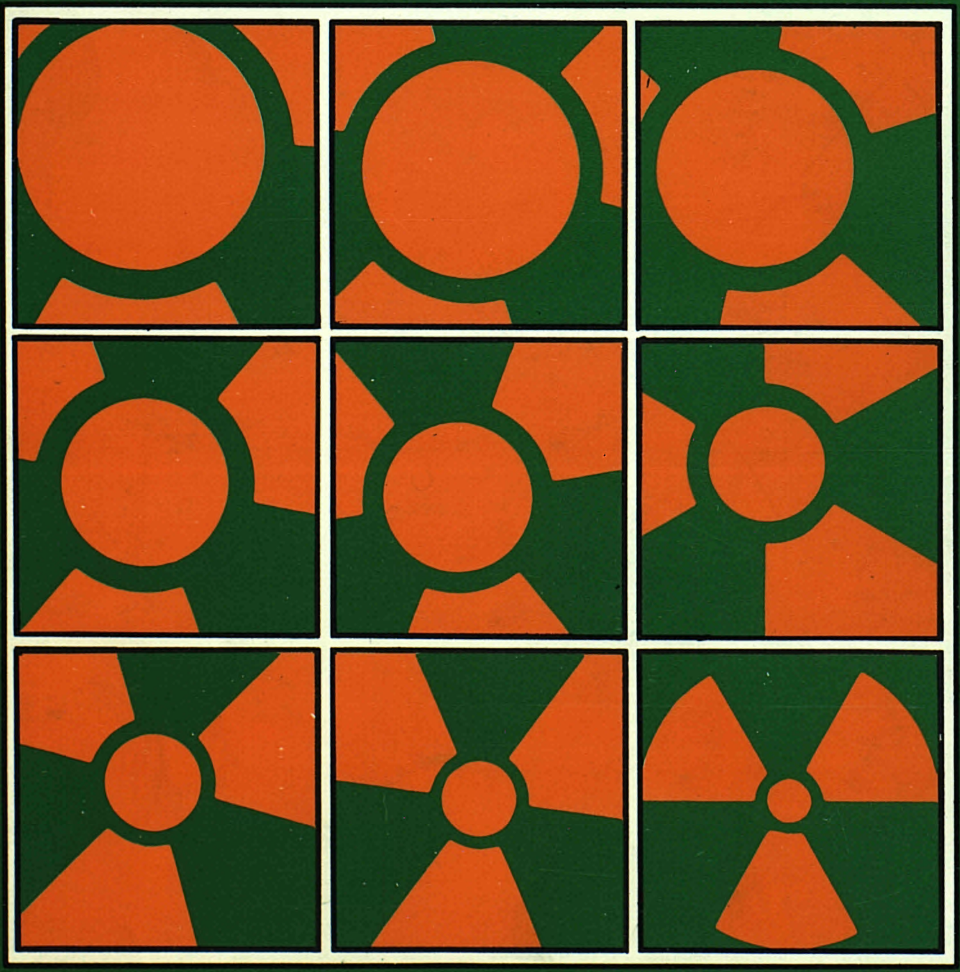
ISSN 1018-5593

European Commission

nuclear science and technology

Community's research and development programme on radioactive waste management and storage
Shared-cost action
(1990-94)

Annual progress report, 1993



Report

EUR 15853 EN

European Commission

Community's research and development programme on radioactive waste management and storage
Shared-cost action
(1990-94)
Annual progress report, 1993

Directorate-General
Science, Research and Development

1994

Published by the
EUROPEAN COMMISSION

Directorate-General XIII
Telecommunications, Information Market and Exploitation of Research

L-2920 Luxembourg

Cataloguing data can be found at the end of this publication

Luxembourg: Office for Official Publications of the European Communities, 1994

ISBN 92-826-8397-4

Printed in Belgium

CONTENTS

PROGRESS OF THE R&D WORK

FOREWORD

This report covers the progress of research work and activities started and developed during 1993 in the framework of the five-year programme (1990-1994) of the European Atomic Energy Community on "**Management and Storage of Radioactive Waste**". This R&D programme has been adopted by decision 89/664/EURATOM of the Council of the Ministers of the European Union on 15 December 1989.

The Council Decision, together with the technical content and the indicative Community financial contributions for the individual sections of the programme, has been published in the Official Journal of the E.C., Nr. L395, 30.12.1989, p. 28-32.

The initial total amount of funding allocated to the programme of 79.6 million ECU over the five-year period, has been reduced to 76.5 million Ecu.

The programme is subdivided in :

Part A : Waste management and associated R & D projects
- A1: Studies of management systems (Task 1)
- A2: Waste treatment (Task 2)
- A3: Safety of the multi-barrier system of geological disposal (Task 3, Task 4 and Task 5)

Part B : Construction and/or operation of underground facilities

A call for research proposals has been launched (O.J. of E.C. Nr. C55/4, 7 March 1990) to implement Part A of the programme through shared-cost research contracts with public organisations or private firms established in the Member States. Multipartner projects have been encouraged.

Contract negotiations for the selected research proposals lead to the signature of 115 contracts for both Part A and Part B of the Programme. The number of research projects running in 1993 are 100.

The European Commission is responsible for implementing and managing the programme and is assisted in this task by the Management and Coordination Advisory Committee "Nuclear Fission energy - Fuel cycle/processing and storage of waste" (see the annexed list of the Members of the Committee).

In addition to shared-cost research contracts, the programme also includes study contracts, awards of training and mobility grants, as well as international co-operation agreements with states outside the European Union.

The co-operation among various teams within the Member States has considerably been promoted by the numerous multi-partner research projects.

The presentation and discussion of the work carried out during periodical progress meetings of working groups of the various projects assures the exchange of information within contractors and representatives of public and private institutions in the Community which are interested in the specific research area.

In order to provide a world wide information on the Community's activities in the field of the radioactive waste a biannual newsletter "EC-FOCUS" is edited.

In this report, the objectives, the working programme and a synopsis of progress and results obtained for each contract in 1993 are presented as prepared by the contractors, under the responsibility of the project leader(s).

The European Commission wishes to express its gratitude to all scientists who have contributed to this report.

The previous annual progress reports of the programme are : EUR-11089 (for 1986); EUR-11482 (for 1987); EUR-12141 (for 1988); EUR-12761/Vol. 1 and 2 (for 1989), EUR-14418 EN (for 1991) and EUR-15132 EN (for 1992). The overall results achieved including the progress of work for 1990 during the programme 1985-1989 have been presented and discussed at the third European Community Conference on Radioactive Waste Management and Disposal - Luxembourg, September 17-21, 1990 (Proceedings published under EUR-13389 - Elsevier Appl. Science Publisher).

N. CADELLI
Head of the Programme
"Management and Storage of Radioactive Waste"

MEMBERS OF THE MANAGEMENT AND COORDINATION ADVISORY COMMITTEE
NUCLEAR FISSION ENERGY
FUEL CYCLE/PROCESSING AND STORAGE OF WASTE [1]

(during 1993)

BELGIUM	Th.	VAN RENTERGEM
	G.	DEDEURWAERDER
DENMARK	K.	BRODERSEN
	S.	HOE
FRANCE	J.	LEFEVRE
	P.	RIEUTORD
GERMANY	M.	BLOSER
	H.G.	RIOTTE
GREECE	S.	AMARANTOS
IRELAND	C.	HONE
	F.	TURVEY
ITALY	G.	GROSSI
	F.	MORSELLI
LUXEMBOURG	C.	BACK
NETHERLANDS	H.	CORNELISSEN
	J.W.A.	VAN ENST (Chairperson)
PORTUGAL	A. J.	DA CONCEICAO SILVA
	C.	RAMALHO CARLOS
SPAIN	J. L.	ROJAS DE DIEGO
	M.	RODRIGUEZ PARRA
UNITED KINKDOM	S.M.	STEARN
	P.J.	HUBBARD
COMMISSION	H.J.	ALLGEIER
	J.	VAN GEEL
	T.	Mc MENAMIN (Secretary)

---

[1] This Committee was established by the Council Decision of 29 June 1984 dealing with structures and procedures for the management and coordination of Community research, development and demonstration activities (OJ N° L 177, 4.7.1984, p. 25).

PART A

WASTE MANAGEMENT AND ASSOCIATED R&D PROJECTS

A1 : STUDIES OF MANAGEMENT SYSTEMS

A2 : WASTE TREATMENT

A3 : SAFETY OF THE MULTI-BARRIER SYSTEM OF GEOLOGICAL DISPOSAL

A1: STUDIES OF MANAGEMENT SYSTEMS

Task 1

"Studies of Management Systems"

* List of contract
* Introduction to Task 1

Topic 1 : System studies

Topic 2 : Harmonisation of radioactive waste management practises and policies

Topic 3 : Comparative assessment of disposal practices in various management schemes for toxic and radioactive waste

Topic 4 : Information

Topic 5 : Transmutation studies

TASK 1 - LIST OF CONTRACTS

Topic 1 : **System studies**

Contract	
FI2W-CT90-0058	Treatment study of contaminated sodium with a view to decommissioning of FBR.
FI2W-CT90-0067	Studies of minimising transport of spent fuel.
FI2W-CT92-0119	Study of the retrievability of radioactive waste from a deep underground disposal facility.

Topic 2 : **Harmonisation of radioactive waste management practices and policies**

FI2W-CT90-0060	Assessment and proposal for activity limits for release of very low-level radioactive waste to landfills.
FI2W-CT90-0066	Definition of reference level for exemption of wastes, suitable for incineration.

Topic 3 : **Comparative assessment of disposal practices in various management schemes for toxic and radioactive waste.**

FI2W-CT90-0042	Comparison of safety assessment methods for toxic and radioactive wastes.
FI2W-CT90-0045	Study concerning the evaluation of toxic elements present in nuclear wastes.
FI2W-CT90-0061	Disposal of radioactive waste and toxic waste in underground repositories.
FI2W-CT91-0110	Use of methods and programmes developed in nuclear field for treatment and disposal of toxic and hazardous wastes.

TASK 1 - LIST OF CONTRACTS

Topic 4 : Information of the public

FI2W-CT90-0036	Study of a communication strategy aimed at achieving a possible better understanding of the consequence of radioactive waste management in a well defined group of public.
FI2W-CT90-0043	Information of the public in the field of decommissioning waste. Study of strategies and means for specific information.
FI2W-CT90-0074	The evolution and implementation of a public information strategy on radioactive waste management.
FI2W-CT91-0105	A public information campaign to support a proposed national deep repository for low and intermediate level radioactive waste.

Topic 5 : Transmutation studies

FI2W-CT91-0103	Transmutation of long-lived radionuclides by advanced converters.
FI2W-CT91-0104	Participation in a CEC strategy study on nuclear waste transmutation.
FI2W-CT91-0106	Potentialities and costs of partition and transmutation of long-lived radionuclides.

INTRODUCTION TO TASK 1 - STUDIES OF MANAGEMENT SYSTEMS

A. Objective

The system studies concern the evaluation of various scenarios for the management of different types of waste. Harmonisation work mainly involves the development of common waste management criteria and schemes. Waste from dismantling operations and spent fuel where these are considered as waste are included as well as the development of analytical models for minimising transport of waste. An additional topic is the evaluation of the possibilities offered by transmutation to reduce the inventory of long-lived radionuclides. Information of the public in all fields of radioactive waste management and disposal is a further topic.

B. Research performed under previous programmes

System studies have been performed by comparing various management schemes for particular categories of wastes or groups of waste streams; the comparisons were based on evaluation of costs and radiological consequences to workers and the public. The management alternatives were studied for:

- solid plutonium contaminated waste,
- alkaline liquid wash waste from fuel reprocessing and zircaloy-hulls,
- reactor waste (waste from normal operation of light-water reactors),
- waste management implications of direct spent fuel disposal and disposal after reprocessing.

Activities in the field of harmonisation of practises covered a review on "Objectives, standards and criteria of radioactive waste disposal in the European Community", the development of criteria for exemption from regulatory control for radioactive waste not linked to the nuclear fuel cycle, and first approaches to waste equivalence.

C. Present programme (1990-1994)

Studies are performed under five headings corresponding to specific research topics.

Topic 1 : System studies

The system studies are based on the comparison of possible management schemes, with the definition of waste inventories at origin, an analysis of the subsequent steps in the possible management routes (treatment, transport, interim storage and disposal), evaluation of costs and determination of radiological consequences. The sensitivity of each scenario to modifications in waste quantities, release limits, and waste acceptance criteria is also evaluated.

The main waste streams concerned are radioactive waste arising from decommissioning of nuclear installations, tailings from uranium-treatment, spent fuel declared as being waste and very low level waste candidate to being exempted from regulatory control.

Topic 2 : Harmonisation of radioactive waste management practices and policies

The main field of activity is the development of the scientific basis for developing criteria for exemption of particular waste streams from regulatory control. Particular disposal routed considered are incineration and disposal at industrial waste burial sites.

Topic 3 : Comparative assessment of disposal practices in various management schemes for toxic and radioactive waste

Studies are performed which compare radioactive waste management schemes to management practises for waste streams involving radioactive isotopes in material not linked to the nuclear fuel cycle and toxic waste mixed with radioactive elements. Particular attention is paid to disposal of toxic and mixed waste in salt formations.

Topic 4 : Information of the public

Studies on strategies allowing efficient information to be given to the public, and on how a good degree of penetration through various media may be reached are in progress. Development of information materials (booklets, visual, aids, etc.) is also part of the activities.

Topic 5 : Transmutation studies

After having established the inventory of long-lived radionuclides produced for a given reactor capacity in considering the spent fuel as a waste, the possibilities of reducing the inventory of long-lived actinides and fission products by partitioning and transmutation are calculated. The conventional routes are irradiation in thermal reactors with MOX-fuel and a mix of light-water-reactors and fast reactors, with long-lived radionuclides added in a homogeneous or heterogeneous way. Advanced possibilities considered are based on accelerator driven spallation devices.

Title :	Treatment Study of Contaminated Sodium with a View to Decommissioning of FBR
Contractors :	CEA - SIEMENS - FRAMATOME
Contract N° :	F12W - CT90-0058
Duration of the contract :	from April 1991 to April 1993
Period covered :	January 1993 - April 1993
Project Leader :	C. Latgé (CEA - coordinator) N. de Seroux (Framatome) H. Hanebeck (Siemens)

A. OBJECTIVE AND SCOPE

In the Fast Breeder Reactor (FBR) decommissioning studies, sodium management is a major problem. Sodium becomes an important waste which must be taken into account in the final process. To handle this specific topic, a cooperative working group has been formed, with the French "Commissariat à l'Energie Atomique" (CEA), FRAMATOME and SIEMENS. CEA is the project leader.

The scope of work is based on a step by step approach, using available data and experimental results with regard to the sodium inventory, sodium purification and waste treatment.

The aim of this particular development program is to highlight optimized scenarios for sodium destruction and recycling, based on a technical and an economical approach. Moreover a Research & Development (R&D) orientation will be provided to improve the selected scenarios and to allow a better understanding of fundamental processes.

B. WORK PROGRAMME

To perform the above scope of work, five main stages were defined :

a : Inventory of the sodium needs :
The sodium balance, based on sodium needs for future FBR programs and existing wastes to be treated, is the starting point from which the problem is tackled and from which the scenarios to be highlighted later on are set.

b: Assessment of sodium behaviour and characteristics :
From an estimated contamination, provided by mathematical models which are validated using experimental data, predictions are established for the behaviour and characteristics of the sodium to be treated.

c: Sodium purification :
Purification processes are examined with regard to the predicted quantities of contaminated sodium and the associated storage and transportation techniques. The R&D needs are defined, according to the required level of knowledge in the waste treatment domain.

d: Analysis of the scenarios and their main parameters :
Using the previous steps as a reference, the main parameters of the scenarios are reviewed, with both a technical and an economical vision. This twofold approach allows the working group to highlight arguments to select and describe the scenarios to be analysed.

e: Optimized scenarios :
These processes, having been defined as suitable scenarios for sodium treatment, are described. Further needs for R&D programs are highlighted, to improve the processes efficiency.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.I. STATE OF ADVANCEMENT

The cooperative working group was assigned in April 1991 the task of sodium management in the decommissioning studies environment.

Four semestrial reports were published on November, 1991, /1/, on April, 1992, /2/, on September, 1992, /3/ and on May, 1993, /4/.

Two Annual Progress Report were published on 1991, /5/ and on 1992, /6/.

The Reference /4/ is the final part of the study and deals with the last point of the work programme. The different scenarios identified in the previous work were assessed and a comparison between themselves was established following the different hypotheses.

Finally, the conclusion recommends a scenario for each of the cases which have been identified.

C.II. RECALLING OF THE SCENARIOS

The selected scenarios for the sodium treatments were defined in the previous work /6/, either to reuse the sodium, or to dispose the sodium.

The scenarios were separated in two groups :
- one or several FBR are to fill up with sodium --> scenarios of sodium reuse and scenarios of sodium disposal + new sodium supply.
- no FBR are to fill up with sodium --> scenarios of sodium disposal or sodium sale in industrial field when it is desactivated.

The possible scenarios are summarized and are identified with letters, in table I for primary sodium and in table II for secondary sodium. The selected steps are : storage, purification, processing, final destination.

The basis hypotheses about radioactivity aspects are :
- sodium is considered non radioactive when its radioactivity is below 10 Bq/g,
- radioactivity of the contaminated sodium at the final shutdown of the reactor is given in table III,
- a radioactivity decade decreasing is obtained with one RVC filter for the caesium, and with one cold trap for the tritium,
- a radioactivity decade decreasing is obtained with about 8 to 9 years of storage for 22 Na.

C.III. COMPARISON CRITERIA FOR THE SCENARIOS

In the aim to compare the costs of the different scenarios for reuse or for dispose the sodium coming from the large Fast Breeder Reactors, criteria of comparaison have been identified and classified in several items.

a) Assessment items of the costs generated by the sodium reuse :

- purified sodium with radioactivity below 10 Bq/g :
  - . purification system
  - . biological shielding addings for storage
  - . storage and surveillance during 30 years

- . transport of the sodium to an other site, if necessary

- partly purified sodium :
  - . purification system
  - . small biological shielding addings for transfer
  - . low increasing of the operators number
  - . controlled area in place 7 months early
  - . low decontamination of the test equipment
  - . transport of the sodium to an other site, if necessary

- no purified sodium.
  - . biological shielding addings for transfer
  - . increasing of the operators number
  - . controlled area in place 7 months early
  - . decontamination of the test equipment
  - . transport of the sodium to an other site, if necessary

b) Assessment items of the costs generated by the sodium disposal :
- . purification system
- . supply of the sodium disposal loop
- . biological shielding addings for transfer and storage, if necessary
- . low increasing of the operators number during transfer
- . operation of the process
- . decontamination of the sodium disposal loop
- . transport of the aqueous sodium hydroxide

c) Assessment items of the savings generated by the sodium reuse :
- . cost of new sodium
- . shorter sodium supply timetable
- . no transport of sodium if the new reactor is on the same site

d) Assessment items of the savings generated by the sodium disposal :
- . none

e) Comparison of the sodium reuse and the sodium disposal interests :

The sodium reuse avoids :
- to buy new sodium,
- to supply loops for sodium contaminated disposal,
- to dispose it and to treat the sodium hydroxide from the disposal.

It allows also to decrease sodium supply duration for the new plant.

The sodium disposal allows to treat contaminated sodium. Then new sodium can be used for new reactors and tests can be performed without contamination of the equipment and without controlled area.

C.IV. DEFINITION OF THE COST ITEMS FOR THE SCENARIOS

Several items of the costs of the scenarios were identified and assessed. They are listed hereafter.

a) Sodium purification

The sodium purification was assessed taking into account :
- 1 RVC filter is needed for 1 decade of purification of caesium
- 1 cold trap is needed for 1 decade of purification of tritium

The treatment of each filter or trap is taken into account.

b) Biological shielding addings of the storage tanks

They are quoted according to the purification level of the stored sodium.

c) Storage of the sodium

Two types of sodium storage are identified :

- short storage time : the sodium is stored in existing tanks of the plant with biological shielding addings. This storage is foreseen for 5 years. Then the sodium is reused or disposed.
- long storage time : the sodium is stored in specific shielded tanks in a new building. This storage is foreseen for 30 years. Then the sodium radioactivity in 22 Na is below 10 Bq/g and the sodium can be reused without radiological constraints (caesium and tritium were previously purified down to 10 Bq/g).

d) Transport of the sodium

It is composed of 2 parts :

- the mobile tanks : they are assessed taking into account the required biological shielding to comply with the transport regulations.
- the travels : they are quoted according to their number and an average distance of 500 km.

e) Transport of the sodium hydroxide

It is composed of 2 parts :

- the mobile tanks are not specific and are supplied by the transport company.
- the travels : they are quoted according to their number and an average distance of 500 km.

f) New sodium

The new sodium cost was assessed with the informations from the "Métaux Speciaux - Pechiney" company in FRANCE, which provided sodium for PHENIX and CREYS-MALVILLE.

C.V. PROPOSITION OF SCENARIOS FOR THE TREATMENT OF PRIMARY SODIUM

The results of the assessment of scenarios for the treatment of the primary sodium is given on the table IV.

Scenarios were classified in the following categories hereafter :

- 1° category : Reuse of the sodium in a new plant which is on the same site than the old plant
- 2° category : Reuse of the sodium in a new plant which is on another site than the old plant
- 3° category : Contaminated sodium disposal of the old plant and new sodium supplying for the new plant

a) 1° category scenarios for the primary sodium

The scenario of contaminated sodium reuse in a new plant on the same site is adventageous, with a purification level of 90 % of caesium and tritium which allows to limit the constraints of the radioactivity. Storage sodium decay of 5 years is sufficient, unless the new plant is not ready.

Starting of sodium filling of the new plant can be delayed because this operation is very fast when the two plants are on the same site. So problems linked to works in controlled areas (due to radioactivated sodium presence) are limited.

Sodium purification in caesium and tritium with a purification level of 90% can be easily realised and is not very expensive. This operation allows to reduce the dose rates to 50 µGy/h (green area) at a distance of 3 m from the sodium pipes. Moreover, the radioactivity concentration of the sodium can be maintained at a normal level during the new plant operation because the decay half period is quite long.

b) 2° category scenarios for the primary sodium

In this case, the scenario of contaminated sodium reuse in an new plant on another site is also advantageous. Sodium purification level needs to be 98 % in caesium and tritium and the sodium has to be stored during 5 years to reduce the 22 Na radioactivity. Then, the sodium radioactivity is low enough to allow the transport in good conditions (19 tonnes of sodium can be transported at each travel by road).

To store the sodium longer than 5 years is not interesting because the caesium radioactivity begins dominating and decreases slowly.

c) 3° category scenarios for the primary sodium

In this case, the new plant is filled up with new sodium. The total cost of the scenario is the cost of the new sodium and the cost of the old sodium becoming.

The most interesting solution to reuse the sodium out of a new nuclear plant is in industrial field. Sodium purification level needs to be 99,99 % in caesium and tritium and the sodium has to be stored during 30 years to reduce its own radioactivity. Then, the sodium radioactivity below 10 Bq/g allows to reuse it with possible conditions. The economical interest is linked to the price level of sale. If the price of sodium below 10 Bq/g could be near of industrial sodium price, the purification cost should be covered by the sale. However, it is difficult to know if this project could be realized when the shutdown of a large plant will happen.

In case of no possibility of sodium reuse in industrial field, contaminated sodium can be disposed with the NOAH process. The analysis of the scenario including the sodium disposal on the site of the old plant and of the scenario including the sodium disposal on the site of the NOAH process wastes treatment did not give any significant difference.

In this case, it is difficult to conclude for this category scenario because a lot of factors are unknown. However, sodium reuse in industrial field is more economical than sodium disposal but is uncertain.

d) Scenario selection results for the primary sodium

There is a new plant to fill up with the primary sodium of a shutdown plant. The results of the selection are given hereafter. (1 MECU = 1 million of ECU)

Scenarios	Costs
Reuse on the same site than the old plant --> scenario F	5,7 MECU
Reuse on an other site than the old plant --> scenario D	10,75 MECU
Sodium disposal + new sodium supply --> scenarios H and I	26,65 to 27,15 MECU

New sodium needed to fill up a power plant as EFR (Europeen Fast Reactor) is about 2050 tonnes for the primary circuit. The cost of this sodium is about 16 MECU. Sodium reuse is largely more economical than sodium disposal, with a ratio of 30 % to 60 %.

C.VI. PROPOSITION OF SCENARIOS FOR THE TREATMENT OF SECONDARY SODIUM

The results of the assessment of scenarios for the treatment of the primary sodium is given on the table V.

Scenarios were classified in the same categories than for the primary sodium.

- 1° category : Reuse of the sodium in a new plant which is on the same site than the old plant
- 2° category : Reuse of the sodium in a new plant which is on another site than the old plant
- 3° category : Contaminated sodium disposal of the old plant and new sodium supplying for the new plant

a) 1° category scenarios for the secondary sodium

The solution of sodium reuse in a new plant is advantageous. When the two plants are on the same site, the sodium can be transfered directly, possibly via a buffer storage tank. However, the cost of the constraints for the draining, the transfer and the filling up of the new plant due to the contamination is higher than the sodium purification cost in tritium to obtain a radioactivity below 10 Bq/g. Then, it is preferable to purify to avoid these constraints, unless the available time for the process is too short. Furthermore, contamination of the test equipment in sodium is avoided.

b) 2° category scenarios for the secondary sodium

When the sodium has to be transported to an other site, the preferable solution is to purify in tritium to obtain a radioactivity below 10 Bq/g to avoid constraints for the draining, the transport and the filling up of the new plant due to the contamination.

c) 3° category scenarios for the secondary sodium

The most interesting scenario remains to reuse the sodium in industrial field. Sodium purification level needs to be of 99,99 % of tritium and the sodium does not need storage period. Then, the sodium radioactivity is below 10 Bq/g to allow to be reused with specific conditions. However, as for the primary reuse, it is difficult to know if this project could be realized when the shutdown of a large plant will happen.
In case of no possibility of sodium reuse in industrial field, contaminated sodium can be disposed with the NOAH process but this solution is less economical.

d) Scenario selection results for the secondary sodium

There is a new plant to fill up with the secondary sodium of a shutdown plant. The results of the selection are given hereafter.

Scenarios	Coûts
Reuse on an other site than the old plant --> scenario M	2,25 MECU
Reuse on the same site than the old plant --> scenario N	3 MECU
Sodium disposal + new sodium supply --> scenario P	13,75 MECU

New sodium to fill up a power plant as EFR is about 1050 tonnes for the secondary circuit. The cost of this sodium is about 8,5 MECU. Sodium reuse seems largely more economical than sodium disposal, with a ratio of 4.

Scenario M is less expensive than scenario N because the sodium is purified below 10 Bq/g what allows to avoid the specific constraints due to the sodium contamination.

C.VII. CONCLUSION

This study allowed to verify that solutions can be proposed presently to treat large volumes of contaminated sodium, whatever the becoming of the FBR could be in the future.

However, solutions that were presented in the study will need to be adapted in the future to take into account possible evolutions of knowledges and regulations that can significantly modify the results.

In all cases, sodium reuse in nuclear field was shown as the preferable solution compared with the sodium disposal. Sodium reuse in industrial field is also possible, mainly for the secondary sodium.

References :

/1/ CCE - Gestion et stockage des déchets radioactifs - Traitement du sodium contaminé - Rapport semestriel N°1 - FRAMATOME - NOVA X 005 807 000

/2/ CCE - Gestion et stockage des déchets radioactifs - Traitement du sodium contaminé - Rapport semestriel N°2 - FRAMATOME - NOVA X 006 067 000

/3/ CCE - Gestion et stockage des déchets radioactifs - Traitement du sodium contaminé - Rapport semestriel N°3 - FRAMATOME - NOVA X 006 123 000

/4/ CCE - Gestion et stockage des déchets radioactifs - Traitement du sodium contaminé - Rapport semestriel N°4 - FRAMATOME - NVTMK DC 93.116

/5/ Treatment of contaminated sodium with a view to decommissioning of FBR - CCE - Community's research and development programme on radioactive waste management and storage - Annual Progress Report, 1991 - EUR 14418 EN

/6/ Treatment of contaminated sodium with a view to decommissioning of FBR - CCE - Community's research and development programme on radioactive waste management and storage - Annual Progress Report, 1992 - EUR 15132 EN

TABLE I
SCENARIOS FOR THE BECOMING OF THE CONTAMINATED SODIUM
PRIMARY SODIUM

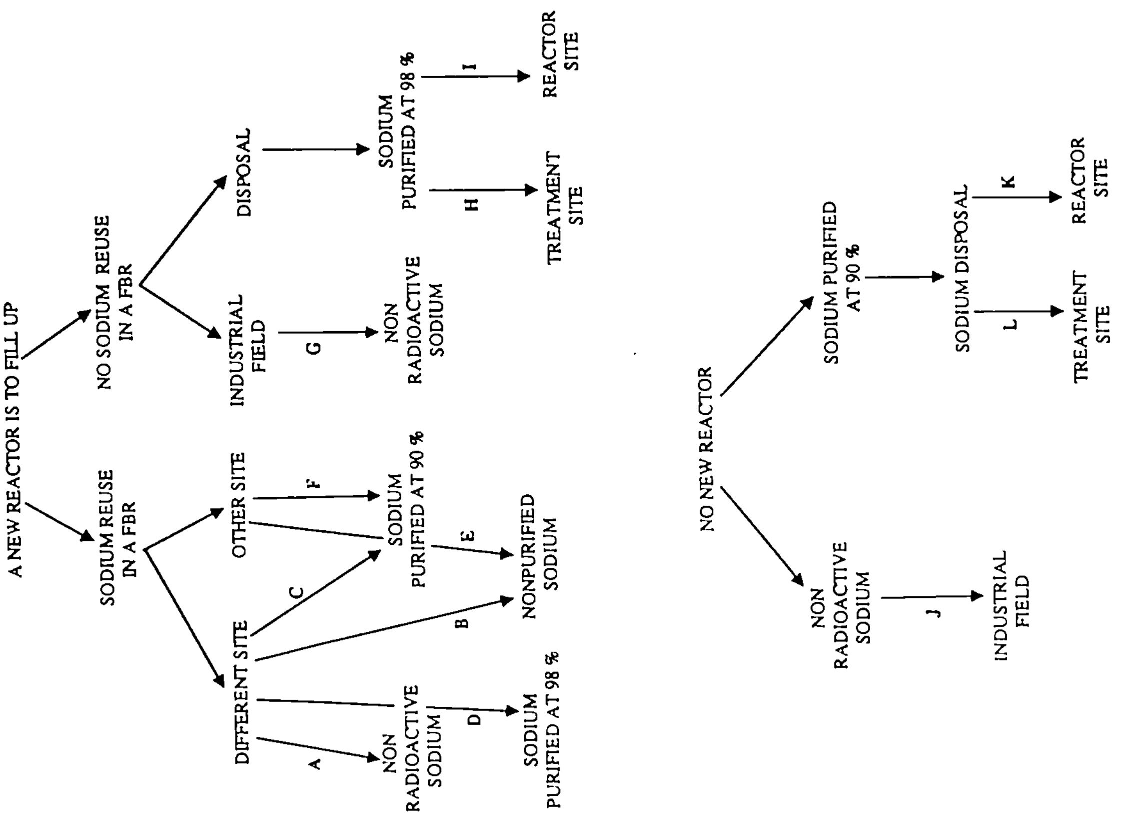


TABLE IV
COSTS ASSESSMENTS OF THE SCENARIOS
PRIMARY SODIUM

A NEW REACTOR IS TO FILL UP

Scenarios	Costs (MECU)
E - Reuse of nonpurified sodium on the same site	5
F - Reuse of purified sodium at 90 % on the same site	5,7
B - Reuse of nonpurified sodium on an other site	9,7
C - Reuse of purified sodium at 90 % on an other site	10,1
D - Reuse of purified sodium at 98 % on an other site	10,75
A - Reuse of non radioactive sodium in an other site	14,1
Sodium cost for EFR primary circuit	16,4
G - Reuse of nonradioactive sodium in industrial field	26,3
I - Sodium disposal on the treatment site	26,65
H - Sodium disposal on the reactor site	27,15

(1 MECU = 1 million of ECU)

NO NEW REACTOR

Scenarios	Costs (MECU)
J - Reuse of nonradioactive sodium in industrial field	9,9
L - Sodium disposal on sodium hydroxide treatment site	10,25
K - Sodium disposal on reactor site	10,65

TABLE V
COSTS ASSESSMENTS OF THE SCENARIOS
SECONDARY SODIUM

A NEW REACTOR IS TO FILL UP

Scenarios	Costs (MECU)
M - Reuse of non radioactive sodium in an other site	2,25
N - Reuse of nonpurified sodium on the same site	3
Sodium cost for EFR secondary circuit	8,4
P - Sodium disposal on the sodium hydroxide treatment site + new sodium cost	13,75

NO NEW REACTOR

Scenarios	Costs (MECU)
O - Reuse of non radioactive sodium in industrial field	0,15
P - Sodium disposal on sodium hydroxide treatment site	5,35

TABLE II
SCENARIOS FOR THE BECOMING OF THE CONTAMINATED SODIUM
SECONDARY SODIUM

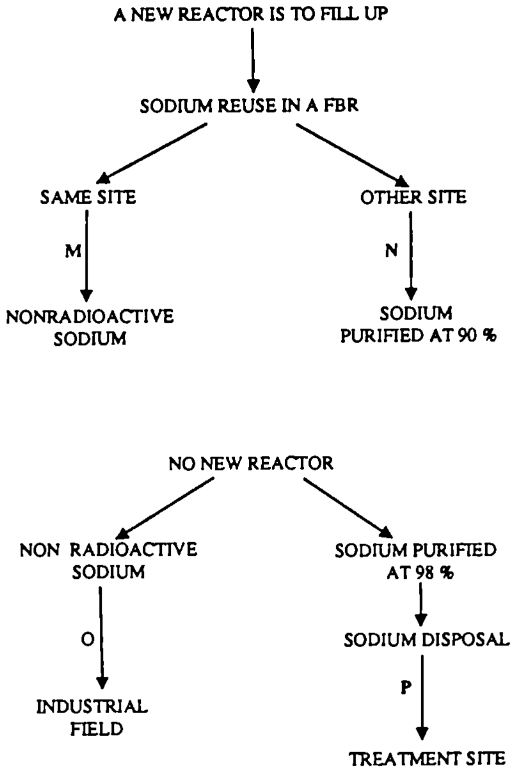


TABLE III
PREDICTED RADIOACTIVITY OF THE PRIMARY SODIUM
OF CREYS-MALVILLE (3 300 T) AT THE FINAL SHUTDOWN

Radionuclides	T 1/2	Radioactivity (Bq/kg)	Total radioactivity (Bq)
Na 22 (β^{+}, gamma)	2,62 years	$1,33.10^{7}$	$4,4.10^{13}$
Cs 134 (β^{-}, gamma)	2,1 years	$1,25.10^{7}$	$4,1.10^{13}$
Cs 137 (β^{-}, gamma)	30 years	$8,95.10^{7}$	$29,5.10^{13}$
Tritium (β^{-})	12,3 years	$3,35.10^{7}$	11.10^{13}
	TOTAL	15.10^{7}	49.10^{13}

Title:	Studies of Minimising Transport of Spent Fuel
Contractor:	BAeSEMA
Contract No:	FI2W-CT90-0067
Duration of Contract:	from 1st September 1991 to 31st May 1993
Period Covered:	Jan 1st 1993 to May 31st 1993
Project Leader:	Richard J Greathead

A. OBJECTIVES AND SCOPE

This study has been carried out within the framework of the European Commission's radioactive waste management research programme. The aim of the work is to establish a methodology and software tools for examining the implications for cost, environmental impact and safety of minimising the transport of spent nuclear fuel and associated materials using multi attribute analysis and linear programming techniques. This sets a number of general objectives:

- to obtain realistic data and develop a model database of the overall setup for generating, storage, processing and disposal of irradiated spent fuel in Europe, as existing and postulated for the future, and to define a potential network of transport channels between the sites and facilities involved;
- to generate a small number of realistic "basic" scenarios, founded on the overall setup, reflecting different options for the spent fuel management cycle, and suitable for testing and demonstrating the methodology and software tools developed;
- to develop the software tools required to model the scenarios, including the linear programming model to minimise transport aspects and database tools to process and evaluate input and output;
- to carry out illustrative analyses and sensitivity studies on the basic scenarios and variants, and report on the findings of the study.

B. WORK PROGRAMME

Task 1 - Formulation of the Problem

This considers and documents the high level conceptual design of the model and the general study strategy, including the financial and environmental/safety impacts to be taken into account, the basic scenarios to be studied, the constraints to apply (storage capacities, flask capacities, etc) and aspects of transport to be minimised (cost, dose, etc).

Task 2 - Data Requirements

A detailed documented definition of the data requirements.

Task 3 - Data Collection

The collection, collation, inclusion in a structured database and documentation of the best available data meeting the requirements identified above.

Task 4 - Model Development

The design and development of the software for the linear programming transport minimisation model and the supporting database programs which pre-process the input data defining a scenario to be studied and post process and evaluate the output from the linear program. This task also included testing and trials.

Task 5 - Illustrative Analyses

Performance of illustrative analyses and sensitivity studies on the basic scenarios and variants, and preparation of the final report.

C. PROGRESS AND OBTAINED RESULTS

Statement of advancement

All tasks are now competed. Tasks 1, 2, 3 and some of 4 were completed prior to the start of 1993 and the rest of Task 4 (Model Development) and Task 5 (Illustrative Analyses) were completed successfully in 1993.

Progress and Results

1. Formulation and Data Requirement (Tasks 1 and 2)

In Task 1, "Formulation of the Problem" and Task 2 "Data Requirements" the nature and purpose of the study are defined, and the data required specified (Refs 1, 2).

Overview of Definition (Model Description)

In summary, it was proposed that linear programming techniques be used to minimise various types of "impact" (quantity, financial cost, occupational collective dose, public collective dose, accident risk, or a normalised and possibly weighted combination of these "impacts") associated with transport of the various materials arising during spent fuel management. The main types of material considered are:[1]

- spent fuel;
- conditioned spent fuel;
- vitrified high level waste; and
- low and intermediate level wastes.

These are transported between:

- reactors;
- storage facilities;[2]
- reprocessing plants;
- plants for conditioning of spent fuel for direct disposal and
- final disposal facilities.

Different modes of transport may be available, i.e. mainly sea (requiring the availability of specialised ships), mainly rail or mainly road, and a variety of flasks may be used for transporting a given material.

Once the permutation of material flows which minimises the required transport impact has been determined (i.e. the quantity of specific materials, of a specific age[3], flowing between specific facilities, via specific routes, in specific containers and for each timestep) the effect of adopting this transport strategy on other stages in the cycle, i.e. storage, processing and disposal, can be evaluated. This is done by calculating the financial cost, doses, etc associated with the flow, and where appropriate stock, of each material at each facility in the scenario (the flows and stocks into/in facilities are also calculated during minimisation).

The model can be constrained by putting realistic limits on the storage and handling capacities of the facilities and limits on the quantity of material which can be carried via specific routes. Minimum and maximum age limits for dispatching or receiving materials at a specific facility can be enforced and the capacity of the flasks can be varied according to the age of the material (i.e. flask capacity can be reduced, possibly to zero, for materials with higher thermal and radiation outputs).

The model is also constrained to generate a minimum, time dependent, amount of nuclear energy in each nation. This level is set using published forecasts for installed capacities (Ref 3). Individual reactors are constrained to perform within lower and upper limits (load factors) and may burn

---

[1] Highly Active Waste Liquor is also defined in the model, but is never involved in intersite shipment. Highly Active Waste Liquor must be included because its storage represents a delay between reprocessing and vitrification. This delay is variable and will affect the time flow of materials.

[2] Including Highly Active Waste Liquor Tanks at reprocessing facilities.

[3] Time after discharge from the reactor.

Uranium Oxide (UO) or Mixed Uranium/Plutonium Oxide (MOX) fuels to different burnups. Within these limits, the model is free to determine the output from individual reactors which, in conjunction with other decision variables, leads to minimum transport impact.

This type of model allows a wide range of study options:
- study of siting policies for new facilities;
- evaluation of the effect of removing or introducing trans-national border transport restrictions or changing the requirements to return waste to its country of origin;
- comparison of localised versus centralised storage strategies;
- examination of the cost benefits of delayed reprocessing, delayed disposal, etc (the model permits investment discounting);
- comparison of direct disposal versus reprocessing management options;
- comparison of the influence of storage facility type or flask type;
- examination of the effect of opting for higher burnups or burning mixed oxide fuels ;
- examination of choice of transport mode (sea, road or rail) studied; etc.

The model can be used in either a strategic capacity for evaluating spent fuel cycle options or in an operational mode for detailed transport planning. In this study, emphasis is placed on its potential application to strategic planning. Demonstration of its potential as an operational tool is limited by lack of detailed data for transport and current model size restrictions.

For this study, it was proposed that the main effort be directed at comparing two basic scenarios, namely a reprocessing orientated management route and a direct disposal orientated management route. It is assumed that waste must be either returned to its country of origin or its disposal permitted at the most favourable site in transport terms, i.e. the best technical, as opposed to political, solution. Variants on the basic scenarios and sensitivity studies are also examined, including the influence of siting of the facilities, flask sizes, choice of timestep, etc.

The original proposed scope of the model included the UK, Germany, France and Sweden (introduced because of that country's use of sea transport as the main transport mode). The data model was developed for these countries and published (Ref 3). However, limitations on the size of model which could be handled by the available versions of the linear programming software lead to reducing the final scope to:
- inclusion of reactors, processing, storage and disposal facilities in Germany and the UK;
- use of French reprocessing facilities and disposal facilities; but
- exclusion of French reactors and all Swedish facilities (although ships based on the Swedish vessel MS Sigyn are introduced).

The impacts originally specified included accident risk. However, obtaining a full and consistent set of accident risk data, for both transport and facilities, and introducing it into the code, presented budgetary difficulties and source data problems. In principle, treatment of accident risk (or other risk or dose parameters such as Maximum Individual Risk) is exactly the same as for other impacts already included in the model (financial cost, occupational collective dose, and short and long term public collective dose) and its exclusion does not invalidate the demonstration of the methodology or software.

The main development languages chosen are the FOXPRO database management language and the MAGIC/LAMPS matrix generating and linear programming language. The EXCEL spreadsheet package is available for producing charts. This software is mounted on DELL 486 DX 50 computers, or similar.

Summary of Data Requirements for Running Model

Once the purpose of the model and its functional specification were outlined, it was possible to define the data requirements. These are not specified in detail here, but include the following main categories.
- Forecast nuclear power generating requirements for each country included in the model and (largely hypothetical) schedule of individual reactor power up/down dates, installed capacity and ranges of load factors which will permit these requirements to be met.
- Fuel burnup data.
- Siting of existing and proposed/hypothetical reactor, storage, processing and disposal facilities and the availability of local road, rail head and port facilities.
- Storage capacities of stores (including At Reactor stores) and final disposal facilities, and how they depend on time.

- Initial stocks at stores.
- Input and output handling capacities at all types of facility (storage At Reactor and Away From Reactor, processing and disposal), and how they depend on time.
- Conversion coefficients between input and output materials during processing.
- Flask capacity (as a function of material and its age), availability data and the ability of facilities to receive/dispatch different types of flask.
- Ship capacity, availability and journey frequency data.
- Connection capacity.
- Unit generalised costs (financial, occupational collective dose, public collective dose, etc per unit of material transported, handled or stored) for transport channels and for each facility, according to material, flask type, etc.

2. Data Collection (Task 3)

Data were collected from many different sources, including small sub-contracts, private communications, reports on earlier CEC contracts and the open literature. It was then collated into a self consistent data model of the nuclear power generation and spent fuel management scene in the countries of interest.

The data has been entered into a computer based "model database" managed by a purpose designed database management system written in the FOXPRO database language. FOXPRO's report writing facilities have been used to directly generate a data report containing all the data on which the study is based (Ref 3).

The quality of data is variable and difficulties were encountered in determining the context in which reported values should be interpreted. The final objective with respect to data collection has therefore been to ensure self consistency, rather than absolute correctness, and to justify by reasoned argument the setting of relative values between data. These aspects are considered in detail in the data report (Ref 3).

Comprehensive referencing in the data report ensures traceability of all data used in the study back to source.

3. Model Development (Task 4)

The design specification of the computer model can be found at Ref 4. In summary, the model can be divided into four main components:

- The database management system used to organise, maintain, report on, and edit the full-scale and scenario databases.
- The pre-processor which uses a subset of the large model database to generate a refined data model of the particular scenario to be studied and converts the format into the lists and tables which are read into the minimisation stage. This component is written in the FOXPRO database management language.
- The minimisation programs which use the MAGIC/LAMPS matrix generation facility and linear programming language to minimise the transport impact of interest.
- The post-processor (evaluator), which takes the flows and stocks, etc output during minimisation and multiplies them by the appropriate generalised cost coefficients to evaluate the costs, doses, etc (impacts) for each facility. It also allows breakdown of the transport and facility impacts according to material, flask type, time, etc. This is written in the FOXPRO database management language.

During development, problems arose with the MAGIC matrix generator in connection with memory and processing time limits imposed by LAMPS. The solution tried was to "decompose" the model into smaller parts. However, initial runs using a decomposed version of the model indicated that whilst the memory problem was resolved it would typically take 100 hours to generate the networks and perhaps 100 hours to optimise. This is not considered practicable. Effort and time constraints did not permit further experimentation and it was decided to revert to the earlier formulation but using later versions of MAGIC/LAMPS with increased capacity. This will not permit solution of the full scale model for Germany, France, the UK and Sweden, and therefore smaller, idealised, but still realistic subsets of the full scale model are used.

A User Guide to the model has been prepared [ref 5].

4. Illustrative Analyses (Task 5)

A number of illustrative analyses have been run examining two basic scenarios. One basic scenario has a low total capacity for conditioning (~400 tonnes of spent fuel per year) whilst the other has a relatively high total capacity for conditioning (1000 tonnes of spent fuel per year). These are respectively referred to as the basic **reprocessing orientated scenario** and the basic **direct disposal orientated** scenario. A 40 year generating period is considered. Storage, processing and disposal facilities are available for up to 60 years beyond cessation of generation. For most scenarios (i.e. those in which the burnup of Uranium Oxide fuel in LWRs and AGRs is assumed to be 33 and 20 GWd/tHM respectively) 22,000 tHM of spent fuel are generated in the UK and 36,200 tHM in Germany. The rate of investment discounting applied in the majority of scenarios is 4%. It is considered that these scenarios provide recognisably realistic and feasible simulations of nuclear power generation and spent fuel management in Germany and the UK.

The ways in which the model can be used are numerous and some illustrations of the type of results which can be obtained are shown in Table 1. This indicates the scenario variations found with the lowest and highest cost and dose impacts for the complete spent fuel management cycle.

As can be seen, of the scenario variations studied, the cheapest turns out to be a direct disposal orientated scenario, minimised on transport cost, with a high UK flask storage capacity (for spent fuel, conditioned spent fuel and vitrified high level waste), costing 14,467 MECU[4]. This compares with the highest cost scenario found, which was a reprocessing orientated scenario costing 20,907 MECU for which transport Occupational Collective Dose was minimised. In this case, direct disposal is cheaper even though wastes are forced to be returned to their country of origin, which was not the case for the reprocessing orientated scenario. Generally, direct disposal was found to be significantly cheaper than reprocessing. The same direct disposal orientated scenario also performed well in terms of Occupational Collective Docs and Public Collective Dose for the complete spent fuel management cycle.

However, it performed badly in terms of the Long Term Public Collective Dose resulting from circulation of discharges from operating facilities and long term release of radionuclides from disposal facilities. This is due to the larger quantity of conditioned spent fuel disposed of in a deep repository situated in granite in the UK compared with other scenarios where more material is disposed of in a repositoriy situated in a German salt dome, which is predicted to have lower release rates.

In several cases, minimising transport impact, which generally forms only a small percentage of the overall impact, leads to a large increase in the impact for the complete spent fuel management cycle. For example, if transport doses, instead of transport costs, are minimised, the quantity of spent fuel disposed of directly decreases (due to the much greater number of transports of conditioned spent fuel needed, compared with vitrified high level waste, for the same amount of original spent fuel, and the relatively small effect decay has on reducing dose compared with the effect investment discounting has on reducing financial costs). This leads to an increase in cost for the complete cycle of more than 3,000MECU.

5. References

1) "Outline Requirements for Radioactive Waste Transport Minimisation Model - Discussion Paper", R Greathead, BAeSEMA Document Reference C2148/TN.1, October 1991.
2) "Radioactive Waste Transport Minimisation Model : Definition and Data Requirements", R Greathead, A R James, BAeSEMA Document Reference C2148/TR/1, April 1992.
3) "Radioactive Waste Transport Minimisation Model : Data", R Greathead, R Davies, A R James, BAeSEMA Document Reference C2148/TR/2, January 1993.
4) "Radioactive Waste Transport Minimisation Model : Design Specification", R Greathead, A R James, BAeSEMA Document Reference C2148/TS/2, August 1992.
5) "Radioactive Waste Transport Minimisation Model : Users and Programmers Guide", R Davies, D Nichols, R Greathead, A R James, BAeSEMA Document Reference C2148/TU/1, June 1993.
6) "Radioactive Waste Transport Minimisation Model : Final Report", R Greathead, A R James, D Nichols, BAeSEMA Document Reference C2148/TR/3, November 1993.

---

[4] 1 MECU = 10^6 ECU.

Table 1 Illustrative Results - Scenarios with Maximum and Minimum Impacts for Complete Cycle

Impact Type	**Scenario**	**Total Impact**
Lowest Cost for Complete Cycle	Direct Disposal Orientated: All materials returned to country of origin: High UK flask storage capacity: Scenario minimised on transport Cost	14,467 MECU
Highest Cost for Complete Cycle	Reprocessing Orientated: Materials need not be returned to country of origin: Scenario minimised on transport Occupational Collective Dose	20,907 MECU
Lowest Occupational Collective Dose for Complete Cycle	Direct Disposal Orientated: All materials returned to country of origin: High UK flask storage capacity: Scenario minimised on transport Cost	324.9 man Sv
Highest Occupational Collective Dose for Complete Cycle	Reprocessing Orientated: All materials returned to country of origin: Scenario minimised on transport Cost	478.6 man Sv
Lowest Public Collective Dose for Complete Cycle	Direct Disposal Orientated: All materials returned to country of origin: High UK flask storage capacity: Scenario minimised on transport Cost	1181.0 mav Sv
Highest Public Collective Dose for Complete Cycle	Reprocessing Orientated: Materials need not be returned to country of origin: Scenario minimised on transport Occupational Collective Dose	2712.2 man Sv
Lowest Long Term Public Collective Dose for Complete Cycle	Direct Disposal Orientated: Materials need not be returned to country of origin: Scenario minimised on transport Occupational Collective Dose	797,558 man Sv
Highest Long Term Public Collective Dose for Complete Cycle	Direct Disposal Orientated: All materials returned to country of origin: High UK flask storage capacity: Scenario minimised on transport Cost	9,740,233 man Sv
Lowest Normalised Total for Complete Cycle	Direct Disposal Orientated: Materials need not be returned to country of origin: Scenario minimised on transport Occupational Collective Dose	3.064
Highest Normalise Total for Complete Cycle	Reprocessing: Materials need not be returned to country of origin: Storage capacities of key stores unlimited: Scenario minimised on transport Cost	4.366

Title:	Study of the retrievability of radioactive waste from a deep underground disposal facility
Contractor:	ECN
Contract no:	FI2W-CT92-0119
Duration of contract:	July 1992 to March 1994
Period covered:	January 1993 to December 1993
Project leader:	J. Prij

A. OBJECTIVES AND SCOPE

Retrievability of radioactive waste emplaced in a deep repository in a geological formation has received increasing attention during recent years. Arguments in favour of keeping waste retrievable are that more suitable sites might be found, that technological advances and/or reduced fission material availability would give an incentive for extracting valuable materials from the waste, or that an economically feasible way could be found to transmute long-lived radionuclides to short-lived ones.

The Member States of the European Community have not, up to date, included provisions for retrievability in their regulatory framework or in recommendations for disposal of waste. Other countries, like the United States, ask for an access to conditioned waste to be guaranteed for some decades.

Two conditions govern the option to retrieve radioactive waste packages from a deep repository:

- the packages should not be damaged (by pressure from the host rock, or due to corrosion, or other processes)
- the position of the package and the nuclide inventory must be known, and this knowledge has to be kept alive.

As those two conditions can be met for a few centuries at the best, provisions for retrievability makes sense only for up to 300 years (a widely used design limit for corrosion resistance of over-packs). During these few centuries, retrievability may be realised by keeping the access to the waste packages open, by maintaining in operational condition the access shafts and the main galleries. A second possibility is to dispose the waste in a suitable overpack and abandon the repository after backfilling, closing and sealing. In this case the waste must be re-mined from the surface. Although this re-mining will be very costly it is obvious that there will be a point in time, where the cost of keeping the repository in operating condition will be higher than those of re-mining from the surface to reach the waste packages in a closed repository. By way of illustration this break-even point is represented in Figure 1.

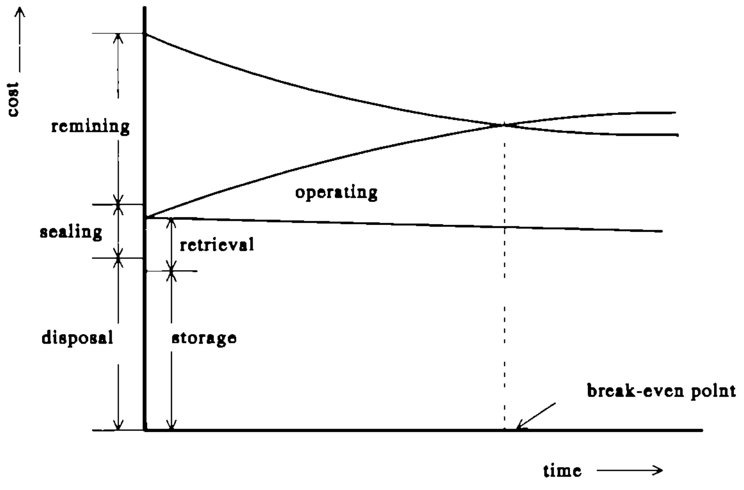


Figure 1 *Cost comparison for retrievable storage and re-mining after final disposal.*

The objective of this study is to collect existing data on retrievability of heat-generating long-lived waste and to produce an un-biased set of data on implications in terms of cost when deciding adoption of a retrievability strategy.

B. WORK PROGRAMME

Present state of the retrievability option

Existing information on retrievability of radioactive waste will be collected in EC-Member States and other countries having a nuclear energy production programme. This review will include regulations, recommendations and even opinions as long as they have been expressed in open literature or in open working documents of national or international bodies. Attention will be paid to aspects of non-proliferation for direct disposal of spent fuel being declared as waste.

Overview of expected modifications because of opting for retrievability

This overview will examine aspects concerning design and fabrication of waste packages, design of the repository, operation and maintenance of the repository and associated equipment, surveillance and control of the installation, and maintaining a documentation system when changing from final disposal to retrievability.
For these factors an estimate of additional costs and occupational exposure will be attempted. Evaluations about radiation protection and long term safety to the environment will be made without carrying out detailed performance assessment calculations.

Detailed evaluations for a reference disposal scenario

A detailed evaluation under realistic conditions will be made in performing a comparison between the costs of retrieval of the waste from a suitable deep underground repository (including the annual costs of keeping the repository open) and the costs of re-mining the waste from a final deep underground repository (including the costs of closing and sealing).

The **assumptions** and **boundary conditions** are:

- The study is restricted to HAW (high level radioactive waste). The quantity of HAW is based on 20 GW installed nuclear power (in standard LWR NPP's) operating for a period of 30 years (scenario and data as in studies /1/ and /2/).
- Two types of waste management strategies will be considered:
  - . direct disposal of all spent fuel
  - . disposal of the HAW from reprocessing all the spent fuel
- One loading sequence of the waste into the repository will be considered.
- The disposal concepts will be chosen based on current state of the mining and disposal techniques.
- Three types of host rock will be considered: clay, granite and rock salt.
- One retrieving and one re-mining strategy will be selected.

The **activities** to be carried out are:

- select feasible **final disposal** and **retrievable storage** concepts for each of the three host rock formations,
- assess the feasibility of the selected options: concise safety evaluations will be performed with regard to radiation protection and long term safety to the environment,
- select a feasible **retrieval** and **re-mining** concept for each of the three host rock formations,
- assess the feasibility of retrieval for the concepts chosen with respect to maximum temperatures and stability of the mine-building after retrieval,
- determine the total costs of each option selected:
  - . for the retrievable options the total costs are the annual costs to guarantee the retrievability, and the costs of the retrieval
  - . for the final disposal concepts selected the total costs are the costs of closing and the costs of re-mining.
- evaluate the costs in present day value and determine for each of the host rocks the break-even point at which re-mining is more favourable from an economical point of view. This evaluation will be based on the present-day society and present day estimates of the economical parameters such as interest rates.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

An evaluation has been made of several methods for the actual retrieval of the waste from a closed and backfilled storage facility. Based on cost, proven technology, and safety for the environment and the personnel, a method of retrieval has been selected. For all three host rock types a detailed planning of the underground facilities has been made and estimates of the cost for each stage in the planning are being made. The complete break down of the planning has been produced as a set of computer worksheets, linked together to form an integrated and flexible tool. For the repository in rock salt the economical evaluation has been finished and the conversion of the worksheets to the repository in clay and granite is being carried out.

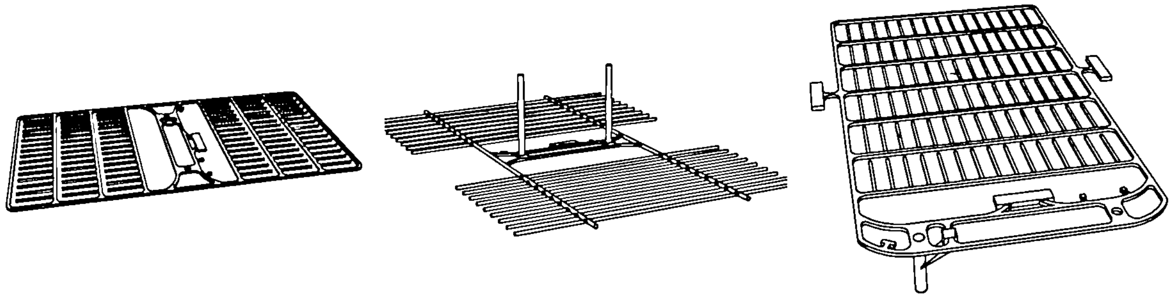
Progress and results

The method selected for the actual retrieval of the heavy waste container has been denoted as 'drilling and pulling'. This method comprises the following steps:

- Determine the exact position of the waste container using radar sonar or careful exploration drilling.
- Remove the backfill in front of the waste container by means of a continuous miner or road header.
- Once the front of the container has been reached a small layer of backfill around the container is removed by drilling a series of holes around the container leaving only a small part below the container as a support.
- Pull the container on a transport vehicle by means of hydraulic rams attached to pulling lugs on the container or by means of an artificial clamping device.

This method has been selected mainly because it requires minimal unprotected labour in the vicinity of the hot container and all parts of the operation can be considered as proven technology.

Based on this retrieval method and on the concept of storage of the waste galleries the layout of the repository in the three host rock formations has been determined. The selected layout for the three cases is represented in Figure 2.



Granite Clay Rock salt

Figure 2 *Lay-out of the different repository concepts*

In granite and clay the repository consists of a system of main and cross galleries. From the cross galleries the disposal tunnels will be driven. In the salt mine the mined salt can be used directly as backfill medium and therefore in the salt option the emplacement of the waste will start during construction of the repository. In this way the salt mined in the latter phase of construction can be used as backfill in the earlier galleries and expensive shaft transport and surface storage is avoided. For this reasons underground storage rooms have been planned in the salt repository.
In the case of a repository in clay all underground rooms have to be concrete lined. This implies that underground room is expensive compared to granite and salt, and that special tunnelling machines have to be used, preferably operating from within a shield to avoid instability of the newly mined surface. The economics of this method of tunnelling requires long straight tunnels because crossings and angles are expensive. Therefore the repository in clay consists of main galleries only, from which long cross galleries will be driven in which the waste will be stored.

The economical evaluation of the results for a repository in clay shows that the position of break even point is very sensitive for the real return rate.
Therefore the preliminary results for a repository in rock salt are presented in Figure 3 as a graph giving the break-even year as a function of the real return rate.

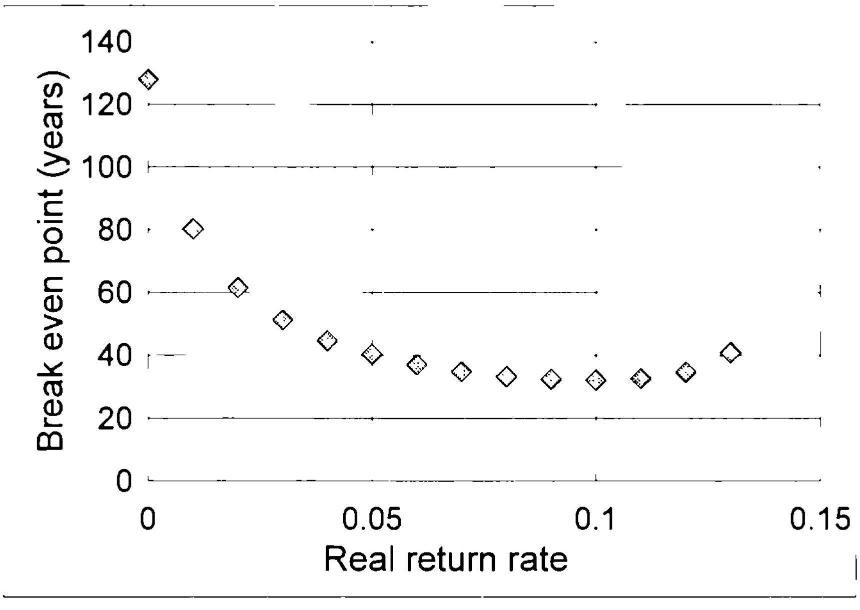


Figure 3 Break even year as a function of the real return rate.

References

/1/ J. Malherbe: Management of radioactive waste from reprocessing including disposal aspects, EUR-13116 (1991), Office for Official Publications of the EC, Luxembourg.

/2/ P. Ashton et al: Analysis of scenarios for the direct disposal of spent nuclear fuel-disposal conditions as expected in Germany, EUR-12953 (1990), Office for Official Publications of the EC, Luxembourg.

ASSESSMENT AND PROPOSAL FOR ACTIVITY LIMITS FOR RELEASE OF VERY LOW-LEVEL RADIOACTIVE WASTE TO LANDFILLS

Contractor	: CEA/IPSN, France, and ONDRAF, Belgium
Contract n°	: FI2W-CT90-0060
Duration of contracts	: April 1991 - June 1993
Additional program	: June 1993 - December 1994
Period convered	: 1 January 1993 - 31 December 1993
Project Leader	: Ph. GUETAT (CEA/IPSN)

A. OBJECTIVES AND SCOPE

In the frame of studies dealing with low level wastes destinations, the project aims to establish acceptance criteria for municipal and industrial landfill.
Correspondances between levels of exposure and levels of radioactivity will be established.
From this work, it will be possible to derive activity concentration and surface activity levels for acceptance criteria to landfill disposal.
A complementary study will investigate the implications of disposal management in a specific landfill which receive only very low level radioactive waste, and will evaluate the economic aspects of this approach.

B. WORK PROGRAMME

The initial program included :

-Phase 1 : Analysis of landfill disposal practices of industrial and municipal waste. A particular attention will be paid to the regulatory context and to the conditions encountered in the different installations.

Phase 2 : Development of a radioprotection code CERISE, in order to establish the relations between exposure and radioactivity of waste, including a data bank of dose conversion factors.
Evaluation of the exposure of workers and public resulting from the water pathway using the code GEOLE (geosphere) and the code ABRICOT (biosphere).

Phase 3 : Establishment of the correspondance between exposure and activity concentration in the one hand or surface activity in the other hand.
Proposal of levels of radioactivity for the waste acceptance in the different types of landfill and for different dose criteria.
Final report.

The additional program includes :

-Review of the existing information of the volumes and radionuclides content in very low level radioactive waste,
-Review of operating data of a landfill including working conditions,
-Evaluation of radiological impact and determination of acceptance criteria in the case of landfill disposal of very low level radioactive waste,
-Economical investigation and determination of monitoring procedures.

C.PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The initial program is achieved and final report is definitely accepted by CEC.

The additional program is beginning but only few new data, concerning quantities and isotopic composition, have been get from fuel companies. Some preliminary calculations were performed.

Progress and results

Initial program.

The scenarios presented by the annual progress report 1993 have been selected for the calculation. In all cases the exposure parameters have been determined on the basis of practical operating procedures and measurements of dust concentration at different workplaces. Computer codes CERISE, GEOLE AND ABRICOT have been developped to assess the radiological impact of landfill sites.

The radioactivity concentration and the surface contamination derived for landfill disposal are given in tables 1 and 2 (for a selected number of radionuclides only). The results are also presented in figures 1 for the radioactivity concentration levels and in figures 2 for the surface contamination levels.

It is easy to see two groups of radionuclides for which the levels are lower :

- radionuclides with high gamma energy, such as Na22, Co60, Ag110m ; the limiting scenarios are those involving external irradiation .
- alpha emitters, such as Pu239 and Am241 ; the limiting scenarios are those where inhalation is involved.

For the other radionuclides, the derived levels are very variable, and there is multiple dominant pathways.

The derived levels in terms of surface contamination are always higher than those in terms of radioactivity concentration (sometimes an order of magnitude).

The derived levels for Belgian and French landfills (water pathway not taken into account) are comparable, and in most cases differ from no more than a factor of 10.

The water pathway is not limiting for the Belgian landfill. For the french landfill, it only seems to be significant for tritium.

Additional program.

For the complementary program on specific landfill, the work carried out include :

- Determination of dose limits to be taken into account for the calculation,
- Review of new scenarios to be considered ,
- Selection of input parameters to be used in computer codes.

Some preliminary calculations have been carried out.

List of publications

Ph.GUETAT (CEA/IPSN), L.BAEKELANDT (ONDRAF)
CECcontract N° FI2W-CT90 00 60.Annual Progress Report 1992 (EUR 15132)

J.M.ASSELINEAU, Ph.GUETAT, Ph.RENAUD (CEA/IPSN), L.BAEKELANDT, B SKA (ONDRAF/NIRAS)
CECcontract N° FI2W-CT90 00 60.Final report. October 1993.

TABLE 1

Specific activity level, in Bq/g.

	Belgian Results		French Results		
Radionuclides	Class 1	Class 3	Class 1	large Class 2	small Class 2
H3	8,2E+05	2,5E+06	1,3E+05	1,3E+05	1,3E+04
C14	7,1E+03	2,1E+04	3,6E+03	1,1E+04	1,1E+03
Na22	1,9E+00	2,6E+00	3,0E+00	8,9E+00	3,6E+00
P32	1,9E+03	2,5E+04	1,1E+04	2,6E+04	7,8E+03
S35	1,4E+04	1,4E+05	1,9E+05	7,8E+04	2,4E+04
Cl36	3,1E+03	3,1E+04	1,1E+04	7,8E+03	2,5E+03
Mn54	5,0E+00	6,7E+00	7,7E+00	2,3E+01	9,2E+00
Fe55	1,8E+05	1,4E+06	1,1E+06	3,3E+06	4,2E+05
Co60	1,6E+00	2,2E+00	2,5E+00	7,5E+00	3,0E+00
Ni59	6,4E+04	6,4E+05	3,8E+05	1,1E+06	1,1E+05
Ni63	3,0E+05	1,2E+06	1,7E+05	4,4E+05	4,4E+04
Sr90+	2,3E+02	6,8E+02	7,0E+01	1,3E+02	1,3E+01
Nb94	2,6E+00	3,5E+00	4,1E+00	1,2E+01	3,2E+00
Tc99m	1,7E+03	2,3E+03	4,2E+04	2,0E+03	3,1E+03
Tc99	2,4E+02	7,1E+02	1,2E+02	3,6E+02	3,6E+01
Ru106+	2,1E+01	2,9E+01	3,3E+01	9,6E+01	3,8E+01
Ag108m+	2,5E+00	3,3E+00	3,8E+00	1,1E+01	3,1E+00
Sb125+	1,1E+01	1,4E+01	1,7E+01	5,0E+01	2,0E+01
I125	2,6E+03	5,6E+03	3,6E+03	3,6E+03	1,2E+03
I129	8,3E+02	2,5E+03	4,3E+02	7,0E+02	1,3E+02
I131	1,4E+01	1,8E+01	2,3E+01	5,9E+01	2,5E+01
Cs134	2,7E+00	3,6E+00	4,2E+00	1,3E+01	5,0E+00
Cs137+	7,6E+00	1,0E+01	1,2E+01	3,6E+01	1,2E+01
Pm147	9,4E+03	9,4E+04	6,8E+04	2,0E+05	2,8E+04
Sm151	1,5E+05	1,9E+05	2,3E+05	6,6E+05	7,9E+04
Eu152	3,0E+00	4,0E+00	4,6E+00	1,4E+01	5,6E+00
Eu154	3,4E+00	4,5E+00	5,3E+00	1,6E+01	6,3E+00
Ra226+	1,6E+00	2,1E+00	2,4E+00	7,3E+00	1,9E+00
U235+	1,7E+01	2,0E+01	2,4E+01	7,0E+01	1,1E+01
U238+	2,4E+01	2,6E+01	3,3E+01	9,5E+01	1,2E+01
Np237+	8,9E+00	1,0E+01	1,3E+01	3,6E+01	5,4E+00
Pu238	1,4E+01	1,4E+01	1,9E+01	5,2E+01	6,1E+00
Pu239+	1,4E+01	1,4E+01	1,9E+01	5,2E+01	6,1E+00
Pu240	1,4E+01	1,4E+01	1,9E+01	5,2E+01	6,1E+00
Pu241+	9,1E+02	9,6E+02	1,2E+03	3,5E+03	4,1E+02
Am241	1,4E+01	1,4E+01	1,8E+01	5,2E+01	6,1E+00
Cm244	2,3E+01	2,4E+01	3,1E+01	8,7E+01	1,0E+01

TABLE 2

Surface activity level, in Bq/cm²

	Belgian Results		French Results		
Radionuclides	Class 1	Class 3	Class 1	large Class 2	small Class 2
H3	9,1E+05	9,1E+06	5,56E+05	4,2E+06	8,3E+05
C14	1,1E+03	2,2E+03	2,92E+03	8,8E+03	1,8E+03
Na22	1,4E+01	1,9E+01	4,01E+01	1,2E+02	4,6E+01
P32	5,9E+01	6,9E+01	3,64E+02	1,0E+03	2,5E+02
S35	1,1E+03	2,3E+03	3,03E+03	9,0E+03	1,8E+03
Cl36	1,1E+02	1,4E+02	7,06E+02	2,1E+03	4,4E+02
Mn54	3,5E+01	4,7E+01	1,05E+02	3,1E+02	1,2E+02
Fe55	4,5E+03	5,3E+03	3,68E+04	1,1E+05	2,3E+04
Co60	1,3E+01	1,7E+01	3,75E+01	1,1E+02	4,3E+01
Ni59	1,2E+03	1,3E+03	1,31E+04	3,9E+04	8,1E+03
Ni63	3,4E+04	9,8E+04	4,99E+04	2,2E+05	4,4E+04
Sr90+	3,5E+01	4,5E+01	2,08E+02	6,2E+02	1,5E+02
Nb94	1,9E+01	2,5E+01	5,26E+01	1,6E+02	6,0E+01
Tc99m	5,2E+03	6,9E+03	2,19E+05	1,0E+04	1,5E+04
Tc99	5,6E+02	1,1E+03	1,64E+03	4,9E+03	9,8E+02
Ru106+	3,4E+01	5,0E+01	1,50E+02	4,5E+02	1,3E+02
Ag108m+	1,6E+01	2,1E+01	5,21E+01	1,6E+02	6,1E+01
Sb125+	6,5E+01	8,7E+01	1,73E+02	5,2E+02	1,8E+02
I125	5,6E+02	9,8E+02	5,67E+02	3,0E+03	6,9E+02
I129	1,5E+02	9,8E+02	1,10E+02	7,3E+02	1,5E+02
I131	7,3E+01	1,1E+02	1,82E+02	4,8E+02	1,5E+02
Cs134	1,9E+01	2,5E+01	5,14E+01	1,5E+02	5,7E+01
Cs137+	5,1E+01	6,8E+01	1,17E+02	3,5E+02	1,1E+02
Pm147	7,9E+02	1,6E+03	2,14E+03	6,4E+03	1,3E+03
Sm151	2,5E+04	6,5E+04	4,72E+04	1,7E+05	3,4E+04
Eu152	2,1E+01	2,8E+01	7,41E+01	2,2E+02	8,3E+01
Eu154	2,5E+01	3,3E+01	6,48E+01	1,9E+02	7,0E+01
Ra226+	1,2E+01	1,6E+01	3,19E+01	9,6E+01	2,8E+01
U235+	1,2E+02	2,1E+02	2,41E+02	7,2E+02	1,9E+02
U238+	4,3E+01	6,1E+01	2,04E+02	6,1E+02	1,5E+02
Np237+	2,2E+01	1,4E+02	1,65E+01	1,1E+02	2,2E+01
Pu238	3,6E+01	3,6E+02	2,22E+01	1,7E+02	3,3E+01
Pu239+	3,6E+01	3,6E+02	2,22E+01	1,7E+02	3,3E+01
Pu240	3,6E+01	3,6E+02	2,22E+01	1,7E+02	3,3E+01
Pu241+	1,8E+03	1,8E+04	1,11E+03	8,3E+03	1,7E+03
Am241	2,7E+01	2,5E+02	1,67E+01	1,2E+02	2,5E+01
Cm244	5,4E+01	5,4E+02	3,33E+01	2,5E+02	5,0E+01

FIGURE 1

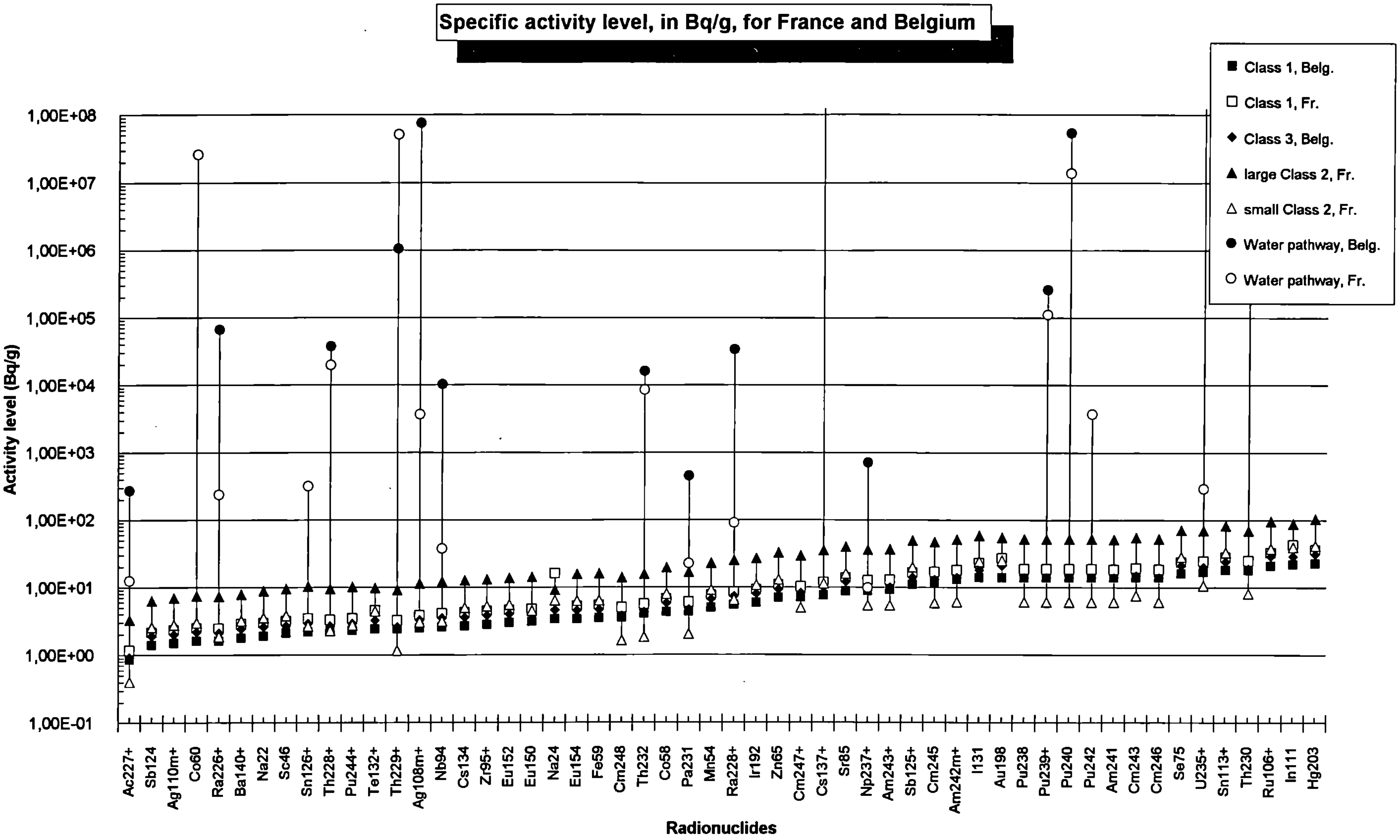

Specific activity level, in Bq/g, for France and Belgium
■ Class 1, Belg.
□ Class 1, Fr.
◆ Class 3, Belg.
▲ large Class 2, Fr.
△ small Class 2, Fr.
● Water pathway, Belg.
○ Water pathway, Fr.
Activity level (Bq/g)
1,00E+08
1,00E+07
1,00E+06
1,00E+05
1,00E+04
1,00E+03
1,00E+02
1,00E+01
1,00E+00
1,00E-01
Ac227+
Sb124
Ag110m+
Co60
Ra226+
Ba140+
Na22
Sc46
Sn126+
Th228+
Pu244+
Te132+
Th229+
Ag108m+
Nb94
Cs134
Zr95+
Eu152
Eu150
Na24
Eu154
Fe59
Cm248
Th232
Co58
Pa231
Mn54
Ra228+
Ir192
Zn65
Cm247+
Cs137+
Sr85
Np237+
Am243+
Sb125+
Cm245
Am242m+
I131
Au198
Pu238
Pu239+
Pu240
Pu242
Am241
Cm243
Cm246
Se75
U235+
Sn113+
Th230
Ru106+
In111
Hg203
Radionuclides

FIGURE 1 (cont.)

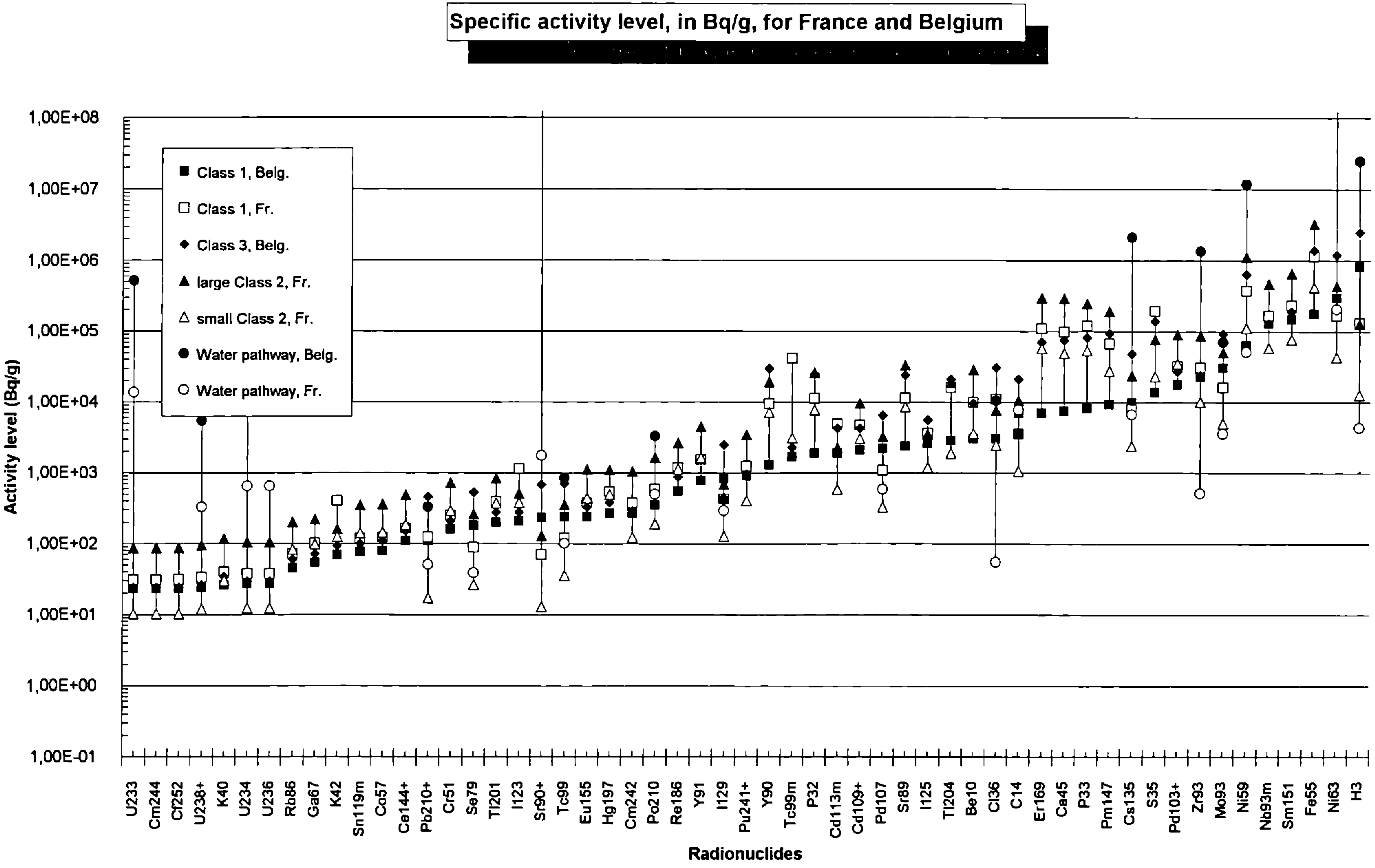


FIGURE 2

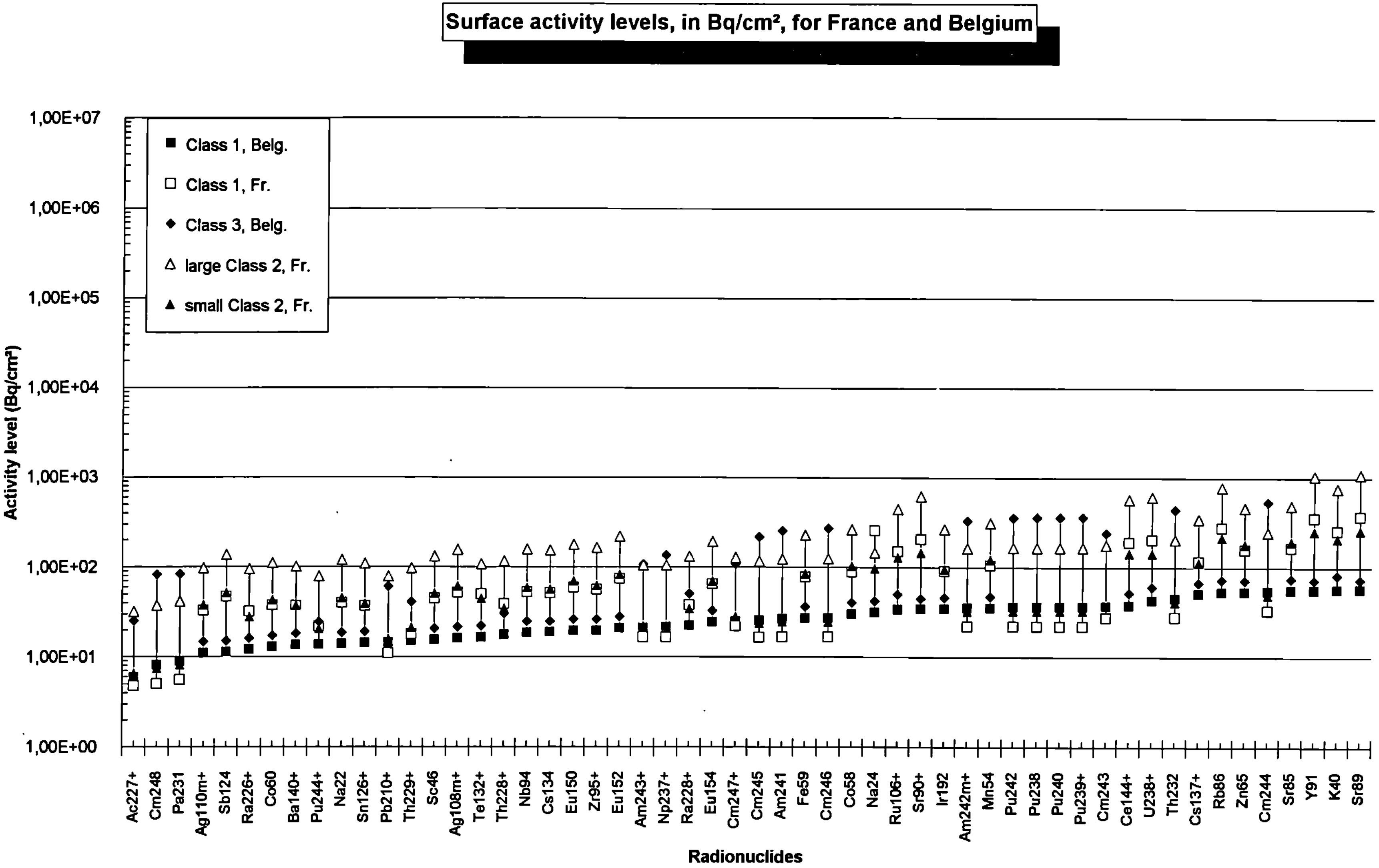
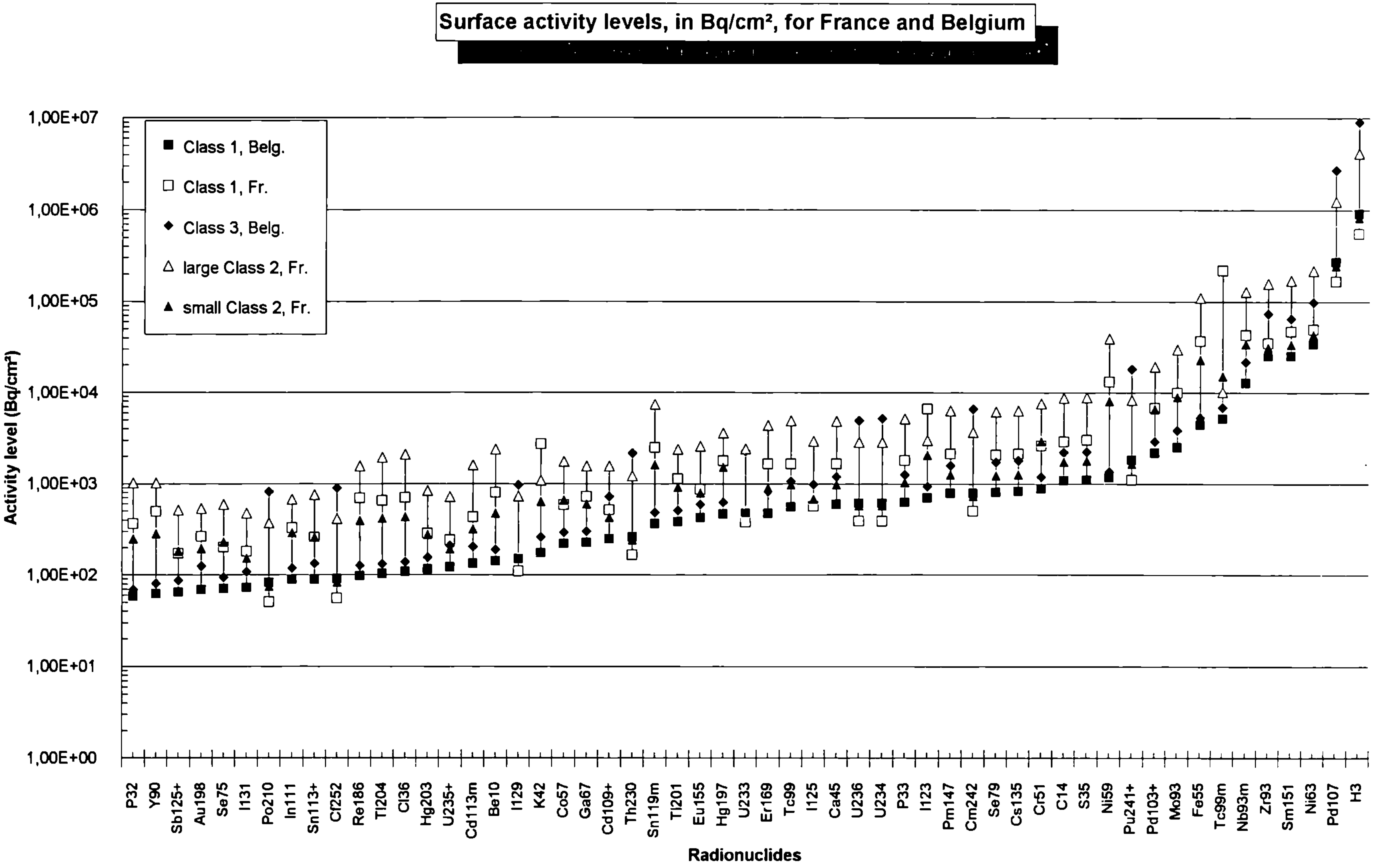

Surface activity levels, in Bq/cm², for France and Belgium
■ Class 1, Belg.
□ Class 1, Fr.
◆ Class 3, Belg.
△ large Class 2, Fr.
▲ small Class 2, Fr.
Activity level (Bq/cm²)
1,00E+07
1,00E+06
1,00E+05
1,00E+04
1,00E+03
1,00E+02
1,00E+01
1,00E+00
Ac227+
Cm248
Pa231
Ag110m+
Sb124
Ra226+
Co60
Ba140+
Pu244+
Na22
Sn126+
Pb210+
Th229+
Sc46
Ag108m+
Te132+
Th228+
Nb94
Cs134
Eu150
Zr95+
Eu152
Am243+
Np237+
Ra228+
Eu154
Cm247+
Cm245
Am241
Fe59
Cm246
Co58
Na24
Ru106+
Sr90+
Ir192
Am242m+
Mn54
Pu242
Pu238
Pu240
Pu239+
Cm243
Ce144+
U238+
Th232
Cs137+
Rb86
Zn65
Cm244
Sr85
Y91
K40
Sr89
Radionuclides

FIGURE 2 (cont.)



DEFINITION OF REFERENCE LEVEL FOR EXEMPTION OF WASTES SUITABLE FOR INCINERATION

Contractor : CEA, IPSN/CEN-FAR, France, and
EMPRESARIOS AGRUPADOS, MADRID, Espagne
Contract n° : FI2W-CT90-0066
Duration of contract : 1 January 1991 - 30 June 1993
Period convered : 1 January 1993 - 31 December 1993
Project Leader : O. CAHUZAC (C) - F. ANDALUZ (1)

A. OBJECTIVES AND SCOPE

In the frame of studies dealing with low level wastes destinations, the project aims to give correlation between waste activity levels and the individual doses due to their incineration.

The study for establishing radiological protection criteria in the case of incineration of very low radioactive waste involves :

- The identification of possible waste management scenarios includes : sources terms, incinerator data, composition of waste streams, mode of disposal or reuse of the residues.
- The establishment of dose levels correspondes to incineration of very low radioactive burnable material in a classical installation.
- The establishment of environmental pathways and dose assessments for each scenario defined.

From this work, it will be possible to derive activity concentrations corresponding to acceptable level for incineration without special precaution.

IPSN (France) and EA (Spain) collaborate to this study, EA investigates specially biological and organic wastes produced in Spain.

B. WORK PROGRAMME

Four steps are looking for :

1. Data Acquisition and Analysis :

1.1 Data collect and analysis of base information of incinerator types, processes and working conditions.
1.2 Definition of the characteristics of burnable very low level radioactive wastes and excepted quantities.

2. Analysis

Sampling and dust in situ measurement.

3. Evaluation of the radiological impact :

3.1. Definition of scenarios corresponding to significant pathways for workers and members of public.
3.2 Adaptation of computer code CERISE to specific case of incineration.

3.3 Assessment of individual doses for the workers and radiological impact to the public as a function of quantities, waste activities and, incinerator and site characteristics.

4. Correlation between activity levels and individual doses

4.1. Individual doses caused by unitary activity concentration of the waste in the considered scenarios.

4.2 Determination of the wastes' average activity corresponding to the individual dose clearance level.

4.3 Determination of practical limits by groups of the nuclides.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The project is carried out during 1992 has been focused on the completion of item 3 and 4. A draft version of the final report has been submitted for the comment of CEC.

Progress and results

In order to evaluate the possibility of very low level waste incineration, two different approaches have been investigated :

A- The first one studied by **IPSN** is a generic study which can be applied to any type of incinerators in the French context. It consists in determining the derived activity concentrations for very low level wastes to be incinerated without any conditions in any non nuclear incinerator.

Detail results per scenario are presented in the form of an effective individual annual dose for a unit specific activity of the incinerated waste corresponding to the different steps of incineration procedures and disposal or reuse of incineration byproducts. The activity concentration derived in the limitative scenarios has been evaluated for induced annual doses of 10 μSv for the population and 50 μSv for workers.

The results are listed in **figure 1** for the four types of incinerators :

- household refuse incinerator,
- industrial waste incinerator,
- cement plant incinerator,
- hospital refuse incinerator.

This approach allows applications for all waste types and can remain valid for a relative long time. This method may be, in some cases, more drastic than necessary.

B- The second one carried out by **Empresarios Agrupados** is a specific study applied to biological and organic waste incinerated in an hospital incinerator in the Spanish context. It is based on an impact assessment in conditions as realistic as possible but nevertheless conservative. realistic but conservative situation. The advantage is to be consistent with the present practice. The application is only valid for the radionuclides presently used.

The **table 2** shows the activity concentration (Bq/g) derived for each type of radionuclide in the limitative scenarios, calculated for a reference annualdose level of 10 μSv and 50 μSv.

In **Table 1,** we can see the beta emitters H-3, C-14, P-32 and S-35 cause maximum doses to individuals residing in the incinerator surroundings ; in this scenario, the main exposure pathway consists of contaminated food ingestion.

The rest of the radionuclides causes maximum doses to the workers of the incinerator. The ash worker is the most affected.

The activity concentration derived from the beta emitters range between 4 and 5 orders of magnitude.
The activity concentration derived from the rest of the nuclides range between 2 and 3 orders of magnitude with the exception of the values 2.18E+4 and 1.10E+12 which correspond to the I125 and Tc-99m radionuclides, respectively.

According to the spectrum, the total activity concentration concerning biologic solids and organic liquids are calculated : the results can be seen in **table 2**.

figure 1 : Specific radioactivity clearance level for four types of incinerators

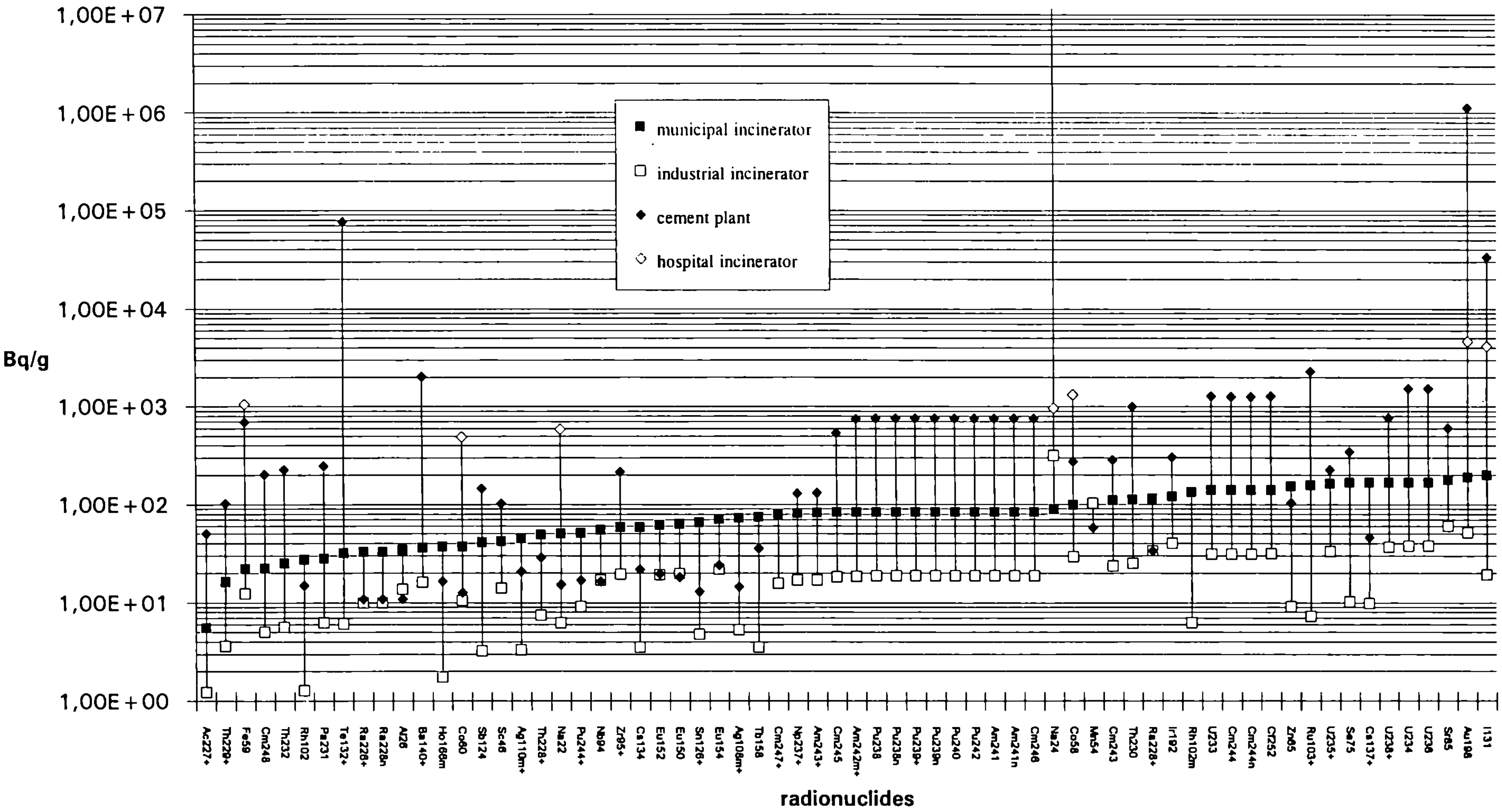


figure 1 (cont.) : Specific radioactivity clearance level for four types of incinerators

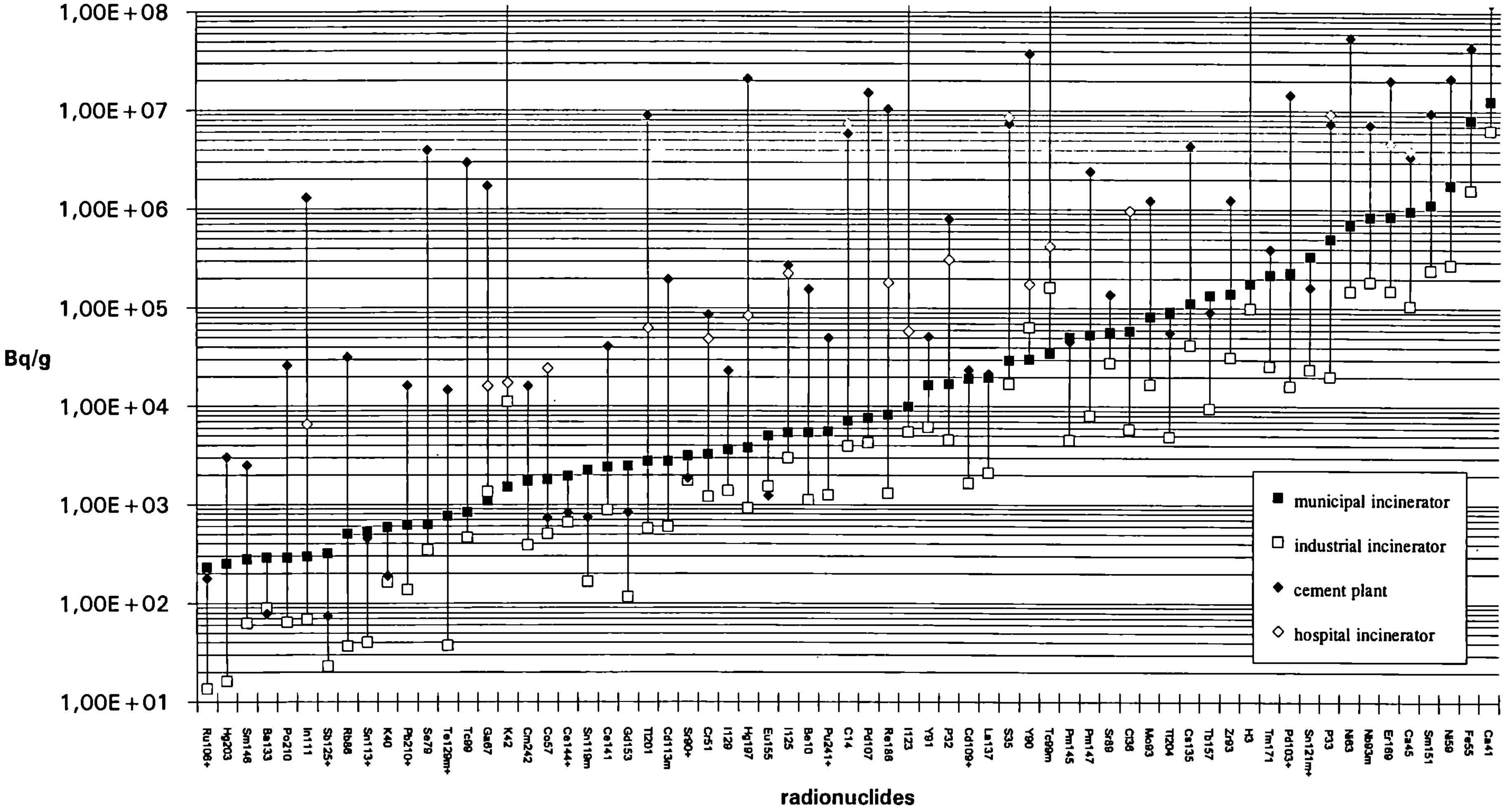


TABLE 1

Doses (Sv/a) caused by the incineration of biological solids and organic liquids (containing 1 Bq/g) in the different scenarios of the practice and derived activities (Bq/g)

ANNUAL DOSES IN THE SELECTED SCENARIOS (Sv/a)																
	furnace loader			ash worker						Public of the incineration surroundings						
Nuclide	ext.expos.	inhalation	total	ext.expos.	inhalation	hands	face	sec.ing.	total	ext.expos.*	inhalat.	ingestion	total	limitative dose	limitative scenario	derived concentr. (Bq/g)
H3	0,00E+00	7,15E-14	7.15E-14	0,00E+00	1.81E-13	0,00E+00	0,00E+00	3.97E-14	2.21E-13	2.26E-12	2.26E-12	1.19E-11	1.64E-11	1.64E-11	public	6.09E+05
C14	0,00E+00	2.23E-12	2.23E-12	0,00E+00	5.64E-12	0,00E+00	7.97E-11	1.24E-12	8.66E-11	0,00E+00	3.58E-13	9.54E-10	9.54E-10	9.54E-10	public	1.05E+04
P32	0,00E+00	1.21E-11	1.21E-11	0,00E+00	5.16E-11	6.65E-10	2.89E-10	6.85E-12	1.01E-09	7.27E-12	1.71E-11	5.03E-10	5.27E-10	5.27E-10	public	1.90E+04
S35	0,00E+00	2.56E-12	2.56E-12	0,00E+00	1.26E-11	0,00E+00	1.47E-10	1.22E-12	1.61E-10	0,00E+00	3.60E-12	7.71E-11	8.07E-11	8.07E-11	public	1.24E+05
Ca45	9.31E-17	6.95E-12	6.95E-12	1.26E-16	3.47E-11	3.69E-12	2.70E-10	3.76E-12	3,12E-10	0,00E+00	4.88E-13	1.17E-11	1.22E-11	3.12E-10	ash worker	1.60E+05
Sc46	3.10E-07	3.00E-11	3.10E-07	4.15E-07	1.48E-10	1.51E-10	3.34E-10	8.10E-12	4.16E-07	5.49E-11	2.11E-12	2.56E-11	8.26E-11	4.16E-07	ash worker	1.20E+02
Cr51	4.12E-09	3.27E-13	4.12E-09	5.19E-09	1.52E-12	1.02E-11	2.04E-12	1.80E-13	5.20E-09	3.01E-13	2.30E-14	6.04E-13	9.28E-13	5.20E-09	ash worker	9.61E+03
Co57	1.74E-08	1.02E-11	1.74E-08	2.37E-08	5.10E-11	3.44E-11	2.58E-11	1.50E-11	2.38E-08	8.72E-12	7.12E-13	4.67E-11	5.61E-11	2.38E-08	ash worker	2.10E+03
Co58	1.45E-07	1.85E-11	1.45E-07	1.93E-07	9.07E-11	9.55E-11	7.65E-11	2.70E-11	1.93E-07	2.35E-11	1.31E-12	8.62E-11	1.11E-10	1.93E-07	ash worker	2.59E+02
Fe59	1.76E-07	1.35E-11	1.76E-07	2.29E-07	6.50E-11	1.27E-10	3.00E-10	1.16E-11	2.30E-07	1.65E-11	9.55E-12	3.77E-11	5.52E-11	2.30E-07	ash worker	2.18E+02
Sr85	7.33E-08	4.79E-12	7.33E-08	9.73E-08	2.34E-11	4.37E-11	1.01E-11	2.09E-12	9.74E-08	1.19E-11	3.36E-13	6.67E-12	1.89E-11	9,74E-08	ash worker	5.13E+02
Tc99m	4.55E-17	1.07E-22	4.55E-17	3.83E-21	3.30E-26	1.01E-24	8.90E-24	1.38E-26	3.84E-21	5.20E-23	1.15E-23	1.07E-21	1.13E-21	4.55E-17	ash worker	1.10E+12
Ru103	5.64E-08	8.79E-12	5.64E-08	7.31E-08	4.19E-11	4.24E-10	1.88E-10	4.04E-12	7.38E-08	6.59E-12	6.18E-13	1.32E-11	2.04E-11	7.38E-08	ash worker	6.78E+02
In111	1.03E-08	1.63E-13	1.03E-08	5.96E-09	3.47E-13	2.96E-12	6.51E-12	1.24E-13	5.97E-09	8.26E-14	1.18E-14	9.36E-13	1.03E-12	1.03E-08	ash worker	4.85E+03
I125	1.54E-09	3.52E-11	1.58E-09	2.04E-09	1.71E-10	1.64E-11	3.28E-12	5.87E-11	2.29E-09	1.03E-10	4.97E-12	3.76E-10	4.84E-10	2.29E-09	ash worker	2.18E+04
I131	3.15E-08	2.78E-11	3.15E-08	3.20E-08	1.04E-10	1.28E-10	1.70E-10	3.87E-11	3.24E-08	1.36E-10	3.98E-12	3.27E-10	4.67E-10	3.24E-08	ash worker	1.54E+03
Ce141	4.66E-09	8.90E-12	4.67E-09	5.96E-09	4.18E-11	1.21E-09	4.03E-10	4.24E-12	7.62E-09	9.33E-13	6.27E-12	1.40E-11	1.56E-11	7.62E-09	ash worker	6.56E+03

*for H3 this is the immersion dose

TABLE 2

TOTAL DERIVED ACTIVITY CONCENTRATION (L_m) FOR BIOLOGICAL SOLIDS AND ORGANIC LIQUIDS (Bq/g)

BIOLOGIC SOLIDS

des (i)	g at source $(a'_m)_m/a_t$ =	f_i	ed concentration (L'_m)	L'_m = k_i for biol	ogic solid ($1/\Sigma k_i$)
	578	,97E-01	6,09E+05	,88E-07	
	48	,47E-02	1,05E+04	,35E-06	
	1166	,01E-01	1,90E+04	,16E-05	
	12	,19E-03	1,24E+05	,99E-08	
	0,8	,12E-04	1,20E+02	,43E-06	
	0,8	,12E-04	9,61E+03	,29E-08	
	31	,59E-02	2,18E+02	,29E-05	
	0,8	,12E-04	5,13E+02	,03E-07	
	0,8	,12E-04	6,78E+02	,08E-07	
	5	,58E-03	2,18E+04	,18E-07	
	96	,94E-02	1,54E+03	,21E-05	
	0,8	,12E-04	6,56E+03	,28E-08	
	1940 (a_t)	,99E-01		,45E-04	**6,92E+03**

ORGANIC LIQUID

des (i)	g at source $(a'_m)_m/a_t$ =	f_i	ed concentration (L'_m)	L'_m = k_i for biol	ogic solid ($1/\Sigma k_i$)
	454	,99E-01	6,09E+05	,19E-07	
	165	,81E-01	1,05E+04	,73E-05	
	19	,09E-02	1,90E+04	,10E-06	
	250	,75E-01	1,24E+05	,21E-06	
	3	,30E-03	1,60E+05	,06E-08	
	2	,20E-03	9,61E+03	,29E-07	
	0,2	,20E-04	2,10E+03	,05E-07	
	0,2	,20E-04	2,59E+02	,48E-07	
	0,03	,30E-05	2,18E+02	,51E-07	
	15	,65E-02	1,10E+12	,50E-14	
	2	,20E-03	4,85E+03	,53E-07	
	910,43	,00E+00		,32E-05	**4,31E+04**

Title:	Comparison of Safety Assessment Methods for Toxic and Radioactive Wastes
Contractor:	Intera Information Technologies Ltd.
Contract No.:	FI2W-CT90-0042
Duration of Contract:	March 1991 - December 1994
Period Covered:	January 1993 - December 1993
Project Leader	Richard Little (Intera) and Carlos Torres (IMA/CIEMAT)

A. Objectives and scope

The need for safety assessments of waste disposal stems not only from the increasing implementation of regulations requiring the assessment of environmental effects but also from the more general need to justify decisions on protection requirements. Just as waste disposal has become more technologically based, through the application of more highly engineered design concepts and through more rigorous and specific limitations on the types and quantities of the waste disposed, so too must the assessment procedure become more sophisticated. It is the overall aim of this study to improve the predictive modelling capacity for post-disposal safety assessments of land-based disposal facilities through the development and testing of a comprehensive yet practicable assessment framework.

Within this project the disposal of toxic, radioactive and mixed hazardous wastes is considered. The term "toxic wastes" is interpreted broadly to include any kind of liquid or solid non-radioactive waste which could give rise to some detrimental environmental effects, post-disposal. The associated work programme is being undertaken jointly by Intera Information Technologies, Environmental Division, United Kingdom, and Instituto de Medio Ambiente of Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (IMA/CIEMAT), Spain.

B. Work programme

B.1. To review the different waste types and to compare and contrast concepts and methods adopted for their land based disposal.

B.2. To review the kinds of criteria adopted for authorising disposals, in so far as they relate to post-disposal environmental impact.

B.3. To review the different assessment methods which have been used to assess post-disposal environmental impacts and to evaluate the advantages and disadvantages of alternative assessment methods.

B.4. To identify the types of post-disposal impact which might arise and use a scenario analysis, according to a well defined procedure, to determine how such impacts may arise.

B.5. To develop and enhance a practicable framework for assessment of post-disposal safety for disposal of wastes to land-based facilities taking full account of existing methodological developments.

B.6. To test the application of the framework on a representative set of example disposals. Illustrations will reflect realistic problems of environmental assessment.

C. Progress of work and obtained results

State of advancement

During 1993, the final work programme item of the original contract has been completed. It involved the testing of the assessment framework (the Safety Assessment Comparison (SACO) Framework (Figure 1)) on the representative set of example disposals /1/. In addition a temporal and monetary extension to the existing contract has been agreed with the Commission. The extension allows for the further development and testing of the SACO framework. Development work includes the identification and collation of generic information to support the framework, the enhancement of scenario analysis procedures used within the framework, and the development of the SACO assessment code. The enhanced framework will be tested on a new set of as realistic as possible disposals using data from shallow and deep disposal systems, and uranium mill tailings. Work under the extension will be undertaken during 1994.

Progress and results

1. Testing the Assessment Framework (B.6.)

It was decided that the following approach to testing the assessment framework should be adopted. The test cases should:

- be undertaken for radioactive, toxic and mixed hazardous waste in a range of disposal facilities;
- be designed specifically to reflect realistic problems of environmental assessments (for example, any lack of comprehensive waste and site characterisation data);
- illustrate the benefits of the application and benefits of the SACO framework, in particular the SACO assessment code, rather than rigorously test all aspects of the framework.

Three broad categories of test cases were identified: shallow disposal; deep engineered disposal; and the special case of uranium mill tailings. For the shallow disposal system test case, municipal solid waste and low level radioactive waste disposals were considered, whilst for the deep system the disposal of transuranic waste was considered. Both radioactive and other hazardous contaminants were considered for the uranium mill tailings.

Relevant data for the test cases have come from a number of sources /2/, /3/, /4/ and /5/. Data from international intercomparison exercises have been used for the radioactive waste disposal cases and the uranium mill tailings. These exercises have been established to test and compare the performance of assessment codes and therefore are ideal for the testing of the SACO code. This approach to testing the code has several advantages:

- the test cases have been derived independently from the SACO project;
- many of the data were derived from real sites such as the Waste Isolation Pilot Plant (WIPP) in New Mexico, USA, or represent data which will typically be available when assessing a real site;
- the results obtained using the SACO code can be compared with those obtained from other assessment codes.

Comparable international intercomparison exercises have not been undertaken for municipal waste and therefore readily available data were limited. However, it was possible to obtain details of representative municipal waste types from a review of the open literature. For facility design, geosphere and biosphere characteristics, it was decided to use appropriate data from the radioactive waste test cases.

Since it was the aim of the tests to illustrate the application and benefits of the framework rather than rigorously demonstrate all its aspects, the following approach, which reflects the various steps of the SACO framework (Figure 1), was adopted:

- describe the available data relating to the waste, disposal facility, geosphere and biosphere (Step 1 of the framework);

- identify the assessment end point(s) and collect any additional data which are relevant (Steps 2 and 3 of the framework);

- describe the conceptual model(s) of the disposal system which has been developed from the available data and which is relevant to the assessment end point(s) (Step 4 of the framework);

- identify combinations of possible features, events and processes (scenarios) which are relevant to the assessment end points, group the scenarios, and reduce the number for analysis (Steps 5 and 6 of the framework);

- analyse the scenarios using the SACO assessment code and evaluate the results. Where appropriate compare the results with the other assessment codes which have been used (Steps 7-11 of the framework).

A detailed description of the application of the SACO framework is given in /1/; an abridged version is presented below for the shallow disposal test.

Available data

Three disposal types were considered: the disposal of radioactive waste in an engineered facility (vault); the disposal of radioactive waste in a minimally engineered facility (trench); the disposal of non-radioactive waste (municipal solid waste, MSW) in a trench.

The trenches are assumed to have been excavated from drift deposits and the only barrier which has been engineered is a covering cap. The wastes have been loose tipped in the form of miscellaneous trash materials (paper, plastics, metals, etc) and there has been no backfilling of voids. For the vault, engineered features include: a cap incorporating a rolled clay layer; drummed waste in a concrete matrix; backfill between drums; and a reinforced concrete top, base and sides to the vault. Contaminants are assumed to uniformly contaminate the matrix in the drums.

Below each disposal facility is a 1 m thickness unsaturated zone succeeded by a 10 m thick aquifer in which groundwater flows horizontally. 500 m down the watertable gradient, groundwater discharges into deep soil and then to surface soil and river water. Humans practice a range of activities in the area including: farming of crops and cattle; abstraction of river water for irrigation, and human and cattle consumption; and fishing. The crops, animal products and fish are consumed by the local population.

Assessment end points

The end points considered relate to the escape of contaminants to the aquifer and their subsequent transport in groundwater. They are:

- the release rate of radionuclides from the landfill into the groundwater - this will allow comparison of the radionuclide release rates from the trench with those from the vault;

- the concentration of each heavy metal in groundwater, river water, soil, and air - this will allow comparison of concentrations in various media with illustrative environmental quality standards which should not be exceeded;

- the annual individual radiation dose received by humans from radionuclides - this will allow comparison of the dose with regulatory limits.

- the intake rates of heavy metals by humans - this will allow comparison of the intake rates with guide levels which should not be exceeded.

Conceptual model

From the information given above, it is possible to identify a range of contaminant release and transport media, primary and secondary biosphere receptors, human health effects of exposure to contaminants, and the associated contaminant release, transport and exposure mechanisms which are appropriate to the groundwater related end points. These can be represented in a conceptual model of the disposal system and its processes (Figure 2). A similar conceptual model can be adopted for each of the cases considered.

Scenario identification

A number of scenarios resulting in the escape of contaminants in groundwater, contamination of various media, and human uptake can be identified. The full set of scenarios considered is illustrated in Figure 3. For the purposes of Test Case 1, it is proposed to combine these scenarios and assess them together for each disposal system.

Results and analysis

The conceptual model and scenarios described above were assessed using the SACO assessment code /6/. Results are presented and analysed below for each assessment end point.

Release Rate of Radionuclides from the Landfill to the Groundwater: Figure 4 summarises the results for Cs-137. The magnitude of the peak release rate is lower and occurs later for the vault disposal. This reflects the greater containment offered by the vault in comparison to the trench which allows Cs-137 to decay further before release. However, this increased containment does result in a potentially interesting environmental problem. Due to the slower release of radionuclides, the rate at which the flux of radionuclides from the vault decreases can be significantly slower than the rate of decline for the trench (Figure 4). This in turn results in the vault flux exceeding the trench flux at times in the future. However, in this case, the release rate is significantly lower than the peak trench release rate and hence does not result in higher environmental concentrations.

Heavy Metal Concentrations in Various Media: Table I shows modelled peak heavy metal concentrations in the groundwater, top soil, air and river water and contrasts them with illustrative environmental quality standards (EQSs). For all three metals the concentrations are well below the relevant EQSs, with the exception of groundwater concentrations which are only an order of magnitude below the EQSs. Therefore, if this were a real case, it might be advisable to monitor any groundwater used for irrigation or human consumption until the concentrations had fallen several orders of magnitude below the EQSs. There would not appear to be any need for potentially expensive groundwater remediation to be undertaken. Concentrations in the groundwater are high compared with those in other media due to the relatively limited attenuation and dilution of the metals before they reach the aquifer. Once in the aquifer they are considerably attenuated and diluted before reaching the top soil, air and river.

Dose to Humans from Radionuclides: The lower concentrations of Th-230 in the surface environment for vault disposals result in lower doses by about an order of magnitude (Figure 5). However, although both doses from trench and vault disposal are still rising at end of the simulation time (90,000 years), it can be seen that peak concentrations for not only the vault but also the trench can be expected to be significantly below the dose limit of 0.1 mSv y^{-1}. Again, these results could be used to help judge the need for the engineered features of the disposal system.

Intake of Heavy Metals by Humans: It can be seen from Table II that Zn intake is the first peak after 20,000 years, followed by Pb at 80,000 years and Fe at 120,000 years. This is due to differences in the sorption of the heavy metals in the geosphere, with Zn being the least sorbed and Fe the most sorbed. Both Zn and Pb peak intakes are well below the guide levels (there is no guide level for Fe). For all three heavy metals, the consumption of contaminated grain is the most important exposure pathway, with in the intake of cattle produce (beef and milk) being the next most important.

List of publications

LITTLE, R.H., GROGAN, H.A, SMITH, G.M. and TORRES, C., Land Disposal Practices in Europe and North America. J. Inst. Water and Env. Man. 7, 354-362.

LITTLE, R.H., TORRES, C., CHARLES, D., GROGAN, H.A., SIMÓN, I., SMITH, G.M., SUMERLING, T.J. and WATKINS, B.M., Post-Disposal Safety Assessment of Toxic and Radioactive Waste: Waste Types, Disposal Practices, Disposal Criteria, Assessment Methods, and Post-disposal Impacts. EUR 14627 (1993).

LITTLE, R.H., TORRES, C., SIMÓN, I. and SMITH, G.M., Quantitative Assessment and Its Relevance to Waste Disposal. International Conference on Environmental Pollution, Sitges (Barcelona), 28 September - 1 October 1993. Proceedings Vol 2, pp 525-532.

TORRES, C., SIMÓN, I., AGÜERO A., LITTLE, R.H. and SMITH, G.M., Metodologia (SACO) para la Evaluacion Comparativa de la Seguridad de los Sistemas para la Disposicion Final de los Residuos Toxicos y Radiactivos. 19th Annual Reunion of Spain Nuclear Society, Caceres, 6-8 October 1993. Proceedings pp 390-392.

TORRES, C., SIMÓN, I., LITTLE, R.H., SMITH, G.M. and AGÜERO A., Safety

Assessment Comparison Assessment Methodology for Toxic and Radioactive Wastes (SACO Version 1.0). International Conference on Nuclear Waste Management and Environmental Remediation, Prague, Czech Republic, 5-11 September 1993. Proceedings Vol 3, pp 589-598.

References

/1/ INTERA and IMA/CIEMAT, Intera Report IE2732-8 (Version 1.0) (1993)

/2/ IAEA, Co-ordinated Research Programme on the Safety Assessment of Near-surface Radioactive Waste Disposal Facilities (NSARS). Specification for Test Case 1 (1991)

/3/ NEA/OECD, PSACOIN Level 2 Exercise Problem Specification and Questionnaire for Stage 1. NEA Probabilistic System Assessment Group, NEA/OECD, Paris (1992)

/4/ NEA/OECD, PSACOIN Level 1b Intercomparison. NEA Probabilistic System Assessment Group, NEA/OECD, Paris (1993)

/5/ BIOMOVS, BIOMOVS II Uranium Mill Tailings Basic Scenario Version 1.07, SSI, Stockholm (1993)

/6/ INTERA and IMA/CIEMAT, Intera Report IE2732-6 (Version 1) (1992)

Table I: Heavy Metal Peak Concentrations from the Trench Disposal of MSW Compared with Illustrative Environmental Quality Standards (EQSs) (after /1/)

	Top soil conc. mg kg^{-1}	Soil EQS mg kg^{-1}	Groundwater conc. mg l^{-1}	Riverwater conc. mg l^{-1}	Water EQS mg l^{-1}	Air conc. mgm^{-3}	Air EQS mgm^{-3}
Fe	1E-9	1E+3	2E-2	1E-11	2E-1	3E-14	1E+0
Zn	2E-6	3E+2	4E-1	2E-11	5E+0	4E-11	5E+0
Pb	3E-7	2E+3	2E-2	2E-12	5E-2	7E-12	2E-1

Table II: Heavy Metal Intake from the Trench Disposal of MSW (after /1/)

	Peak Intake mg d^{-1}	Time of Peak y	Guide Level mg d^{-1}
Fe	4.4E-10	1.2E+5	No level
Zn	2.0E-6	2.0E+4	1.4E+1
Pb	3.3E-10	8.0E+4	5.0E-1

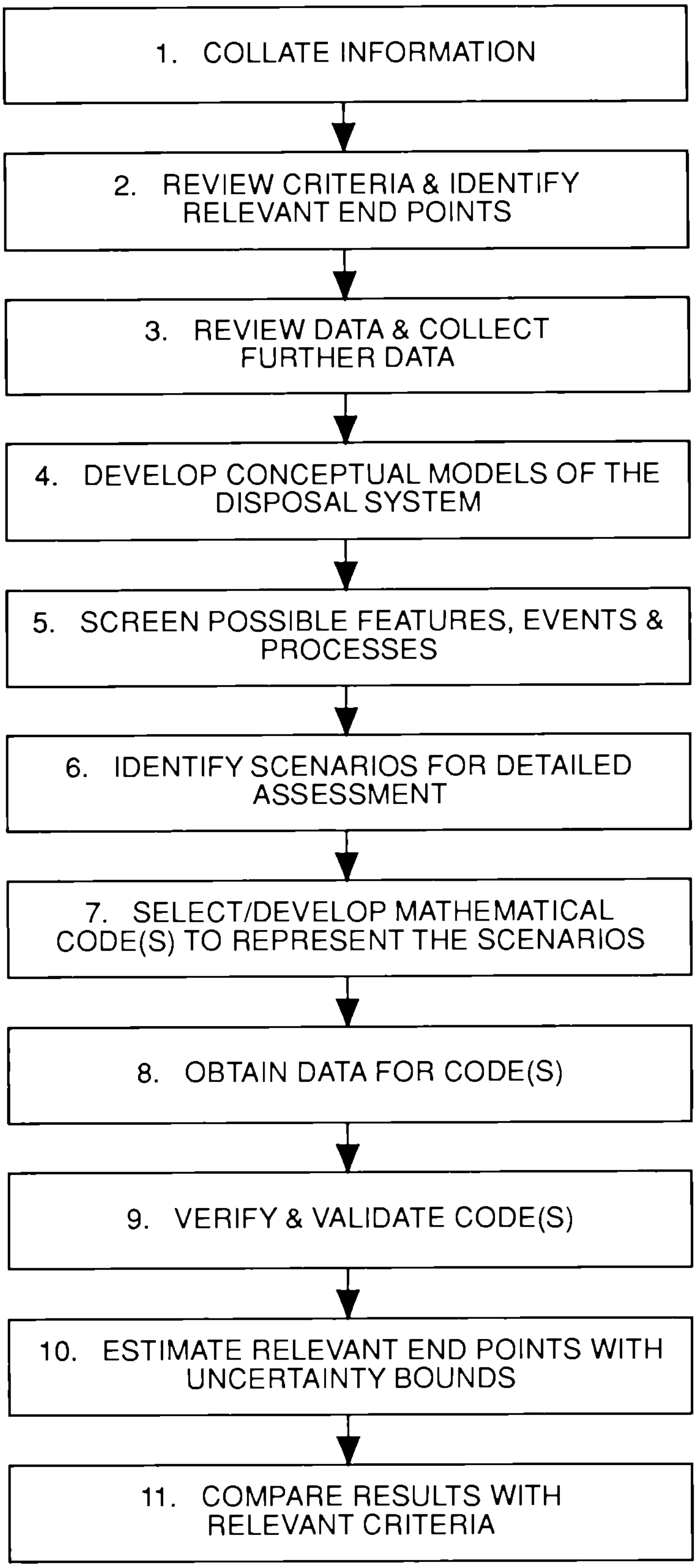


Figure 1: The SACO assessment framework (after /1/)

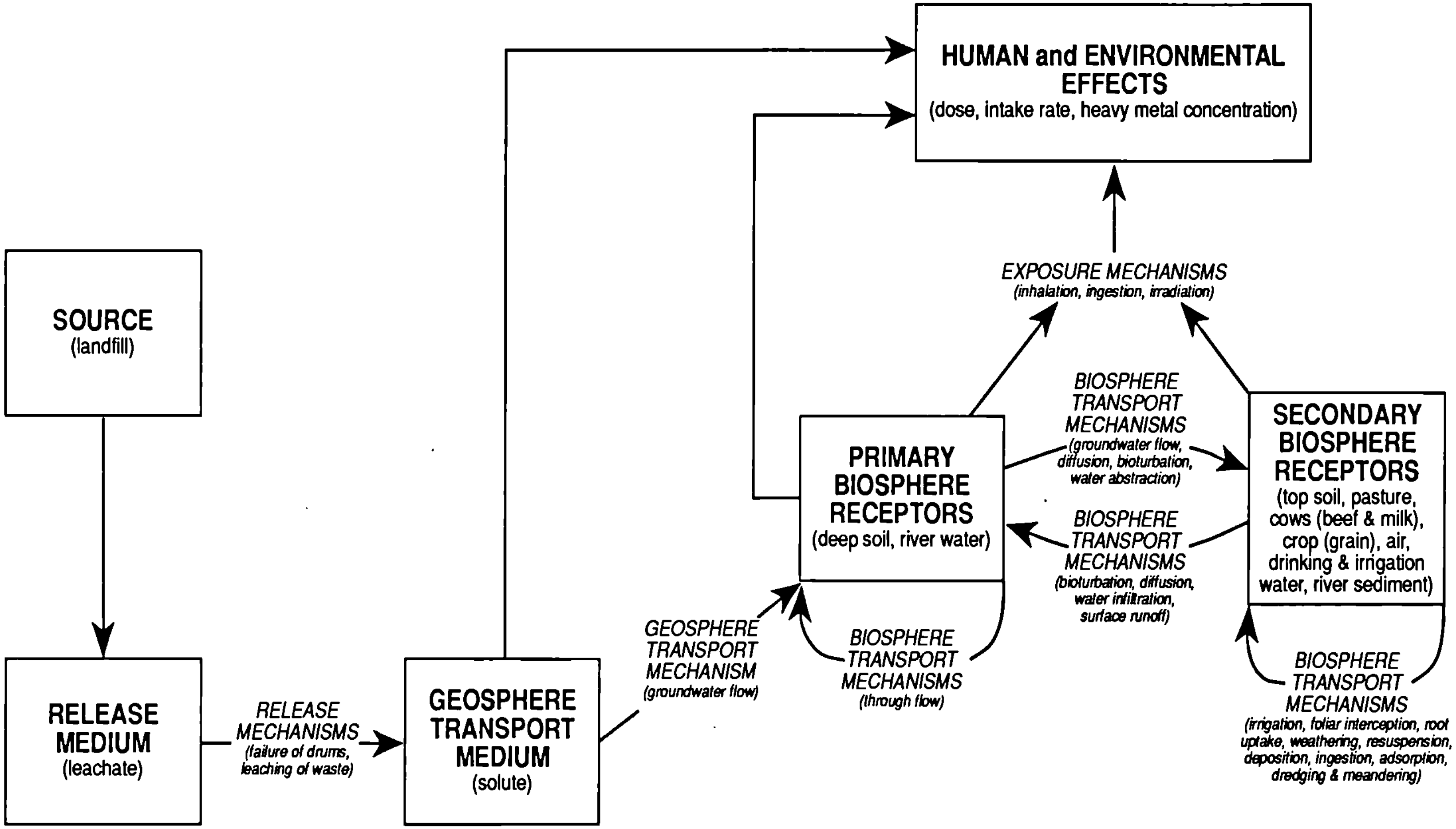


Figure 2: Conceptual model of the shallow disposal system and its processes (after /1/)

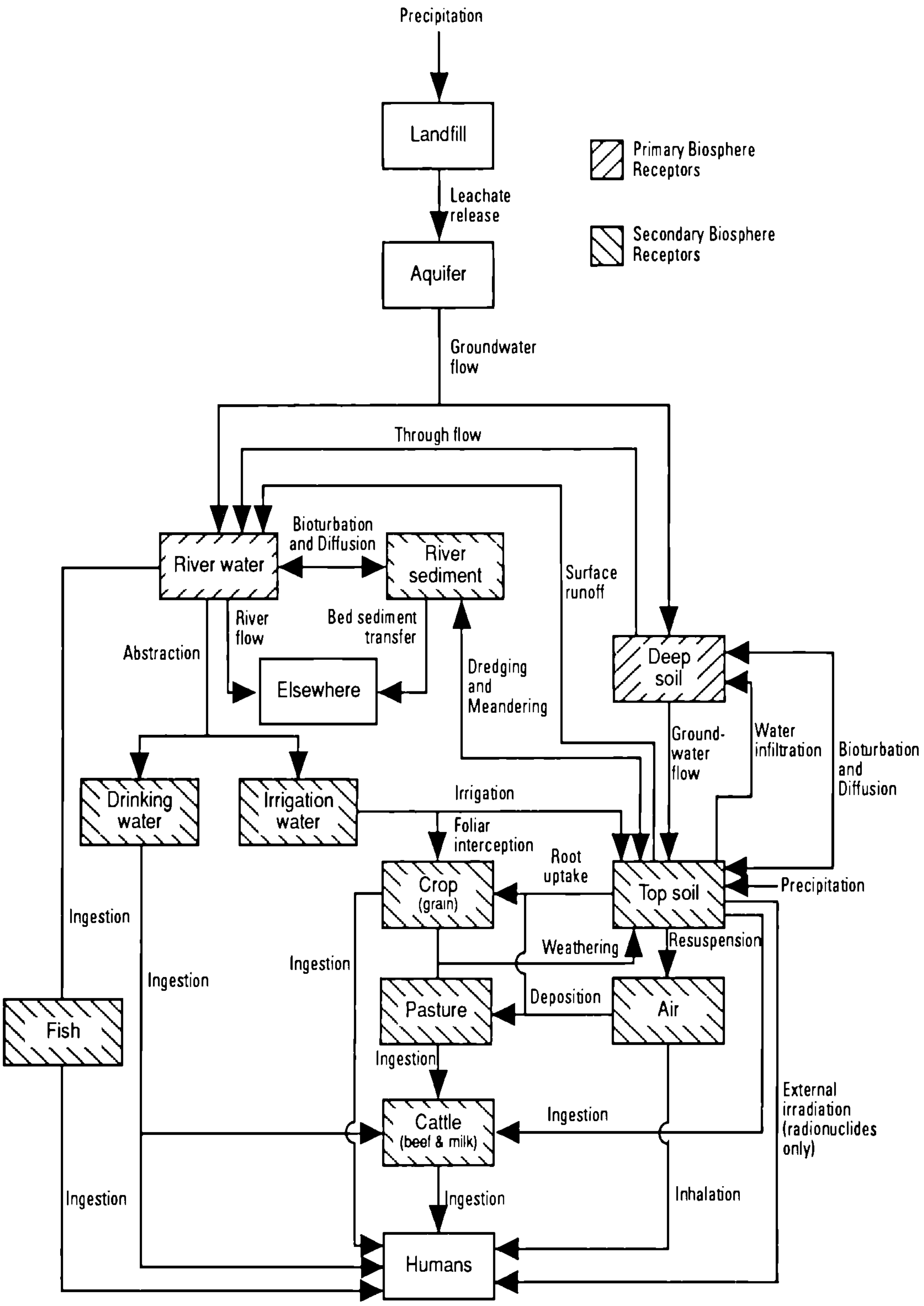


Figure 3: Scenarios analysed using the SACO assessment code (after /1/)

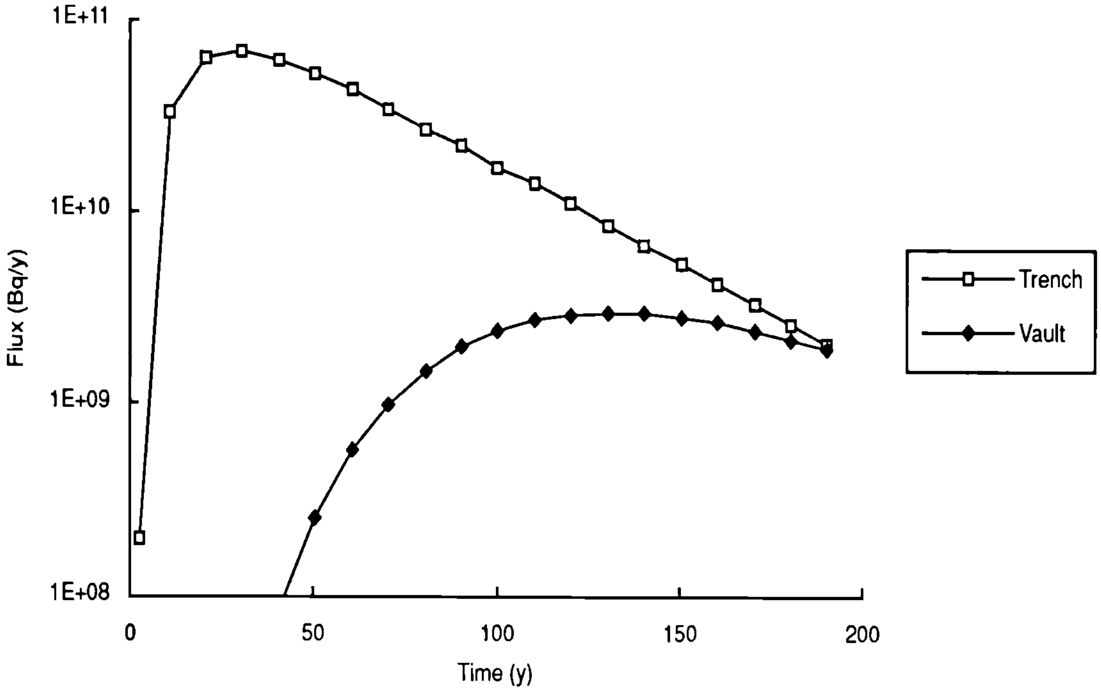


Figure 4: Cs-137 release rate to the aquifer from trench and vault disposals (after /1/)

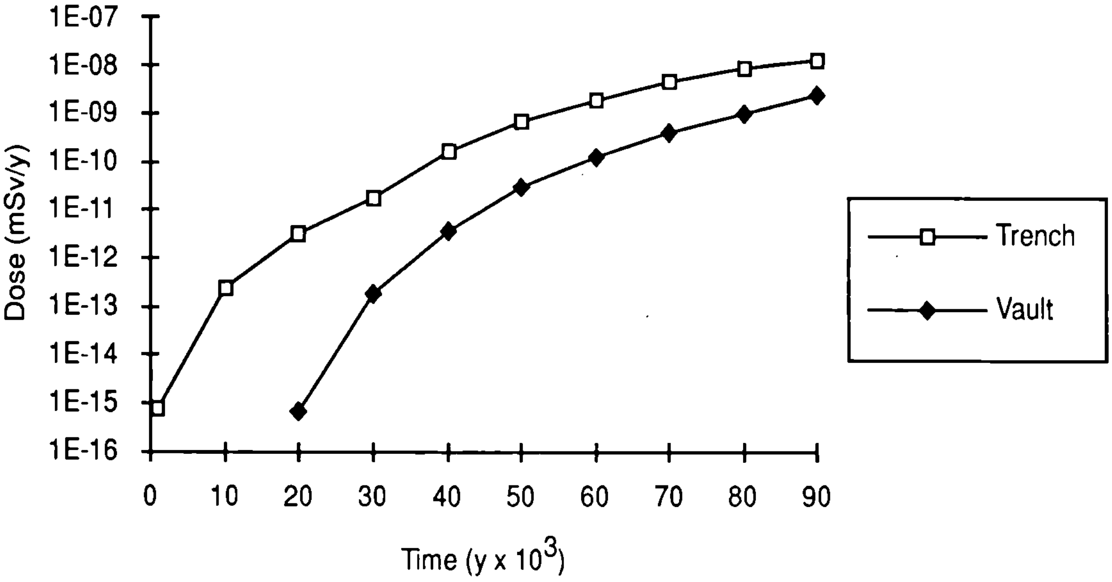


Figure 5: Dose from Th-230 from trench and vault disposals (after /1/)

Title : Study concerning the evaluation of toxic elements present in nuclear waste

Contractor : ONDRAF/NIRAS, Place Madou, 1 btes 24/25 B-1030 BRUSSELS

Contract nr : FI2W-CT90-0045

Duration of contract : from 01.04.1991 to 31.03.1993

Period concerned : 01.01.1992 to 31.12.92

Project leader : A. De Goeyse

A. Objectives and scope.

The management of radioactive waste is mainly determined by the safety conditions of the final disposal. Those safety conditions must cover the radiological aspects but also the chemical toxicity aspects coming either from the radioactive isotopes or from the non radioactive compounds of the waste.

The aim of the study is to make an evaluation of those chemical elements and of their quantity in the different waste streams.

The different waste streams will be identified systematically (per producer and per category) making a segregation between them based on the production process (operational, technological, dismantling, packaging, conditioning,...).

The chemical properties of the identified waste streams will be included in a general databank covering the identification and quantification, the physico-chemical properties, and the radiological characterization of the nuclear wastes.

To define the field of the inventory and to structure the inquiry, we take advantage of the experience of similar works performed in other European countries.

The evaluation and characterization of the chemical toxicity of nuclear waste is performed in collaboration with Indaver N.V. (Antwerp-Belgium), a mixed treatment plant company for chemical waste.

B. Work programme.

1. Selection of toxic elements, in particular heavy metals, in function of the present local, national and european legal context.
2. Qualitative review of the origin of heavy metals in nuclear waste, following the next classification :
   - raw radioactive waste
   - packaging
   - conditioning matrix
3. Quantitative inventory of the heavy metals in radioactive waste from several producers; Quantitative evaluation of the heavy metals used in the packaging and the conditioning of the waste, based on the available prognoses for the complete Belgian nuclear program.
4. Definition of measurements or evaluation methods to identify and quantify the toxic elements in nuclear wastes.
5. Improvement of the specifications for acceptance of radioactive waste to be treated and definition of toxic elements & limits (orders of magnitude) acceptable for the admission of waste on a shallow land burial, referring to the operation criteria in force for conventional landfilling of industrial waste.
6. Preventive actions to avoid the use of toxic elements in the nuclear facilities and their consecutive presence in radioactive waste.

C. Progress of work and obtained results.

State of advancement.

The information of the remaining selected producers has been collected during the first six months, except for Belgoprocess. Thanks to a limited prolongation of the contact, the results of Belgoprocess were obtained after summer.
The report was sent for comments to the Commission end of 1993.

Progress & results :

1. Heavy metals in radioactive waste from several producers.
   . Additional information has been provided by Electrabel about lead and zinc in dismantling waste. The final amounts for the seven Belgian power plants are as follows :
   24 500 kg lead
   65 450 kg zinc.

   These amounts are to be considered with caution for the following reasons :
   + the chemical composition of the impurities in the lead used is such that only short-live isotopes can be generated by activation of them, resulting in a high probability of exemption at the moment of dismantling
   + the most quantities of zinc will only be contaminated in case of accident during the life cycle of a unit.

   . A wide range of metals has been identified in the waste of IRE (Institut des Radio-Elements, Fleurus),
   like Al (ca 200 kg/year) and Cu (ca 30 kg/year) in normal production waste ;
   Cu (3 000 kg) and Pb (200 kg) in technological waste ;
   Al (30 000 kg), B (1 000 kg), Be (0,1 kg), Cu (75 000 kg), Pb (1 680 t) and Zn (60 000 kg) in dismantling waste.

   . The CEN-SCK (Centre d'Etudes Nucléaires, Mol) has limited the inventory to waste in stock, identifying : 4 000 kg Be
   some hundred kg of Cd
   87 kg of Hg

   . Belgoprocess has performed an inventory of cadmium, mercury, lead and zinc on site I (including the ex-Eurochemic reprocessing facility) and on site II (ex- waste division of CEN-SCK). The results are summarized on table 1 and are to be carefully considered because significant amounts could be exempted.

2. Heavy metals in packaging, and conditioning matrix.
   Considering the current Belgian nuclear programme and based on a 100 % reprocessing of used nuclear fuel, an evaluation of the metals used for the packaging (zinc from galvanized drums and lead from canisters) and for the conditioning (boron in glass matrix) gave the next estimates :
   3,2 t lead
   1 109 t zinc
   114 t boron

3. Comparison of the shallow land burial for radioactive waste with a landfill disposal site for industrial waste.
   The objective of both installations is to reduce to a minimum the impact of waste on the environment.
   The type of toxicity and the physical structure of the waste, the level of safety to guarantee and the period of time involved lead to fundamental differences between both concepts, wich are summarized on table 2.

4. Acceptance criteria and specifications
   In the same order, a review of the existing criteria on heavy metals for industrial landfilling has been performed, and compared with the present specifications applied to radioactive waste. Proposals are made in the perspective of future regulations.

5. Prevention.
   An example is given where general principles of prevention are successfully applied to the daily production of boron-containing effluents generated by a nuclear power plant. Details are given on how general objectives are translated in the reality through motivation, instructions and work organization.

6. Conclusion.

   A wide range of heavy metals has been identified in the Belgian radioactive waste produced during the daily processing of nuclear facilities or foreseen at the moment of their dismantling.

   These obtained results are presently used as input for safety assessment studies of the belgian project for shallow land burial.

   These data will further be combined with the radiological properties of the waste containing metals, aiming to an integral and safety management of the radioactive waste.

Metal	Quantities (kg)	
	Total inventory	Net prevision (not exemptable quantities)
Cd	1 200	220-270
Cu	26 089	≤ 26 089
Hg	2 088	2 088
Pb	405 700	175 000
Zn	9 737	8 137

Table 1 : Heavy metals inventoried and previsions after exemption for Belgoprocess.

	Category 1 landfill site **Indaver**	**Shallow land burial** **NIRAS Project**
Capacity	900 000t	100 000 to 200 000t
Structure	cells	modules
Waste characteristics	bulky stable	packages solid
Draining system	functional drains	control drains (option)
Gas	ventilation shafts	nihil
Usable volume	± 90%	± 50%
Stability	autostable (after compacting)	concrete modules + infilling materials
Bottom waterproofing	clay 2 m geomembrane PE 2,5 mm	waterproof concrete 1 m
Top waterproofing	rubber + bitume 3 mm	geomembrane PVC 1-2 mm clay 2,5 m bitume + fibres cover waterproof concrete 1 m
Total thickness of the cover	1,5 m	5 m + 1 m béton
Operation period	long (> 10 years)	short (< 6 months/set of 10 modules)
Survey period	10 to 30 years treatment of the effluents integrity control	200 years control of the natural outlet integrity control

Table 2 : Main characteristics of a category 1 landfill site and a project-site for shallow land burial

Title:	Disposal of Radioactive Waste and Toxic Waste in Underground Repositories
Contractor:	GSF-Forschungszentrum für Umwelt und Gesundheit,GmbH; Stichting Energieonderzoek Centrum Nederland (ECN)
Contract No:	FI2W-CT90-0061
Duration of contract:	from March 1st, 1991 to February 28th, 1994
Period covered:	January 1st - December 31st, 1993
Project Leader:	Th. Brasser (GSF - Coordinator) A. van Dalen (ECN)

A. OBJECTIVES AND SCOPE

The initial objective of a mutual research project between GSF and ECN is to delineate the statutory boundary conditions pertaining to an underground emplacement of hazardous wastes. At the same time the wastes of relevance to disposal are to be characterized according to type, composition, origin, toxicity, and volume, while taking the particularities of the situation in both countries into due consideration. Assumed potential hazards to the environment emanating from disposal are to be assessed on the basis of these data. The current strategies for an underground storage of hazardous wastes are described and compared with the concepts for the final disposal of radioactive wastes. Reference is taken to the special R&D topics of final disposal, such as the selection of the host rock, investigation of the geomechanical and hydrogeological situation, transport methods, backfilling and sealing techniques as well as the more complex subjects, such as the spreading of toxic agents and the safety analysis. This mutual project is to combine the basic knowledge of the repository concepts for the disposal of radioactive and hazardous wastes.

B. WORK PROGRAMM

2.1 Consideration of legal stipulations for the underground disposal of toxic wastes, based on the aims, requirements, techniques and safety concepts of radioactive waste disposal.
2.2 Description of the types of waste, their composition, origin, toxicity and assessment of their potential hazards to the environment emanating from the emplacement.
2.3 Description of strategies for underground disposal of toxic wastes and comparison with the concepts for radioactive waste disposal.
2.4 Compilation of special requirements on the disposal of toxic wastes in deep geological formations, summarizing those results which can be generally adopted from the R&D work in the field of radioactive waste disposal.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Federal Republic of Germany

2.1 Legal Stipulations

2.1.1 Waste Act (Krw-/AbfG)

The draft of a so-called waste cycle management- and waste act (Krw-/AbfG) in Germany corresponds with the demand of the European community and particularly with the guideline of the council of march 18th, 1991. Besides this the content of the law should counteract to the growing problems of waste management in the Federal Republic of Germany.

2.1.1 Objective

The waste rise faces presently neither quantitatively nor qualitatively a sufficient disposal capacity. To prevent a critical state in disposal-affairs in the near future, production residues must therefore be held as far as possible in an economic cycle so that waste is avoided in greater quantities than up to now. Altogether economic as well as ecological reasons command both, to reduce the waste rise drastically. Thus basic conditions must be created, which can guarantee the problem solution in a social and ecological market economy. To transform these goals the draft of the new waste act follows the demand of the waste act of 1986 of more self-responsibility. The waste cycle management should lie therefore primarily in private hand. The waste management itself has to align with the order of avoidance, recycling (first material then energetic reuse), waste treatment and waste disposal. Producers and distributors have a product responsibility, so that ecological products will be developed and produced and the cycle of material will be closed. The federal government intends to create the necessary basic conditions by legal regulations, whereby the waste cycle management and waste act stands in a narrow connection with further ordinances, for example the technical manual for municipial waste, the technical manual for hazardous waste or the waste combustion ordinance.

In general wastes produced in the Federal Republic of Germany are to be treated and / or disposed of in the country itself. Secondary raw materials can be exploited however in foreign countries also.

2.1.2 Waste Quantities

In the meantime preliminary waste quantity statements for 1990 exist which will be revised by the Federal Statistical Office. According to the environment statistics act every two years elevations occur, which include now for the first time the new federal states also. The last elevation also resulted for the first time with a direct assignment of occurring waste quantities to the respective waste keys. After that altogether about 15 Mio.t of hazardous wastes and residues have occurred 1990, from which 27,8% have been recycled. A compilation of the 62 waste types (after TA Abfall), relevant for underground disposal, expels for 1990 a quantity of about 700.000 t.

2.2 Waste Characterization

The goal of the inorganic analysis and the determination of sum parameters is to prepare a mass balance and to describe the wastes both after their main-,as well as after their trace-element content. After performance of survey analyses a selection of several waste types was characterized by waste-analytical methods. The results have been interpreted above all in regard on the necessity of an underground disposal.

2.2.1 Investigation Procedure

The applied investigation processes for waste characterization are:

* Different chemical solution processes,
* Insolubles residues,
* Water-solubles fraction,
* Drying loss and loss on ignition,
* Ion-chromatography,
* Photometric processes,
* Carbon determination,
* ICP / AES.

Particularly through the comparison of different solution- and detection processes with the help of the ICP / AES and alternative wet-chemical processes it has been determined, in which way the achieved results are depending on the kind of inserted analysis processes and the kind of investigation methods.

2.2.2 Assignment to the Underground Disposal

At all samples investigated (hardening-salts, iron-sulfates, browning-salts, lead-salts and blasting medium residues) the demands are fulfilled, which are put at wastes for an underground disposal. Neither spontaneous combustion nor combustibility or explosibility are to be expected under disposal conditions (temperature, humidity). Smell or degassing could be observed at no sample. At cyanide-containing wastes (hardening-salts) no measurable cyanide-content could be ascertained at measurements in the gas room directly over the sample.

A comparison of the permissible limits for the landfill deposit of hazardous wastes with the concentrations in eluates determined at the samples shows, that the wastes investigated are not associated to injustice to an underground disposal. Already the determined loss on ignition excludes some waste types from landfill disposal. The limit of 10% soluble fraction hold the investigated lead-salts and blasting medium residues, but the permissible zinc-, lead- and cadmium contents are exceeded by individual samples. All nitrite-containing waste types and, in addition, the group of browning-salts contain so much nitrite, that they should be protected from solution effectively. The standard value for sulfate is exceeded by iron-sulfate wastes around 7 - 8 - fold; determined cyanide-contents lie likewise far over the standard value. Generally the anion-contents contribute in larger extent to the exclusion of landfill disposal than the metal ingredients.

2.3 Disposal Concepts

As suitable for underground disposal of special hazardous wastes particularly cavities in salt rocks are examined. In Germany there are altogether five large salt districts, in which today potassium- and / or rocksalt is mined and in which there are mines with large cavity volume:

- The flat bedded and thin evaporites of triassic origin in Baden-Württemberg.
- The flat bedded evaporites of Zechstein in Hesse and Thüringen, the potassium district at Werra and Fulda.
- The middle-german district with Zechstein salts mainly of the Stassfurt-series.
- The north-german district (Zechstein, predominantly Leine-series).
- The Wesel district at the Niederrhein.

Beside salt rocks however also the qualification of hardcoal mines for the disposal of residues, for instance from power plants is under exploration. Indeed the geological safety of the jointed Carboniferous strata is essentially slight, since already during the operational phase saline formation waters must be pumped, so that the mines are not floveled. Also the overburden layers of Emschermergel with a thickness of several hundred meters do not form a complete barrier. Thus one can dispose of no special hazardous wastes without further investigations , unless the hazardous content of the wastes is consolidated or fixed by special processes in a matrix, e.g. in concrete or pozzuolan.

The development in former ore mines is similar, from which only four in the western federal states still exist. Since here however only a relatively slight output is to be recorded, also the created cavities for disposal options are essentially more insignificant.

Cavities, which have been resulted from the underground mining of evaporites like anhydrite / plaster, lime and dolomite, serve likewise for the diposal of power plant residues.

Stratigraphy e.g. is very well known at the sites of former mines. Main aquifers, which were not essential for the safety of the mine itself, but which could be however, on the other hand, essential for the long term safety of a disposal mine, are however investigated up to now only insufficiently.

Beside the disposal of residues and wastes in mines in the federal state of Lower Saxony the possibility of a disposal in salt caverns has been studied. Thereby one concentrates particularly on salt domes near the coast, because the salt freight occurring at the solution process could be derived in the sea.

2.4 R&D - Transfer

Beside the promotion of research works in the field of final disposal of radioactive waste and special hazardous waste by single projects also institutional research works are accomplished in three National Research Centres (GFE) of the BMFT (GSF, KFA and KfK). But the programs of these GFE are aligned, as far as waste specific, still predominantly on radioactive waste. The whole topic is, in addition, also an element of the R&D -

program of the Federal Institute for Geosciences and Natural Resources (BGR).

2.4.1 Federal Institute for Geosciences and Natural Resources (BGR)

One point of main effort of research within the BGR is the achievement of physical material laws of the host rocks, particularly on the thermomechanical behaviour of salt rock and backfilling material. An important step thereby is the development of experimental methods for the determination of material parameters as well as the further development of test- and measuring technology for lab-and in-situ - investigations, since only the knowledge of the conformities and specific parameters allows a sufficing exact forecast of the long-term behaviour of the host rock.

2.4.2 GSF-Forschungszentrum für Umwelt und Gesundheit

The GSF-Research Center for Environment and Health with the Institut für Tieflagerung (institute for deep disposal, IfT) since 1965 develops and tests techniques for the final disposal of radioactive waste in the Asse salt mine. For non heat-producing, weak- and middle-radioactive waste processes have been developed, which are meanwhile concept elements for the planned disposal site in the former iron mine Konrad and in the salt dome of Gorleben. Furthermore methods for the safety analysis of underground disposal have developed and are already utilized as part of authorization processes. The experiences, which have been achieved in the area of final disposal of radioactive waste, further will be transfered on the underground disposal of chemically - toxic wastes. Summing up the GSF - IfT presently is working on following topics:

- Development of safety-related technical basic conditions,
- Investigation of the efficacy of geotechnical barriers,
- Investigations on long term safety under worst case conditions,
- Development of safety-analytical methods for the long-term safety.

2.4.3 Research Centre Jülich (KFA)

In the KFA predominantly the institute for chemical technology (ICT) deals with questions of the operational safety and the long-term safety of an underground disposal. Beside this contributions to the characterization of HTR-fuel elements come from the hot cell area of the institute for reactor raw materials (IRW-HZ). Work emphases are characterization and treatment of HTR - and MTR-fuel elements and from wastes for the final disposal.

Heat producing radioactive wastes must be disposed of by a technology which is considering the special waste characteristics. The investigations concentrate on the final disposal of MAW and from HTR / MTR-fuel elements , e.g. in drilled boreholes, and include particularly the detailed description of the effects connected with the backfilling with crushed salt like load denudation, gas development and -migration.

2.4.4 Nuclear Research Centre Karlsruhe (KfK)

In the KfK the works of the institute for nuclear treatment- and disposal-techniques (INE) include the development of concepts and processes for the immobilization of radionuclides (waste conditioning), works on the optimization of the barrier effect of waste products as well as the investigation of the chemical behaviour of radionuclides in the near- and far-field of an underground disposal. Essential contributions to the long-term safety deliver:

- material investigations at waste skeins
- near-field investigations, including the effect the radiation field
- development of material laws to the description of thermal and thermodynamical effects in an enlarged near-field.

2.4.5 Outlook

Between the german National Research Centres there is no narrowly determined division of the research activities in the field of long-term safety of underground disposal. The Research Centre Jülich (KFA) and the Nuclear Research Centre Karlsruhe (KfK) pursue especially research works in the area of waste characterization, liberation behaviour as well as conditioning. The GSF-Research Centre for Environment and Health works at themes concerning disposal technique as well as long-term safety. The BGR pursues beside this site-specific research works (e.g. Gorleben, Konrad) with the above described questioning; works are accomplished also for the Federal Office of Radiation Protection (BfS) according to an agreement between the Federal Ministries BMU, BMWi and BMFT.

2.4.6 Further R&D - Tasks

In Germany a promotion-programm for the ecological disposal of hazardous wastes and / or residues in deep geological formations is discussed presently, which includes both radioactive as well as special hazardous wastes and / or residues. Hereby the legal and administrative separation with the treatment and disposal of radioactive and non-radioactive wastes should be given up. Among experts the opinion exists, that despite of the status already reached in this area further research and development is necessary to heighten the available standard of knowledge through application- orientated basis research, particularly for the protection of man and environment, particularly:

- to improve the requirements for a demand-orientated provision of underground disposal sites for heat producing radioactive wastes,
- to develop the current possibilities of waste characterization and classification relevant for underground disposal as well as to support the preparation of underground disposal sites through application-orientated research,
- to show evidence of safety of underground disposal as inclusively and verifiably as possible, also to increase the acceptance within the public,
- to develop further scientific and technical concepts for the treatment and disposal of hazardous wastes.

The proposed promotion-program thereby emphases the following topics:

1. Waste characterization and -classification,
2. Safety demands,
3. Characterization of potential host formations and locations,
4. Quality assurance,
5. Work and environment protection,
6. Incident analysis for the operational phase,
7. Scenario analysis,
8. Geochemical effects in the nearfield,
9. Behaviour of geotechnical barriers,
10. Behaviour of host rock, mine openings and backfill material,
11. Transport processes in the geosphere,
12. Development of methods and calculation programs for long-term safety analysis,
13. Strategies for validation and quality assurence of calculation programs.

The Netherlands

Introduction

About two years ago the government announced a public discussion on wastes and waste disposal. The main reason was the resistance of the public to accept a large underground facility for waste disposal, both radioactive and high toxic chemical waste. Pending the discussions the government could not give indications or instructions how to handle the disposal of wastes without giving the impression of partiality. There was no progress in law-making concerning underground disposal. It is not without reason that the reaction of the government is cautious concerning waste management in view of the involvement of local, provincial and state authorities in the past.

2.1 Legal Aspects

On May 14 this year the standpoint of the government was published on the use of the underground for disposal of toxic waste, both radioactive and toxic chemical. Principle of living with waste is that the isolation from the environment is inspectable and controllable. Controllable implicates also retrievable for reuse, detoxification, removal to a safer storage. The retrievability is not limited in time e.g. the closure of the underground facility.

The production of toxic chemical or radioactive waste in the future for new processes or products has to be justified. The value of the product for the society should outbalance the economic and social costs of the accompanying waste.

It is announced in the standpoint of the government that export of wastes for the purpose of disposal elsewhere will be ended in 1996. This will have implications for the waste characteristics and amounts as is given by the yearly review of the institute for chemical waste data collection.

2.2 Waste Characterization

Chemical waste to be stored retrievable underground mentioned in the governmental document concerns the high toxic (C-1) and medium toxic (C-2). High toxic chemical waste (class C-1) is not allowed to be stored in an above-ground facility. This waste consists of residues of natural gas production containing mercury and its compounds, metal hardening salts, and residues from fluorescent lamps. These wastes amount to about 300 - 600 tons yearly. Storage is underground in the Herfa-Neurode salt mine, a facility considered suitable for retrieval of the wastes.

Medium toxic chemical waste (class C-2) can be stored in an landfill facility under the condition of inspectable and controllable isolation from the environment. The so-called C-2 facility consisted of a concrete vault of 125,000 m^3. Sections of this facility are in use for the storage of sludges from industrial processes, pigments, soluble salts, heavy metals, ashes from chemical (organic) waste incineration. The total of these wastes amounts to 30,000 tons yearly.

Extrapolation to the future of amounts and qualities of chemical waste is less certain, due to:

- Revision of laws and rules,
- Less industrial waste by more efficient processes,
- Less waste by disappearance of products, processes and industries,
- More waste by import of raw materials and ores of lower quality,
- More or less success of the recycling industries,
- The acceptance of waste materials as raw materials for other purposes (replacing original used materials).

2.3 Disposal-Mine Concept

Earlier concepts for a disposal mine in a salt formation are in view of the declaration of the government regarding underground disposal not valid anymore. High and medium toxic wastes have to be retrievable anytime, even long after the operational period of the underground facility. The decision to take back or not the waste is left to the future generations.

Reasons for retrieval mentioned are:

- Use of waste as raw material,
- Detoxify for safety reasons,
- Remove to a safer site (calamity).

Other conditions of the government are: inspectable and controllable (from remedial action to retrieval). The other important factor concerns the fact that the mine or facility will not be state owned. The fact that the mine will be private owned means that the waste storage / disposal has to be done on a commercial basis. The equivalent of the nuclear option (a mine for waste only) is far to expensive. The amounts of C-1 andC-2 wastes produced yearly, about 30,000 tonns, is much to small for the investment of a complete mine.

2.4 R&D Transfer

For several decades investigations were made to ensure the disposal of nuclear waste. Experimental engineering in a salt dome, practical experience with low level waste disposal, calculations of stability, creep of salt for rooms, caverns etc. For the long term safety prediction calculation programmes were developed validated by using measured data from natural analogs. For a particular disposal site a lot of information is needed on the geologic formation to be used but also on the surrounding formations to predict for the far future the behaviour and displacement of the waste components in case of dissolution.

The transfer of knowledge from nuclear waste disposal R&D is most important for the formulation of the mine-law and -rules. Up till now it is not allowed by law to bring underground other materials as removed from the place or material necessary for the mine exploitation.

The nuclear experience and R&D work may be helpful to formulate the legal conditions for chemical waste storage / disposal underground. Some points to be regulated are:

- The ownership of the wastes during the operational phase of the mine,
- Idem after closure but no decision on retrieval,
- Idem after declared not retrievable,
- Retrieval on request by who, and at whose expense,
- The conditions of the mine suitable to receive wastes,
- The construction of the rooms, caverns,
- The conditions for waste and wasteform for acceptation,
- Description of the working conditions,
- Description of techniques and measures for mining, inspection, control, and retrieval,
- Material choice for backfill, barriers, closures,
- Administration of the wastes and their location in the mine.

2.4.1 Stability of Salt Structures

The long-term safety of a final disposal depends partly on the engineered structure in the salt formation, including the closure techniques used but also on the geologic stability of the salt formation. The studies completed for the nuclear waste disposal in the early eighties were focussed on salt diapirism, subrosion and the influence of an ice-cap during the coming ice-age. The origin of salt diapirism was supposed to be the difference inspecific weight between rock salt and the overlying sediments.

Sufficient lithostatic pressure and the plastic behaviour of salt were used to make calculations of diapiritic growth. Mass flow of salt was estimated from the subsidence of the surrounding sediments. The picture used for calculations in a flat deltaic structure with originally about horizontal sedimentary layers. Structures below the Zechstein salt were not taken into account. The calculated growth values are in the range of generally accepted results of about 0,1 - 0,5 mm per year.

The discovery of substantial amounts of oil and gas in northern Europe initiated intensive studies of the geology. The presence of oil in northern Germany was already known for three hundred years from seepings. As drilling is very expensive a good knowledge of the underground structure is of help to avoid "dry wells". A very detailed study was necessary because the underground proved to be very complex and fragmented resulting in alarge number of relative small gas and oil fields. Gas and oil are collected in permeable layers covered by impermeable formations.

For most of northern Europe this means that the history can be constructed starting with the permocarboniferous of about 300 Ma ago. A large amount of information is given in the journal Tectonophysics 107 (1987) devoted to compressional Intra-Plate Deformations in the Alpine Foreland.

Inside a salt formation a number of salt minerals is present and it has been noted that during the existance of the formation recrystallisations occur. Herrmann suggests a relation with diapirism and cites the results of age determinations by Potassium-Argon and Rubidium-Strontium measurements. In the neighbourhood of Hannover in potassium salt ages of 130, 100, 75, 63 and 40 - 20 Ma were found. These ages are in coincidence with theorogenic pulses of Late Kimmerian (130), Austrian (100), Subhercynian (75), Laramide (63) and Pyrenean, Alpine (40-20 Ma).

Salt flows under pressure and it seems that the pressures of orogenic pulses are the main origin of salt displacements. Thinner layers act as gliding planes for the upper sediments as was found in the Tabular Jura in Northern Switzerland. The same effect has been observed in the region of the Broad Fourteens basin in the North Sea west of The Netherlands.

Due to the relation of growth of salt diapirs in periods of tectonic pulses and the location of the diapirs in relation to the topography of the basement rocks there is strong evidence for the tectonic origin of salt domes. Horizontal pressures and differences in heights in the basement structure are the most important factors for the presence and location of the salt structures in the Permian Basins.

In the discussions on conditions the simplified cross-section pictures are misleading. The basement in reality is complex and the diapir has in most cases a very elongated structure according to faults in the basement.

The condition that major faults in the neighbourhood of the salt dome may not be present is not real because of the origin of a salt dome is due to the presence of height differences at the basement. These differences are due to faults. Also the basement is very fragmented in the Alpine foreland, a fault is always nearby.

Recently the public opinion has been shaken by a tectonic event near Roermond in The Netherlands and the neighbouring parts of Germany and Belgium. The centre of the earthquake was at the south-eastern end of the Central-West Netherlands basin. This event is due to subsidence. In the scientific opinion Northwest Europe is a very stable region and it has to be explained that in geologic times the earth crust has been not so quiet. The influence on a saltdome however is small to negligable.

Title: Use of methods and programmes developed in nuclear field for treatment and disposal of toxic and hazardous wastes

Contractor: NUCLEO S.p.a. - SNIA Tech.
Contract n°: FI2W-CT91-0110
Duration of contract: from 1.1.1992 to 30.6.1993 (extended to 30.9.1993)
Period covered: from 1.1.1993 to 30.9.1993
Project leader: Francesco Lo Giudice (NUCLEO S.p.a. - Co-ordinator)
V. Pellecchia (SNIA Tech.)

A. OBJECTIVES AND SCOPE

Aim of the research is to make a general overview of the industrial wastes (on technical and regulatory point of view) to identify toxic and hazardous wastes. This research has identified refuses containing asbestos (RCA) as the wastes more suitable for the compaction and immobilization process, widely considered a good balance between technical and economical features for low activity radwastes management.
Experimental tests have been carried-out to verify the feasibility and the convenience of the proposed process. The target was to demonstrate the possibility to decrease significantly the volume of incoming wastes, so reducing costs related to the disposal and in the same time to have a final product more easily disposable in less restrictive category dump, according to Italian regulation.
Results of experimental tests have been used to set-up the definitive input data for the basic design of a pilot plant able to treat about 12,000 m^3/y of incoming RCA, developed with the same criteria as it was a nuclear facility.
Final economic consideration has shown that the processed wastes can be disposed in less restrictive category dump, allowing a cost saving of about 20 % (wastes decategorisation).
Of course this means that also on environmental point of view, it has been reached a good result because the decategorisation allows to dispose the wastes in safer more ecological way.

B. WORK PROGRAMME

According to the technical Annex of the Contract the following steps have been carried-out:

1. selection of THW featured by an environmental impact similar to low activity radwastes;
2. selection of the radwastes treatment processes, already adopted in industrial scale, to be transferred to THW both technical and economical point of view;
3. testing of the whole treatment process including: shredding of RCA, compaction and final embedding in cement matrix.
4. pilot plant basic design development
5. final report including : test report, design and plant description, cost/benefit evaluation.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1.1 State of advancement

A technical survey on the toxic and hazardous wastes has been carried out to select the categories suitable to be processed with the methods and techniques up to now adopted for low and intermediate level radioactive wastes, taking into account the current regulation for safe management and disposal.

The research identified the Refuses Containing Asbestos (RCA) as more suitable for the volume reduction and embedding processes, which are widely used in radioactive wastes field owing to their convenience and technical ease.

We have mainly focused our attention on RCA considering the wide utilization of asbestos in the last decades, before discovering its toxicological properties dangerous for public health, so pushing many Countries to ban asbestos based materials, dispose them and replace with alternative materials. In first instance the research was pointed to investigate the real amount of RCA to be adequately disposed of.

Successively the basic criteria for RCA volume reduction and embedding process have been drawn, by starting functions and requirements of a treatment pilot plant. To confirm the fixed design data, a preliminary experimental campaign was performed in full scale by employing real RCA samples and equipment of NUCLECO in the ICS 42 facility, where a similar process is qualified for solid radwaste treatment. The above mentioned campaign gave results not completely satisfactory, so forcing us to modify the process and optimize the treatment either in terms of reliability and cost saving.

Consequently a second experimental campaign was carried out to verify the process modification and hence to assign the ultimate data to review the preliminary basic design. Considering future applications on industrial scale of defined treatment, the plant capital and running costs evaluation was done, as well as the costs/benefits comparative analysis for untreated/treated RCA disposal. In summary, the main targets achieved are:

* a final volume reduction factor of 2.5, if compared to untreated RCA to be disposed of;

* a final product, featured by a lower environmental impact and disposal in less restrictive dumps, according to the rules in force in Italy;

* about 20% cost saving on RCA disposal, in comparison with the current costs for untreated refuses.

1.2 Progress and results

The results of the first experimental campaign, carried-out in 1992, showed that the increase of compacting load over a specific value of about 20 bar, is not justified by the VRF increase and by the consequent higher cost of equipment needed. In fact the values of VRF achieved do not take in consideration the spring-back effect, typical of this material, which partly decreases the volume reduction immediately measured after pressing.

In practice an effective VRF of 5 can be achieved by shredding and then compacting the RCA at low pressure load (about 10 bar), thus confirming the expected value. A second negative result, not deeply investigated in advance, was remaked: the poor compactness of pressed material, independent from the pressing load. This unexpected effect, that makes very difficult the handling inside overpacks of pressed RCA, is mainly due to nature of mineral asbestos itself and also to plastic fragments inside; in fact the low friction coefficient between adjacent plastic layers, inside compacted material, cuts any inner linkage.

During the second experimental campaign, carried-out in the reference period, to override these troubles, process alternatives were investigated:

1. plastic removal before shredding and pressing. This operation produced a compacted material not enough stiff to ensure a safe handling towards the overpack;
2. adding of cement binder to shredded RCA and adequate mixing, before pressing, to improve the handling of the material and contemporarily to reduce spring-back effect. This last trial produced good result in terms of spring-back reduction, but still not satisfactory results for the handling purpose.

To verify the most severe operating conditions, RCA with a negligible water content were processed. A considerable quantity of refuses was collected and divided into two streams: with and without plastic inside. In first instance, the shredding operations were performed on both streams, without adding any binding agent, and attaining a nearly 2 volume reduction factor (VRF), as already found during the first experimental campaign.

Successive pressing operations on both streams, performed by an hydraulic press, resulted in a pressed material characterized by unsatisfactory compactness as necessary for a proper handling towards overpack, moreover the pressed material with plastic inside showed an appreciable spring-back effect, so partially vanishing the VRF recorded immediately after pressing.

The same operations, performed on shredded RCA mixed with a cement binder (Portland 425 cement, water, fluidifier) before pressing, showed, at the press outlet, a VRF slightly lower than the corresponding value found in the no binder trial and the spring-back effect was less evident.

This notwithstanding, the compactness was not yet enough to ensure a satisfactory and safe handling in all overpacking conditions.

To avoid any trouble it was finally decided to test the direct pressing in overpack, by compacting, one upon the other, RCA calibrated amounts (about 50 litres), fed in sequence inside the concrete overpack.

A first run test was carried out without adding any binder to the shredded material; once more, an appreciable spring-back effect was observed, particularly on refuses containing plastics fragments, so decreasing the final VRF achievable immediately after compaction.

A further in overpack pressing test, carried out by adding and mixing about 10% (by volume) cement binder to shredded RCA, gave a final VRF very close to the value achievable on material immediately after pressing. At the end of the second experimental campaign all overpacks produced in the different tests were top sealed by pouring cement mortar, duly qualified and used for radwastes embedding.

After an adequate setting and curing time (28 days), all produced overpacks were cut both axially and radially.

The gathered specimen gave the following results:

a) overpacks containing material pressed outside by means of hydraulic press, without binder, loaded inside overpack, and top sealed with mortar showed a satisfactory waste embedding only on the upper third of the overpack. This result is due to the uncomplete downward mortar penetration, although the overpack was strongly shaken on a vibrating table during mortar pouring;
b) overpacks, containing the same material as per point a), but mixed with cement binder, showed a better embedding quality, even if their preparation was rather uncertain, due to the handling problems described before;

c) overpacks with shredded material, pressed inside without binder, showed the same uncomplete mortar in deep penetration, as the case a), and a worse VRF due to the spring-back effect as described above;
d) overpacks containing shredded material, mixed with cement binder and directly pressed inside, showed a satisfactory and a quite uniform RCA embedding quality all along the axial/radial directions. The final VRF was very close to the value obtained in case a), approximately 2.5.

Looking through the results above listed, it was taken the decision that the treatment alternative tested under case d), is the best compromise between final product quality and adequate VRF.

A further advantage of this alternative is the good capability of the cement binder to retain asbestos fibres also in the matrix core, thus ensuring a satisfactory fibres containment, also in accidental events during transport and disposal, which could generate the failure of the overpack walls, taken as main containment.

The main results obtained during the second experimental campaign are the following:

- the shredding operation of RCA, before pressing, allows to achieve an effective VRF higher than the value achievable only by pressing. This is due to the material bulk density increase, as reduction of dead volume inside the RCA packages;
- the binder addition allows to retain the free fibres and to reduce significantly the spring-back effect after pressing.

The use of a cement paste as binder, is the most effective and economical way to reduce the free fibres in the inner matrix, making possible to consider this waste as declassified one.

During experimental trials, carried-out on quite dry wastes, an unusual cement paste, made with a very high water/cement (w/c) ratio was used to replace the large amount of water absorbed by wastes. This water absorption gave a positive result in reducing the spring-back effect on pressed material before cement setting.

Of course, the amount of cement binder may be reduced when processing wet RCA coming from dismantling activities: in this case the w/c of binder must be proportionally adapted to the water content inside the waste itself. Experimentally, we saw that, also processing RCA completely dry, the necessary amount of binder was a small percentage (about 10% vol.) of the shredded refuses.

It is important to underline that the binding action of the cement paste is not pointed to achieve a high mechanical strength, but mainly to embed the free fibres.

As already stated after preliminary trials, it was confirmed that a high pressing load, achievable with supercompacting hydraulic press (i.e. 1,500 tons), does not provide VRF values proportional to the applied load, because of following spring-back negative effect. In particular, applying pressures over the range of 10 bar, the VRF values have no significant increase.

In conclusion, it was verified that this low load of compaction, corresponding to the above range (lower than 10 bar), is adequate to obtain a total VRF not lower than 2.5.

The sealing mortar, prepared with a recipe already qualified and used to embed nuclear LL wastes, assures the long term full containment of the pressed material.

After visual inspection of sealed overpacks there was no evidence of bleeding water or cracks on the top. After curing time, the final gross weight average of overpacks was approximately 700 kg.

As result of the above experimental trials, a volume reduction factor (VRF) close to 5 has been reached in good compliance with the values of in-drum pressing of solid low level radwastes, widely used in nuclear facilities.

This numeric figure is very important, because the overpacking operation approximately halves this value and consequently the effective VRF of RCA leaving the plant, for final disposal, is about 2.5 times lower than the volume of incoming untreated refuses.

On the other hand, considering the overpack tare, the mass of binder and sealant, a consistent weight increase by a factor near 2.3 was found.

This aspect, apparently negative, is well balanced by the lower disposal cost for declassified wastes.

Quantitatively this important result allows to consider the RCA treated in this way as a waste disposable in less restrictive class dump (cat. II type B), according to the Italian and Community rules.

2. PILOT PLANT DESCRIPTION

The plant capacity of 12,000 m^3 per year overrides the normal size concept for a pilot plant and is very close to the design of an industrial installation. This is mainly due to the optimisation of some process operations and to the availability of standard equipment from market (i.e. the shredder machine of adequate power to shear the RCA):

- the confinement within the different zones is achieved by separate filtration and ventilation systems for Zone I (RCA process line) and Zone II (plant). So the containment is implemented in two different ways: statically by physical separation of the different zones and dynamically by increasing the negative pressure between outer environment/Zone II/Zone I;
- the above ventilation systems also provide for the total capture of the free flying asbestos fibres;
- to assure suitable conditions in working areas of Zone II during winter the heating is provided in operative areas;
- the volume reduction of RCA is achieved by physical operations, in particular by shredding refuses as preliminary step and then pressing the shredded material inside the concrete overpack.

2.1 Process description

All the material born during RCA shredding is gathered by gravity inside a weighing hopper, which cuts off power to shredder unit when reaching a set amount, corresponding to a pressing stroke inside the overpack. It is positioned beneath the end of the mixing and transferring auger conveyor. In the same hopper it is pumped a calibrated minimum amount of cement binding paste (coming from make-up plant) for a proper embedding of asbestos fibres; the water/cement ratio of cement binder is set in reference to moisture of incoming RCA. Of course, setting of w/c ratio is related to the RCA incoming homogeneous batch.

The quantity transferred for each pressing stroke strictly depends from the volumetric mass of RCA incoming batch and is set by operator on the weighing hopper through the process computer (PLC) on the basis of reference values established by experimental trials.

3. FINAL CONSIDERATIONS

- A final volume reduction by 2.5 ratio, in reference to untreated RCA, is achievable through the process;
- about 20% cost saving on RCA disposal is certainly a promising goal.

In terms of environmental impact we must account the following further advantages:

- the disposal of treated RCA inside lower category dumps makes available more space in II Cat., type C dumps, for other kinds of toxic-hazardous waste otherwise not easily and economically disposable.
- the release of asbestos fibres to the environment given by treated RCA is strongly lower than corresponding rate born from untreated ones, mainly taking in account that life time of II Cat., type C dumps is not indefinite.
- the future trend of rules in force is pointed to consider the embedded asbestos materials as inert wastes, so making possible their disposal in II Cat., type A dumps, less expensive and with a smaller impact to the environment.

TITLE: Study of a communication strategy aimed at achieving a possible better understanding of the consequence of radioactive waste management in well-defined group of public

Contractor: ONDRAF/NIRAS, Belgium
Contract n°: FI2W-CT90-0036
Duration of contract: 45 months : from 01.04.91 to 31.12.94
Period covered: January-December 1993
Project leader: V. Vanhove

A. OBJECTIVES AND SCOPE

Starting from the hypothesis that the information of the public on radioactive waste management is confronted with prejudice and ignorance, the study tries to establish whether it is possible, by working out and disseminating an argumentation that is well adjusted to a specific target group, to reduce obstacles to information and to induce the public to understand and accept the approach of ONDRAF/NIRAS.

Beside the first phase of the study which is aimed at identifying the target group and determining the origin and state of knowledge of the target group regarding the subject, the global objective is to perform an in-depth study of the system of knowledge transfer with the aim of evaluating, both qualitatively and quantitatively, the methodology worked out. The same methodology will be applied later on for other target groups.

The global objective is divided into two parts :

1. distribution (introduction and implementation) of the documentation and argumentation developed ;

2. registration and follow-up of the resulting changes in public opinion and attitudes towards the subject.

B. WORK PROGRAMME

The following work programme has been followed :

1. development of the pedagogical package for the teaching staff and for the students

2. elaboration of the introduction and mailing strategy

3. elaboration and start-up of the Information Centre Isotopolis

4. elaboration and implementation of a qualitative pretest of the pedagogical package and of the visit to Isotopolis

C. PROGRESS OF WORK AND RESULTS OBTAINED SO FAR

State of advancement

During the period considered, the pedagogical package - both for the students and for the teaching staff - were finalized. The concept and content of Isotopolis, the information centre in Dessel (province of Antwerp, located on the nuclear site of Belgoprocess, ONDRAF/NIRAS' industrial subsidiary) were finalized as well. By December 1993, Isotopolis was ready for inauguration. Six schools already paid a visit to Isotopolis and evaluated one of the brochures - "Handling Radioactivity" - as part of the pretest of the global project.
In November a first mailing was sent out to all high schools in the country (two last years of secundary education in Belgium) to introduce the project. By the end of December this mailing was followed by a second mailing containing more detailed information on the project and a reply card for ordering information kits and/or making reservations for a visit to Isotopolis.

The information project has two components :

1. the information package, presented in a written form and composed of three brochures (Handling Radioactivity, Managing Radioactive Waste, Disposal of Radioactive Waste) and information files on ONDRAF/NIRAS and Belgoprocess. A glossary will be developed early 1994 ;

2. a visit to the information centre on radioactive waste management, Isotopolis, in Dessel, which is the pivot of the information project, where visitors are confronted with the reality of the radioactive waste management issue in an interactive and visual way. The success of the information and knowledge transfer to the target group largely depends on the guides who show the visitors around in the Information Centre.

Structure of the information package

Considering the innovative and experimental character of the study, the actions are conducted in several phases :

1. a qualitative pretest on national level and on local level (Mol, Dessel and Geel, province of Antwerp). This action is justified by the establishment of the Information Centre. Determination of the sample is entirely based on the experience of the first phase of the study;

2. distribution (introduction and implementation) of the information package on national level in the two last years of secondary education (1200 schools) ;

3. the assessment of the information and knowledge transfer will be made in 1994.

By the end of December 1993, 185 students had visited Isotopolis (of whom 95 visited Isotopolis and 90 used the combination of the "Handling Radioactivity" brochure and Isotopolis). Another 85 students evaluated the brochure "Handling Radioactivity". Since the pretest was not finished at the end of the month, no results are available yet.

Title : Information of the public in the field of decommissioning waste
Study of strategies and means for specific information

Contractor : CEA Saclay - Direction du Cycle du Combustible (DCC)
Contract N° : F12W-CT90-0043
Duration of contract : June 91 - May 94
Period covered : January - December 93
Project leader : Mrs. Danièle Gerster

A OBJECTIVES AND SCOPE

DCC/UDIN is the nuclear installations dismantling unit of CEA and manages most of its waste. The nature and importance of the waste justifies public information. UDIN is in good position to yield technical and economical information.

The first step of the work consists in searching and defining a good media dissertation and producing a pilot operation of communication.

The results expected will form a practical contribution to solve sociological problems issued by waste management, whether they are hazardous or not.

The economical benefits expected from this information will be tied to human analysis, positive and intelligent, in solving conflicts related to waste management in the European Community.

To answer public needs for information, several partners were selected :

- University of Paris-Orsay to translate technical information into common ("popular") language.
- A group of sociologists explore and explain the fears and hopes of the public.
- A movie maker skilled in technical, didactic and TV films.

B WORK PROGRAMME

The programme of the study is approximately structured according to the following steps :

B1 : Selection of partners, define basis of discourse and iconographic data ; evaluation of application to actual dismantling plants (e.g : G2-G3, Rapsodie).
B2 : Analysis of similar actions evolving in other fields ; investigation of results, definition of the basis of the discourse.
B3 : Investigation of different fields ; selection of targeted public ; acceptance of such a public ; approach and motivation of (media) "atypique" persons and evaluation of their reactions to the proposal discourse.
B4 : Methodology of pilot operation : study of original communication charter ; meetings with support producers.
B5 : Development of adaptation operations and validation of the elaborated processes.
B6 : Final Report with global recommendations. Drafting of Annexes according to the discourse and transposable actions.

SUMMARY

It was pointed out, in the conclusions of last year's progress report, that :
- there is a need for outside information on dismantling and its waste ;
- it is necessary to firstly inform relays of opinion, including nuclear operators ;
- company staff is a vector that has never been specifically contemplated ;
- pictures are a convivial mean to comfortably transfer a lot of information.

It was then decided to perform an inquiry through interviews of the personnel working on dismantling projects of CEA's nuclear facilities, to produce a video film on dismantling and its waste, to distribute the film to the company staff, together with an information file, and then to hear about their reactions via a questionnaire.

The period from April to September 1993 was devoted to the inquiry, the writing of the information documents, and the preparation of the movie script.

The film was produced between October and December and the whole package has been submitted to a selection of the personnel during January 1994.

Copies of the video, the file and the questionnaire are sent together with this report.

PROGRESS REPORT

1 - The inquiry

a) Selection of facilities : a reactor and a laboratory

The inquiry has been carried out in March and April 1993 on two facilities of CEA, presently under dismantling : GGR reactors (G2 - G3), and a laboratory : RM2 (radiometallurgy).

The gaz graphite reactors were commissioned in 58-59 and stopped in 80 (G2) and 85 (G3). The dismantling project will reach stage 2 at the end of 1993.

The plutonium radiometallurgy laboratory (1965 - 1980) devoted to the study of irradiated fast reactor fuel, was highly contaminated with α emitters and fission products. Most dismantling operations must be remotely performed. Level 3 is expected to be reached at the end of 1994.

b) Selection and behaviour of people

As it was not possible to interview everybody, two criteria of selection were adopted ; we agreed to choose people being :
- volunteer for answering questions,
- still working on the project.

18 thorough interviews were performed, based on a preestablished interview guide worked out by a sociologist in cooperation with CEA's Communication Division and with the Fuel Cycle Division which is in charge of the Dismantling Unit.

The average interview time was two hours instead of one as planned ; this is a good yardstick of the interest they take in their work (upon which those people discoursed at length) and of their willingness to think over matter of information, inhouse communication, communication of the public at large, reliability of media, etc..

c) Content of interviews

Main subjects addressed were :

- interest in the job,
- general knowledge in dismantling, and in nuclear technical activities at large,
- sociability and openmindedness,
- need for information,
- feeling about communication.

d) Results

If communication towards the outside was the central point in this inquiry, it remains true that the content of the interview is also filled with opinions about internal communication : organization and content of work, perception of the future in this field of activity. For site-work staff, concern about employment is preponderant.

It is generally agreed that information is available, but not precise knowledge of where and how to get it, nor the definite will to make efforts to obtain it. Differences exist between different sites and projects. Concision and synthesis are wanted in the transmission of information. Comparisons with other types of activities are requested because "people are mainly interested in consequences, but find it hard to master concepts such as radiation, contamination, etc...".

Regarding external communication, some distrust is expressed towards professional's communication, even if it is admitted that it is necessary.

TV is considered as a powerful medium (some people think that one can write just anything, but pictures "it is the truth").

TV is also considered as under-used (and ill-used) as far as nuclear and safety are concerned : efforts devoted to nuclear safety, security, radiation protection, are not assessed at their true value by journalists and public alike : "in the nuclear field, it is a belt, plus suspenders, plus safety pins !".

Regarding waste, some incertainties and even inaccuracies are sometimes expressed. Though this subject is practically never brought up spontaneously, it is in the case of dismantling considered as "a key topic", as well from the public opinion standpoint, as from the operationnal worksite standpoint.

The reuse of materials from dismantling remains the most controversial topic.

The focusing of public opinion on waste from nuclear power generation (and not from hospitals or non-nuclear industries) is badly perceived.

If during extraprofessionnal discussion, dismantling does not raise any problem in itself, on the contrary "nuclear waste represent a hot topic, it is unacceptable, discussions become bitter".

The necessity of explaining the origin of the various materials and ultimate waste produced in the dismantling operations, and how they will be managed thus appears very clearly ; it is the main goal assigned to the video film to be produced.

2 - THE CONTENT OF THE VIDEO MOVIE

The video film explains in about ten minutes :

- what is dismantling : leaving the site as clean as possible, with different stages, accessible to the public or to any kind of activity ;
- what kind of facilities are to be dismantled : reactors, plants, laboratories ;
- what are the alternative strategies : wait until the activity has decreased by several orders of magnitude, or immediate action, to what level ?
- what are the techniques available : mapping of radioactivity, decontamination, disassembling, cutting into pieces, conditionning of liquid and solid waste, including specific materials like graphite or sodium, decreasing volumes, characterisation of waste;
- destination of waste and miscellaneous materials : separate and condition the waste according to their type and activity level, control, specify and store them in specialized installations ; recycle non radioactive products and materials when possible, in the nuclear industry.

The important point for public opinion is obviously the consequences of a dismantling operation : in terms of safety and radiation protection of public and environment but eventually also in terms of professional activity in the region (employment). One of the criteria which seems particurlarly sensitive in the opinion nowadays, is the assumed effects of low doses on living organisms ; may be because we do not have yet a sufficient scientific knowledge in this matter.

This subject would in itself require a complete study and argumentation, but we considered it was definitely outside the scope of the present work.

3 - FINAL STAGE OF THE PROGRAMME

The video movie has been completed at the end of December 1993, and is being handed over the personnel (40 persons) of UDIN, CEA's dismantling task force, together with an information booklet dealing of waste management, a file of documents about dismantling techniques and strategies, and a questionnaire to fill, about reaction of the audience to the video movie.

This questionnaire is a mean to measure the efficiency of this communication action in terms of public impact, in order to draw conclusions about the adequation of this kind of action with the original objectives.

The answers to the questionnaire will be analysed at the end of the first trimester (1994) and the final synthesis report of this contract will be available before the end of the first semester.

Title:	The evolution and implementation of a public information strategy on radioactive waste management
Contractor:	GCI London
Contact n°:	FI2W-CT90-0074
Duration of contract:	from: June 1991 to: February 1995
Period covered:	January - December 1993
Project leader:	

A. *OBJECTIVES AND SCOPE*

GCI London is responsible for the creation and implementation of a communication programme covering four principal areas:-

1. The evolution of an EU policy on the public information aspects of radioactive waste disposal
2. The sharing of communications lessons learned by national agencies within the European Union
3. The provision of a resource base of complementary, pan-European communications materials
4. The creation of a multicountry, complementary education programme

The envisaged practical application is for the Commission to complement the communication activities of the national waste agencies where appropriate.

B. *WORK PROGRAMME - 1993*

1. Publications

Origination, production and distribution of A4 report in various language versions; production and distribution of language versions of existing A5 leaflet.

2. Video

Origination, production and distribution of 11' video.

3. Education Programme

Creation and implementation of a multilingual, multimedia education programme.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

1. State of advancement

Through 1993 *GCI London* have delivered the communication materials as scheduled.

The objectives and scope of the education programme were agreed, a specialist sub-contractor appointed following submission of competitive bids, and initial development work completed. The education programme is scheduled for completion in 1994.

2. Progress and results

(i) communications materials

All communications materials were produced with the cooperation and input of the national waste management authorities, enabling *GCI London* to compile an accurate survey of radioactive waste management throughout the European Union.

The publications and video have effectively complemented national waste agencies' communications strategies. Their take up of the publications is demonstrated by the production and distribution figures set out in tables I - IV.

(ii) Education programme

The purpose of the education programme is to educate schoolchildren in selected Member States on the reality of radioactive waste management.

The educational objectives of the programme distinguish it from other communication activities. There is an absolute necessity to provide balanced, objective, credible information on the issue in order for it to be considered suitable for use by teachers.

An approach oriented towards public relations, or which serves as an apologia for the nuclear industry, would result in a waste of resources and severely damage the credibility and authority of the European Commission.

The major constraints governing the programme are:-

- *the narrow curricular base in EU schools*

  Radioactive waste management comes under various sections of the national curricula, such as physics, geography, social studies, economics, environmental studies. In addition, curricular requirements vary by region and country.

- *negative perceptions of radioactive waste management as part of nuclear industry*

  Public opinion is initially hostile to nuclear generation of power and associated industries. The goal of the education programme is to challenge this hostility, enabling children to understand the complexity of the issues involved. The children will be encouraged to reach their own independent conclusions regarding the reality of radioactive waste management.

- *sheer volume of educational materials produced by other industries and interest groups*

  Many industries/interest groups produce educational materials targeted at schools, claiming that they are essential aids to teaching standard subjects.

- *the complexity of radioactive waste management necessitates different levels of teaching adapted to different age groups*

  An understanding of radiation is at the foundation of a comprehension of the tasks involved in effective radioactive waste management. Most children, however, are not taught the requisite physical concepts until the ages of 13 - 15. Attitudes to environmental issues, however, develop in children from an early age - sometimes from the age of 4 upwards.

To avoid all these problems, *GCI London* are developing a multilingual, interactive, mulitimedia exhibit for educational use in European museums. Teachers and schools will be targeted through an allied education pack.

The exhibit is branded as a product of the European Commission, and has teenage video arcade feel to attract children in the museum environment. Personalised to each user through an identity ticket, the interactive nature of the exhibit will enable each child to progress at his or her own speed. Furthermore, the interactive, multimedia programme adapts automatically to the age of the child when he/she logs on.

The exhibit will be premiered at the Edinburgh Science Festival at the end of March. Negotiations for siting are continuing with the national Science Museum in London, and are scheduled to be opened with Braunschweig regional museums and public bodies in April.

Of the national waste agencies, *ENRESA* (Spain) and *ANDRA* (France) will be associated at the evaluation stage, whilst *ONDRAF/NIRAS* (Belgium), *BfS* (Germany) and *UK NIREX* (UK) have participated in the development of the programme. Additional materials have been sourced from *AEA Technology* and *Nuclear Electric* in the British nuclear sector.

A5 LEAFLET

Title: *Managing Radioactive Waste*
Total number of copies produced: 47 900

Table I. A5 leaflets produced under contract

Language	Quantity	Delivered to	Distributed by
English	10,000	Mr Schaller	C.E.C.
French	2000	Mr Schaller	C.E.C.
German	1000	Mr Schaller	C.E.C.
Dutch	1500	Mr Schaller	C.E.C.
Italian	500	Mr Schaller	C.E.C.
Spanish	1000	Mr Schaller	C.E.C.
TOTAL	16,000		

Table II. A5 leaflets requested by and paid for by national waste agencies

Language	Quantity	Delivered to	Distributed by
English	20,000	UK Nirex	UK Nirex
English	5000	Scottish Nuclear	Scottish Nuclear
English	500	ENRESA	ENRESA
English	100	ONDRAF	ONDRAF
French	100	ONDRAF	ONDRAF
French	500	ENRESA	ENRESA
French	200	NAGRA	NAGRA
German	500	NAGRA	NAGRA
Spanish	5000	ENRESA	ENRESA
TOTAL	**31,900**		

A4 REPORT

Title: *Managing Radioactive Waste in the European Community*

Total number of copies produced: 22 000

Table III. A4 reports produced under contract

Language	Quantity	Delivered to	Distributed by
English	5000	Mr Schaller	C.E.C.
French	1000	Mr Cadelli	C.E.C.
German	1000	Mr Cadelli	C.E.C.
Spanish	1000	Mr Cadelli	C.E.C
Russian	2000	Mr Cadelli	C.E.C.
TOTAL:	10,000		

Table IV. A4 reports requested by and paid for by national waste authorities

Language	Quantity	Delivered to	Distributed by
English	10,000	UK Nirex	UK Nirex
German	1000	Interforum Germany (I.G.)	I.G.
Spanish	1000	Forum Atomico Espanol (F.A.E.)	F.A.E.
TOTAL:	12,000		

A public information campaign to support a proposed national deep repository for low and intermediate level radioactive waste

Contractor:	BNFL (UK), UNIVERSITY OF SURREY (UK), INSTITUTE SYMLOG (F)
Contract No:	F12W/CT91/0105
Duration of contract:	1 November 1991 to 30 April 1995
Period covered:	1993
Project Leaders:	M Bold (BNFL) P Allen (University of Surrey) C Mays (Institute SYMLOG)

A. Objectives and Scope

The primary objective of the campaign is to gain support in Cumbria for a radioactive waste repository at Sellafield through the dissemination of factual information in various forms to the public.

Opinion polls have established an initial baseline level of support which represents an appropriate yardstick for evaluating the effectiveness of the campaign as it progresses. Analysis and comparison of data gathered from subsequent polls and interviews will enable change in support to be measured.

A second objective is to generate information in a suitable form for detailed consideration by other European Community Member States by assisting them to produce similar programmes of their own. The comparison of the baseline opinion data in the United Kingdom and France is the principal method for fulfilling this objective.

B. Work Programme

This involves opinion surveys and the development and production of appropriate information material. The main components of the campaign are:

i. Opinion Research

a. The University of Surrey Robens Institute has conducted detailed research work, obtained baseline measures of public understanding and reactions to the siting of the Repository at Sellafield and identified particular concerns by a survey conducted in Cumbria.

b. The Institute is evaluating the various publicity media available for the BNFL information campaign and advising on the most effective methods to communicate to the public.

c. The Institute will also conduct follow up surveys to assess the effectiveness of the campaign in terms of changes in the knowledge and attitudes of the Cumbrian people.

ii. International Comparisons

a. The Institute SYMLOG de France has carried out detailed research work involving comparisons of Cumbrian public opinion data and French public opinion data concerning the siting of a radioactive waste repository.

b. The Institute is comparing the public opinion data with the interview data from appropriate officials concerned with radioactive waste management in France and the UK.

c. The Institute would also compare institutional approaches and the extent to which their policies are appropriate, given public views.

C. Progress of Work and Obtained Results

1. REPORT BY UNIVERSITY OF SURREY ROBENS INSTITUTE

1.1 Survey within West Cumbria

The University of Surrey, Robens Institute, carried out further analysis of the results of a survey carried out in the West Cumbria area. A representative sample of 744 people from 3 geographical zones within West Cumbria was surveyed in order to provide a baseline of public views. The principle findings were as follows:

- Regarding the stability of the population, urban residents in the coastal zone (Zone 1) tended to have been in the area the longest, while rural residents in the inland zones (Zones 2 and 3) tended to have been there for a shorter length of time. However, both these groups of people expressed a desire to stay in the area.

- The majority (84.9 percent) had heard of the proposed deep Repository, but for those who had no connections with the nuclear industry this proportion depended on distance from the proposed site with fewer aware of the proposal inland from Sellafield.

- Although most had heard about the Repository, few claimed to know very much about it. Those in Zone 1 and particularly those with an employment connection (almost half of those in Zone 1) tended to attribute more knowledge to themselves. Main information sources were TV and newspapers.

- 47 percent indicated that they were opposed to the Repository but a very similar number (41.4 percent) were undecided. People in the coastal zone, those with an employment connection, and men tended to be less opposed; zone being the most reliable predictor of attitude. Those under 24 and over 64 were less certain of their view.

- An increase in self-attributed knowledge was not associated with either an increase in opposition to, or acceptance of the Repository. Those in favour were not necessarily better informed, and as many of those who opposed the Repository as welcomed it were well informed. It cannot be assumed, therefore, that information alone will result in increased support.

- Objections which the respondents thought might be raised against the Repository mainly concerned safety/risk aspects. Also, over half the sample ranked health risks as the most important siting issue.

- In addition, men, those who knew quite a lot about the Repository, and those in favour of both nuclear power and the Repository, felt that geology was more important. Conversely women, those who knew little or nothing, and those against, ranked health and environmental issues as more important. This indicates the existence of very different constituencies of people who might be targeted with information about the proposals. Their opinions vary considerably and their responses to information will differ substantially.

- Coastal residents and those with an employment connection thought that the taking into account of local opinion was more important than did other groups, while inland respondents with no such connections tended to think that environmental and health issues were more important.

- The majority of people (66 percent) did not think that their views would be taken into account. However, more of those from the coastal area, and more of those already supporting both nuclear power and the Repository, were prepared to believe that their views would be heard.

- However, only approximately half the sample showed some degree of confidence that the right decision would be made. Those in Zone 1, with an employment connection, pro-nuclear and pro-Repository, and those claiming more knowledge tended to be more confident.

- Regarding perceived information requirements, the respondents expressed a need for information on most of the issues, in particular safety issues. Those with an employment affiliation generally required less information. Zone 3 respondents wanted more information about geology, monitoring arrangements, safety procedures, the probability of future contamination, and recovery potential. Those against nuclear power wanted more information than those in favour, on relative costs, monitoring arrangements, gaps in scientific knowledge and the probability of future contamination. The uncommitted group, which may be influenced the most easily, felt they wanted more information about future contamination, safety, monitoring arrangements, and transportation. Those opposing the Repository required more information on all of the issues.

- The respondents were most confident in the competence of NRPB, BNFL, Department of Environment, and environmental groups to deal with the waste problem, and local authorities and contractors the least. Regarding trustworthiness to tell the truth, environmental groups, NRPB, and the Department of Environment were again rated highest, but contractors and NIREX were rated the lowest.

- Coastal residents tended to have more confidence and trust in most of the groups, but particularly BNFL and the nuclear power industry. People's opinions varied most concerning BNFL. Those with an employment affiliation had more confidence and trust in BNFL, NIREX, Department of Environment, contractors and the nuclear power industry. Those claiming some knowledge of the Repository and both pro-nuclear and pro-Repository respondents tended to express more trust and confidence in all of the groups, except environmental groups.

- Overall the sample had slightly less confidence in the *competence* of local authorities and environmental groups but less *trust* in BNFL, NIREX and the nuclear power industry.

- The majority (72.3 percent) did not think that the public are told enough. Although fewer people in the coastal zone, with an employment connection, in favour of both nuclear power and the Repository, and fewer women tended to agree with this.

- Half the respondents claimed to have thought about the waste issue, but only 9.3 percent seriously. Zone 1 people had thought about the issue the least, and Zone 2 people the most. Therefore, degree of thought is not associated with distance from Sellafield. Also those with no employment connection and those against both nuclear power and the Repository, had thought about the issue *more*.

- 37 percent of the sample had visited the Sellafield Visitors Centre. Half of these were coastal zone residents, and a higher percentage had an employment connection and a greater degree of knowledge about the Repository. Twice as many of those in favour of nuclear power had visited and 65 percent of those supporting the Repository. This suggests that the Centre may well attract those who are already pro-nuclear.

- The Centre was rated very highly overall, particularly by those with an employment connection, with quite a lot of knowledge about the Repository, and by those in favour of nuclear power and the Repository, and those uncommitted. The Centre, therefore, has some potential to influence the latter group.

- 51.2 percent of the sample were in favour of nuclear power generally, 27.4 percent against, and 21.4 percent were undecided. More of those in favour were from the coastal zone, and had an employment connection. Men were slightly more pro-nuclear.

- Half of those in favour of nuclear power had not formed a definate opinion regarding the Repository. However, those more in favour of nuclear power claimed to know more about the Repository than the other groups.

- Few of the sample (only 4.1 percent) were, or had been, members of environmental groups. Of these, the majority were from the inland zones, had no employment connection, and were against both the Repository and nuclear power.

These results provide a general picture of the attitudes and beliefs of the people of West Cumbria in relation to both nuclear power in general and more specifically the proposed deep Repository. The survey indicates that the most important characteristics of the population with respect to attitudes about the Repository were distance from the Sellafield site, employment connection with the nuclear industry, attitudes to nuclear power generally and degree of knowledge about the Repository. Fewer effects were found for age, sex, and qualifications.

In general, those in the coastal zone (Zone 1), with an employment connection, in favour of nuclear power and the Repository, and who attributed themselves with quite a lot of knowledge about the Repository, tended to see the waste issue in a more positive and favourable light, and tended to perceive health and safety issues as less salient.

However, it is important to emphasise that knowledge itself is not a factor giving rise to increased support, particularly for the Repository. Many of those who are against both nuclear power and the Repository claimed to know quite a lot about the latter.

Another important finding was that environmental groups were rated most highly in the survey, both for competence and honesty, compared with NIREX. The industry was viewed as competent but was not trusted.

Finally, the survey might be taken to indicate a considerable degree of apathy concerning the Repository. Although the majority of respondents were against the Repository, most were not actively opposed, and a large number were undecided. However, interest in the issue is indicated by the number of comments given in response to the open ended questions. These comments tended to be negative, suggesting suspicion and mistrust. Likewise, respondents were not particularly trusting of certain relevant groups, and largely felt that their views would not be heard and that the right decision would not be made.

Consequently, although the survey does give the impression of a certain degree of acceptance of the Repository, and of nuclear power in general in the area, this is much more likely to be a thin veneer of acceptance, disguising the feeling that people have no choice, and that they are largely powerless to alter the situation.

The concerns expressed over representation of local views, the lack of trust and the apparently pervasive belief that the right decision will not be made all point to the paramount importance of a visibly just decision process for the siting of the Repository. It would seem to be especially important to study the public perception of that process.

1.2 Analysis of responses to NIREX advertising

This survey involved the qualitative analysis of the responses to the NIREX newspaper advertisement campaign, which concerned proposals for the national deep Repository for radioactive waste at Sellafield. The advertisements invited the public to send in questions to the Sellafield Repository Project Information Unit at Whitehaven. In total, 112 responses were received, 30 (26.8 percent) were from people living in Cumbria, the rest (73.2 percent) included several from outside the UK.

The responses were content analysed in order to reveal concerns and information needs, and attitudes and perceptions of the Repository Project. The Cumbrian and non-Cumbrian responses were analysed separately in order to explore differences between the two areas, which were expected to be a function of distance from the proposed site (Allen and Marston, 1993).

Cumbrian Responses

The analysis of the subject matter of the Cumbrian responses indicated that the principal concern of the respondents was the possible effects of earthquakes and other seismic activity upon the Repository. The following issues were also referred to a number of times: environmental damage, risk to future generations, the Repository advertisements, site suitability and selection, and secrecy and dishonesty surrounding Sellafield's operations.

The responses tended to be specific and rather informed, suggesting that the respondents already possessed some knowledge of the relevant issues. There were also references to aspects of Sellafield and the nuclear industry in general which were not directly related to the Repository Project. This shows that people do not tend to consider the Repository Project in isolation, but in the context of related issues, about which they may already have formed strong opinions.

There appeared to be two main reasons for respondents replying to the advertisements, and hence two types of response: firstly, there were questions to which the respondents expected answers, and secondly, there were comments through which respondents expressed their opinions, fears and objections. Although more Cumbrian respondents asked genuine questions, 23.3 percent of the responses were comments, and a further 26.7 percent were questions which incorporated comments. Consequently, the reply slip fulfilled a dual role by providing both information and a channel for communication.

The responses were also analysed regarding the likely attitudes of the respondents, which might be inferred from the general tone of the response. Just over half of the Cumbrian responses were 'neutral', in that they did not obviously indicate an attitude, and most of these were questions. 40 percent however were 'critical' of the subject matter of their response, particularly regarding the issues of site selection and suitability, secrecy surrounding operations at Sellafield, leaks and accidents, and both general risks and risks to future generations. The high proportion of comments and of 'critical' responses indicates that many Cumbrian respondents were concerned. However, two respondents expressed their support for the Project.

When the responses were geographically divided into the zones identified for the Cumbrian survey (Allen and Marston, 1993), the Lakeland area (Zone 2) yielded the most responses overall, while fewer responses were received from the coastal area (Zone 1); although here there were more comments and 'critical' responses, indicating their concern. This was perhaps a result of a resigned attitude towards the nuclear industry in this area, as previous studies have indicated. Further attempts at facilitating public involvement might therefore be appropriate.

The relatively few questions from Zone 1 could also be taken to indicate some support for the Repository, since the Cumbrian survey indicated that those in favour of the Repository typically required less information. Consequently attitudes may be more polarised in this area.

The actual language used by the respondents included several terms with negative connotations, such as *'dump'* used instead of Repository, and overtones of scepticism and distrust, even within some of the 'neutral' type responses. Attitudes towards the Repository therefore seem to be more complex than simply 'for' and 'against'. There were also frequent references to 'uncertainty', particularly to whether NIREX could 'guarantee' no risks resulting from the Repository Project.

Sex differences between the responses were also discovered, with 72 percent of the total Cumbrian respondents being male. Women however made more 'critical' comments. This provides further evidence to support earlier suggestions that women tend to be more anti-nuclear. Women referred more frequently to 'safety' and the 'retrievability' of the waste.

Non-Cumbrian Responses

The issues inherent in the responses from the rest of the UK and overseas were more diverse. Many were also particularly detailed and specific, again indicating considerable knowledge. A quarter of the responses, on the other hand, were requests for general information, and several for educational material, presumably from those who knew little about the Project. The reply slip therefore served both those needing general and specific information.

Non-Cumbrian concerns included: details about the waste, water movement and earthquakes, surface storage, and in particular funding/costs of the Repository. There were no references to the latter amongst the Cumbrian set, where more people mentioned safety, environmental damage and secrecy/credibility of the nuclear industry. These differences are presumed to be due to proximity to the proposed site.

All but two of the non-Cumbrian responses were questions, therefore there were definite differences in the use of the reply slip between the two areas, with many Cumbrian respondents apparently requiring a means of expressing their attitudes and objections. As a result, most of the non-Cumbrian responses were characterised as 'neutral' regarding attitude, although of those that were not, the majority were 'critical'.

An analysis of the language again revealed sceptical overtones, particularly regarding the funding/costs of the Repository. However, there were no references to *'dumps'* as with the Cumbrian set. Allusions to 'uncertainty' were again a re-current theme.

An analysis of the geographical distribution of the non-Cumbrian respondents showed that responses were received from all over the country, but in particular from the general vicinity of nuclear waste generating sites, especially around the Capenhurst/Springfields/ Heysham sites. Proximity to these sites may have increased awareness of the waste issue.

Again more men (71 percent) responded to the advertisements, and again 'retrievability' was a more female concern. However, amongst the non-Cumbrian responses fewer 'critical' comments came from women, compared with those in Cumbria.

The advertisements and reply slip were therefore somewhat successful in eliciting concerns and information needs. The most frequent questions overall referred to earthquakes and various other geological and hydrogeological aspects of the Repository. Other issues which recurred throughout the responses were: high level waste, foreign waste, secrecy surrounding Sellafield's operations, retrievability of the waste, and expense of the advertisements.

The reply slip also served a dual purpose in providing both information to the general public, and in enabling the expression of opinions and objections, hence facilitating a two way correspondence between the public and the nuclear industry. The analysis also revealed some characteristics of the respondents. Overall, many of the respondents already possessed knowledge of the relevant issues, the majority being men. Outside of Cumbria, most respondents asked 'neutral' type questions, few being critical, and many were relatively close to nuclear waste generating sites. Many of those who responded from Cumbria, however, were 'critical', particularly women. The advertisements therefore achieved a flow of information, despite the fact that they provoked criticism from a few.

2. <u>REPORT BY THE INSTITUTE SYMLOG DE FRANCE</u>

Institute SYMLOG de France, has carried out two levels of international comparison. People responsible for informing the public on radioactive waste management issues in France and the UK were interviewed. Also, a detailed report has been produced comparing Cumbrian and French national opinion survey data.

The overall result of the analysis first pointed to an apparent acceptance of an underground repository in the Sellafield area based on a professed lack of concern about the disposal of radioactive waste in comparison to other environmental problems. However, there is a great diversity of view underlying this result and in terms of presenting information, a unified audience does not exist. Target audiences requiring different types of communication can be identified.

When comparing the UK and French results, West Cumbrians described themselves as less likely than the French to take personal resistive action to the siting of a repository.

Questions relating to the Cumbrian's perceived competence and credibility of the people responsible for a Sellafield repository siting, showed relatively high levels of confidence and trust compared to the French, indicating that many of the officials involved had become familiar to the local community. The respondents were, however, suspicious of the amount of information given and whether the views of the population would be taken into account.

The problem of radioactive waste disposal combines a series of issues. These include technological, economic, environmental and social aspects.

As communities are faced with more and more issues, there will be less willingness to entrust the problems to the "experts" without a measure of input from the community.

It is important to secure an effective information exchange between the general public and the officials involved in the project. The range of issues covered and the mix of information exchange forums should reflect the diversity of the persons and concerns present in the community.

West Cumbrians appear to regard environmentalists - both militant and members of the establishment - highly, and value their apparent desire to "save" the environment. The low rate of militant group membership in the sample indicates that such groups do not fully comply with residents concerns or personal convictions.

Further research is recommended to explore the public's perceptions of "protecting the environment".

In order to test the generalisation of these action conclusions, and permit their transfer to other Community Member States as well as to other waste management issues, Institute SYMLOG would suggest:

i Similarly detailed site-specific public opinion research in a French community pre-selected to receive a repository or laboratory.

ii Communication policy-building seminars for decision makers on the basis of comparative data.

iii Design of background material aids for creating recommended interactive community risk management forums.

3. REPORT BY BRITISH NUCLEAR FUELS plc (BNFL)

The main responsibility of BNFL in this campaign is the co-ordination of a comprehensive information service to the general public in Cumbria on the proposed radioactive waste repository at Sellafield.

The Sellafield Repository Project Information Unit continues to coordinate the public relations functions associated with the repository. It is based at Sellafield and includes personnel from UK NIREX Ltd.

The provision of information in the area around the investigations is handled primarily from the Repository Information Office at Whitehaven, 18 kilometres north of the Sellafield site.

Much of the requirement for information has been centred around the decision to bring forward the development of an underground Rock Characterisation Facility - a free standing phase, separate from the actual repository itself. Exploratory work will take place in an area known as Longlands, near Sellafield. Planning application has now been approved allowing NIREX to drill a total of 13 exploratory boreholes at Longlands. Conditions of the planning approval specify that only two rigs between 35m and 50m high can be used at the same time. Drilling will last for a maximum of three years with a further four years post-drilling testing. Experience has shown that this is a conservative estimate and other borehole work has been quicker.

Drilling at the existing boreholes in the area was largely completed in 1993 with most of the work now concerned with post-drilling testing.

Drilling was begun at Longlands during 1993 and the results will enable decisions to be taken on the precise location and specification of the Rock Characterisation Facility. Sufficient information is expected to be available during the early part of 1994 to allow a formal planning application for the Facility to be submitted. This application could result in a public inquiry stage being entered into.

Public information material is being developed in response to demand for it, taking account of results of further research and the progress of the actual project itself.

The results of an opinion research survey carried out on behalf of NIREX by Priority Search, are now available. This consisted of almost 1000 house-to-house interviews conducted in the Sellafield area.

Those 'supporting' or 'tending to support' the project stress the operational safety of the project as their top concern, followed by effective long-term containment of waste. They also look for the Company to continue to be completely open and honest in its dealings with the community. Local employment is a high priority for those who support the project but was rarely mentioned by respondents who oppose it.

The research indicates that the information programme must concentrate more on safety issues. An advertising campaign was produced which deals with safety issues and invites readers to either comment or ask questions. A number of responses have been received and an analysis of these is contained in the University of Surrey report.

The Sellafield Repository Project Information Unit continues to produce a regular newsletter giving details of the latest developments. These are distributed to Regulatory Authorities, the media, local councillors and as handouts to visitors. To compliment this, there are plans for a free-distribution newsletter which will be delivered to households in the area.

This newsletter is intended to cover progress of the work and give information about forthcoming stages of the project. Information sheets are also produced for a very localised audience in order to keep members of the community, directly affected by the work, informed of progress and plans for future work. These groups are sometimes as small as six or eight people living in the immediate vicinity of the borehole work being carried out.

In addition to providing information from the Whitehaven office, the Repository Information Unit operate a mobile exhibition which is used at local events and shows. Information presented is continuously updated and renewed to reflect the progress of the project. The exhibition unit used at the borehole sites is still in use but consideration is now being given to the information needs at the Rock Characterisation Facility drilling site. The existing exhibition unit will be used in the short term, but an existing building on the site is being considered for a permanent exhibition.

Visits to similar facilities abroad have been arranged for local councillors, politicians and other opinion formers to allow them to see for themselves the extent of the operations and the type of work carried out. These visits have been very well received and have enabled comparisons to be drawn between similar projects and the experience in West Cumbria.

All the information now available from research is providing a sound platform on which to base the strategy for continuing information campaigns. The investigations and subsequent planning application for the Rock Characterisation Facility is the next major phase of the project and relevant information campaigns are either in place or being produced. The details of any future information campaign will be dependent on whether the planning application results in a public inquiry. The objective is to provide a balance of information and community liaison to ensure maximum support for each stage of the work as it progresses. Community reaction and concern is closely monitored resulting in a continuing successful communication programme.

Title: Transmutation of long–lived radionuclides by advanced converters
Contractor: Siemens AG Power Generation Group (KWU)
Contract No: FI2W–CT91–0103
Duration of contract: October 1st 1991 to December 31st 1994
Period convered: 01.01.1993 to 31.12.1993
Project Leader: Dr U. Wehmann

A Objectives and Scope

The study will analyse the possibilities, limits and technological development steps needed for tansmutation of actinides and long–lived fission products in unconventional advanced reactors and other advanced transmutation devices. The notion 'unconventional advanced reactor' means a fast reactor with unconventional fuel or of faster neutron spectrum or a small unit, which mainly will be constructed for transmutation. The other advanced transmutation devices are accelerator driven spallation machines and fusion reactors.

This study is one part of a coordinated partitioning–tansmutation study of a group of organisations: CEA, ECN Petten, ENEA, Casaccia, Siemens.

B Work Programme

1. Large fast reactors with MOX– and metallic fuel, fast zones and high axial leakage
2. Fast reactors, small units
3. Transmutation of fission products
4. Influence of lanthanide admixture to the fuel
5. Spallation machines and fusion reactors

C Progress of Work and Obtained Results

C1 State of Advancement

Referring to programme item 1, the transmutation potentials of MOX– and metallic–fuelled fast reactors have been compared and the influence of minor actinides on the main core parameters has been investigated. A safety related evaluation of these influences is under way.

The transmutation of fission products (Tc^{99} and I^{129}) has been studied (item 3) in a heterogeneous mode and the investigations on the influence of lanthanide admixture to the fuel of fast reactors (item 4) have been started.

The literature study about accelerator driven transmutation devices (item 5) has been extended to the Japanese JAERI concept and the Los Alamos on–site transmuter.

C2 Progress and Results

C2.1 Large Fast Reactors with MOX– and Metal Fuel (Item 1)

The minor actinides (MA) transmutation capabilities of oxide and metallic fuel have been compared, both in an EFR–like fast reactor core with reduced total power of 2600 MW_{th} and a core height of 70 cm. The only differences in the design parameters of both reactors are the fuel properties (type, density, Pu–enrichment). The maximum burnup of 20 % has also been kept constant for both cores.

The efficiency of MA transmutation has been calculated by assuming that 3 % of the heavy metal (HM) is replaced by MA. In the present investigation, Pu is not considered as an actinide waste, it just serves as a driver fuel for supplying high fluxes for MA transmutation.

The calculations have shown that there is no clear advantage for either fuel type, although the MA have a more favourable fission to absorption ratio in the metallic core. This advantage is largely compensated by the smaller capture cross–sections of the MA which reduce the transmutation into Pu–238. Both fuel types have a transmutation half–life of 11 years. A small advantage of the metallic fuel is the higher MA inventory at beginning of life due to the higher fuel density. Therefore, the transmuted MA mass per year is about 15 % higher than for oxide fuel.

The operational and safety behaviour is an additional important criterion for the evaluation of both fuel types. Here the following aspects are important:

- Compared to the oxide fuel the metallic fuel shows some specific advantages, which are based on the higher fuel density, i.e. lower Pu–enrichments, lower loss of reactivity per year due to fuel burnup and a longer fuel residence time. Assuming the same number of cycles per residence time for both cores, the absorber system requirements are reduced so that the control rod worth reduction by 13 % is more than compensated.
- The positive sodium void effect increases for metallic fuel compared to oxide fuel by about 50 – 60 %. The Doppler constant is reduced by about 50 %.

A safety related evaluation of these consequences will be performed in 1994.

C2.2 Transmutation of Fission Products (Item 3)

The fission products Tc^{99} (half–life $2.1 \cdot 10^5$ years) and I^{129} (half–life $1.6 \cdot 10^7$ years) belong to the long–lived nuclides in the high–level waste. Their risk contribution during storage is relatively high because of their pronounced mobility in geochemical environments around the waste repositories. Their transmutation into stable isotopes ($Tc^{99} \rightarrow Ru^{100}$, $I^{129} \rightarrow Xe^{130}$) is therefore of interest.

The one–group capture cross–sections of both isotopes are rather small in a standard fast reactor neutron spectrum. They are below 0.5 barn so that in an average neutron flux of $3 \cdot 10^{15}$ $cm^{-2}s^{-1}$ less than 25 % of the fission products are burnt during a fuel subassembly life of 6 years.

One possibility to increase the capture cross–section of the fission products is to place them in a moderated environment in order to soften the neutron spectrum. This effect was studied by introducing $ZrH_{1.7}$ in the target subassemblies containing Tc^{99}, I^{129} and Cs^{135} and by varying the $ZrH_{1.7}$ content. Figure 1 shows the one–group cross–sections of these isotopes as a function of the $ZrH_{1.7}$ content. The strong influence of the moderator content can be seen, but the fission product content itself has a similar impact. The larger fission product content leads to a spectrum hardening in the target subassemblies so that the capture cross–section is decreasing.

Figure 1 is also showing that the cross–section of Cs^{135} is small even in case of a large moderator content. Therefore, there is no chance for a transmutation of this isotope in a fast reactor.

In addition to the spectral effects indicated in Figure 1 the absolute flux level is also influenced by the contents of fission products and moderator. In general the neutron flux level is decreasing with increasing effectiveness of the fission products. A careful optimisation of the contents of fission products on one side and of the moderator on the other side is therefore necessary and realistic whole–core calculations have to be performed in which the right neutron flux level can be realized.

Within the first step of our study the fission products were concentrated in target subassemblies at the outer boundary of the outer core zone. These positions were chosen in order to avoid major distortions of the main core properties and especially of the reactivity coefficients.

The main result of this study was that the transmutation potential of the peripheral positions is rather poor due to the low flux level although 78 target positions were considered. The following table shows clearly the controversial influence of the fission product content on the transmutation half–life and the absolute masses:

Tc^{99} content	half–life in years	transmutation rate of Tc^{99} in kg/a
20 %	48	68
10 %	31	53
2 %	16	21

These data are valid for a $ZrH_{1.7}$ content of 5 %, but an increase to 10 % is changing the figures by less than 10 %.

In view of the fact that the fast reactor itself produces about 20 kg Tc^{99} per year, the transmutation rates mentioned above are certainly too small. One has therefore to choose inner core positions with a higher neutron flux level.

Basis of the study with in–core target subassemblies was an EFR type core where 84 of the 390 fuel subassemblies were replaced by Tc^{99}. In order to keep the linear rating constant, the total power was reduced to 2600 MW_{th} and the core height was increased to 1.20 m. Tc^{99}–contents of 10 % and 20 % were considered and the $ZrH_{1.7}$–content was varied between zero and 10 %.

In compensation to the cases with peripheral target positions these calculations clearly indicate the advantage of the in–core positions with respect to the absolute transmutation rates. In case of 20 % Tc they reach about 170 kg per year which is sufficiently large compared to the production of about 20 kg per year by this reactor. Consequently, there is a net transmutation rate of 150 kg per year which corresponds to the production rate of about 5 LWRs with 1300 MW_{el}. This results is quite acceptable.

The transmutation half–lives of the in–core positions are, however, comparable to those of the peripheral positions since the advantage of the higher flux level of the incore positions is largely compensated by the smaller capture cross–section due to the harder in–core spectrum. Half–lives of about 25 years can be realized.

For the case described above the sodium void and Doppler effect were calculated with a fission product content typical for an end of equilibrium cycle state. It turned out that the sodium void effect of the Tc^{99} containing core is 10 % smaller than that of the core without Tc^{99} although it has a larger core height. This can be explained by the much higher Pu–enrichment and the heterogeneity of the core with 84 Tc^{99} subassemblies. On the other side the higher enrichment causes the Doppler effect to drop by almost 30 %.

The transmutation of I^{129} has also been studied. The main result is that the efficiency of the fast reactor with moderated I^{129} targets in form of SnI_2 is smaller than that for Tc^{99}, but the net transmutation rate is still large enough to eliminate the production of 2 LWRs with 1300 MW_{el}.

C2.3 Spallation Machines (Item 5)

Table 1 compares the main features of three accelerator driven transmutation concepts, the Los Alamos ATW concept, the Brookhaven PHOENIX concept and the JAERI concept. The JAERI concept is more sticking to technologies now available and is by far less ambitious with respect to the beam current.

The high k_{eff}–values between 0.9 and 0.95 require much care regarding criticality safety and the high power density and large total powers are similar to those of commercial power reactors. One has therefore to doubt whether considerable credit of the subcriticality of these systems for simpler licensing or better public acceptance compared to present reactors can be taken.

C.3 List of Publications

W. Timm, F. Sperber
Consistent Comparison of Metallic and Oxide Fuel for Minor Actinide Transmutation in a Large EFR Type Fast Reactor
Proceedings of the 3rd working group meeting on Targets and Fuels, Karlsruhe 1993.

Characteristic Features	ATW	PHOENIX	JAERI
accelerator			
proton energy	1.6 GeV	1.6 GeV	1.5 GeV
beam current	250 mA	104 mA	39 mA
electrical power	900 MW	410 MW	146 MW
target/blanket modules			
number	4	8	1
target	solid tungsten/lead	sodium cooled rods of minor actinide oxide	solid tungsten
actinide blanket	actinide slurry in tubes passing through D_2O		sodium cooled rods of actinide alloy
neutron spectrum	thermal	fast	fast
k_{eff}	about 0.95	about 0.9	about 0.9
actinide inventory of the system	1.3 t minor actinides and plutonium	23 t minor actinides	3.2 t minor actinides and plutonium
transmutation rate per year of the system			
actinides	2.5 t minor actinides and plutonium	2.6 t minor actinides	0.25 t minor actinides (plutonium not mentioned)
fission products	0.3 t technetium and iodine	0.3 t iodine	–
number of LWRs, whose waste is transmuted	7.5 plutonium, minor actinides, iodine, technetium	75 minor actinides and iodine	8 minor actinides (plutonium not mentioned)
net electrical power production of the system	1000 MW	850 MW	100 MW

Table 1: Comparison of ATW, PHOENIX and JAERI transmutation systems

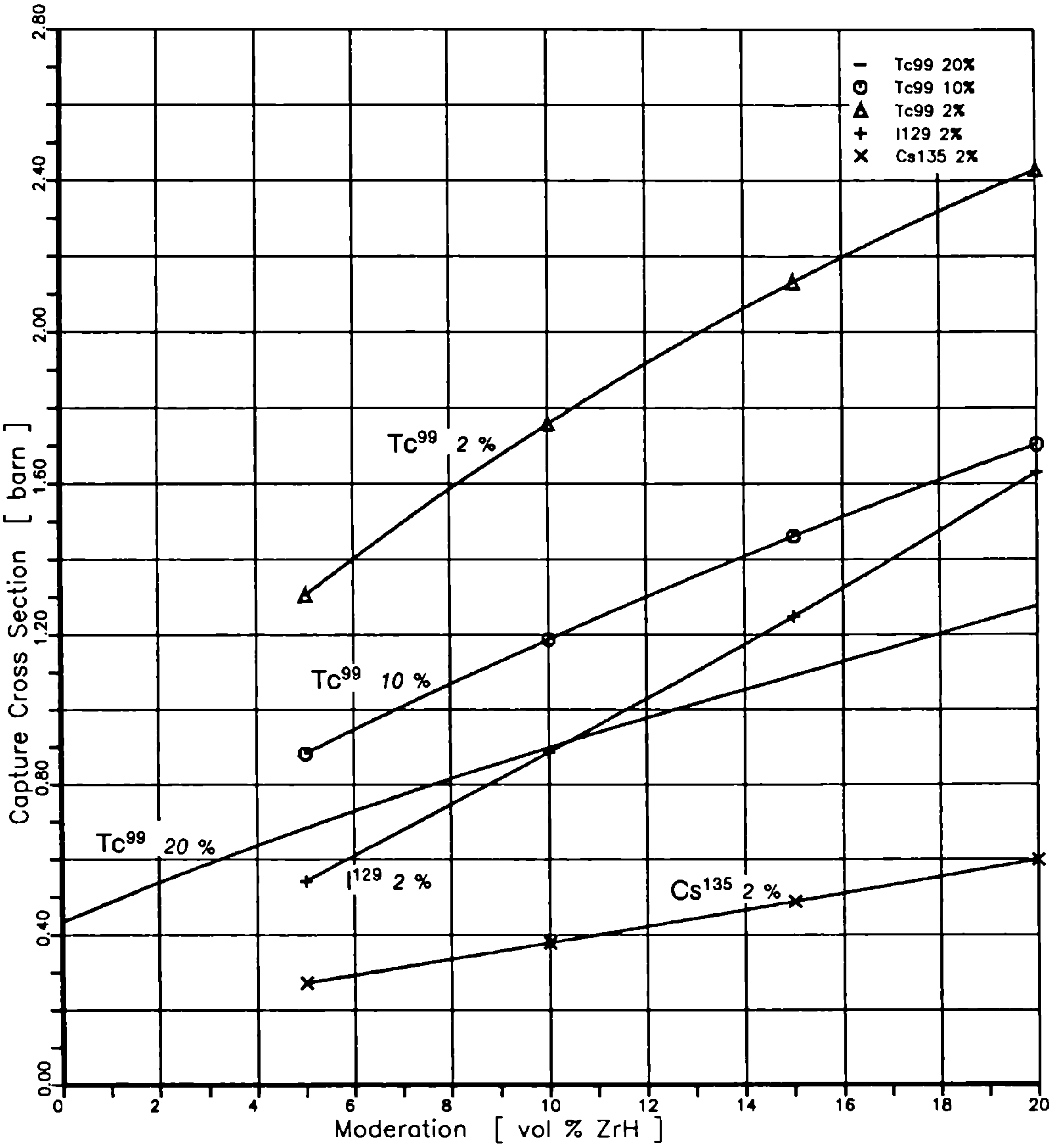


Figure 1: One–Group Capture Cross–Sections for Tc^{99}, I^{129} and Cs^{135} in Dependence on Moderator Content

Title: Participation in a CEC strategy study on nuclear waste transmutation
Contractor: Stichting Energieonderzoek Centrum Nederland-ECN
Contract No: F12W-CT91-0104
Duration of contract: from 1 November 1991 to 31 December 1994
Period covered: The calendar year 1993
Project Leader: K. Abrahams

A. OBJECTIVES AND SCOPE

This contract "Participation in a CEC strategy study on nuclear waste transmutation" has first of all as an objective the improvement of the nuclear data base for inventory calculations, which are needed in strategy studies on nuclear waste transmutation. A second contribution to the CEC strategy study will be in the form of a paper on: "Transmutation of long-lived fission products as a means of reducing the leakage dose risk of stored nuclear waste". Both objectives fit into the research program RAS, for the study of "Recycling Actinides and Fission Products" of the Netherlands Energy Research Foundation ECN. In this way ECN intents to contribute to international evaluations of recycling options for the nuclear waste problem. The program RAS is focused on studies on strategies and scenarios, on reactor physics research, on small scale demonstrations of possibilities for transmutation, and on the nuclear parameters, which are relevant to this.

Since November 1993 Belgonucleaire has joined these efforts of ECN as sub-contractor. In the form of an associated study Belgonucleaire identifies the possibilities as well as the constraints and limitations for a programme of recycling waste products in PWR reactors of current design with MOX fuel. This study subdivides into three parts, related respectively to the physics of recycling actinides, to the impact on fuel fabrication, and to the physics of recycling fission products. The present contract is in turn placed in the frame of broader CEC strategy studies on nuclear waste transmutation, together with the contract F12W-CT91-0102, to CEA, and the contract F12W-CT91-0103 to Siemens respectively.

B. WORK PROGRAMME

2.1 Preparation of a nuclear data base for actinides and fission products, which is needed for the experimental verification of technological aspects of transmutation

2.2 Preparation of derived data in order to assess the ORIGEN nuclear data library for transmutation studies.

2.3 Performing sample burn-up calculations for several scenarios with the updated ORIGEN nuclear data library.

2.4 Investigation of possibilities of transmutation of long-lived fission products, and Physics of fission products recycling (associated study by Belgonucleaire)

2.5 Extended feasibility study for the transmutation of fission products

2.6 Physics of actinide recycling (associated study by Belgonucleaire)

2.7 Impact on fuel fabrication (associated study by Belgonucleaire)

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In coordination with CEA and Siemens the work on three Community contracts is being harmonized. These three contracts all regard studies on possibilities to reduce the long-term radio-toxicity of nuclear waste. The ECN work is focused on the preparation of common data sets and standardized libraries for relevant nuclear data as well as on a study of possibilities for transmutation of long-lived fission products. The original contract expired November 1993, but it was extended to allow more time for in-depth studies of fission product transmutation and for an extension of the work on validation of the working libraries. At the same date Belgonucleaire was associated to the ECN contract with studies on usage of MOX fuel for transmuting plutonium and americium. Possibilities for multiple (successive) recycling of Am in the form of a homogeneous extended MOX fuel $(UPuAm)O_2$ are considered. Particular attention will be paid to the composition and the reactivity on voiding in a PWR in case of once, twice, and three times recycling. With compositions resulting from these calculations the dose rates will be derived for some critical stages of fuel fabrication and the necessary extra shielding as well as the margins to criticality will be evaluated. Recycling the long-lived fission products Tc-99 and I-129 in target pins in PWRs with and without extra moderation has been included into the Belgonucleaire contract. Calculations by Belgonucleaire are being performed in close cooperation with ECN through short-term delegations.

Work programme 2.1 and 2.2 (Common data sets)

In the period 1991-1993 a nuclear data base has been prepared, which is in accordance with the most recent European JEF-2.2 library. This nuclear data base is intended for an experimental verification of some scenarios, and mainly relates to nuclear data on actinides and long-lived fission products. Existing codes and libraries (based upon JEF-2.2) have been evaluated. Most of these data have been extracted from the available libraries. For burnup calculations, the code ORIGEN is being reviewed together with its working libraries of cross sections, ICRP-61 toxicity data, yields and decay constants. In addition to an assessment of the existing ORIGEN nuclear data library for transmutation studies, some new data have been inserted in the ORIGEN library, which will include the inspected and updated relevant fission yields as well as a number of cross sections from the EAF-file. Extensions of the library also concern data, which are relevant to the effect of important traces.

Some nuclides like Ce are relevant in relation to applications in matrix materials, which are inert during irradiation. Other nuclides in new materials, to be used in cladding of targets for irradiation, as well as the product-nuclides of the transmutation of I-129 and Tc-99 (Xe and Ru isotopes) are equally relevant. Therefore ECN is extending previous work by inspection and by addition of data for all relevant nuclides. This work includes the calculation of multi-group constants in XMAS structure for these nuclides.

During this year some evaluations on one-group cross sections have been made for actinides and fission products. The main achievements regarding this data evaluation are presented in ref. [1]. Validation of the ORIGEN nuclide libraries with some burnup calculations on a PWR and a fast reactor have been included. Another part of the original contract includes a study of the transmutation rates of Tc-99, I-129, and Cs-135 in several reactors such as the High Flux Reactor, the Phénix reactor and a power reactor of the LWR type. These studies are being extended to more in-depth calculations, which also include the CANDU reactor.

Work programme 2.3 (Sample burn-up calculations for actinides)

Apart from this contract, ECN makes an effort towards small-scale demonstrations of transmutation possibilities at the Petten High Flux Reactor (HFR), which is an ideal test reactor for the study of transmutation with thermal neutrons. This effort in itself is not subject to the present contract, but it is strongly related and relevant to this contract. In order to support these demonstrations, sample calculations on the transmutation of an americium in the High Flux Reactor in Petten have been made [1, 11].

Sample burnup calculations on americium transmutation.
Computer simulations of irradiations in a thermal neutron flux of 1.3 x 10^{14} cm^{-2} s^{-1} have been made. A 10 grams sample containing Am_2O_3 with a ratio Am-241/ Am-243 equal to 2.6 is given as an example. Irradiation of this AmOx sample in the HFR was supposed to last for 40 HFR cycles of 4 weeks. This is quite a long irradiation time and it has to be investigated yet whether such a long irradiation time in the HFR can be achieved with an americium sample (with respect to behaviour of sample and cladding during and after irradiation as well as with respect to sample handling after irradiation). Figure 1 gives the fission power as a function of irradiation time. This fission power reaches a first peak after about one HFR cycle, and this maximum is due to fissioning of $Am\text{-}242^m$ directly after it has been formed by neutron capture in Am-241. Almost all Am-242, which is formed during the irradiation quickly decays to Cm-242, which subsequently decays (with a half life of 160 days) to Pu-238. After Pu-238 has been formed, another neutron capture leads to the fissile isotope Pu-239. This leads to a high fission power in the sample after about 500 days as is shown in fig.1. Neutron capture in Am-243 leads to Am-244, which decays to Cm-244. Another capture in Cm-244 leads to Cm-245 which is fissile again and gives a contribution to the fission density after about 400 irradiation days. Together with a 70% reduction of the total actinide mass, the corresponding long-term toxicity decreases likewise. As can be seen from table I the toxicity also decreases with about 70%, if one considers a cooling down period of at least hundred thousand years.

Table I: Radiotoxicity (Sv) of the AmOx samples (before and after irradiation and after several subsequent periods of cooling down in storage)

Period (yr)	Unirradiated	5 cycles	40 cycles
100	4.82E+05	6.14E+05	1.17E+05
1000	1.23E+05	4.19E+04	1.07E+04
10.000	6.63E+03	6.50E+03	3.80E+03
100.000	3.85E+02	7.36E+02	1.42E+02
1000.000	1.63E+02	1.31E+02	2.39E+01

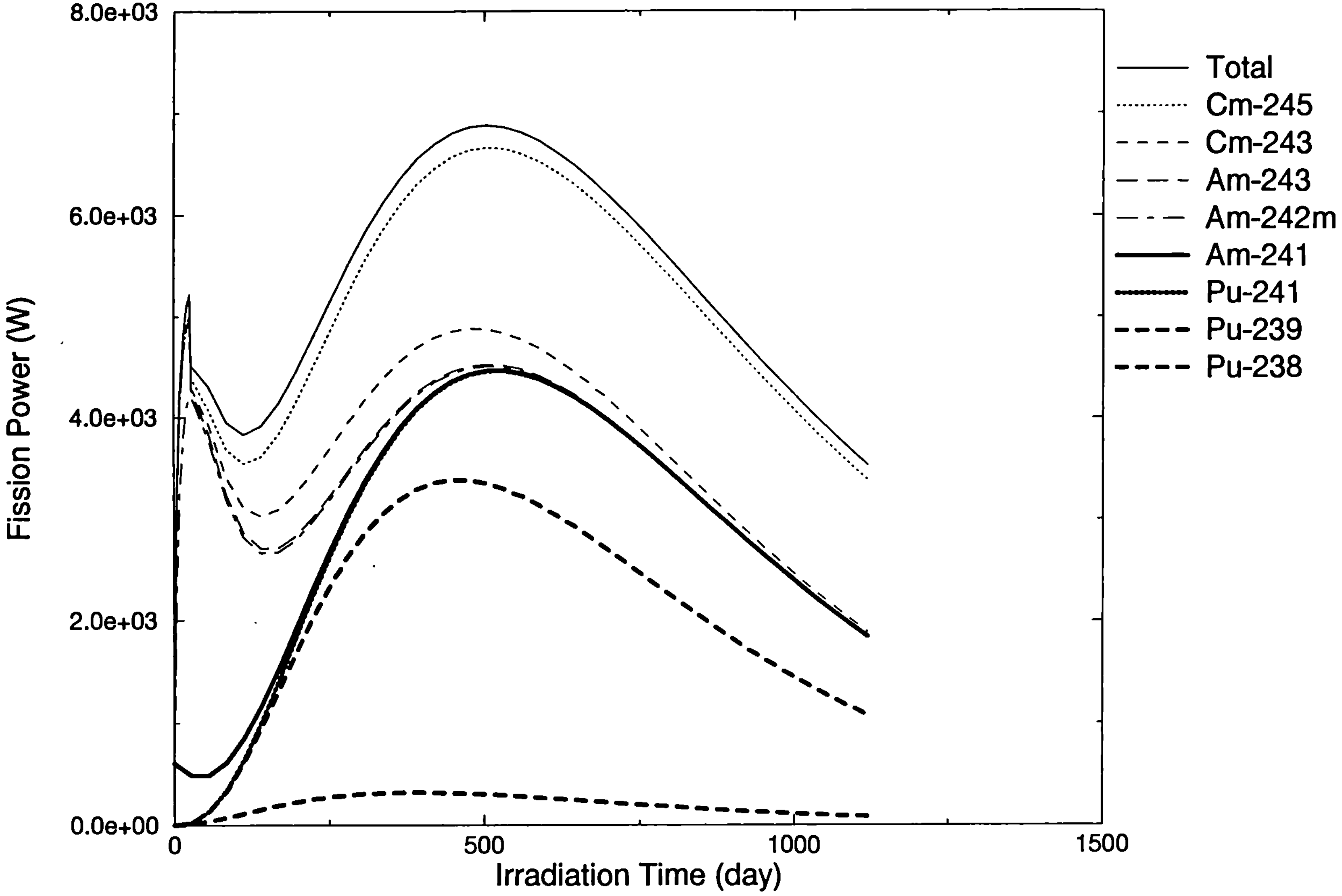


Figure 1: Fission power of a sample containing 10 grams of AmOx during 40 HFR cycles

Work programme 2.4 (Investigation of transmutation of long-lived fission products)

Besides the above mentioned nuclear data activities, some strategy studies on fission product transmutation have been performed. In these studies the transmutation scenarios were connected to geological deposition scenarios, in which the radiation dose is related to the mobility of long-lived fission products in a repository. It has been shown that the partitioning and transmutation would enable the reduction of the dose risk from the long-lived and geo-chemically mobile fission products Tc-99 and I-129. This reduction would result from the transmutation of Tc-99 and I-129 by neutron capture to harmless Ru-100 and to equally harmless Xe-130. It is intended to submit a report on fission product transmutation under coordination with the partners. In order to start the work a discussion-paper has been written on strategies of transmutation of fission products. This paper has been presented and discussed at the Technical Committee Meeting on "Safety and Environmental Aspects of Partitioning and Transmutation of Actinides and Fission Products" of the IAEA [2]. This work is to be extended in the frame of the new contract, but some preliminary conclusions have been drawn already such as:

On the risk reduction and costs of recycling Tc-99.
One of the problems with technetium is that it is an element which does not occur in nature, and one has little experience with its behaviour in the eco-system. It has been shown in ref. [2] that total transmutation of technetium could save future mankind some risk due to possible leakage of this radionuclide during very long storage times. In this way one might avoid a leakage-risk which, though it is rather small, may exceed the leakage-risk for actinides for most geological storage facilities. Practical applications however would require that costs of recycling Tc-99 are kept small with respect to the current fuel cycle costs. This seems possible, provided that chemical partitioning and reprocessing costs for Tc are low.

On the risk reduction of I-129, and on isotopic dilution.
Justification for transmutation of actinides is not necessarily based on the wish to avoid leakage-risks, but it is mainly based on fears for loss of integrity of repositories by human intrusion or by natural catastrophes. Similar concerns could to a smaller extent also be applied to justify transmutation of I-129. Moreover similar arguments based on the wish to reduce the leakage-dose risk could be given for I-129 as well as for Tc-99. However two points disfavour the transmutation of iodine: First of all the upper limit of the leakage-dose due to long-term global I-129 contamination is orders of magnitude lower than that for Tc-99. Secondly, iodine is an element which is rather abundant in nature and therefore the technique of isotopic dilution could perhaps be applied to reduce local dose rates. If one would dilute the I-129 with about a factor of 500 with natural iodine, the resulting admixture might have a radiological impact smaller than for example the free amount of potassium in the biological cycle of any living creature. Such a small toxicity has never harmed life as far as we know, and high costs and risks of transmuting I-129 should balance this marginal risk. The conclusion could be that isotopic dilution is preferable, if it were to receive public acceptance. In the meantime both partitioning/transmutation and isotopic dilution strategies ought to be evaluated.

Recommendations
For the time being it is recommended to study technetium, its dose consequences and its ecology, as well as its chemical nature especially in the solid state. If human intrusion

or other disturbances are taken into account, the actinides determine the maximum value of the expected individual dose rates. Actinides and the safeguarding problems have been dominating the discussion on transmutation of nuclear waste. The fact that safeguarding procedures should be accounted for in the partitioning of actinides, might also influence the scenarios for partitioning the fission products from the actinides.

On the issues related to public acceptance
Most discussions on nuclear waste, and also the present discussion are based on average quantities. Any such probabilistic assignment of risk creates suspicions, and public confidence in predictions that range over more than a few hundred of years is clearly diminishing. It should therefore be realized that the acceptance problem is too complex to be approached in a purely scientific/technological way. As it nevertheless is necessary to sketch a frame in which the waste problem could be approached, one should start to investigate whether transmutation of Tc-99 and I-129 is technically/economically feasible.

Work programme 2.5 (Extended feasibility study of fission product transmutation)

By simple reasoning it is easy to show that fission-product transmutation is most likely to be practical if one uses capture of thermal neutrons. For any process with charged particles the cross sections are orders of magnitude smaller due to Coulomb repulsion. To demonstrate incineration methods in a high thermal neutron flux, several calculations have been performed on transmutation with accelerators and reactors. Extended studies have been made on the transmutation of fission products. This study includes energy-, mass-, and cost-balance for transmutation scenarios (costs of reprocessing are excluded for the time being). Similar to the sample calculations, which support the demonstrations for actinide transmutation at the HFR, also some in-depth calculations have been performed on heterogeneous transmutation facilities for long-lived fission products, and matrices inert to irradiation with thermal neutrons [3,11]. Refs. [3,11] treat the following: a) Pure accelerator methods (with high energy proton beams and a spallation target), b) Pure reactor methods (e.g. an HWR in a simple calculation), and hybrid methods c) Accelerators with sub-critical assemblies.

Below the three methods are discussed shortly starting with method a):
Without a fission booster each 1.5 GeV neutron produces less than 30 neutrons even in heavy targets like tungsten or lead. Suppose the accelerator efficiency is about 50% (a very optimistic statement). In this case the price of one thermal neutron is about 1500/(30 * 0.5) = 100 MeV, if this price would be expressed in terms of electrical energy. As this electrical energy had to made from thermal energy, one would have required about three times more energy. Because it is too optimistic and even unrealistic to assume that each neutron will transmute a technetium nucleus, one will need much more than 300 MeV thermal energy for each technetium nucleus to be transmuted. In case that this 300 MeV would have been generated by means of a nuclear reactor, this would mean that more than one fission in the reactor is needed to transmute one technetium nucleus at the accelerator. Following this reasoning it seems obvious that method b (direct transmutation of technetium in a reactor) is much more economic in case that one excess neutron also becomes available for each fission in the reactor itself. Clearly the reactor method is more direct, and further it is also more economical because the 200 MeV, which is generated by fission, can still be used to generate electricity in the "pure reactor scenario" (this electricity is no longer needed to transmute

the technetium nucleus with an accelerator!). Because a high flux of thermal neutrons is most relevant for fission-product transmutation, one thinks in terms of neutron boosters. These are sub-critical systems with fissionable material, in which each neutron from the primary accelerator-target system might produce up to ten secondary fission neutrons. In fact it has been shown that such a sub-critical system will be more economical than any system without a booster. Combinations of an accelerator and a booster seem to approach the economy of the reactor method more closely if the setup is more close to criticality. However it can be shown by arguments of safety as well as mass and energy flows that hybrid systems are not favoured at the moment [3,11].

List of publications

[1] J.L. Kloosterman, Validation of New ORIGEN-S Libraries, NFA-ACT-93-10, and New Working Libraries for Transmutation Studies, Proceedings of the conference Global '93, p. 1229.

[2] K. Abrahams, Transmutation of Long-Lived Fission Products, contribution to the meeting of the Technical Committee IAEA on the transmutation of nuclear waste Vienna 29/11 - 2/12/93, also published as memo NFA-ACT-93-09.

[3] A.J. Janssen, Transmutation of Fission Products in Reactors and Accelerator-driven Systems: Some Critical Remarks, ECN-R-94-xxx to be published and also included in ref. [11].

[4] R.J.M.Konings et al, Technological Aspects of Transmutation of Technetium and Iodine. Proc. of the GLOBAL '93 conference, September 1993, Seattle page 1260.

[5] K.Abrahams, J.H.Bultman, E.H.Cordfunke, H.Gruppelaar, A.J.Janssen, W.M.P.Franken, H.Th.Klippel, R.J.M.Konings, J.L.Kloosterman en J.Smit, Transmutatie van Kernafval. Report for the 1993 dossier Nuclear Energy.

[6] "Transmutatie van Kernafval", Standpunten van de Begeleidingscommissie Programma Recyclage van Actiniden en Splijtingsprodukten (RAS), Report for the 1993 dossier Nuclear Energy.

[7] J.L. Kloosterman, A.J. Koning, K. Abrahams en H. Gruppelaar, "Onderzoek Nucleaire Gegevens voor Transmutatie", concept of C-93-067.

[8] J. Bultman, C.L. Cockey and T.Wu, Actinide Burning and Breeding in Metallic and Oxide Fuelled ALMR Cores, Proceedings of the conference Global '93, p. 136.

[9] J. Bultman, Reduction of Nuclear Waste by Introducing Advanced Liquid Metal Reactors, Proceedings of the conference Global '93, p. 170.

[10] J. Bultman, PRISM: Option for burnup of radioactive waste? Petten 10-12-93.

[11] K.Abrahams, Participation in a CEC strategy study on nuclear waste transmutation, Progress report under contract No. F12W-CT91-0104, first semestrial period 1993.

Title : Potentialities and costs of partition and transmutation of long-lived radionuclides

Contractor : CEA
Contract n° : F12W-CT91-0106
Duration of contract : 39 months, from October 1991 o December 1994
Perio covered : January - December 1993
Project Leader : CEA - Fuel Cycle Direction

A. OBJECTIVES AND SCOPE

The purpose of this conceptual study is to analyse the different strategies of waste management aiming at reducing contents of long lived radionuclides by partitionning and transmutation ; tecnical ways and costs will be evaluated.

In a first step reference scenario will be defined ie to draw up an inventory of long lived radionuclides produce by the European installed or foreseen reactors and estimate radiotoxicity of such nuclides.

In a second step will be estimated the expected decrease of radionuclides stockpile according to two mains scenarii : first one using presently known or available technologies, second one taking into account all foreseen innovative technologies.

B. WORK PROGRAM

The program is divided in two main part : technical studies to find the best way of stochpiles reducing and economical studies to evaluate the cost of partitionning

The different items of this program are the following :

1.- References scenarios : (treated in the previous report)

. definition of involved reactors (number, type, ...)
. evaluation of produced radionuclides (Am, Np ...)
. potential radiotoxicities

2. - Step one : available technologies : (present report)

. separations :
    . definition of processes
    . evaluation of efficiencies and losses
    . costs
. transmutation :
    . in FBR
    . in PWR

3. - Step two : foreseen technology :
    . same items than for 2

C PROGRESS OF WORK AND RESULTS

This report presents the phase two of the working program.

1. - The principal hypothesis

The studies concern the tranmutation of Neptunium and Americium in LWR's or FBR's representing respectively the scenario RP 1-1 and the scenario RP 1-2.

Neptunium and Americium are irradiated either in homogeneous mode :

. RP 1-1 : in PWR (UOX) fuels containing 1 % of each actinide, which will be reprocessed.

. RP 1-2 : in FBR (MOX) fuels containing 2,5 % of each actinide, which will be reprocessed.

or as heterogeneous targets which will be irradiated at a maximum acceptable level then disposed of :

. RP 1-1 : specific targets (clusters containing actinide oxide rods) are placed in the guides of a UOX fuel assembly.

. RP 1-2 : specific targets (intert matrix) are placed in the first radial blanket

The reprocessing iosses are :

U = 0.3 %, Pu : 0.5 %, Np : 5 %, Am : 5 %

The targets are not reprocessed

2. THE MATERIAL BALANCE OF REPROCESSING WASTES

The material balance for scenarios RP 1-1 or RP 1-2 are compared with those for scenario R2 or R3 (the equivalent scenario without transmutation).

The table shows the cumulative (tons) reprocessing wastes (U losses, Pu losses, Np losses, Am losses and Cm) in 2100.

Reprocessing wastes	R2	RP 1-1 (Hom)	Rp 1-1 (Het)	R3	RP 1-2 (Hom)	RP 1-2 (Het)
U losses	470	470	470	420	420	420
Pu losses	22	22	22	23	23	23
Np losses	100	12	10	94	11	9
Am losses	420	27	25	247	24	20
Cm	65	108	51	40	54	30

Americium recycling results in increased Curlum production (+ 65 % for the recycling in the PWR (UOX) fuels and + 35 % for the recycling in the FBR (MOX) fuels). In the event of heterogeneous recycling, allowance must also be made for the curium contained in the irradiated Am targets : the end results is approximately the same as for homogeneous recycling.

3. POTENTIAL RADIOTOXICITY (INGESTION) BALANCE

The results were normalized with respect to the R1 results (open cycle)

Two radiotoxicity inventories were performed :

- a "waste" inventory including the radiotoxicity due to nuclear materials suitable for ultimate disposal (losses, waste reprocessing),
- a "cycle" inventory including the radiotoxicity due to nuclear materials throughout the fuel cycle (industrial facilities, interim storage, reactors and wastes).

Figures 1 and 2 show the evolution of the potential ingestion radiotoxicity beginning in the year 2100 for scenarios R2, RP 1-1 and R3 1-2 in the "waste" and "cycle" inventories.

3.1. Comments on the scenarios RP 1-1 and RP 1-2

- Comments on the "Cycle" Inventory
  - The "waste" represents less than 20 % of the overall radiotoxicity after the first 100 years. The most important items are irradiated fuel and targets (both in interim storage and in the reactors) up to 10_6 years ; depleted uranium accounts for most of the radiotoxicity thereafter.
  - The gains over scenerios R2 and R3 are not significant : for the scenario RP 1-1, the radiotoxicity increases during the first 100 years due to Cm production.
  - Interim storage of the irradiated targets penalizes the heterogeneous mode scenario compared with the homogeneous mode.
  - The Np and Am recycled don't degrade the radiotoxicity of the cycle inventory.
- Comments on the "Waste" Inventory
  - Both recycling modes provide equivalent gains.
  - Significant gains (by a factor of 6) over scenarios R2 or R3 are obtained for two time periods :
    - between 10_2 and 10_3 years, a period when most of the radiotoxicity is attributable to Am,
    - between 5 x 10 5 and 5 x 10 6 years, a period when most of the radiotoxicity is due to Np.
  - For the other short and medium-term time periods, the increased Cm production appreciably limits the gains.
  - Compared with scenario R1, the gain is by a factor of 10 to 50 beyond the first 100 years.

4 SEPARATION COMPLETION OF THE ECONOMIC PART OF THE STUDY

This part consists in comparing the costs of a cycle using current techniques, such as those implemented today in France, with a cycle management ensuring separation and then incineration of minor actinides (neptunium and americium). The options to be assessed are the two advanced reprocessing scenarios of level 1 (RP1):

. RP1-1 in which the plutonium and the minor actinides (Np and Am) are incinerated in PWR reactors,

. RP1-2 in which the incineration is performed in FBR reactors.

The results are given in relative value with respect to a reference cycle operation. The reference scenarios are the following[1]: Reprocessing without separating the minor actinides and recycling all the plutonium (apart from the losses) in a PWR reactor (scenario R2) and FBR reactor (scenario R3). This comparison is made by determining the cost of the different unit operations in the fuel cycle.

At the level of the reactors, the transmutation of actinides is performed in the same type of power generating reactor mix as that making up the reference for the study, without it being necessary to make any noticeable modifications. Therefore, for the "reactor" part of the cycle, there is no investment or operating overcost in the RP1 scenarios. However, it may be necessary to modify a part of the fuel, particularly the enrichment in uranium 235 or plutonium, but these cost increases are included in the overall cost increase of the fuel cycle.

The cycle expenditures are assessed by multiplying the various flows of matter per year by the unit cost of each operation. These costs, essentially drawn from national or international studies (exclusive of reprocessing costs and fuel fabrication costs which have been assessed in the framework of the study) correspond approximately to market prices.

This approach, in which discounted cost is not taken into account, allows to weigh the relative importance of the different steps of the cycle in the scenario studied. However, this does not allow to integrate the cost of the cycle thus determined in the kWh as it is assessed by a different economic procedure.

4.1. Procedure

The annual expenditures of a cycle for each scenario are determined from services and material balances and from the unit costs determined for each operation in the fuel cycle. This calculation requires two or three successive steps, depending on the operation involved:

- **Step 1** / determination of the construction cost of the production facilities corresponding to each operation of the cycle (presented in the Progress Report, 1st semester).

- **Step 2** / based on these costs, determination of the corresponding unit costs (presented in the Progress Report, 1st semester).

---

[1] The direct storage scenario without reprocessing (scenario R1) is taken as reference for the comparisons in terms of radiotoxicity only.

For the reference scenarios, we have direct access to the unit costs of each operation in the cycle, as they have already been studied in a national (CEA, DIGEC) or an international (OECD) framework and correspond approximately to market prices. However, some adjustments are necessary to take particularities into account (case of the scenario R2[2]).

For the other scenarios, two operations of the cycle vary, reprocessing and actinide fuel fabrication.

- Step 3 / determination of annual cycle expenditures.

4.2. Results

The economic comparison between the different scenarios may be made at each step :

-Step 1, comparison of reprocessing plant construction cost RP1-1/R2 and RP1-2/R3.
The results are summarized in the following table :

RELATIVE COST INCREASE	
(RP1-1-R2)/R2	0,23<**0,35**<0,47
(RP1-2-R3)/R3	0,28<**0,48**<0,68

-Step 2, comparison of the unit costs of the reprocessing operation and the actinide fuel fabrication operation.
The results are summarized in the following tables :

Reprocessing costs

The reprocessing cost is directly proportional to the construction cost, so the results of step 2 are the same then step 1(see §4-1).

RELATIVE COST INCREASE	
(RP1-1-R2)/R2	0,23<**0,35**<0,47
(RP1-2-R3)/R3	0,28<**0,48**<0,68

Minor actinide Fuel Fabrication for homogeneous recycling

we considered two values of cost in order to carry out a sensitivity study

The first reflects the fact that the fabrication of UO_2 + NpO_2 or AmO_2 fuel will cost at least as much as MOx fuel, and that even under ideal circumstances, some modifications would be necessary, resulting in a minimum cost supplement of 10%. The second figure doubling of the cost assumes that the "glove box" technology implemented in the MOX plant must be abandoned, and that a different "shielded line" technology must be developed, with a major impact on fabrication costs. These figure of + 100% must not be taken too literally, as it was not obtained by a serious evaluation but is only postulated to assess the sensitivity of the overall results to a significant increase in the actinide fuel fabrication cost.

Relative Unit Cost Increase of Minor Actinide Fuel Fabrication Compared with:	
UOx fuel	2.6 < **2.9** < 5.5
MOx fuel[1]	0.1 < **0.2** < 1.0

The bold numbers will be used as the reference for the remainder of this investigation,

-**Step 3,** comparison of expenditures, RP1-1/R2 and RP1-2/R3

The comparisons were made from three types of balances without any discounted cost :

*Yearly balances, showing the evolution of cycle expenditures year by year,

* cumulated balances over the duration of the scenarios, allowing the effects of inertia of the scenarios to be taken into account.

* current year balance, taken at the end of the period to be as close as possible to a stable state. This type of comparison is significant of thes differences of nature between scenarios.

`The main results are indicated in the following table:

Basis	(RP1.1 - R2)/R2		(RP1.2 - R3)/R3	
	Typical Year	Cumulative	Typical Year	Cumulative
High Estimate	54%	44%	52%	29%
Reference	**33%**	**27%**	**28%**	**17%**
Low Estimate	21%	17%	11%	7%

Under the assumptions of this study, compared with the conventional fuel cycle scenarios, the partitioning/transmutation scenarios imply a cycle cost supplement ranging from 20% to 55% for the PWR scenario, and from 10% to 50% for the FBR scenario.

5 "IMPLEMENTATION OF ADVANCED TECHNIQUES AND KNOWLEDGE" SCENARIO (RP2)

Reprocessing process RP2

The principle of the process proposed was described in the Progress Report of the First Semester.

The three main points are recalled here:

Types of fuel and targets to be reprocessed:

- PWR UOX fuels,
- FBR MOX fuels,

---

[1] *The cost of MOx fuel fabrication is roughly 3.25 times that of UOx fuel.*

- dedicated FBR fuels (initial Np 5%),
- initial targets AmO_2 40% in MgO from dedicated FBRs,
- targets PbI_2 and metallicTc from dedicated FBRs.

Process options: The main options chosen are:

- Desorption of iodine at the level of the dissolution operation. The iodine is recovered at the output of the plant as a lead iodide precipitate PbI_2.

- For the U, Pu and Np cycles, the TBP is replaced by a monoamide.

- Separation of technetium in the form of pertechnetate (TcO_4^-) at the level of the first cycle.

- Direct separation FP/minor actinides in a single cycle is obtained by using picolinamides.

- As for RP1, the Am/Cm separation is done by acting on the selective extraction phenomenon of americium in the oxidized state, the solvent used is the same monoamide as that of the U, Np and Pu cycles.

Separation efficiency:

- U and Pu 99.9%
- Np, Am, Cm 99.5%
- I, Tc 90%

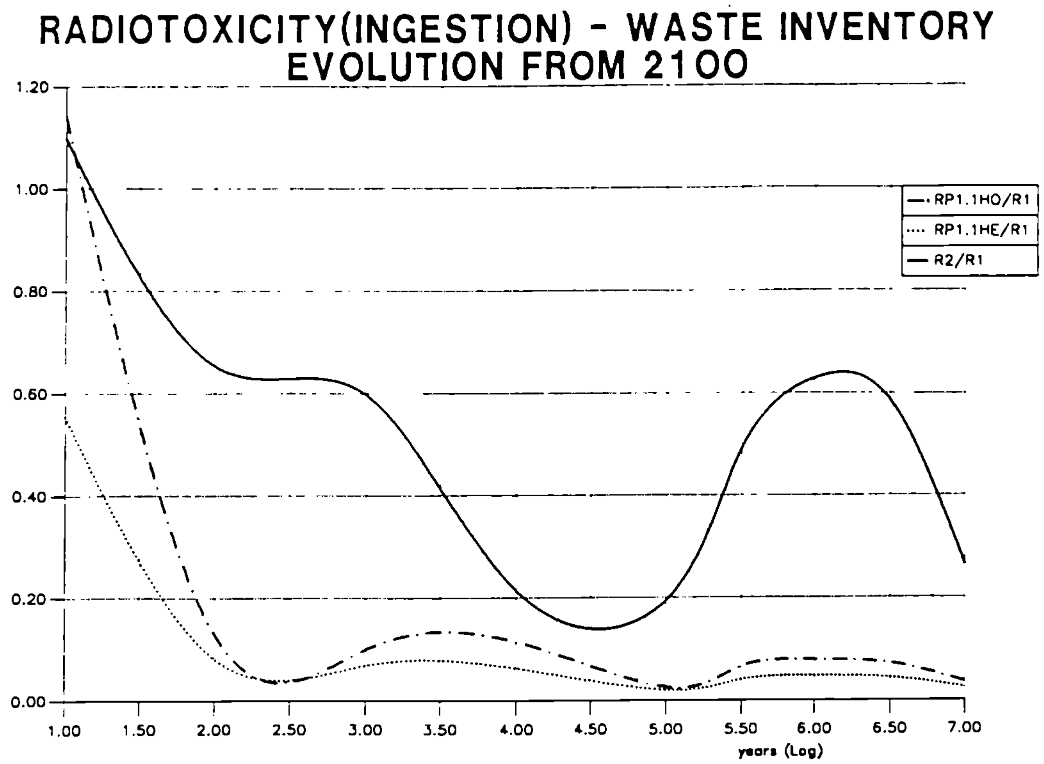
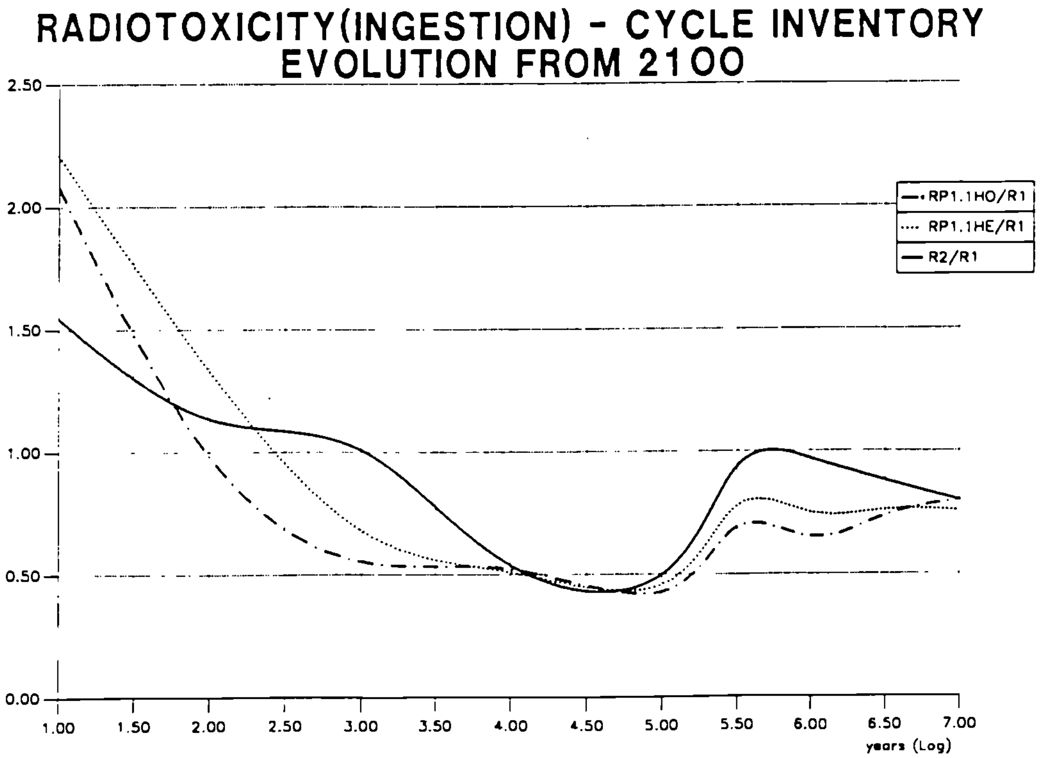

RADIOTOXICITY(INGESTION) - WASTE INVENTORY
EVOLUTION FROM 2100
1.20
1.00
0.80
0.60
0.40
0.20
0.00
RP1.1HO/R1
RP1.1HE/R1
R2/R1
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
years (Log)

Fig 1


RADIOTOXICITY(INGESTION) - CYCLE INVENTORY
EVOLUTION FROM 2100
2.50
2.00
1.50
1.00
0.50
0.00
RP1.1HO/R1
RP1.1HE/R1
R2/R1
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
years (Log)

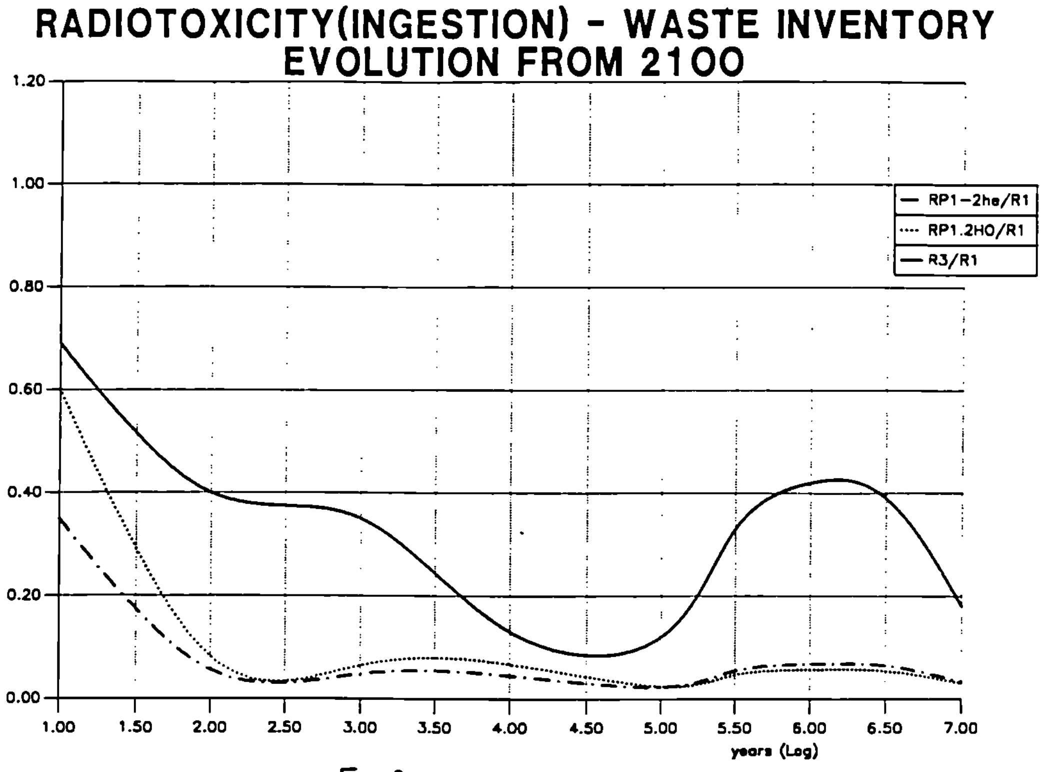
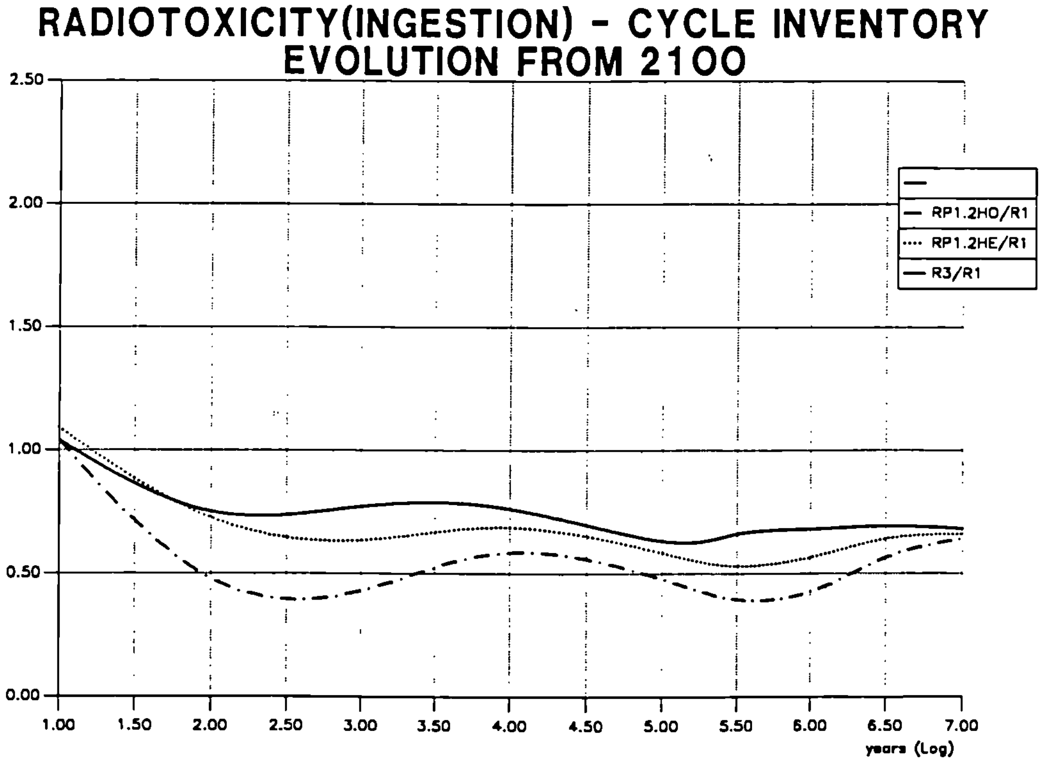

RADIOTOXICITY(INGESTION) - WASTE INVENTORY EVOLUTION FROM 2100
1.20
1.00
0.80
0.60
0.40
0.20
0.00
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
years (Log)
RP1-2he/R1
RP1.2HO/R1
R3/R1

Fig 2


RADIOTOXICITY(INGESTION) - CYCLE INVENTORY EVOLUTION FROM 2100
2.50
2.00
1.50
1.00
0.50
0.00
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
years (Log)
RP1.2HO/R1
RP1.2HE/R1
R3/R1

A2: WASTE TREATMENT

Task 2

"Treatment of Radioactive Waste"

* List of contract
* Introduction to Task 2

Topic 1	:	Minimization of radioactive discharges
Topic 2	:	Reduction of waste volumes to be disposed of
Topic 3	:	Waste de-categorisation and actions at the source
Topic 4 *	:	Spent fuel conditioning for disposal
Topic 5	:	Potentialities of transmutation of long-lived radionuclides

* No activity running on this topic

TASK 2 - LIST OF CONTRACTS

Topic 1 : Minimization of radioactive discharges

FI2W-CT90-0054	Improvement in the performance of the conventional treatment of liquid effuents by co-precipitation.

Topic 2 : Reduction of waste volumes to be disposed of

FI2W-CT90-0053	Wet oxidation of organic containing wastes.
FI2W-CT90-0057	Advanced processes for the treatment of low level liquid wastes at a pilot plant scale.
FI2W-CT91-0095	Process design and feasibility study for incineration under pressure, condensation and effluent treatment of radioactive waste.
FI2W-CT91-0100	Melting of incinerator ashes using a microwave furnace.
FI2W-CT91-0108	Treatment of radioactive solvent waste by catalytic oxidation.

Topics 3 : Waste de-categorisation and actions at the source

FI2W-CT90-0062	New macrocyclic extractants for radioactive waste treatment : Ionizable crown ethers and functionalized calixarenes.

Topic 5 : Potentialities of transmutation of long-lived radionuclides

FI2W-CT90-0047	Partition of radioactive wastes.
FI2W-CT91-0112	High-level liquid waste partioning by means of completely incinerable extractants.

INTRODUCTION TO TASK 2: TREATMENT OF RADIOACTIVE WASTE

A. Objectives

Improvement of radwaste management schemes by means of new treatment processes allowing :

- the minimization of radioactive discharges into the environment;
- the reduction of the waste volumes to be disposed of;
- the de-categorisation of waste packages in terms of disposal routes;
- the removal of long-lived radionuclides from high level waste for partitioning and/or transmutation purposes.

B. Research topics investigated within the programme 1985-1989

Investigations were carried out on volume reduction techniques for liquid waste from reactor operation, spent fuel reprocessing and from research centres. The work was focused on ultrafiltration techniques, electrochemical ion-exchange and chemical precipitation coupled with centrifugation.
Research work was devoted to the waste de-categorisation for making easier conditioning, transport and disposal operations of a number of alpha and MLW, particularly on :

- treatment flow-sheets relying on solvent extraction;
- chemical precipitation and inorganic ion-exchange techniques;
- exhaustive decontamination of solid alpha waste by leaching with electrogenerated Ag(II).

New immobilisation matrices (modified sulphur cement, ceramics and new cement formulations) have been investigated for various wastes like incinerator ashes, ion-exchange resins, sludges, dissolver residues.
Actions taken at the source of production (MOX fuel fabrication plant) for reducing alpha waste arisings also played an important part in this programme. Quality assurance schemes for waste products in conditioning facilities for cementation, drying and compaction were elaborated and critical parameters for disposal criteria selected.

C. The present programme 1990-1994

At the beginning, Task 2 comprised 13 research contracts, four of them being multinational. In 1993, the work has been progressing for 10 contracts, two of them being completed and one cancelled. The following topics have been covered:

Topic 1 : minimization of radioactive discharges

- Setting up of a downstream treatment processes for low level liquid effluents at the La Hague reprocessing plant (CEA Cadarache).
- Radium recovery from uranium tailings (LNETI).

Topic 2 : Reduction of waste volumes to be disposed of

- Recovery of boron from PWR low level liquid waste by electrodialysis, reverse-osmosis, distillation, ion-exchange and electrochemical ion-exchange as alternative treatments (Laborelec, AEA Harwell and CEN/SCK).
- Volume reduction of alpha-bearing incinerator ashes by microwave furnace and melting processes for spent fuel zircaloy hulls in a cold crucible (CEA-Valhrô).
- Ion-exchange resins destruction by H_2O_2 (AEA-Winfrith) and by incineration with oxygen under pressure (Bertin, CEA-Cadarache and INITEC).
- Treatment of liquid waste by distillation and wet oxidation (ENEA Saluggia).

Topic 3 : Waste de-categorisation and actions at the source

- Evaluation of decontamination performances of leaching technique with nitric acid and electrogenerated Ag(II) on different solid alpha-bearing wastes (CEA-FAR).
- De-categorisation of medium-level reprocessing concentrates by using "tailor-made" macrocyclic extractants (calixarenes and crown-ethers). This multipartner project associates CEA-Cadarache with the Universities of Barcelona, Belfast, Mainz, Parma, Strasbourg and Twente.

Topic 4 : Conditioning of spent fuels in view of their direct disposal

There are no activities running on this topic.

Topic 5 : Potentialities of transmutation of long-lived radionuclides

- Development and testing of enhanced treatment scheme for separation of long-lived radionuclides from high level liquid waste. This co-ordinated research programme is being carried out by CEA-FAR and KfK.

Title : Improvement in the performance of the conventional Treatment of Liquid Effluents by Co-Precipitation
Contractor : CEA-DCC
Contract N° : FI2W/CT90/0054
Duration of Contract : From May 1st to April 30th 1995
Period Covered : January-December 1993
Projet Leader : FROMONT Michel, FEDERICI Véronique

A. *OBJECTIVES AND SCOPE*

The capacity of treatment of the COGEMA irradiated fuel reprocessing plant at The Hague is to be progressively increased from 400 to 1600 tonnes a year. The regulations concerning the release of radioactive effluents into the sea remain unchanged, that is to say they authorize :

- 45000 Ci (1665.10^3 GBq) for all radioelements (except tritium) including 6000 Ci (222.10^3 GBq) for Sr90 and Cs137;
- 45 Ci (1700 GBq) for α emitters.

The efficiency of radioactive liquid effluent chemical treatment should therefore be improved.

At present, the Liquid Effluent Treatment Plant (so called STE3) implements a process involving a chemical co-precipitation for low activity (act.$\beta<5$ Ci/m^3) and medium activity (act.$\beta<300$ Ci/m^3) radioactive effluents and a neutralization, followed by filtering for any effluents suspected of the slightest radioactivity (act.$\alpha<10^{-4}$ Ci/m^3, act.$\beta<10^{-2}$ Ci/m^3).

In association with the treatment plant (STE3) operators who are to supply actual radioactive effluents, we propose to implement complementary treatments in a hot laboratory, using for example mineral exchangers, organic extractants and chemical precipitation, the application of which, in the STE3 plant at The Hague, should entail only minor modifications to the existing process.

B. *WORK PROGRAMME*

The work programme consists of :

- the caracterization of the chemical forms of the radioelements to be removed,
- the insolubilization of these radioelements by means of mineral exchangers in powder form (oxydes, sulfates, phosphates, ...), of supported organic extractants (active carbon, silica) and of precipitation treatments.

- the study ot the separation of the insolubilized activity by means of the most appropriate processes : tangential filtering, centrifugation or columns used singly or in series.

- the carrying out of tests on a radioactive pilot mock-up (1/60 scale).

C. PROGRESS OF WORK AND OBTAINED RESULTS

- State of advancement

The evolution of the radioactive liquid effluents discharged into the channel by the STE/La Hague shows a reduction of 30% of the active effluents and of 50% of the suspect effluents (so called "V"), but the distribution stays almost unchanged : 27% of 90Sr, 23% of 127Sb, 17% of 106Ru and 3% of 137CS. To reduce the released activity, we focused therefore our attention to these radionuclides. Moreover. V effluents should be investigated as they account for 21% of the discharged alpha activity, although they represent only 6% of β activity. With complementary treatments implementation in view, our goal is to obtain a decontamination factor of the order of 10.

During the previous period (1992), we have shown that Sr90 and Sb125 could be removed by means of titanium or zirconium oxides, used in situ precipitation, or in preformed precipitates or with solid compounds in powder or in pellets.

Considering these results, we studied the fixation of the two radionuclides in column filled with sodium titanate pellets. Then, we considered the elution of Sr by nitric acid, the quantity of sodium which is released and the re-use of the materials.

For Ru106, coupling active carbon and ion-exchanger or polyvinylpyridine was investigated, but results are disappointing with at best a decontamination factor of 5.

PROGRESS AND RESULTS

1. STRONTIUM REMOVAL ON COLUMN

Sr removal can be achieved by percolation of the A effluent after STE3 in a column filled with 3,2 ml of sodium titanate pellets. Before, the effluent pH is increased until 12, which is the most effective value for the removal. The effluent is also spiked with Sr85 for γ analysis. After percolation at a flow-rate 32 ml/h of the effluent in the column, γ activity of the effluent, which is shown on Figure 1, is measured as a function of the volume. Considering the ratio v between the effluent volume and the adsorbant volume, this figure can be divided into three parts :

- 0 < v <1000, DF is equal to 12 for 3,3 liters of effluent,
- 1000 < v < 2000, DF decresases from 12 to 2,7 for 6,4 liters,
- v > 2000, DF remains constant and equal to 2,7.

This method is also effective to treat 3,2 liters of effluent contaminated by strontium with only 3,2 ml of sodium titanate pellets. Same results were obtained for a V effluent.

2. STRONTIUM ELUTION

We also investigated the fate of the contaminates pellets. The first possibility is their embedding by ceramisation. The second alternative we have chosen is the elution of the pellets by nitric acid 0,1 M (this concentration has been optimized). The previous column which has removed Sr85 from the effluent is treated by nitric acid at a flow-rate 12 ml/h. Figure 2 is related to the eluted activity as a function of the ratio v.The peak has a maximum for v equal to 15. All the activity is eluted for v equal 70 (245 ml of nitric acid). This has been confirmed by integration of the different peak areas corresponding to the removal and the elution. During Sr elution, sodium is also eluted. Its concentration is around 3,5 g/l, which is similar to the sodium concentration in the effluents. An other advantage is the pellets re-use.

3. ANTIMONY REMOVAL

Sr removal on sodium titanate pellets has been studied in the same manner. Previous experiences implied that the effluent pH must be acid for a better efficiency of the treatment. A column filled with 3,2 ml of material gave the results in the table I. When the effluent is at pH 7 and the pellets at pH 5, DF are below 2. We also decreased the pH (5 for the effluent and 2 for the pellets), but DF are still closed to 2 when the flow-rate is 32 ml/h. Decreasing it to 12 ml/h increased DF to 3. These bad results were attributed to the contact time between the effluent and the pellets, which is still too low.

4. RUTHENIUM REMOVAL

Electrophoresis indicates that Ru106 is under three forms in the effluent at pH 9 (a neutral, a slightly anionic and an anionic forms). Two adsorbants were also used in so far as to increase DF, one for the active carbon and an anionic exchanger. DF is equal to 3,4 for the active carbon alone and remains constant with the ion-exchanger (Table II). It was better to use polyvinylpyridine PVP in a second step, because DF increased from 3,4 to 5,4. But results remain disappointed, so that more experiences have to be achieved to improved Ru removal.

LIST OF PUBLICATIONS

No publications other than progress reports dealing with the work under with contract.

WET OXIDATION OF ORGANIC CONTAINING WASTES

Contractor :	AEA Technology
Contract No :	F12W/CT90/0053
Duration of Contract :	March 1991 to March 1995
Period covered :	January - December 1993
Project Leader :	Dr N S Holt

A. OBJECTIVES AND SCOPE

A wet oxidation process for the destruction of organics from intermediate level radioactive wastes has been developed in parallel by AEA Technology (Decommissioning and Waste Management) for the treatment of reactor sludges from the Winfrith Steam Generating Heavy Water Reactor, and by Nuclear Electric for the treatment of spent organic ion exchange resins from their nuclear power stations.

The process, which is based on catalysed reaction with hydrogen peroxide, has already been subject to experimental investigations up to 10 - 50 kg non-active resin batch using pilot scale plant for the above applications.

The main objective of this programme is to demonstrate the feasibility of wet oxidation treatment on a range of real radioactive wastes by the design, construction and operation of a fully active mobile pilot plant (50 - 100 kg / day capacity).

The key organic wastes identified for possible investigation include :

- Ion exchange resins from power reactor operation
- Decontamination liquors
- Mixed reactor sludges from WSGHWR
- Solvents and scintillants
- Cellulose containing soft wastes

B. WORK PROGRAMME

The programme consists of the following tasks :

Task 2.2	Analysis of literature data and assessment of candidate wastes in UK and EC context
Task 2.3	Evaluation of previous experimental results
Task 2.4	Completion of wet oxidation experiments
Task 2.5	Appraisal of alternative plant concepts
Task 2.6	Evaluation of complete treatment schemes
Task 2.7	Design, construction and operation of a mobile active wet oxidation pilot plant
Task 2.8	Drawing-up of flowsheets
Task 2.9	Analysis of safety and economic aspects

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

By the end of 1992, the second year of the project, literature reviews, non-active laboratory studies and analysis of previous experimental data were complete. A final detailed design for a mobile pilot plant to treat radioactive organic wastes had been produced, and the construction phase of this plant had commenced.

In the year covered by this report (January - December 1993), the construction of the mobile pilot facility was completed, after significant delay. The plant was successfully transported 200 km from the construction site to the Winfrith research centre by road. During the final quarter of the year the mobile wet oxidation plant has been installed and all components tested during commissioning trials. The first reactions between hydrogen peroxide and organic ion exchange resin (non-radioactive) were carried out in December 1993 as part of the commissioning procedure.

Ion-exchange resin waste from a UK Magnox power station has been treated at laboratory scale. The mass of organic carbon present in the sample was reduced by 97% after wet oxidation treatment.

The non-radioactive commissioning programme for the plant has received safety approval under the terms of the UK Nuclear Installations Inspectorate's licensing procedures.

Progress and Results

Task 2.2 Analysis of Literature Data

Task completed 1992. The findings of a comprehensive literature survey on wet oxidation research were presented.

Task 2.3 Evaluation of Previous Experimental Results

Task completed 1992. The studies of AEA Technology and Nuclear Electric relating to wet oxidation prior to this programme were reviewed.

Task 2.4 Completion of Wet Oxidation Experiments

This task has now been completed with the laboratory treatment of real radioactive waste. The waste sample used, from a UK Magnox power station, consists mainly of spent cation exchange resin. Both organic and inorganic ion exchange materials are present in the waste, in proportions varying throughout the waste storage tank. In the sample used, the principal component (87% by volume) was Lewatit DN, a caesium specific cation exchange resin. The phenol-formaldehyde polymeric structure of this resin is functionalised with sulphonic acid exchange sites. The other significant component of the waste mixture is AW500, a synthetic zeolite again used for selective caesium removal. The bulk specific activity of the waste has been measured at 245 kBq g^{-1} dry weight. The principle radionuclide present is ^{137}Cs, with a specific activity of 212 kBq g^{-1} (1990 values). The organic carbon content of the sample used was measured at 95 g kg^{-1}.

After reaction of a 200g batch of the sample with 800g of 17.4 M hydrogen peroxide solution, under reflux conditions and a reaction pH of 3.5, the organic carbon present in the sample was reduced to 0.6g over a 4 hr period, representing a 97% reduction in organic carbon. This test suggests that irradiated and aged Lewatit DN resin may be effectively treated by wet oxidation. The reaction efficiency relative to stoichiometric peroxide consumption was 35%, which is at the lower end of the expected range for batch wet oxidation reactions.

Task 2.5 Appraisal of Alternative Plant Concepts

Completed in 1992. Semi-continuous addition of waste throughout an extended reaction period emerged as the preferred option.

Task 2.6 Evaluation of Complete Treatment Schemes

This task requires data from non-radioactive and trace radioactive pilot plant trials, available in 1994, to progress.

Task 2.7 Design, Construction and Operation of a Mobile Active Wet Oxidation Pilot Plant

During 1993 the construction of the mobile pilot plant has been completed. The plant was delivered to AEA Technology's Winfrith site in early August, with some instrumentation incomplete. A detailed description of the mobile plant and the commissioning activities completed is given below:

2.7.1 Plant Description

The plant is fully contained within a single ISO transport container, with a mass of 8.4 te.

The main part of the plant, containing the majority of the radioactive inventory, is housed in a glass reinforced plastic containment glovebox. This section includes the jacketed reaction vessel, waste feed hopper, the feed and discharge pumps and the plate coil heat exchanger. The design waste throughput for the plant is 50 - 100 kg per day, dependant on waste type, with a maximum activity within the containment of 0.1 TBq (2.7Ci) as ^{60}Co. The containment box, is maintained slightly below atmospheric pressure by a vent fan.

The steam and gases produced by the wet oxidation reaction pass through a heat exchanger. This is cooled by a closed circuit air blast cooler to minimise the dependence of the plant on external water supply. The air blast cooler is mounted within the plant for transport but its operational position is external to the plant.

Condensed water from the process may be stored in the distillate tank. Non-condensed gases pass through a packed tower acid scrubbing column and circular High Efficiency Particulate Air filter (HEPA) before discharge to the atmosphere.

Heat to initiate the process is supplied by a compact steam boiler. Both high pressure steam or cold water can be supplied to the reaction vessel jacket for heating or cooling respectively.

2.7.2 Control and Instrumentation

The operation of 10 pumps, over 30 actuated valves, and several heaters and fans are controlled directly by the computer system. In addition, over 100 data channels from temperature sensors, gas analysers, flow meters and pressure transducers are monitored and logged by the computer system. The software programming to allow remote operation of the plant by a single operator has been completed over the period covered by this report. Commissioning operations are controlled using a hierarchical set of mimic screens, each controlling individual plant systems or operations. A second VDU provides the operator with real time measurements from plant instrumentation.

A second control system, with permanent wiring and independent of the computer system has also been installed, which provides safety trips under maloperation conditions.

2.7.3 Commissioning Programme

The non-active commissioning of the plant has commenced, and testing with simulant resin and hydrogen peroxide has begun. An outline of the sequence of commissioning operations that have been carried out are given below.

- Connection and demonstration of plant services e.g. power supply, lighting
- Verification of computer control function
- Functional test of all manual and actuated valves
- Leak testing of all plant items and calibration of level indicators
- Testing of all key safety trips
- Steam boiler commissioning
- Trial operation using water only
- Demonstration of resin feed / discharge system with inactive simulant.
- Passivation of hydrogen peroxide circuit
- Trial operation with inactive simulants

The first waste type to be investigated as part of the non-radioactive commissioning was a mixed anionic / cationic bead resin. This resin was used at a UK power station for non-active water treatment. A short trial reaction with 20 kg of this material has recently been completed, allowing parameters such as instrument performance, heat transfer rates, exothermicity and gas generation rates to be evaluated under close to design conditions. Although not the principle aim of this test, an overall reduction in the organic carbon content of the resin by 94% was achieved.

Task 2.8 Drawing up of Flowsheets

This task is awaiting data from mobile plant operations, and will be progressed in 1994.

Task 2.9 Analysis of Safety and Economic Aspects

The economics of wet oxidation treatment will be evaluated following radioactive plant operations in 1994 / 5.

Prior to delivery of the mobile plant, a detailed safety submission was produced to justify the commissioning of the plant. This was approved under guidelines laid down by Her Majesty's Nuclear Installations Inspectorate (NII). Information gained from non-radioactive plant operation will be required to confirm the safety of future radioactive operations.

2.9.1 Main Hazards

The main hazards identified with plant operation are a radiological hazard and chemical hazard to the operators. With the maximum design inventory of 0.1 TBq as ^{60}Co, the estimated dose to plant operators is 1.2 mSv/yr assuming a distance of 10 metres between operator control point and containment glovebox, and the provision of a 50mm thick lead wall (or equivalent). Control of the plant is currently possible at up to 15 metres from the containment box, and this distance may be increased further if necessary.

Hydrogen peroxide, the main chemical hazard, is stored externally to the plant in a purpose built storage tank. This minimises the amount of hydrogen peroxide present in the mobile plant and reduces the potential for decomposition hazard.

2.9.2 Safety Systems

The main safety related components and systems fitted on the plant are shown below :

- Housed in ISO container with appropriate vibration and shock protection for fixed items
- Reaction vessel constructed of glass lined steel. Stainless steel pipework throughout. Gaskets and polymers selected for radiation tolerance.
- A passive pressure relief system is provided via a water filled lute in case of overpressure.
- A pressure relief valve is incorporated within the hydrogen peroxide feed line, venting into the containment box drip tray.
- Distillate, scrubber liquor and off-gas discharge lines have sampling points.
- Hydrogen peroxide is stored external to the plant and supplied by a dedicated feed line.
- A full wash down system, including spray balls within the reaction vessel is fitted to the plant.
- Hard wired safety trips are incorporated to prevent peroxide addition under fault conditions e.g. loss of agitation, high reaction vessel temperature, excess foaming. These are supplemented by software controlled alarms for improved reaction control. Rapid cooling may be provided via the reaction vessel jacket and emergency cooling by the scrubber circuit.
- A glass reinforced plastic containment box held at slightly depressed pressure is fitted around all plant items containing significant quantities of radioactive material.
- The control console is connected to the plant by a 10 metre long 'umbilical cord', allowing remote operation.

List of Publications

/1/ HOLT, N.S., "Wet oxidation of organic containing wastes - Fourth semestrial report", AEA D&W Report CPDD(92)P034 (1993)

/2/ TWISSELL, M.A., "Wet oxidation of organic containing wastes - Fifth semestrial report", AEA D&W Report CPDD(93)P111 (1993)

/3/ TWISSELL, M.A., "Wet oxidation mobile active pilot plant - PreCommissioning Safety Report", AEA D&W Report CPDD(93)P060 (1993)

ADVANCED PROCESSES FOR THE TREATMENT OF LOW LEVEL LIQUID WASTES AT A PILOT PLANT SCALE

Contractors : LABORELEC (B) - SKC-MOL (B) - AEA-HARWELL (UK) - LNETI (P)
Contract n° : FI2W - CT90 - 0057
Duration of contract : from April 1/1991 to 31/12/1994
Period covered : 1993

Project leader :		
	Coordinator	R. ROOFTHOOFT
	SCK	P. DE REGGE
	AEA	A. TURNER
	LNETI	J.P. GALVAO

A. OBJECTIVES AND SCOPE

The objectives of the programme are :

a) Eliminate boron from low level liquid waste of PWR plants. Five processes will be evaluated (electrodialysis, reverse osmosis, distillation, ion-exchange and electrochemical ion-exchange).

b) Demonstrate the capabilities, reliability and cost-effectiveness of these processes for the treatment of real PWR wastes over realistic time scales at representative throughputs. As a part of this, it is a key goal to achieve low activity discharge levels (< 2 MBq/m^2) and high waste volume reduction factors (> 500) in a cost-effective way. An additional goal will be to obtain purified boric acid with less than 1 ppm Cl^- and a B-recovery of more than 75 %.

c) Evaluate electrochemical ion-exchange (EIx) on wastes from a nuclear research center (Harwell) in comparison with the flocculation/sand filtration process currently used for the removal of Cs, Co and α-emitters.

d) Evaluate electrochemical ion-exchange and reserve osmosis for the removal of Ra and other heavy metals from uranium mine tailing wastes in comparison with flocculation.

B. WORK PROGRAMME

First the composition of the waste streams will be identified. To select the optimal equipment batch experiments are carried out on simulant wastes. On the basis of these, bench-top experiments will be realized, firstly with simulant and then with genuine waste.

On basis of the obtained information one or more pilot plants will be designed and built. They will be used for testing on real waste :
- at Doel or Tihange PWR-stations
- at Harwell research laboratories
- on the Portuguese site Sacavem for uranium mine tailing wastes.

The processes which will be evaluated are :
1) electrodialysis
2) reverse osmosis
3) distillation
4) ion exchange
5) electrochemical ion exchange.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C1. State of advancement

Tests at the labo scale on genuine waste have been concluded.

- E-D and EIX at Doel
- EIX 1) Sacavem mine tailing waste 2) long term testing electrodes
- flocculation has been tested as well as pretreatments before R.O.
- distillation at SCK on genuine waste from Doel (2 experiments).

Two pilot plants have been constructed at Doel. The first by Laborelec : the pilot consist of an ultrafiltration followed by a unit for electrodialysis. The second by AEA-Harwell : it consists of a unit for electrochemical ion exchange which will take its water after treatment by UF (Laborelec plant). A full safety report on the two plants has been presented to the Doel power plant operator. The inspection by the authorities has been performed in November '93 and the plant started in December. A third pilot plant is in construction (SCK-CEN).

Laborelec and LNETI have performed tests in September in Urgeiriça with an R-O equipment (production of pure water : 130 l/h)

Another test has been performed by LNETI with the same pilot in December '93.

A pilot plant based on volatilization at elevated temperature and pressure has been developed by SCK. It was planned to order all equipment before the end of the year 1993. This pilot will be installed in Doel.

C2. Progress and results

a) E-D

The tests with a bench scale unit (Corning unit) followed by the EIX were finished by Laborelec in the first months of the year at Doel.

A pilot plant consisting of an EDR module protected against fouling by an ultrafiltration unit and a conventional filtration has been built in Doel. All the informations necessary to the follow-up of the treatment are collected in a database system with alarm system. This plant was authorized to start in December. The first test has been performed on LNA waste. It shows that :

1) Decantation and filtration over 10 µ filter cartridges : the biggest part of the activity is caused by Co-58 and Co-60. The activity of the waste is taken out for about 92 % after decantation and filtration over 10 µ-cartridges. See table I.

2) Ultrafiltration over Romicon cartridge :
- in the permeate most of the insoluble parts have been removed.
- about 2 % of the initial activity of the waste solution is remaining. See table I.

3) First tests with an Aquamite I electrodialysis unit :
- the unit concentrates further the Cs-134 and Cs-137 isotopes still in the permeate after the ultrafiltration.
- Co-58, Co-60 and Mn-54 that remained are not concentrated.
- during the first tests we also noticed that the efficiency of the electrodialysis process was decreasing.

- this problem could be caused by the presence of a big dose of surfactants, which would form a coating on the electrodes or saturate the resins that are in the stack with sulfonates.
- further tests need to be done to see if reversing the polarity of the current on the stack (every 20 minutes) can solve this problem and if the surfactant used is containing sulfonates.
- some results of electrodialysis, once through. See table II.
- some results of electrodialysis, recirculating the product water back in the feed-tank. See tables III and IV.

b) EIX

A pilot plant has been completed and commissioned in Harwell. CEIX membranes have been loaded with cobalt ; it has been demonstrated that bound cobalt may be removed by running under acid conditions, thus enabling solution volume reduction factors in excess of 4500.

Long term testing of small electrodes has been continued.

No sign of passivation is found after more than 30 months constant cycling of electrodes in precious metal oxide coated titanium meshes. This is equivalent to 4.5 years continuous operation under EIX conditions.

Long term tests of AEIX flow cells have continued. The cell treating a feed with high level of chloride (150 ppm Cl-) is now showing degradation in both physical appearance and EIX performance. No degradation has been noted with low chloride solutions.

A pilot plant has been constructed and delivered in Doel. It will take its water after treatment by ultrafiltration (Laborelec plant). The agreement for start-up has been obtained in November after inspection by AIB-Vinçotte.

c) Reverse osmosis

Laborelec and LNETI have performed tests in Urgeiriça with a R-O equipment and on genuine waste solutions. The membranes which were used,were of the composite type in a Rochem module based on discs. The solutions which had to be treated contained very high amounts of iron which result in fouling of the membranes. However the fouling is easily eliminated by flushings and cleanings with citric acid (adjusted to pH 4 with NH_4OH). A reconcentration test had to be stopped because of an important increase of pressure. Citric cleaning was not efficient and a precipitation of $CaSO_4$ was suspected.

Other tests and cleanings of the membranes have been performed by LNETI with the same plant in Urgeiriça in December.

d) Distillation

Two bench scale continuous experiments on genuine waste (LNA water Doel) were carried out. The pilot is based on the volatilization of boric acid at elevated temperature and pressure. The volume treated for each test is 150 l. The results of the experiments are a high decontamination factor (≥ 1000) and a good volume reduction factor (≥ 630).

A parametric study of the boric acid distribution between the vapour and the concentrate has been performed to measure the importance of pH, temperature and boric acid concentration.

A pilot plant is in construction.

e) Ion exchange

Ion exchange was not successful and has be abandoned.

Activities in MBq/m³ ; Table I

	Waste before treatment	Waste after decantation filtration 10 µ	Waste after ultrafiltration
global γ	221	17,4	3,7
Co-58	66,20	3,44	0,20
Co-60	80,97	6,06	0,34
Cs-134	1,60	0,54	0,54
Cs-137	2,00	0,68	0,74
Mn-54	5,40	0,66	0,64
Nb-95	2,70	-	-
Sb-124	0,80	-	-
Σ	159,67	11,38	2,46

Table II

Volume	Concentrate			Product		
treated (l)	λ µS/cm	B ppm	Cl⁻ ppm	λ µS/cm	B ppm	Cl⁻ ppm
0	390	-	-	-	-	-
50	894	-	-	92	-	-
103	1438	45,6	157,8	86	106,1	8,0
206	2010	-	-	107	114,3	10,0
422	3360	58,6	334,4	212	109,2	12,3
577	3770	66,2	447,3	353	115,1	24,8
680	3950	-	-	279	113,0	22,0
783	4120	69,6	500,6	358	112,6	26,1
Feed	667	121,6	63,3			

Table III

Hour	Volume treated (l)	T2 (feed)		T3 (concentrate)	
		pH	λ (µS/cm)	pH	λ (µS/cm)
0	0	7,74	624	9,25	265
30'	52	7,67	554	7,8	1111
1 h 07'	116 l	7,55	443	7,9	1412
1 h 47'	185 l	7,38	342	8,0	1640
2 h 07'	220 l	7,28	288	8,0	1756
3 h 15'	338 l	7,03	178,3	8,0	1988
3 h 48'	395 l	6,93	140	8,1	2070
4 h 17'	445 l	6,83	115	8,1	2120
5 h 17'	549 l	6,03	77,7	8,1	2200
6 h 17'	653 l	5,92	53	8,1	2260
7 h 17'	757 l	5,89	36,4	8,1	2290
8 h 17'	861 l	5,84	26,8	8,1	2330
9 h 17'	965 l	5,82	23,5	8,1	2320
10 h 32'	1095 l	5,85	16,8	8,1	2340
12 h 32'	1303 l	5,89	12,4	8,1	2360
13 h 17'	1381 l	5,90	11,8	8,1	2360
14 h 17'	1485 l	5,92	11,4	8,1	2360

Table IV

	Waste : begin test	Waste : after test
B (ppm)	110,0	86,3
Cl^- (ppm)	57,2	0,433
global γ (MBq/m^3)	3,2	0,16

Title	Process design and feasibility study for incineration under pressure, condensation and effluent treatment of radioactive waste	
Contractors	BERTIN & Cie (F), CEA-Cadarache (F) and INITEC (SP)	
Contract N°	F12W-CT91-0095	
Duration of contract	From July 1991 to June 1994	
Period covered	January 1993 - December 1993	
Project leader	C. LEONARD	BERTIN & Cie, Coordinator
	J.F. DOZOL	CEA
	S. ALAMO	INITEC

A. OBJECTIVES AND SCOPE

The main objective of this reseach is the evaluation of the technical feasibility of the combustion of a range of organic wastes containing radioactive elements, by means of oxygen under pressure, using a new type of incinerator relying on the recent technical developments achieved within the MESMA (Autonomous Energy Module) project.

In particular, the study will have to demonstrate that this new type of incinerator enables a quantitative destruction of organic wastes while only releasing inactive-gases (in terms of radioactivity and chemical toxicity).

The work to be performed is focused on the study of the adaptation of a closed loop for combustion under pressure operating at 60 bar - including the setting-up of a suitable off-gas treatment - to incineration of organic waste, and mainly of spent ion-exchange resins.

BERTIN has to adapt the process, developed for the MESMA project, to the case of waste incineration. In particular, a test bench for spent ion-exchange resins incineration has to be realized. The CEA will make a review of the possible waste to be processed, and will perform laboratory incineration and treatment trials.

INITEC participates to the design of the incineration test bench and to the trials.

B. WORK PROGRAMME

According to the additional clause of the contract, the work programme has been modified and comprises five distincts steps.

1. Identification of radioactive waste which could be incinerated : different organic wastes will be analysed. The choice will take into account the incineration characteristics as well as the interest in removing organic elements from the waste (amount produced, existing solution of removal, ...).

2. Drawing-up of process flow-sheets for incineration of spent ion-exchange resins. The best process and its main operating parameters will be defined.
3. Treatment and conditioning study of secondary waste generated during the incineration process : ashes, dust, liquids and gases (uncondensable gases and the release of under pressure storage tanks).
4. Bench-scale tests : after realization of a specific test bench, various incineration and treatment trials will be performed to confirm the hypothesis made for the drawing-up of process flow-sheets.
5. Technical evaluation : based on the results of bench-scale tests, this last step will permit to conclude upon the feasability of the process.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. State of advancement

Work carried out over the last year has made it possible to :

- define the whole process for thermal destruction of spent ion-exchange resins, including treatment of secondary waste : the flow-sheet corresponding to a 10 kg/h pilot plant has been established (Steps 2 and 3)
- size, erect and tune up the incineration test bench (Step 4)
- performe preliminary incineration tests at atmospheric pressure (Step 4)

2. Progress and results

2.1. Defining of the process

2.1.1. Incineration process

The incineration process, the scheme of which is given in figure 1, is composed of :

- a furnace

The furnace, a fluidized bed, is equipped with a waste feeding system (endless screw) and with a gas circuit (O_2 + recirculated gases) devoted to fluidizing the waste and supplying oxygen for combustion. The internal temperature is controlled at around 1000°C by the action of the recirculated gases (variation of flowrate by variation of the rotary speed of the surpressor). Oxygen flowrate is regulated to obtain 7 % oxygen excess in the exhaust gases in order to achieve a complete combustion.

- a quench / scrubber

This device has 3 functions :

- cooling/condenser function : cooling of combustion gases from 1000°C to 40°C by water injection into this gas. During this, water resulting from the waste combustion is also condensed
- dedusting function : recovery of dust (lithium, bore, radioelements oxides) in the condensed water
- scrubbing function : recovery and neutralisation of sulphur oxides by soda and partially of nitrogen oxides

The washing solution is stored in the quench tank. Part of it is sent to the liquid treatment system. The other part is cooled round 30°C before being re-injected into the quench. A continuous soda supply keeps the pH of the washing solution constant.

- a scrubber

A bubble scrubber is set downstream from the quench in order to complete the recovery and neutralisation of gases. A continuous soda supply keeps the pH constant. A liquid exhaust circuit is devoted to discharge sulphur and nitrogen saltz to the liquid treatment system.

- a recirculated gases circuit

Downstream from the scrubber, the prior part of clean gas is recirculated to the furnace by the surpressor.

- an exhaust gas circuit

In order to keep the incineration pressure constant (from 1 to 60 bar), part of combustion gases have to be discharged outside by means of an exhaust gas circuit comprising a heater, a filter, devoted to recover radioelements which may still be contained in the gases and a discharging device.

2.1.2. Treatment process for secondary waste

The composition of the secondary waste generated during the incineration of spent ion-exchange resins (quench and scrubbing of combustion gases) is expected to be :

- water	:	88 %
- soda saltz	:	10 % (Na_2SO_4, $NaNO_3$, $NaHCO_3$)
- metallic oxides	:	2 % (Boron and Lithium)
- radioelements	:	(Cs, Co, Mn, Sb)

The treatment of the secondary liquid waste must fulfil two requirements :

- simplicity of implementation
- minimization of the waste volume

Chemical precipitation complies with these requirements. The radionuclides (mainly 60 Co) can be precipitated either by increasing the pH (with caustic soda) or by adding a cation that is not very soluble in sulphate of carbonate/bicarbonate medium, calcium for instance.
Precipitating only with NaOH must lead to the smallest volume of sludge ; sodium being very soluble, only transition cations will precipitate.

2.1.3. Flow-sheet of a 10 kg/h pilot plant

Calculation shows that the mass reduction factor of the waste (mixture of anionic and cationic ion-exchange resins) would be round 10. Main results are shown on figure 2.

2.2. Incineration test bench

In order to validate the assumptions made in establishing the flowsheet of the 10 kg/h pilot plant, a test bench has been sized and erected (figure 3).

2.3. Preliminary atmospheric pressure trials

Preliminary incineration tests, performed at atmospheric pressure and with air instead of oxygen/CO_2 mixture, led to a fusion of a part of the furnace because of a too high temperature (> 1300°C).
After some modifications of operating conditions, good control of the combustion temperature has been obtained and no fusion appeared any more.
Resin combustion is complete and no soot can be observed in combustion gases at the outlet.

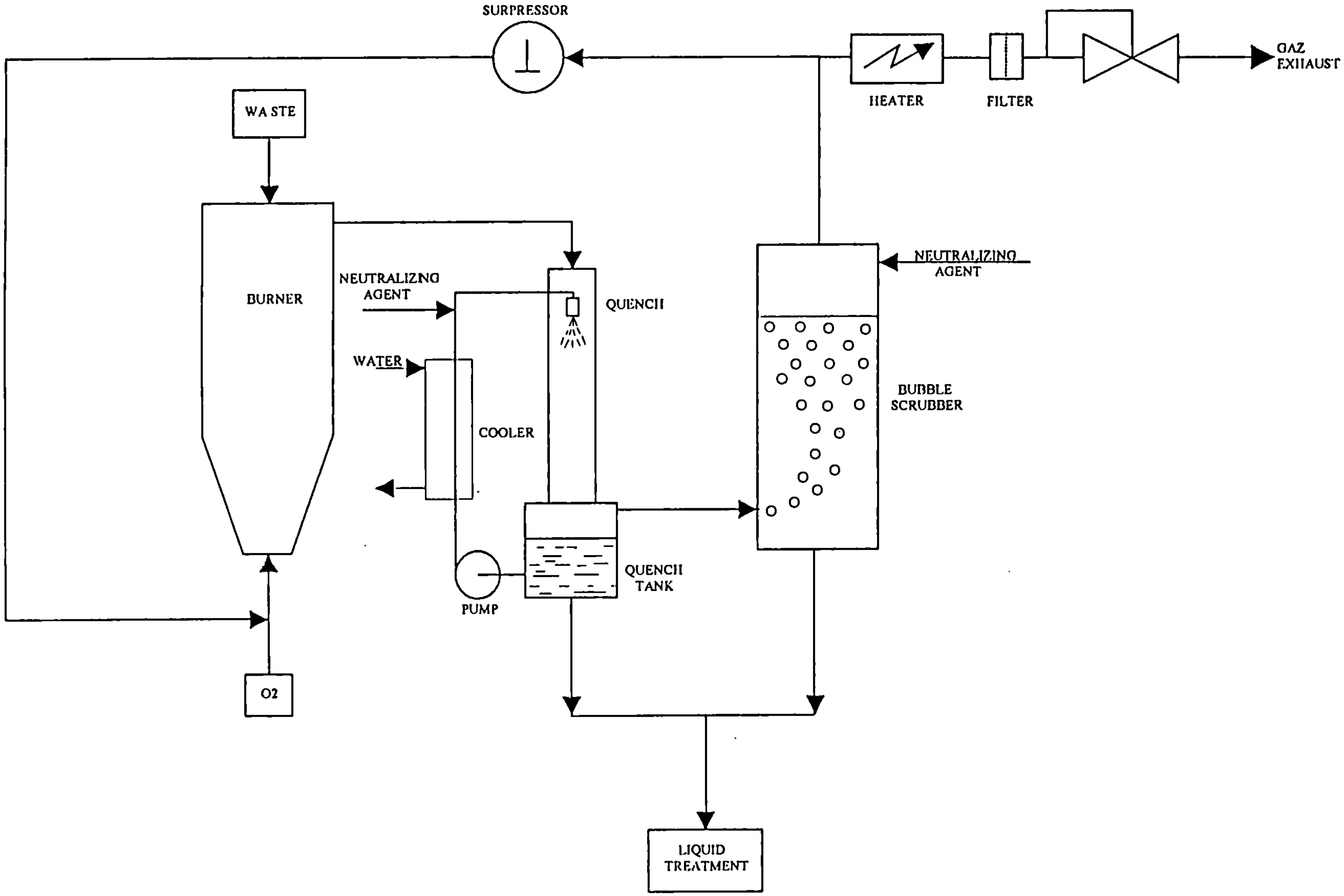


Figure 1 : scheme of the incineration process

Figure 2 : flowsheet of the process

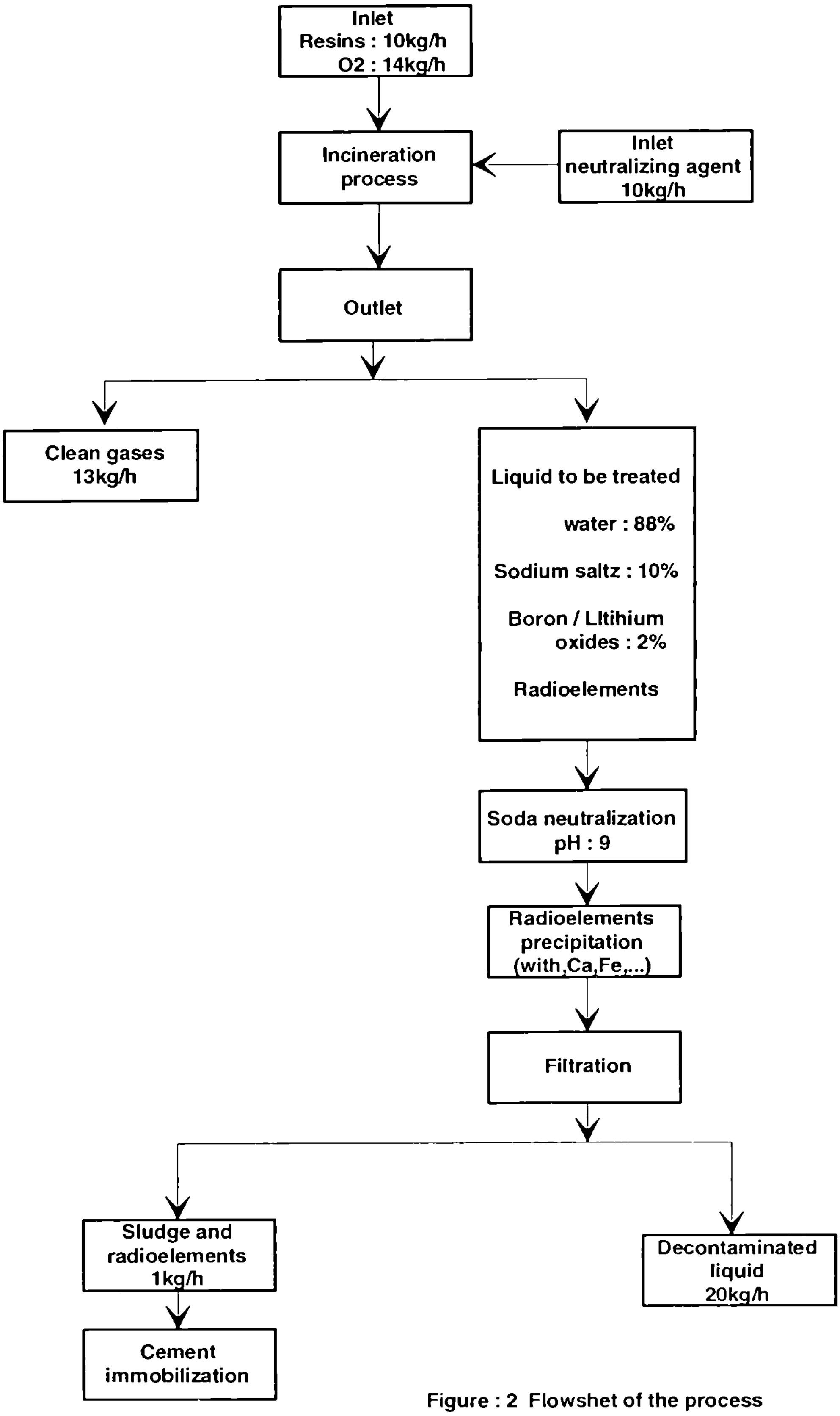
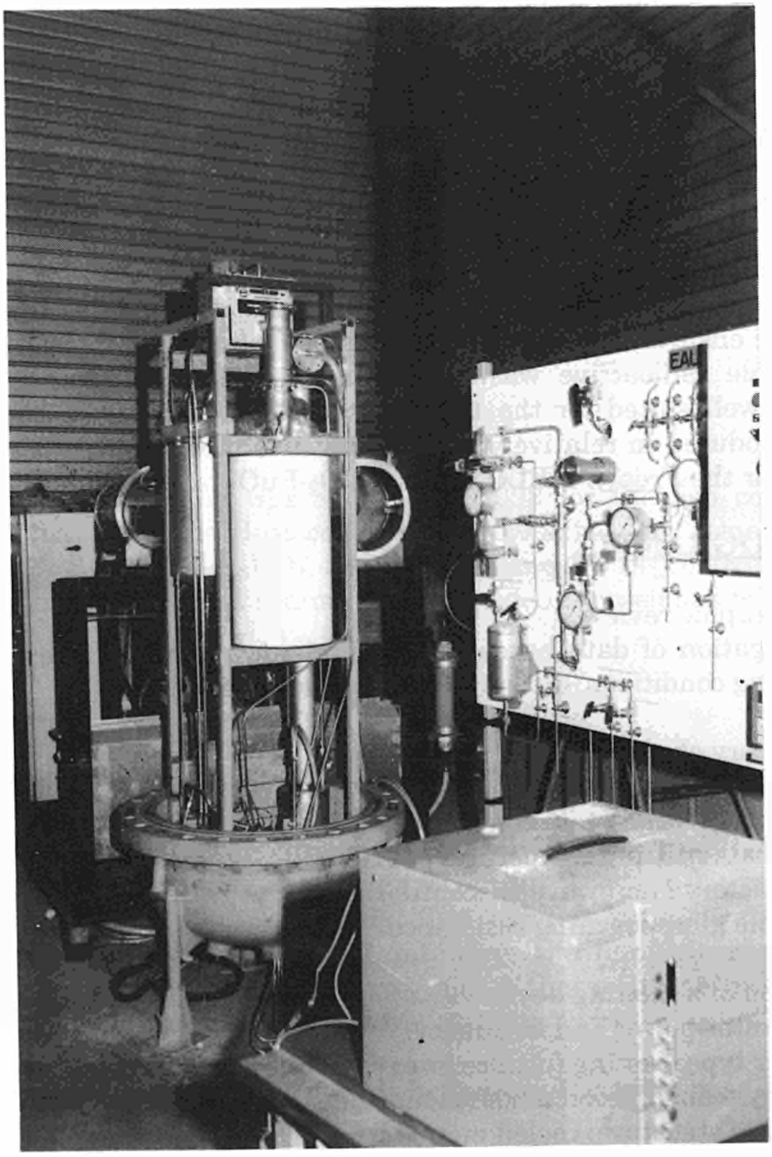


Figure : 2 Flowshet of the process

Figure 3 : global view of the bench tests installation



MELTING OF INCINERATOR ASHES USING A MICROWAVE FURNACE

Contractor:	CEA DCC/DRDD/SCD
Contract No:	F12W-CT91-0100
Duration of Contract:	July 1991 – July 1995
Period Covered:	January – December 1993
Project Leader:	J.J. Vincent

A. OBJECTIVES AND SCOPE

The purpose of this investigation is to design, build and test an inactive prototype microwave melting facility for incineration ashes, with a capacity not exceeding a few kilograms per hour.

The microwave melting technique will significantly reduce the ash disposal volume while ensuring chemical and mechanical stability comparable to that of the most favorable radioactive waste containment matrices. This technique is also particularly well suited for the treatment and conditioning of radioactive ashes, which are produced in relatively small quantities (about 10 m^3 per year) based on projections for the French MELOX mixed UO_2-PuO_2 oxide fuel fabrication plant.

B. WORK PROGRAMME

B.1 Bibliographic review.
Interrogation of data bases covering microwave melting (existing processes, operating conditions, dielectric properties of materials).

B.2 Laboratory study.
Specification and development of a glass composition for ash incorporation compatible with certain constraints:
- moderate melting temperature (1100°C),
- satisfactory microwave susceptibility,
- suitable glass leaching resistance.

B.3 Selection of a melting device.
- Generator power and frequency.
- Melter type: casting furnace or expendable crucible furnace.
- Energy transmission mode: monomode or multimode.
- Crucible structure: cooled metal or refractory material.
- Glass casting mode: batch or continuous.
- Microwave cavity design.

B.4 Design and construction of the melting facility.

B.5 Testing and development.

B.6 Technical and economic assessment.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Task B1 (*bibliographic review*) was completed in 1993.

Task B2 (*laboratory studies*). After developing and testing the glass composition in 1992, laboratory tests continued in 1993. The glass formulation was improved and the final composition was subjected to leach testing under nonradioactive conditions.

Task B3 (*selection of a melting device*). The reference solution remains, the monomode, cooled metal melter operating at 915 MHz. Nevertheless, the work undertaken in 1992 to develop other melting devices continued in 1993.

Task B4 (*design and construction of the melting facility*). The 915 MHz reference melter was built and delivered to the SCD in July (SGN was the prime contractor).

Task B5 (*testing and development*). The first melting tests were conducted after installing the 915 MHz melter.

Progress and Results

Task B2. Laboratory Studies

- *Improving the Glass Formulation*

A standard composition was adopted in 1992 for the ash containment glass (Table I). At that time, the glass consisted of 40% ashes; the remaining 60% was a mixture of 26% SiO_2, 33% H_3BO_3, 33% Na_2CO_3 and 8% Fe_3O_4. When the glass was fabricated, the boric acid and sodium carbonate decomposed according to the following reactions:

$$2\,H_3BO_3 \Rightarrow 2\,B_2O_3 + 3\,H_2O$$
$$Na_2CO_3 \Rightarrow Na_2O + CO_2$$

The gas released by these reactions caused the flashes observed during casting tests in the prototype facility at Cadarache.

In order to mitigate this problem, the vitrification additive (SiO_2, Na_2CO_3 H_3BO_3) was no longer added in powder form, but as glass frit containing 33% of SiO_2, 33 % of Na_2O, 33 % of B_2O_3. The ash/frit ratio for the new mixture (designated C_0) was 50/50. While maintaining the final glass composition, this formulation significantly reduced the gas release that would be incompatible with a melting process implementing microwave heating.

- *Boiling Water Leach Test of Nonradioactive Ash Containment Glass at Atmospheric Pressure*

From a safety standpoint, the most important property of a containment glass is its aqueous corrosion resistance and containment integrity. The development of a microwave ash melting system cannot be separated from the quality of the process glass (electromagnetic susceptibility, process temperature, etc.); qualification of the leaching behavior of the reference ash containment glass was thus indispensable.

A "Soxhlet" leaching device, consisting of a boiler topped by a condenser, is used to select and characterize containment glasses. A glass test specimen is exposed to water at the boiling point under atmospheric pressure. Two types of tests are conducted: dynamic and static.

- *For dynamic testing*, the specimen is placed in a boat beneath the condenser, exposed to the condensed (demineralized) water stream; this prevents the aqueous medium from reaching saturation, which would limit glass corrosion. Dynamic tests provide information on the initial corrosion rate.
- *For static testing*, the specimen is placed directly in the boiler and is therefore exposed to an aqueous leaching medium that gradually becomes enriched in leaching products: the corrosion rate thus progressively diminishes. Static tests take account of the drop in the corrosion rate as the medium reaches saturation, and are therefore more representative of glass behavior under actual repository conditions.

The results obtained for the ash containment glass were compared with the data available for the R7T7 reference glass, which has been fully characterized in our department.

- Dynamic leach testing indicated that corrosion (i.e. the normalized mass loss NL) of the ash containment glass was three times greater than that of R7T7 glass. In other words, the initial (maximum) corrosion rate of the ash containment glass is three times higher than for R7T7 glass. The normalized total mass NL(M) and boron mass NL(B) losses measured after 28 days of leaching were as follows:

NL(M) = 160×10^{-4} g·cm^{-2} for the ash containment glass
to compare with : 56×10^{-4} g·cm^{-2} for R7T7 glass.

NL(B) = 225×10^{-4} g·cm^{-2} for the ash containment glass
to compare with : 72×10^{-4} g·cm^{-2} for R7T7 glass.

- The 28-day static leach test revealed that, without leachate renewal, corrosion of the ash containment glass was low, practically identical with that of R7T7 glass. The corrosion rate thus drops considerably as the water medium becomes saturated:

NL(M) = 16×10^{-4} g·cm^{-2} for the ash containment glass
to compare with : 16×10^{-4} g·cm^{-2} for R7T7 glass.

NL(B) = 26×10^{-4} g·cm^{-2} for the ash containment glass
to compare with : 24×10^{-4} g·cm^{-2} for R7T7 glass.

The ash containment glass may therefore be considered to be of good quality. Although the normalized mass losses under dynamic leaching conditions were three times higher than for R7T7 glass, they are indicative only of the initial corrosion rate. Static leach tests, which are more representative of actual glass behavior, were fully comparable with R7T7 glass.

Task B3. Selection of a Melting Device

At the present time, the reference solution remains a monomode, cooled metal melter operating at 915 MHz (Figure 1). Nevertheless, alternative microwave melting processes (in-can melting at 2450 MHz) continue to be investigated.

The cooled metal melter option operating at 915 MHz was selected for a number of reasons.

- The program target (a melting rate of 15 kg of ashes per hour) requires a microwave power rating of about 25 kW. As the power output from a microwave generator is inversely proportional to the frequency, the specification requirement can only be met by 434 MHz or 915 MHz generators. As the former raise a number of technological problems in use, we naturally opted for the latter.

- Monomode operation was selected because it ensures the highest power densities while providing uniform heating.
- Microwaves directed parallel to the surface were adopted rather than perpendicular or oblique waves to increase the melting surface area and minimize hot spots.
- Having selected these two techniques, we opted for a continuous casting melter using a cooled metal structure to limit corrosion.
- Finally, the melter is primarily a research and development facility, for which a modular design was most appropriate. The applicator comprises five separate sections; the ends may be reversed to direct the microwaves at the casting nozzle or at the opposite side. The nozzle itself features a slotted opening with an interchangeable strap to adjust the height of the glass melt.

Task B4. Design and Construction of the Melting Facility

SGN, the prime contractor, delivered the 915 MHz melter to Marcoule in the summer of 1993, and acceptance testing began in September.

Task B5. Testing and Development

- *915 MHz Melter*

The unit was assembled in the SCD technological test facility. The melter was connected to a 25 kW 915 MHz generator and to a previously calibrated feed system before acceptance testing, including the formation of the holdup (the glass heel in the reactor) and an initial casting test.

About 2¼ hours were required to form the holdup with about 5 kg of molten glass. No electric arc was observed during this preliminary phase (unlike the test at 2450 MHz). The melt exhibited satisfactory thermal homogeneity, and its slightly dark orange color and viscous appearance showed that little or no overheating occurred.

This observation was confirmed by the casting test. The relatively viscous liquid stream was 20 to 30 mm in diameter as it exited from the casting nozzle. The nozzle was not cooled, so the glass remained fluid: plugging only occurred once. Visual observation showed no unmelted ashes in the glass (unlike the 2450 MHz melter). After cooling, however, the glass did not appear sufficiently refined. This may be attributable to the short residence time, to the absence of overheating, or to an extended digestion time. The average throughput during the first test was 2.8 $kg \cdot h^{-1}$, well below the potential melting capacity.

It is important to note that the 915 MHz generator does not include a return power indicator, making it impossible to adjust the applicator impedance using the tuning piston. This situation would have been intolerable with the 2450 MHz melter (repeated short-circuits), but was not too penalizing at 915 MHz: only one generator shutdown occurred due to overheating of the filaments. A measurement diode will be added at the water load outlet; coupled to a milliwattmeter it should indicate the order of magnitude of the return power and thus allow us to tune the system impedance.

- *2450 MHz In-Can Melter*

Along with the 915 MHz melter tests, we also conducted in-can melting tests at 2450 MHz. The initial tests in a cylindrical multimode cavity did not produce glass of sufficient quality to meet nuclear containment requirements: a layer of completely unmelted ashes was found at the glass/melter interface, and the glass contained numerous ash inclusions.

In view of the poor results obtained with a multimode cylindrical crucible, we turned to an energetically more favorable solution in the form of a monomode in-can melter using a rectangular RG 112U waveguide as a resonant cavity (Figure 2). Unfortunately, the results were no less unsatisfactory than in the multimode configuration. The results demonstrate the technological feasibility of an in-can microwave melting process for vitrifying a mixture of incineration ashes, but they also show that a good containment matrix is very difficult to obtain.

Table I - Selected Glass Composition

SiO_2	37.0 %
Al_2O_3	12.4 %
Na_2O	16.6 %
B_2O_3	15.2 %
CaO	5.0 %
Fe_3O_4	5.0 %
CeO_2	2.9 %
Fe_2O_3	0.3 %
ZnO	1.9 %
TiO_2	0.1 %
MgO	1.4 %
BaO	0.4 %
Cl	1.3 %
C	0.1 %
S	0.4 %

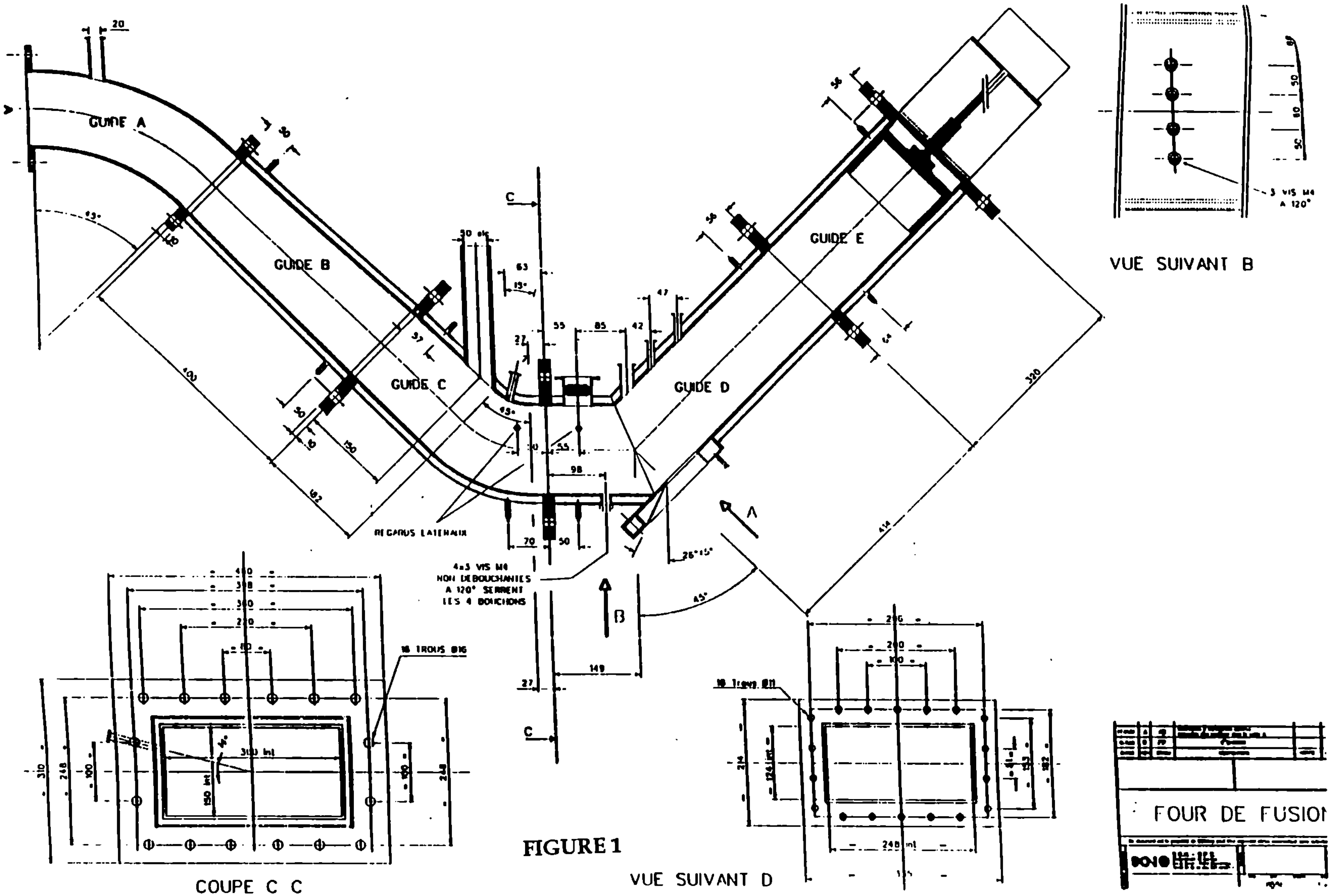

GUIDE A
GUIDE B
GUIDE C
GUIDE D
GUIDE E
VUE SUIVANT B
3 VIS M4 A 120°
REGARDS LATERAUX
4x3 VIS M4 NON DEBOUCHANTES A 120° SERRENT LES 4 BOUCHONS
A
B
C
C
45°
26°15'
400
320
414
16 TROUS Ø16
310 Int
150 Int
COUPE C C
10 Trous Ø11
124 Int
248 Int
VUE SUIVANT D
FOUR DE FUSION

FIGURE 1

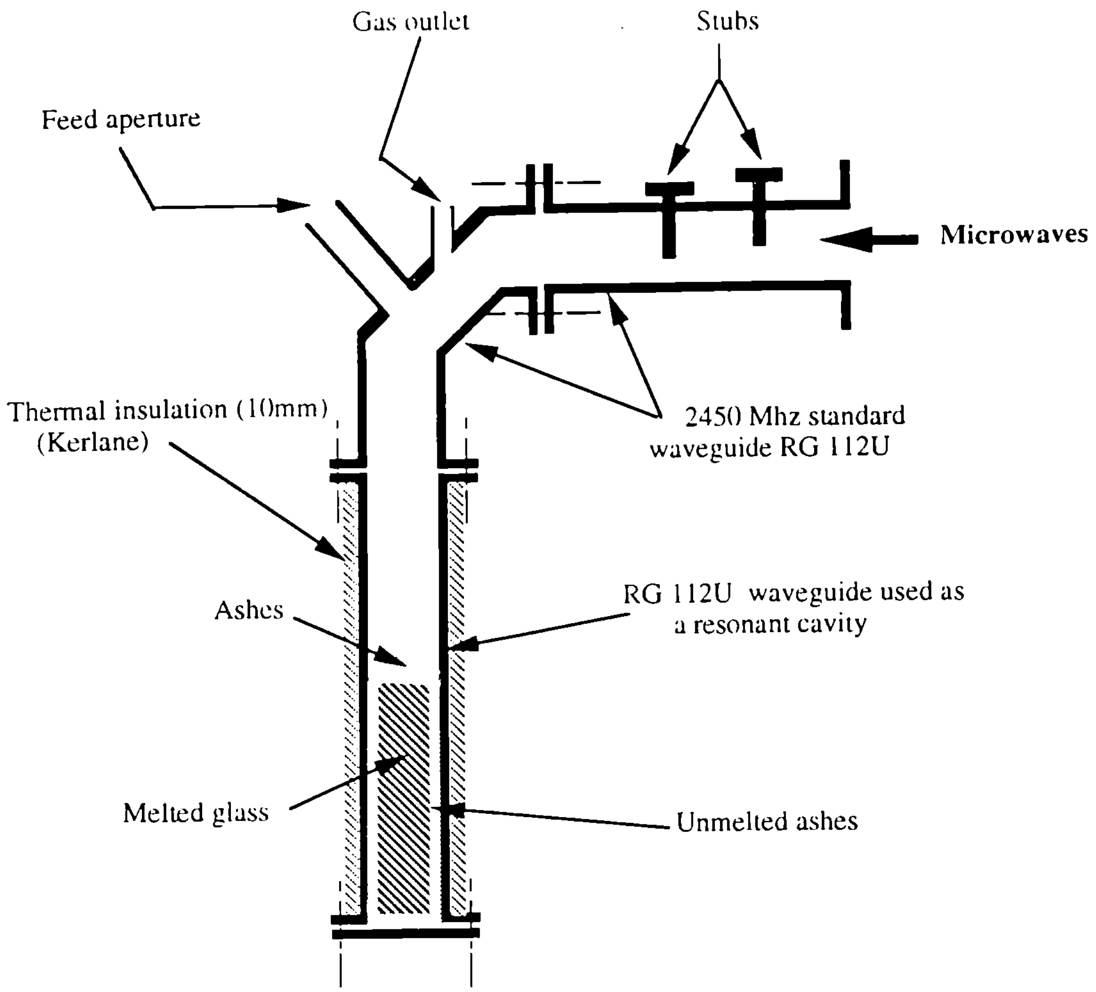


Fig. 2 : Ash vitrification using a 2450 Mhz monomode in-can melting process

Title: Treatment of radioactive solvent waste by catalytic oxidation
Contractor: ENEA
Contract N°: FI2W-CT91-0108
Duration of contract: from 1 October 1991 to 31 March 1994
Period covered: January - December 1993
Project Leader: Alfredo LUCE

A. OBJECTIVES AND SCOPE

As a result of past reprocessing campaigns performed in the EUREX pilot plant (Saluggia, Italy), about 26 m^3 of spent solvent were produced. Taking into account the difficulty to process this waste type (a mixture of tri-butyl-phosphate, tri-capryl-amine, kerosene and methyl-benzenes) according to existing technologies (e.g. Incineration), this research activity aims at setting-up a suitable treatment process capable of reaching three major objectives:
1) reduction of the waste volume by a factor at least equal to 10;
2) oxidative destruction of the reduced volume waste;
3) compatibility of the processed waste with conventional immobilisation matrices like cement.

For the specific purpose, it is intended to investigate the potentialities of the combination of distillation with wet oxidation. Scope of the distillation is the reduction of the waste volume, producing a non contaminated distillate, to be conventionally incinerated without containment, and a bottom residue, containing all the activity, to be processed by wet-oxidation.

The research activity comprises the implementation of the following items:
1) Laboratory scale distillation tests using genuine samples of EUREX spent solvent waste.
2) Wet oxidation experiments both on laboratory scale with genuine waste and on bench scale with simulated waste, using hydrogen peroxide in presence of a catalyst.
3) Cementation tests of the aqueous waste arising from the wet oxidation.
4) Preliminary design of a full scale treatment plant.

B. WORK PROGRAMME

The work programme includes the following tasks:

1. Conduction of laboratory scale distillation tests with genuine waste coming from the EUREX plant storage. Scope of the tests is the optimisation of the operating parameters in order to get a DF of the top fraction which satisfy incineration criteria in conventional plants.

2. Wet oxidation experiments

2.1. Laboratory-scale experiments. These experiments are conducted using the bottom product generated during distillation tests of the genuine solvent waste.

2.2. Bench scale experiments. These experiments involve processing of 3-5 litres batches of inactive simulated waste in order to quantify the scaling-up effect and to optimise the process parameters which enable a minimisation of the final aqueous waste volume.

3. Conduction of cementation tests using ordinary Portland cement (possibly with inorganic additives) on the inactive aqueous waste coming form the wet oxidation bench-scale experiments.

4. Preliminary design of a full scale treatment plant for processing the whole stock of the EUREX solvent waste, including the distillation section, the wet oxidation section and the interface with the cementation plant.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The following tasks of the research contract have been completed in line with the time schedule:
1) Distillation experiments.
2) Wet oxidation laboratory experiments.
3) Wet oxidation bench scale experiments.

The experimental results are so far quite satisfactory; the feasibility of the distillation as method to drastically reduce the volume of the waste has been demonstrated. More than 88% of the solvent waste can be distilled with a negligible rising of the activity, so that the top product of the distillation can be conventionally incinerated according with the environmental radioactivity receptivity.

The bottom residue of the distillation can be treated by wet oxidation with hydrogen peroxide producing an aqueous stream to be discharged and an aqueous residue to be cemented.

The 4th task (Cementation tests) is at a good stage of completion. Cementation tests of the aqueous residue, coming from the bench scale experiments, are in progress in a cold technological hall of ENEA Casaccia site (Rome).

Last task (Preliminary design) has been initiated with the assistance of an Engineering Company and the conclusion of the task is expected within the time scheduled.

Progress and results

1. Distillation Tests

The distillation tests have been successfully completed and fully described in the previous reports, showing that more than 88% of the solvent waste can be distilled with a negligible rising of the activity.

The distillation tests has been carried out inside a laboratory fume hood. The equipment is completely borosilicate glass made, and consists of Reboiler (Volume = 2 l), distillation column, phase separator and condenser.

Several hot tests have been carried out utilising quantities of genuine waste ranging between 0.6 and 5 litres in batch steam distillation. Efforts have been made to maximise the decontamination factors and to minimise the operating time.

The described tests confirm the feasibility of the distillation process in order to obtain a substantial volume reduction of the waste before the chemical treatment.

Table I shows a resume of the main data concerning the distillation of the entire stock of Solvent Waste to be distilled, with the global expected ripartition of the activity between the streams.

Table I - Ripartition of the Activity

	$\alpha + \beta$		β (n.v.)		α		Volume
	(Bq)	(Ci)	(Bq)	(Ci)	(Bq)	(Ci)	(l)
S.W.	2.25E+10	0.608	4.39E+09	0.119	1.31E+09	0.0355	25000
Distillate	2.21E+07	5.98E-04	7.52E+05	2,03E-05	1.55E+04	4.19E-07	22125
Residue	2.25E+10	0.608	4.39E+09	0.119	1.31E+09	0.0355	2875

n.v. = non volatile radionuclides

The achieved results show that the distillate can be conventionally incinerated, because all the residual activity can be completely released to the atmosphere without any filtration according with the authorised discharge limits of the EUREX plant for the gaseous effluents. The respect of the authorised discharge limits assures that the discharged activity is much below the limits of the local environmental receptivity.

2. Wet Oxidation Experiments

2.1. Laboratory scale experiments

Laboratory scale experiments with real waste have been conducted using the bottom products of the distillation tests. The same installation used for the distillation tests has been used, with some modification, especially studied for the new safety requirements. So the reboiler has been used as reactor, while the packed column as a high efficiency demister.
The above equipment is installed inside a laboratory fume hood; due to the safety consideration about explosion hazard, the reactor is ventilated with N_2, in order to maintain the possible flammable gases always below the explosion limits; this gas also provide a bubble mixing of the liquid. External peristaltic pump is used to continuously feed H_2O_2 to the reactor. Heating is provided by a laboratory electric heater.
3 batches have been conducted, each batch processing 100 ml of the organic residue of the distillation tests; the organic waste is introduced into the reactor together with 2 g of ferrous sulphate in 100 ml demineralized water. Heating is provided to keep the temperature at the boiling point (about 100 °C). The stirring is provided without mechanical devices, but with the inlet of the N_2. A continuous feed rate of 100 ml/h 40 % m/v hydrogen peroxide is maintained.
The distillate is completely condensed and the aqueous phase is collected and periodically sampled while the organic one is recirculated to the reactor.
Table II shows the main informations coming from the tests.

Table II - Main Data of Hot Laboratory Experimental Tests

	Test 1	Test 2	Test 3
Real Waste (l)	0.1	0.1	0.1
- Beta-tot. (Bq/l)	~ 8.00E+06	~ 8.00E+06	~ 8.00E+06
- Beta n.v. (Bq/l)	~ 1.50E+06	~ 1.50E+06	~ 1.50E+06
- Alfa (Bq/l)	~ 4.50E+05	~ 4.50E+05	~ 4.50E+05
H_2O_2 40% fed (kg)	4.50	3.40	2.80
H_2O_2 consumption (kg/l of waste)	45	34	28
H_2O_2 average feed rate (kg/h)	0.10	0.10	0.10
Catalyst (g) (ferrous sulphate)	2	2	2
Reaction Temperature (°C)	100	100	100
Organic Residue (l)	0.020	0.020	0.030
Aqueous Residue (l)	0.300	0.400	0.200
Aqueous Distillate (l)	3.300	2.600	2.000
- Beta-tot. (Bq/l)	230	265	320
- Beta n.v. (Bq/l)	≤13,5	≤13,5	≤13,5
- Alfa (Bq/l)	1.3	1.7	1.5

The global efficiency of the reaction seems to be lower than for the bench scale experiment, and the organic residue is bigger. The explanation is the minor efficiency of the stirring method, which confirm that the vigorous stirring is essential for the process.
There are no information about the losses of radioactivity with the off-gas, but from Tab.II we note that the rising of the radioactivity with the aqueous distillate is extremely low, so we believe that the off-gas also should be very slightly contaminated, and only with volatile low radiotoxicity nuclides (e.g. ^{3}H, ^{14}C) so to be compatible with the discharge limits.

2.2. Bench scale experiments

Bench scale experiments with simulated waste have been conducted in order to quantify the scaling-up effect and to determine the process parameters which enable a minimisation of the final waste volume. Tests involve processing of 3-10 litres batches of inactive simulated waste with about the same composition of the bottom product of the distillation, of course without contamination.
All the equipment (see Fig. 1) has been installed inside a cold technological hall of the EUREX plant and consists of:

- Reactor borosilicate glass made, volume = 30 l, equipped with stirrer, heating, pH-meter, temperature measurement, off-gas condenser, sampling.
- On-line monitoring of the off-gas flow-rate and composition, referring to main gaseous decomposition products (CO_2, CO, O_2).
- Other equipment: dosimetric pumps, instrumentation, data acquisition, etc.

Two campaigns of bench scale wet oxidation tests have been carried out; Table III shows the main experimental average data.
From the experimental results of the two campaigns some consideration can be done:

1) The best reference operational procedure seems to be as follow:
- batch loading of the organic waste togheter with the catalyst solution;
- continuous feeding of H_2O_2 and distillation conditions;
- continuous discharging of the aqueous distillate;
- batch discharging of the residue in the reactor; eventual supplementary evaporation for volume reduction.

2) The exothermicity of the reaction is quite enough to keep the temperature of the reactor at the operating level (98÷100 °C) for long time, also providing an evaporation which can automatically remove the aqueous excess from the reactor. External heating is necessary during the less efficient step and also to provide an evaporation to keep low the final aqueous residue in the reactor.

3) 20÷24 kg H_2O_2 40% are necessary for the almost complete "destruction" of 1 litre of organic waste, but big quantities of soluble degradation organic compounds are still present in the aqueous distillate, as the high TOC values demonstrate.

4) TCA is by far the most reactive component of the mixture, in the sense that it is very quickly decomposed to intermediate molecules. The big reactivity of the mixture, observed at the beginning of the batch, is essentially due to the presence of the TCA.

5) It seems that the quantity of organic phase in the reactor doesn't influence the reactivity, because the reaction happens at the interface with the aqueous phase, so that the more soluble organic substances are more reactive (e.g. TCA, which is more soluble in the acidic aqueous media).

6) A small quantity (2÷3 % of the initial volume) of very viscous unreactive residue is found in the reactor at the end of the batch. Conditioning hypotheses are being studied for this fraction.

7) The addition of fresh organic during a batch, continuously or discontinuously, doesn't influence significantly the global efficiency of the process.

8) The reduction of the H_2SO_4 doesn't decreases the efficiency very much, but the lower acidity allows the precipitation of ferrous-ferric phosphates.

Table III - Average Results of Bench Scale Experiments

Operative Parameter	Average Batch
Simulated Waste (l)	3÷10
H_2O_2 consumption (kg/l of waste)	20÷24
H_2O_2 feed rate (kg/h)	3÷4
Catalyst (g/l of waste)	20
H_2SO_4 96%	0.5 % of the H_2O_2
Reaction Temperature (°C)	98÷100
Organic Residue (%)	2÷3
Aqueous Residue (l/l of waste)	2÷4
Aqueous Distillate (l/l of waste)	16÷19
TOC Aqueous Distillate (mg/l)	5000÷6000
TOC Aqueous Residue (mg/l)	200÷300
Solid Residue	small amount powdery precipitate

3. Cementation Tests

Cementation tests have been started in the second half of the year, in order to determine the compatibility of the wet oxidation product with conventional immobilization matrices.
The major problem of this task comes from the high salts content of the aqueous solution (sulphates, phosphates, etc.). Efforts have been done in order to find an appropriate alkaline solution for neutralization step. Neutralization with sodium hydroxide and calcium hydroxide seems to be the best procedure which enables the precipitation of calcium sulphate and phosphate, which can be inglobated in the cement without significant influence on its properties.

4. Preliminary Design

A preliminary design of a full scale plant for processing the EUREX solvent waste has been started. The design will include the distillation section, the wet oxidation section and the interface with the cementation plant. A flow sheet will be drawn up, including mass and radioactivity balances and all the steps up to the production of cemented blocks.

On the basis of the design of the full scale treatment plant, a detailed assessment of the safety implications of the process will be made, including the practical means to prevent the effect of an unexpected growing up of unreacted hydrogen peroxide within the reactor.

List of publications

/1/ A.LUCE, F.TROIANI, Treatment of Radioactive Solvent Waste by Catalytic Oxidation, CEC Contract N° FI2W-CT91-0108, Third Progress Report, April 1993.
/2/ A.LUCE, F.TROIANI, Treatment of Radioactive Solvent Waste by Catalytic Oxidation, CEC Contract N° FI2W-CT91-0108, Fourth Progress Report, September 1993.

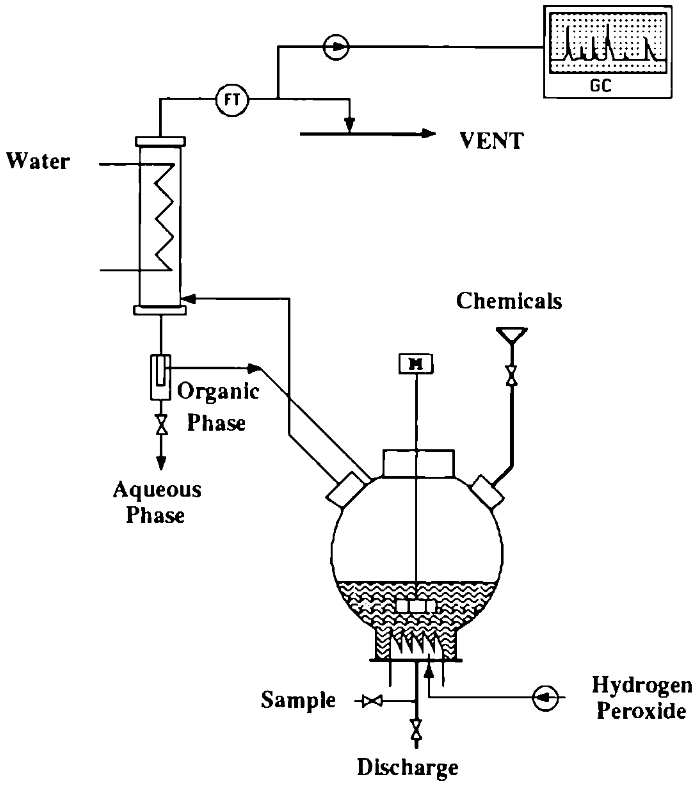


Figure 1 - Bench Scale Scheme of Installation

Title :	New macrocyclic extractants for radioactive waste treatement : ionizable crown ethers and functionalized calixarenes
Contractors	CEA-Cadarache (F) - Universities of : Barcelona (E), Parma (I), Mainz (D), Belfast (G.B), Twente (NL) and Strasbourg (F)
Contract n°	F12W-CT90-0062
Duration of contract	January 1991 - August 1995
Period covered	January 1993 - December 1993
Project leader	Coordinator : J.F.Dozol (CEA-Cadarache) (F) F.Lopez Calahorra (E), A. Mc Kervey (G.B), V. Boehmer (D), R.Ungaro (I), M.J.Schwing (F), D.Reinhoudt (NL).

A. OBJECTIVES AND SCOPE

The principal aim of this research consists in perfecting the schemes of decontamination of real liquid wastes : medium level reprocessing concentrate and more generally liquid wastes arising from reprocessing plants.

The objective of this research is to selectively remove actinides, cesium and strontium from high salinity wastes arising from reprocessing operations in order to minimize the volume of wastes to be disposed of in a geological formation.

It is intended to investigate the potential of new classes of organic extractants under development in different university laboratories.

Four laboratories (Parma, Belfast, Mainz, Twente) are working on the basic research on calixarenes. Synthesis of these macrocyclic compounds from the various p-alkyl-calixarenes will be carried out in order to obtain very strong and selective extractants for long-lived radioactive cation such as strontium, cesium and actinides. The Barcelona laboratory synthesizes crown ethers which possess pendant ionizable groups. Compared with classical crown ethers, the presence of these groups facilitates the extraction or transport of metal ions.

The four laboratories working on calixarenes and already collaborating in more basic research, and the laboratory in Barcelona which synthesizes crown ethers, provide functionalized calixarenes and ionizable crown ethers for EHIC and CEA which in turn test these different products.

The CEA is the coordinator of the project, begun on September the first 1991, with six contractors, the Universities of : Barcelona (Pr F. Lopez Calahorra), Belfast (Pr M.A. Mc Kervey), Mainz (Pr V. Boehmer), Parma (Pr R. Ungaro), Twente (Pr D. Reinhoudt), Strasbourg (Pr M.J.Schwing).

B. WORK PROGRAMME

1- The EHIC Strasbourg tests all the macrocycles synthesized in the frame of the contract, after this screening (or simultaneously) the most promising products undergo extra tests in Cadarache.

2- The four universities (Belfast, Mainz, Parma, Twente) working on the synthesis and basic research of calixarenes devote their efforts to prepare selective extractants for actinides cesium and strontium and work in close collaboration,

3- The University of Barcelona synthesizes crown ethers with pendant ionizable groups such as phosphoric and sulfonic in order to allow for the removal of cesium and strontium from a highly acidic solution.

4- During the first two years, synthesis, basic studies, measurements of characteristics and of distribution coefficients of nuclides between organic and aqueous phases have been carried out.

5- The new process defined with functionalized calixarenes or ionizable crown ether will be compared with the process using C.M.P.O. and neutral crown ethers.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1- State of advancement

Since the beginning of the contract more than 60 macrocycles have been synthesized by the several Universities involved in the project and screened at the EHIC Strasbourg. About 30 were tested at Cadarache with nuclides in simulated liquid waste.

2 - Progress and results obtained in the various laboratories

2.1- European Higher Institute of Chemistry of Strasbourg

In 1993, besides the continuation of the investigation of calix-crowns, hexaesters and modified crown-ethers, the study of some new calixarenes containing phosphorous groups has been started, as well as the study of the complexation of Th(IV) as a model for tetravalent actinides. 26 compounds have been tested by cation picrate extraction experiments, from a neutral aqueous solution to dichloromethane, by determination of the stability constants in methanol and of the rate of transport of metallic thiocyanates, between two aqueous phases through a thick liquid membrane of dichloromethane.

2.1.1- Extraction, transport and complexation of alkali, Sr^{2+} and Eu^{3+} cations by various ligands

a- Calix[4]-crowns (from Parma) and calix[5]-crowns (from Mainz). Nine calix[4]-crowns with different conformations (mobile, cone, 1,3 alternate), residues on the unbridged positions and crown-sizes have been examined. The results confirm the better efficiency of the 1, 3 alternate calix[4]-crowns-6 for the extraction and complexation of the larger alkali ions especially Cs^+. The introduction of two ester or amide functions on the unbridged positions slightly enhances the extraction of Sr^{2+} and Eu^{3+}, but to a greater extent, that of Na^+. The phosphonate derivative is not effective for all the cations investigated. None of these compounds is suitable for Sr^{2+} or Eu^{3+} removal. Among the four calix[5]-crowns studied, only three are Cs^+ selective, but however less than the tetramers.

b- Hexaesters (from Belfast). The high performance of the dealkylated hexaesters for Cs^+ removal has been confirmed by transport experiments. The transport of Cs SCN has been demonstrated to be diffusion controlled.

c- Calix-spherands (from Mainz). Three calix-spherands, substituted with ester and amide functions, have been tested. They show high extraction levels for Na^+ and Cs^+, Sr^{2+} and Eu^{3+} are also well extracted.

d- Phosphorous containing calixarenes (from Belfast). Four new calixarenes bearing phospine and phosphine oxide groups have been tested in extraction towards Na^+, Cs^+, Sr^{2+}, some lanthanides and some transition and heavy metal ions. A calix[4]phosphine reveals to be extremely selective for Ag^+ but is not effective for Cs^+, Sr^{2+} or Eu^{3+}. On the contrary, all the phosphine oxide derivatives are Eu^{3+} selective, the best one being the hexamer.

2.1.2- Extraction and complexation of Th(IV)

Seven of the previously studied calixarenes and the three phosphine oxides have been tested in extraction and in complexation towards Th(IV). At this stage, the phosphine oxides seem to be promising.

2.1.3- Modified crown-ethers (from Barcelona)

The complexing properties of four new compounds for alkali and alkaline-earth cations have been tested in methanol. The results show that the introduction of one negative charge (sulphonate) on the benzo 18 C6 leads to only little changes on the selectivity profile in the alkali series. However, when this charge is more distant or when a second one is introduced, the complexation level is decreased. With the alkaline-earth cations the effects are globaly more important.

2.2- CEA Cadarache

Three classes of calixarenes were particularly studied en 1993 :
- The calix[4]arene crown prepared at Parma.
- The p tert butyl calix arene diphenyl phosphine oxide synthesized at Belfast.
- The calix[6]arene hexa ester synthesized at Belfast.

Unfortunately this last class of compounds which is very efficient and selective towards cesium was not stable in very acidic nitrate media.

The calix[4]arene crown 6, in the 1.3 alternate conformation, displayed exceptional selectivity for cesium, particularly the octyl and isopropyl derivatives. Diluted in NPOE or NPHE (10^{-2} M) they allow us to transport cesium selectively and quantitatively from a concentrate to water. A joint patent was registered with the Parma group.

Repeated transport of cesium carried out with the octyl derivative, in which both aqueous solutions were renewed every day while the membrane remained the same, displayed the lipophilic character of this compound since 40 transport experiments were possible ; a permeability decrease was observed during the first runs.

The efforts of the Twente group were devoted to increasing the lipophilicity of these products by synthesizing an NPOE derivative. Unfortunately repeated experiments carried out with the NPOE derivative did not display any perceptible increase of lipophilicity. Calix arene diphenyl phosphine oxides were very effective for the removal of actinides from simulated liquid waste,particularly the hexamer : the distribution coefficients were much higher than those obtained with CMPO. However, for the hexamer the transport kinetics of actinides is lower than for CMPO ; this low permeability is no doubt due to insufficient stripping of the cations even in a complexing medium.

2.3- University of Twente

Calix[4]crown-6 derivatives 1.5, synthesized in Parma and Twente, were succesfully applied in supported liquid membranes to transport Cs^+. The K_{ex} and D_M values are :

	Derivatives	K_{ex} (M^{-1})	D_M ($m^2.s^{-1}$)
1	R = n-propyl	1.35E-3	1.49-E-11
2	R = i-propyl	1.20E-3	1.21E-11
3	R = n-octyl	1.07E-3	1.49E-11
4	R = o-NPOE	1.49E-3	1.23E-11
5	R = CH_2COOEt	1.07E-4	1.29E-12

Selectivity experiments show a very high initial selectivity (24 h) for Cs/Na of approximately 3 x 10^4 for 1.4 ; the di-ester 5 has a much lower selectivity (1.1 x 10^4) which can be explained by an affinity from the carbonyl group for Na^+.

Because of the common-anion-effect it is possible to transport more than 50% of the $CsNO_3$ from a solution of 10^{-3} M $CsNO_3$/ 1M $NaNO_3$ (the presence of the large amount of NO_3 acts as a pump for the $CsNO_3$). Compounds 1.4 (as 0.01 M solutions in NPOE) transport approximately 75-80 % of $CsNO_3$ from a 10^{-3} M $CsNO_3$ /1M $NaNO_3$ mixture in 4 days. The selectivity over 4 days is approximately 8000.

Durability experiments indicate that there is no partition of the extractant into the water. The small increase in flux can be explained by the loss of a small amount of membrane solvent.

2.4- University of Belfast

The objectives of the University of Belfast during 1993 were to extend the range of new chemically modified calix[4]-,[5]-, and [6]arenes with ligating functional groups for screening as extractants for cesium, strontium, thorium and the lanthanides. The work of the University of Belfast during this period has concentrated almost exclusively on the synthesis of calixarenes with phosphine and phosphine oxide groups attached to the lower rim. Procedures have been developed for converting the free calixarenes, both with p-tert-butyl and p-H substituents, into derivatives of the type calix-$OCH_2CH_2PPh_2$ and calix-$OCH_2CH_2P(O)Ph_2$. These transformations have been completed with the tetramers and hexamers and work on the pentamers and octamers is close to complexion. A tetramer phosphine oxide in the partial cone conformation has also been synthesized. Some of these compounds have already been screened in Strasbourg and preliminary extraction studies have also been carried out in Cadarache. The results of these measurements are contained in the reports of the groups in Strasbourg and Cadarache. Work has also continued on the preparation of ester and amide derivatives of the various calixarenes.

2.5- University of Mainz

2.5.1- Calixcrowns :

1,3-crownether and -benzo crownether derivatives were synthesized from t-butylcalix[5]arene by reaction with the detosylates of tetra-, penta- and hexaethylene glycol and of 1,2- and 1,3-bis (hydroxyethoxyethyl)benzene in acetonitrile using CsF as base in yields of 50-80 %. They were further converted to trimethylether and tri-ester derivatives by alkylation with methyliodide (yields of 65-90 %) and ethylbromoacetate, respectively. The latter reaction is complicated by the formation of different stereoisomrers and optimum conditions for the formation of the desired cone-conformation are not yet found.

Studies to attach various further functional groups (e.g. acid, amide, phosphonate, phosphine oxide) onto the three remaining OH-groups of a calix[5]crown are on the way.

2.5.2- Spherand calixarenes

By condensation of 2,2'-dihydroxy-5,5'-di-t-butyldiphenol with formaldehyde under alkaline conditions a cyclic trimer and a cyclic tetramer is available in which diphenol units are linked via methylene bridges. Further alkylation of the phenolic OH-groups with ethylbromoacetate leads to ether derivatives. Conditions were found to convert the trimer exclusively into the hexaester with C_2 - symmetry (while the D_3 -isomer was not yet obtained). Further functionalities were obtained by hydrolysis (CH_2COOH), transesterification ($CH_2C(O)OEt$) and aminolysis ($CH_2C(O)NHR$) of the initial hexaethylester. A complete etherification of all eight OH-groups is also possible with the tetramer, but conditions for the formation of a single stereoisomer (not necessarily important in this context) were not yet found.

2.5.3- Calixarenes with functional groups similar to CMPO

0-Alkylation of t-butylcalix{4]arene (C_{10} - C_{10}), ipso-nitration and reduction of the nitrogroups gave in good overall yields the p-aminocalix[4]arene ethers (in the cone conformation), which can be easily reacted with chloroacetylchloride. The subsequent Arbuzov-reaction with triethylphosphite (successful with model compounds) gave not yet satisfactory results with the calix[4]arene. A clean formation of the desired NH-C(O)-(CH_2-P(O) - structures at the "upper rim" was possible, however, using the anhydride of Ph_2-P(O)-CH_2- COOH or $(EtO)_2$-P(O)-CH_2-COOH.

2.5.4- New calixarene structures

Various alkylidene bridged diphenols (including as bridge for instance CH-CH_2-P(O)-$(OHC_2)_2$ were synthesized. They can be incorporated into calix[4]arenes by the "2+2"-fragment condensation. Their use in one-pot procedures is presently studied, with the aim, to find an easy access to calixarenes with additional functional groups at the methylene bridges.

2.6- University of Parma

During 1993 the attention of Parma group has been devoted to the removal of cesium and actinides. For the first objective calix[4]arene-crown-ethers having different conformations have been synthesized. In particular it has been found that calix[4]arene-crown-6 fixed in the 1,3-alternate conformation are much more selective toward cesium cation than other isomers or flexible compounds. The exceptional cesium/sodium selectivity found for this class of compounds, which is much superior to known ionophores, led to the filing of a patent.

Some work was also devoted to provide this new class of cesium selective ligands with reactive functional groups in order to attach them to the membrane phases and allow transport studies (in Enschede).

For the removal of actinides the attention has been devoted to the synthesis of calixarenes bearing phosphonate, phosphine oxide and phosphonamide groups.

A systematic study on model compounds for the high yield synthesis of such compounds has been performed.

Derivatives from p-tert-butylcalix[6]arene bearing six phosphonate ($PO(OEt_2)_2$ or phosphine oxide ($POPh_2$) groups have been synthesized together with calix[4]arene crown ethers in the cone conformation having the same binding groups.

2.7- University of Barcelona

1) In its effort to synthesize crosslinking crown ether polymer by imprinting polymerization University of Barcelona has successfully obtained ten different polymers with monomeric unit guest complexed to crown ether unit host. The template cation or molecule can be easily removed by subsequently washing with dilute acid in aqueous organic solvents.

2) The extraction behavior toward alkali metal ions (Li+, Na+, K+, Rb+ and Cs+) of all the polymers have been tested under batch extraction conditions. Most of the polymers exhibit good extraction capacity of cations. Some of them, exhibit good selectivity toward cesium.

3) The extraction medium plays an important role in the extraction behavior of the polymers. The polarity and solvation ability of extraction medium will have an influence on the swelling ability of the polymers which in turn affects the accessibility of cations toward the polymer chain.

4) The effect of the template cation (Cs+) has not been proved yet clearly due to the shortage of the data where other cations are used as template as compared. It could be attractive to use potassium ion as template which may be favorable for the orientation of the conformation of crown ether cycles. The counteranion shows an effect on controlling the hole size of polymer matrix. As a result this leads to the increase of selectivity toward cesium.

5) The strongly acidic repeating unit (sulfonate type) can behave as a component for the improvement of hydrophilicity of polymer matrix. This characteristic allow the polymers to extract cations in aqueous medium, even in water.

Title: **Partition of Radioactive Wastes**

Contractor: Kernforschungszentrum Karlsruhe - KfK (D)

Contract n°: FI2W-CT90-0047

Duration of contract: from 1st March 1991 to 28th February 1995

Period covered: from 1st January 1993 to 31st December 1993

Project leader: Z. Kolarik

A. OBJECTIVES AND SCOPE

- Separation of long-lived actinides and fission products would reduce the radiotoxicity of Purex process high-level wastes. This would lower the costs and risks of final waste disposal.

- The aim of the work is to obtain distribution data, which are applicable to the development of a solvent extraction process for the separation of plutonium, neptunium, americium, curium and technetium from the highly active Purex waste solution (HAW). The target decontamination factors are 50000 for Am and Cm, 1000 for Pu and 100 for Np.

- Application of solvent extraction for treatment of highly radioactive materials is well developed. Existing knowledge of the chemistry and engineering of the method can serve as a starting point for the project work.

B. WORK PROGRAMME

1. Search for extractants or complexants which make it possible to separate transplutonides from fission lanthanides by solvent extraction.

2. Measurement of distribution and, eventually, kinetic data for selected transplutonides and lanthanides, and the working out of a proposal of a flowsheet.

C. *PROGESS OF WORK AND OBTAINED RESULTS*

State of advancement

The experimental work was concentrated on the search for solvent extraction systems, in which transplutonides could be separated from fission lanthanides. Selective extraction of transplutonides(III) over lanthanides(III) was the preferential mode of the separation. The separation was attempted by the extraction of solvated salts other than nitrates, using tributyl phosphate (TBP), n-octyl(phenyl)-N,N-di-isobutylcarbamoylmethylphosphine oxide (OΦD(iB)CMPO) and Schiff bases as solvating extractants. Dialkylthiophosphinic, dialkyldithiophosphinic, dialkyldithiophosphoric and carboxylic acids were used as acidic components of the solvent extraction systems. Am(III) and Eu(III) were used as representatives of the transplutonide and lanthanide groups respectively. Di(2-ethylhexyl) dithiophosphoric acid with TBP present was the only extractant combination, which under particular circumstances extracted Am(III) over Eu(III) with a significant effectiveness. With other extractant combinations the Am(III)/Eu(III) separation factor was as low as ≤ 2.

Progress and results

1. Extraction of transplutonide(III) and lanthanide(III) salts other than nitrates

We have previously shown /1/ that di(2-ethylhexyl) dithiophosphoric acid (HDEHDTP) extracts Am(III) with a good separation efficiency over Eu(III). We further have shown that the separation factor strongly decreases with decreasing Eu(III) concentration in the system. According to our opinion, the phenomenon can satisfactorily be explained so that the HDEHDTP complex of Eu(III) is self-associated predominantly in the aqueous phase. On the other side, Musicas /2/ supposes that a preparation of HDEHDTP contains a strongly extracting impurity which does not distinguish between Am(III) and Eu(III). HDEHDTP itself can separate the two elements only at higher Eu(III) concentrations, when the impurity is saturated by Eu(III). To assess the plausibility of the explanations, we fitted a mathematical model for each of them to the experimental data. The fit between the calculation and experiments was very good, when the formation of complexes with a Eu(III) to HDEHDTP ratio of 4:2 in the aqueous phase and 1:3 and 4:12 in the organic phase was supposed. The behaviour of Am(III) at increasing Eu(III) concentration was well described by partial copolymerization of Am(III) with Eu(III) in both phases, i.e. by the reaction of one Am^{3+} ion with one tetrameric Eu(III) complex. A worse fit between the calculation and the experiment was obtained in assuming the presence of a strongly extracting impurity in the HDEHDTP preparation. Moreover, optimization of the fit implied an implausibly high extracting power of the impurity in comparison with HDEHDTP.

Unsatisfactory results were obtained with bis(2,4,4-trimethylpentyl) dithiophosphinic acid, which is commercially available under the trade name Cyanex 301. The extrac-

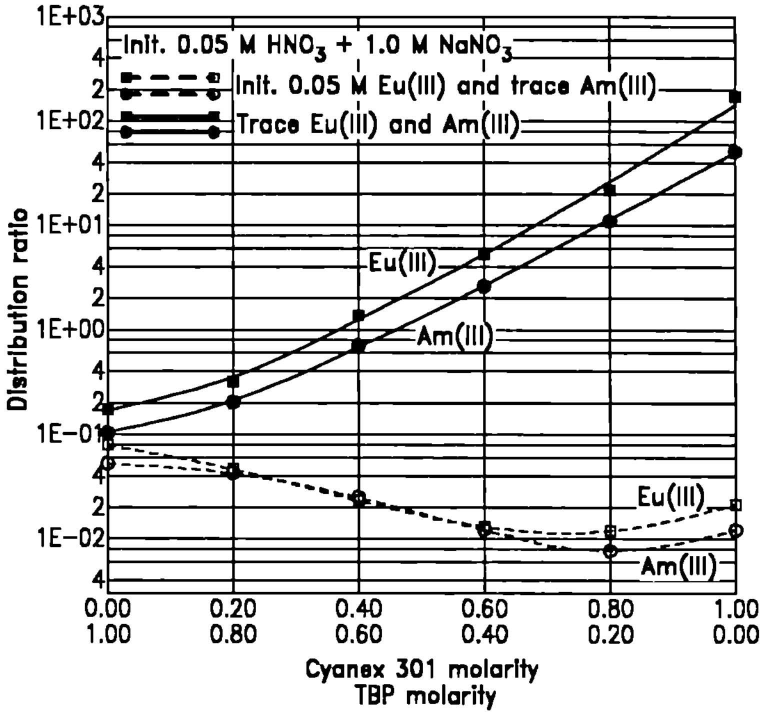


Figure 1. Extraction of Am(III) and Eu(III) by 1.0 M (Cyanex 301 + TBP) in dodecane: Trace or macro amounts of Eu(III) were present initially in the aqueous phase. Room temperature.

tant is said by the producer to be more stable toward oxidation than HDEHDTP. It is seen in Figure 1 that, contrary to HDEHDTP, the extractant does not separate trace Am(III) from macro amounts of Eu(III) in the presence of TBP. Obviously, TBP does not prevent copolymerization of the Am(III) complex of Cyanex 301 with the Eu(III) complex in the aqueous phase. Similar disappointing results were obtained in analogous experiments with bis(2,4,4-trimethylpentyl) monothiophosphinic acid, commercially available as Cyanex 302.

The Cyanex 301 extractant neither separates Am(III) from Eu(III) in the presence of OΦD(iB)CMPO as a solvating extractant. OΦD(iB)CMPO acts as a strong synergist in the system, but the difference between the distribution ratios of Am(III) and Eu(III) is very small at 0.1 M HCl in the aqueous phase and at 0.1 M OΦD(iB)CMPO and 0.1 to 0.45 M Cyanex 301 in the organic phase. Addition of thiocyantes to the system supports the extraction of Am(III) and Eu(III) and also improves the Am(III)/Eu(III) separation. At 0.1 or 0.2 M HCl in the aqueous phase as well as 0.1 M OΦD(iB)CMPO and 0.2 M Cyanex 301 in the organic phase, two thiocyanate ions appear to participate in the formation of the extracted Am(III) and Eu(III) species at >0.05 M NH_4SCN. The Am(III)/Eu(III) separation factor tends under these condition to reach a value of 6, which is lower than the sepa-

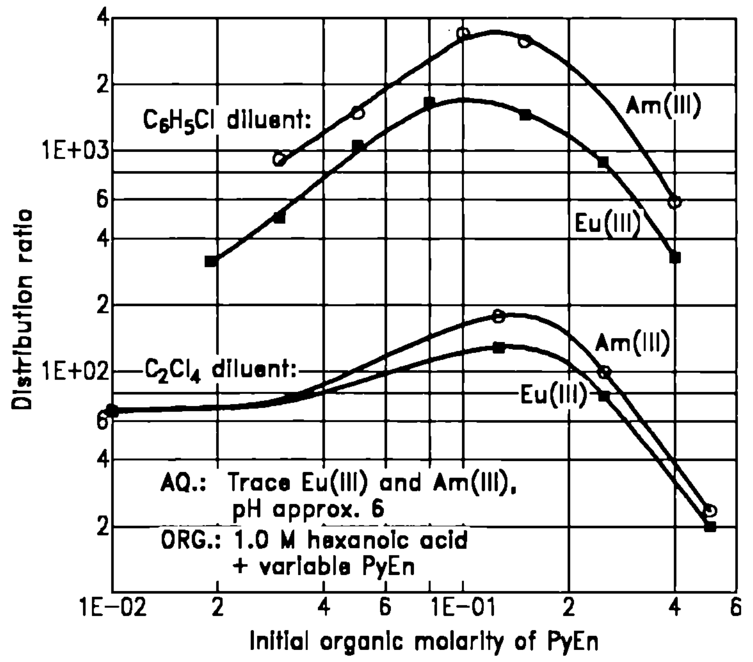


Figure 2. Extraction of Am(III) and Eu(III) in the presence of a pyridinyl substituted Schiff base: Effect of the Schiff base concentration on the distribution ratio of Am(III) and Eu(III). The Schiff base, PyEn, is N,N'-bis(2-pyridinylmethylene)-1,2-ethanediamine. Room temperature.

ration factor 8 to 12 attained in the extraction of Am(III) and Eu(III) thiocyanates by OΦD(iB)CMPO /3/. Trioctylmethylammonium chloride (0.01 to 0.1 M) acts as an antagonist at 0.05 M HCl in the aqueous phase and 0.5 M Cyanex 301 in the organic phase, and the separation of Am(III) from Eu(III) is not improved.

Since sulfur donor extractants did not give satisfactory or at least promising results as reagents for the separation of transplutonides(III) from lanthanides(III), we directed our attention to nitrogen donor compounds. We synthesized Schiff bases and other compounds, and this work is still in progress. Only preliminary distribution experiments with Am(III) and Eu(III) were performed, in which Schiff bases were tested as solvating agents. Hexanoic acid, a precursorily chosen extractant, was taken as an acidic component of the extracted complexes. Figure 2 shows the results obtained with a tetrafunctional Schiff base with only nitrogen donor atoms included in its molecule. The trend to a selective extraction of Am(III) over Eu(III) is little pronounced, but it possibly can be improved by varying the acidic component and diluent in the system. Practically no trend to an Am(III)/Eu(III) separation is exhibited by a tetrafunctional Schiff base with two nitrogen and two sulfur donor atoms in the molecule (see Figure 3).

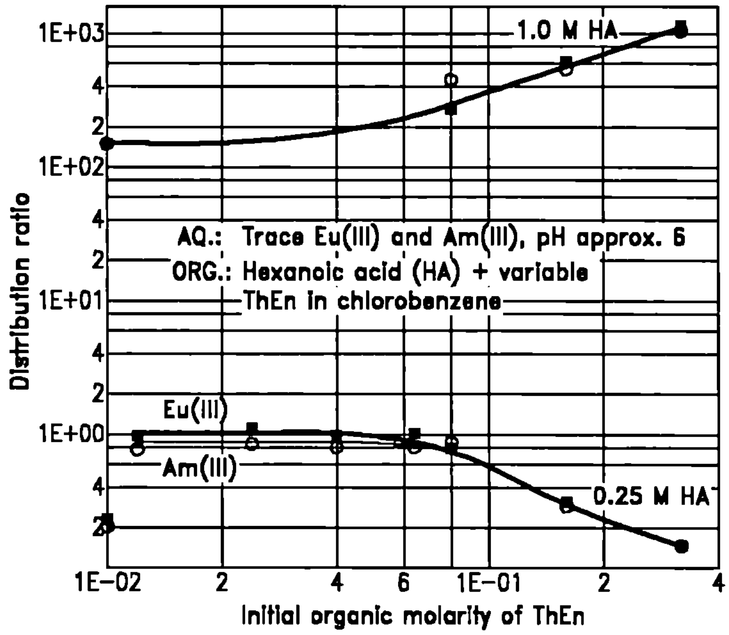


Figure 3. Extraction of Am(III) and Eu(III) in the presence of a thienyl substituted Schiff base: Effect of the Schiff base concentration on the distribution ratio of Am(III) and Eu(III). The Schiff base, ThEn, is N,N′-bis(2-thienylmethylene)-1,2-ethanediamine. Room temperature.

2. References

/1/ COMMISSION OF THE EUROPEAN COMMUNITIES, *Annual progress report 1992 on the community's research and development programme on radioactive waste management and storage, shared-cost action (1990-1994)*, EUR 15132 (1993), pp. 195-9.

/2/ MUSIKAS, C., personal communication.

/3/ COMMISSION OF THE EUROPEAN COMMUNITIES, *Annual progress report 1991 on the community's research and development programme on radioactive waste management and storage, shared-cost action (1990-1994)*, EUR 14418 (1992), pp. 165-9.

Title	**High-level liquid waste partitioning by means of completely incinerable extractants.**
Contractor	CEA-Fontenay-aux-Roses ; University of Reading
Contract N°	FI2W-CT91-0112
Duration of Contract	October 1991-September 1995.
Period covered	January -December 1993.
Projects leaders	Dr. C. MADIC (CEA, Coordinator) Dr. M.J. HUDSON (University of Reading)

A. OBJECTIVES AND SCOPE

The main objective of this research is the demonstration of the suitability of new types of diamides as well as triazine-based compounds for the removal of actinides from high level liquid waste and the subsequent purification of minor actinides from rare earths respectively. Other types of extracting agents will be also considered for the same purposes.

In terms of decontamination performances, these extractants have to demonstrate properties at least equivalent to bifunctional organophosphorous extractants (like CMPO) for actinide removal and to the combination of HDEHP with DTPA for the separation of lanthanides from trivalent actinides. These requirements are in addition to the requirement to be completely incinerable in order to avoid secondary wastes.

This research, which is closely coordinated with those currently under study at KfK Karlsruhe, should result in the preparation of flow-sheets for HLLW partitioning and hot testings of these flow-sheets.

B. WORK PROGRAMME

This study will include the implementation of the following steps :

B.1. Synthesis of new organic extractants (diamides, triazine-based, hydroxamic acids...).

B.2. Determination of their extracting properties and extraction performances on simulated HLLW.

B.3. Quantification of the exractants stability in the long term towards chemical attack and irradiation.

B.4. Preparation of possible partitioning flow-sheets on the basis of the results from B2.

B.5. Verification of two flowsheets at least through counter-current experiments with simulated HLLW in order to validate decontamination and separation performances of extractants in view of partitioning experiments with genuine HLLW.

B.6. Scaling-up of the preparation procedure for diamides, triazines and other extractants.

B.7. Definition and verification of solvent regeneration treatments.

B.8. Cooperation with laboratories working on HLLW partitioning in the framework of Task N°2 of the EC Programme.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the year 1993, many interesting results have been obtained in the framework of this research programme. Among these, the most interesting and promising results are as follows :

Synthesis of extractants ***(B.1) :***

Diamides :

A new, efficient and inexpensive route has been successfully established for the synthesis of diamide molecules. It is based on the reaction between malonyl ester and amine.

TPTZ derivative :

The new high pressure route, developed for the synthesis of the TPTZ, gives low yields for the preparation of the trimethylPTZ (TMPTZ). Nevetheless, few grams of pure TMPTZ were successfully prepared.

Determination of the extractant properties ***(B.2) :***

Diamides :

It has been shown that loading capacities of the solvents, (a mixture of diamides in solution with industrial aliphatic diluent (TPH)) when extracting solutes like nitric acid or U(VI), Nd(III) and Fe(III) nitrates, are greatly improved with an increase in the length of the central alkyl group of the diamide molecule.

For the first time, the structure of a complex between a diamide and La(III) nitrate was established, which shows a coordination number of ten for La(III) and the bidendate character of the diamide.

TMPTZ :

It was shown than, as expected, TMPTZ in combination with alpha-bromocapric acid shows improved properties, in comparison with the TPTZ itself, for the separation between Am(III) and Eu(III).

Hot tests of the DIAMEX process ***(B5) :***

Three hot tests have been successfully conducted using the DIAMEX process to decontaminate a genuine HLLW.

Progress and results

B.1. Synthesis of new organic extractants

Diamides :

An entire new method of synthesis of the diamides has been developed utilizing the malonyl ester. The malonylesters are very much less expensive and less reactive than the corresponding malonyl dichloride and so a direct controlled route for the synthesis has been developed. The malonyl ester is mixed with the amine of choice and both are heated together at 120 °C for several hours.

Several malonamide extractants were also prepared by PANCHIM, a small french chemical company. Moreover, seven kilogrammes of dimethyldibutyltetradecylmalonamide were synthetised by PANCHIM for the development of the DIAMEX process (see below).

TMPTZ :

Trimethylpyridinetriazine was found difficult to synthetize by the high pressure route newly developed for TPTZ itself. Nevertheless, as mentioned above, a few grams of pure TMPTZ have been prepared and its extracting properties studied. To explain the problems encountered in that synthesis, the existence of an intermediate compound was confirmed by preparing a solid complex with copper dichloride and resolving its crystal structure.

Alpha-hydroxycapric acid :

Alpha hydroxycapric acid, to be used in synergistic mixture with TMPTZ, was synthetised from capric in two steps. The intermediate compound was alpha-bromocapric acid. The synthesis was easy to conduct.

B.2. Determination of the extracting properties of the new molecules

Diamides :

For the optimization of the formula of the diamide (malonamide) extractant, one of the major properties to be studied concerns the loading capacities of the solvents, composed of malonamide solutions in an aliphatic hydrocarbon diluent like the TPH (used in COGEMA's La Hague plants), during the extraction of various solutes such as nitric acid, U(VI), Nd(III) and Fe(III) nitrates. The loading capacities related to these solutes have been determined for several dimethyldibutyl(alkyl)malonamides. It was shown that an increase of the length of the central alkyl group of the malonamides induces a large increase in the loading capacities of the solvents. For example, the solvent loading capacities for nitrate salts can be improved by a factor close to four when the tetradecyl group is replaced by the octadecyl one.

It was also confirmed that the introduction of an ether function in the central group improves the affinity of the extractant towards Am(III) nitrate.

A very interesting result was obtained which concerns the determination of the crystal structure of the complex formed between N,N,N'N' tetraethylmalonamide and lanthanum (III) nitrate. This structure shows that the metallic ion possesses a coordination number of ten ; in the complex the two diamide molecules are bound to the metallic center through their two oxygen atoms. That structure will be helpful in the future for the realization of the molecular modeling studies.

TMPTZ :

It has been known for a long time that nitrogen donor atom ligands can react with An(III) more intensely than with Ln(III). Of course, in both cases, the intensity of these interactions are lower than those observed for oxygen donor atom ligands. It was shown in the past at the CEA, Fontenay-aux-Roses, that the tripyridyltriazine (TPTZ) ligand, in synergistic mixture with an organic acid is an interesting system for the separation between An(III) and Ln(III) by selective extraction of An(III). However, this system suffers some drawbacks like the tendency of the TPTZ to be stripped into the aqueous phase and the low aqueous nitric acidity required to achieve sufficient An(III) distribution coefficients. The newly synthetised TMPTZ shows improved properties in comparison with that of his parent compound TPTZ. Of course, it will be interesting to continue to increase the lipophilicity of the TPTZ derivatives, for example by using longer alkyl substituents than the methyl ones as used in the TMPTZ.

B.5. Hot tests of the DIAMEX process

Instead of running counter-current tests of the DIAMEX process with synthetic HLLW, it was considered more interesting to carry-out real hot tests. The objectives of these hot tests were limited. The first objective was to identify, using a real active effluent, the main problems to be solved for the design of a DIAMEX optimised flow-sheet. The other objectives were :

- to demonstrate the extractability of the An(III) from a real HLLW with alpha decontamination factors at least equal to 100,
- to decontaminate the An fraction of the fission products which possess high affinity for the solvent, by operating special scrubs.

The hot tests were conducted during the month of June 1993 in the hot-cell CYRANO, in close cooperation with the staff members of the service SPHA. The HLLW used during these hot tests was an effluent produced in february 1993, during the reprocessing of a MOx irradiated fuel by the PUREX process. Before implementing the hot tests it was necessary to define :

- a purification method for the solvent, made of a 0,5 mol/L solution of DMDBTDMA in the TPH, which when impure has the ability to form stable emulsions,
- the hydrodynamic conditions for the circulation of the organic solvent flow into the mixer-settlers batteries.

Three hot tests were realized during the two weeks campaign. The main results of these tests can be summarised as follow :

- the alpha DFs of the HLLW were very good (comprised between 300 and 1000) and always larger than that defined as the objective,
- Zr(IV), which possesses a good affinity for the solvent, can be efficiently scrubbed using ketomalonic acid as the complexing agent,
- no third phase formation occurred during these tests,
- the stripping of the actinide alpha emitters from the loaded solvent was easy and quantitative.

During these tests several problems were also identified. Among these, the most important seem to be :

- the limited separation factor between Cm(III) and the ruthenium,
- the poor stripping behaviour of the extracted Ru,
- the failure to scrub Mo(VI) from he solvent using hydrogen peroxide as a complexant,
- the degradation of the solvent by the high doses received, creates stable emulsion problems.

B.8. Cooperation with EC laboratories

Dr. M. HUGON (Brussels) suggested to establish a collaboration with *Dr. GLATZ*, from TUI (Karlsruhe, Germany), in order to study the retention behaviour of actinide species in the DIAMEX's solvent according to its radiolysis. For that purpose, a first contact happened in October 1993 at the TUI and the basis of the future collaboration discussed.

Part A3

Task 3

"Characterisation and Qualification of Waste Forms, Packages and their Environment"

* List of contracts
* Introduction to Task 3

Topic 1	Waste form characterisation and performance
Topic 2	Containment and barrier properties of the near-field (including modelling)
Topic 3	Radionuclide assay : development of standard methods and equipment for specific applications
Topic 4	Quality control of waste conditioning

TASK 3 - LIST OF CONTRACTS

Topic 1 Waste form characterisation and performance

FI2W-CT90-0012	The behaviour of Pu, Am, Np and Tc during the corrosion of the Cogema glass R7T7 in salt solutions.
FI2W-CT90-0020	Consequences associated with gas production in geological repositories (PEGASE).
FI2W-CT90-0025 + 0007	Characteristics of bitumenized radioactive waste.
FI2W-CT90-0026	Natural analogues of bitumen matrices in a deep repository.
FI2W-CT90-0027	Aqueous corrosion of nuclear glasses: influence of disposal conditions.
FI2W-CT90-0028	Effect of insoluble active dissolution fines on fission product glasses.
FI2W-CT90-0031	The corrosion of nuclear waste glasses in a clay environment: mechanisms and modelling.
FI2W-CT90-0032	Basic leaching for pure Beta long-lived emitters in radioactive wastes.
FI2W-CT90-0055	Chemistry of the reaction of as-fabricated and high burnup spent UO_2 fuel with saline brines.
FI2W-CT90-0077	Container properties ensuring safety : gas emission, biodegradation, corrosion.
FI2W-CT90-0094	Gas generation in supercompacted waste products.
FI2W-CT90-0099	Impact of additives and waste streams constituents on the immobilisation potential of cementitious materials.
FI2W-CT93-0124	Source aspects of leaching mechanisms of ions incorporated in cement or polymer.

TASK 3 - LIST OF CONTRACTS

Topic 2 Containment and barrier properties of the near-field (including modelling).

FI2W-CT90-0022	The effect of microbial activity on the near and far fields of a deep repository.
FI2W-CT90-0030	Corrosion of selected packaging materials for disposal of heat-generating radioactive wastes.
FI2W-CT90-0035	Theoretical and experimental study of degradation mechanisms of cement in the repository environment.
FI2W-CT90-0040	The performance of cementitious barriers in repositories waste in practice.
FI2W-CT91-0096	Completion of the corrosion programme in Boom clay (in situ experiments).

Topic 3 Radionuclide assay : development of standard methods and equipment for specific applications.

FI2W-CT90-0010	Determination of fissile material in waste package by neutron transport interrogation.
FI2W-CT90-0034 + 0109	Inventory and characterisation of important radionuclides for safety and storage-correlation to key nuclides easy to measure in waste types.

Topic 4 Quality control of waste conditioning.

FI2W-CT90-0009	Construction and testing of a computer tomography assembly for routine operation.
FI2W-CT90-0014	Behaviour of low-level radioactive waste under fire accident conditions.
FI2W-CT90-0019	Test for process control during treatment of low and medium radioactive waste in practice.
FI2W-CT90-0021	Establishment of non-destructive or partially destructive test procedures for determining the characteristics of waste containers.
FI2W-CT90-0023	Non-destructive characterization of radioactive waste packages by advanced radiometric methods.
FI2W-CT91-0107	High Energy Accelerator Tomography

INTRODUCTION TO TASK 3 - CHARACTERISATION AND QUALIFICATION OF WASTE FORMS, PACKAGES AND THEIR ENVIRONMENT

A. Objectives

- Determination of the relevant properties and performances of waste forms and their environment (Characterisation)
- Development and validation of models and data bases describing the long-term evolution of disposed waste (Modelling)
- Improvement of the control of radioactivity in the waste and the quality of waste products/packages.

B. Research topics dealt with the 1985-1989 Programme

In the previous programme, the following main research actions were pursued:

- Characterisation of low and medium level wastes:
  Eleven waste forms were selected for joint investigation and specified as reference formulations for conditioned LLW and MLW. Many of the characteristics of these waste forms relevant to the long-term safety in different disposal environments were determined with simulates and, as far as available, with real waste specimen.

- Testing and evaluation of high active and special alpha-bearing waste forms:
  During the period 1985-1989 the development of new candidate waste forms for the High Level Liquid Waste Stream was reduced in favour of extended testing and evaluation of the industrial reference borosilicate formulations. Corrosion, nuclide leaching, radiation damage and thermal stability were investigated in laboratory test series with inactive and spiked simulates.

- Study of container and buffer/backfill materials:
  The coordinated action on container corrosion launched in the second programme was concluded: corrosion rates and mechanisms of carbon steel, Ti-Pd and Hastelloy were determined under representative conditions.
  A variety of argillaceous and cement-based buffer materials were tested to determine suitable formulations for the various repository options.

- Development of a standard waste hostrock interaction test:
  The Repository Systems Simulation Test which permits the testing of HLW glass formulations in conditions representative of geological disposal was developed and validated in a Round-Robin campaign by 14 laboratories.

- Development of methods for the Quality Assurance of Waste Packages:
  Non-destructive test methods such as computer tomography and active neutron interrogation techniques for assaying alpha emitters as well as techniques and procedures for sampling solidified waste were the most important items of a wide range of R & D projects.

C. Present programme (1990-1994)

1. Waste form characterisation and performance

- Characterization of heterogeneous waste forms
- Effects of radiation, corrosion, biodegradation, etc. on waste form stability
- Gas generation by corrosion, radiolysis and biodegradation
- Effect on inclusions on waste form crystallisation and stability
- Chemistry of reaction of spent fuel with saline brines
- Mechanisms of nuclide release under repository conditions

2. Containment and barrier properties of the near-field

- Effect of microbial activity on the near-field
- Theorical and experimental study of degradation mechanism of cement in the repository environment
- Modelling and testing of the hydration of backfill and sealing materials
- Corrosion of selected packaging materials for disposal of heat generating radioactive waste

3. Radionuclide Assay: development of standard methods and equipment for specific application

- Establishment of a European basis for the determination of relevant nuclide concentrations in industrial LLW and MLW: Study of existing methods and compilation of data bases, evaluation of currently used scaling factors and correlation.
- Development of equipment and methods for the assaying of LLW and MLW including the validation of scaling correlations for relevant emitters.
- Development of methods for measuring(checking)the nuclide inventory of conditioned TRU-wastes

4. Quality control of waste conditioning

Research actions to develop methods permitting the measurement and certification of compliance with quality requirements/criteria. Subjects being addressed include:

- Establishment of sampling procedures and techniques
- Verification of chemical composition
- Detection of unwanted or undeclared substances
- Detection/measurement of waste/matrix interaction, gas generation and release, container corrosion and swelling
- Measurement of physical properties of waste products and packaging
- Homogeneity, thermal stability, etc.

D. Programme implementation

At present the above topics and areas of research are being tackled under 26 contracts, the majority of which are multi partner and trans-european. Further details are provided in the summary reports presented hereafter.

Title : **Retention of Pu, Am, Np and Tc in the Corrosion of COGEMA* Glass R7T7 in Salt Solutions**

Contractor: Kernforschungszentrum Karlsruhe (D)
Contract: FI2W-CT90-0012
Duration of contract: January 1991 - December 1994
Period covered: January 1993 - December 1993
Project leader: W. Lutze, B. Grambow, Institut für Nukleare Entsorgungstechnik - KfK

A. Objectives and Scope

High-level radioactive waste from the reprocessing of German spent fuel is vitrified at La Hague. Glass blocks will be returned to Germany and must be disposed in the deep underground eventually. The repository is expected to be located in the Gorleben salt dome. the repository constitutes a system of technical and natural barriers (multibarrier system) against the release of radionuclides. The glass is the most central technical barriers. A detailed understanding of the glass performance must be obtained for all conceivable accidental conditions including contact with water. The respective results shall be used to describe source terms in the framework of safety analyses.
The subject of this investigation is to study the chemical durability of the highly radioactive French borosilicate glass R7T7 in one of the three German "standard" salt solutions as a function of time and temperature. This work complements previous investigations on the durability of a very similar but non-radioactive CEA glass by measuring the release behaviour of Pu, Am, Np and Tc.

B. Work programme

The work programme was described in detail in the Annual Report 1992 (1). The corrosion test conditions were: powered CEA R7T7 glass (4,8 g, average grain size 86 µm) shall be corroded under static conditions in 25 mL (S/V 10000 m-1) of a Mg rich salt solution at 110, 150 and 190°C for 45, 90, 180, 360, 720 and about 1000 days. Briefly the work programme consists of installing the host-cells to prepare glass powder, to handle Tantalum lined autoclaves filled with an Argon atmosphere and install equipment for separating and sampling solid and liquid phases at the end of the tests. The solution samples will be analyzed for the actinides and Tc99. The analytical techniques were developed to extract and analyze the actinides and Tc99 from the highly concentrated salt solution. Corrosion layers shall be analyzed using SEM, and host phases for radionuclides will be searched for and analyzed (if possible).

---

* We were advised by CEA Marcoule to use a different designation for the glass. The glass investigated here was fabricated by CEA Marcoule closely simulating the chemical composition of the glass produced by COGEMA at La Hague in their vitrification plants. In the text, the glass from Marcoule is designated CEA R7T7.

During analyses and evaluation of the results of the first four experiments it became obvious that an extension of the work programme was necessary in order to be able to evaluate the retention of radionuclides during glass corrosion. This extension consists of fully and completely analysing the mass distribution (mass balance) of radionuclides among the surface alteration layer on the glass, the aqueous phase and material sorbed on the vessel walls. When analysing the aqueous phase, we distinguished between truly dissolved material and particulate or colloidal material. A description of the procedures of analysing solid and solution phases is given in Fig. 1.

C. Progress of work and obtained results

State of advancement

1. All experiments, except some of the 45 day and 90 day experiments were started.
2. The analyses of radionuclide inventories of the as delivered glass R7T7 was completed
3. The analyses of radionuclide distribution between the leachate, the surface alteration layer and the reaction vessel walls are close to completion for a 45 day and a 300 day experiment at 190 °C. The analyses of the 90 days experiments were started.
4. A crystalline alteration product, a rare earth elements containing powellite, was identified in the 45 day test performed at 190°C..
5. Results of radioactive and inactive glass are compared.

Progress and results

Analyses of the as delivered glass

Preliminary results of the glass analyses were reported in the Annual Report 1992 [1]. The data were completed by analysing Sr-90 and by repeating the analyses of Np237 and Am243/Np239 which was necessary, due to the low concentrations of theses nuclides in the glass, and the associated large uncertainties in the analyses values. The results are in excellent agreement with the value given by CEA Marcoule. The final analyses values are given in the Annual Report 1993.

Analyses of leachates, filter residues, plate out of reaction vessel and surface alteration layers

During glass dissolution, radionuclides are either mobilized (truly dissolved or colloidal) or are retained in immobile phases (sorption or precipitation on the reaction vessel walls (Ta), on the surface alteration layer or in particulate matter which may remain suspended in solution. A new analytical procedure (Fig. 1) was established with the aim to perform a complete mass balance. The new procedure provides for the identification of the radionuclide contents of the various phases after test termination. To the knowledge of the authors it is the first time, that a full mass balance of radionuclide distribution is attempted with a radioactive glass. A new technique was employed which allowed the separation of the pristine glass from its surface alteration layers by means of suspension in ethylene glycol within an ultrasonic bath.

The surface layer particles were separated from the residual glass particles by different sedimentation rates. In order to avoid contamination by the radioactivity content of the leachate, all immobile phases were washed cautiously. Solid phases were dissolved in HNO_3/HF prior to radiochemical analyses. A minimum of 6 samples are obtained per experiment: two solution samples (450 and 1.8 nm filtered), two solutions of dissolving filter residues, one solution containing the dissolved surface alteration layer and one solution containing the sorbed or precipitated material from the reaction vessel walls. Results of the two solution samples are given in terms of the normalized elemental mass loss NL in [g/m^2] (normalization by surface area and by radionuclide inventory of the glass). Results of analysing immobile phases are also given in terms of NL units. The ratio of the NL values of immobile phases to the NL value of the mobile phase is the retention factor. The NL values of immobile phases are summed up together with the NL value of the leachate. The sum values are a direct measure of the extent of matrix dissolution (gram altered glass per m^2) and for all nuclides these sums should be equal, provided that a given element is not seggregated and is not susceptible to alkali/ion exchange. Hence, a criterion for a good mass balance is provided by the comparison of these NL sum value.

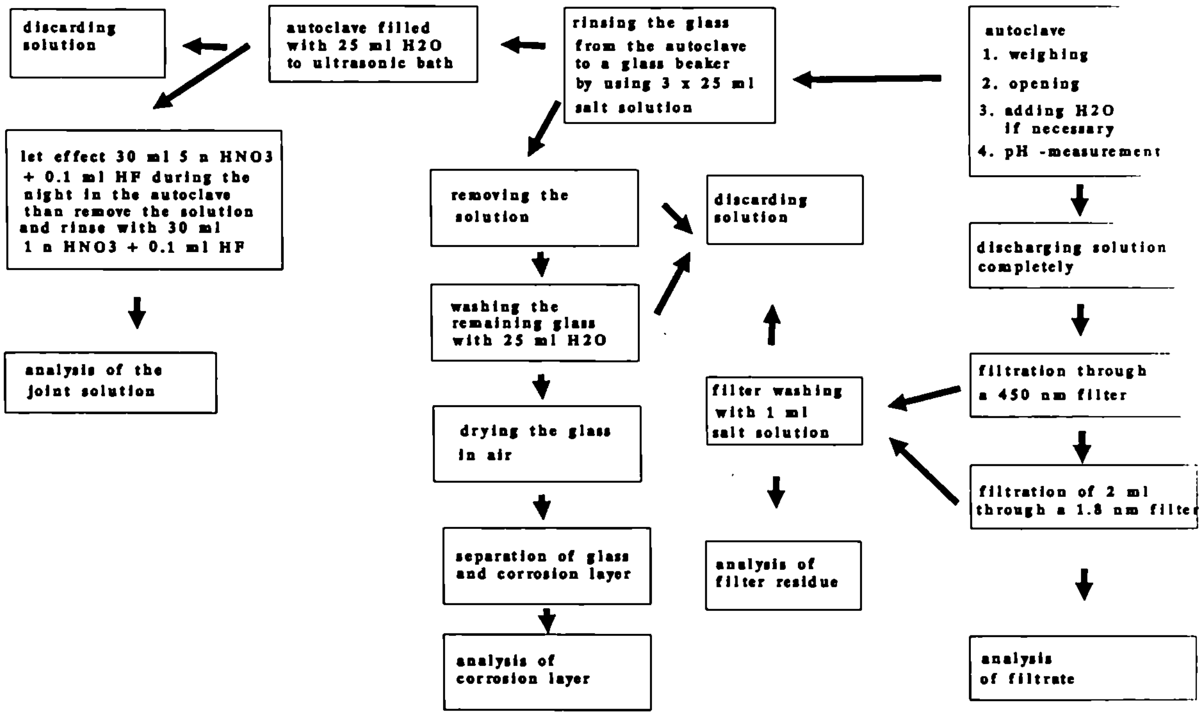


Fig. 1: Scheme of sample preparation after termination of a glass corrosion test

Results of the corrosion tests:

As an example the results of a glass corrosion experiment performed for a duration of **45 days** at a temperature of 190°C are shown in Table 1. The pH value measured was 5.4 (corrected for liquid junction and referred the pH convention of Pitzer). Unfortunately, the rinsing solution of the tantalum container could not be analysed because it got lost during manipulation in the hot cell. There is rather good agreement in the summed NL values of the various nuclides, indicating that the mass balance was performed successfully. Hence, the contribution to the mass balance of the radionuclides sorbed onto the vessels walls may be rather small. This is also true for colloidal and particulate matter. The mean value of the summed NL values of the various nuclides, i.e. the extent of matrix dissolution is 3 g/m^2. The results show that a large fraction (>90%) of the inventory of the trivalent actinides and rare earth elements Am, Cm and Eu in the altered glass mass is retained in the surface alteration layer. Nevertheless, more than 50 % of Cs, Tc, Sr and Co are released into the aqueous phase. Surprisingly, also a quite high amount of about 30% of Pu is found in solution.

As a second example results of a **300 day** test performed at 190°C are given in Table 2. The pH was 3.8. The mean value of the NL sums of the various nuclides (not considering Eu, Pu and Sb, whose mass balance appeared to be incomplete), i.e. the extent of matrix dissolution is 7.8 g/m^2. In the leachate we found 98 % of the Co-60, 90 % Sr-90, 64 % Tc-99, 96 % of the Cs-isotopes 134/137, 62 % of the Europium-isotopes 154/155, 99,5 % Np-237, 76 % Am-241 and 66 % Cm-244. In comparison to the 45 day experiment, the high amounts of trivalent actinide (Am 241, Cm 244) and rare earth elements in solution (Eu 154/155) can probably be explained by the high mobility of these elements at the low pH value of 3.8. The data for Pu are still puzzling. The mass balance for Pu is not complete. Only about 12 % of the Pu content of the altered glass mass was recovered in the analysed phases, distributed to equal amounts between surface alteration layer and material plated out at the walls of the reaction vessel.. Work is continuing for finding the missing Pu.

Identification of solid alteration products

A tantalum metal plate (1 cm by 0.5 cm) has been added to each experiment, in order to study plate out effects at the reaction vessel walls. For the 45 day experiment, the metal plate was recovered after terminating the experiment. The metal was rinsed with distilled water to remove the salt solution. A typical scanning electron micrograph of a small fraction of a gold plated area is shown in Figure 2. The metal surface is covered with µm-sized crystals. Additionally, adhering glass particles were found. This is because the metal contacted the glass powder during the experiment. EDX-analyses indicate that a calcium molybdate phase (powellite) rich in rare earth elements (Nd, La) has been formed, similarly as in corresponding experiments with inactive R7T7 glass, as reported in the literature [2]. The EDX system is not capable of analyzing a potential content of Am241 in this phase, as the content of Am in the glass is only 0.01 wt%, which is much lower than that of the rare earth elements.

A parallel experiment with non-radioactive R7T7-glass under the same experimental conditions has shown that another phase was formed on the tantalum plate. Main components are Al, Mg and Si . Figure 3 compares the EDX spectrum of this phase with that of the surface alteration layer analysed in a similar experiment and identified as a gel layer containing saponite. The composition is rather similar, indicating that the gel layer which typically forms on the glass surface may also form offset of the glass surface on other, energetically preferred sites such as the vessel walls.

Comparison of reaction behavior of the active glass to inactive glass

The results from the ongoing work complement previous work with an inactive simulated R7T7 glass which was undertaken under the same experimental conditions [3]. The inactive experiments were performed at S/V ratios ranging from 10 to 10000 m^{-1} for periods as much as 3 years. A large data base was generated. Figure 4 shows the observed pH evolution in brine 2 (the leachant used in the present work) as a function of the amount of dissolved glass per unit of solution volume. The data for the radioactive glass obtained in the present work are included. The amount of glass dissolved per unit area is calculated from the mean value of the summed NL values of the various nuclides. As can be seen, there is excellent agreement in two cases and rather poor agreement in one case (the 45 day test described above, the high pH value of this test may explain the good retention of trivalent actinides). The time dependence of the reaction and the release of Pu and of Am is given in Fig. 5 together with respective data for B, Li, Si and Nd of the inactive tests. The concentrations of the elements and nuclides in solution are normalized to the respective inventory in the glass ("Normalized concentration" = NL value of a nuclide times the S/V ratio of the test) and are plotted agains the product of the square root of time and the S/V ratio. This modified time scale allows to plot results of experiments obtained at various S/V ratios and experimental durations in a single diagram [4]. The extent of matrix dissolution in the radioactive experiment ("Reaction, active") is in excellent agreement with the boron and Li data measured in the inactive experiment indicating that the time dependence of reaction is the same for active and inactive tests. This diagram may also be used directly for long-term extrapolations.

The results in Fig. 4 and 5 clearly show that results of active and inactive experiments are similar, hence, the large data base generated for the inactive glass [3] can also be used quantitatively to explain and frame results of the active experiment and, consequently, long-term predictions can be based to a large extent on the results obtained from the inactive tests. With respect to actinide behavior and behavior of Tc, one may tentatively say that neither Np237, Cm244, Am241 nor Tc99 may be retained to a significant extent in immobile glass corrosion products (Fig. 5, and Table 2). Hence, the release of these elements from the glass is probably controlled by the kinetics of glass dissolution and consequently, Fig. 5 may be used for long-term extrapolations. This, however needs confirmation by the results of the ungoing work. No statement can yet be made on the behavior of Pu.

References

[1] W. Lutze, L. Kahl, E. Bohnert, A. Dietl, P. Dressler, V. Toth, Retention of Pu, Am, Np and Tc in the corrosion of COGEMA glass R7T7 in salt solutions, Annual Report 1992.

[2] A. Rother, W. Lutze, P. Schubert-Bischoff, "Characterization of lanthanoid phases formed upon dissolution in salt solutions", Mat. Res. Soc. Symp. Proc., Vol. 257 (1992) pp. 57-64.

[3] W. Lutze, R. Müller, W. Montserrat, Mat. Res. Soc. Symp. Proc. Vol. 112 (1988) and Vol. 127 (1989)

[4] B. Grambow, R. Müller, "Chemistry of Glass Corrosion in High Saline Brines"; Mat. Res. Soc. Symp. Proc. Vol. 176 [1990]

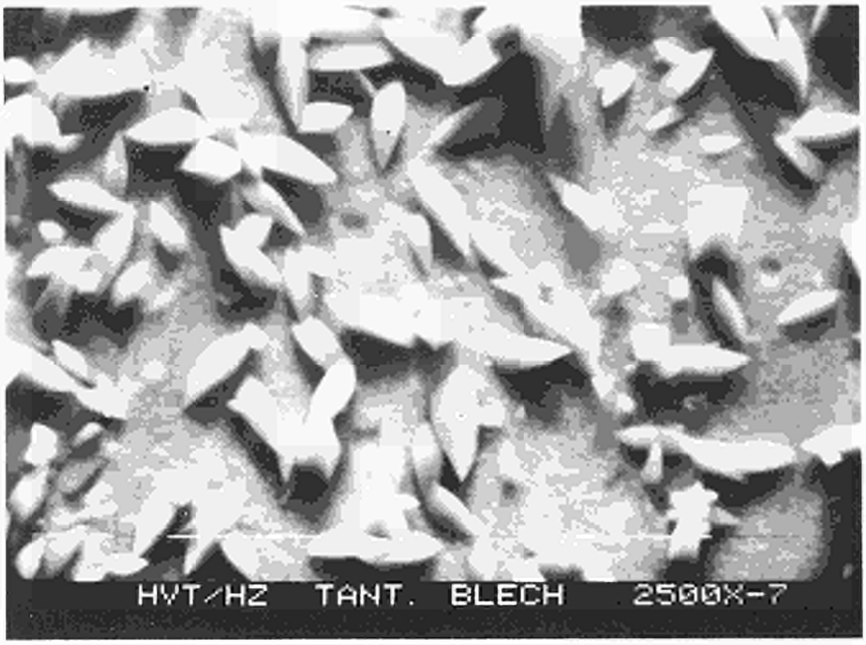
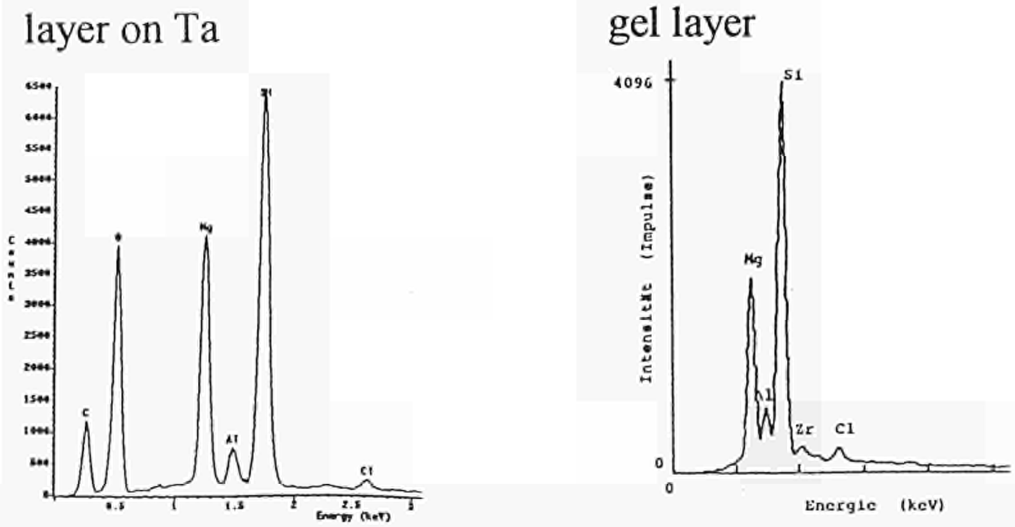


Figure 2: SEM micro graph, 2,500X. Ca,Nd,La-molybdate (powellite-type)crystals on a tantalum metal plate after 45 days of corrosion of glass R7T7 at 190°C in salt solution.


layer on Ta

gel layer

Figure 3: EDX spectrum of the layer of alumino-magnesium-silicate formed on a Ta-metal plate in a 90 day glass corrosion test, compared with the EDX spectrum of the surface alteration layer on the glass measured in a similar experiment

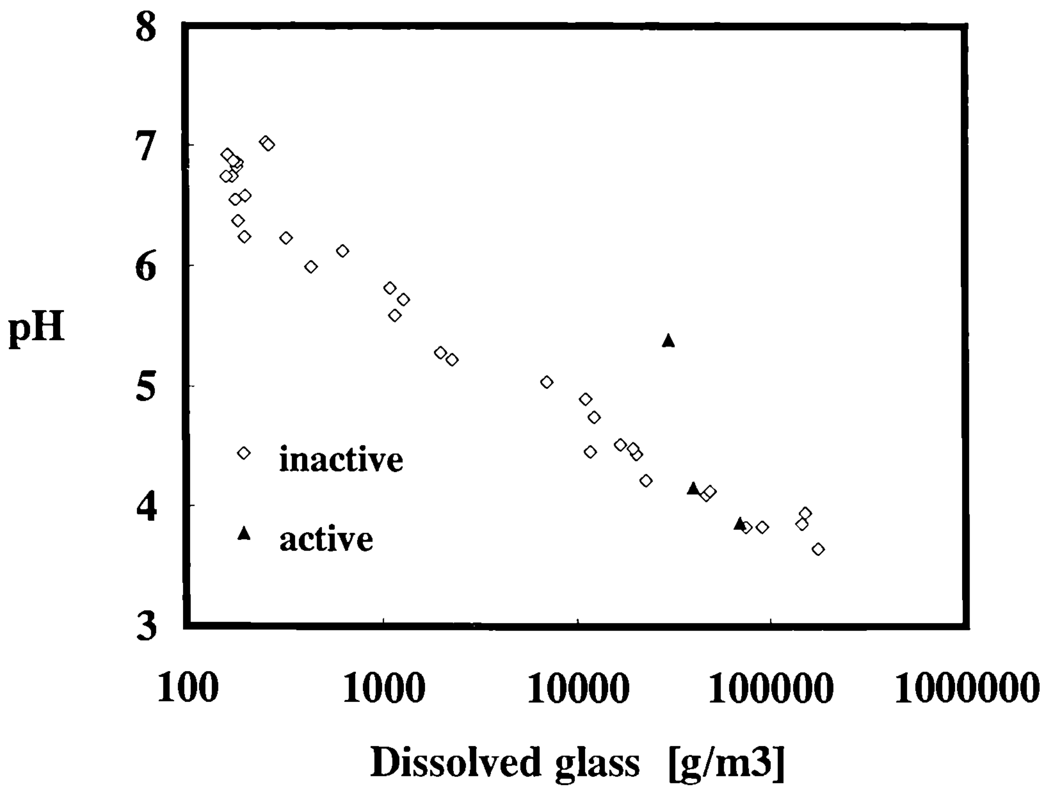


Fig. 4: Comparison of pH values obtained in the present corrosion test with high active CEA-glass R7T7 with the pH evolution in coressponding tests with the inactively simulated glass R7T7 [3, 4].

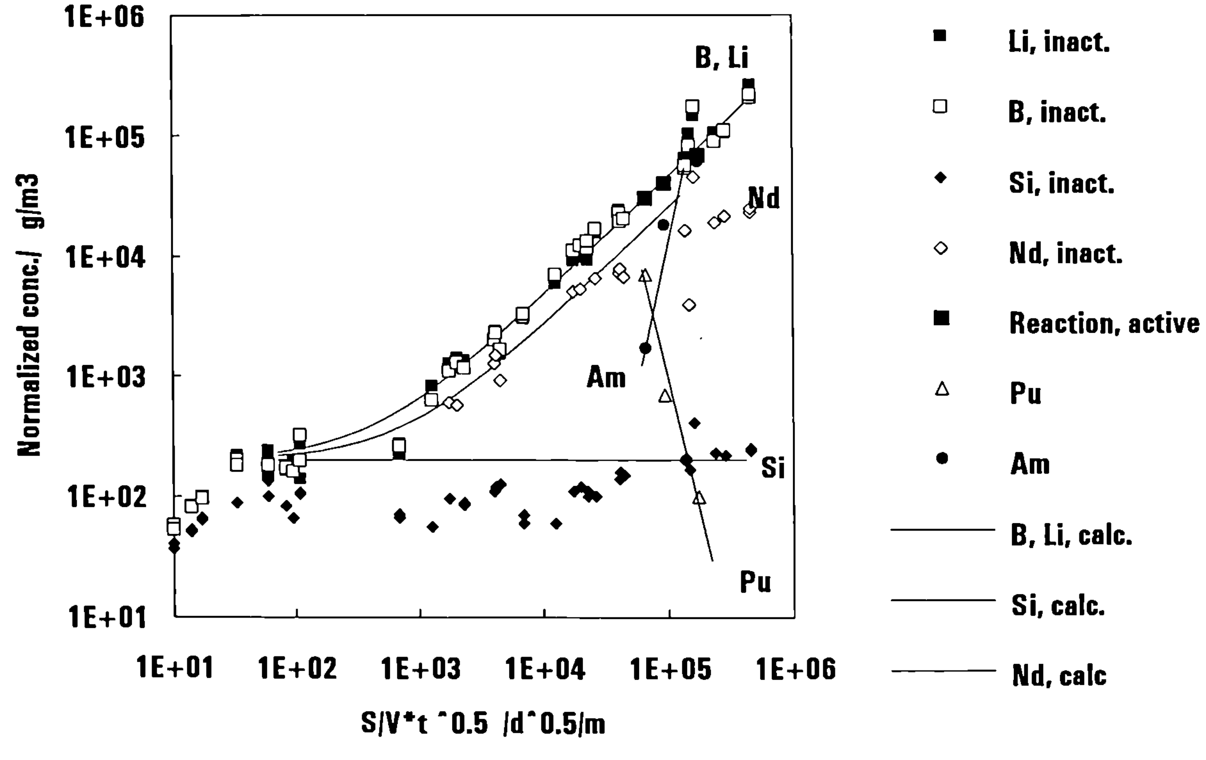


Fig. 5 Time dependence of the reaction of the inactive and active glass. The concentrations of the elements and nuclides in solution normalized to the inventory in the glass plotted versus the product of the square root of time and the S/V ratio. The extent of matrix dissolution in the radioactive experiment: "Reaction, active"

TABLE 1: CORROSION OF THE CEA-HLLW-GLASS R7T7 - Time: 45 d - Temperature: 190°C

	in solution		on filters		plate out : container	corrosion layer	Sum	Balance
	450 nm	1,8 nm	450 nm	0,18 nm				
	NL g/m2	NL g/m2	NL g/m2	NL g/m2	NL g/m2	NL g/m2	NL *	
Co-60	2.26	2.11	b	0.005	n	1.99	*4.25*	143 %
Sr-90	1.60	1.51	b	0.003	n	1.10	2.70	91 %
Tc-99	0.75	0.69	b	0.034	n	0.36	*1.11*	37 %
Sb-125	0.12	0.12	b	0.002	n	0.39	*0.51*	17 %
Cs-134	1.46	0.7	< 0,001	0.014	n	1.89	3.35	113 %
Cs-137	1.66	0.73	< 0,001	0.013	n	1.82	3.48	117 %
Eu-154	0.11	b	< 0,001	0.017	n	2.50	2.61	88 %
Eu-155	0.09	0.02	< 0,001	0.019	n	2.35	2.44	82 %
Np-237	0.19	0.06	b	b	n	3.26	3.45	116 %
Pu-238	0.76	0.58	< 0,001	0.027	n	1.78	2.54	85 %
Pu-239/240	0.73	0.63	b	0.024	n	1.94	2.67	90 %
Am-241	0.19	0.05	< 0,001	0.030	n	3.86	4.05	136 %
Am-243	0.07	0.03	b	0.043	n	n	*0.14*	5 %
Cm-244	0.33	0.29	b	0.027	n	2.13	2.46	83 %

* = sum of NL covers the columns 2, 6, 10 and 12

b = below detection limit

n = not measured

m = to be measured

Mean: 2.98

TABLE 2: CORROSION OF THE CEA-HLLW-GLASS R7T7 -
Time: 300 d - Temperature: 190°C

	in solution		on filters		plate out: container	corrosion layer	Sum	Balance
	450 nm	1,8 nm	450 nm	0,18 nm				
	NL g/m2	NL g/m2	NL g/m2	NL g/m2	NL g/m2	NL g/m2	NL *	
Co-60	9.23	7.82	0.026	0.13	0.06	0.12	9.44	121 %
Sr-90	7.22	5.64	0.066	0.07	m	0.11	7.99	103 %
Tc-99	4.00	3.63	0.043	0.04	m	1.81	6.24	80 %
Sb-125	0.03	0.02	0.023	0.01	0.24	1.53	*1.82*	23 %
Cs-134	6.79	6.31	0.082	0.15	0.07	0.21	7.15	92 %
Cs-137	7.49	6.34	0.089	0.15	0.05	0.07	7.70	99 %
Eu-154	1.93	1.48	0.070	0.02	0.12	0.99	*3.11*	40 %
Eu-155	2.13	1.71	0.076	0.02	0.12	1.06	*3.39*	44 %
Np-237	10.67	b	0.050	b	m	b	10.72	138 %
Pu-238	0.008	0.007	0.003	0.01	0.45	0.42	*0.88*	11 %
Pu-239/240	0.011	0.008	0.004	0.01	0.48	0.46	*0.96*	12 %
Am-241	6.10	4.88	0.198	0.56	0.30	1.47	8.07	104 %
Am-243	6.10	b	0.145	b	m	b	6.25	80 %
Cm-244	4.26	4.57	0.098	0.04	m	1.22	6.46	83 %
						mean	7.78	

* = sum of NL covers the columns 2, 6, 10 and 12

b = below detection limit

n = not measured

m = to be measured

Title: Consequences of gas production in geological repositories (PEGASE)
Contractors: ANDRA, ENRESA, GRS
Contract n°: FI2W-CT90-0020
Duration of contract: from August 1st 1991 to July 31st 1994
Period covered: January - December 1993
Project leaders: Mrs. Sylvie VOINIS (ANDRA Coordinator)
Mr. Miguel A. CUNADO (ENRESA)
Mr. Wolfgang MULLER (GRS)

A. Objectives and Scopes

This project intends to model the overall impact of gas production in the near-field and in particular on the groundwater flow, the durability of engineered barriers and on the radionuclide migration. The wastes forms will include spent fuel, vitrified wastes, medium level waste. The different rock formations envisaged are granite rock and salt. This project is divided in four stages.

1. Description of processes
2. Analyze of gas transport mechanisms
3. Modelling of the system
4. Calculations in specific disposal conditions

B. Work programme

B.1. Description of processes

This step will consist in identifying the mechanisms for gas formation in the different waste repositories considered in the project scenarios from bibliographic or experimental studies and to establish the common data for the development of the models and for calculations.
Analytical laws will be defined through this study to be integrated in the future modelling.

B.2. Analyze of gas transport mechanisms

The transport concerns the near-field and the host-rock. A listing of the main phenomena will be identified and studied.

B.3. Modelling of the system

The modelling will be based on specific developments or on already existing models for the different repository conditions considered by each participant.

B.4. Calculations

The calculations will be performed for the repository conditions defined by the participants. The aim of these calculations is to verify that engineered barriers and wastes matrix are still playing their safety role in the presence of gas. The other aim is to discuss the results and their consequences on the future research.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1. Task one

C.1.1. Data reference and bibliographic synthesis

On the basis of an exchange of informations; working group 1 (ANDRA/ENRESA/GRS) created for task 1 has finished two reports :

- Data reference : the characteristics of wastes, concepts are described in this chapter.See progress report 1
- Bibliographic synthesis : a compilation of the description concerning the potential gas formation mechanisms is finished.See progress report 3

This synthesis has been used for the establishment of the gas formation codes.

C.1.2. Gas formation codes

Two codes have been developed. The name of the first one is GASFORM which has been developed by ENRESA/INITEC. It evaluates the consequences associated with the production of gas in underground storage facilities for radioactive waste. The model is intended to include spent fuel; glasses, and intermediate level wastes.

The model calculates the gas generation due to the following mechanisms : canister corrosion, cladding corrosion, microbial degradation, external radiolysis, internal radiolysis, radioactive decay and water vaporization. The scheme in annex 1 shows the structure of GASFORM code.

The six mechanisms can be classified in the following way : 1-surficial generation that includes steel corrosion, zircaloy corrosion, internal radiolysis and radioactive decay; 2-volumic generation that includes external radiolysis and microbial degradation.

Some examples of calculations are described in the progress report 4 and are shown in the figures 1 and 2.
The next work on this code will be at first to finalise the manual guide and at second to complete the verification tests. Some improvment on the user interfaces will be also made.

An another code has been developed by GRS. Its name is GABI. GABI's code is in charge to calculate the gas formation due to the corrosion canister and internal radiolysis. Concerning the corrosion, two anaerobic metal corrosion reactions can be selected for inner and outer container corrosion.

Numerous parameter variations were calculated with GABI code. It appeared that additional features were desirable for improved calculations of the radiolytical gas production. By this time the GABI code was completely restructured and revised due to exceeding memory requirements. The code can now be run in an overlay structure on any 386-PC or higher without additional features. Testing of the new version is under way.
The figure 3 gives an example for a reference case for HAW calculated with the new version.

The comparaison between these two codes will be made in 1994 du to the delay of the code verification.

C.2. Gas transport

C.2.1. Transport in salt

The TOUGH code has been used to clarify decisive parameters by sensitivity analyses. Some calculations are presented in the progress report4. Since TOUGH is not able in its present version to include tme dependant source terms for gas generation, appropriate modifications have been started.

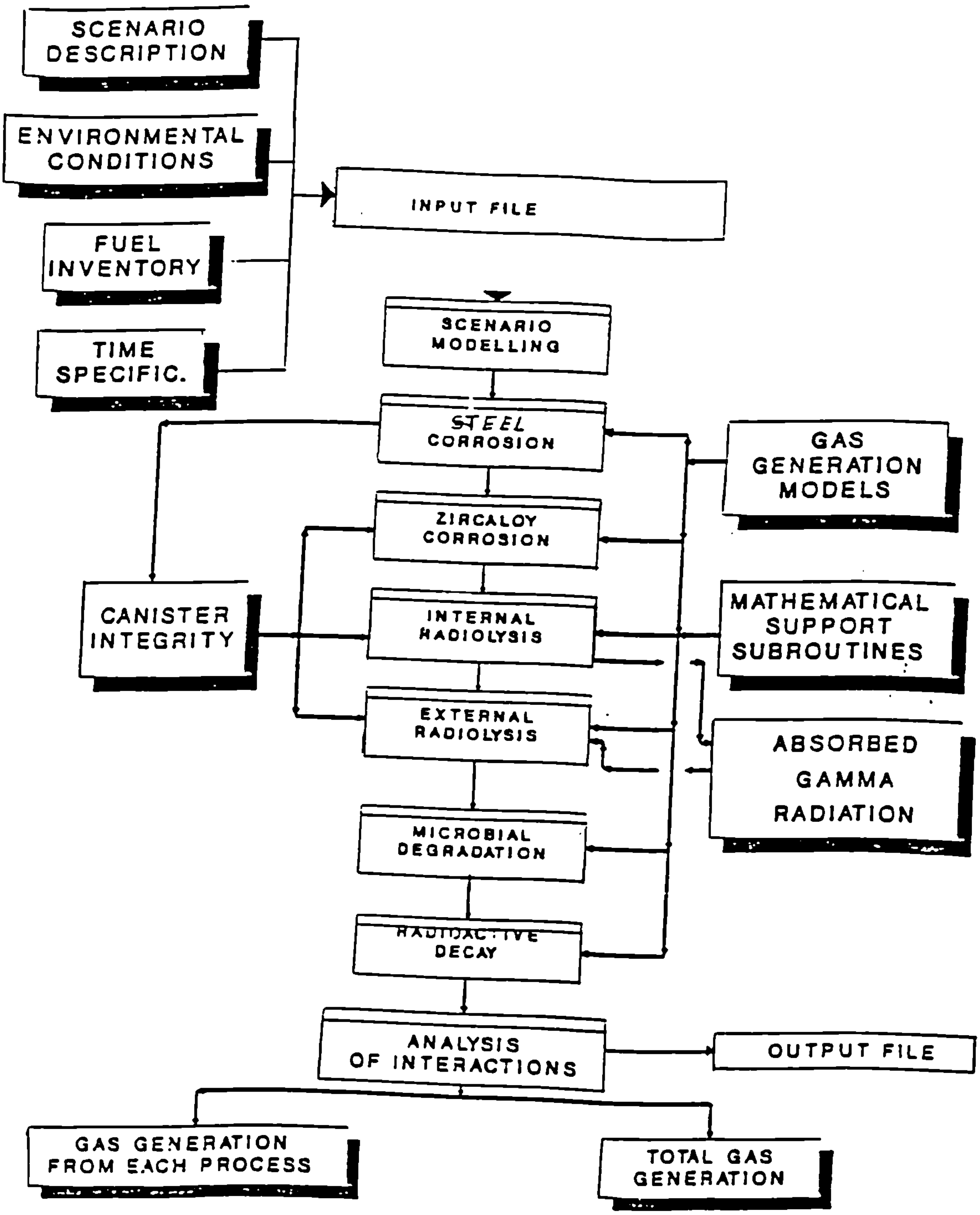
A preliminary mathematical model for the description of two-phase transport phenomena in a salt repository with the PHOENICS code has been developed and is tested. This work was performed by a subconstractor. A final version of the mathematical model is still pending.

C.2.2. Transport in granit

A physical analysis has been made to determine the predominant phenomena and parameters to be integrated in the global codes.After making this physical analysis, it has been decided to use the code TOUGH2 that corresponds to most of the specifications required and presented in the next progress report.

In the annexe 2, the diagram of the coupling between TOUGH and GASFORM is presented. It results of the analysis of GASFORM and TOUGH codes. The work concerning the coupling will be made during the first part of this year and some test will be input before june.

ANNEX 1


SCENARIO DESCRIPTION
ENVIRONMENTAL CONDITIONS
FUEL INVENTORY
TIME SPECIFIC.
INPUT FILE
SCENARIO MODELLING
STEEL CORROSION
ZIRCALOY CORROSION
INTERNAL RADIOLYSIS
EXTERNAL RADIOLYSIS
MICROBIAL DEGRADATION
RADIOACTIVE DECAY
ANALYSIS OF INTERACTIONS
CANISTER INTEGRITY
GAS GENERATION MODELS
MATHEMATICAL SUPPORT SUBROUTINES
ABSORBED GAMMA RADIATION
OUTPUT FILE
GAS GENERATION FROM EACH PROCESS
TOTAL GAS GENERATION

ANNEX 2

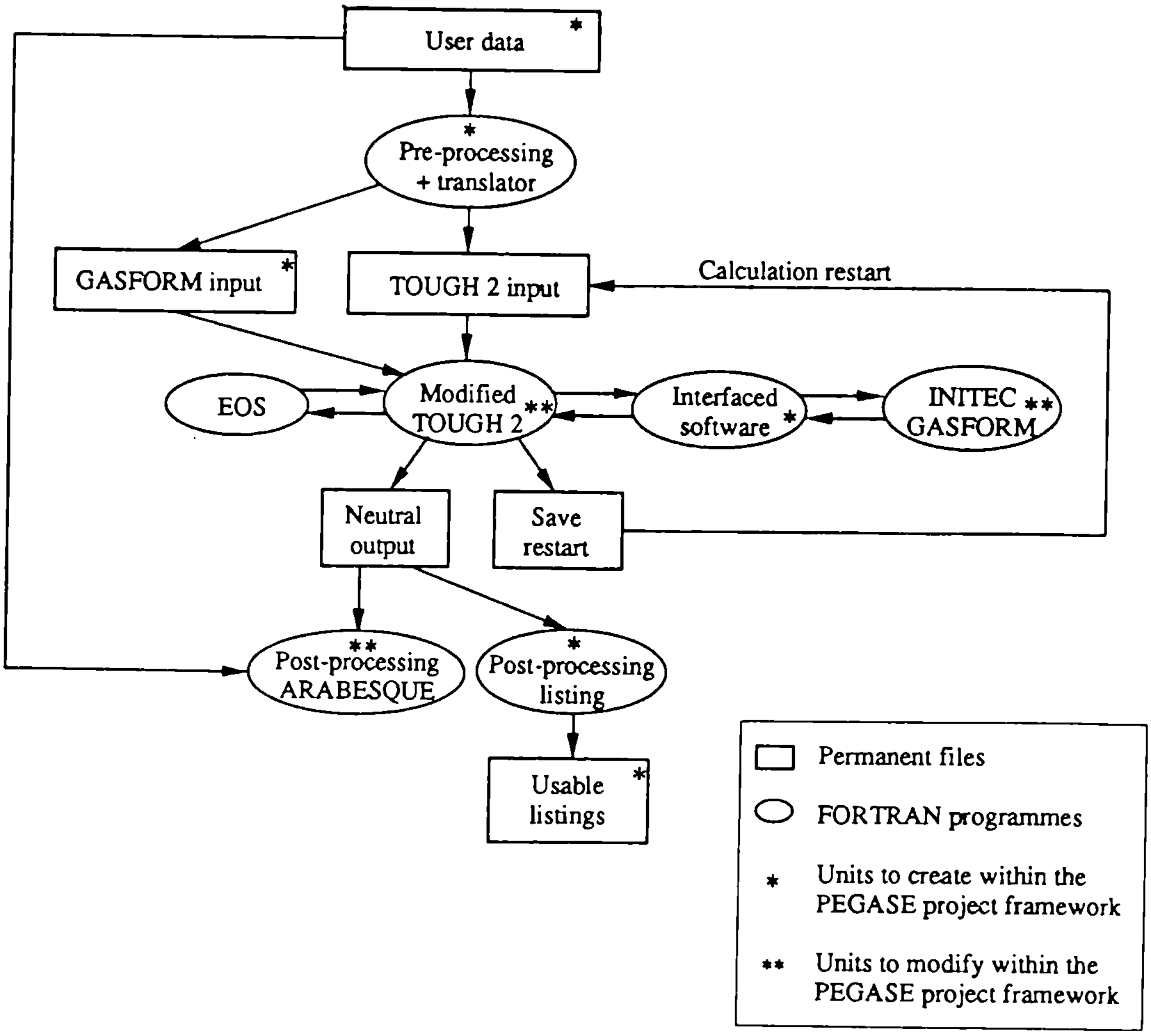

User data *
* Pre-processing + translator
GASFORM input *
TOUGH 2 input
Calculation restart
EOS
Modified TOUGH 2 **
Interfaced software *
INITEC GASFORM **
Neutral output
Save restart
** Post-processing ARABESQUE
* Post-processing listing
Usable listings *
Permanent files
FORTRAN programmes
* Units to create within the PEGASE project framework
** Units to modify within the PEGASE project framework

Figure 1 : ENRESA CASE
SURFACIC CALCULATIONS

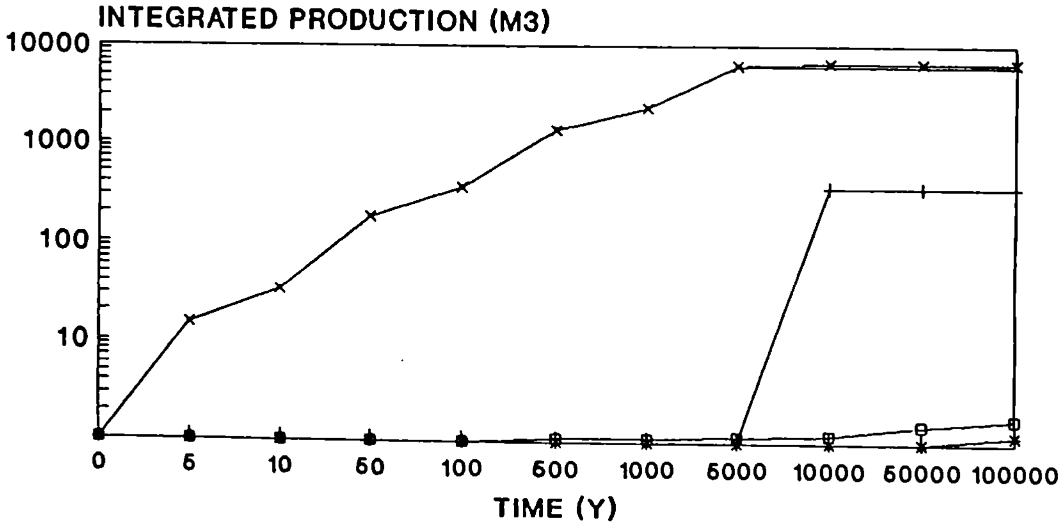
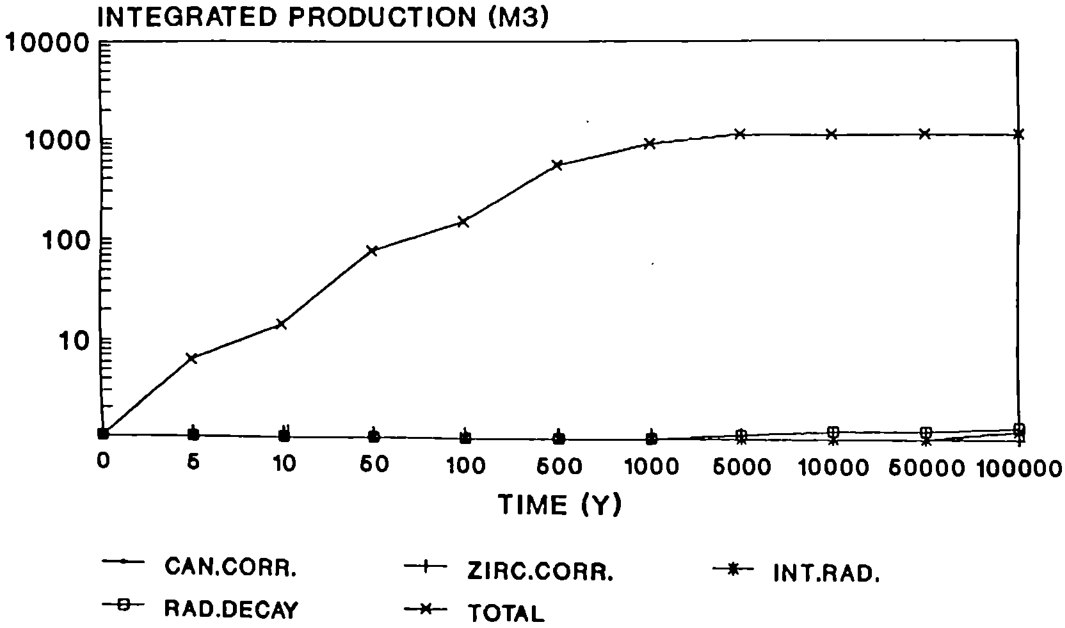


Figure 2 : ANDRA CASE
SURFACIC CALCULATIONS



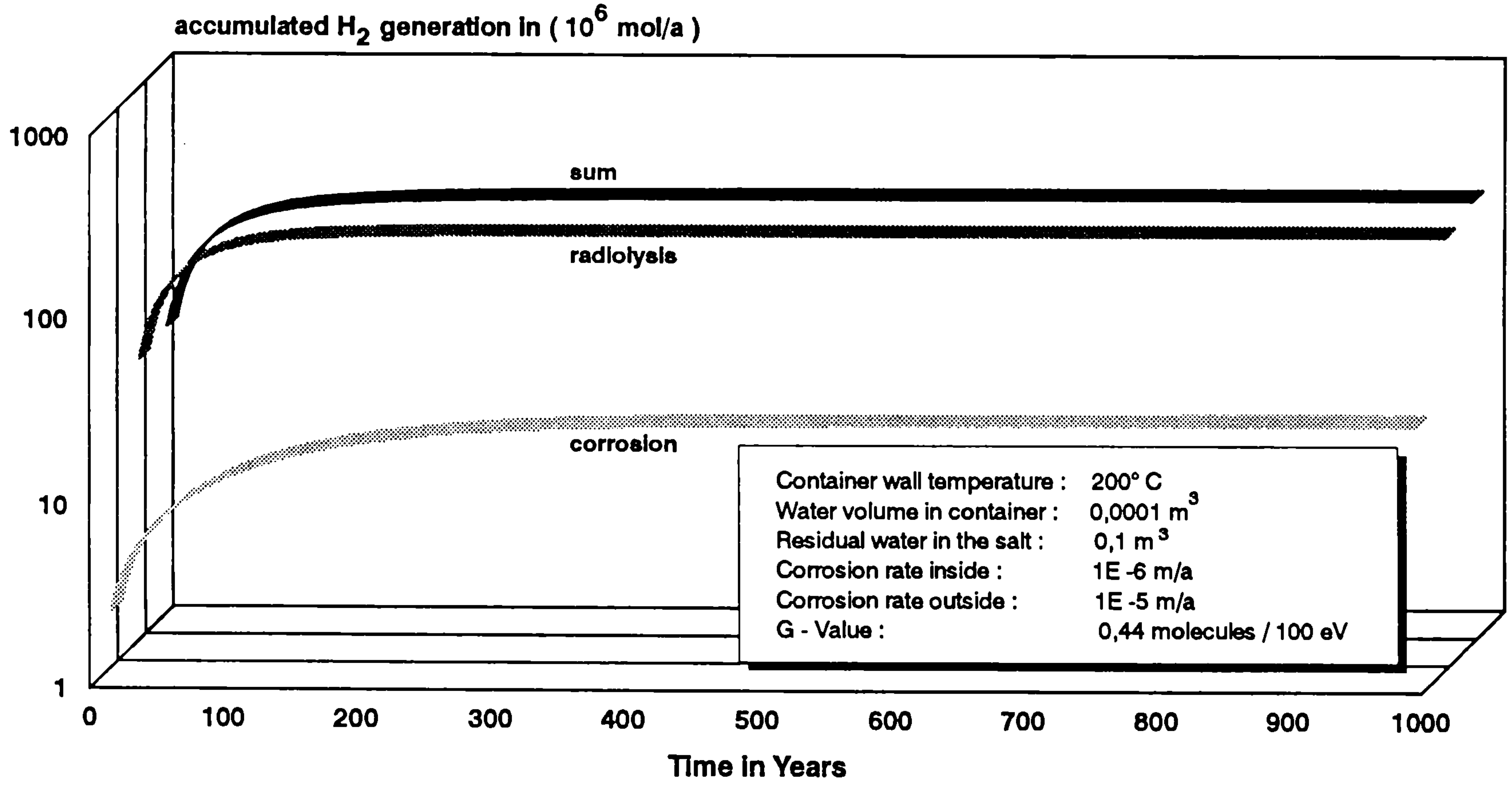


FIGURE 3 : GAS GENERATION OF A HAW CONTAINER IN A VERTICAL BOREHOLE IN SALT

Title: **Characteristics of bitumized radioactive wastes**
Contractors: **CEA/DCC (Cadarache et Saclay), SCK/MOL, NIRAS-ONDRAF, RISO NATIONAL LABORATORY**
Contract n°: **FI2W-CT90-0025 + 0007**
Period covered: **January - December 1993**
Project Leader: **M. Brunel**
Task Leaders: **MM. Van Iseghem, De Goeyse, Nomine, Brodersen**

A. OBJECTIVES AND SCOPE

The objective of this study is to investigate the leaching behaviour of the bitumen encapsulation of representative and homogeneous reprocessing sludges or concentrates wastes under geological disposal conditions.
The influence of the bitumen matrix and the type of waste treated will be closely examinated.
The present study will include realistic disposal scenarios and comparison of Eurobitum and M80/100, M40/50 and MR90/40 will be possible in regards to efficiency confinement of radioactivity.
The tests that should enable us to evaluate encapsulation stability are steady leaching tests in different media conditions constituted by water (CEA Cadarache and SACLAY), by a cement/clay mixture and clay/clay water mixture (SCK Mol and CEA SACLAY) with different size samples from a few cm^3 to the full size bitumen block.
Understanding of water uptake in and release of dissolved materials when bitumenized materials are disposed of under saturated as well as unsaturated conditions and quantification of swelling pressure and leaching phenomena are improved by RISO NATIONAL LABORATORY.
The small size samples of bitumenized coprecipitation sludges will be prepared by CEA Cadarache.

B. WORK PROGRAMME

B.1. Sampling

Samples are taken from an inactive and an active drum or are fabricated in suitably equipped shielded cell. The size of the samples is between 20 cm^3 and 200 l.

B.2. Inactive leaching tests

Tests are carried out by SCK Mol Laboratory in a cement/clay mixture and a clay/clay water mixture, at 23°C and 40°C, for duration until 480 days. Emphasis will be on leaching kinetics of inactive waste constituents.

B.3. Active leaching tests

Tests are carried out in similar conditions as B.2 (media, temperature, duration) by SCK Mol for the small samples (20 cm^3) and by CEA SACLAY for 200 l, 20 l, 2 l and 0,2 l samples. Leaching tests in water will be performed on 0,4 l samples in static and uncontinuous conditions by CEA Cadarache and on 200 l, 20 l, 2 l and 0,2 l for CEA SACLAY. Emphasis will be on leaching processes and kinetics of the active waste constituents.

B.4. Migration of water and ions through membranes of bitumized products

Uptake of water into bitumenized waste is important for the understanding of the long-terw behaviour of the material. Diffusion of tritiated water and ^{134}Cs ions is studied using membranes made from pure bitumen, bitumen mixed with crystals of soluble salts such as $NaNO_3$ or with insoluble sludge particles, for example $BaSO_4$. the measurements of the amounts of diffused materials are supplemented by measurement of the electrical conductivity over the membrane. This gives additional information about the migration mechanisms and the quality of the membranes.

B.5. Swelling and swelling pressure

Unrestricted swelling, water uptake and Na-leaching from samples of bitumenized materials containing soluble salts are followed using a weighing technique and chemical analyses of the leachants. The materials are simplified versions of typocal waste products. This makes it possible to investigate the influence of single parameters such as bitumen type, salt content, crystal size, presence of sludge particules, etc.

Pressure development due to water uptake in confined samples of similar materials is also investigated using a technique where swelling caused by water penetrating through a cement mortar barrier results in replacement of mercury from a bottom reservoir up in a long capillary tube.

B.6. Model describing water uptake and leaching

A research model describing the water uptake in bituminized materials containing soluble salts has been developed. The dynamics of the swelling and the generation of an internal solution-filled pore structure are modelled on teh micro-scale. Some simplifying assumptions about geometry of the system, etc. are made. The water is supposed to be transported as vapour through the bitumen films surrounding the crystals. Diffusivities for tritiated water obtained in the above-mentioned membrane experiments are utilized.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The status of progress has not been forwarded to the Commission for 1993.

Title :	**Organic matter and uraninite from the Oklo natural fission reactors - Natural analogue of radioactive waste-containing bitumen and UO_2 irradiated fuel.**
Contractors :	CEA/DCC/DESD Cadarache, CREGU-CNRS Nancy
Contract N° :	FI2W - CT90 - 0026
Duration of contract :	June 1991 - December 1995
Period covered :	January 1993 - December 1993
Project leader :	P. Holliger, DESD/SCS - CEA Cadarache
Co-contractor :	P. Landais, CREGU-CNRS Nancy
Co-worker :	O. Ruau, CREGU ; C. Menet-Dressayre, CEA

A. OBJECTIVES AND SCOPE

The objective of this research program is the investigation of the effects of radiation on the chemical changes in the structure of organic matter (OM), specifically in the Oklo U-ore deposit and its associated natural fission reactors. Studies have shown that sedimentary organic matter associated with uranium may be altered by irradiation related to (i) the natural decay of ^{238}U and (ii) the ^{235}U fission process. Such modifications must be studied by a non-destructive, in-situ technique because of the technical difficulties related to the extraction and the isolation of the organic matter. Specular reflectance Fourier transform micro infrared spectroscopy (micro FTIR) appears to be an efficient tool for microscale studies (Rochdi and Landais, 1990, Landais and al., submitted). It provides information on oxygenated, aliphatic and aromatic species abundance ratios for 200 X 200 microns large regions of organic matter on polished section samples. The morphology and texture of bitumens and mineral inclusions are first observed by optical microscopy in order to select specific areas for subsequent analysis by micro FTIR (Holliger and Landais, 1993a, 1993b). The combination of petrographic, spectroscopic and isotopic ($^{13}C/^{12}C$) studies allows the different types of organic matter from the different zones of the Oklo basin to be distinguished. New organic matter-rich samples from the core of Reactor Zone 9 (RZ.9) are now prepared. The aim is to compare the structure of OM from two different zones of nuclear criticality (RZ.9 and RZ.10) in order to discriminate different types of OM and/or functioning of the reactors (temperature, water as moderator,...). Finally, ion bombardment with varied ions of appropriate mass and energy was performed on samples from the reactor core and outside the reactor in order to detect some structural modifications of the OM.

B. WORK PROGRAM

B. 1.1	Sampling and petrographic observations (by using electron microscope and reflected light microscope)
B. 1.2	In-situ characterization of the organic matter, by using specular reflectance Fourier transform micro infrared spectroscopy.

B. 2.1	Characterization of the OM and uraninite from nuclear reactor 10 : uranium and fission products containments (isotope data and ion microprobe cartography).
B. 3.1	Experimental study of radiation effects: Pb and He implantation experiments on the Oklo samples

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The main features of this work during this year have been as follows:

- Collection and petrographic description of new samples throughout the Oklo and Okelobondo uranium ore deposit : in, in the vicinity and outside the Reactor Zones. Based on morphology and textures, the bitumens in a reactor facies can be characterized in three groups: - (1) non-mineralized anisotropic bitumens with mosaic texture (mesophase type) forming droplets and aggregates, - (2) mineralized bitumens which occur at a pressure solution seams and secondary pores of the rock and - (3) mineralized isotropic bitumens with a very low reflectance, which frequently form an outer rim of the latter type; this textural type is regarded to be a product of bitumen oxidation.
- Chemical analysis of OM by Energy Dispersive X-ray analysis (EDX)
- Isotopic abundances (uranium, fission products) of some OM-rich uranium samples performed by Inductively Coupled Plasma - Mass Spectrometry (ICP/MS) and Secondary Ion Mass Spectrometry (SIMS).
- A correlation between fission rates (depletion in ^{235}U) and enrichment in ^{13}C on OM samples from the reactor core; the isotope fractionation line observed on samples collected in gallery D.81N (RZ.10) clearly shows that OM was present during reactions in this portion of reactor.
- A study based on specular reflectance Fourier Transform micro InfraRed spectroscopy (FTIR) allows to underline chemical differences in organic matter from the Oklo basin. Even though no radiogenic halo around the uraninite inclusions are seen, one can observe differences related to the distance of the sample from the natural reactors.
- Raman spectra were obtained only from two points on a sample from RZ.10. Because of very low quality of the record (integration time only 10 s) an interpretation of the results is very difficult. None the less, in both cases the character of Raman spectra point to a very low degree of structural ordering. In all other samples, the destruction of bitumens (decolorisation and burning) was so quick, that even at a minimum power of the laser beam no spectra have been obtained.
- Ion bombardment was performed on Oklo OM samples by using either ion implanters for low energy heavy ions (Pb^{2+}, 1 keV/a.m.u.) or accelerators for high energy ions (He, 1.2 MeV). But, difficulties occurred on some samples because the bitumens of Oklo revealed to be quite fragile in the high vacuum conditions necessary for ion bombardment and analysis, and to ion beam effects. Another difficulty was due to the relative brittleness of some bitumens which tend to break into small pieces during the leaching experiments, notably when performed at high temperatures (> 100°C). However good results were obtained using He bombardment, on D.81N samples (RZ.10): optical differences are visible on the OM between irradiated and non irradiated areas.

Progress and results

B.1.1 Sampling and petrographic observations

- Organic Matter occurrences

The polished sections were studied using a reflected light microscope and an electron microscope. According to the results of the optical studies, the whole set can be described as:

I. samples of massive bitumen with small inclusions of uraninite, galena and chlorite. This group comprises samples GL 2898 (front 299 D, zone 8), GL-3097 (RZ.8, north part); D 81N-190392/ 2 (RZ.10); Oklo Fond I ; D.75- 2029 (R.Z. 16),

II. Strongly mineralized bitumen samples with relicts of host sandstone: OP.100, OP.1029 (Okelobondo, north part),

III. Samples formed by droplets and lobate aggregates of the bitumen with uraninite inclusions, in a fine grained matrix consisting of authigenic, well crystallized chlorite ("facies argile de pile", RZ.10),

IV. Samples formed by several pods of U-mineralized black bitumen and strongly chloritized and carbonatized high strained greywacke (ES.24, Oklo, south part)

V. Host mineralized sandstone with few dropletss of bitumen "trapped" in intergranular spaces: SF 85 (Oklo, RZ.10),

VI. Weakly mineralized or non-mineralized bitumens with relicts of host sandstone: SD.97 (Oklo, south part), SD.37 (Oklo, RZ.13), OD.13 (Okelobondo, south part).

- The Uranium - Organic Matter relationship

Mineral inclusions within OM often consist of uraninite, radiogenic galena and chlorite. Uraninite forms either slightly corroded and sometimes brecciated grains in the matrix, or occurs together with chlorite in thermal cracks and fissures. In latter case it is frequently silicified and replaced by coffinite.

In accord with observations, the origin of bitumen can be seen in the processus of hydrothermal (not necessary radiolytic) degradation of the Francevillian kerogen. The bitumens were mobilized and expelled from the source rocks in liquid or semi-liquid stage, together with a highly reducing hydrothermal solution which was rich in dissolved Si, Al, Fe and Mg. Due to reducing character of the hydrothermal system, the uraninite was partly passively transported by bitumens, partly dissolved and recrystallized together with chlorite in the bitumen thermal fissure network in time or after its solidification. No radiation haloes were formed around the uraninite grains, as the matrix was irradiated before solidification stage. The final stage of bitumen evolution is represented by small zones of oxidation and silicification, which document a slightly more oxidizing, alcaline character of the vaning stage of the hydrotermal activity.

B.1.2 Infrared micro spectroscopy

- Introduction

The samples selected for the present study come from various zones of the basin, including (i) samples noted MO.1 and MO.3 (RZ. 8-9), (ii) MO.14 and MO.15 (RZ. 10) and (iii) MO.22 (ES.24, out of the reactor zones). This report summarizes the results of specular reflectance micro FTIR on polished sections of bitumens from the "facies pile" (Gauthier-Lafaye and Weber, 1978).

- Materials and methods

The micro FTIR analyses are performed on a Nicolet System 800 Fourier transform spectometer. This device is equiped with an NIC-Plan microscope, which is fitted with a 250 µm diameter narrow-band MCT (mercury-cadmium-telluride) detector cooled to 77K. The objective magnification allows 70 to 400 µm diameter areas to be analyzed. The interferogram is recorded by accumulating 128 to 600 scans over 50 to 240 s. Reflectance spectra are transformed using the regular Kramers-Krönig procedure to obtain absorbance index spectra. The available spectral range lies between 4000 and 700 cm^{-1} and the spectral resolution is 8 cm^{-1}(appendix 1). The assignments of the main I.R. bands are determined by the reference to the works of Robin et al., 1977 and Guiliano and al., 1988 (table 1 in appendix 2). The band area quantification is obtained by the commonly used valley to valley integration mode (Robin and al., 1977 and Kister and al. 1988). Band ratios have been calculated in order to determine the relative proportion of oxygenated, aliphatic and aromatic species.

- Results and discussion

For each sample, several representative regions (five in general) of the organic matter on the polished section have been chosen for characterization by micro FTIR. The values obtained from aliphatic species (ν CH_{ali} between 3000 and 2800, δ CH_{ali} between 1500 and 1350 cm^{-1}, δ CH_2+CH_3 between 1500 and 1420 cm^{-1} and δ CH_3 between 1420 and 1350 cm^{-1}), aromatic (ν C=C at 1600 cm^{-1} and γ CH_{aro} between 900 and 700 cm^{-1}) and oxygenated ones (ν C=O near 1710 cm^{-1}) are used in following ratios.

Aliphaticity ratios :

- dali / garo : δ CH_{ali} / γ CH_{aro}
- dali / c=c : δ CH_{ali} / ν C=C
- ali / c=c : ν CH_{ali} / ν C=C
- ali / garo : ν CH_{ali} / γ CH_{aro}

These different ratios take into account the relative content of aliphatic species versus aromatic species and thus give information on the maturity of the organic matter of the sample. The weaker the value of the ratio is, the more mature the sample is.

Branching and/or substituents length ratio :

- CH3 / CH3+CH2 : δ CH_3 / δ (CH_3 + CH_2)

This ratio is relative to the average length of alkyl chains substitued on aromatic rings. The greater the value of this ratio is, the shorter and/or more branched the alkyl substituents are.

Oxidation ratios :

- c=o / dali : ν C=O / δ CH_{ali}
- c=o / ali : ν C=O / ν CH_{ali}
- c=o / c=c : ν C=O / ν C=C
- c=o / garo : ν C=O / γ CH_{aro}

This group of ratios provides data on the oxidation degree of the organic matter of the samples. Data deduced from the infrared ratios reveal that :

- several samples contain a rather homogeneous organic matter in terms of maturity and oxidation degrees : MO.1, MO.14 and MO.22. On another hand, sample MO.3 seems to contain at least two types of organic matter with the same maturity but with different oxidation degrees. Sample MO.15 presents various types of organic matter with different maturity and oxidation states.
- on sample MO.15 the effect of the matrix embedding bitumens has been emphasized when recording the spectra of various homogeneous zones of organic matter near and far from the matrix. Qualitative and quantitative IR data evidence no differences that can be related to the distance from the matrix.

Table 2 (appendix 2) gives the average value of the different IR ratios for each sample. Accordingly to these data, a radar diagram is drawn in order to give a relative global characterization of the samples (appendix 3).

One can notice that MO.1 and MO.22 present the greatest oxidation state acordingly to the higher values of the oxidation ratios than for the other samples. Moreover, their weaker values of the aliphaticity ratios underline their higher maturity. The samples from zone 10 (MO.14 and MO.15) have nearly the same average value for all the calculated ratios except for ratios dealing with aliphatic moieties (v CH_{ali} band areas). Organic matter maturity of these samples is weaker than in the other studied samples accordingly to the higher aliphatic ratios values. Finally, the last sample (MO.3) exhibits both intermediate maturity and oxidation states.

Such a microscopic analysis allows to characterize the organic matter of the samples from the different zones of the Oklo basin. The organic matter of the samples MO.14 and MO.15 collected close to one another in zone 10 presents low oxidation and maturity degrees. Moreover, bitumens of MO.1 and MO.3 collected in zone 8 and zone 7 show higher maturity and oxidation states. Some differences are noticed between these two samples, with MO.1 organic matter (zone 8) more oxidized and more mature than MO.3 (zone 7). Finally, bitumen of sample MO.22 (out of the reaction zone) displays high oxidation and weak aliphaticity ratios.

- Conclusions :

This study based on specular reflectance Fourier transform micro infrared spectroscopy allows to underline chemical differences in organic matter from the Oklo basin. Even though no radiogenic halo around the uraninite inclusions are seen, we can observe differences related to the distance of the sample from the natural reactor. IR datas are transformed in ratios in order to determine oxidation and maturity of the samples. Thanks to microscopic approach some chemical changes, like oxidation zones are noticed in the organic matter of the same sample. The study of more samples from the different zones of the Oklo basin and the combination with other micro analysis techniques such as electron microprobe may lead to a better understanding of the phenomena occuring in this basin.

B.2.1 Characterization of the U-rich OM : chemical and isotopic measurements

- Energy Dispersive X-ray (EDX) analyses

Microanalyses by energy dispersive technique were carried out on uraninite, coffinite, clay minerals within massive OM and microcracks at the microscale level (C. Menet, 1993). Firstly, Pb/U ratios were estimated in uraninite grains in order to evaluate the diffusivity of radiogenic lead in the different samples. Secondly, sulfur contents of the OM were measured on different areas, free of U, on the most of the samples. S results were presented in a previous report (Holliger and Landais, 1993b). It appears that no S is detectable in D.81N samples (core of RZ. 10), while S contents are a few wt.% in the other samples. Petrographic observations show that OM from D.81N samples, is a black and lustrous bitumen with numerous small inclusions of uraninite; uraninite is often corroded and replaced by coffinite (e.g. sample 202092/11II). The OM matrix is generally silicified; fractures and cracks are filled with quartz and clay minerals (mainly Fe-Mg chlorite). Quartz grains appear as relicts and were altered by the effect of hot fluids; these fluids were probably those of a convecting hydrothermal system related to nuclear reactions. So, OM from these samples could be contemporain with the nuclear process; this was confirmed by C isotopic analyses.

- Organic Matter Fission Products containment

Quantitative and isotopic analyses were performed on U-rich OM powdered samples by using ICP-MS technique in order to check Fission Products (FP) distributions relative to U. In these organic-rich portions of reactors (RZ.8-9, RZ.10), uranium and fissiogenic isotopes are held in uraninite grains which became enclosed in viscous bitumen during criticality (Nagy et al.,1991). Rare Earth Elements are specially well retained (>98%) in the structure of uraninite as shown in Fig.1. Other fissiogenic elements (e.g. I, Te,..) also present in the samples from RZ.10 could have formed mineral assemblages approaching equilibrium under highly localized physicochemical conditions, as suggested by Curtis et al. (1989) and could have been trapped subsequently in solid bitumen phase at the end of nuclear reactions.

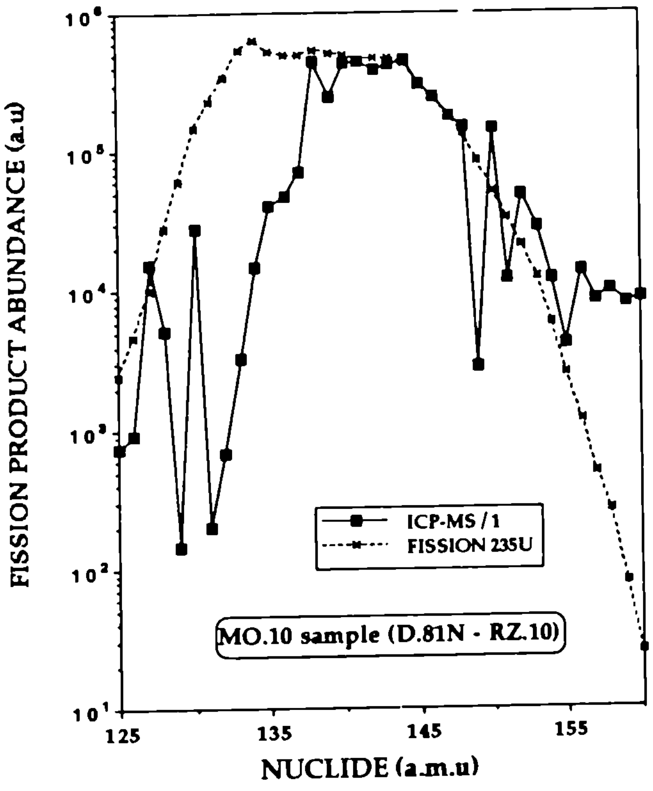


Fig.1 - Degree of retention of fissiogenic isotopes compared to the 235U fission curve range 125-160 atomic mass units (a.m.u.)

- $^{13}C/^{12}C$ on powdered samples

Twenty selected powdered samples (referenced MO) were analyzed for their $\delta^{13}C$ values (J.L. Michelot, University of Orsay, France) and $^{235}U/^{238}U$ ratios (C.Riglet, CEA Cadarache). By definition, $\delta^{13}C = [(R_{sample} / R_{standard}) - 1] \times 1000$, where $R = {}^{13}C/^{12}C$ and the standard is PDB; the absolute $\delta^{13}C$ analytical precision is of about ± 0.1 per mil. Figure 2 shows a diagram ($^{235}U/^{238}U$, $\delta^{13}C$); samples are divided in five groups according to their genesis. Okelobondo samples have normal U isotopic compositions (0.726% ± 0.001%) and $\delta^{13}C$ values in the range -23.0 to -29.2 per mil, which are typical of kerogen and bitumen from the Oklo Fa formation (Cortial et al.,1990). All the analyzed samples including those highly depleted in ^{235}U (RZ.8-9, SF.85 from RZ.10), give δ^{13}C values lower than -22, except the high-grade samples from D.81N gallery in the core of RZ. 10. These latter samples show δ^{13}C values of -9.6 to -18.6 per mil correlated with the ^{235}U depletion. Because the OM and uraninite grains (^{235}U-depleted to-day) were deposited simultaneously during nuclear reactions, as confirmed by petrographic observations, the radiation effects were particularly important; the radiation dose which was absorbed in OM was of about 10^{12} to 10^{13} rads (depending upon ^{235}U locally consumed see Holliger and Landais, 1993). These radiation effects may have induced important changes in the structure of the OM by bond-breaking, ionization and formation of ^{13}C-depleted volatile products. FTIR analyses performed on two of these samples (MO.14 & 15) exhibit a weaker maturity and higher aliphatic ratio values (see B.1.2).

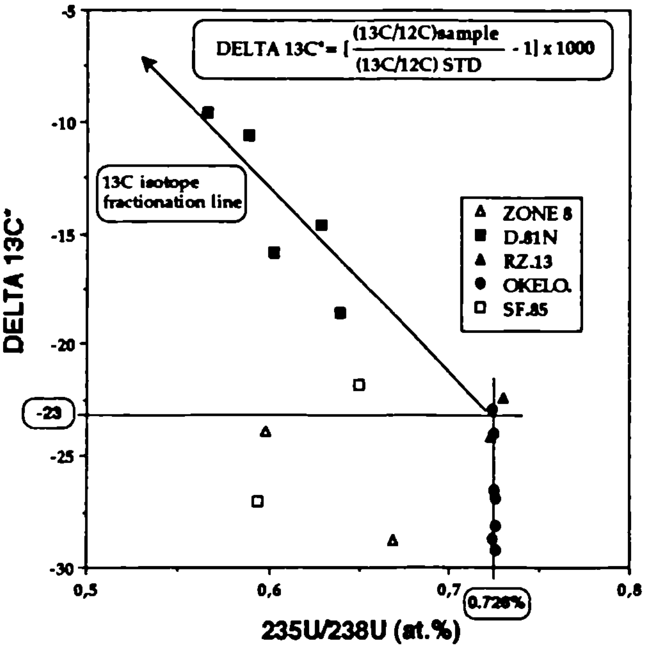


Fig.2 - Plot of 13C as a function of 235/238 and the isotope line fractionation induced by nuclear reactions for D.81N samples.

B.3.1 Irradiation experiments

- Introduction

This part of the programme relies on ion bombardments with He and Pb of appropriate mass and energy in order to simulate alpha particles, alpha recoils and fission fragments. Changes in the structure of the OM as a function of radiation effects is expected; calibrations obtained could help us to interpret the direct characterization of samples naturally irradiated during the functioning of reactors.

- Experimental procedure and optical results

Six polished sections were used for ion bombardment. Before irradiation, a part of the surface of the sample was covered with a grid (mesh: 100 µm x 100 µm) partially masking the ion bombrdment in order to compare irradiated and non irradiated areas. Irradiating conditions were as follows:

- for Pb: energy 200 keV, courant 15 µA, dose 1.13x10^{12} ions/s/cm^2, vacuum 5x10^{-7} torr, T at the surface of the sample <100 °C. Ranges of fluence: 10^{12}, 10^{13}, 10^{14}, 10^{15} Pb/cm^2
- for He: energy 1.2 MeV, ranges of fluence: 10^{13}, 10^{14}, 10^{15}, 10^{16} He/cm^2.

Optical observations allow us to observe that the print of the grid is visible on some OM areas from samples MO.14, 15, 18 and 32 for the highest values of He ion bombardments (10^{15} and 10^{16} He/cm^2). Forthcoming in situ analyses by FTIR and the ion microprobe will be used for detecting textural changes in the OM (if any).

Bibliography

Cortial F. ,1985. Les bitumes du Francevillien (Protérozoïque inférieur du Gabon, 2000 Ma) et leurs kérogènes. Relations avec leurs minéralisations uranifères. Thèse Univ. Louis Pasteur, Strasbourg, 183 p.

Cortial F., Gauthier-Lafaye F., Lacrampe-Couloume G., Oberlin A and Weber F., 1990. Characterization of organic matter associated with uranium deposits in the Francevillian formation of Gabon (lower proterozoic). Org. Geochem., v.15, n°1, 73-85.

Curtis D., Benjamin T., Gancarz A., Loss R., Rosman K., De Laeter J., Delmore J.E. and Maeck W.J. (1989). Fission product retention in the OKLO natural fission reactors. Applied Geochemistry, vol.4 : 49-62

Gauthier-Lafaye F. and Weber F., 1978. Etudes minéralogiques et pétrographiques effectuées à Strasbourg sur les réacteurs naturels d'Oklo, *in:* Les réacteurs de fission naturels, IAEA-TC-119, Vienna.

Gauthier-Lafaye F., 1979. Contrôle géologique de l'exploitation des zones de réaction 7-8-9 , OKLO - Gabon. Avril 1978- Septembre 1979. Internal Report, Univ. Strasbourg, Fr.

Guiliano M., Mille G., Kister J. and Muller J.F., 1988. Etude des charbons français déminéralisés et de leur macéraux. Chim. Phy., 85, 10, 963-970.

Holliger P., 1992. Les nouvelles zones de réaction d'Oklo : datation U-Pb et caractérisation in-situ des produits de fission à l'analyseur ionique. Programme "OKLO-Analogues Naturels", CEA Int. Rep. CEN. Grenoble/ DEM n°01-92, 42 p.

Holliger P. and Landais P., 1993a and 1993b. Organic matter and uraninite from the natural fission reactors - Natural analogue of radioactive waste-containing bitumen and UO2 irradiated fuel. CEA Int. Rep., DSD. 93-84, 29 p., 8 pl. and DSD. 93-101, 26 p.

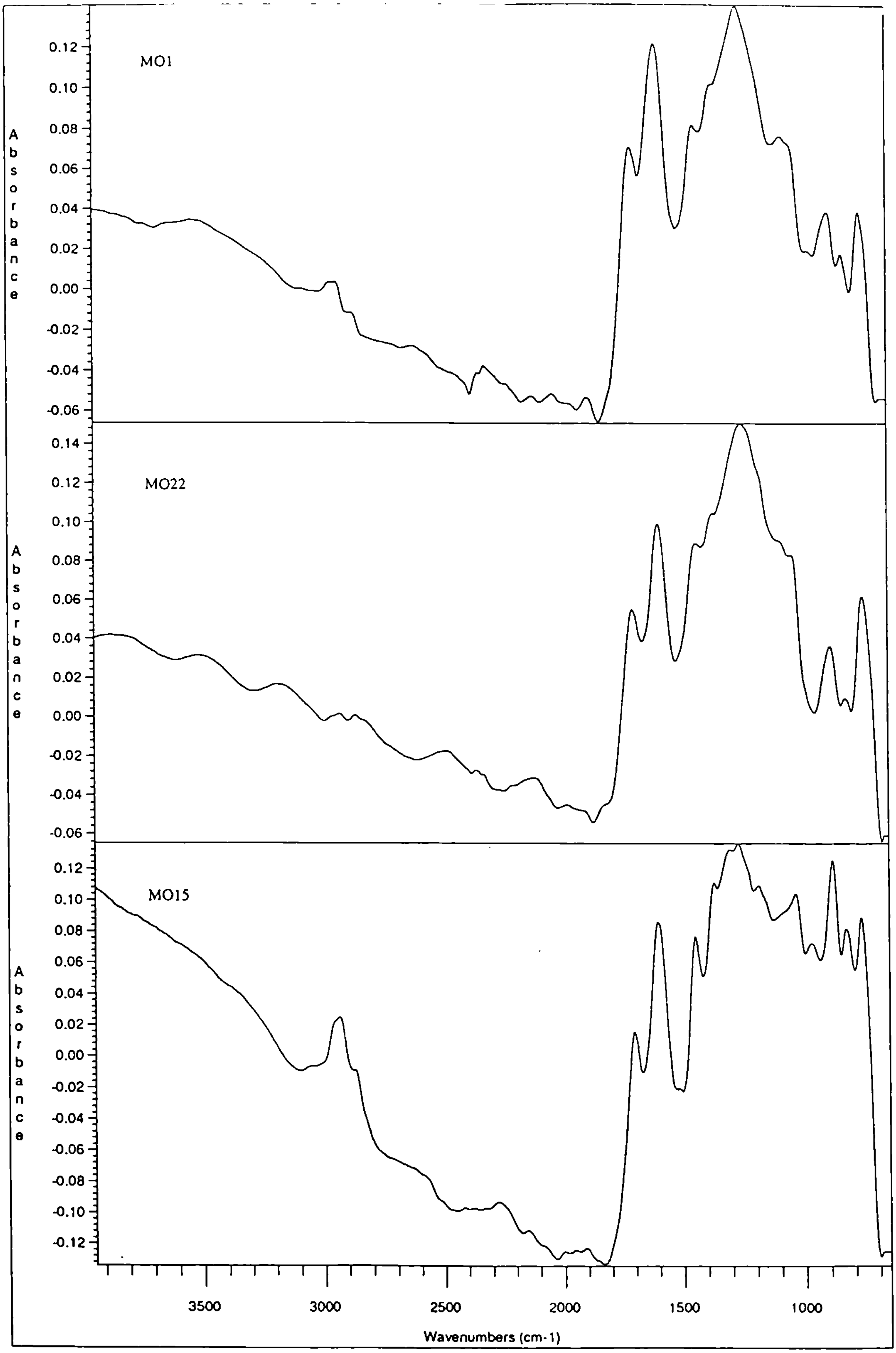
Kister J., Guiliano M., Mille G. and Dou H., 1988. Changes in the chemical structure of low rank coal after low temperature oxidation or demineralization by acid treatment. Fuel, 67, 1076-1082.

Landais P., Gardette J.L., and Rochdi A., submitted. Organic matter analysis by specular reflexion FTIR microspectroscopy. Bull.SNEAP.

Menet C., 1993. Matières organiques et uraninites des réacteurs fossiles d'Oklo: Analogues naturels des bitumes d'enrobage et du combustible irradié. Matières organiques et paragenèses minérales. CEA Internal Report, SCS. 93-30, 48 pages.

Robin P.L., Rouxhet P.G. and Durand B., 1977. Caractérisation des kérogènes et de leur évolution par spectroscopie infrarouge: fonctions hydrocarbonées. Advances in organic geochemistry, R. Campos and J. Goni eds, Enadisma, Madrid, 693-716.

Rochdi A. and Landais P., 1991. Transmission micro-infrared spectroscopy. An efficient tool for microscale characterization of coal. Fuel, vol 70, 367-371.


MO1
MO22
MO15
Absorbance
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
-0.06
0.14
-0.08
-0.10
-0.12
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

Appendix 1

Band (cm-1)	Vibration type	Chemical species	Abbreviation
3050	Stretching	Aromatic CH	aro
2955	Stretching (asymetric)	CH3	
2929	Stretching (asymetric)	CH2	
2870	Stretching (symetric)	CH3	ali
2855	Stretching (symetric)	CH2	
1735	Stretching	C=O Esters	
1702	Stretching	C=O Carbonyl, Carboxyl	C=O
1655	Stretching	C=O Conjug. ketones	
1600	Stretching	C=C	C=C
1460	In plane deformation	CH3 + CH2	CH3 + CH2
1380	In plane deformation	CH3	CH3
875	Out of plane deformation	Aromatic CH (1H adj)	
825	Out of plane deformation	Aromatic CH (2H adj)	garo
755	Out of plane deformation	Aromatic CH (4H adj)	

Table 1 : Assignment of absorption bands in IR spectra of organic matter

Samples	ali / c=c	ali / garo	dali / garo	dali / c=c	CH3 / CH3+CH2	c=o / ali	c=o / dali	c=o / c=c	c=o / garo
MO 1 Average	0.220	0.204	0.139	0.150	0.272	2.693	3.750	0.563	0.523
MO 3 Average	0.320	0.201	0.192	0.314	0.291	1.763	1.783	0.556	0.345
MO 14 Average	0.426	0.158	0.157	0.449	0.291	1.751	1.353	0.587	0.203
MO 15 Average	0.827	0.347	0.179	0.428	0.270	0.583	1.127	0.483	0.202
MO 22 Average	0.107	0.074	0.139	0.197	0.155	5.213	2.629	0.518	0.365

Table 2 : Average IR ratios values for the five samples

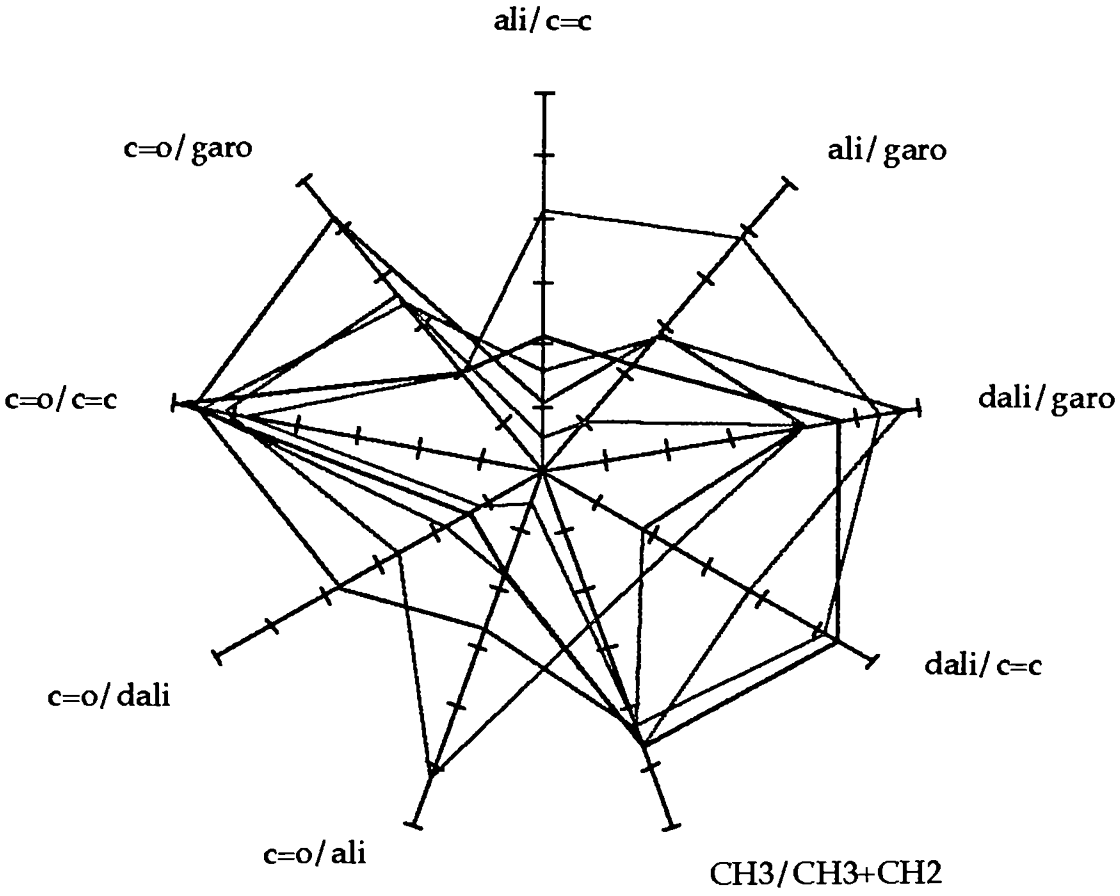
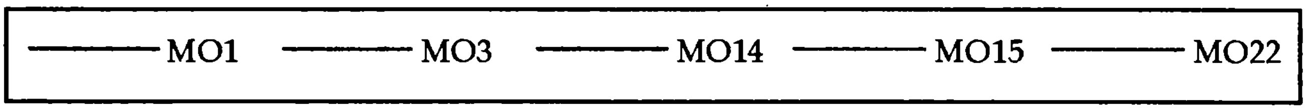


Figure : Chemical species average repartition in the five samples



Appendix 3

AQUEOUS CORROSION OF NUCLEAR GLASSES: INFLUENCE OF DISPOSAL CONDITIONS

Contractor:	CEA - CE Valrhô, DRDD/SCD
Contract No:	FI 2W 0027
Duration of Contract:	April 1991 - April 1995
Period Covered:	January - December 1993
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Geological disposal of vitrified high-level waste packages will expose the containment glass to multiple complex chemical reactions (involving the host rock, the engineered barrier materials and the nuclear glass) due to the presence of the water vector in the repository environment. The presence of environmental or local site materials affects (increases or decreases) the glass matrix corrosion rates and the degree of radionuclide containment. It is therefore essential to characterize and quantify the potential reaction mechanisms in a geological disposal complex. The investigation begins at laboratory scale; the experimental approach also allows the development of a nuclear glass dissolution model applicable to actual repository conditions.

Three major avenues of research will be investigated in a programme combining an experimental approach and modeling of relational processes: ① basic research on aqueous corrosion of nuclear glass; ② the effect of the host rock on R7T7 glass alteration; and ③ the development of models describing glass behavior in repository conditions.

B. WORK PROGRAMME

B.1 Basic research on aqueous corrosion of nuclear glass

1. The effect of glass composition on the initial dissolution rate, the solubility limit and equilibrium pH, and the role of new phases on glass dissolution kinetics will be investigated by varying the concentrations of the following components: MgO, SiO_2, Al_2O_3, B_2O_3 and fission product oxides.
2. Role of exterior ions: metallic cations (Al, Fe, Zn, Pb and Mg) and canister corrosion products; effect of the ionic strength.
3. Investigation of the interface gel layer: physical and chemical properties, thermodynamic properties and stability.

B.2 Influence of the disposal site

1. Equilibrium limits with various host materials: granite, clay (ref 448 and 802), schist and salt.
2. Parameter experiments at 90°C in the presence of schist (different types and grain sizes), clay, granite or salt (clear halite and cloudy halite).
3. Integral experiments with granite, clay and schist.

B.3 Development of a glass behavior model

1. Mechanistic model
2. Geochemical model (thermodynamics and kinetics of R7T7 glass dissolution, interactions between R7T7 glass and corrosion products, interactions between R7T7 glass and host materials: granite, clay or schist).

C. PROGRESS OF WORK AND OBTAINED RESULTS

Task B1: Basic Research on Aqueous Corrosion of Nuclear Glass

Effect of Glass Composition

The effects of MgO and SiO_2 on the aqueous corrosion stability of the glass were discussed in the preceding reports. The effects of the Na_2O, B_2O_3, Al_2O_3 and fission product oxide concentrations on glass corrosion are now being investigated through experiments with glass powder at high glass surface-area-to-solution-volume (*SA/V*) ratios (20 000 m^{-1}).

Role of External Ions

- *Effect of Metallic Cations*

The effects of metallic cations (Al, Fe, Zn, Pb and Mg) on the corrosion kinetics of R7T7 glass were assessed in two experimental configurations.

- Tests were conducted at low *SA/V* ratios under static conditions at imposed pH values, using a single cell from which all solution samples were taken. The initial solution was double-distilled water to which metallic cations were added in variable concentrations. The highly diluted test medium corresponded to a very slight degree of reaction progress, allowing us to investigate the effects of the cations on the initial glass dissolution rate R_0.
- Tests were also conducted at high *SA/V* ratios using glass powder with flowing solution. A different cell was used for each type of solution; samples of the outflowing solution were taken at regular intervals; the inflowing solution contained H_4SiO_4 at 90% of the saturation value with respect to the glass, as well as variable concentrations of metallic cations. All these experiments were carried out in duplicate. The high degree of reaction progress allowed us to assess the effect of cations on the glass dissolution rate under near-saturation conditions.

Most of the first series of tests in dilute media have now been completed, while some of the tests in saturated media have not yet been initiated. The test results will be discussed in the 1994 Semiannual Report.

- *Effect of Canister Corrosion Products*

A number of the R7T7 glass dissolution experiments in the presence of corrosion products from the NS24 (PC) steel canister have been completed and the alteration solutions analyzed. The test conditions were the following:

- 0.5 g of NS24 (previously altered in *aqua regia*) were placed in contact with R7T7 glass in water at 90°C and 50 m^{-1} for 1, 3, 7, 14, 28, 56, 84, 126, 186, 273 and 364 days;
- additional tests were conducted with 50 mg and 5 mg of NS24.

The test results were discussed in the 1992 Semiannual Report.

The experiments on the effects of simple oxides and hydroxides (Fe, Ni, Cr and Ti) have been completed, as have the tests to assess the effects of the temperature (50°C and 70°C) and the presence of "siliceous" additives (smectite, bentonite and silica gel). The test results are now being interpreted, and will be published in a later report.

- *Effect of Ionic Strength*

The effect of the ionic strength on the initial corrosion rate is now being investigated. R7T7 glass corrosion experiments were conducted with the following brine solutions: NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$ and $CaSO_4$. The alteration solutions are currently being analyzed.

Investigation of the Interface Gel

The R7T7 glass alteration gels are currently being analyzed.

Task B2: Influence of the Disposal Site

Equilibrium limits with various host materials

Experiments to determine the equilibrium limits of R7T7 glass in the presence of 5 environmental materials (granite, two clays, schist and salt) were conducted at 90°C with an *SA/V* ratio of 5800 m^{-1} for durations of 7 days to 1 year. All the experiments have been completed and the results have been analyzed (they will be presented in a later report).

The first results show that each medium imposes a different pH, different elemental concentrations in solution, and different degrees of glass corrosion. Although the two clay media were the most aggressive with respect to R7T7 glass during the first six months, very low corrosion rates were reached after one year in all the test media.

At the present time, no direct relation has been established between the pH, the Si concentrations and the glass corrosion rates.

Parameter experiments at 90°C

- *Alteration in the Presence of Schist*

The results of this investigation were discussed in the 1992 Annual Report.

- *Alteration in the Presence of Clay*

R7T7 glass alteration in two natural clays sampled from deep underground sites was studied for 1, 2, 3 and 6 months at 90°C. The clay was ultracentrifuged after the test to recover the leachate and perform elemental determinations and pH measurements. The results of this investigation will be presented in a later report.

- *Alteration in the Presence of Granite*

The results of this investigation were discussed in the 1992 Annual Report.

- *Alteration the Presence of Salt*

R7T7 glass corrosion tests are currently in progress with two types of salt, at temperatures of 90°C and 150°C, at an *SA/V* ratio of 70 m^{-1} for durations of 7, 14, 28, 42, 56, 70, 84, 91, 120 and 180 days and for 1 and 2 years. Only the 1 and 2-year tests have not yet been completed. The alteration solutions have been analyzed and the crystallized phases identified by X-ray diffraction.

Integral Experiments

The "TAV 6" experiment simulating a granite repository environment has been in progress for over 9 years. Glass alteration remains very slight, and is controlled by the pseudo-flow due to the solution sampling procedure. Four integral clay tests were initiated in 1992: two of them will be terminated after 6 months, and the others after 2 years. Two integral schist tests were also initiated in 1992 for periods of 6 months and 2 years.

Several integral "TAV"[1] experiments are included in this task to simulate different repository environments:

- Granite: the ongoing TAV 6 experiment was initiated over 10 years ago, in September 1983.
- Clay: 4 TAV experiments (TAV 21 to 24) were initiated in November 1992 with clays from two different formations encountered at different depths (448 m and 802 m) in the same borehole. The disposal concept selected for these tests was discussed in the 1992 Annual Report. Two of these tests were terminated after 8 months, and the other two are scheduled to be terminated after 24 months.
- Schist: a TAV experiment was initiated in November 1992, and a second will begin in January 1994.

The results of the TAV tests will be presented at a later date, when all the experimental findings are available.

Task B3: Development of a Glass Behavior Model

Mechanistic Model

This model was discussed in the 1993 Semiannual Report. The effect of the major parameters were quantified by simulations at 90°C using the LIXIVER code. We showed that the initial dissolution rate r_0 has very little effect on the calculated concentrations after the first three months. The pH affects the glass solubility C* and thus has only a very limited influence at values below 9. The CO2 partial pressure directly affects the glass dissolution rate by modifying the pH. The apparent silicon diffusion coefficient in the alteration film proved to be the most sensitive parameter taken into account by the LIXIVER code: very slight D variations result in very different calculated element concentrations.

A comparison between the calculated and experimental results showed that it was impossible to fit the short-term values (up to 90 days) using only a single diffusion coefficient for the entire experimental period. The parameter study showed that the only way to account for the experimental concentrations was to postulate a high D value for the first few days of dissolution, and a lower value for the longer intervals.

Geochemical Model

The results of geochemical modeling with the KINDIS code of R7T7 glass at 90°C in water in contact with different clays, and in contact with flowing water, are presented in detail in the 1993 Annual Report. The simulations were performed in collaboration with the CNRS (Surface Geochemistry Center, Strasbourg).

---

[1] *TAV: a French acronym for "Glass Alteration Test"*

List of Publications

1. N. GODON, T. ADVOCAT, P. JOLLIVET, F. DELAGE, S. GIN and E. VERNAZ, *Effect of Geological Repository Parameters on Aqueous Corrosion of Nuclear Waste Glass*, CEC Contract FI 2W CT 90 0027, 1992 Annual Report, CEA document SCD/93-01 (1993).
2. P. JOLLIVET, F. DELAGE, T. ADVOCAT, N. GODON and E. VERNAZ, *Effect of Geological Repository Parameters on Aqueous Corrosion of Nuclear Glass*, CEC Contract FI 2W CT 90 0027. Semiannual report: January-June 1993, CEA document SCD/93-22 (1993).

Effect of Insoluble Active Dissolution Fines on Fission Product Glasses

Contractor:	CEA - CE Valrhô, SCD
Contract No:	FI 2W - 0028
Duration of Contract:	March 1991 to February 1995
Period Covered:	January 1993 to December 1993
Project Leader:	N. Jacquet-Francillon

A. OBJECTIVES AND SCOPE

Insoluble particles, known as fines, present in fission product solutions consist of cladding fragments or undissolved fission products, notably platinoids. At La Hague, these fines are vitrified with the fission product solution in the T7 facility. Platinoids are found in soluble or insoluble form with other particles. Regardless of their initial state, the platinoid elements ruthenium, rhodium and palladium are insoluble in the glass.

As a result, the amorphous glass mass contains heterogeneous inclusions comprising notably highly radioactive Ru and Rh, with substantial thermal power. It is therefore necessary to ascertain whether the SON 68 18 17 L1C2A2Z1 reference glass composition is a suitable containment matrix for these active insoluble dissolution fines. The experimental programme will include the fabrication and characterization of glass rods containing actual active fines.

B. WORK PROGRAMME

B.1 Development of an analysis method for glass containing dissolution fines.
B.2 Development of a nondestructive gamma-scanning method to measure the radionuclide distribution and the true activity.
B.3 Fabrication of glass rods containing actual active fines; quantification of the fines, and notably the platinoids, in the glass.
B.4 Preparation of test specimens after gamma scanning.
B.5 Measurement of glass containment properties at room temperature and at 90°C; determination of glass alterability at 90°C.
B.6 Leaching of test specimens at 100°C in Soxhlet devices.
B.7 Characterization of glass microhomogeneity.
B.8 Repeat steps B.4 through B.7 on glass samples submitted to a heat treatment cycle.

C. PROGRESS OF WORK AND OBTAINED RESULTS

Progress and Results

A glass composition designated A130, containing actual fines from dissolution of fuel irradiated in the Advanced Prototype Boiler (CAP) at Cadarache, was produced in the Vulcain cell. The principal characterization tests specified in the contract have been completed on this sample.

- After heat treatment at 780°C, the same phases were observed in the heat-treated glass as in the as-cast specimens: platinoids in the form of ruthenium oxide or ruthenium metal, and palladium metal together with tellurium, chromites and calcium molybdate crystals.
- The crystallization density increased from less than 1% in the as-cast sample to 2.8% after heat treatment, probably because of the development of the calcium molybdate phase.

A second glass composition designated A131, containing fines from reprocessing fuel from the *Phénix* fast breeder reactor at Marcoule, was also produced in the *Vulcain* cell. This sample is currently being characterized.

- Gamma scanning showed a uniform ^{125}Sb and ^{137}Cs distribution in the glass, although a slight excess of ^{106}Ru was observed at the end of the casting phase.
- Specific activity measurements by gamma scanning differed from the expected activity calculated from the analysis results of the fines suspension for the following radionuclides: ^{106}Ru,^{125}Sb and ^{137}Cs. The gamma scanning results were 2 to 3 times higher than expected.
- The glass was submitted to acid dissolution (first in a mixture of HCl and HNO_3, then in HF) and analyzed by ICP and α and β spectrometry.
  The glass composition determined by chemical analysis was as expected.
  Radiochemical analysis confirmed the gamma scanning results, i.e. specific activities 2 to 3 times higher than expected for ^{106}Ru,^{125}Sb and ^{137}Cs.
  This acid dissolution method is unsuitable for analysis of the platinoids.
- Leach testing at 90°C showed satisfactory aqueous corrosion resistance. Corrosion was congruent and increased in a linear manner over 21 days. The glass corrosion rate calculated from the mobile element release rates was 0.15 $g{\cdot}m^{-2}d^{-1}$. The normalized mass losses for the platinoid elements after 21 days were about 600 times lower than for boron.

THE CORROSION OF NUCLEAR WASTE GLASSES IN A CLAY ENVIRONMENT : MECHANISMS AND MODELLING

Contractor :	NIRAS/ONDRAF Brussels
Contract N° :	FI2W0031
Duration of contract :	March 1991 - February 1995
Period covered :	January 1993 - December 1993
Project leader :	R. Gens (NIRAS/ONDRAF, coordinator)
Project leader SCK :	K. Lemmens

A. *OBJECTIVES AND SCOPE*

The present project is the third part of a programme which started in 1981. This programme studies the performance of various simulated HLW-glasses in one of the reference repository environments, the Boom clay, with the aim to elucidate corrosion mechanisms in clay media and to propose a source term for the radionuclide release into the nearfield. The objective of the present project is to enlarge the already existing database by the use of corrosion accelerating test conditions (accelerated tests) and more complex media (integrated tests) and to model the long term interaction between glass and clay environment, which is the final goal of the project. In the accelerated tests, SA/V (glass surface area to solution volume) and temperature are used as the corrosion accelerating parameters. To obtain a high SA/V the glass is powdered. In the integrated tests glass corrosion is studied in the presence of canister/overpack corrosion products and backfill.

The S.C.K./C.E.N (Mol, Belgium) was appointed for the practical execution of the programme.

B. *WORK PROGRAMME*

B.1. Inactive accelerated tests: powdered samples of glasses SON68 and SM539 are exposed to distilled water (DW), synthetic interstitial claywater (SIC) and a mixture of 500 g Boom clay and 25 g Fe_2O_3 per liter synthetic interstitial claywater (called "CCSICM + CP"). The SA/V values are 500, 2500 and 10000 m^{-1}, the experimental temperatures are 40, 90 and 150°C. The maximum test duration is 720 days.

B.2. Active accelerated tests: grains of glasses SON68 and SM539 are exposed to the same media as sub (B.1.). The glasses were doped with either Pu/^{134}Cs/^{90}Sr or ^{237}Np/^{99}Tc/^{55}Fe/^{241}Am. The SA/V value is approximately 400 m^{-1}. The experimental temperature is 90°C. The maximum test duration is 360 days.

B.3. Inactive integrated tests: a first series of powdered samples of glasses SON68 and SM539 is exposed to a mixture of 250 g Ca-bentonite, 250 g Boom clay and 25 g Fe_2O_3 per liter synthetic interstitial claywater. A second series of powdered glasses is exposed to a mixture of 397 g Boom clay, 21 g Cibelcor P40 cement and 21 g Fe_2O_3 per liter synthetic interstitial claywater. The SA/V values are 500 and 2500 m^{-1}. The experimental temperatures are 40, 90 and 150°C. The maximum test duration is 720 days.

B.4. Active integrated tests: grains of glasses SON68 and SM539 are exposed to a mixture of 250 g Ca-bentonite, 250 g Boom clay and 25 g Fe_2O_3 per liter synthetic interstitial claywater. The glasses are doped with the same radionuclides as for the active accelerated tests. SA/V, temperature and test durations are also the same as sub (B.2.).

B.5. Modelling of the dissolution behaviour of the glass matrices in the studied clay disposal surroundings.

Table I shows an overview of the 1991 - 1995 test programme.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Most tests with inactive glass samples were finished by the end of 1993. This is the case for the accelerated tests and the integrated tests with addition of bentonite. Most tests with addition of cement were also finished by this date. A selection of the accelerated and integrated tests in SIC and CCSICM+CP will however be restarted for durations of 1 and 2 years, because the concerning test containers of the first test series had lost more than 10 % of their original water content.

The accelerated and integrated tests with the Pu/^{134}Cs/^{90}Sr doped glasses were finished. The accelerated and integrated tests with ^{237}Np/^{99}Tc/^{55}Fe/^{241}Am doped glasses had been started, but none of the tests was finished.

In the course of 1992, it had been decided already that the existing computer codes for the simulation of the corrosion experiments of this programme had to be adapted to comply with recent findings. In 1993, the subsequent steps to reach this goal were pointed out.

Progress and results

B.1. Inactive accelerated tests

All accelerated tests with inactive glass samples were finished. Results are available for the tests with duration up to 360 days. Based on boron and litium plots as a function of the scaling factors SA/V.t and SA/V.$t^{0.5}$ (SA is the surface area of the glass sample, V is the leachate volume, and t is the test duration), diffusion appears in general to be rate limiting for the corrosion of SON68 and SM539 in DW and SIC. In CCSICM+CP, no general conclusions can be drawn so far. For the reason mentioned above, the results for the tests of 360 and 720 days in SIC and CCSICM+CP at 90°C of 360 days are probably not reliable. Most of these tests will be restarted.

B.2. Active accelerated tests

The tests with glass samples, doped with Pu, ^{134}Cs and ^{90}Sr are finished. There are indications that, for the tests in CCSICM+CP, the Pu and Am concentrations in solution, after filtration over 100000 MW cut-off membranes, increase with increasing SA/V. The radionuclides are released more congruently in the clay containing mixtures than in pure SIC. This is especially clear for glass SM539. For this glass, Pu is released at about the same rate as Cs and Sr in CCSICM+CP.

The tests with $^{237}Np/^{99}Tc/^{55}Fe/^{241}Am$ doped glasses were started in december 1993.

B.3. Inactive integrated tests

The integrated tests with inactive glass samples until 360 days were finished, except for the tests with cement at 150°C, for which only the duration of 90 days had been reached.

Results are available for the tests with bentonite at 40 and 90°C for the tests up to 360 days, and at 150°C for the tests up to 90 days. In general the solution pH is lower for the mixture of bentonite and Boom clay than for the mixture with only Boom clay (CCSICM+CP). Based on the boron concentrations in the solution, the glass corrosion rate would increase as a result of the partial replacement of Boom clay by bentonite at 40 and 90°C. At 150°C, the data are contradictory. At 90°C, the mass losses of the glass coupons do not show the same trend as the B data, but yet we do not consider these mass loss data as decisive.

Results are available for the integrated tests with cement at 40 and 150°C up to 90 days and at 90°C up to 180 days. In the tests with cement, the solution pH was higher than in CCSICM+CP. The glass coupon mass losses tend to be lower than in cement-free mixtures.

For the reason mentioned above, the results for some of the tests of 360 and 720 days in SIC and CCSICM+CP at 90°C of 360 days are probably not reliable. These tests will be restarted.

B.4. Active integrated tests

The tests with glass samples, doped with Pu, ^{134}Cs and ^{90}Sr are finished. The Pu concentration in solution tends to be smaller than in CCSICM+CP until 180 days, but the difference is small after 360 days, as a result of a strong increase in the bentonite containing mixture. The Am concentrations in solution and the ratio of the mobile leached Am over the total leached Am are lower in the bentonite mixture than in CCSICM+CP. This may be an indication for a higher binding capacity of the bentonite mixture for Am. The total released activities are not much influenced by the addition of bentonite.

The tests with $^{237}Np/^{99}Tc/^{55}Fe/^{241}Am$ doped glasses were started in december 1993.

B.5. Modelling

In 1992, we decided already that simulation of the data with the GLASSOL code could not be succesfull, because this code assumes a constant long-term corrosion rate, whereas a diffusion controlled long-term is more probable. In the course of 1993, a working scheme was pointed out for the adaptation of the model and to gain some supplementary necessary information. It consists of the following :

(1) determination of the diffusion and sorption of Si in Boom clay mixtures by means of flow-through and percolation experiments with ^{32}Si
(2) application of the PHREEQE geochemical code on the system glass-claywater, in order to obtain information about the secondary phases that are formed in the solution.
(3) modelling of the corrosion in distilled water and clay-claywater media at 90°C. This comprises the elaboration of a conceptual and a mathematical model, and the application of the mathematical model.

Table I : Overview of the corrosion tests of the 1991-1995 programme

Test Conditions	Accelerated tests		Integrated tests	
	Inactive	Active	Inactive	Active
Temp (°C)	40 90 150	90	40 90 150	90
Media	DW SIC CCSICM+CP	SIC CCSICM+CP	BC+SIC+CP+BF1 BC+SIC+CP+BF2	BC+SIC+CP+BF1
SA/V (m^{-1})	500 2500 10000	400	500 2500	400
Duration (days)	20(1,2) 28(1,3) 90 180(1) 360 720(3)	90 180 360	20(1,2) 28(1,3) 90 180(1) 360 720(3)	90 180 360

DW : distilled water
SIC : synthetic interstitial claywater
CCSICM: concentrated clay - synthetic interstitial claywater mixture
BC : Boom clay
CP : corrosion product (Fe_2O_3)
BF1 : backfill bentonite
BF2 : backfill cement
(1) : not at 40°C
(2) : not at 90°C
(3) : not at 150°C

<u>Title</u> : **Basic Leaching Tests for Pure β Long-lived Emitters in Radioactive Wastes**

Contractor	:	CEA Cadarache
Contract No	:	F12W/CT-90/0032
Duration of contract:	:	01.05.1991 to 30.04.1994
Period covered	:	01/01/1993 to 31/12/93
Project leader	:	C.Riglet (CEA Cadarache)

A. OBJECTIVES AND SCOPE

The technical solution under study to store long-lived radioactive wastes consists in :
- embedding the wastes in suitable confining matrixes (glass, cement, bitumen);
- and burying the coats in stable geological sites in which the radioactivity will decrease naturally.

The evaluation of the confining capability of the matrixes used - determined by implementing leaching tests - will enable us to assess the reliability of the process. Safety studies indicate that the long-term risk mainly stems from long-lived radionuclides.

In this context, the research contract is related to a basic leaching study of pure β and α long-lived emitters in real and simulated wastes, in order to collect basic information about these radionuclides which are critical for the safety analysis of disposal storage. No reliable data are available at present for these species.

B. WORK PROGRAMME

B.1. (CEA - CIEMAT)
- Working organization
- Setting-up of a working programme
- Harmonization of the leaching procedures

B.2. (CEA)
- Definition and manufacturing of the samples
- Implementation of the leaching experiments
- Collection of the data and interpretation

B.3. (CIEMAT)
- Selection of the types of wastes, the cement formulae and of the elements to be taken into account

- Implementation of the leaching experiments with simulated wastes
- Optimization of the analytical procedures
- Collection of the data and interpretation

B.4. (CIEMAT)

- Implementation of the leaching experiments with real resins
- Collection of the data and interpretation

B.5. (CEA - CIEMAT)

- Interpretation of the data
- Comparative study of the various experiments
- Final evaluation

C. PROGRESS OF WORK AND RESULTS OBTAINED

STATE OF ADVANCEMENT

B1 : This task has been completed.

B2 : CEA programme

In 1993, the last evaporator concentrate / cement coats were manufactured. Table I shows the state of advancement of the various leaching tests in progress :

- As mentioned previously, all leaching tests of evaporator concentrate / bitumen coats were stopped after a leaching period of 180 days, in view of the drastic degradation of the samples in contact with water and the consequent high releases of the embedded elements ;
- For the "STE3 LH" sludge / bitumen samples, the scheduled leaching period of 455 days was completed in both demineralized and Evian waters as well as in leachants at pH of 6 and 8 ;
- As regards the "STE3 LH" and evaporator concentrate / thermo-setting resin (RTD) coats, a leaching period of 365 days was completed in both demineralized and Evian waters, and in water with EDTA ;
- The scheduled leaching tests for the evaporator concentrate / cement samples were carried out as soon as the 3-month curing period was completed. A cumulative period of 45 days was reached in both demineralized and Evian waters.

Furthermore, considerable chemical characterization work of the leachates as well as collection and interpretation of the data was realised.

B3 and B4 : CIEMAT programme

The experimental work is also proceeding favourably. The reference leaching tests in demineralized water at different temperatures (25, 40 and 50°C) and the tests performed in "El Cabril" underground water and in leachants containing complexing agents (EDTA and TMA at 40°C) were completed during the period under review. Almost all the analytical results are now available.

As far as the leaching tests with real resins are concerned, a cumulative leaching period of more than 200 days was achieved, but few analytical results are available at this time.

B5 : CEA – CIEMAT

From the data obtained from the reference leaching tests of ion-exchange resin embedded in cement, calculations were made in order to verify that the leachability of the cemented specimens was controlled by a diffusion process.

PROGRESS AND RESULTS

B.2.1. Manufacturing of the samples :

Results concerning the bituminous coats reported in the 1992 annual report showed much lower leachability of ThO_2 compared to UO_2, leading to an undetectable release of Th whatever the leaching conditions. In the **evaporator concentrate / cement** samples therefore, thorium was replaced by europium and ruthenium. In addition, radioactive ^{137}Cs, ^{106}Ru and ^{152}Eu were also added to the samples in order to allow more sensitive radiochemical detection of those elements.

The synthetic waste / cement mixture was made according to the same formula as that used to embed the evaporator concentrates from the PWR nuclear power plant. The manufacturing process included the following sequences :

- Preparation of the solid phase, the composition of which is reported in Table II ;
- Preparation of the mixing phase (without any radioelement), the composition of which is reported in Table III ;
- Addition of the radioelements ;
- Mixing and homogenization ;
- Casting of the samples.

Because of the presence of sodium borate at high concentrations in the wastes, the drying period was considerably increased (72 hours instead of 4 hours), and the curing period was set at 3 months instead of the usual 28 days.

B.2.2. Implementation of the leaching tests :

Leaching tests of the evaporator concentrate / cement coats in demineralized and Evian waters are in progress. The leaching procedure as well as the analytical operating conditions are extensively described in the 1991 annual report. Three leaching renewal steps (3, 12, 30 days) have been completed for each of the two implemented tests. Nevertheless, the results are not yet available.

B.2.3. Collection of the data and interpretation :

Leachants at pH 6 and 8 (pH controlled by a CO_2/HCO_3^- buffer), lead to a gradual degradation with time of the **"STE3 LH" sludge / bitumen** samples, unlike to the demineralized and Evian water media. From the chemical characterization of the altered layer, it appears that the degradation stems from premature chemical ageing (change in the composition of the generic families of the matrix) of the bitumen in contact with leachants containing high concentrations of bicarbonate ions (as described in the literature in the case of sodium hydroxide solutions). Whatever the leaching conditions, the leaching rates of the elements studied tend to a constant limit. The orders of magnitude are 4.E-07 cm/day for U, 3.E-06 cm/day for Tc and 8.E-06 cm/day for I.

The **evaporator concentrate / bitumen** coats undergo drastic degradation in contact with the leachant, because of the dehydration of the embedded salts at the manufacturing stage followed by a rehydration during the leaching stage. This results in poor confinement of the wastes in the bitumen. Those experiments were stopped after a leaching period of 180 days.

"STE3 LH" sludge and evaporator concentrate/thermo-setting resin coats :

No major degradation of those samples was observed, whatever the leaching conditions.

Among the elements studied, only the leachability of uranium is slightly affected by the nature of the leachant : the global increase of the releases in solutions containing CO_3^{2-} and EDTA is probably connected to the formation of highly stable complexes in those media.

The leaching rates of the elements U, Tc and Cs in the evaporator concentrates (of about 2.E-06, 3.E-04 and 3.E-04 cm/day respectively) are higher by a factor of 5 to 10 as compared to "STE3 LH" sludges. In contrast, neither the composition of the leachants, nor the nature of the matrix, nor the nature of the waste affect the leaching rates (of about 2.E-07 cm/day) of I. Thorium, which is highly insoluble, was never detected in any of the leaching tests carried out until now.

B.3.1. Reference leaching tests :

Because of visible degradation (cracking and crumbling) of the formula 2 specimens (observed at the end of the leaching stage), the leaching parameters of the ^{63}Ni and ^{90}Sr incorporated into these samples are much higher and much more erratic than in the formula 1 samples.

However, the leaching parameters of the β emitters studied and also of the non-radioactive elements seem to be quite independent of the leaching temperature (between 25°C and 50°C). The cumulative leached fraction data show rather a slight increase of leachability with temperature but this variation is not significant enough from the point of view of the incremental leaching rate.

The leaching data fit the well-known diffusion equation derived from Fick's laws pretty well and the calculated diffusion coefficients (Table IV) decrease with the radii of the hydrated ions. These correlations are in accordance with a process strongly controlled by a diffusion phenomenon.

B.3.2. Leaching tests with complexing agents :

The incremental leaching rates and the cumulative leached fractions, were calculated with the analytical results from both Formula 1 and Modified Formula 2. Some of these data are reported in Table V. Graphic representations of the incremental leaching rate data of ^{63}Ni are shown in Figure 1.

EDTA solutions, as compared to demineralized water, produce a higher modification of the leachability of the β emitters studied and also of the majority of the non-radioactive elements in both Formula 1 and Modified Formula 2 samples. However, the Modified Formula 2 specimens are less affected by the effects of EDTA than the Formula 1 samples.

Except for ^{63}Ni and Al in Formula 1 samples, solutions of trimethylamine (degradation products of ion-exchange resins), when compared to demineralized water, do not produce a significant change in the leachability of either the β emitters studied or the non-radioactive elements.

A slight decrease of the leachability of ^{90}Sr, ^{63}Ni and Al is observed when the "El Cabril" underground water is used as a leachant.

B.4.1. Leaching tests with real resins :

The very first data show that, in both Formula 1 and Modified Formula 2 specimens, the leaching rates vary according to the following order :

$$^{137}\text{Cs} < {}^{90}\text{Sr} < {}^{63}\text{Ni} < {}^{60}\text{Co}$$

As expected, the leachability of those radionuclides decreases as the radii of the hydrated ions increase.

In both Formula 1 and Modified Formula 2 samples, the leachability remains lower in the "El Cabril" underground water than in demineralized water.

TABLE I

STATE OF ADVANCEMENT OF THE LEACHING TESTS IN PROGRESS.

Matrix	**Wastes**	**State of advancement**							
		Leaching conditions							
		Demineralized water	EVIAN water	Water pH = 6	Water pH = 8	Water with EDTA	Water at 25, 40, 50°C	Water with complexants from REI	"EL CABRIL" water
Bitumen	"STE3 LH" sludges	455 days End	455 days End	455 days End	455 days End				
	Evaporator concentrates	180 days End	180 days End	180 days End	180 days End				
RTD	"STE3 LH" sludges	365 days	365 days			365 days			
	Evaporator concentrates	365 days	365 days			365 days			
Cement	Evaporator concentrates	45 days	45 days						
	Synthetic resins					*455 days End*	*455 days End*	*455 days End*	*455 days End*
	Real resins						*270 days*		*270 days*

CEA Programme *CIEMAT Programme*

RTD : Thermo-setting resin
REI : Ion-exchange resin

TABLE II

MANUFACTURING OF THE EVAPORATOR CONCENTRATE / CEMENT COATS : Composition of the solid phase.

Components	**Concentration (% w./cement coat)**
Cement CPA55	54.1
Sand from Fontenay	39.7
Lime	3.18
AgI	0.003
TOTAL	**96.98**

TABLE III

MANUFACTURING OF THE EVAPORATOR CONCENTRATE / CEMENT COATS : Composition of the mixing phase.

Element	**Chemical form**	**Concentration (% w./cement coat)**
B	H_3BO_3	2.47
Na	NaOH	0.46
Cs	CsCl	0.009
Ru	$RuCl_3$	0.0035
Eu	$Eu(NO_3)_3$	0.0043
U	$UO_2(NO_3)_2$	0.074
	TOTAL	**3.02**

TABLE IV

EXPERIMENTAL RESULTS FOR THE IMMOBILIZED ION-EXCHANGE RESINS : REFERENCE LEACHING TESTS - FORMULA 1 : CALCULATED DIFFUSION COEFFICIENTS

TEMPERATURE	CONSTITUENT	SLOPE	INTERCEP	CORRELATION COEFFICIENT	EFFECTIVE DIFFUSION COEFFICIENT
25 °C	K	1.34 E-2	2.35 E-1	0.9585	8.65 E-5
	Na	6.53 E-3	1.70 E-1	0.9948	2.05 E-5
	Sr-90	1.09 E-3	3.27 E-2	0.9871	5.73 E-7
	Ca	1.07 E-4	7.74 E-4	0.9776	5.52 E-9
	Mg	1.78 E-5	1.16 E-3	0.9248	1.53 E-10
	Al	2.02 E-5	1.78 E-3	0.9369	1.97 E-11
	Fe	2.39 E-5	-1.05 E-4	0.9689	2.75 E-10
	Ni-63	5.22 E-6	-2.77 E-5	0.9769	1.31 E-11
40 °C	K	1.27 E-2	3.29 E-1	0.9997	7.77 E-5
	Na	6.63 E-3	1.84 E-1	0.9778	2.11 E-5
	Sr-90	8.15 E-4	7.20 E-2	0.9995	3.20 E-7
	Ca	8.56 E-5	9.32 E-4	0.9501	3.53 E-9
	Mg	7.03 E-5	3.14 E-4	0.9048	2.38 E-9
	Al	4.37 E-5	1.94 E-3	0.9780	9.20 E-10
	Fe	1.43 E-5	5.14 E-6	0.9670	9.85 E-11
	Ni-63	4.46 E-6	-5.30 E-6	0.9595	9.59 E-12
50 °C	K	1.44 E-2	3.84 E-1	0.9998	9.99 E-5
	Na	5.91 E-3	2.38 E-1	0.9894	1.68 E-5
	Sr-90	6.11 E-4	8.56 E-2	0.9811	1.80 E-7
	Ca	1.13 E-4	1.15 E-3	0.9372	6.16 E-9
	Mg	2.53 E-5	8.16 E-4	0.9003	3.08 E-10
	Al	4.99 E-5	2.36 E-3	0.9617	1.20 E-9
	Fe	1.35 E-5	1.75 E-5	0.9435	8.78 E-11
	Ni-63	1.27 E-5	-6.39 E-5	0.8983	7.77 E-11

TABLE V

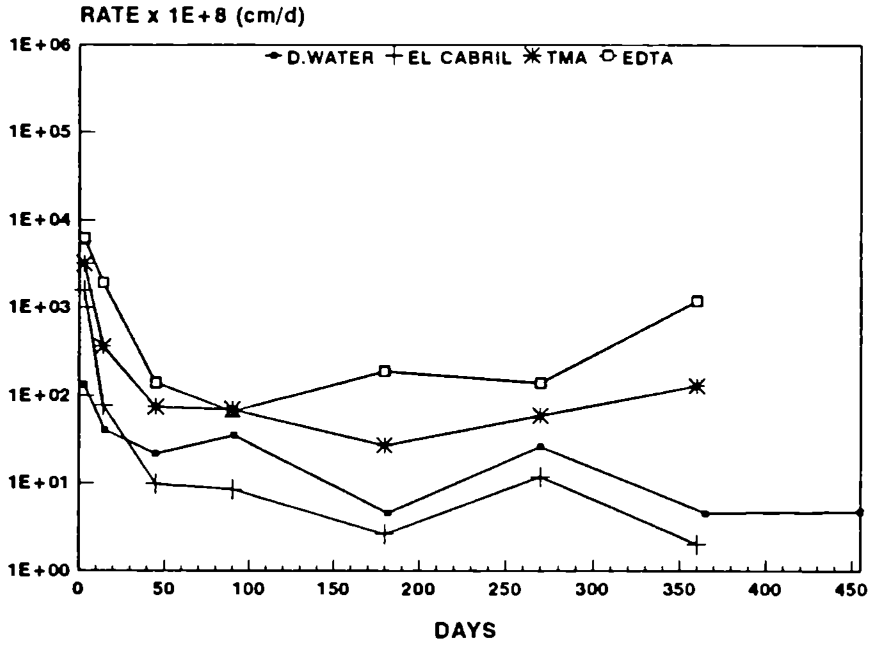
EXPERIMENTAL RESULTS FOR THE IMMOBILIZED ION-EXCHANGE RESINS : LEACHING TESTS WITH COMPLEXING AGENTS - FORMULA 1 : INCREMENTAL LEACHING RATES (in cm/day)

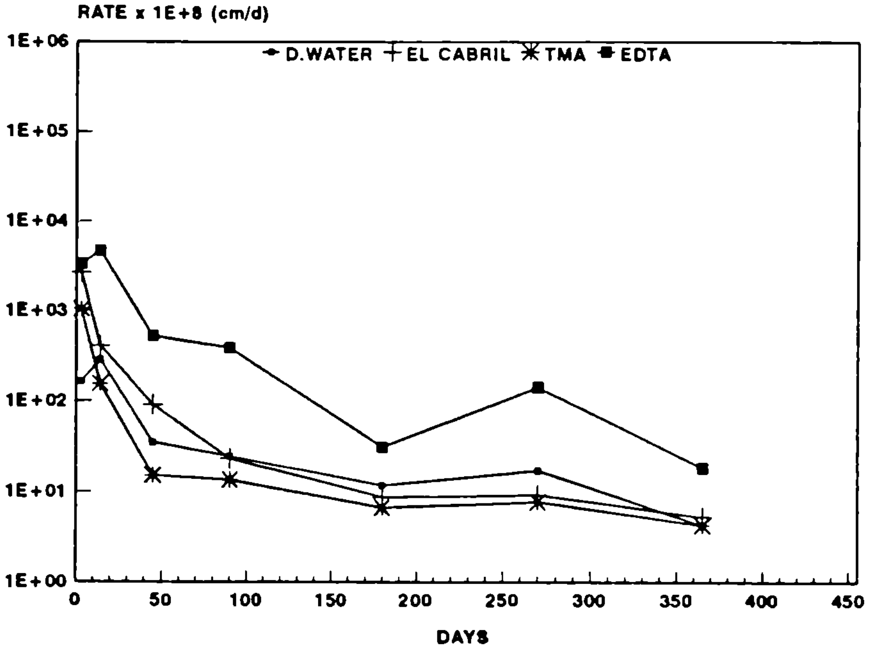
ELEMT	AGENT	CUMULATIVE LEACHING TIME (DAYS)							
		3	14	45	90	180	270	360	452
K	EDTA	2.2E-1	3.9E-1	4.6E-1	5.5E-1	6.6E-1	7.0E-1		
	TMA	2.0E-1	3.8E-1	5.0E-1	5.5E-1	5.9E-1	6.2E-1		
	E.C.W.	2.0E-1	3.0E-1	4.0E-1	4.8E-1	5.4E-1	5.7E-1		
	D. W.	1.9E-1	3.3E-1	4.0E-1	4.5E-1	5.1E-1	5.4E-1	5.7E-1	6.0E-1
Na	EDTA	2.4E-1	4.3E-1	5.2E-1	6.4E-1	8.8E-1	9.6E-1		
	TMA	2.1E-1	4.0E-1	5.4E-1	5.8E-1	6.2E-1	6.5E-1		
	E.C.W.	2.1E-1	3.4E-1	4.6E-1	5.4E-1	6.3E-1	6.7E-1		
	D. W.	1.2E-1	1.9E-1	2.2E-1	2.4E-1	2.8E-1	3.0E-1	3.1E-1	3.2E-1
Sr 90	EDTA	2.8E-2	4.5E-2	5.7E-2	6.8E-2	8.1E-2	8.5E-2	8.8E-2	
	TMA	3.1E-2	4.4E-2	4.8E-2	5.1E-2	5.6E-2	5.8E-2	6.0E-2	
	E.C.W.	2.0E-2	2.1E-2	2.3E-2	2.5E-2	2.8E-2	3.1E-2	3.3E-2	
	D. W.	5.9E-2	6.9E-2	7.4E-2	8.0E-2	8.3E-2	8.6E-2	8.8E-2	8.9E-2
Ca	EDTA	1.1E-2	1.5E-2	1.8E-2	2.1E-2	2.7E-2	3.2E-2		
	TMA	2.4E-3	2.5E-3	2.5E-3	2.8E-3	3.0E-3	3.4E-3		
	E.C.W.	3.0E-4	3.6E-4	3.8E-4	6.5E-4	9.6E-4	1.3E-3		
	D. W.	7.4E-4	1.0E-3	1.7E-3	1.8E-3	1.9E-3	2.5E-3	2.6E-3	2.7E-3
Mg	EDTA	1.3E-4	2.4E-4	4.4E-4	9.4E-4	1.5E-3	1.7E-3		
	TMA	1.1E-4	1.6E-4	2.2E-4	4.1E-4	5.7E-4	8.2E-4		
	E.C.W.	Mg concentrations in leachaetes and in "El Cabril" water were similar							
	D. W.	4.9E-4	6.4E-4*	8.6E-4*	9.9E-4	1.1E-3	1.7E-3	1.7E-3	1.7E-3
Al	EDTA	9.3E-3	1.1E-2	1.2E-2	1.2E-2	1.2E-2	1.2E-2		
	TMA	7.5E-4	3.0E-3	3.5E-3	4.0E-3	4.2E-3	4.4E-3		
	E.C.W.	2.9E-4	3.6E-4	4.6E-4	5.7E-4	6.3E-4	6.6E-4		
	D. W.	1.0E-3	2.0E-3	2.3E-3	2.4E-3	2.5E-3	2.6E-3	2.8E-3	2.9E-3
Fe	EDTA	4.8E-5	3.3E-4	4.1E-4	7.0E-4	9.7E-4	1.1E-3		
	TMA	6.7E-5	1.1E-4	1.3E-4	2.0E-4	2.2E-4	2.2E-4		
	E.C.W.	7.8E-5	1.2E-4	1.3E-4	2.4E-4	2.7E-4	3.0E-4		
	D. W.	3.0E-5	1.0E-4	1.4E-4	1.6E-4	1.8E-4	2.3E-4	2.7E-4	3.3E-4
Ni 63	EDTA	2.4E-4	5.1E-4	5.6E-4	6.0E-4	8.2E-4	9.8E-4	2.4E-3	
	TMA	1.2E-4	1.7E-4	2.0E-4	2.4E-4	2.7E-4	3.4E-4	4.9E-4	
	E.C.W.	6.1E-5	7.2E-5	7.6E-5	8.0E-5	8.3E-5	9.7E-5	9.9E-5	
	D. W.	5.1E-6	1.1E-5	2.0E-5	4.0E-5	4.6E-5	7.0E-5	8.1E-5	8.8E-5

E.C.W.: "El Cabril" underground water. D.W.: Demineralized water.

FIGURE 1

LEACHING RATES OF ^{63}Ni :
Leaching tests with complexing agents
Formula 1 (up) and Modified Formula 2 (down)





Title: **Chemistry of the Reaction of Fabricated and High Burnup Spent UO_2Fuel with Saline Brines**
Coordinator: Kernforschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgungstechnik, B. Grambow, A. Loida, N. Müller, H.Geckeis, K. Friese
Participant: Empresa Nacional de Residuos Radiactivos S.A., Departamento de Ingenieria (ENRESA), J. Gago
Subcontractor: Universidad Politecnica de Cataluña (UPC), I. Casas, J. de Pablo, J. Giménez, M.E. Torrero
Contract No. **F12W/0055**
Duration of contract: 1.3.1991 to 28.2.1995
Period covered: 1.1.1993 - 31.12.1993
Project Leader: B.Grambow

A. Objectives and Scope

The research program aims at characterization and qualification of the chemical durability of unprocessed high burnup UO_2 fuel as a barrier against radionuclide release for disposal sites in salt formations. The reaction behavior of the fuel with saline brines is going to be studied as a function of time, temperature, redox potential, and surface area in order to give insight into the corrosion mechanisms and sources of radionuclide release. Additionally, the solubility of unirradiated UO_2 in salt brines is studied for comparison with the reaction behavior of the irradiated material in order to identify radiolysis and burnup effects and in particular to identify and quantify solubility effects in the degradation of the fuel matrix. Eventually, the ongoing work will provide a basis for modeling, bridging over the gap between experimental results and performance assessment for long-term storage of the fuel in a repository in salt formations in case of brine intrusion.

B. Work Program

I. General preparations, analytical techniques, and sample preparations

II. Characterization of the durability of spent UO_2-fuel in saturated NaCl brines

III. Solubility tests with unirradiated UO_2

IV. Modeling of the reaction behavior of spent fuel with salt brines

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the reference year high burnup spent fuel samples (single mm-sized fragments, cm-sized pellets, μm-sized powders) were corroded in non buffered NaCl solutions (initial pH ca. 7) under Ar-atmosphere, partially in the presence of metallic iron powder (effect of the corroding canister) under static conditions. The accumulated corrosion time has reached about 500 days. Samples of the leachate were taken after 40, 110, 200 and 440 days. Radiochemical separation techniques were employed and leach solutions were analyzed. Additionally, sampling and analyses of fission and radiolysis gases, which were released or formed in the course of corrosion were performed.

Dissolution tests with unirradiated UO_2 in different salt brines have been carried out, in order to study such effects as pH, initial sample treatment, redox potential on UO_2 corrosion. As a function of time, corroded solid samples were investigated by means of X-ray Photoelectron Spectroscopy in order to study the oxidation state of their surface. A preliminary model is being evaluated describing the effect of oxidation state of uranium and corrosion rates rates on UO_2 dissolution.

Progress and results

I. General preparations, analytical techniques, and sample preparations

Hot cell equipment was improved, in particular an apparatus was designed, constructed and tested, allowing remote automatic solution sampling with a syringe. A centrifuge was installed in the hot cell and used for ultrafiltration of solution samples. The sampling of gases, formed in the course of corrosion were carried out by means of a system of two gas collecting cylinders (stainless steel, 50 cm^3, preevacuated to 10^{-6} mbars), which were connected with the interior of the autoclave by one of the ball valves, located on the lid. Analyses of the gas samples were performed by using a quadrupole mass spectrometer (BALTZERS). Radiochemical analyses and separation techniques were employed allowing analyses of the nuclides Pu238, Pu239/240, Pu241, Am241, Am243, Cm244, Cm242, Np237, Np239, Tc99, Cs 134, Cs137, Ru106, Ag110m, Eu154, Eu155, Ce144, Sr90, Sb125 and Uranium.

II. Characterization of the durability of spent UO_2-fuel in saturated NaCl brines

Corrosion tests comprise (1) "washing" steps, where the Cs gap inventory should be removed by exposing the fuel to the leachant (95% saturated NaCl or deionized water) under Ar atmosphere for two periods of one month and afterwards replacing the total solution volume by fresh leachant. Subsequently (2) static corrosion of the fuel samples is initiated. Aliquots of the solution are sampled periodically under Ar atmosphere and the time dependence of the spent fuel dissolution behavior is deduced exclusively from analyses of filtered and ultrafiltered solution samples. At test termination the final solution volume will have been reduced to about half of its initial value, solid samples will be analyzed for surface alteration effects and in particular for identification of solid reaction products.

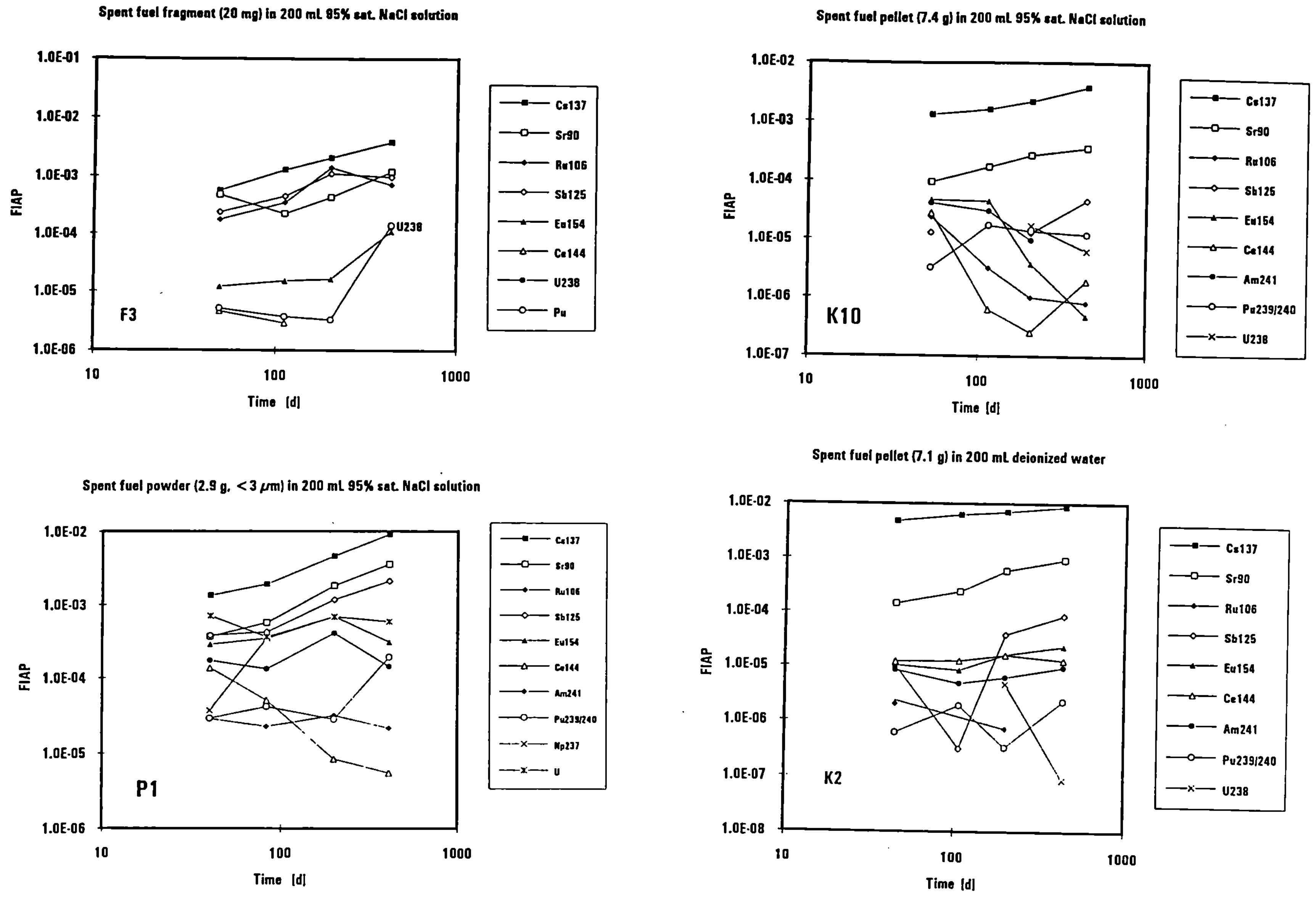


Fig. 1: Fraction of inventories of various radionuclides in the aqueous phase (FIAP), obtained after exposure of spent fuel samples for 440 days to 200 mL 95% saturated NaCl solution. Note: Samples were washed twice in the leachant for periods of 1 month each. Data from wash solutions are not included in the Figures (see annual report 1992). Zircalloy cladding remained attached on samples K 2 and K 10, zircalloy cladding was added to sample P 1.

II. 1. Radionuclide release into the aqueous phase.

The cumulative Cs releases ("gap release") from pellet sized fuel/cladding segments and from individual fragments are similar (about 2% of the total inventory), indicating that Cs is homogeneously distributed on all fracture surfaces and solution has penetrated all fractures within the fuel segment. With powdered fuel, all grain boundaries are expected to be exposed to the solution and the major Cs release occurs within few minutes of ultrasonic cleaning. Cumulative release is about 3.5% of the inventory, of which 1.5% (=3.5% - 2% gap inventory) may be attributed to release from grain boundaries.

For the other nuclides the results from dissolution of powdered fuel, a fuel pellet and an individual fragment in 95% saturated NaCl solutions are given in Fig. 1 (next page) expressed as FIAP-values (Fraction of the inventory in the aqueous phase). Respective data of dissolving a fuel pellet in deionized water are included for comparison. The released quantities of matrix bound radionuclides Sb125, Eu154, Am241, Pu239/240, Sr90, Ru106 and Ce144 are in most cases between $3*10^{-4}$ and $3*10^{-6}$.

Results from analyzing ultra filtered and micro filtered solution samples were the same for Ag, Sr, Sb, and Cs and differ slightly for actinides, Ru and rare earth elements but never by more than a factor of three. Colloid formation was not enhanced in the presence of fuel powder or of iron.

Effect of iron

The effect of iron and/or iron corrosion products on the mobility of radionuclides is illustrated by the data given in Fig.2. The presence of iron effectively reduces the solution concentration of all radionuclides, except of Cs and fission gases (see above). The cumulative release of Cs was more than 4% of the inventory after 200 days, a value higher than the sum of gap and grain boundary inventories of fuel powder. The decrease in radionuclide mobility may indicate increased stability of the fuel matrix at the lower redox potential or may be due to the fact that radiogenic oxygen is effectively consumed by iron corrosion. However, low release of other fission products and of actinides may alternatively be a result of sorption on iron. More work is necessary, before the effect of iron can be understood.

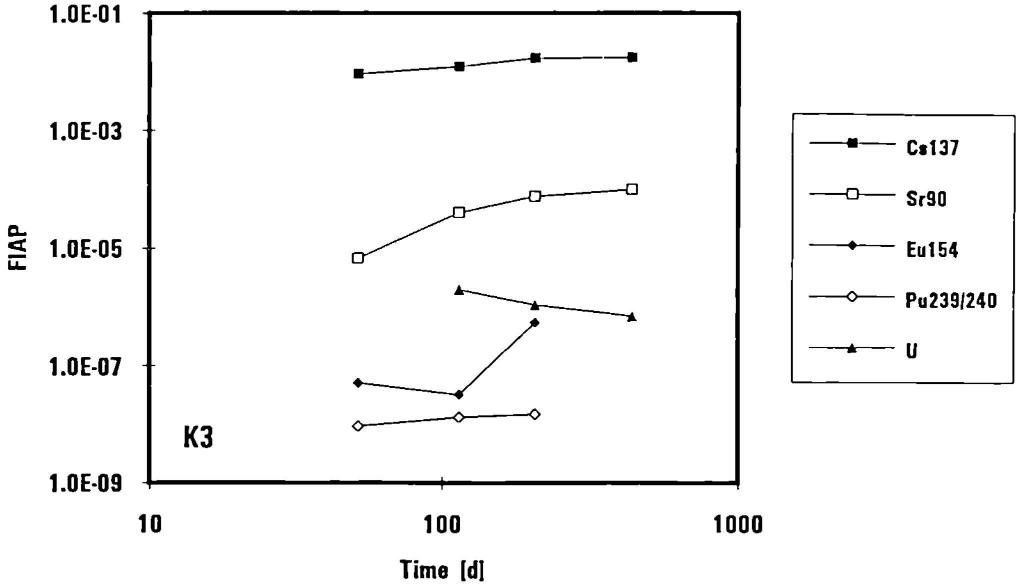


Fig. 2: Effect of the presence of iron (8.5 g powder, grain size < 10 µm) on the dissolution process of a fuel pellet (7 g) in 200 mL 95% saturated NaCl solution. Fraction of inventories of various radionuclides in the aqueous phase (FIAP)

II.2 Release of fission and radiolysis gases.

The fission gases Xe and Kr were measured in isotopic ratios which match predictions by the KORRIGEN code. H_2 gas was detected in all experiments, resulting from radiolysis and in the presence of iron additionally from the corrosion of iron. Radiolytic H_2 production is directly proportional to fuel sample mass and independent on the sample geometry. In a half year 2.9 g of powder generated ca. 3 Vol% H_2 whereas 7 g pellets generated 7 Vol% H_2 in 200 mL gas volume of ca.1 atm). This finding may help to distinguish between alpha- and gamma-radiolysis. As the escape depth of alpha-particles out of the fuel is limited to few µm, one would expect much higher specific H_2-production for powdered fuel samples than for fuel pellets, if H_2 radiolysis resulted mainly from alpha-radiolysis. This is not the case and we may use this as an indication that mainly gamma-radiolysis is responsible for H_2-formation. About 30% less H_2 was produced in the experiments using deionized water when compared to NaCl solutions. Only traces of N_2 (<0.2 Vol%) where observed in the reaction vessel, indicating effective sealing of the autoclaves against the hot cell atmosphere. Oxygen contents in experiments with fuel pellets were about 1 Vol%, clearly resulting from radiolysis, because air is absent. The measured partial pressures of Kr and Xe were compared with the fission gas inventories calculated by the KORRIGEN code. In the experiment K 4 (spent fuel pellet + Fe-powder) 4% of the Kr and 6.6% of the Xe inventory were released within 60 days whereas in the comparing experiment K3 (spent fuel pellet + Fe-powder) the respective numbers are 8% for Kr and 13.7% for Xe after 139 days.

II.3 Behavior of radionuclides in the spent fuel corrosion process

Sr90 release data were found to be useful in indicating the kinetics of the degradation of the fuel matrix. Release of Tc99, Np237 and Sb125 occured with a similar rate than that of Sr, hence, release of these elements is controlled by the kinetics of the degradation (oxidation, dissolution) of the fuel matrix. Preferential release of Cs134/137 was observed, representing release from grain boundaries. Even at low reaction progress values (experiments with single mm sized fragments in large solution volumes) the solution concentrations of U, Pu, Am, and REE were significantly lower than anticipated from the extent of fuel matrix dissolution. Concentrations are controlled by a combination of sorption, precipitation and coprecipitation phenomena. The maximum concentrations of Pu and U in the tests are close to reported solubility limited concentrations in pure 5m NaCl solutions, whereas Am concentrations remain more than five orders of magnitude lower than the solubility limit of the expected stable phase $Am(OH)_3$.

The presence of iron effectively reduces the solution concentration of all measured radionuclides (except Cs).

III. Solubility tests with unirradiated UO_2

The dissolution of unirradiated UO_2 has been studied as a function of pH and initial sample treatment under oxidizing conditions, with special attention to the U(VI)/U(IV)-ratio on the samples surface.

UO_2 samples (7,8 g) with particle sizes of 100 - 300 and 900 - 1100 µm were corroded into 150 mL of 0,01 m $NaClO_4$ in different Teflon vessels at room temperature. The pH values were adjusted to 4 or 8 by addition of $HClO_4$ or CO_2-free NaOH solutions. Oxidizing conditions were achieved by using 5% O_2 in N_2 flux.

The release of uranium was found to be significant lower at pH 8, compared to that obtained at pH 4. A decrease of release rates is observed in both cases after a relatively fast initial dissolution. The moles of uranium released at pH 4 and pH 8 as a function of time are shown in Fig.3.

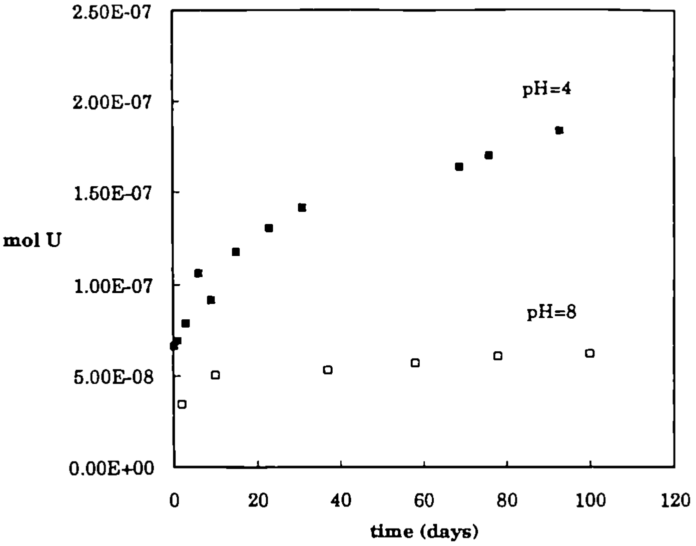


Fig. 3: Release of uranium after corrosion of unirradiated UO_2 (7,8g) into 150 mL of 0,01 m $NaClO_4$ at pH 4 and pH 8 as a function of time

The rather high initial release has been explained taking into account an oxidized surface layer, which dissolves very easily. The presence of the oxidized surface layer was verified by treatment of one sample with diluted perchloric acid prior to the corrosion test. Uranium release was significant lower in that case, because the oxidized surface layer was removed.

Solid samples of corrosion experiments at pH 4 and pH 8 were removed at different times and investigated by means of X-ray Photoelectron Spectroscopy with respect to the U(VI)/U(IV)-ratio on the samples surface. Results from the solid surface characterizations are summarized in Table 1.

Table 1: Results from XPS investigations of the surface of corroded unirradiated uranium oxide.

Time (days)	% U(VI)	% U(IV)	pH
0	60	40	8
2	12	88	8
4	23	77	8
37	38	62	8
102	39	61	8
0	71	29	4
20	27	73	4
100	10	90	4

The corrosion behavior of unirradiated UO_2 in a NaCl-rich brine was studied as a function of oxygen partial pressure.The size of the UO_2 particles was 1 mm, the specific surface area was found to be 0,0016 m^2/g (BET). Reducing conditions were achieved by bubbling hydrogen into the experimental vessel using a Pd catalyst, anoxic conditions were maintained with nitrogen and an air flux was used to obtain oxidizing conditions.

Under reducing conditions an initial short increase of the uranium concentration of the leachate was observed, followed by a decrease, attributed to the precipitation of U(IV)-hydroxides, and finally constant U-concentrations. The final value agrees with the solubility of UO_2 determined in 5 m NaCl - solutions at the same conditions. Under oxidizing conditions the dissolution rates were measured before and after replenishment. The following different stages can be distinguished: (1) 7,3 E -7 mol /m^2d (first stage: dissolution of an oxidized layer), (2) 3,2 E -8 mol /m^2d (second stage: dissolution of "low" oxidized uranium oxide), (3) 2,6 E -8 mol /m^2d (third stage: dissolution after replenishment). Similar rates before and after replenishment may be interpreted, that a surface with the same oxidation state is dissolving. XPS analyses resulted in a surface composition of $UO_{2,4}$, which is close to that of $UO_{2,1}$, obtained in dissolution tests with $MgCl_2$-rich brine (Q-brine). This might be an indication, that the dissolution mechanism of UO_2 in brines and diluted solutions is similar. Under anoxic conditions a second dissolution rate, lower than under oxidizing conditions can be calculated: 6,2 E -9 mol /m^2d.

These results obtained in terms of total uranium concentration in NaCl brines are plotted as a function of contact time in Figure 4.

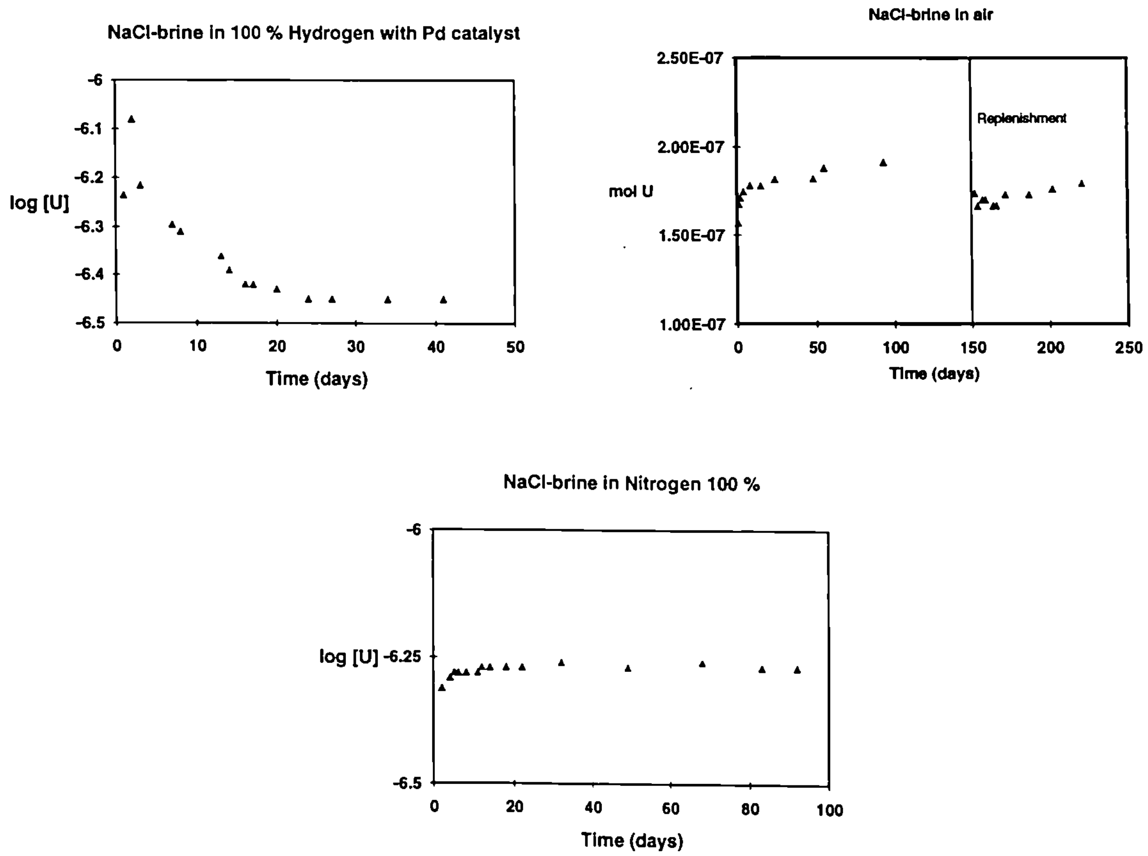


Fig.4: Uranium concentration in NaCl-brine after corrosion of UO2 under reducing, oxidizing and anoxic conditions as a function of contact time.

Title:	Container properties ensuring safety : gas emission, biodegradation, corrosion.
Contractor:	CEA Saclay
Co-contractor:	AEA Technology Harwell
Contract n°:	FI2W-CT91-0077
Contract duration:	October 1991 - October 1994
Period covered:	January 1993 - December 1993
Project leader:	P. LESSART (CEA Cadarache-coordinator), A. ROSEVAER (AEA)

A. Objectives and Scope

The knowledge of possible evolution of conditioned waste during intermediate storage, handling and deep repository is necessary to warrant the safety of workers and to define the conditions for storage and disposal. These conditions can depend on production of gases and of chemical compounds able to promote degradation or biodeterioration phenomena.

The origin of gas production can be:

- the waste itself, producing radon and gases from alpha and gamma radiolysis,
- the chemical or micro biological corrosion of embedding matrix and structural material,
- the radiolysis of organic compounds included in the waste.

Living micro-organisms can also produce complexing agents and organic or material acids able to promote corrosion and to modify the oxydo-reduction conditions and the pH of the repository.

A part of this project is concerned with assessing the effects of alkali tolerant micro-organisms on a cement based matrix.

B. Work programme

Four laboratories are collaborating for this contract, one of them being from AEA Technology Harwell and the others from DSD CEA Cadarache.

Programme 01: biocorrosion of cement and bitumen used as embedding matrix. Acid and gas production. Physico-chemical modifications of the material.

Programme 02: gas production by an genuine concrete conditioned waste with high content of radon producers.

Programme 03: effects of organic complexing agents in concrete and bitumen conditioned wastes on the gamma radiolysis gas production.

Programme 04: the aim is to determine the form in which the microbial cells attach to the alkaline surface and the extend to which this change the physical and chemical properties of the cement. This will provide data to assist in setting design criteria for cement based materials used to condition the pore water chemistry in a radwaste repository.

C. PROGRESS WORK AND OBTAINED RESULTS

Programme 01 : Biocorrosion of cement and bitumen

As a conclusion of a bibliographical study, micro-organisms exist in a deep repository before man intrusion, and, furthermore, after intrusion. All the elements necessary for microbial life exist in a nuclear waste repository. During repository evolving after setting-up and sealing, oxygen concentration decreases and even if at the beginning only aerobic microbes may develop modifying the physico-chemical characteristics of the repository, after a long term, anaerobic conditions become probable.

Programme 01 a : Biocorrosion of bitumen

Bitumen is a complex mixture of different heavy hydrocarbons that can be susceptible of biodeterioration because of its organic content.

The first part of this study corresponds to the identification of natural anaerobic microbial strains that can be found in soils polluted by hydrocarbons. Two samplings were done on such soils and, using medium described by literature, in a first step, we identify and separate fermentative, denitrifying and sulphate reducing micro-organisms. In accordance with the redox conditions they need and due to the presence of nitrates and sulphates in the wastes, these micro-organisms will probably be the first to developp in the repository when anaerobic conditions take place. No research Will be done on microbes producing methane because they grow very slowly compared with the previous one and their growth will take place only after a sufficient decrease of the rH.

Microbial growth is evaluated qualitatively by measuring the produced gas (CO_2, N_2O and N_2 for denitrifying microbes, CO_2 and H_2S for sulphate reducing bacteria, CO_2 for fermentative micro-organisms), decrease of nitrates or sulphate concentrations, and microscopic observation.

The second part of this studycorresponds to first quantitative experiments carried out using a denitrifying bacteria (*Pseudomonas* strain) and "bitumen powder". This is obtained by deposit of bitumen on silica gel (high ratio surface/volume, see previous reports). Hydrocarbons are partly oxidised into CO_2 while Nitrates are reduced into Nitrites, N_2O and N_2.

The first results obtained have allowed the choice of the operating conditions for anaerobic bitumen degradation by denitrifying bacteria.

A method has been developed in order to obtain better measurement of the total amount of produced CO_2.

In these experimental conditions, most of the gas production (CO_2, N_2O and N_2) takes place during the 100 first hours. At that moment, in the solution, we can notice an accumulation of nitrites that may inhibit the biodegradation.

Programme 01b : Biocorrosion of cement

The aim of this work is to study the cement deterioration induced by mineral or organic acids produced by alkali tolerant micro-organisms. In France, concretes planned to be used as embedding matrices are based on CPA 45 and CLC 55 cement.

Cement samples, 80mm diameter, 10mm thick, have been manufactured by DSD/SCS Laboratory of CEN Saclay, specialised in concrete studies, according to AFNOR NF P15402. Special devices were built for these experiments.

Cement samples are completely immersed in a mineral media inoculated by :

- a mixed culture of fungi (*Trichoderma viride* and *Aspergillus niger*) using glucose (an intermediate product of cellulose degradation) and producing several organic acids,
- a mixed culture of *Thiobacillus* strains, growing on thiosulphate (a soluble reduced sulphur source) and producing sulphuric acid.

Growth conditions were determined for these two micro-organism groups. Both fungi and *Thiobacillus* were adapted step by step to alkaline conditions.

Experiments are now carried out for about 600 days.

Chemical analysis of the solution are made every two weeks.

From first results, it appears that we must distinguish the experiments done with fungi from those done using Thiobacillus :

Fungi action :

- for CLC based samples immersed in the fungi culture medium, but without fungi (control experiments), pH stays quite stable, near 12 during more than 100 days, while for CPA based samples in the same conditions, this pH stability is observed during about 210 days. Then the pH decreases slowly from 10 to 8.
- a growth of fungi, corresponding to a a decrease of pH near 8 or even a lower value, is observed after 50 to 80 days of culture in medium containing CLC based samples, and after about 100 days in contact of CPA samples. After fungi growth takes place, the pH decreases irregularly from about 6 or 7 to 4 or 5.

Thiobacillus effects :

- for CLC based samples immersed in the Thiobacillus culture medium, but without Thiobacillus (control samples), pH decreases from 12 to 8 during the 200 first days and then stays quite stable near 8 until day 550, while for CPA based samples in the same conditions, a linear pH decrease from 12 to 10 is observed during about 550 days.

- a growth of Thiobacillus, corresponding to a decrease of pH near 6 or 7, is observed after 50 to 80 days of culture in medium containing CLC based samples, and after about 320 days in contact of CPA samples. Then pH stability between 5 and 4 can be noticed.

Samples under action of fungi have lost between 60 and 80% of their initial Calcium content after 600 days and many percents of Aluminium, and , as a result, have lost their mechanical properties.

For samples under action of Thiobacillus, the Calcium lost rapidity is quite constant when pH stability is achieved. After 550 days, the Calcium lost is only of 8% for CPA samples and of 18% for pure CLC or CLC containing ashes samples.

In order to better explain the microorganisms action, other analysis are done. Complete interpretation is expected for the end of June.

Programme 02 : gas production by actual waste package

The studied waste is a radioactive residue of uranium ore resulting from the extraction of lanthanides, Uranium and Thorium. In this waste, two main radioactive families must be taken into account, those of ^{238}U and ^{232}Th. This of ^{235}U can be neglected due to the initial low content of this isotope in the ore. Corresponding to the chemical treatment in order to extract the interesting compounds, the natural radiochemical balance in the ore has been broken, and a new distribution is establishing in the waste, with Radium as starting point.

Two isotopes of this nuclide are present in this waste, the ^{226}Ra and the ^{228}Ra, that give both a radioactive gas by decay : the ^{220}Rn and the ^{222}Rn.

Corresponding to the half life of daughters of ^{226}Ra and ^{228}Ra, the equilibrium for the ^{222}Rn is rapidly obtain while it will be obtained only after 20 years for ^{220}Rn. The aim of this study is to determine the radon quantity in the gaseous phase (over the solid waste) and to describe its release from the solid to the gas.

The radiochemical composition of the waste is known and allows the calculation of the total production of Rn in the solid phase. Its release (described by the leak rate) depends on the experimental conditions and on the physical properties of the waste : it is a function of the mean run time for the gas in the waste and of a retention factor.

The curve of Radon release, after replacement of the free volume atmosphere over the waste by air, was drawn, allowing the experimental measurement of the Radon leak rate using the MARCO device (see previous reports).

The ^{222}Rn content in the gas sample is determined using flasks (provided by the French Centre de Radio protection dans les Mines) with inner walls coated by Zinc sulphur activated with Silver (this compound emits photons under alpha radiations). Three hours after sampling, an equilibrium is reached in the flask between ^{222}Rn and its short life daughters ^{218}Po and ^{214}Po that are alpha emitters, while the activity of ^{222}Rn and ^{216}Po (its daughter) is negligible.

Two series of measurements have been done. The first takes place in February and March in order to evaluate the maximum content in ^{222}Rn after equilibrium between the solid and the gaseous phase. The second, with the objective to determine the time necessary for the establishment of this equilibrium, takes place in December.

It was shown that the greatest quantity of ^{222}Rn in the gaseous phase is always lower than the total production in the solid phase and can reach about 30% of this. A long time is necessary for the achievement of the equilibrium of radon between the solid and the gas phases.

Programme 03 : effects of organic complexing agents in concrete and bitumen conditioned waste on the gamma radiolysis gas production

The objective of this study is to determine the amount of produced gases by external gamma radiolysis on bitumen containing TBP and cement containing EDTA.

Effects of TBP on gas production from bitumen

Gamma irradiation of bitumen 80/100 containing 0%, 2.5% and 4.2% of TBP is now completed. We chose to study TBP concentration much higher than those possible in actual waste with the objective to enhance its effects. In order to explain the first obtained results, gamma irradiation is also made on pure TBP and bitumen containing only 0.4% TBP, and pure bitumen sampled from the same lot.

Indeed, results obtained for the same referenced bitumen (for example, for 80/100 Vacuum residue), many physical characteristics may vary (including TBA and penetration). Under radiation, different behaviour are demonstrated, so only an evolving can be noticed, never an absolute value.

Conditions of sample fabrication, irradiation (in aerobic conditions) and gas analysis were determined. The reproducibility of gas production during gamma irradiation can be evaluated to 15%. The total irradiation dose corresponds to the cumulated dose after 300 years in a Intermediate Level Waste repository.

Literature reports that :

- TBP is an electron scavenger,
- radiolysis yield of hydrogen from pure TBP, measured in various experimental conditions, is comprised between 1 and 2.5 molecules per 100eV, that corresponds to a production rate of 2.33 to 5.8 l/kg per MGy, the mean value being about 3.4 l/kg per 1 MGy total dose.

From our experiments, gas production rate for pure TBP is about 2.5 +/- 0.4 l/kg per 1 MGy total dose (1.1 molecule/100eV), and Hydrogen is the main radiolytic gas.

Samples containing high TBP content present a higher gas production rate than pure bitumen, but effects becomes important only for the higher TBP content. Hydrogen concentration in radiolysis gases is quite the same that for pure bitumen and near 95%. CO production rate is quite constant while CH_4 production increases slightly with TBP content. No difference can be noticed for production rate of the other gases (CO_2, C_2H_4, C_2H_6).

For sample containing 4.2% and 2.5% of TBP, the total gas production is respectively of 710 and 610 ml/kg per MGy.

A new sample containing only 0.4% of TBP was studied. For this concentration, no effect on gas production can be noticed, while, for the upper concentrations, total gas production rate appears to be lower than this resulting from the additivity law.

The physical characteristics of bitumen are greatly modified by high TBP contents : they become softer (flowing effect of TBP) and therefore less apt to swell. By opposition, swelling effect is very important for sample containing only 0.4% TBP.

Programme 04 : Biodeterioration of concrete

This project is concerned with the growth of micro-organisms on and within cement based matrices typical of those to be used in the disposal of Low and Intermediate Level Waste (ILW/LLW).

Different microbial strains were isolated from soil which had been exposed to an cellulose alkaline hydrolysate for several years. Colonisation of cement and plastic surfaces by alkali-tolerant organisms in a fed batch reactor were described in the previous reports.

Cell growth in the resulting biofilm utilised the six-carbon, polyhydroxy acids, isosaccharinic acid (ISA : one of the main products obtained by alkaline hydrolysis of cellulose, the technical source used is clarified black liquor), and caused the pH of the liquid phase to decrease. The experiments focused on the development of methods to monitor the build up of the biofilm and the rate at which key nutrients might diffuse through the cement matrix to the growing cells.

In a repository situation, the biofilm will be very thin and so methods of detecting very small amounts of cellular material have been evaluated.

From Scanning Electron Micrographs (SEM) of samples taken from these experiments after 3 months of operation, it is apparent that a network of long filamentous organisms had colonised the surface and that shorter rod type cells were established on this primary layer. The apparent distribution of microbial cell strains is modified. Non-biological material such as the crystals of sodium sulphide also became enmeshed in this framework to give the fully developed biofilm. The organisms attach well to both the smooth surface of plastic and to the interconnected porosity of the cement based matrix.

One hour after inoculation, in a static test, it was found $2*10^3$ viable cells attached per mm^2 and the cell number increase steadily over the following week to $6*10^6$ per mm^2. Clarified black liquor, i.e. ISA and by products from alkaline hydrolysis of cellulose, was used as the only carbon source, and a total consumption of ISA was noticed.

Cell growth was only noted on the surface of the concrete and not within the pores. This was thought to be the result of either exclusion of cells or nutrient or the fact that the inner pores were a relatively extreme environment compared with the bulk phase (i.e. the nutrient content was very low and the pH very high).

Ten distinct types of microbial colony were identified on the plates used for viable counts. Irrespective of the source of inoculum, during the first days, we observed a colonisation by long filamentous type micro-organisms. The development of a thick polysaccharide biofilm then takes place (first month), in which are dispersed a few short and filamentous type rods. Then, depending on the source of inoculum, two kind of microbial population are predominant : either a Bacilli type rod, or long filamentous cells.

Measurement of effective diffusion rapidity through concrete of nitrates and sorbitol (molecular size similar to ISA) were carried out. Both these solutes were chosen to be stable for long period in the alkaline conditions and to sorb strongly on the cement matrix. Diffusion measurement of sorbitol (organic compound which molecular weight is similar to ISA but that is not used for microbial growth) shows that its diffusion rapidity is 1500 times lower than the nitrate one.

From effective diffusion coefficient measurement, it would appear that there are a number of well connected pores through which most of the transport occurs, and a substantial number of interconnected but tortuous and narrow pores which contributed little to the through diffusion in this experiment.

The diffusion experiments confirm that the concrete is porous to solutes typical of the most important nutrients likely to be found in the repository. Thus, there is no reason why organisms in localised niches should not be capable of growing on solutes generated or originating in remoter parts of the repository. In addition, this growth may be possible both at the edges of the blocks and also within the bulk concrete, provided that the nutrients are not scavenged by any intervening biofilm.

A number of physico-chemical methods have been developed to study the changes as the biofilm and associated inorganic precipitates builds up on the surface of the concrete.

The hydraulic permeability is expected to changed markedly with the formation of a surface biofilm, but it is not yet clear since the measurement itself will perturb the system by altering the biofilm. Other electrical methods are being developed in order to investigate the biofilm development. These are conductivity (measurement of the cross section area through which conduction can take place), potential measurement between two regions with a chemically different environment, and electro-osmosis measurement (applying an electric field induces a liquid flow through a fixed bed or a tube). An alternative approach to electro-osmotic flow is to measure the electrical potential induced by applying a hydraulic pressure, nevertheless the first results show that this effect is probably too small to use for monitoring changes on concrete and the apply of a hydraulic pressure has the potential disadvantage of mechanically perturbing the biofilm.

Various experimental devices were adapted to conductivity measurement. The "Notional Pore Area" for the concrete specimen tested was 11% of the disk area, i.e. the specimen had the same conductivity as a pore-free specimen with a single hole of area 11% of the disk area. This compares with a relative pore volume of 21% estimated by measuring water uptake and implies that not all pores are through-pores and/or the pores are tortuous rather than direct. Surprisingly, the conductivity rose consistently over the first 30 days. This rise may result from slow equilibration between the composition of the pore liquid with the free liquid. The free diffusion experiments indicate that nitrate diffuses relatively quickly compared with even relatively small organic. However, in a preliminary experiment in which an SS2 culture was drawn through a disc of reference backfield the conductivity rose from 6.5 to 9.9 mmho suggesting that the increased conductivity from biopolymers may dominate over any effect due to occlusion.

The EMF was measured between the top surface and the medium in the disk, before and after scraping the top cube surface to expose clean concrete. Although the faces of the cubes tested were discoloured in patches, no visible growth of microbes was apparent. The results were quite variable, but there was a clear finding that in the presence of a biofilm there was a measurable EMF step, the free surface of the film being negative with respect to the concrete. Values of over 100 mV were measured on several samples and although freshly wetted raw concrete also showed a "skin potential", this was never more than 30 mV.

In the mini-reactors, The EMF measurement showed a similar pattern to that seen with conductivity. The potential may be caused by differential movement and sorption of macromolecules within the pores and the different chemical potential of the free ions needed to maintain electrical neutrality (e.g. the Donan effect). This observation emphasises that sorption of macromolecules must be allowed for in estimating changes arising from biofilm formation but that a measurable effect from surface coating is possible.

Electro-osmosis is the induced flow of liquid through a fixed bed or a tube, under the influence of an applied electric field. In special experiment, using KCl 0.1M as the electrolyte, the resulting osmotic flow was 0.07 ml per hour, too small for accurate measurement. No adaptation for measurement in situ was done.

An alternative method of measuring electro-osmotic effects has been assessed. Classically the electric charge of the solid, its z (zeta) potential, is measured by either (i) measuring the flow of the medium when an electric field is set up in it, or (ii) measuring the EMF across it when the medium is forced through under pressure. This approach has been examined by applying a hydraulic pressure and measuring the resulting EMF generated across a porous solid. The first tests indicate that this effect is probably too small to use for monitoring changes on concrete and has the potential disadvantages of perturbing the biofilm and being difficult to apply *in situ*. It will not be pursued further.

A third, potentially more convenient, way of estimating zeta potential is by measuring the EMF across the solid when a salt concentration gradient is set up in it. Preliminary results indicate that sensitivity of the method is high enough. In the bioreactor studies, one can monitor the combined effects of (unknown) z potential and some unknown salt gradient, especially with regard to progressive changes, and try to make inferences about one or other or both. Work on this approach will continue since as z potential depends on the chemical nature of the porous solid (concrete and films) it should give useful information as the biofilm develops.

From this various experiments it appears that :

- Natural microbial populations will form biofilms on the surface of concrete
- The alkaline degradation products of cellulose are utilised as a nutrient source
- The carbon source will be converted mainly to carbon dioxide and partly to polysaccharides and biomass
- Simple nitrogen and carbon sources can diffuse through the concrete matrix and be consumed
- The build up of the biofilm can be monitored by electrochemical methods and by electron microscopy.

Title:	Gas Generation in Supercompacted Waste Products
Contractor:	Forschungszentrum Jülich (KFA)
Contract.No.:	FI2W-CT 91-0094
Duration of contract:	from 01.10.1991 to 31.01.1995
Period covered:	from January to December 1993
Project Leader:	R.Odoj
Executants:	H.Heimbach, K.Kroth, H.J.Steinmetz, J.Wolf

A. OBJECTIVES AND SCOPE

The quality Controll Office for Radioactive Waste (PKS) was established due to a long-term contract between the Research Centre Jülich (KFA) and the German Federal Office for Radiation Protection (BfS). Ist main appointments are the qualification of conditioning processes for radwaste products and the implementation of radioanalytical quality control on waste packages prior to disposal in underground repositories. In this context adequate low gas release rates from waste products have to be guaranteed to minimize the release of radioactive and/or chemical reactive gases in the environment or the atmosphere of a disposal mine.

Because of radioanalytical decomposition as well as due to electrochemical reactions, supercompacted radwaste pellets often generate considerable amounts of hydrogen. This effect may lead to significant pressure buildup in waste drums or other containers. As part of the EC-project PEGASUS the PKS investigates methods to exclude unacceptable hydrogen by waste pellets as well as methods to decrease hydrogen by physical or chemical removal from the drum atmosphere.

B. WORK PROGRAMME

As comprised in the proposed time schedule of Fig.1, the programme for the project „Gas Generation in Supercompacted Waste Products“ includes seven main working items:

Item 2.1 Time dependend measurements on gas formation in supercompacted pellets
2.2 Heating of pellets under different conditions (p,T,t)
2.3 Measurements of gas generation after thermal treatment
2.4 Testing materials for hydrogen absorption (physical reaction)
2.5 Evaluation and tests of materials reacting with hydrogen (chemical reaction)
2.6 Proposal of technical procedures to avoid hydrogen release
2.7 Discussion and final report

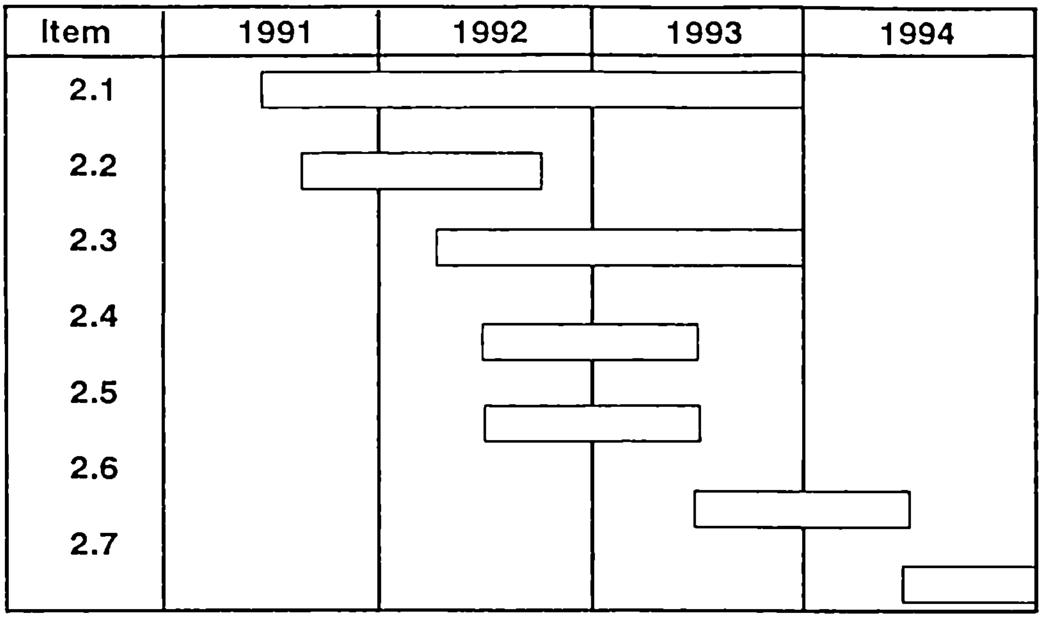


Fig.1 Proposed time schedule of the project.

C. PROGRESS OF WORK AND RESULTS

C.1 Measurements of gas generation at various experimental conditions (Items 2.1-2.3)

The measurements on release rates of hydrogen from supercompacted pellets of different composition at 25°C and 70°C (repository temperature) have been continued. The hydrogen production in general does not exceed 120 l H_2 in the first 100 days at 25°C and additional 110 l H_2 after storage at 70°C. Only with wet pellets, mainly constisting of shreded metall, up to 1300 l hydrogen (58 mol H_2) were liberated in the first 100 days. After an additional 400 hours at 25°C, most of the pellets still produced hydrogen, but the final release rates did not exceed 1.0 ml H_2 / hour.

After 500 days storage at 25°C, mixed waste pellets were heated up to repository temperature. By heating up, a short rapid decrease of hydrogen in the drum atmosphere could be observed followed by a release of H_2 at nearly the same amount as from the pellets in the first days. This interesting increase may be due to changes in hydrogen-adsorption at the pellet materials and establishing of a new solubility equilibrium after a constant temperature distribution has been reached in the drum.. After continuous heating for 50 days at 70°C, the pellets yielded additional 14-110 l H_2.. Further long time experiments are in progress.

C.2 Evaluation and tests of hydrogen absorbers (items 2.4-2.5)

For the removal of hydrogen from drum atmospheres both catalytical recombination of hydrogen and oxygen or chemical oxidation of hydrogen under formation of water appear to be technically usable. In order to avoid the formation of explosive hydrogen in air mixtures during a hypothetical core melt accident in LW Reactors, KFA Jülich developed highly efficient recombination catalysts which showed activity even at 5°C /1/. Based on these experiences catalysts containing palladium or platinum were tested. Among the tested chemical absorbers, manganese dioxide, surface activated with one percent silver (as Ag_2O) by an in-house developed preparation technique, was selected as an effective low-cost hydrogen absorption material. Under defined laboratory conditions its full capacity was determined to be 206.7 l H_2 / kg NPT.

Recombination of hydrogen and oxygen under formation of water has been investigated at 25 °C. Pilot tests on "cold burning of hydrogen" on mainly palladium or platinum containing surfaces were performed using a small scale laboratory arrangement with a 200 ml stainless steel pressure vessel. The vessel contained catalytically active nets of standard geometry in an air-atmosphere, which was charged to about 200 mbar overpressure with 10 % hydrogen in nitrogen. Especially palladium or platinum containing wash coated copper nets of DODUCO GmbH (Germany), each containg 0.5 mg of the precious metal per cm^2, proved to be effective. Using the Pt-catalyst, about 50 % and using the Pd-catalyst about 80 % of the total hydrogen amount could be recombinated to water within 10 minutes. Further kinetic measurements are in progress.

Taking into consideration oxygen consuming corrosion processes, drum atmospheres might not in any case contain enough free oxygen to recombinate all the arising hydrogen. Therefore full scale field investigations were focused on absorption by silver activated manganese dioxide. The investigations were carried out on a ordinary 200 l waste drum, in which an air atmosphere was charged with 35 l hydrogen from 1000 mbar to 1160 mbar. The reaction between hydrogen and MnO_2 (used as finely divided powder) was continuously monitored by measuring the pressure decrease in the drum.

The experiments, performed so far at room temperature, showed that „hydrogen-burning“ by activated manganese dioxide occures with high initial reaction rates. Fig. 2 contains the typical graphs for the pressure decrease. As an interesting result, the time-dependent absorption was determined by the position of the absorber. Placing the MnO_2-powder near the lid of the drum, about 90 % of the total hydrogen amount could be absorbed within 90 hours. Placing the absorber at the bottom of the drum a lower absorption rate was observed. These different results may be caused by the accumulation of the light hydrogen gas in the upper part of the drum.

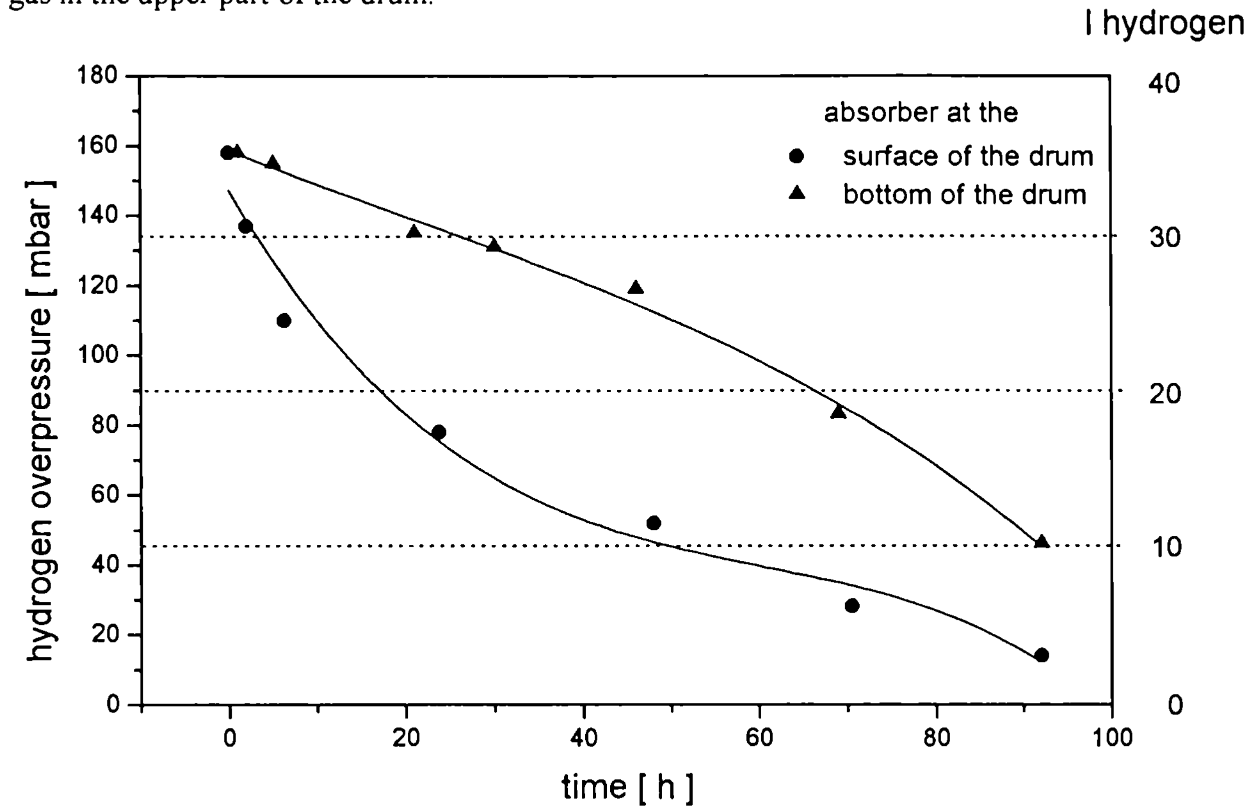


Fig.2 In-drum hydrogen absorption using silver-activated manganese dioxide. (field experiment with 200 l waste drum and 1 kg MnO_2).

C.3 Proposal of technical procedures (item 2.6)

Following a proposal of KFK Karlsruhe, the reduction of hydrogen overpressure in radioactive waste containers could be governed by using a safety-valve analog device, integrated in the wall or the lid /2/. This unit contains a catalyst for cold burning of hydrogen with oxygen from the surrounding air, but cannot hinder tritum and other radioactive gases from escaping into the environment. In contrast on the basis of the new investigations at KFA the proposed drum-integrated "hydrogen absorption unit" works without safety valve in the lid breaking the sealing of the drum.

A schematic drawing of a prototype is shown in Fig. 4. The unit comprises either catalytically active nets (Version B) or MnO_2 (Version A). A bursting disk is integrated under the lid of the unit and protects absorber or catalyst from being deactivated or poisoned until significant hydrogen overpressure accures. To avoid mechanical damage of the bursting disk, it is covered by a metallic net or a punched metallic disk. Water resulting from the catalytical recombination or the chemical oxidation will be absorbed by molecular sieve and a comparable drying agent inside the unit.

Taking in consideration the accumulation of the light hydrogen gas in the upper part of the drum this unit should be fixed on the inner side of the lid of the drum or container. Currently prototypes of Version A and Version B absorption units are in construction and will be tested in 1994. A german patent was applied for in December 1993. The application of a european patent is foreseen.

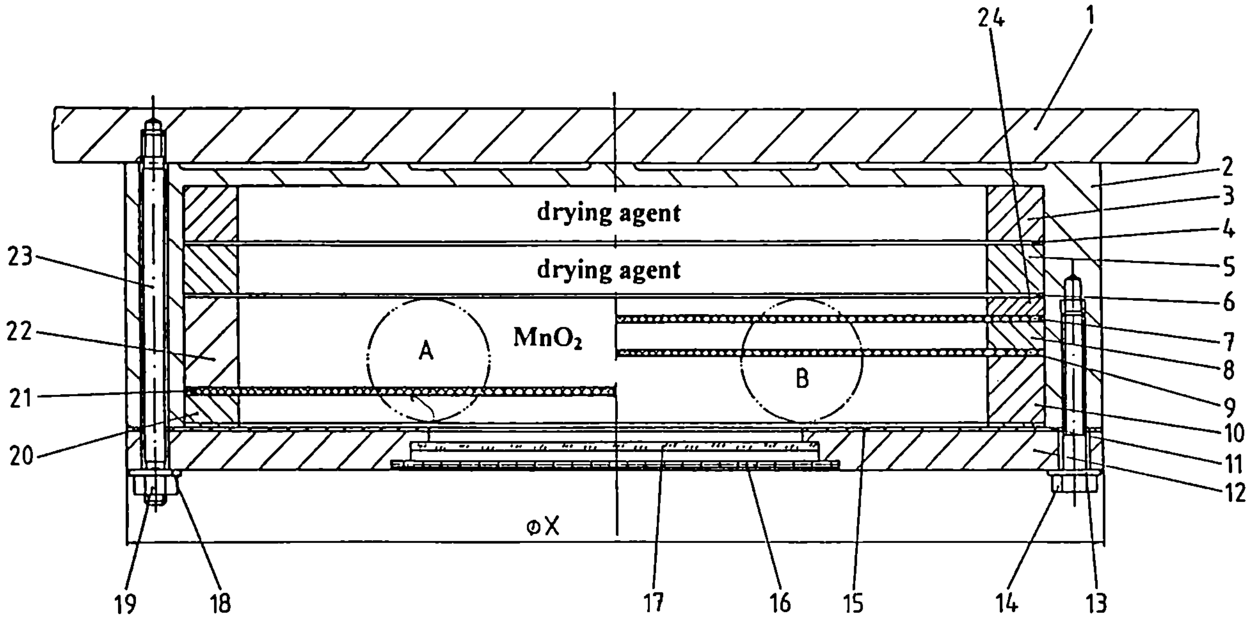


Fig.3 Schematic drawing of the proposed hydrogen absorption unit
[1]=lid of waste container, [2] wall of the unit, [12]= cover of the unit, [17]=bursting disk, [16]= metallic net or punched disk, [11,15]=rubber rings, [3,5,8,10,20,22,24]=distance elements, [4,6]=separation layers, [17]=bursting disk, [13,14,18,19]=screw joints,
Version A: [21]=separation net, *Version B*: [7,9]=catalyst coated nets

D. REFERENCES

1. K.H.Klatt, H.Wenzl, A.K.Chakraborty, Deutsche Patentschrift DE 3604416 C2 (1990-04-19). Kernforschungsanlage Jülich GmbH.

2. R.Köster, M.Kelm, W.Pfeifer, W.Hempelmann, Deutsche Offenlegungsschrift DE 3904149 A1 (1990-08-23). Kernforschungszentrum Karlsruhe GmbH.

Title:	**Impact of Additives and Waste Stream Constituents on the Immobilisation Potential of Cementitious Materials.**
Contractor:	University of Aberdeen, Aberdeen, Scotland, UK. AB9 2UE Free University of Berlin, 14195 Berlin 33, Germany (partner) AEA Windscale, Cumbria, England. CA20 1PF (partner)
Contract No.:	F12W/0099
Duration of Contract:	October 1991 - December 1994
Period Covered:	January 1993 - December 1993
Project Leader:	Prof. F.P. Glasser (UA) Prof. G. Marx (FUB) Dr. M. Angus (AEA)

A. OBJECTIVE AND SCOPE

The objective of this tri-coordinated research programme is to determine the interactions between waste and cementitious materials, in real waste forms, and also to explain the sorption phenomena of transuranics and relate laboratory data to the performance of realistic cemented waste forms within a repository.

The studies will be used to strengthen the links between empirical studies e.g. leaching, and more fundamental aspects. They will also be used to determine the impact of waste itself, both active and non-active, on the properties and performance of the encapsulating cement.

Various techniques will be used in the measurement of the aqueous phase and solid phase compositions of cement and blended cement, using inactive controls as well as formulations containing real wastes. Separation factors will be calculated for various isotopes in the above systems. The sorption processes for certain transuranics will be determined on pure cement phases and the role of certain organic complexing agents will be determined. The impact of selected inorganic ions on cement performance at longer ages will also be measured. The above experiments will be carried out at three isotherms: ambient (~ 22°C), 55°C and 80°C.

B. WORK PROGRAMME

B.1 Preparation of blended cements incorporating radioisotopes and process chemicals.

B.2 Trial runs at elevated temperatures on pore fluid expression device.

B.3 Pore fluid extraction of the samples prepared under B.1 and measurement of radioisotope sorption for the various cement blends.

B.4 Determine the effect of organic additives/real wastes on the sorption potential of the various cement blends.

B.5 Synthesis and characterisation of phase pure cement hydrates for sorption studies.

B.6 Measure the sorption of Eu(III) or Am(III), U(VI), Th(IV), Np(V) and Pu(VI) on synthetic cement hydrates, ettringite, C-S-H, tobermorite and hydrotalcite. The effect of organic additives on the sorption capacity will be determined.

B.7 Study the specific nuclide interactions (Ni, Cs, Cl and I) with cementitious materials.

B.8 Study the impact of chloride, carbonate and sulphate on cement performance.

B.9 Study the impact of organic additives/process chemicals on cement performance.

B.10 Verification of mineralogy of phase pure cement hydrates used in B.6.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of Advancement

In the period under review all of the above tasks are underway with tasks B.1, B.2 and B.5 completed. A problem that has been encountered with task B.6 is that some of the hydrates have altered in to various other compounds due either to the temperature or the solutions they have been contacted with. This is not seen as a major problem as long as the new products are identified and the sorption capacities of the alteration products are determined. It is important to note these changes since they may reflect what will happen to the hydrates in a repository environment. In task B.6 most of the work has concentrated on work at 25 and 55°C in double distilled water and in saturated NaCl solution. Work at 85°C and the effects of organic additives will be carried out over the next year. The bulk of task B.3 has been completed and work is well underway for B.4. Task B.7 is underway with most of the work concentrating on Ni and Cs. In task B.8 most of the work has concentrated on the impact of chloride. Task B.9 has begun and most of the work to date has centred on the effects of citric acid and oxalic acid. Much time has been used in developing the relevant analytical techniques. Task B.10 is ongoing throughout the project and the phase purity of the hydrates is determined as and when the samples become available from task B.6.

Progress and Results

Tasks B.3 and B.4 Sorption Experiments on Real Cements Containing Waste Materials.

Work is reported on the extraction and analysis of pore fluid from repository cements using a high force hydraulic press. Work has concentrated on the following areas during 1993;

- The effects of organics arising from cellulose degradation on the pore fluid concentrations of radioisotopes of plutonium, tin and thorium.
- The effect of EARP (Enhanced Actinide Removal Plant) floc simulant (an iron-based floc used to remove actinides from process streams in the UK) on the sorption of radioisotopes of chlorine, iodine, tin, thorium and plutonium.
- To provide characterisation information on the various cement blends used in the project under the appropriate curing conditions

The test matrix for work with the cellulose organics has involved four different sources of organics:-

- neat cellulose, purchased directly from a chemical supplier and added at a rate of 15 wt.% with respect to the dry cement used.

- degraded cellulose, prepared by leaching 40g of tissues and 360g crushed backfill with 500ml water at 80°C for 30 days. This was added to give a cellulose addition of 1% with respect to dry cement used.
- iso-saccharinic acid (ISA) a known cellulose degradation product. This was added at two concentrations; 0.001 and 0.01 moles per 150g cylinder of cement.
- simulated plutonium contaminated material, which was prepared in the laboratory by cutting up all the constituent materials, see Table I, in to small pieces. A total mass of 66.68g of PCM simulant was added to each 150g cement cylinder.

These materials are all sources of cellulose or cellulose degradation products. Three cement formulations have been investigated; 3:1 PFA:OPC, 3:1 BFS:OPC and UK Nirex 'Reference Vault Backfill. The cylinders were prepared with saline groundwater simulant and cured at 80°C for 28 days under anaerobic conditions.

Three variations of EARP floc was used in the sorption experiments; an aged floc and 2 fresh flocs. The fresh flocs were subjected to different mixing regimes; addition of the radioisotopes at the point of mixing the floc and cement together and addition of the isotopes before flocculation. The cement blend used was a 1:1 PFA/OPC mixture. The samples were cured as described above for the organics.

No increase in Pu solubility was observed as a result of adding ISA or cellulose leachate. However, with a very large addition of neat cellulose there is a significant increase of approximately 2 orders of magnitude. Addition of PCM simulant produces a smaller increase in Pu solubility, at levels planned by BNFL for the encapsulation of combustible PCM, . There is no significant decrease in sorption with the addition of leachate but with large additions of neat cellulose there is a significant decrease in Th sorption for all three cement blends. In contrast, decreased sorption of Sn is only observed with large additions of cellulose to 3:1 PFA/OPC.

The aged EARP floc results are similar to results obtained previously for isotopes in cement with no added floc. The sorption was higher for Cl, I and Sn with fresh floc than for aged floc, but was lower for fresh floc with Th and Pu.

Some characterisation work on non-active samples of 3:1 PFA/OPC and backfill containing organic additives were investigated at Aberdeen University. Methods include X-ray diffraction (XRD), scanning electron microscopy (SEM), total organic carbon (TOC) and inductively coupled plasma mass spectrometry (ICP-MS). A limited amount of HPLC work was carried out by AEA Harwell.

Task B.6 Sorption Experiments on Phase Pure Cement Hydrates.

In the time period covered FG Radiochemistry of FU-Berlin finished the experiments on the sorption of neptunium on the four cement components: hydrotalcite, ettringite, C-S-H gel and tobermorite in water, saturated NaCl solution and Q-brine at 25°C. The sorption experiments on thorium and uranium on the four cement components in the three systems at 55°C have been completed. Results have been obtained for the sorption of plutonium on hydrotalcite in water at 25°C. Experiments on europium were started at 55°C with the 4 cementitious sorbents in water and saturated NaCl solution. Results have been obtained for europium sorption in Q-brine at 55°C.

Freundlich and Langmuir isotherms could be applied to the data obtained. From the results obtained from these experiments on speciation it can be shown that for thorium at high pH only $Th(OH)_4$ is present in water and in saturated NaCl solution; the ion constituent is a single ionic species in this case. Within the pH range 3-5, $Th(OH)_4$ competes with $Th(OH)_2^{2+}$ and to a much lesser extent with $Th(OH)_3^+$. Chlorocomplexes do not exist at these conditions, however, if the pH is changed, not by adding NaOH but by dilution with saturated NaCl solution, a variety of chlorocomplexes will exist, the leading part played by $ThCl^{3+}$ at lower pH and $ThCl(OH)_4^-$ at higher pH. The species $ThCl(OH)_2^+$ exists at intermediate conditions. With respect to the speciation of neptunium, the results show that NpO_2^+ is the dominant species at lower pH in saturated NaCl solutions. At very high pH, $NpO_2(OH)_2^-$ plays the leading part. Within the relevant pH range, from 10 - 11, NpO_2OH must be taken into account as well as NpO_2^+ and $NpO_2(OH)_2^-$ which have about equal concentrations. In water NpO_2^+ is the dominant species, even at pH 10, negatively charged complexes are only present at very high pH values ($pH \approx 12$). For uranium, only the species $UO_2(OH)_2$ exists at higher pH in water. At lower pH $(UO_2)_2(OH)_2^{2+}$ plays the leading part followed by UO_2^{2+} in acidic media.

The physical chemical constants obtained from Langmuir's isotherm allow the sorption ability of the four cementitious materials to be compared with each other in the three different electrolyte solutions.

The results obtained from the sorption experiments on thorium, uranium and neptunium show that the sorption of the ion constituent of these elements on the various cementitious materials is higher in saturated NaCl solution than in water. This behaviour may be due to the chlorocomplexes formed. This is the case for neptunium and uranium but not for thorium. In order to confirm this assumption the surface of the cement components needs to be investigated by the use of instrumental methods. The main factor, which drastically decreases the solubility of the selected actinides in these systems, is the high pH resulting from dissolved cement components.

B.7 Specific Nuclide Interactions with Cementitious Materials.

Most of the work to date has centred the interaction of Ni and Cs.

Blended cements with the compositions OPC, 9:1 BFS/OPC, 3:1 PFA/OPC and a backfill mix were prepared with a w/c ratio of 0.5. Nickel was added to the mix water to give a concentration of either 0, 5000, 50000 ppm Ni (as the nitrate salt). The cylinders were prepared in duplicate and cured for 24h at 25°C. They were then stored at 25° and 85°C for 3 months and 1 month respectively. After this time the pore fluid was expressed under nitrogen, and OH and Ni concentrations determined (see Table II). At 0 and 5000 ppm Ni additions, the Ni levels in the pore fluid are effectively the same. There is more Ni in the OPC pore fluid than in the blended cements. This may be due to a significant Ni content in the OPC. Elevated temperature reduces the Ni concentration in the pore fluid except at the highest loading.

XRDs were made of the solids to identify any possible Ni containing phase. Only at the highest Ni loading is there a change in the XRD. Identification of the phase(s) responsible for incorporating/sorbing Ni was attempted using TEM. Dispersed samples did not show any distinct Ni containing phase(s), although the Ni seemed to be uniformly dispersed within the sample. It may have been present as small $Ni(OH)_2$ particles adhering to the surface of other cement hydrates. Initial X-ray element maps of polished sections of the high Ni samples showed Ca-rich regions bounded by a Ni-rich layer. This may be $Ca(OH)_2$ coated with $Ni(OH)_2$.

Fragments of the above cements (prior to pore fluid expression) were ground and used for leaching experiments at a w/s ratio of 50. Samples were stored for 2 months at 25° and 85°C. Unfortunately the samples stored at 85°C dried out. Ni concentrations in the samples at 25°C were found to be <10 ppb.

The work with Cs has centred on sorption experiments. Several authors have demonstrated that OPC has very little potential to absorb Cs./1-4/ However, well-cured PFA/OPC blends have the best potential for absorbing Cs./2,4/ The exact phase responsible for this enhanced sorption is not known. McCulloch found that C-S-H with a C/S ratio < 1.0 shows enhanced sorption over gels with a C/S 1.1 - 1.7./4/ Tobermorite was also found to have a high sorption capacity.

In this work we have measured the sorption potential of various, phase pure, cement hydrates that can be potentially found in well-cured PFA blended cements. The phases studied were; hydrotalcite, gehlenite hydrate, C-S-H (C/S = 1.0, 1.4 and 1.7), tobermorite, jennite, C-A-S-H gel (C:A:S = 1), gismondine all at 25°C and "zeolite precursor" at 25" and 85°C. Gismondine showed the best sorption capacity followed by C-A-S-H gel, tobermorite and jennite, C-S-H showed moderate sorption with C/S = 1.0 performing best. Hydrotalcite and gehelnite hydrate showed no measurable sorption. The results are for selected hydrates are shown in Tables III - VI.

B.8 Impact of Chloride on Cement Performance.

Most of the work to date has been identifying which chloride phases are stable in a cement environment, finding out their solubility either from literature or synthesising the compounds and determining the solubility. This data was then used to determine the range of chloride concentrations that the various phases were stable. This was done using thermodynamic computer models. /5/.

In the CaO-Al_2O_3-$CaCl_2$-H_2O system at 25°C seven hydrates were found to be stable:- $Ca(OH)_2$ [CH], $Al(OH)_3$ [AH_3], $Ca_3Al_2(OH)_{12}$ [C_3AH_6], $3CaO{\cdot}CaCl_2{\cdot}15H_2O$ [3-1-15], $CaO{\cdot}CaCl_2{\cdot}2H_2O$ [1-1-2], $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$ [F.S.] and $CaCl_2{\cdot}6H_2O$. The numbers in [ ] are abbreviations for the phases. The order in which these phases occur is:-

	[Cl] < 0.009 mol/Kg	: AH_3, C_3AH_6, CH
0.009 <	[Cl] < 0.011 mol/Kg	: AH_3, C_3AH_6, CH, F.S.
0.011	[Cl] < 3.285 mol/Kg	:AH_3, F.S., CH
3.285	[Cl] < 6.427 mol/Kg	AH_3, F.S., 3-1-15
6.427	[Cl] < 8.001 mol/Kg	AH_3, F.S., 1-1-2
8.001	[Cl] < 8.0158 mol/Kg	$CaCl_2{\cdot}6H_2O$, F.S., 1-1-2
8.0158	[Cl] < 8.016 mol/Kg	$CaCl_2{\cdot}6H_2O$, 1-1-2
	[Cl] >8.016 mol/Kg	$CaCl_2{\cdot}6H_2O$

As can be seen from the above data, Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) occurs at quite low chloride concentrations and persists over a wide range of concentrations. It is believed that this will be the dominant chloroaluminate phase under repository conditions, unless the groundwater has very high levels of chloride. The effect of adding sodium to this system is has yet to be determined.

B.9 Influence of Organic Additives on Cement Hydration.

The hydration and interaction of OPC in the presence of citric acid have been investigated. It has been proposed that retardation results from the adsorption of the citrate species, the strong retarding effect generally being attributed to the presence of an α or β-hydroxy carboxylic entity./6/ It is known that calcium, aluminium and iron ions are all potentially capable of chelating with hydroxy acids although these complexes are not very strong./7/ Thus organics are of interest because they appear in process waste streams and may interfere with cement hydration. They may also form strong complexes with radionuclides leading to their increased solubility.

The results clearly indicate that small additions, < 0.15% wt.% citric acid/OPC, have a powerful retarding action. At higher concentrations, 0.3%, the retarding effect is so powerful that set may not take place. In the presence of 0.05 wt.% citric acid the rate of heat evolution is decreased and there is a short retardation of approximately 2 hours. As the concentration of citric acid is increased up to 0.15 wt.%, a gradual decrease in the rate of heat evolution is observed. OPC with 0.15 wt.% citric acid addition sets in 14½ hours, an increase of 10 hours.

Cement cylinders containing citric acid were prepared with OPC to a w/c = 0.4. Three concentrations of citric acid were studied; 0.05, 0.10 and 0.15 wt.%. Control samples containing no citric acid was also prepared. These samples were cured at 25°C at 100% RH. Fluid was extracted from the cylinders either by filtration or by means of a high pressure squeezing device, "pore fluid expression". The samples were filtered after the initial mix, ~ 10 minutes, at set point (time depends on the citric acid concentration), 96 and 168 hours. The pore fluid was analysed for major cations and anions and also for citrate. The results show that citrate concentrations drop rapidly until set point and thereafter slowly increases. The citrate concentration at set point is ≈250 ppm regardless of the initial citrate concentration of the mix water. Other trends that emerge are that hydroxyl ion concentration increases with increasing citric acid concentration whilst calcium and sulphate slowly decrease.

Cement Nomenclature:- C = CaO A = Al_2O_3 S = SiO_2 H = H_2O M = MgO $\bar{S}$ = SO_3

Abbreviations:- OPC - Ordinary Portland Cement BFS - Blast Furnace Slag
PFA - Pulverised Fly Ash

References.

/1/ Komarneni, S. and Roy, D.M., *Cem. Conc. Res.*, 11, 789-794 (1981)

/2/ Crawford, R.W., McCulloch, C.E., Angus, M., Glasser, F.P. and Rahman, A.A., *Cem. Conc. Res.*, 14, 595-599 (1984)

/3/ Anderson, K., Torstenfelt, B. and Allard, "Sorption and Diffusion Sudies of Cs and I in concrete", Chalmers University of Technology, Goteborg, Sweden. (1981)

/4/ McCulloch, C.E., "The Immobilisation of Cs in Cement Based Matrices", PhD Thesis, University of Aberdeen, Scotland. (1985)

/5/ Revvertegat, E., Glasser, F.P., Damidot, D., Stronach, S.A. and Adenot, F. Commissariat à l'Energie Atomique (CEA), N.T./SCS 93.13, 1992. (Annual Report for CEC Contract No. F12W-0035, 1992)

/6/ Double, D.D., *Trans. Royal Soc. Lon.*, Series A 310, 53-66 (1983)

/7/ Sillen, L.G. and Martell, A.F., *Chem. Soc. Lon.*, Special Publ., 17, 1964

Tables.

Table I. Composition of PCM Simulant

Material	Amount (g)
White gloves	5.13
Black gloves	5.13
Marigold™ gloves	5.13
Kleenex™ tissues	1.34
Cotton cloth	1.34
Brown paper	1.34
Polythene bags	8.66
PVC sheet	38.61
TOTAL	**66.68**

Table II. Solubility of Ni in Blended Cement Pore Fluid.

Cement formulation	Ni added in mix water (ppm)	3 months at 25°C		1 month at 85°C	
		[Ni] ppm	[OH] mmol/l	[Ni] ppm	[OH] mmol/l
OPC	0	1.0	625	0.4	288
	5000	0.9	550	0.3	173
	50000	-	-	-	-
9:1BFS/OPC	0	0.3	103	0.1	70
	5000	0.3	70	0.1	43
	50000	1.9	-	1.5	25
3:1 PFA/OPC	0	0.4	140	0.1	23
	5000	0.3	60	0.2	5
	50000	1.5	<10	1.8	5
Backfill	0	0.3	170	0.1	135
	5000	0.4	123	0.2	83
	50000	1.6	50	-	50

Table III. Sorption Capacity of Gismondine for Cs.

Sample	gismondine		
Weight of hydrate	0.5 g		
Volume of solution	100 ml		
Initial Cs (ppm)	1.3	133.0	1329.1
After 18 days (ppm)	0.03	1.33	638.0
R_D (ml/g)	8467	19800	216.6

Table IV. Sorption Capacity of C-A-S-H gel for Cs.

Sample	C-A-S-H gel		
Weight of hydrate	1.0 g		
Volume of solution	100 ml		
Initial Cs (ppm)	9.68	100.0	1006.0
After 24 days (ppm)	4.43	50.10	732.2
R_D (ml/g)	118.5	99.60	37.39

Table V. Sorption Capacity of Tobermorite for Cs.

Sample	Tobermorite		
Weight of hydrate	1.0 g		
Volume of solution	100 ml		
Initial Cs (ppm)	9.68	100.0	1006.0
After 24 days (ppm)	5.31	89.14	984.1
R_D (ml/g)	82.30	12.18	2.23

Table V. Sorption Capacity of Jennite for Cs.

Sample	Jennite		
Weight of hydrate	0.5g		
Volume of solution	100 ml		
Initial Cs (ppm)	9.68	100.0	1006.0
After 24 days (ppm)	8.57	96.13	983.1
R_D (ml/g)	25.90	8.05	4.65

Report Compiled by A. Kindness 26/1/94

Title: **Some Aspects of Leaching Mechanisms of Ions Incorporated in Cement or Polymer**

Contractor: NCSR "Demokritos", 153 10 Athens, Greece
Contract No.: FI2W-CT93-0124
Duration of Contract: from 1 March 1993 to 28 February 1995
Period covered: 1 March-31 December 1993
Project Leaders: S.G. Amarantos and J.H. Petropoulos

A. OBJECTIVES AND SCOPE

The present work aims at further elucidation of some mechanisms which govern the elution, by water, of some important ions from solids simulating solidified low or medium level radioactive wastes.

The distribution of Sr ion in the cement matrix after a long period of leaching as well as the physicochemical state of water within the pores in this matrix is under investigation.

In the work concerning polymers the experimental study of the sorption and diffusion behavior of a model polymer-NaCl-H_2O system will permit the more detailed application and testing of the theoretical approach describing the elution of salts of both high and low solubility embedded in hydrophobic matrices, taking into account the concurrent imbibition of water.

B. WORK PROGRAMME

B.1 Cement

B.1.1 Distribution of Sr.
B.1.1.1 Experiments with specimens containing inactive Sr in the form of $SrSO_4$.
B.1.1.2 Experiments with specimens containing Sr-90 in the form of $Sr(NO_3)_2$.
B.1.2 Physicochemical state of water.
B.1.2.1 Thermogravimetric and differential scanning calorimetry measurements.
B.1.2.2 Porosimetry measurements.

B.2 Polymer

B.2.1 Sorption and diffusion experiments with NaCl in polymer films and parallel measurements of the rate of water sorption.
B.2.2 Equilibrium water uptake by polymer films at different relative humidities and salt content.
B.2.3 Study of ion transport using Na-22 and Cl-36 tracers.

B.3 Modelling and interpretation of results

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The distribution of non-eluted Sr along the diffusion axis in cement specimens previously subjected to leaching with distilled water for several years was studied. The Sr was initially incorporated in the form of inactive sparingly soluble $SrSO_4$. The results showed deviation from the perfectly uniform distribution of the embedded salt in the cement matrix which is assumed theoretically. Similar studies with Sr-90 incorporated in the cement specimens as $Sr(NO_3)_2$ as well as thermogravimetric (TGA), differential scanning calorimetry (DSC) and mercury porosimetry measurements for the characterization of the state of water in cement will be carried out in the next phase of the program.

The experimental work with model polymer-salt-H_2O systems included measurements of sorption and diffusion of NaCl in cellulose acetate films. $\sqrt{t}$ kinetics was obeyed in some cases but appreciable deviations therefrom were found in other cases. The rate of water sorption by the film during salt elution was also measured. Work on the determination of equilibrium water vapor uptake by polymer films at different relative humidities was begun using neat polymer films.

Progress and Results

1. Cement specimens

B.1.1.1 Distribution of Sr along the diffusion axis of specimens containing (inactive) $SrSO_4$.

Cylindrical specimens (diameter ≅height ≅4 cm) from previous elution studies /1/, initially containing about 3.1% by wt of Sr as $SrSO_4$ were used. They had been subjected to leaching by distilled water (with one flat surface of the specimen exposed to leachant) at 30°C. The methods used involved either stagnant leachant which was renewed periodically or leachant which was continuously renewed in the manner described in Ref. /1/. CO_2 was excluded during preparation and leaching of the specimens. The latter were cut into slices or ground up progressively normal to the diffusion axis, until the Sr content of successive slices or samples of powder did not vary significantly. Sr content was determined by atomic absorption after dissolution in 3M HNO_3. Examples of the concentration profile of Sr determined by grinding are presented in Figures 1 and 2 where x is the distance from the surface exposed to leachant and the Sr content refers to dried sample. The dotted line represents the initial concentration of Sr in the specimen (assumed to be uniform along the length of the specimen), as estimated from the total amount of Sr found in leachates and that remaining in the specimen. In both cases the diffusion front is not sharp as predicted by the Higuchi model /1/, which assumes that the embedded salt is perfectly uniformly dispersed throughout each cross-section of the specimen. This is attributable to the fact that the embedded salt is at least partly in the form of particulate aggregates (as is confirmed by the visual observation of "spots" on the ground surface of the specimens which have been shown by atomic absorption to contain a very high proportion of Sr).

2. Polymer specimens

B.2.1 Sorption and diffusion experiments with NaCl in polymer films and parallel measurements of the rate of water sorption.

Two types of polymer films (of thickness 120 or 300 µm) were used, namely (a) as prepared in neat form (normal films) or (b) films originally loaded with particulate NaCl (11 or

20% by wt), which was subsequently removed by elution (salt-depleted films) /2/. Normal or salt-depleted films were equilibrated at 25^oC with concentrated NaCl solutions containing 0.05, 0.12 or 0.25 g/cm^3 of salt solution and were then subjected to elution by distilled water with stirring at 25^oC. The amount of desorbed salt was determined by measuring the electrical conductivity of the eluting bath. The water content of the films at the beginning of, or during, the elution experiment was estimated gravimetrically. Some sorption and diffusion results are summarized in Table I were K_p and k_s are partition coefficients. In particular, K_p=C/c, where C and c are the salt concentrations in the polymer and external solution respectively (expressed in g/cm^3 of polymer or of solution respectively), while k_s is the ratio of salt concentration in the water imbibed by the polymer (in g/g of sorbed water) to the external salt solution concentration (also in g/g of water). C_{W0} and $C_W{}^0$ denote the water content of the polymer in equilibrium with salt solution and with water respectively; D is the diffusion coefficient calculated from the slope of the linear part of the elution curves of Figure 3a.

The values of K_p, k_s and D as well as the water content, of salt-depleted films are generally higher than those of normal films (i.e. films with zero initial salt load). This, no doubt, reflects the fact that in salt-depleted films the volume initially occupied by the salt particles is available for occupation by imbibed water. The values of Kp, $C_W{}^0$ and D of normal films agree reasonably well with those found by others (e.g. Ref. /3/) and do not differ significantly at the two concentrations (c=0.05 and 0.12 g/cm^3) studied. Table I also shows that the water uptake C_{W0} of films equilibrated in the most concentrated NaCl solution (0.25 g/cm^3) is substantially lower.

Some representative elution curves are presented in Fig. 3a, where the fraction of salt desorbed $\Sigma\alpha_n/A_o$ is plotted vs the square root of elution time t. Fickian kinetics is obeyed, except in the case of films equilibrated with the most concentrated NaCl solution (the corresponding D values in Table I have been put in parentheses, because they are indicative only). In particular, the middle portion of the elution curve in the latter case exhibits a marked acceleration effect attributable to the concurrent influx of water. The kinetics of the latter is presented in Fig. 3b.

B.2.2 Equilibrium water uptake by polymer films at different relative humidities and salt content.

Normal films (~120 µm thick) were first equilibrated with distilled water, dried by evacuation and then equilibrated at 25^oC with atmospheres of progressively higher relative humidity. The water regain of the film was estimated gravimetrically and the resulting sorption isotherm is presented in Fig. 4 (the point corresponding to RH=100% was determined by immersion in distilled water). Reasonable agreement of our results with those given in the literature /4/ was found.

References

/1/ POTTIER, P.E. and GLASSER, F.P., Editors, Characterization of low and medium level radioactive waste forms, Final Report - 2nd CEC Program 1980-84, EUR 10579 EN (1986); p. 133-140.

/2/ AMARANTOS, S.G., PAPADOKOSTAKI, K.G. and PETROPOULOS, J.H., Report No. EUR 13543EN (1991).

/3/ HEYDE, M.E., PETERS, C.R. and ANDERSON, J.E., J. Colloid Interf. Sci., **50**, 467 (1975).

/4/ TOPRAK, C., AGAR, J.N. and FALK, M., J. Chem. Soc., Faraday Trans. I, **75**, 803 (1979).

TABLE I. SORPTION EQUILIBRIA AND KINETIC PARAMETERS OF POLYMER FILMS

c (g/cm^3)	Original salt load of film (% by wt)	K_p	k_s	C_{WO} (g/g)	C_W^0 (g/g)	$D \times 10^9$ (cm^2/s)
0.05	0	0.0336	0.186	0.153	0.155	1.5
	11	0.0758	0.361	0.192	0.200	3.7
	20	0.131	0.510	0.248	0.273	8.3
0.12	0	0.0320	0.199	0.146	0.150	1.0
0.25	11	0.0585	0.381	0.130	0.201	(35)
	20	0.0545	0.339	0.128	0.260	(18)

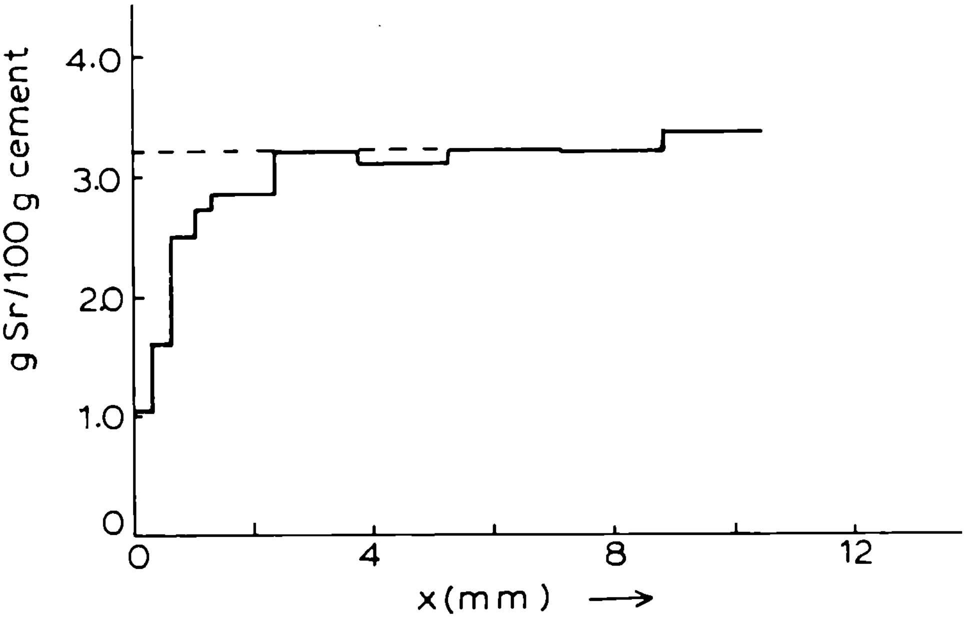


Figure 1. Distribution of non-eluted Sr in cement samples after 19 months of elution at 30°C by stagnant distilled water.

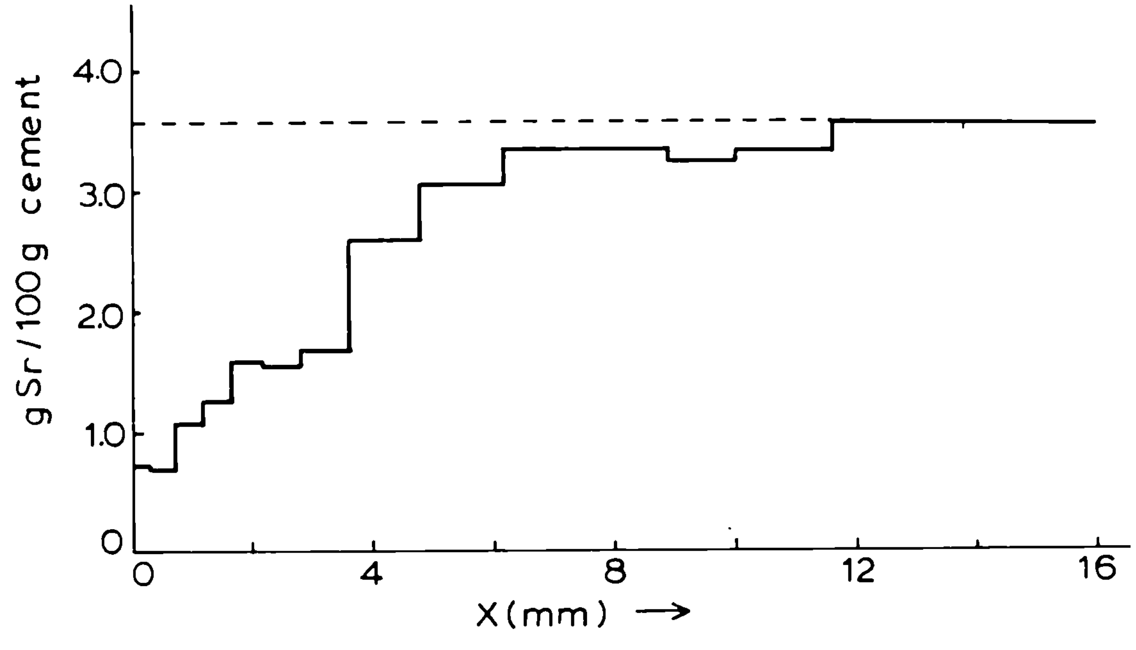


Figure 2. Distribution of non-eluted Sr in cement samples after 74 months of elution at 30°C by continuously renewed distilled water.

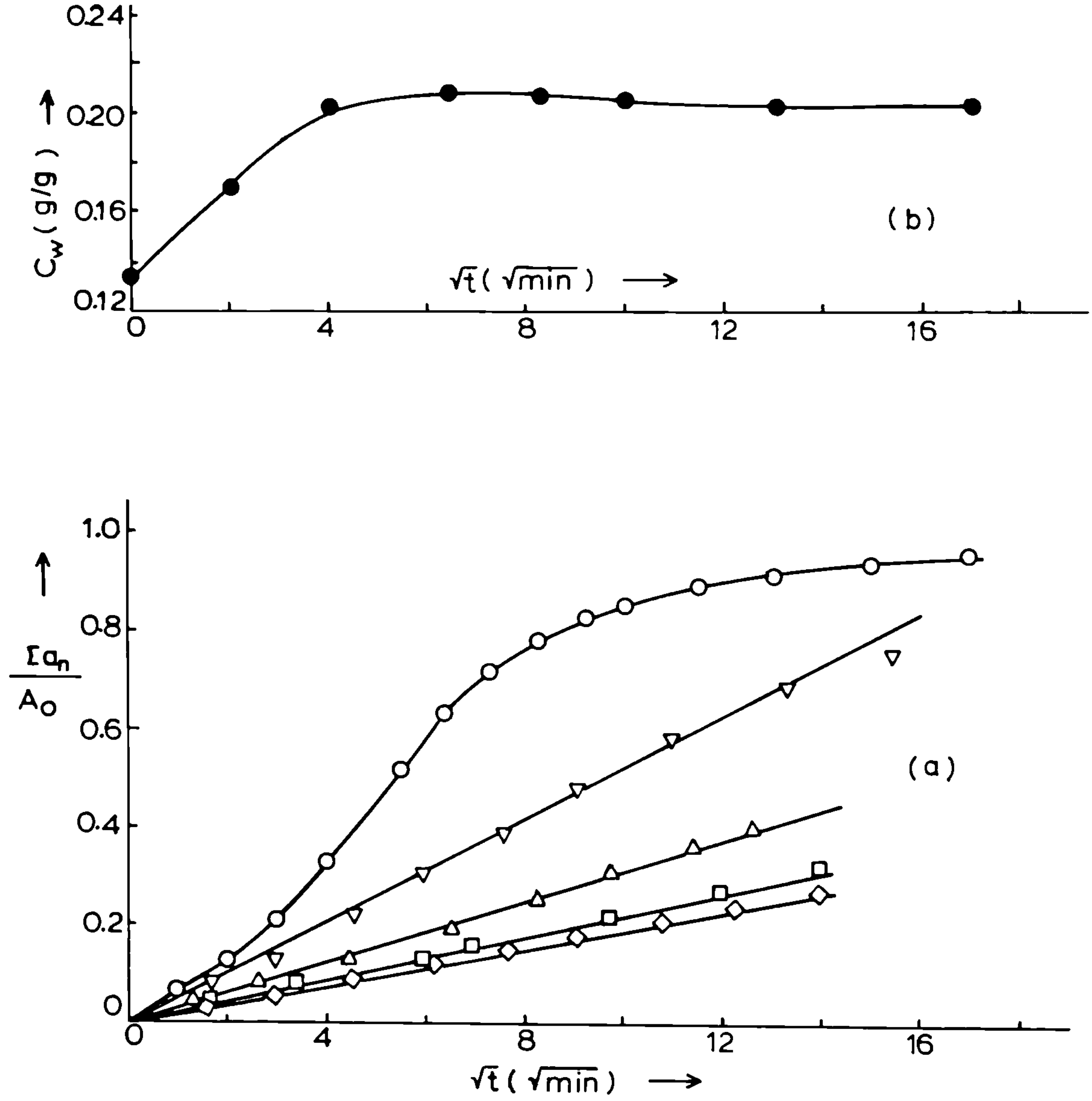


Figure 3. (a) Elution curves of normal (□, ◊) or salt-depleted films of original salt content 11 (Δ, o) or 20% (∇) by wt, equilibrated in a NaCl solution of concentration 0.05 (□, Δ,∇), 0.12 (◊) or 0.25 (o) g/cm^3. Film thickness: 300 μm.
(b) Water uptake (during salt elution) of the film equilibrated in the 0.25 g/cm^3 salt solution.

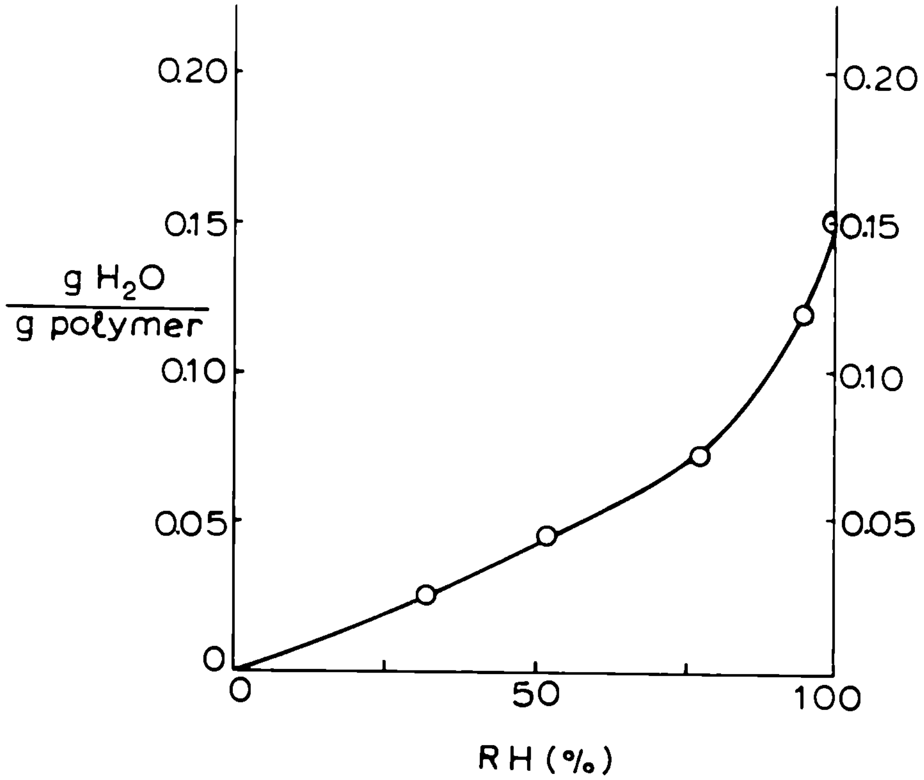


Figure 4. Water regain of a neat polymer film equlibrated at different relative humidities

Title :	The effect of Microbial Activity on the Near and Far Fields of a Deep Repository
Contractor :	DCC/Dir CEA Saclay
Contract N° :	FI2W-CT90-0022
Duration of Contract :	October 1991- October 1993
Period covered :	January 1993 - December 1993
Project Leader :	M P. LESSART DSD/SEP/SEATN CEA Cadarache
Co-workers :	Mme LIBERT, M. BESNAINOU, MM SPOR, TRESCINSKI, BILCOT

A. OBJECTIVES AND SCOPE

Micro-organism can produce organic or mineral acids that can promote corrosion and complexing agents that can modify the characteristics of the repository. So, radionuclides that have been immobilised by cement or bitumen embedding matrix can be leached either as soluble ions or soluble complexes (effects of the corrosion of the matrix). This leads to an increase of their mobility.

On the other hand, micro-organisms can decrease the mobility of initially soluble species by sorption on the cell membrane or on polymers (especially polysaccharides) produced by cells, and also by bioaccumulation in the cell.

The objective of the present work is to determine the global effect of microbial presence on the mobility of radionuclides supposed immobilised in the near field (clay or cement).

The experiments are realised on pure cement cylindrical samples or on fine mote of clay, containing U (introduced as Uranyl nitrate) or Cs (introduced as Cesium chloride). The organic acid producing micro-organisms growth on cellulose, one carbon source that can be found in nuclear waste.

B. WORK PROGRAMME

Literature survey.

Pilot plant design and realisation, hydraulic tests, choice of working conditions.

Metabolism study of cellulolytic micro-organisms

Leaching of U and Cs contained in cement or clay matrix by the culture medium containing micro-organisms.

Study of the different effect of direct and indirect microbial action on radio nuclide mobility or retardation.

C. PROGRESS WORK AND OBTAINED RESULTS

I Literature survey

From literature, it can be conclude that all elements necessary for microbial growth (such as S, P, Ca, Mg, Fe as substratum, or Cu, Mn, Co, Zn, Mo, Ni, Se, V...as oligo element, electron donors and electron receivers) exist in a deep repository. They are more or less available but micro-organisms have a very important adaptation ability that make them able to develop special metabolism in order to make the element assimilable if they need it for growth.

When environmental conditions are too bad for growth, a lot of micro-organisms have the possibility of becoming spores or resting cells, that is a non developing state in which they can stay for a very long time, until environment becomes less unfavourable for growth.

II working condition and metabolisms of Trichoderma viride

They have been described in details in previous reports. *Trichoderma viride*, using cellulose as the only carbon source, which may be representative of nuclear waste, they produce a lot of organic acids, 14 of them being identified by HPLC analysis, but, very rapidly, the total production is very low. The culture medium is a low mineral content solution, nearly representative of ground water.

Two different liquid flows around the samples are used. Twice are more higher than those expected in a deep repository in which water renewal will be very low. They were chosen in order to allow a modelisation of leaching of cement constituents.

III Pilot plant leaching experiments

The pilot plant has been described in details in the annual report of January 1992 and is now under use for 16 months.

Two liquid flows on the cement or clay samples were chosen, corresponding respectively to a main residence time in contact with the sample of about 1 and 4 days for cement experiment. Corresponding to swelling of clay when put in contact with water, it has not been possible to determine the free volume for clay columns, nor the mean residence time. Moreover, despite of being totally and constantly immersed, preferential liquid ways developed, corresponding to gas bubbles accumulation between the clay grains.

On the top of cement containing both Cs or U, when leaching by a solution containing micro-organisms, a polysaccharide biofilm can be noticed. A precipitation of Phosphate and Carbonate on the cement samples can be noticed specially on the top of the samples, while Carbon is produced (micro-organisms and metabolites, including carbonates). The layer of Calcium carbonate is thicker at the top of the cement columns (up to 100µm) than at the bottom. A thin Calcium phosphate layer (about 10µm) also develop under the previous Calcium carbonate layer.

III.1 Leaching of cement samples containing Uranium

Initial pH of mineral solution is about 6.5 to 7. It is unchanged when dropping on cement despite of acid production by fungi, due to the very small amount of produced acid and to the buffer capacity of the solution. Nevertheless, immediately after the solution is in contact with cement, pH increases to 12.5-13 at the beginning of the experiment (due to the mobility of $Ca(OH)_2$ and other alkaline compounds content), and is still greater than 10 after 12 months leaching.

Three slices were taken from the cement sample, one from the top, one from the middle and the third from the bottom. Compared with initial cement content, first results show that there were no effects on MnO and TiO2 content, but an important leaching of K, Na and Mg to a lesser extend, this last being precipitated on the surface as a phosphate of Ca and Mg. No decrease of Ca or other major component contents was noticed after 6 and 12 months of leaching except within the first outer 0.2 mm which porosity is increased. No leaching of Uranium was noticed. No effects can be noticed on Cl^- leaching. The greater the liquid flow around the cement is, the greater the effects.

Some pores at the surface of the sample seems to be sealed by the previous Calcium phosphate compound and by Calcium carbonate.

III.2 Leaching of cement samples containing Cesium

Compared with cement samples containing Uranium, the conclusions are the same except for Sulphate that is leached in this case, and for Cl^-, that was much more concentrated in the cement (Cesium was incorporated into the cement as Cesium Chloride). But these effects are noticed only for the higher liquid flow and have to be confirmed.

Within about 0.2 mm from the surface, most of the Cesium seems to have been leached from the matrix which porosity is increased. After 6 months leaching, the leached Cesium is concentrated at the periphery of cement, included into a Phosphate of Mg and Cs (chemical composition : $CsMgPO_4$). After 12 months, most of the Cs has been leached from this compound.

Precipitation of Calcium phosphate and carbonates seems also to have sealed some outlying pores.

III.3 Leaching of clay samples containing Uranium

Leaching of clay by mineral or organic acid

Desorption experiments were carried out with a suspension of clay in a stirred reactor. For the same acid, desorption increases with H^+ concentration. Compared with sulphuric acid, all tested organic acid always lead to a greater Uranium desorption, phenomenon that cannot be explained only by complexing properties (such a result is obtained using acetic acid that cannot be considered as a complexing chemical).

Leaching in the laboratory pilot plant by acid produced by fungi growing on cellulose

As for experiments on cement, sorption of Phosphate from the solution and no modification of Cl^- concentration, and a slight desorption of Sulphate can be noticed.

We can notice a slight sorption of K, no effects on Mg and Na, and a solubilisation of Ca.

Only the sorption of Phosphate and desorption of Potassium increase when liquid flow increases. No solubilisation of Uranium was noticed, most of the leached Uranium being probably caught by cells (sorption on the cell walls).

III.4 Leaching of clay samples containing Cesium

Leaching of clay by mineral or organic acid solutions

These experiments were carried out with a suspension of clay in a stirred reactor. As expected, there is no effect of the complexing properties of the acids but only an effect of pH of the solution.

Leaching in the laboratory pilot plant by acid produced by fungi growing on cellulose

For clay containing Cesium, the same effect of Phosphate sorption can be noticed.

For cations, the effects increase with the liquid flow. A sorption of Potassium can be noticed, but no effect on Calcium nor on Magnesium, and a leaching of Sodium. Despite of the effects of Cesium on clay structure, it seems that small amount of Sodium were still present in the clay and are displaced by Potassium (contained in the culture solution).

IV Study of the different effects of direct and indirect microbial action on radio nuclide mobility

For better understanding of the various possible action of micro-organisms on Uranium, we develop two different experimental apparatus to measure respectively direct and. indirect effects. They were described in the January 1993 annual report.

IV.1 Direct microbial action on radio nuclide mobility

Direct effect measurements need that radionuclides and micro-organisms are in contact one with the other.

For this experiment, *Trichoderma viride* is put as a suspension into a mineral medium containing Uranyl nitrate and stay in contact during 1 day.

At the end of the experiment, the culture medium is filtered and the total amount of U or Cs, adsorbed and bioaccumulated, is measured in the biomass by "washing" them using a diluted acid solution (desorption of ions only absorbed on cell wall).

For *Trichoderma viride*, as expected, despite of no microbial growth, it appears that Cesium is mainly bioaccumulated while Uranium is adsorbed on cell walls (a few percent for both nuclides).

IV.2 Indirect microbial action on Radio nuclide mobility

The objective of this study is to determine the increase of radio nuclide mobility by chemical issued from cellulose biodeterioration. This needs radionuclides and micro-organisms be separated.

Indirect effects have been measured using a 2 compartment device (see previous report) separated by a microporous membrane (0,45 µm polyvinylidene difluoride membrane) allowing the free diffusion of ions and molecules. Cells are grown in one compartment while Uranium or Cesium included in the matrix, are in the other.

Produced organic acids diffuse through the membrane and lead to the desorption of U initially incorporated in the matrix.

Solubilized nuclide can diffuse through the membrane of polyvinylidene and an accumulation on the cell wall or on polymers excreted by cells occurs.

In the case of Uranium incorporated into cement, only a very small amount (about 1%) is dissolved, most of it being adsorbed into polymers excreted by cells. The important production of polymers leads to fouling of the membrane and stops the experiment.

For Cesium incorporated into clay, the pH of the solution was not low enough to solubilize it.

Preliminary conclusion

From first results, cement is a very efficient barrier against Uranium migration, while clay is much more better than cement to avoid Cesium migration.

After 12 months leaching, it is impossible to distinguish the specific effect of micro-organisms on leaching of Uranium from clay or cement.

Nevertheless, solubilisation of Uranium incorporated into clay as UO_2^{2+} is greater using organic acids than using mineral ones. So, it seems that micro-organisms can increase the mobility of Uranium.

By opposition, accumulation of Uranium into polymers excreted by cells can be noticed, that leads to a decrease of Uranium mobility.

Up to now, it is too early to conclude about the global effect of micro-organisms on mobility of Uranium which is a balance between these two effects. Experiments prosecutes.

As a first approach, it seems that there is no specific effect of micro-organisms on solubilisation of Cesium both from cement or clay.

Title: Corrosion of Selected Packaging Materials for Disposal of Heat-Generating Radioactive Wastes

Contractors: KfK Karlsruhe, ENRESA Madrid
Contract No.: FI 2W-CT-90-0030
Duration of contract: January 1991 - December 1994
Period covered: January 1993 - December 1993
Project Leader: E. Smailos, KfK-Karlsruhe, Germany

A. OBJECTIVES AND SCOPE

In previous corrosion studies, carbon steels and the alloy Ti 99.8-Pd were identified as promising materials for heat-generating nuclear waste packagings acting as a barrier in a rock-salt repository. To characterize the corrosion behaviour of these materials in more detail, a research programme including laboratory-scale and in-situ corrosion studies has been undertaken jointly by KfK and ENRESA/INASMET. Besides carbon steels and Ti 99.8-Pd, also Hastelloy C4 and some Fe-base materials will be examined in order to complete the results available to date.

The research programme has two objectives:

- Investigation of the influence of essential parameters on the corrosion behaviour of the materials in disposal relevant salt brines. These parameters are: temperature, gamma radiation and selected characteristics of packaging manufacturing (KfK).
- Investigation of the resistance of carbon steels to stress corrosion cracking in an $MgCl_2$-rich brine at various temperatures and strain rates by means of the slow strain rate technique (ENRESA).

B. WORK PROGRAMME

B.2.1 Corrosion studies on the unalloyed fine-grained steel in three salt brines (two $MgCl_2$-rich, one NaCl-rich) at 150°C and gamma dose rates of 1 Gy/h and 10 Gy/h (laboratory-scale immersion tests, KfK).

B.2.2 Corrosion studies of two low-alloyed steels (TSt E 460, 15 MnNi 6.3) in three salt brines at 150°C (laboratory-scale immersion tests, KfK).

B.2.3 In-situ corrosion studies on specimens of Fe-base materials, Ti 99.8-Pd and Hastelloy C4 in rock salt at rock temperature (reference experiments, KfK).

B.2.4 In-situ corrosion studies on tubes of carbon steel, Ti 99.8-Pd and Hastelloy C4 provided with selected container manufacturing characteristics in rock salt/brines at 90°C-200°C (KfK).

B.2.5 Statistical analysis of corrosion data (KfK).

B.2.6 Stress corrosion cracking studies on unalloyed and low-alloyed steels (fine-grained steel, TSt E 460, 15 MnNi 6.3) in an $MgCl_2$-rich brine at various temperatures (25°C, 90°C, 170°C) and slow strain rates (10^{-4} - 10^{-7} s^{-1}) (ENRESA / INASMET).

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

In the period under review, gamma irradiation-corrosion studies of up to about 6 months at 10 Gy/h and 150°C, and stress corrosion cracking studies at slow strain rates (10^{-4}-10^{-7} s^{-1}) and 90°C were performed on three preselected carbon steels in disposal relevant salt brines. Moreover, results were obtained from long-term in-situ corrosion studies (maximum test duration 9 years) on carbon steel, Ti 99.8-Pd, Hastelloy C4, Ni-resist D4 and Si-cast iron. In the in-situ experiments, besides metal sheets, tubes of the above-mentioned materials provided with selected container manufacturing characteristics were tested in rock salt and rock salt plus brine at temperatures of 32°C-200°C.

PROGRESS AND RESULTS

B.2.1 Irradiation-corrosion studies on the unalloyed steel TStE 355 in brines (KfK contribution)

The long-term gamma irradiation-corrosion studies on the unalloyed fine-grained steel TStE 355 (0.17 wt.% C; 0.44 wt.% Si; 1.49 wt.% Mn; bal. Fe) were continued by examination of the 166-day specimens. The steel was investigated for general and local corrosion in three disposal-relevant salt brines (two $MgCl_2$-rich, one NaCl-rich) given in Table I at 150°C and a realistic gamma radiation field of 10 Gy/h (10^3rad/h) for the thick-walled container discussed. The experiments were performed in the spent fuel storage pool of KFA Jülich. The radiation source were spent fuel elements with a gamma energy spectrum similar to that of 10-year-old vitrified HLWC. For comparison, also experiments without radiation were conducted. All investigations were carried out at a brine volume - to specimen surface ratio (V/S) of 2 ml/cm^2.

The integral weight losses and the corrosion rates of the steel after an 166-day exposure to irradiated and unirradiated brines of 150°C are compiled in Table II. For comparison, also the results of previous studies /1/ lasting 100 days have been entered. All values are average of 3-4 specimens. In both cases with and without radiation, the integral corrosion rates of the steel in the $MgCl_2$-rich brines 1 (Q-brine) and 2 are siginificantly higher than in the NaCl-rich brine 3. The highest corrosion rate was obtained in the $MgCl_2$-richest brine 2, the lowest in the NaCl-rich brine 3. The higher corrosivity of the $MgCl_2$-rich brines compared to NaCl-rich brine is attributed to their higher HCl concentration. This could be explained by the higher Cl^- concentration and the hydrolysis of the Mg^{2+}. The acceleration of the steel corrosion in brines containing high amounts of $MgCl_2$ is in agreement with the results reported by Westerman et al. /2/.

The imposition of a 10 Gy/h radiation field on the 150°C brine environments increases the average integral corrosion rates of the steel specimens in the brines 1 and 2 from about 69 µm/a to 124 µm/a, and from 170 µm/a to 221 µm/a, respectively. In the brine 3, the corrosion rate in the 10 Gy/h irradiated environment (14.6 µm/a) is very closed to the value in the unirradiated system (19.2 µm/a).

Surface profiles and metallographic examinations of corroded specimens have shown that the steel is resistant to pitting corrosion in both irradiated and unirradiated brines. In all brines, a non-uniform general corrosion was observed. However, the measured maximum penetration depth of this uneven corrosion corresponds to the values of the average thickness reduction.

In general, it can be stated that the corrosion rates determined so far for the steel in irradiated and unirradiated brine environments imply corrosion allowances technically acceptable for the thick-walled containers discussed. A 10 Gy/h gamma radiation field appears to increase the general corrosion of steel at

150°C in $MgCl_2$-rich brines, whereas in NaCl-rich brine no effect of radiation on the corrosion was observed. For a final statement regarding the influence of a gamma dose rate of 10 Gy/h on the corrosion of carbon steels in 150°C brine environments, the results of the ongoing long-term experiments lasting up to 18 months are necessary.

B.2.3 +
B.2.4 In-situ corrosion studies on selected container materials (KfK contribution)

In the period under review, the long-term in-situ corrosion studies (maximum test duration 9 years) on Ti 99.8-Pd, Hastelloy C4 (a Cr-Ni-Mo alloy), cast steel (0.16 wt.% C) and the Fe-base materials Ni-resist D4 and Si-cast iron were completed. Besides metal sheets of the above-mentioned materials, tubes (500 mm length, 45 mm outside diameter) provided with selected container manufacturing characteristics were investigated. Two types of tubes were examined: Tubes made of Ti 99.8-Pd, cast steel and Ni-resist D4 with the container sealing technique simulated by electron beam (EB) or tungsten inert gas (TIG) welding, and carbon steel tubes with a corrosion protection of Ti 99.8-Pd or Hastelloy C4 simulated by explosion plating.

In these experiments which were conducted in vertical boreholes in the Asse salt mine, the specimens were exposed to rock salt (0.1 wt.% H_2O) and rock salt plus brine (NaCl or $MgCl_2$-rich), respectively, at temperatures of 32°C (rock temperature) and 90°C-200°C (vertical T-gradient in the boreholes). In the experiments with brine, 100 ml of the corrosion medium were filled at the beginning of the experiments in the annular gap between the tubes and the borehole wall. The maximum pressure in the boreholes measured during the experiments was 0.28 MPa which corresponds to a salt brine boiling point of 140°C. This means that the water contained in the brine evaporates at points of elevated temperature (center of the tube) and recondences at the upper cooler end of the tube (90°C).

The essential in-situ corrosion results can be summarized as follows:

- Corrosion of metal sheets and tubes of Ti 99.8-Pd and Hastelloy C4 in rock salt (32°C) and rock salt plus NaCl-brine (32°C-200°C) is negligible small. The same is true also for cast steel, Ni-resist D4 and Si-cast iron in rock salt at temperatures of 32°C-200°C. All materials are resistant to pitting corrosion and their general corrosion rates are only 0.1-1.1 µm/a.
- In rock salt plus $MgCl_2$-rich Q-brine (6.3 years at 32°C), the non-corrosion protected cast steel tube suffers from significant non-uniform general corrosion. The greatest corrosion attack of 570 µm occurred at the lower part of the tube, the smallest of 180 µm existed at the top of the tube (Figure 1). These values correspond to average corrosion rates of about 30 µm/a (top of the tube) and 90 µm/a (bottom), respectively, and imply corrosion allowances technically acceptable for thick-walled containers.

B.2.6 Stress corrosion cracking studies on carbon steels (ENRESA / INASMET contribution)

Further stress corrosion cracking studies were performed on three preselected carbon steels in the $MgCl_2$-rich Q-brine (brine 1) at 90°C and slow strain rates of 10^{-4}-10^{-7} s^{-1}. The steels investigated were: the low alloyed steels TStE 460 and 15 MnNi 6.3 and the unalloyed fine-grained steel TStE 355. The steels had the following composition in wt.%:

TStE 460 : 0.18 C; 0.34 Si; 1.5 Mn; 0.51 Ni; 0.15 V; bal. Fe
15 MnNi6.3 0.17 C; 0.22 Si; 1.59 Mn; 0.79 Ni; bal. Fe
TStE 355 : 0.16 C; 0.41 Si; 1.5 Mn; bal. Fe.

The parent materials for TStE 355 and TStE 460 were hot-rolled and annealed plates, and for 15 MnNi 6.3 forged and annealed disks. The experiments were performed in Hastelloy C-276 autoclaves at an argon pressure of 13 MPa. In order to be able to interpret the results obtained in the brine, additional comparative investigations were conducted in argon as the inert medium. Besides specimens made of the parent materials, also MAG (Metal Active Gas) welded specimens simulating a possible container sealing technique were tested. For the experiments round specimens of 6 mm diameter, finished with 1,000 grade emery paper were used.

Load, position, time and temperature data were logged by the microprocessor that controls the slow strain rate machine. After each test the elongation (E), reduction of area (R.A.), energy, yield strength (Y.S.), maximum load, and true stress at fracture were calculated. To evaluate the resistance of the steels to stress corrosion cracking, metallographic and scanning electron microscopic (SEM) examinations of the fracture specimen surfaces were performed in addition to the tensile experiments.

The results of the slow strain rate tests obtained for the unwelded steel specimens (parent materials) in argon and Q-brine at 90°C and various strain rates (10^{-4}-10^{-7} s^{-1}) are given in Figs. 2 and 3. All values are average of at least two experiments. The values for the yield strength and maximum load in Q-brine are very closed to those in argon. However, a clear decrease of the elongation, reduction of area, energy and true stress at fracture occurs for all steels in Q-brine at 90°C in comparison to argon. This finding is in good agreement with own previous results obtained at 170°C /1/ and those reported by Westerman et al. /2/. Nevertheless, the loss of ductility of the steels at 90°C is lower than that of 170°C. The results obtained for the MAG-welded steel specimens in argon and Q-brine (90°C) show that welding causes only a slight decrease of the ductility of the steels in these media.

In the metallographic examinations of steel specimens tested in Q-brine, a non-uniform general corrosion due to repeated breaking of the corrosion surface layer is observed for all steels both in the unwelded and MAG-welded condition. Secondary cracks typical for stress corrosion cracking were not observed for the hot-rolled steels TStE 355 and TStE 460 under any of the test conditions. For this reason, the reduction of ductility of these steels in Q-brine compared to argon cannot be attributed to stress corrosion cracking. For the loss of ductility in this brine another mechanism such as embrittlement could be responsible. Also in the case of the forget steel 15 MnNi 6.3, no signs of sensitivity to stress corrosion cracking were found in Q-brine at 90°C and strain rates up to 10^{-6} s^{-1}. However, at the slowest strain rate of 10^{-7} s^{-1}, besides a non-uniform corrosion, extensive lateral secondary cracks indicating stress corrosion cracking were observed.

The fracture surface features observed in the scanning electron microscopic (SEM) examinations show a change from a fully ductile manner when steel specimens are tested in argon to a brittle one when the specimens are tested in Q-brine. The embrittlement of the steels in Q-brine at slow strain rates in probably due to the hydrogen produced during corrosion, as already discussed in previous work /1/. It appears that the hydrogen enters the steels in the atomic form, predominantly in zones of high stress level, and causes a loss of ductility. However, this effect does not appear to be serious because the residual reduction of area and elongation at fracture of the steels after testing in the brine environment are still relatively high.

REFERENCES

/1/ SMAILOS, E., FIEHN, B., GAGO, J.A., AZKARATE, I. "General Corrosion and Stress Corrosion Cracking Studies on Carbon Steels for Application in Nuclear Waste Disposal Containers", KfK Report 5166 (1993).

/2/ WESTERMAN, R.E., HABERMAN, J.H. et al., "Corrosion and Environmental-Mechanical Characterization of Iron-Base Nuclear Waste Package Structural Barrier Materials", PNL Report 5426 (1986).

List of publications in 1993

SMAILOS, E., FIEHN, B., GAGO, J.A., AZKARATE, I. "General Corrosion and Stress Corrosion Cracking Studies on Carbon Steels for Application in Nuclear Waste Disposal Containers", KfK Report 5166 (1993).

SMAILOS, E., "Corrosion of High-Level Waste Packaging Materials in Disposal Relevant Brines", Nuclear Technology, Vol. 104, No. 3, pp. 343-350 (1993).

SMAILOS, E., HALM, G., SCHWARZKOPF, W., KÖSTER. R., "Investigations into the Effect of Gamma Radiation on Corrosion of High Level Waste Steel Containers in Salt Brines", Improvements in Material Reliability in the Back End of the Nuclear Fuel Cycle,(Proc. of a Technical Committee Meeting, Vienna 1989), IAEA-TECDOC-686, Vienna, February 1993, p. 97.

SCHWARZKOPF, W., SMAILOS, E., FIEHN, B., KÖSTER, R., "In-situ Corrosion Studies on Selected High Level Waste Packaging Materials under Simulated Disposal Conditions in Rock Salt Formations", Improvements in Material Reliability in the Back End of the Nuclear Fuel Cycle (Proc. of a Technical Committee Meeting, Vienna 1989), IAEA-TECDOC-686, Vienna, February 1993, p. 119.

Table I: Compositions, pH -values and O_2 -contents of the salt brines used in the laboratory - scale corrosion experiments

Brine	Composition (wt.%)							
	NaCl	KCl	$MgCl_2$	$MgSO_4$	$CaCl_2$	$CaSO_4$	K_2SO_4	H_2O
1	1.4	4.7	26.8	1.4	---	---	---	65.7
2	0.31	0.11	33.03	---	2.25	0.005	---	64.3
3	25.9	---	---	0.16	---	0.21	0.23	73.5

pH (25°C): 4.6 for brine 1; 4.1 for brine 2; 6.5 for brine 3
O_2(55°C): 0.8 mg/l for brine 1; 0.6 mg/l for brine 2; 1.2mg/l for brine 3

Table II: Integral weight losses and corrosion rates of the unalloyed fine-grained steel TStE 355 after exposure to the test brines at 150°C

Brine	Test time (d)	Without gamma radiation		With gamma radiation of 10 Gy/h	
		Weight loss (g/m^2)	Corrosion rate (µm/a)	Weight loss (g/m^2)	Corrosion rate (µm/a)
1	100	178.1 ± 8.2	87.5 ± 4	367.7 ± 6.3	173.5 ± 3.0
	166	244.5 ± 15.0	68.8 ± 4.2	430.2 ± 51.7	124.0 ± 14.9
2	100	516.8 ± 20.3	254.1 ± 10.0	441.6 ± 149.4	208.4 ± 70.5
	166	605.3 ± 18.4	170.3 ± 5.2	766.0 ± 74.0	220.9 ± 21.3
3	100	50.5 ± 5.8	24.8 ± 2.9	44.9 ± 5.9	21.2 ± 2.8
	166	68.1 ± 7.1	19.2 ± 2.0	50.8 ± 6.4	14.6 ± 1.8

brines 1 and 2: $MgCl_2$-rich; brine 3: NaCl-rich

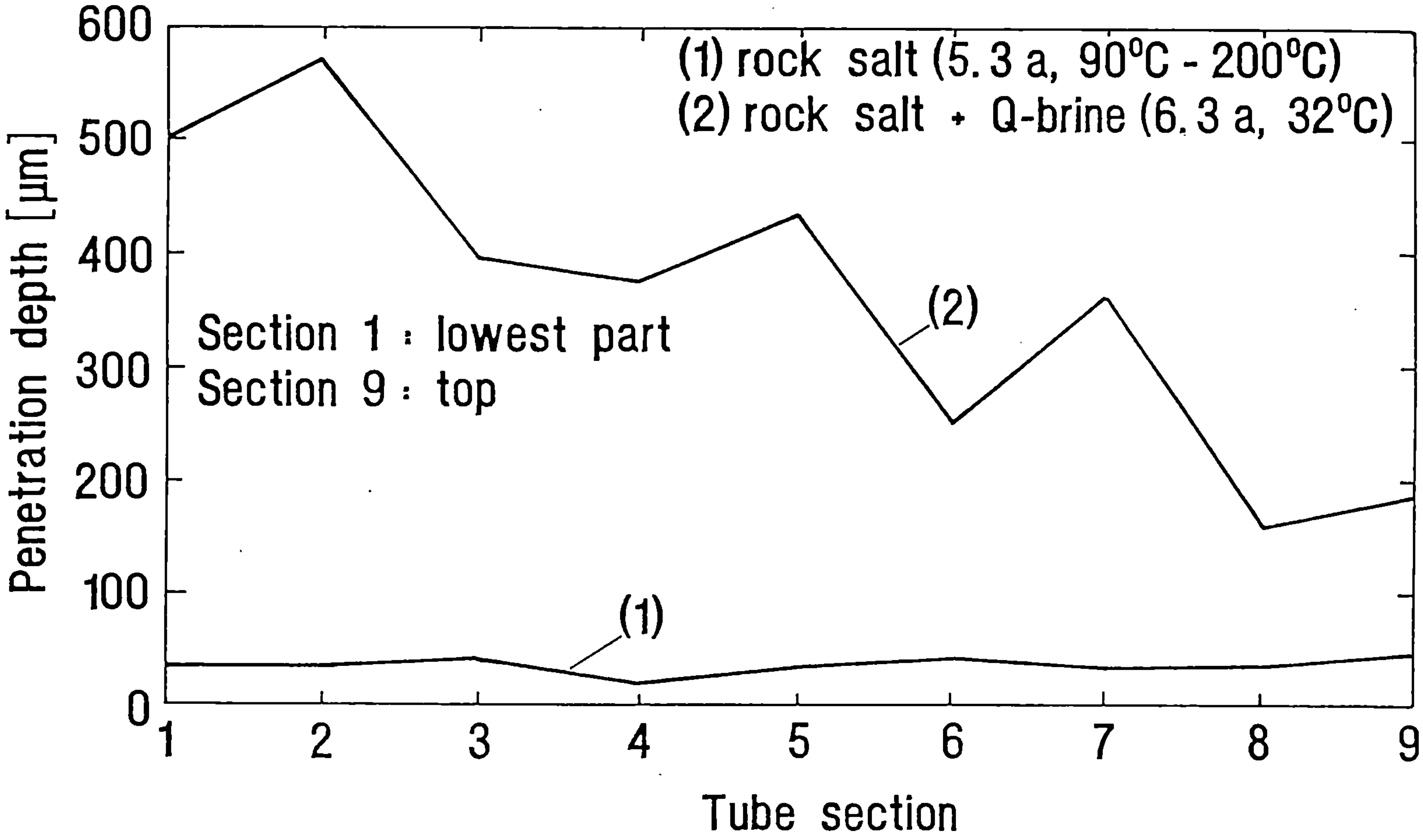


Fig. 1: Surface profilometry results of in-situ tested cast steel tubes. Maximum depth of non-uniform corrosion in rock salt and rock salt + brine

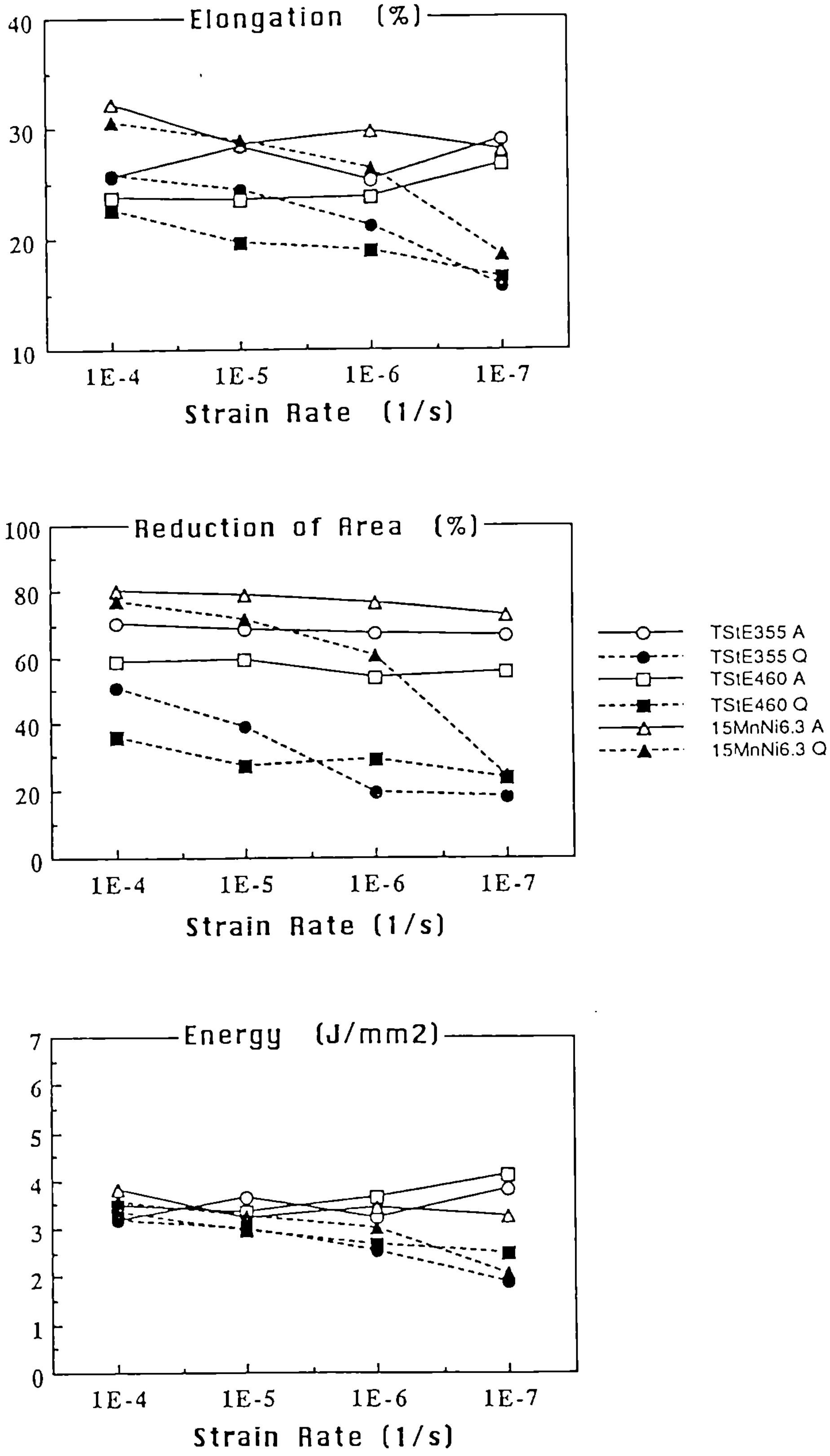


Fig. 2: Elongation, reduction of area and energy versus strain rate for the steels TStE 355, TStE 460 and 15MnNi6.3 tested at 90°C and 13 MPa in argon and Q-brine

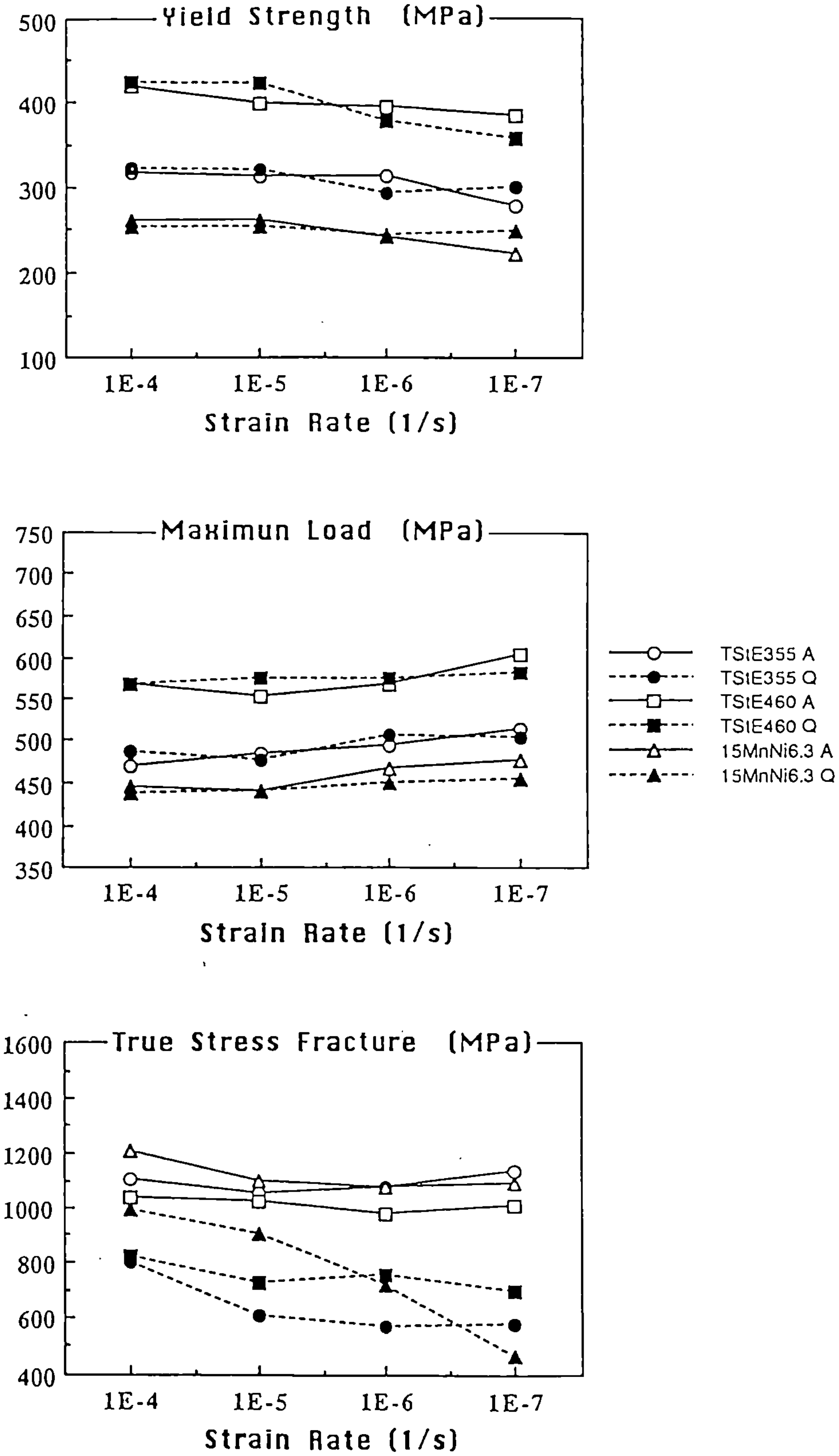


Fig. 3: Yield strength, maximum load and true stress fracture versus strain rate for the steels TStE 355, TStE 460 and 15 MnNI6.3 tested at 90°C and 13 MPa in argon and Q-brine

Title: **Theoretical and experimental study of degradation mechanisms of cement in the repository environment**
Contractor: **Commissariat à l'Energie Atomique/CE. Saclay/DCC/DSD/SCS**
Contract: **FI2W-CT90-0035**
Duration of contract: **January 1991-December 1994**
Period covered: **January - December 1993**
Project leader: **Mme Revertegat, CEA/CE Saclay/DCC/DSD/SCS**

A. OBJECTIVES AND SCOPE

The object of the research program supported by CEC contract number FI2W-CT90-0035 is to estimate the long-term corrosion of concrete used for waste disposal and to determine the mechanisms involved. Therefore we are developing a corrosion model based on the different mechanisms involved, in which it will be possible to introduce storage conditions specific to each site (type of corrosive solution, cement composition, storage temperature...)

B. WORK PROGRAMME

1. Investigation about degradation mechanisms involved when the cement paste is corroded by a solution including aggressive ions:
    - study of phase diagrams to determine which phase may coexist and acquisition of the thermodynamic data necessary to solve the model in the different possible cases (study of equilibria as functions of aggressive ions and temperature)
    - study of degradation processes of cement pastes submitted to various aggressive environments (chlorides, sulfates, carbonates)

2. Testing of the local equilibrium hypothesis (by checking that the kinetics is effectively governed by diffusion)

3. Modelling of cement paste degradation:
    - mathematic writing of the model equations built on physico-chemical laws
    - numerical resolution of the model by a microcomputer program: in a first step, a simplified algorithm is developed i order to validate the model equations
    - model validation
    - algorithm extension to resolve any case (modelling of Cl, SO_2 and carbonates attack and taking into account the main reactions of precipitations and dissolutions occurring)

4. Application to cement clay interaction: resolution of the generalized model and comparison with experimental results

C. PROGRESS OF WORK AND OBTAINED RESULTS

The status of progress has not been forwarded to the Commission for 1993.

Title	The Performance of Cementitious Barriers in Repositories
Contractor(s)	AEA Industrial Technology (co-ordinator) Riso National Laboratory Bundesanstalt fur Material Forschung und Prufung
Contract N°	FI2W-0040
Duration of Contract	from 1 May 1991 to 30 April 1994
Period covered	1 January 1993 to 31 December 1993
Project Leader	Dr A.W. Harris

OBJECTIVES AND SCOPE

Cementitious materials are likely to be used in waste disposal facilities to help retain radionuclides by acting as chemical and physical barriers to migration. Current source term calculations are based on the homogeneous repository assumption. This is unlikely to be true in reality since cementitious materials will crack, leading to inhomogeneities in mass transport and chemistry. The impact of these inhomogeneities will depend upon reactions with groundwater that can lead to the healing of cracks, to the benefit of the physical barrier performance, and sealing of concrete surfaces, to the detriment of chemical performance.

Validated models and supporting data for the physical and chemical barrier performance of cementitious materials will be developed and used to examine the simpler models employed in safety assessments. The mechanisms of crack healing within cementitious materials under repository conditions will be investigated. An assessment of the impact of cracks and inhomogeneities on the source term will be made. The reference repository will be based on the designs provided by Nirex and hence will be realistic.

WORK PROGRAMME

Task 1 - Healing of Cracks by Cementitious Materials

Sub-task 1.1 - Experiments on crack healing
Sub-task 1.2 - Modelling of crack healing

Task 2 - Cement-groundwater interactions

Sub-task 2.1 - Diffusive cement-groundwater interactions
Sub-task 2.2 - Perfusive cement-groundwater interactions
Sub-task 2.3 - Modelling cement-groundwater interactions

Task 3 - Barrier Properties of the Inhomogeneous Repository

Sub-task 3.1 - Chemistry varying with position and time
Sub-task 3.2 - Effect of fissures on the source term
Sub-task 3.3 - Validation of source term model

PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The contract is generally progressing according to expectation. During the year progress has been made in all tasks including the commencement of all sub-tasks within Task 3. Some delays have been encountered in the modelling tasks due to lack of available time (Task 1) and difficulties in verification and validation (Task 3). The process of validating the models developed under Task 3 commenced towards the end of the year and will continue during 1994.

An additional piece of work be added to the contract to be performed by Dr V. Balek at the Rez Nuclear Research Institute in the Czech Republic. This work will be concerned with the study of diffusion in reaction layers using radon measurements. Approval for this work has been received and it will be carried out during 1994.

Progress and results

Task 1 - Crack Healing

Sub-task 1.1 - Experiments on crack healing

The experiments performed at Risø National Laboratory have principally been concerned with crack filling in cementitious barriers due to the flow of calcium bicarbonate solutions through cracks. A total of 25 different specimens have been studied covering a variety of crack geometries and material and solution compositions.

The mechanisms which determine whether a crack will close are now fairly well understood. The tendency to crack closure increases with the concentration of readily diffusing alkali metal hydroxides in the cementitious material and is also increased by the presence of side cracks approximately perpendicular to the main crack and the direction of flow. Such side cracks, or the more complex crack systems present in partially crushed specimens, function as additional sources of the hydroxyl ions necessary for the precipitation of calcium carbonate from the bicarbonate solution. It is expected that the closure of a crack in this manner would improve the performance of a cementitious barrier in a radioactive waste repository.

In contrast, when the hydroxyl ions are supplied through the dissolution of calcium hydroxide or calcium silicate hydrate (CSH) gel from the cementitious material adjacent to the crack, a relatively thin and protective layer of calcium carbonate crystals is formed on the surfaces of the crack. Under such circumstances the flow of the bicarbonate solution continues virtually unimpeded through the centre of the crack. The formation of such layers may significantly affect the performance of a cementitious barrier through the a modification to the chemistry, and in particular the pH, of the solution flowing in the crack. Such effects are the subject of Tasks 2 and 3.

The characterisation of the crack-filling minerals has been carried-out using chemical analysis and scanning electron microscopy (SEM). The morphology of the precipitates resulting from the flow of tap water was found to be distinctly different from that of the precipitates formed from the calcium bicarbonate solution employed as a groundwater simulant in the majority of experiments. The bicarbonate solution precipitates are primarily rhombohedral, as illustrated in the SEM image shown in Figure 1. In contrast, the precipitates from tap water are either rod-like or flat and tend to be interlocked. It is suggested that the reason for this difference in morphology is the presence of a small but significant quantity of magnesium in the tap water.

In a third type of experiment, employing de-ionised water, crack closure was observed for relatively narrow cracks. The reason for crack closures under these circumstances is presumed to be the formation of a voluminous silica gel as a product of the leaching of CSH gel from the cementitious material.

The influence of de-ionised water on the leaching and re-location of other minerals within columns of granulated hardened cement pastes is currently being studied. These experiments include the use of specimens containing radioactive tracers.

Sub-task 1.2 - Modelling of crack healing

The formation of sealing layers of calcium carbonate crystals on the surfaces of a crack results in a very high hydroxyl ion concentration gradient through the layer. That this must be the case is demonstrated by the consideration of the precipitation reactions, the diffusion coefficients for the appropriate cations and anions and the requirement for the maintenance of electro-neutrality. A numerical diffusion model covering these features has been set up and has been shown to function acceptably. Some difficulties have been encountered with the modelling of the extremely high concentration gradients. The model makes use of a simplified cement chemistry and in unable to model leaching by pure water.

Task 2 - Cement-groundwater Interactions

Sub-task 2.1 - Diffusive Cement-groundwater Interactions

The impact of the reaction layers formed by interaction with groundwaters on the diffusion and sorption properties of cementitious materials is being assessed. The experimental work has concentrated on the reaction between carbon dioxide- and magnesium-bearing solutions and the Nirex reference vault backfill. A series of specimens are being subjected to carbon dioxide-bubbled water, carbon dioxide bubbled magnesium chloride solution and magnesium chloride solution alone to form reaction layers. All exposures have been completed during the current year. Specimens have been exposed to water saturated with carbon dioxide at atmospheric pressure for periods up to 470 days. The specimens exposed to magnesium chloride solutions have been exposed for total time periods of either 120 or 370 days.

The morphology of the reaction layers formed on reference backfill in the presence of carbon dioxide saturated water has been investigated using SEM. The presence of relatively large rhombohedral crystals of calcium carbonate is very apparent. The morphology of the layer is very similar to that illustrated in Figure 1, demonstrating that the morphology is relatively independent of the nature of the cementitious material. The nature of layers makes it difficult to determine a value for the layer thickness. Figure 1 shows that the maximum crystal dimension is of the order of 100 microns, therefore the layer thickness could be of a similar magnitude.

The sorption and diffusion properties are determined using tin and caesium in-diffusion. These species have been selected to be typical of sorbing and non-sorbing elements. The performance of the specimens is characterised by the product of the intrinsic diffusion coefficient and the capacity factor. This value is denoted the diffusion product. Measurements on all exposed specimens have now been completed. The results of the experiments are summarised in Tables 1 to 3. Table 1 gives the results for a series of pristine specimens which provide baseline information. Table 2 demonstrates the effect of exposure to carbon dioxide and Table 3 the effects of magnesium chloride solutions both with and without the presence of carbon dioxide.

Comparison of the data given in Tables 1 and 2 demonstrates that specimens exposed to carbon dioxide bubbled water show a significant change in the value of the diffusion product compared with the pristine material. The diffusion product for tin is increased by a factor of two whereas that for caesium is generally decreased by a factor of between two and ten. The experimental measurements for the specimen exposed for 470 days are continuing and the apparent increase in the diffusion product compared with pristine material is not definite.

In addition to carbon dioxide, the repository groundwater is also expected to contain significant quantities of dissolved magnesium. Previous experiments carried out in Task 2.2 have indicated that the precipitation of magnesium compounds is significant. The experimental measurements on the second batch of specimens, previously exposed to magnesium chloride solutions of 0.01, 0.025, 0.05 and 0.1 M concentration. These solutions were saturated with carbon dioxide by bubbling the gas through them. An additional set of specimens are exposed to 0.1 M magnesium chloride without carbon dioxide. The specimen exposed to carbon dioxide-free solution shows an obvious precipitate and the specimen surfaces have been occluded by a powdery white surface layer. It is believed that the precipitate is magnesium hydroxide (brucite). In contrast, the carbon dioxide bubbled solutions show no sign of a precipitate, although a surface layer similar to that formed on the carbonated specimens is evident. It has been concluded that the interaction between magnesium and carbon dioxide is significant in determining the nature of the surface layers formed on the reference backfill.

Caesium in-diffusion measurements have been carried-out on specimens after 120 and 370 days exposure. Tin diffusion has been determined for 120 days exposure only. The results are given in Table 3. The results for tin exhibited considerable variability but it was apparent that the diffusion product had decreased slightly compared with pristine specimens. The magnitude of the decrease depends on the magnesium concentration. In the case of caesium in-diffusion, the diffusion product is significantly reduced when carbon dioxide was present. In the absence of carbon dioxide, when a magnesium hydroxide layer is expected, there is no decrease in the diffusion product.

It can be concluded that the reaction layers have different properties to the unreacted backfill and that the magnitude of the effect is dependent on a combination of the type of layer formed and the migrating species. In general, carbonate layers give rise to a significant effect whereas magnesium hydroxide is probably ineffective as a diffusion barrier. Observations made under Task 1.1 suggest that the presence of relatively small quantities of magnesium in solution can significantly affect the morphology of the reaction layer. This may provide a mechanism for the effect of magnesium on diffusion rates, magnesium-containing carbonates providing a less protective layer than pure calcium carbonate.

In order that an indication of the relative merits of the various possible compounds be assessed, in-diffusion type measurements have been performed on powder samples of three compounds; calcium carbonate, magnesium carbonate and magnesium hydroxide. These compounds were selected to represent the basic compounds which might be formed for the groundwater composition under consideration. The experiments are currently in progress and results are not yet available. Initial indications are that magnesium hydroxide gives rise to the removal of tin from solution in a very short time, probably through an increase in the sorption of the species.

Sub-task 2.2 - Perfusive Cement-groundwater Interactions

The interaction between groundwater and cementitious material during the flow of the solution through the pore structure of the material may lead to the deposition of reaction products within the pore structure and the preferential dissolution of certain minerals, in particular portlandite (calcium hydroxide). This may give rise to preferential flow pathways within the material and consequently reduce the effective sorption and pH buffering capacities of the backfill.

Initial experiments were performed using the reference vault backfill and either pure water or simulated groundwater. The results of these experiments have been described previously. It was apparent from these experiments that the buffering behaviour of the reference vault backfill was not exactly as expected. In particular, the apparent quantity of calcium hydroxide leached from the specimens was not as great as would be expected from the composition of the material. Examination of the specimens demonstrated that calcium hydroxide was present when the equilibrium pH had fallen below that expected in the presence of this compound. This was provisionally attributed to the microstructure of the reference vault backfill precluding access to the entire inventory of calcium hydroxide. In addition, the use of a calcium hydroxide aggregate gives rise to a bimodal distribution of calcium hydroxide crystallite sizes due to the formation of additional calcium hydroxide during hydration.

The influence of microstructure and the use of the calcium hydroxide aggregate was investigated by producing a number of additional materials omitting one or two of the components of the actual reference vault backfill. Accelerated leaching experiments have been performed on these specimens during the current reporting period and the data are currently being analysed. It was apparent during some of the experiments that the process of casting the materials could give rise to a volume of material which was very much more susceptible to leaching and rapidly gave rise to inhomogeneous flow. The water flowing through such volumes was not buffered by the backfill despite the remainder of the specimen being intact and retaining significant buffering capacity. These readily leached volumes were attributed to more porous regions which occurred at the top of the cast specimens due to settling of material during casting.

It was decided to investigate the potential for the formation of inhomogeneities during casting further. A number of "interface" specimens have been created whereby the specimen was cast in two stages with an interval between castings. These specimens are intended to simulate the process of backfill emplacement in stages and the possible impact of this on the development of preferential flow pathways. In addition, a cylindrical specimen approximately 1 m in length has been cast and the porosity and strength of the material will be profiled to ascertain the size of the potentially porous zone in a more realistically dimensioned specimen.

The specimens cast with a deliberate interface were found to be extremely weak. It was not possible to carry out measurements on these specimens since the interface failed during handling. It can be concluded that the interface between consecutive pours may well provide a significant zone of weakness. A profile of fractional porosity through approximately 1 m of the high-porosity backfill showed no variation in porosity with vertical distance over the length scale available; approximately 5 mm.

Task 2.3 - Modelling Cement-groundwater Interactions

The modelling of the accelerated leaching experiments on the reference backfill has not been extended during the current reporting period since no additional results have been produced. It is expected that the interpretation of the results discussed above, in particular those relating to cement paste and the other materials related to the reference backfill will make further use of this modelling.

Task 3 - Barrier Properties of the Inhomogeneous Repository

Sub-task 3.1 - Chemistry varying with position and time

The large-scale development of inhomogeneities within a repository may result in groundwater flow being substantially or completely confined to cracks. A simple model of the interaction of the interaction between the water flowing in the crack and surrounding backfill was developed as part of the work reported out previously [1]. This model was simplified to the extent that only a single chemical process was considered; the dissolution of calcium hydroxide. The analytical model is not able to simulate the potential of reaction layers on crack surfaces to hinder the interchange of aqueous species between the water flowing in the crack and the backfill.

The development of the advanced model of the behaviour of cracked media based on a two-dimensional version of the CHEQMATE code has continued during the current period. The model, denoted CHEQFRAC, is now operational and is undergoing verification. Initially the model has been verified by comparison with the simplified analytical model developed previously [1].

Sub-task 3.2 - Effect of fissures on the source term

The results of the experimental and modelling work undertaken thus far indicate that significant differences may arise between the performance of a repository in which homogeneous chemical conditions are assumed and one in which the effects of inhomogeneities, especially cracks, are also considered in the modelling of performance. In particular, the time evolution of the repository chemistry is significantly different if a proportion of the groundwater flow is confined to cracks. Any change in the repository performance will be reflected in a modification to the radionuclide source term. It is not intended that the current project will provide a modified source term model which takes account of cracks. However, the potential magnitude of the effect of cracks on the source term will be considered by determining the possible effects of cracks. Suggestions will be made as to how such effects should be incorporated into a source term model.

The primary factor which determines the magnitude of the effect of the cracks will be the actual crack distribution within the repository. The CHEQFRAC model is currently being used to identify the range of crack distributions which can have a significant effect on the performance of the repository. The other significant factors within the model are the various diffusion parameters for the backfill and the reaction layers.

Sub-task 3.3 - Validation of source term model

The aims of this sub-task are to verify the theoretical models of the buffering of water flowing in a crack and to use the models to ascertain the potential impact of flow in cracks on the performance of the near-field.

The necessary experiments must be laboratory-scale simulations of cracks. To this end an experiment has been designed which will consist of a slab of the reference vault backfill which is contained such that water will flow past one face of the slab. The effective crack width will be controlled by spacing a perspex sheet at an appropriate distance from the face. The experiment is intended to determine the chemistry of the water flowing past the slab face as a function of water volume and the quantity of backfill. The experiment will be directly simulated by the theoretical model and the results compared.
A simple experimental apparatus for the verification experiments has now been constructed and an initial run carried out. The principal problem in verifying the models of the

behaviour of water in cracks is that of the extremely slow flow rates expected in a repository. Despite the fact that flow in cracks would be significantly faster than that through a homogeneous medium, due to the concentration of flow into a small volume, the maximum velocity in a crack may be as low as 10^{-6} m s^{-1}. Thus far, the minimum velocity achieved in the experimental apparatus has been more than 10^{-4} m s^{-1}. In addition, the interaction lengths possible in laboratory experiments are of the order of a few tens of centimetres, rather than the metres expected in a repository.

The initial experiments have indicated a maximum pH in the solution after passing through the crack of the order of 11.3. This is in contrast with the expected value of about 12.5 (due to the presence of calcium hydroxide in the specimen). Two possible reasons for the low pH have been identified:

- relatively slow diffusion to the crack;
- failure to achieve equilibrium between solution and solid.

The first of these can be modelled by adjusting the diffusion parameters in the model whereas the second is beyond the scope of the current, thermodynamic-based model. Comparison of the experimental results and the predictions of the model for appropriate conditions should allow the cause of the lower pH to be identified. This is currently in progress.

References

/1/ ATKINSON, A., Nirex Safety Study Report NSS/R287 (1991) (draft).

Table 1 Experimentally measured values of the diffusion product for pristine reference backfill.

Specimen	Diffusion product / m^2 s^{-1}	
	Tin	Caesium
Specimen 1	3.3×10^{-8}	1.8×10^{-10}
Specimen 2	3.7×10^{-8}	3.1×10^{-10}
Specimen 3	4.2×10^{-8}	7.9×10^{-10}
Specimen 4	3.6×10^{-8}	2.9×10^{-10}
Specimen 8	2.5×10^{-8}	3.7×10^{-10}
Specimen 9	3.0×10^{-8}	4.6×10^{-10}
Average	$(3.4\pm0.2)\times10^{-8}$	$(4.0\pm0.9)\times10^{-10}$

Table 2 Experimentally measured values of the diffusion product for reference backfill exposed to water saturated with carbon dioxide.

Exposure / days	Diffusion product / $m^2 s^{-1}$	
	Tin	Caesium
50	$5.1x10^{-8}$	$2.6x10^{-11}$
50	$5.6x10^{-8}$	$4.0x10^{-11}$
120	$4.8x10^{-8}$	$3.2x10^{-11}$
250	$7.2x10^{-8}$	$2.0x10^{-10}$
470	-	$(1.3x10^{-9})$

Table 3 Experimentally measured values of the diffusion product for reference backfill exposed to magnesium chloride solutions.

Exposure / days	Concentration of $MgCl_2$	Diffusion product / $m^2 s^{-1}$	
		Tin	Caesium
120	0.01 M + CO_2	$3.1x10^{-8}$	$2.4x10^{-10}$
	0.025 M + CO_2	$2.2x10^{-8}$	-
	0.05 M + CO_2	$1.6x10^{-8}$	$1.5x10^{-11}$
	0.1 M + CO_2	$1.6x10^{-8}$	$4.0x10^{-13}$
	0.1 M	-	$(1.9x10^{-9})$
370	0.01 M + CO_2	-	$4.5x10^{-10}$
	0.025 M + CO_2	-	$6.6x10^{-12}$
	0.05 M + CO_2	-	$6.6x10^{-12}$
	0.1 M + CO_2	-	$< 5x10^{-13}$
	0.1 M	-	$6.5x10^{-11}$

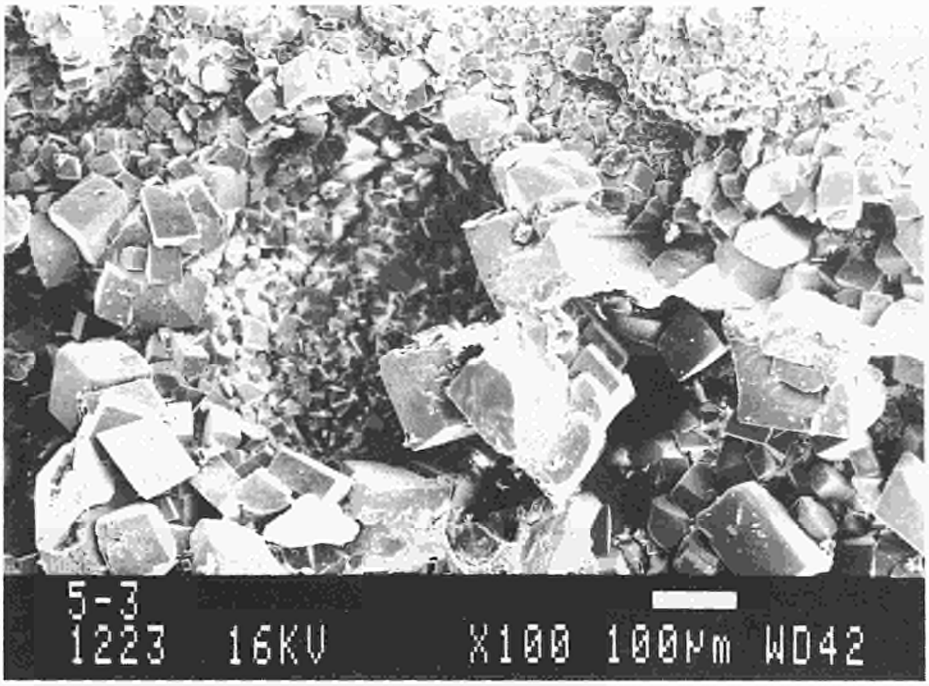


Figure 1 SEM image of the surface of the interior of a cracked specimen of cement mortar after exposure to calcium bicarbonate solution. The largest of the calcium carbonate crystals are about 0.1 mm across and were probably formed around an air bubble.

Completion of the corrosion programme in Boom clay (in situ experiments)

Contractor : ONDRAF/NIRAS, Brussels, Belgium

Contract N° : FI2W/0096

Duration of contract : July 1991 - December 1994

Period covered : January 1993 - December 1993

Project leader : J. Van Miegroet

A. OBJECTIVES AND SCOPE

The in situ corrosion experiments in the Boom clay underground laboratory (Mol, Belgium) were initiated during the 1985-1989 five-year plan to obtain realistic corrosion rates for a large range of metallic and non-metallic materials (glasses, bitumen, concrete, and container- and overpack materials). Different corrosion tubes were installed in the period 1985-1991 or will be installed in the near future. The aim of the present research programme is the completion of the corrosion experiments initiated in the previous programme and the beginning and completion of the operation of two additional corrosion tubes. The experimental work is performed by CEN/SCK.

B. WORK PROGRAMME

1. Monitoring and controlling of the ongoing corrosion experiments.
2. Design, construction and installation of the new corrosion loops.
3. Overcoring and retrieval of the different tubes in due time.
4. Analysis of the metallic and waste form samples and of the surrounding clay.

PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The last corrosion tube of type I (i.e. tube 3) has been overcored and retrieved after a total exposure time of ± 7.5 y at 90 °C. All the samples will be prepared for further analyses.
Two new tubes have been installed in the clay : one type II tube (tube 5b) and one type III tube (tube 10).
The samples of tube 8, which was running under oxic conditions, have been retrieved and the tube has been switched to anoxic conditions from now on referred to as tube 8b. New samples will be placed in the beginning of 1994.
Electron microprobe analyses and Auger electron spectroscopy measurements on a selection of metallic samples from tubes 1 and 4 have been performed.

Progress and results

The last corrosion tube of type I (i.e. tube 3) has been successfully overcored and retrieved on November 16, 1993, after a total exposure time of about 2840 days at 90 °C. (In the type I tubes all samples are placed in direct contact with the clay). Analyses of the corroded samples (mass loss measurements, optical microscopy, stereomicroscopy, scanning electron microscopy, ...) are scheduled for the beginning of 1994. Two glass samples (SON 68 and SM513) had been doped with ^{239}Pu, ^{90}Sr or ^{134}Cs. The clay contacting these doped glass samples has been sampled to investigate the migration profiles of these isotopes. Also, clay samples have been taken from the clay contacting a few non-doped glass samples and overpack materials to study the migration of elemental constituents not normally present in the Boom clay.

Tube 5b has been installed in situ on September 1, 1993, after the vertical opening had been filled with argon to ensure anaerobic conditions around the samples from the beginning of the experiment on. An automatic drainage system, using helium as expulsion gas, has been connected to tube 5b to avoid water accumulation in this vertical tube. The tube will run under anaerobic conditions and at 90 °C, but the connectors on the heating elements and on the thermocouples have not yet been placed. This is scheduled for early 1994.

Tube 8 had been running for several years under aerobic conditions but his phase has been terminated and the samples have been retrieved. Tube 8 will be restarted under anaerobic conditions and the new samples will be placed in the tube during the first semester of 1994. This new test will be referred to as tube 8b. An automatic drainage system similar to the one on tube 5b will also be installed on tube 8b.

A second type III tube (i.e. tube 10) has been successfully installed in the clay on February 17, 1993. (In type III tubes part of the samples is directly exposed to the Boom clay and part is exposed to a concrete atmosphere). An automatic water drainage system has been installed and functions well.

An overview of the metallic and waste form samples placed in the three corrosion tubes 5b, 8b and 10 is given in Table I.

A selection of canister and overpack samples from tubes 1 and 4, retrieved in August 1991 and November 1990 respectively, has been analysed with electron microprobe (EMPA) and Auger electron spectroscopy. The EMPA-technique has been applied to the overpack candidates carbon-steel, Hastelloy-C4 and Ti/0.2 Pd. No surface layer could be detected on Hastelloy-C4 and Ti/0.2 Pd. Different corrosion layers, however, are clearly visible on C-steel samples exposed at clay during 5 years at 16 C (tube 4) and 170 C (tube 1), but also on blank samples (i.e. samples stored in the laboratory under ambient conditions). A typical example of the EMPA is given in Figure 1.

Auger analyses have been carried out on ultrasonically cleaned Hastelloy-C4 and IMI-115 samples. They confirmed the expected presence of thin passivation layers on the samples.

LIST OF PUBLICATIONS

- VAN ISEGHEM P. (1993)
  In-situ testing of waste glass in clay.
  Paper presented at the International Symposium "Scientific Basis for the Nuclear Waste Management XVII", Boston (USA), November 1993.

Table I : Selection of metallic and waste form samples for tubes 5b, 8b and 10 ("as" = as such ; "ht" = heat-treated ; "p" = polished)

	TUBE NUMBER						
SAMPLE	5b*			8b*		10	
	as	ht	p	as	p	as	p
Candidate overpack materials							
Carbon steel (CEC)	3	-	3	3	3	6	3
Hastelloy C4 (CEC)	2	-	2	2	2	2	2
Ti/0.2 Pd (CEC)	2	-	2	2	2	2	1
IMI 115	2	-	2	2	2	2	1
UHB 904L	3	-	3	2	2	4	2
Canister materials							
AISI 309 (Cogéma R7T7)	3	2	3	2	2	2	-
AISI 430 (Eurobitumen)	2	-	2	2	2	2	-
DIN 1-4571 (DWK/Pamela)	2	2	2	2	2	2	-
Waste form samples							
Glass SON68 (Cogéma R7T7)	-	-	3	-	3	-	-
Glass SM513 (DWK/Pamela)	-	-	3	-	3	-	-
Glass SM527 (DWK/Pamela)	-	-	3	-	3	-	-
Glass WG124 (SCK-CEN/FLK)	-	-	3	-	-	-	-
Cement CAC (Cogéma)	2	-	-	-	-	-	-
Cement CPA55R (Cogéma)	3	-	-	2	-	3	-
Cement CBF (Cogéma)	-	-	-	2	-	-	-
Cement Tihange (active)	-	-	-	-	-	3	-
Concrete "gallery"	-	-	-	2	-	-	-
Bitumen "STE" (Cogéma)	-	-	-	2	-	3	-
Eurobitumen (Belgoprocess)	-	-	-	2	-	3	-
Bitumen "Mummie" (Belgoprocess, active)	-	-	-	-	-	3	-

* eight carbon steel samples are also tested for crevice corrosion : four on tube 5b and four on tube 8b

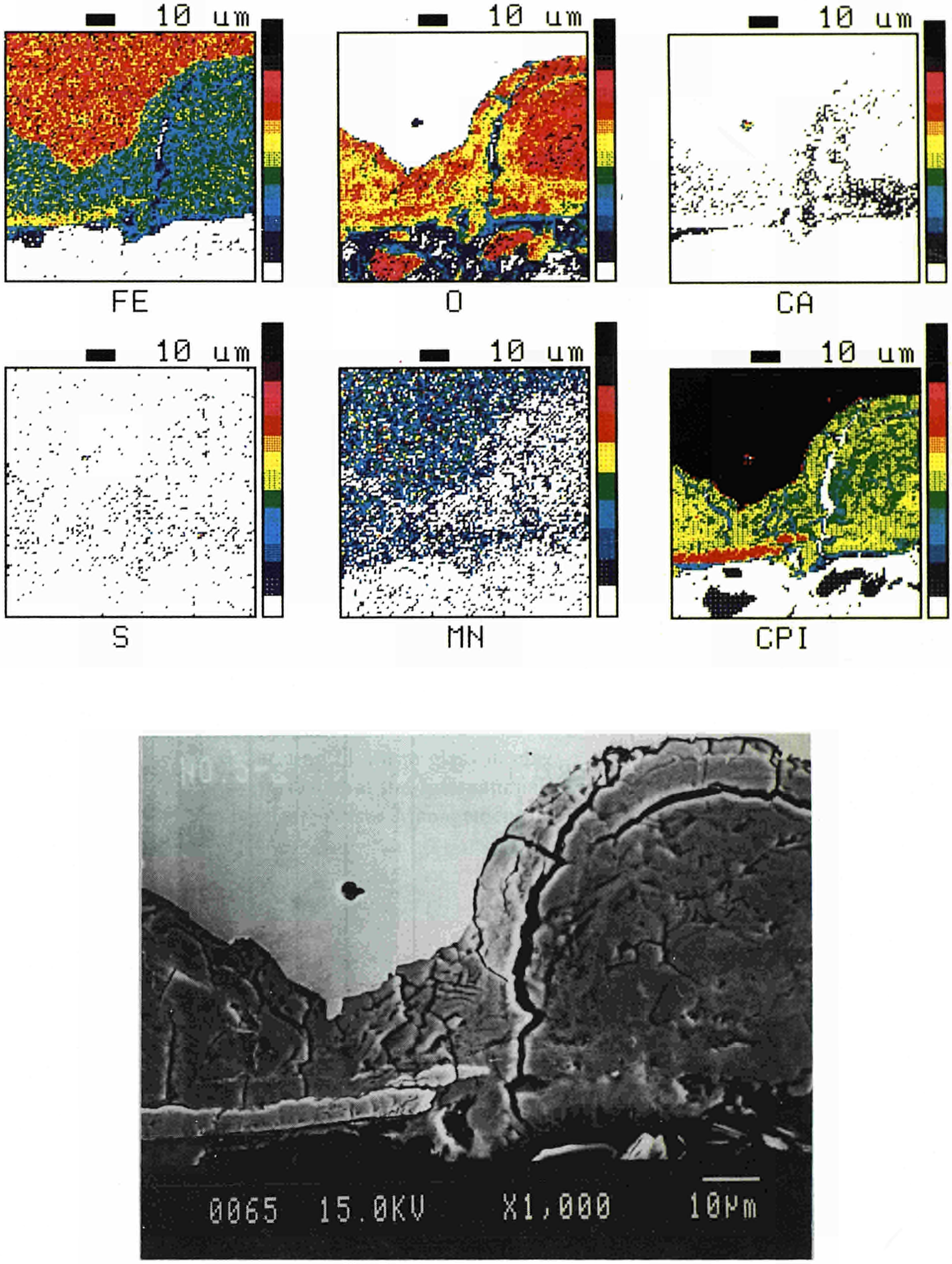


Figure 1. EMPA on the polished cross section of the corrosion layer of a carbon steel sample after five years of corrosion in direct contact with clay at 16°C.

Title: **Determination of Fissile Material by Neutron Transport Interrogation**
Contractors: Forschungszentrum Jülich (KFA)
SCK/CEN Mol
Contract No.: FI2W/0010
Duration of contract: 1 November 1991 to 31 October 1995
Period covered: 1 January 1993 to 31 December 1993
Project leader: R. Odoj
Experiments: P. Filß, J. Kühne (KFA)
Calculations: R. Mandoki, M. Bruggeman, P. Van Iseghem

A. OBJECTIVES AND SCOPE

This research is concerned with non-destructive assay techniques for fissile material determination in waste material mainly in waste drums. The starting point for development work was an assay system at the KFA for fissile material determination by active neutron interrogation with an Sb-Be neutron source. In this assay system the fission neutrons were discriminated from the source neutrons by their transport properties in hydrogenous material. The neutron count rate was composed of a source term and a second term proportional to the fissile material content of the investigated sample. The system directly determines all the fissionable nuclides U-233, U-235, Pu-239, Pu-241. It required shieldings due to the approx. 2 E12 Bq Sb-124 and had detection limits between 1 mg and 1 g fissionable material depending on sample size and matrix composition.
Neutron transport calculations at CEN/SCK Mol are intended to achieve a theoretical understanding and an improvement of the assay system with different neutron sources by modelling the neutron transport properties in the waste drum and the assay system. A replacement of the Sb-Be neutron source by other low energy neutron sources, such as Am-Li, will lead to an assay system with minimum shielding requirements and constant source strength (Am-241, t1/2 = 432.6a, Sb-124, t1/2 = 60.3d). As an additional advantage there is no need for a reactor to reactivate the Sb. The replacement of the Sb-Be neutron source by Am-Li is therefore an important objective of this research.
Passive neutron emission mainly results from spontaneous fission in Pu-238, Pu-240, Cm and Cf isotopes. Counting these neutrons gives information on the presence of these transuranic elements in the waste matrix. Effective recording and evaluating of these neutrons is an objective of this research. The aim of the final assay system is an easy-to-use and reliable instrument for the estimation or determination of the fissile material content of various packages, mainly waste drums.

B. WORK PROGRAMME

B.1. Checking and optimization of the Sb-Be system by comparison with neutron transport calculations.

B.2. Active neutron interrogation with other neutron sources, in particular Am-Li and comparison with neutron transport calculations.

B.3. Modification of the system for passive neutron counting capabilities.

B.4. Test and performance of the active/passive neutron assay system with actual samples, mainly drums with waste from the nuclear fuel cycle.

C. PROGRESS OF WORK AND IMPORTANT RESULTS

C.1. Neutron Transport Calculations

At SCK-CEN Mol the past year was devoted to the installation and application of an improved Monte Carlo code. After a first period of testing material features with the 1-D DTF-IV code [1], use and application of the MCNP 4.2. Monte Carlo code [2] on a DEC workstation was achieved. This aimed at reaching a satisfactory compromise between speed, cost and capacity.

The foremost improvement gained by the use of the MCNP code consists in the possibility of simulating a complex 3-D geometry. Substitution of materials, variation of material thickness and distribution, and their influence on fluxes, reaction rates and efficiencies are accessible to calculation. The results of the calculation are presented here and discussed later together with the experimental results.

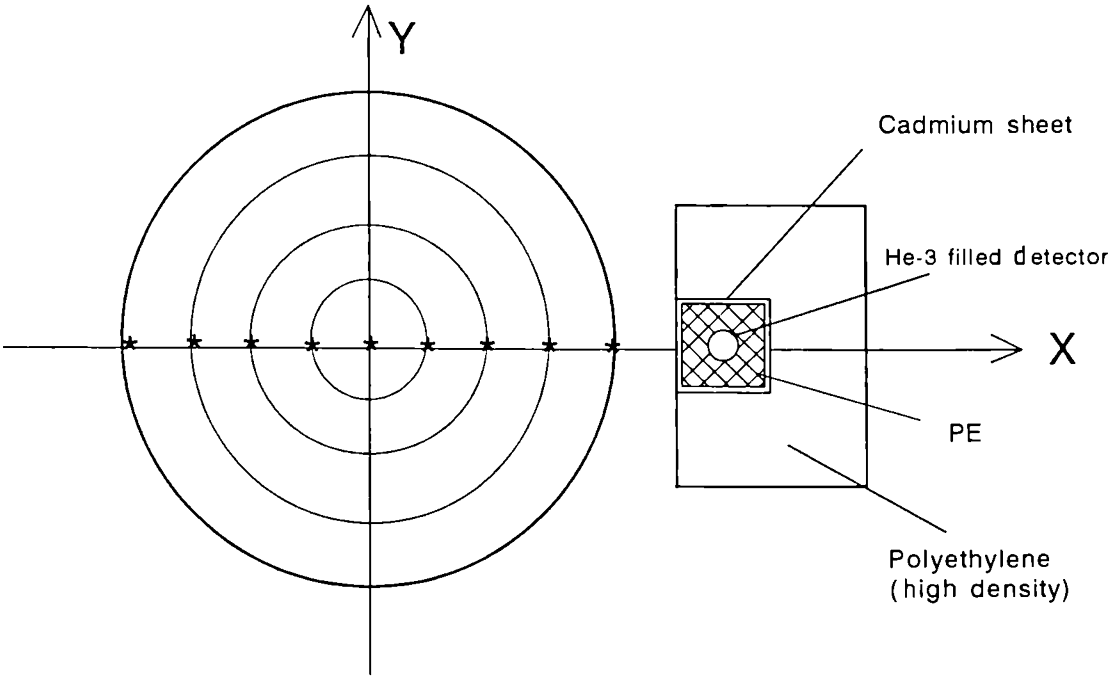


Fig. 1: Passive counting system for calculations

The first calculation was carried out with different neutron point sources (Pu-240, fission neutrons from U-235 and Pu-239) in front of the detector block (Fig.1). The thermalization thickness of the polyethylene block surrounding the He-3-counter was varied from 1 to 8 cm in front of the detector. The distance between the source and the centre of the He-3 detector was 40 cm and corresponds to the distance between the drum and the detector centres. The results are plotted in Figure 2.

Figure 2 shows that an optimum in detection efficiency is obtained with 3 to 4 cm polyethylene in front of (surrounding) the detector. From Figure 2, we also conclude that no major difference arises from the different fission spectra. Only the Pu-240 spectrum was therefore retained for later use. In the next step, the Pu-240 point source was positioned along the X-axis of Figure 1 in the cemented drum facing the He-3 filled detector. These calculations show that only if the source is very close to the detector (along the X-axis) can an optimum in efficiency be observed. After more than 7 cm into the cemented drum, there is no longer an optimal thermalization polyethylene thickness. For a source placed farther than 7 cm into the cemented drum, a "rough" exponential decrease of the efficiency as a function of the polyethylene thickness around the detector is observed for a fixed polyethylene thickness in front of the detector (3.75 cm). Figure 3 shows an exponential decrease of efficiency as a function of the position of the point source on the X-axis in the drums. More than 95 % of the detector response arises from the first half of the cemented drum. On the basis of a Pu-240 point source and a 3 σ signal above the background the NDA for Pu ranges from 50 to 150 mg Pu total. Other calculations with a homogeneous distribution of Pu-240 in the drum lead to an identical order of magnitude for the NDA.

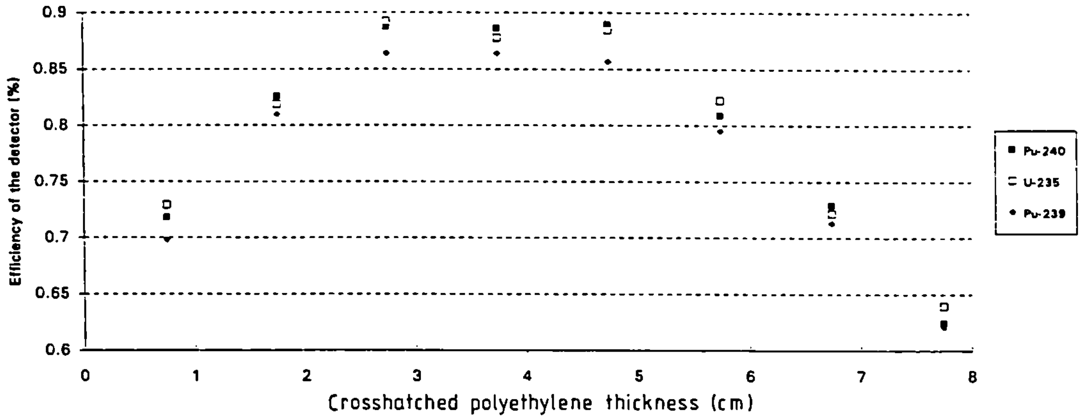


Fig. 2: Efficiency of a 10 bar HE-3 filled detector as a function of the thickness of polyethylene in front of the detector (with point sources at 40 cm)

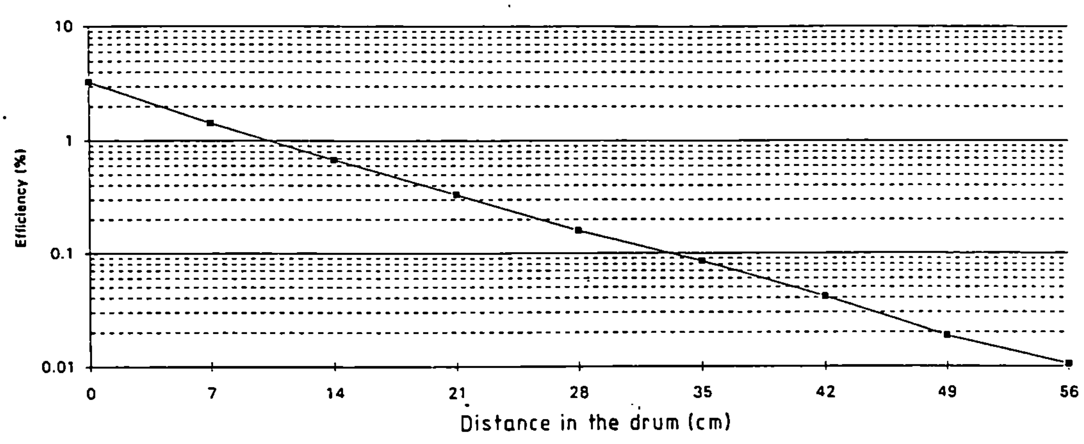


Fig. 3: Detection efficiency (obtained with a Pu-240 source moved on a line perpendicular to the axis of the drum at mid-height)

C.2. Performance of the Passive neutron System

The passive neutron assay system in its present (1993) layout is shown in Fig. 4. The system is light-weight and easy to move to any measuring site. The positions shown in Fig. 5 were used for the measurement of 1 g Pu in a 200 l cemented drum. In a first set of measurements the drum was not rotated but measured with the Pu sample at fixed angles relative to the line of the centre of the drum to the counter tube (angle 0°). The position of the sample was later moved by fixed angles in the measurement shown in Table I. Two points are important to mention.

Fig. 4: Passive assay system (1993)

- The loss of count rate in the inner positions of the cemented drum is in good agreement with the calculations presented in Fig. 3.
- Due to the radial position of the source in the drum typical fluctuations of the count rate over the angular position of the drum are observed.

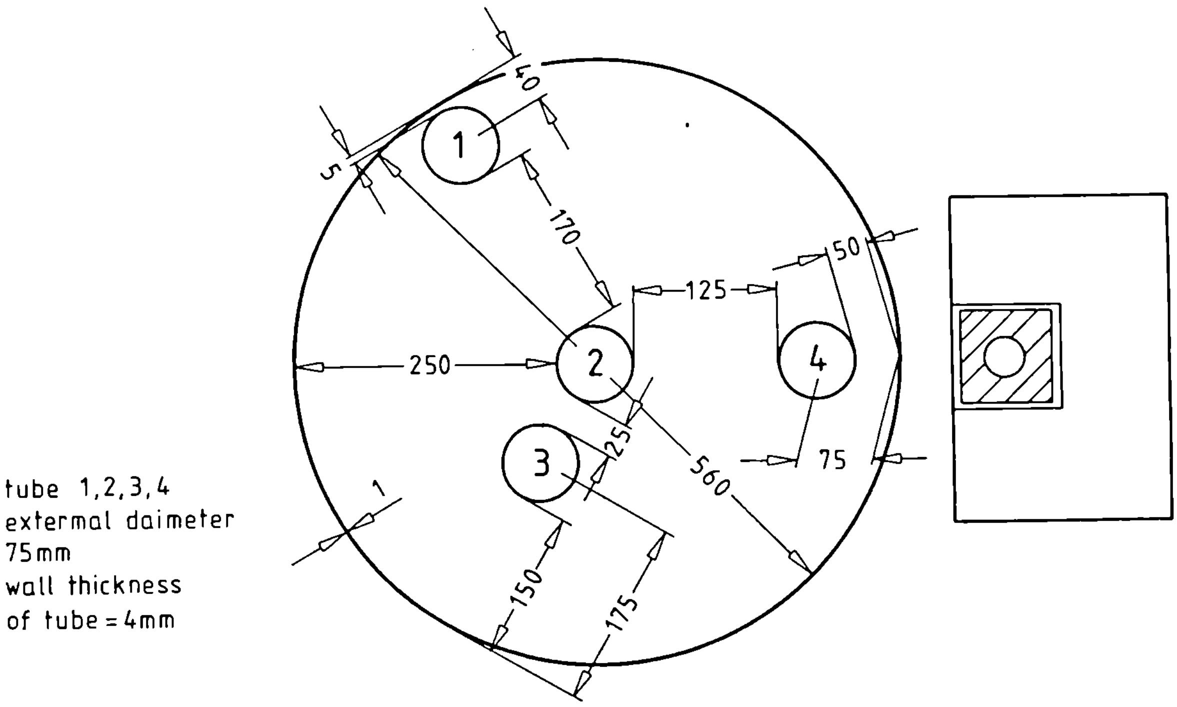
This variation of the count rates Z is in agreement with the calculated alternation α according to Fig. 3, as shown in last line of Table I. The deviation in the case of Tube 1 is understandable because the 90° position is here so far away from the central line and therefore the accessible detector surface is much lower for neutrons from the 90° position than from the 0° position. The peak count rate relative to the 90° count rate or to the average count rate is a significant parameter as well.

Table I
Neutron countrate as a function of the angle relative to the line from the detector to the center of the drum in concrete of σ = 2 g /cm^3, 1 g Pu (190 mg Pu-240). Geometry according to Fig. 3

Net count rates (Z) in s^{-1} (background of 0.27 5^{-1} subtracted)				
angle/radius	Tube 1/r =25cm	Tube 4/r =20cm	Tube 3/r=10cm	Tube2/r=0
0°	5.13	3.35	1.21	
25°	2.93	2.14	1.05	
45°	1.22	1.09	0.78	
90°	0.08	0.19	0.29	
180°	0.00	0.03	0.17	0.37
270°	0.06	0.2ß	0.29	
315°	0.78	1.12	0.67	
335°	3.33	2.37	1.05	
360°	5.13	3.35	1.21	
average	0.83	0.68	0.44	0.37
Z(0°)/Z(aver.)	6.2	4.9	2.8	1.0
Z(0°)/Z(90°)	70	17	4	1
Transport length in concrete from the 90° position to the face of the drum in front of the detector				
	35 cm	32 cm	27 cm	25 cm
alternation α from the 0° position to the 90° position	$\alpha(0.5)/\alpha(35)$ = 35	$\alpha(5)/\alpha(32)$ = 15	$\alpha(15)/\alpha(27)$ = 3.5	$\alpha(25)/\alpha(25)$ = 1

The fluctuation of count rate during rotation, which can be easily observed with this type of counter system is an indication of the radial position of a point source.

Passive and active detection systems generally have a dependence of the count rate on the radial position for high density material. A more sophisticated system at Los Alamos [6] has a count rate variation of 3 for the radial position of the Pu point source at high hydrogen densities. This system more closely resembles the rotating drum discussed in the following Table II.



tube 1,2,3,4
extermal daimeter
75mm
wall thickness
of tube = 4mm

Fig. 5: Test drum with holes for positioning the Pu source

Table II
Count rate (net) from a 1 g Pu point source in different positions of a waste drum.
Length of the He-3 tube (presently) 60 cm
Concrete filling in the drum 77 cm

Axial position	Rotating drum Net count rates in s^{-1} (background $0.13s^{-1}$ subtracted)				
	outside drum	Tube 1	Tube 4	Tube 3	Tube 2
bottom	0.92	0.52	0.40	0.27	0.23
1/4		0.76	0.64	0.41	0.34
1/2		0.83	0.68	0.44	0.36
3/4		0.74	0.61	0.39	0.32
top of filling		0.43	0.35	0.22	0.20

The typical measuring procedure in passive assay is the rotating drum. Results from this kind of measurement are reported in Table II. Here, a count rate variation of a factor of 2 results from the radial position of the Pu point source compared with up to 14 in the case of Table I. The count rate dependence over the radius is lower than for the stationary drum. An average in achieved by the rotation. The indication of the radial position which is obtained in Table I at different angles is lost. The measurement of the count rate fluctuation over the angle according to Table I permits a more precise estimation of the radial position and the average efficiency than the averages reported in Table II.

The dependence on the axial height shown in the columns of Table II is not satisfactory. The count rate at the edges of the concrete filling is approx 1/2 the central values. It will be attempted to overcome this deficiency by using longer counter tubes. The background cannot be considered to be satisfactory either. In a hot cell facility many neutrons arise from spallation in Pb-walls. The present measuring site near a lead wall is therefore not optimal.

C.3. Active neutron system

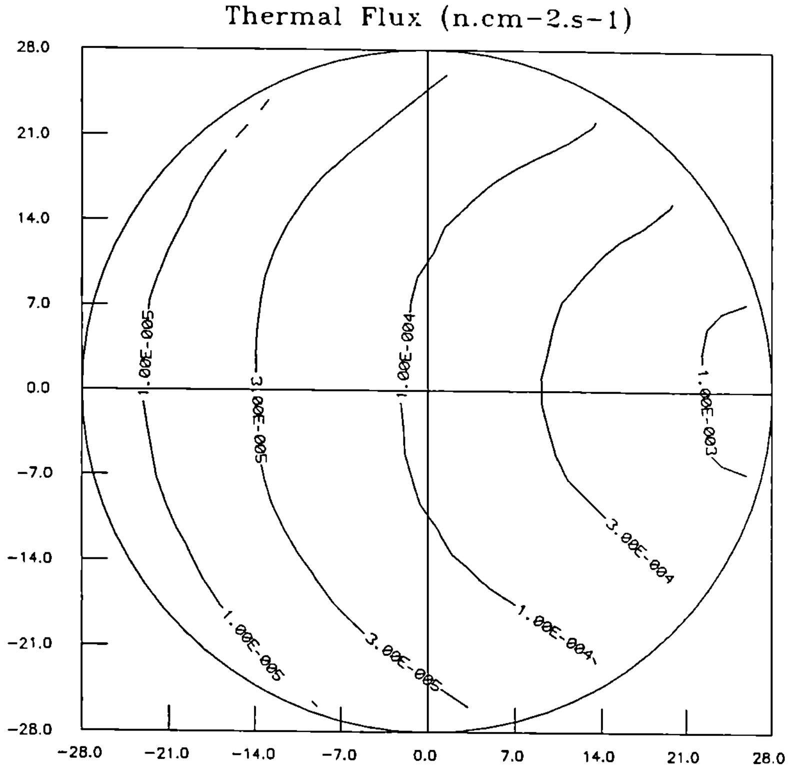


Fig. 6: A typical 2D flux distribution with the Am-Li source (P1) outside of a and at the mid-height of the drum

Two-dimensional calculations of the neutron flux distribution in a drum (Fig. 6) confirm the knowledge that the flux decreases greatly from the region of the neutron source to the opposite side of the drum. It is less by a factor of 100 at the opposite side. This led to the assay system layout proposed in the previous annual report [5] and shown in Fig. 7 and Fig. 8. In the actual testing of this system

- the high source count rate at the detector site from the Am-Li source and
- the count rate from scattered neutrons (no fissile material) in the sample position

play an important role.

Much effort was spent in various geometrical modifications in order to decrease the source count rate and the count rate from scattered neutrons relative to the induced fission count rate. The count rates and count rate relations defined in the following are listed in Table III for the more important modifications.

UG = background count rate without any neutron source and sample in the assay system. (UG is slightly site-dependent)
Q = source count rate with the Am-Li neutron source in the assay system (active system) but without a sample.
Gr = count rate with the neutron source and typical matrix material (but no fissile material) in the sample position (graphite).
Ur = count rate from 1 g U-235 together with the matrix material (typically graphite).
Pu = count rate from 1 g Pu (reactor grade) with the matrix material in the sample position.
T = (Ur-Q)/Q increase neutron count rate by 1 g U-235.
V = (Gr-Q)/(Q) increase of the neutron count rate by the matrix, typically graphite.

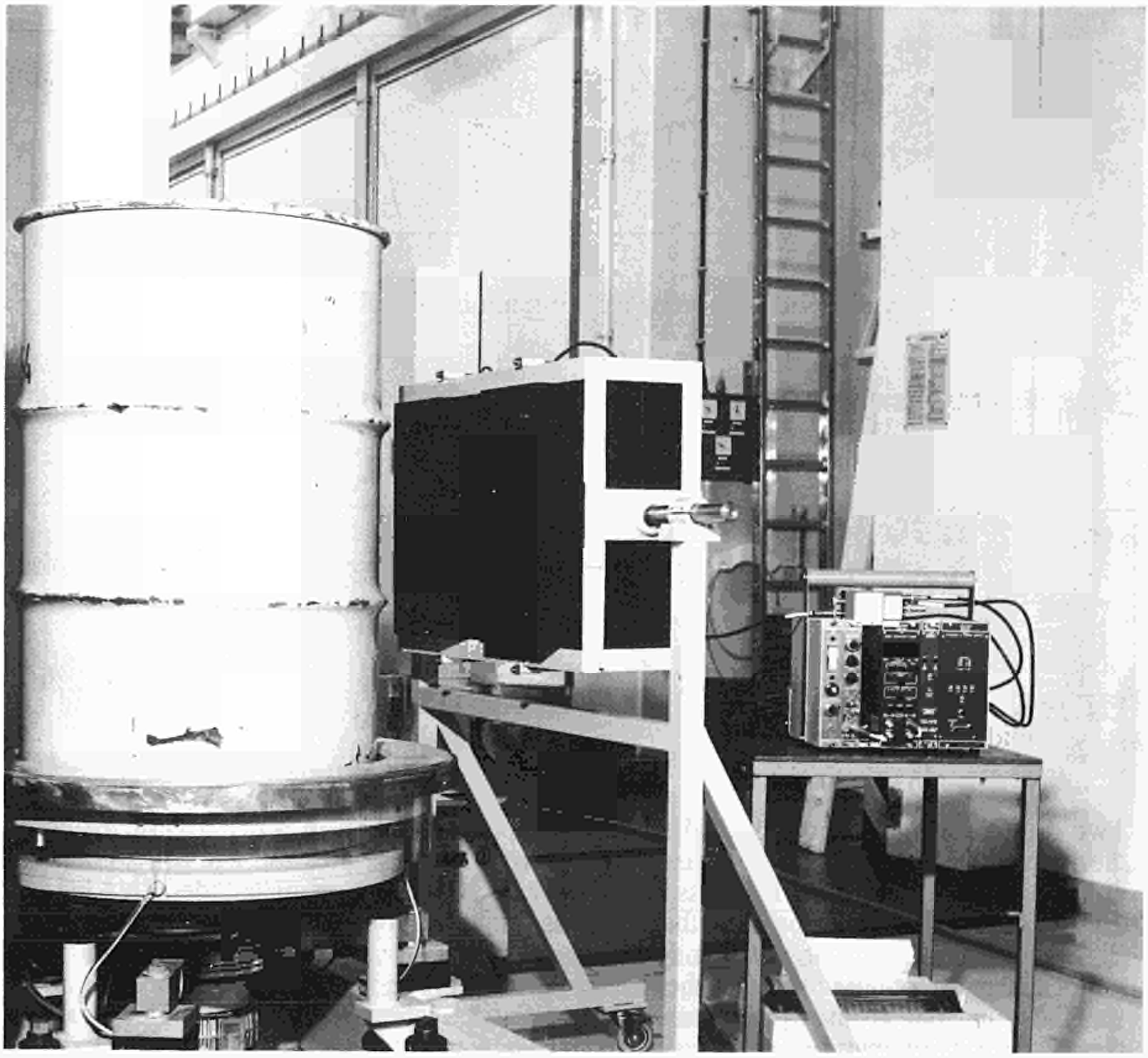


Fig. 7: Active assay system with the Am-Li neutron source
The Am-Li neutron source and the He-3 tube are both contained in the black PE block.

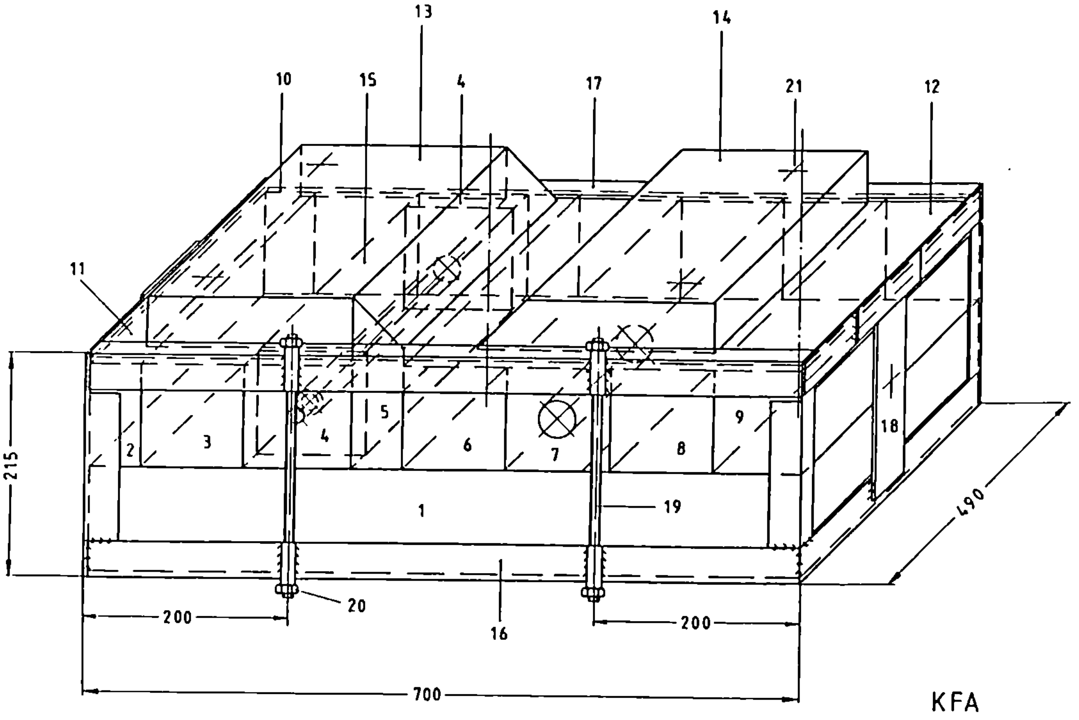


Fig. 8 Present layout (end of 1994) of the active standard assay system

Table III
Changed count rates as a result of five modifications

All count rates in s^{-1}								
	System/Modification	Intention	Q	Gr	Ur or Pu	T	V	Comment
A	Standard assay system with PE	standard system	1.71	1.79	2.03	5 %	19 %	
B	1 g Pu (reactor grade) instead of 1 g U-235	active interrogation of Pu passive count rate from 1 g Pu = 1.2 s^{-1}	1.71	1.79	3.17 = 1.71 + 0.26 + 1.2	5 %	85 % (active +passive)	Additive contribution of passive and active neutrons. Passive neutron rate ~5x active rate
C	Shielding Removed above the Am-Li source Decreased shielding above the counter	increase in count rate	1.52	1.78	1.83	17 %	20 %	Strongly dependent on scattered neutrons (large T)
D	Al in the source and in the transport layer	increase in count rate	4.37	4.42	4.65 = 4.37 + 0.28	1.6 %	6.4 %	Mainly the source count rate is increased. The fission count rate is not much changed.
E	Drum filled with concrete as reflector material	matrix of drum	2.32	2.35	2.66	1.3 %	14.7 %	Increased source count rate by reflection (matrix effects)

In the standard system (A) 1 g of U-235 leads to an increase of 19 % of the source count rate. A 5 % increase is already obtained by a scattering sample of the pure matrix material. When the same system is used for the determination of 1 g reactor grade plutonium, the increase in count rate is 85 %. But this is mainly due to the passive neutrons from the Pu source. Various modifications of shielding (C) did not actually raise the fission count rate (V), but the influence of scattering was drasticaly increased. The replacement of PE by Al (D) increased the source count rate Q, but the influence of uranium and scattering was decreased. A drum filled with concrete acted as a reflector from the beginning. The influence of an additional reflector matrix was decreased, but the influence of fissile material was not better than in the standard assay system (A). Therefore success was limited.

D CONCLUSION

In the case of passive interrogation, an easy to handle system is being developed, which with the one counter design has a special advantage in estimating the position of point sources in drums. The results of calculation and measurement are in excellent agreement. Some points concerning the efficiency at the end of the drum will be improved and drums with different densities will be tested in the next period.

The active system with the Am-Li neutron source suffers from a high source neutron count rate and detection limits of several 100 mg. No significant improvements could be achieved up to now. Intensive calculations with the Cf-252 neutron spectrum indicate no improvement from this type of neutron source.
The use of a completely different neutron source is now being considered.

E REFERENCES

[1] Mandoki R.; "Determination of Fissile Material by Neutron Transport Interrogation", SCK-CEN Annual Report 92, R-2963 (1993)

[2] Forster R.A.; "MCNP Capabilities for Nuclear Well Logging Calculations", CCC-200/MCNP 4 RSIC Code Package (1990)

[3] Auguston-Reilly, "Fundamentals of Passive Non-destructive Assay of Fissionable Material", LA-5651-M (1974)

[4] Filß P.; "Spalturanbestimmung in Abfallfässern und Lagerkannen für bestrahlte Brennelementkugeln durch Interrogation mit Neutronen einer Sb-Be-Quelle und Nachweis der prompten Spaltneutronen", Jül-2027-Ass (1985)

[5] Odoj R.; Determination of fissile material , Annual progress report 1993, XII/233/93-EN, pp. 125 - 129

[6] Menlove H.O. et al.; WDAS Operation Manual..., LA 12292-M, April 1992

Title: **Inventory and Characterization of Important Radionuclides for Safety of Storage and Disposal. Correlation with Key Nuclides that are Easy to Measure in Typical Waste Streams.**

Contractors: CEA Cadarache, GRS-Cologne, ONDRAF/NIRAS, ENEA-Saluggia, ENRESA, AEA-Dounreay.
Contracts No: FI2W-CT90-0034 and FI2W-CT91-0109
Duration of contracts: from May 1991 to September 1995
Period covered: January 1993 - December 1993
Project leaders: A. Raymond, CEA-Cadarache (co-ordinator for contract n° FI2W-CT90-0034) - W. Müller, GRS-Cologne (co-ordinator for contract n° FI2W-CT91-0109) -
R. Gens, ONDRAF/NIRAS - M. Gili, ENEA-Saluggia - A. Morales, ENRESA - A. Yates, AEA-Dounreay.

A. OBJECTIVES AND SCOPE

This contribution to the characterization and the inventory of radionuclides important for the safety of storage and disposal has three main objectives:
- checking and standardisation of operational destructive and non-destructive analytical methods with application to the main waste streams of the participating institutions,
- development of some alternative analytical methods for long-lived radionuclides,
- computation of correlation factors for critical radionuclides to easily measurable key nuclides, through the analysis of the main waste streams of the contractors.

Only low- or intermediate-level wastes originating from both power plants or fuel reprocessing plants are considered in the framework of these contracts.

Samples of each selected waste stream are analysed for both easy-to-measure and critical radionuclides as determined by the national safety assessment of each contractor.

B. WORK PROGRAMME

B.1: Organization - Coordination

- review of the initial situation of the participants.
- list of information to be collected and studied.
- final choice of the list of samples and of radionuclides to be analysed.
- setting up of a working organization.

B.2: Development of analytical methods

- improvement of the current procedures for long-lived radionuclides.

- search for alternative methods as compared to those based on radiation detection.
- development of special procedures for the recovery of radionuclides from solid, low-level technological wastes.
- drafting of some common analytical methods.

B.3: Measurement of wastes from nuclear power plants (CEA, ONDRAF/NIRAS, ENRESA, GRS)

- collection of available results from previous measurements.
- waste sampling and analysis for the radioactive content.
- collection of the necessary relevant information.
- transfer of the corresponding results into the data bank.
- assessment of the results and discussion of possible further improvements concerning the number and the representativity of samples.

B.4: Measurement of wastes from fuel reprocessing plants (ENEA, AEA Technology)

- construction of a non-destructive measurement system for gamma-emitters (ENEA).
- preparation of simulated waste drums.
- tests of the measuring equipments with simulated wastes.
- intercomparison of the tests results (AEA and ENEA).
- destructive and non-destructive measurement campaigns on reprocessing wastes.
- assessment of the results and discussion of possible further improvements.

B.5: data evaluation and processing (GRS)

- evaluation of available results from previous measurements.
- continuous evaluation of the results relevant to this programme.
- implementation of data banks for wastes from both fuel reprocessing and nuclear power plants.
- development of statistical tools for evaluation of results.
- development of individual evaluation codes for each participant.
- testing and optimisation of codes for routine applications.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

B.1: two important extension projects of the original contracts have been proposed and accepted by the CEC. Effective early in 1994, these programmes concern the organisation of an inter-comparison test for destructive analyses and the incorporation of four Hungarian laboratories co-ordinated by Paks Nuclear Power Plant.

B.2: the development or the improvement of analytical methods has concerned the following nuclides: ^{3}H, ^{107}Pd, ^{129}I, ^{99}Tc, ^{90}Sr, ^{94}Nb and Uranium.
B.3: since the beginning of the programme about 50 % (47 out of 93) of the destructive analyses on NPP waste samples have been completed (23 % in 1993 only).
B.4: since the beginning of the programme, 144 results (59 in 1993 only) have been collected from the Dounreay segmented gamma scanner and 7 destructive analyses have been carried out from both Dounreay and Saluggia technological waste samples.
B.5: most of the results obtained in tasks B.3 and B.4 have been transfered to GRS for the common data base and statistically evaluated.

Progress and results

CEA-Cadarache

Development of analytical methods

CEA focused its development work on the analysis of ^{129}I, ^{99}Tc, ^{90}Sr and ^{107}Pd.

For **^{129}I** and **^{99}Tc**, the extraction procedures with crown-ethers previously developed (see the 1991 Annual Progress Report) were associated with Inductively Coupled Plasma Mass Spectroscopy (ICP/MS) as the measurement technique. In term of detection limits, the results obtained on synthetic solutions showed a 20-fold improvement over radiation detection methods for ^{129}I while no significative difference was observed for ^{99}Tc.
However with real waste solutions resulting from the digestion of filter samples in sulfuric acid erratic and non reproducible extraction yields were observed for both nuclides. Solutions to overcome this difficulty are being investigated.
With primary coolant samples, the determination of ^{129}I and ^{99}Tc is readily achievable by ICP/MS, without previous extraction, leading to detection limits of 5 Bq/l (^{99}Tc) and 0.15 Bq/l (^{129}I).

For the analysis of **^{107}Pd** a two-step extraction procedure using phosphine derivatives is being tested in order to get rid of the ^{107}Ag interference prior to determination with ICP/MS.

For the analysis of **^{90}Sr**, the previously described method (separation of this nuclide on an EICHROM specific column and measurement by liquid scintillation counting) has been modified in order to get rid of some interfering nuclides: the measurement is now based on Cerenkov counting of radiations produced by ^{90}Y after that the radioactive equilibrium has been reached.

Analyses of waste samples

In 1993, CEA-Cadarache carried out the radiochemical determination of over 30 radionuclides on:
- two filter cartridges from Cruas N.P.P.
- one primary coolant from Bugey PWR.
- three filter cartridges from Bugey PWR.

Since the beginning of the project about 45 % of the scheduled analyses have been performed.

ENEA-Saluggia

Gamma scanning system

1993 has been dedicated to a modification of the lay-out of the 1.5 l. slave dewar -automatically filled by the 60 l. master dewar- from horizontal to vertical position.

The modification requested more time than scheduled due to a crystal deterioration.

The equipment is now under test at the Italian branch laboratory and it is foreseen to be available by January 1994.

Analytical techniques

During 1993 the procedures for the destructive analyses on solid samples have been set up.

Analytical methods are now available for Cs, Sr, Am, Pu, and U.

Up to now, the method for Tc has only been tested on six different simulated samples, obtained by adding known amounts of ^{99}Tc to the samples; the recovery yields were found to be in the range 89 to 108 %.

Destructive analyses

Destructive analyses on real wastes have been performed upon six samples for ^{137}Cs, ^{90}Sr, ^{241}Am, U and Pu.

Concerning the correlation of the main radionuclides to ^{137}Cs a comparison exercise has been undertaken with HLW-MTR liquid streams, sampled during the same reprocessing campaigns as when these solid wastes were produced.

The preliminary observations showed that:

- the Sr to Cs correlation is not as good as it could be expected for two fission products;
- total Pu seems to have a better correlation than it could be expected for a TRU vs. a fission product like Cs;
- the U behaviour seems to be unpredictable.

ENRESA/CIEMAT

Development of analytical methods

ENRESA/CIEMAT focused their development work on the analyses of ^{129}I, Uranium and $^{89/90}$Sr.

For the analysis of ^{129}I, the direct procedure, without any prior chemical separation, presented in the 1992 Annual Progress Report, has been improved because a long counting time (60 hours) was necessary in order to achieve a sensitive detection limit (20 Bq/g of resin).

For this reason, it has been added a radiochemical separation step, based on the co-precipitation of ^{58}Co, ^{60}Co, ^{59}Fe, ^{54}Mn and ^{65}Zn with Fe^{3+}, Co^{2+} and

Zr^{4+} hydroxides (this step is repeated twice), ^{134}Cs and ^{137}Cs being precipitated as chloroplatinates.

The recovery yields range between 45 and 60%.

The separation factors are higher than 99% for all the radionuclides assayed.

For a counting time of 5 hours, a detection limit of 8 Bq/g has been obtained, which means a 2.5-time improvement over the previous, direct procedure.

For the analysis of **uranium**, it has been developed a procedure based on the separation and purification of uranium by liquid-liquid extraction with ethyl acetate in saline medium (aluminium nitrate/tartaric acid), elimination of ethyl acetate and measurement of uranium concentration by laser fluorescence in the aqueous phase.

The detection limit is 2×10^{-3} microgrammes of uranium, equivalent to 20 microgrammes U/g of resin and 0.5 microgrammes U/mL of evaporator concentrate.

The decontamination factors range from 74% (Sb-125) to >99% in the majority of cases.

For the analysis of $^{89/90}Sr$, the procedure described in the 1992 Annual Progress Report (selective extraction chromatography using a crown-ether) has been slightly improved.

The following parameters have been modified:

- The carrier concentration is increased from 0.6 to 10.0 total mg.
- Strontium is loaded in the column with HNO_3 8M - $Al(NO_3)_3$ 0.5 M instead of HNO_3 3M.
- ^{90}Sr is added as internal standard in order to allow the determination of the chemical yield.

These modifications have resulted in much shorter analysis times and in easier chemical yield determinations.

With real ion-exchange resins samples, all separation factors were found to be > 87% and in most cases > 99%, while the chemical yields range from 58 to 81.6%.

The chemical yields calculated either by gravimetry or by adding ^{90}Sr as an internal standard were in coincidence.

Analyses of waste samples

During 1993, 10 complete sets of results have been otained and transfered to GRS for evaluation:

- one evaporator concentrate from Garona BWR.
- four ion-exchange resins from Cofrentes BWR.
- one evaporator concentrate from Trillo PWR.
- two evaporator concentrates from Asco PWR.
- two ion-exchange resins from Asco PWR.

ONDRAF-NIRAS/C.E.N. Mol

Development of analytical methods

ONDRAF-NIRAS/C.E.N. Mol focused their development work on the analyses of ^{129}I, ^{90}Sr, ^{99}Tc, ^{94}Nb, tritium, ^{238}Pu, ^{241}Am and $^{242/244}$Cm.

For the analysis of ^{129}I, the procedure reported in the 1992 Annual Progress Report has been abandoned because of the unreliability of the results obtained for evaporator concentrates. The new procedure relies on the isotopic exchange between a precipitated iodide compound and the iodide in the supernatant solution. The chemical yield is monitored by adding an ^{125}I spike to the solution and the isotopic exchange is achieved by a redox cycle.

Interfering cations are then precipitated as their sulfides, leaving the iodide in the solution. After filtration the purified iodide solution is concentrated by evaporation to the appropriate volume for liquid scintillation counting of the ^{129}I and gamma-spectrometry of the ^{125}I for the yield determination.

The procedure has been tested on real homogeneous solutions as obtained after the dissolution procedure for evaporator concentrates. The recovery of the iodine throughout the procedure applied to four aliquots is 79.2 % with a reproducibility of 2.4 %. There are no interfering gamma-emitting isotopes observed in the gamma spectrum. A detection limit of 0.05 Bq/ml has been obtained in the measured solution, equivalent to 10 Bq per liter for the original evaporator concentrate sample.

The radiochemical purity obtained after the chemical separation allows measurements by ICP/MS. The results obtained until now however suffer from the interference of ^{129}Xe, which is present in the argon feed gas. Therefore the current detection limit for ^{129}I is only 1.3 ppb, which corresponds to about 8 Bq/l. This offers no advantage with respect to the radiochemical measurements. Efforts are continuing to achieve better detection limits by removing the xenon interferences from the argon gas.

For the analysis of ^{90}Sr, after the separation of strontium by adsorption on an Eichrom Sr.Spec column, ^{90}Y is allowed to reach equilibrium with ^{90}Sr during about two weeks. Yttrium is then precipitated as its hydroxide, the precipitate is dissolved and yttrium is precipitated again as its oxalate and filtered on a counting planchet for beta-counting with a proportional low-level counter.

The adsorption yield on the Eichrom Sr.Spec column has been found to be close to 100 %. The chemical yield of the subsequent precipitation steps is consistently 99 to 100 %. The detection limit for a measurement time of 60 minutes is 1 Bq per liter of homogeneous solution.

For the measurement of ^{99}Tc, the procedure developed by ONDRAF-NIRAS/C.E.N. Mol relies on its adsorption from dilute nitric acid on a Teva.Spec selective column (Eichrom Industries Inc,) and washing out of the interfering radioisotopes. After elution of the ^{99}Tc with 8 M HNO_3, it is measured by liquid scintillation counting. If any ^{60}Co remains as a contaminant, it is removed by extraction with thenoyltrifluoroacetone from a phosphate buffer. The aqueous phase containing ^{99}Tc is then concentrated by evaporation and measured by liquid scintillation counting.

Taking into account the separation yield for ^{99}Tc (73 to 91%) the detection limit for technetium is in the range of 150 to 500 Bq/l in the homogeneous sample solution. This corresponds to the upper limit of the expected ^{99}Tc concentration range in the evaporator concentrate samples. Radiochemical measurements have to be further improved to decrease detection limits by a factor 10 to 50.

For the measurement of ^{94}Nb, the procedure relies on the extraction of niobium with tributylphosphate from hydrochloric acid medium. Therefore the waste solution is evaporated to dryness after addition of niobium carrier and redissolved in 8 M HCl. The niobium is back-extracted in a diluted hydrochloric acid phase. The niobium is measured by high resolution gamma-ray spectrometry. The procedure was standardised to obtain constant recovery yields for niobium as no tracer is added for monitoring the yield.

The experimental detection limit is 48 Bq/l in the initial solution resulting from the dissolution of the waste, when using an aliquot of 50 ml for the analysis. The yield is consistently between 85 % and 90 % and the standard deviation is 5 %.

The **Tritium** procedure as described earlier in the 1992 Annual Progress Report has been abandoned in favour of a double distillation method. The effect of isotopic enrichment has been investigated and a procedure has been developed to minimise this error source.

In practice a quantity of water corresponding to the quantity distilled is added when about 50 % of the liquid has been distilled. The detection limit is 30 Bq per liter of homogeneous solution.

Reliable results have been obtained for evaporator concentrates. For dissolved resin samples however the tritium quantity in the distillate is not decreasing as a function of the distillate number but remains constant at a significant tritium concentration. The reason for this effect is being investigated.

For the measurement of ^{238}Pu, ^{241}Am, ^{242}Cm and ^{244}Cm no specific experiments have been carried out so far but the activity levels have be estimated in order to set the objectives for the radiochemical separation methods to be developed.

Analyses of waste samples

At present 90 % of the samples have been delivered and 47 % of the samples have been dissolved and analysed by gamma-ray spectrometry.

About one third of the samples have been analysed for the first series of critical nuclides (^{3}H, ^{14}C, ^{59}Ni, ^{63}Ni, ^{135}Cs and the uranium isotopes). At present 47 % of the samples have also been analysed for those isotopes of the second series, for which the procedure has been qualified (^{90}Sr, ^{94}Nb, ^{99}Tc, ^{129}I and the americium, curium and plutonium isotopes).

Applying twelve measurement procedures to the total number of thirty samples yields about 360 individual measurement data or data sets. At present 102 have been completed.

AEA TECHNOLOGY-Dounreay

Waste drums data

During 1993, 59 results have been collected from the Dounreay segmented gamma system. Data sheets from measurements have been submitted to GRS for the data base. These drums contain wastes from the disassembly stage of reprocessing from a fast reactor reprocessing plant and the dissolution stage of a research reactor reprocessing plant (ie both prior to solvent extraction stage).

The in-house computer code 'FISPIN' has been used to calculate the total radionuclide activity for each reprocessing run, based on a knowledge of irradiation history. This data is also submitted to GRS for the data base.

Destructive analysis

A 200 litre drum of soft wastes from reprocessing run PR19 was destructively analysed. The content of the drum was loaded into 4 litre containers and each container was measured by gamma spectrometry. As one of the containers contained about 95% of total activity the contents of this was leached in nitric acid.

Radiometric analysis was then carried out on the leachate, and the quantity of 15 radioisotopes determined. The results showed a reasonable comparison between the drum measurement and chemical analysis except for ^{106}Ru which is insoluble in nitric acid. The comparison with FISPIN analysis also showed a reasonable agreement.

A second drum has been identified for destructive analysis and preparations are in hand for this work.

GRS-Cologne: data evaluation and processing

Data base

The amount of data sets available is summarized in table I.

Each data set contains a different number of radionuclides for which measurement results have been achieved. Thus the number of data sets alone gives only limited information about the possibility to establish a correlation between a key nuclide and any other nuclide considered.

Furthermore results below the detection limit normally have to be excluded since their correlation to those above the detection limit in general does not provide meaningful information.

Selection of appropriate key nuclides

It has been checked if there is a need for two or even more key nuclides instead of one and if a separate key nuclide should be chosen for the actinides.

By this time we conclude that it is not recommendable to rely on only one key nuclide because of the loss of quality for the concerned correlations. For other key nuclides the frequency of their measurement in individual samples is too low to replace e.g. ^{137}Cs as a key nuclide.

On the other hand it can be shown, that correlating the actinides to ^{239}Pu would improve the quality of the correlations to a certain extent. Since ^{239}Pu cannot be measured easily from outside of a waste container this is prohibitive for routine purposes. But possibilities to use this observation for further improvement are still under investigation.

Evaluation method

The method applied for routine evaluations has been described already in previous reports. It is based on a correlation by **linear regression of the logarithms of the measurement results** for two different nuclides. Other methods used are (a) the **scaling factor**, the average ratio of the activity of a relevant nuclide and the key nuclide activity, or (b) the **linear regression of activity measurements.**

It has been investigated which of these methods provides the best fit to the evaluated data and thus the most reliable prevision of the activities. In conclusion the evaluation method chosen is still considered as the most appropriate and will be kept for the future.

Qualification of correlations

The linear regression is a mathematical method which is applicable only under certain conditions. Therefore it has to be checked if these condition are met. Further restrictions emerge from practical considerations. The applicability of the method therefore has to be assessed. For this purpose for some characteristic quantities criteria have been set up which are summarized in Table II.

Further restrictions may come from the number of correlated data and the requirement to compare only evaluations based on the same or a comparable data base.

Preliminary results

Carbon-14

Within the CEC, data seem to be widely comparable with one exception. The Belgian data develop a markedly higher slope of the correlation line than the data from all other states. An explanation for this effect is not available. An effect of the scattering of the data can be excluded since the Belgian data alone show an excellent correlation which is comparable or better than the other results. The difference in slope suggests a different source or combination of sources for ^{14}C in wastes from Belgian PWRs compared to the others.

Nickel-63

^{63}Ni is one of the best investigated nuclides of the activated corrosion products. As has been demonstrated already in earlier reports deviations between different states including the United States are small. Figure 1 summarizes the latest results for PWRs.

The evaluation provides four distinct correlations of very high quality (correlation coefficient $R=0.88$ to 0.97). Three of the respective correlation lines nearly fall together, while the German one differs slightly mainly due to a lower slope. A more detailed analysis results in a proportionality constant a for the German data which is two to three times lower than for the residual data. Furthermore the regression coefficient is around 10% lower for the German correlation.

The first observation implies that the ^{63}Ni source in German PWRs is reduced compared to other designs. It can further be shown from these results that the sources of both nuclides are not identical for German PWRs. The opposite conclusion can be drawn for the other states. These statements can be confirmed by measured data.

For BWRs no essential differences can be detected. In contrast to PWR results the quality of the correlations is slightly lower ($R=0.76$ to 0.82) and the non-linearity more distinct (regression coefficient $b=0.56$ to 0.65).

Plutonium-239

^{239}Pu as the most prominent representative of the α-emitters offers a good opportunity to check the applicability and the capability of the evaluation method with a nuclide that is chemically quite different from either of the key nuclides ^{60}Co or ^{137}Cs. A first test shows that in most cases ^{60}Co produces the correlations with the higher quality.

Considering the scatter of the data the results for PWRs are in good agreement. The mathematical description of this is a correlation coefficient of $R = 0.84$ in spite of an obvious non-linearity of the correlation ($b=0.75$). Nearly the same picture develops for BWRs with only a slightly lower quality of the correlation ($R=0.68$).

A comparison of the PWR and BWR correlations reveals the fact that both are practically identical. The presentation in Figure 2 demonstrates that both correlation lines fall together. This means that a common correlation can be used for PWRs and BWRs or in other words that the data of both reactor types can be combined.

Table I: Distribution of the available data sets among different states

State	R	EB	F	C	Total
PWR					
Belgium	14	18	-	-	32
France	12	8	18	-	38
Spain	3	3	-	-	6
Germany	55	51	4	22	132
Sum PWR	**84**	**80**	**22**	**22**	**208**
BWR					
Spain	9	10	-	-	19
Germany	20	22	12	-	54
Sum BWR	**29**	**32**	**12**	-	**73**
Total	**113**	**112**	**34**	**22**	**281**

Table II: Qualification of correlations

Correlation coefficient R	**Regression coefficient b**				
	0.7 - 1.3		0.5 - 0.7 1.3 - 1.5		< 0.5 > 1.5
	ratio of propotionality constant a_m/a				
	< 100	> 100	< 100	> 100	
0.9 - 1	A		E		
0.7 - 0.9	A		E		
0.5 - 0.7	E		E		
< 0.5					

A = fully acceptable

E = conditionally acceptable

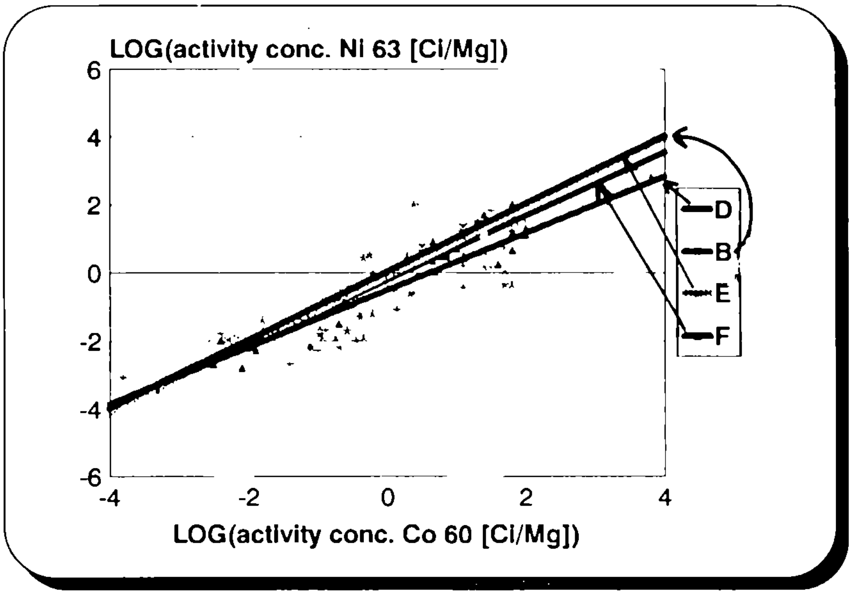


Figure1: Correlation of Ni 63 to Co 60 for European PWRs

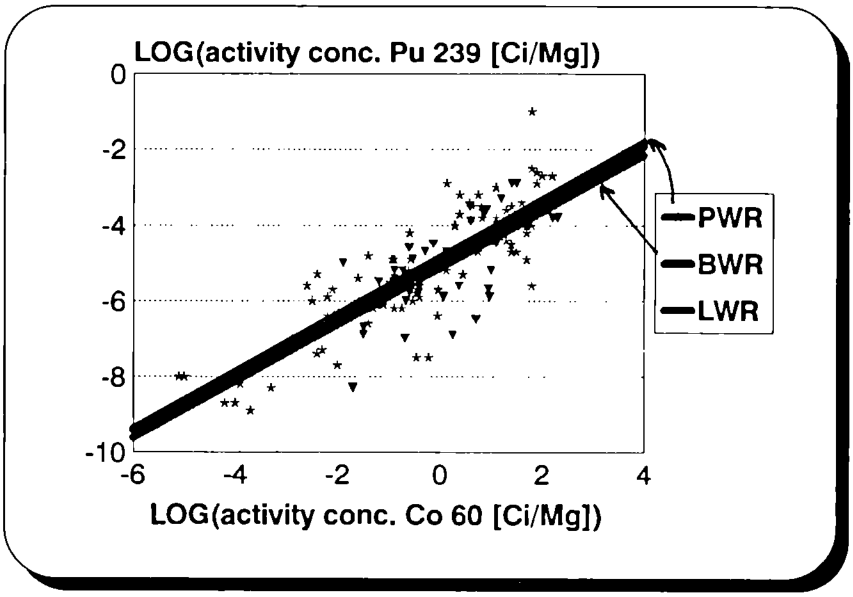


Figure2:Correlation of Pu 239 to Co 60 in European LWR

Title: **Construction and Testing of a Computer Tomography Assembly for Routine Operation**
Contractor: Forschungszentrum Jülich (KFA), FRG
Contract N°: FI2W-CT90-0009
Duration of contract: from 1. Sept. 1991 to 31. Aug. 1995
Period covered: from 1. Jan. 1993 to 31. Dec. 1993
Project Leader: Dr. Reinhard Odoj
Executant: Dipl.-Ing. Peter Eifler

A. OBJECTIVES AND SCOPE

The disposal of barrels containing radioactive waste material into an underground repository has to meet certain requirements of governmental regulations, one of which is the specification of the radionuclide inventory. This can either be achieved by non-destructive or by destructive analysis of the waste containers. If a cemented matrix of relatively high density is used to condition the waste a considerable fraction of the inner radiation is absorbed in the barrel itself. This has to be taken into account in an effort to obtain reliable results if non-destructive methods for the determination of the specific and total activity of the waste barrel are used. For this reason the PKS (Produktkontrollstelle) of the BfS (Bundesamt für Strahlenschutz) located at the KFA (Forschungszentrum) in Jülich, Germany, has been appointed to quality control radioactive waste containers by gamma-scanning and tomography measurements, both non-destructive. The preliminary objective is the direct measurement of the density distribution in shielded structures and heterogeneous fillings with the aim of analyzing the activity distribution and finally to be able to quantify the total activity of the waste drum.

B. WORK PROGRAM

B.1 Modifying the existing passive gamma-scanner to obtain active gamma ray screening capability

- addition of a 7 Ci Co-60 gamma source for transmission measurements;
- modification of the turntable for the drum and upgrading the mechanical system for translatory movement.

B.2 Installing a suitable computer tomography system for the examination of samples with uncommon composition and uncommon density distribution

- development of tomography software for transmission (TCT) and emission (ECT) tomography;
- design of technical equipment in order to synchronize mechanical movement, countrate measurements and absorption data transfer to the computer;
- visualization of the density and activity distribution and estimating the total activity of the waste drum.

B.3 Comparative test measurements

- on dummies with different materials for testing purposes;
- on typical waste drums with inner shielding structures.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the period covered in this report the progress of work can be summarized by:

- mechanical upgrade of the tomography assembly;
- development and installation of the reconstruction software for TCT and ECT (using the Algebraic Reconstruction Technique ART);
- visualization and archivation of the density and activity distribution;
- establishment of the co-operation between computer and hardware devices (detector, mechanical system);
- designing and manufacturing a cement dummy for detailed comparative test measurements;
- comparative test measurements on the dummy and evaluation of the tomographic results.

Progress and results

In order to determine the nuclide inventory of the radioactive waste drum the measurement of the density distribution is necessary (TCT), followed by the analysis of the activity distribution by applying the technique of emission tomography (ECT). In the case of transmission, the intensity of a γ-beam radiated by an external source and attenuated by the object is measured at various positions surrounding the object. Due to the high density of the cement fillings a strong γ-source of 7 Curie Cobalt-60 has been installed within the tomographic assembly (fig. 1). The attenuation coefficients throughout the observed plane of the barrel are calculated by a reconstruction algorithm. In the case of emission, the radiation of γ-sources located inside the drum is monitored by a detector at different positions. In general, the attenuation of the emitted radiation by the material contained in the drum can not be neglected. For this reason the attenuation coefficients obtained from the transmission measurements are applied to correct the emission data. The reconstruction algorithms, required for both TCT and ECT, have been developed, whereas test measurements have been exclusively carried out on TCT.

The setup of the tomography system is of the translation-rotational type (fig 1). The mechanical upgrade of the assembly focused on the installation of a new turntable mounted onto a linear moving bench. The turntable is designed to move waste barrels (200 l) up to 1.5 tons. Its positioning resolution of 0.2° ensures exact positioning, which is necessary in TCT and ECT applications. The turntable as well as the linear moving bench are controlled by stepping motors with very high stepping resolution. It is planned to install vertical moving capabilities in order to examine different planes of the barrel (fig. 1).

Furthermore, the problems implying visualization and archivation of the reconstructed images have been solved. The visualization software enables the operator to quantitatively determine the density and the activity distribution of the object by calibrated scales. For reasons of cost reduction all computer work is carried out on an IBM-compatible PC.

The detector, which was used to collect the quanta passing through the object, is a high purity germanium detector with outstanding energy resolution (efficiency approx. 20%).

To check the performance of the computer software and the accuracy of the mechanical operation a test dummy was designed and manufactured (fig. 2). The dummy has the shape of a disc with a diameter of 560 mm. Its weight is approx. 70 kg. It embodies 3 different materials, different in density (lead, steel and plastic material). These bodies are enclosed by a concrete matrix. Since the size as well as the chosen materials of the dummy are those of a real waste drum precise measurements under realistic conditions were performed. The dummy also contains several holes and hollow spaces, in which it is possible to insert radioactive samples, which is interesting for ECT.

Figures 3-5 show reconstructed images of the density distribution of the test dummy. The image of fig. 3 is set up by a 261x261 pixel matrix. It is based on the data of 156 angle positions, each consisting of 100 scan steps. The number of angle positions (M) and the number of scan steps (N) were chosen to fulfill a so-called sample theorem: $M=\pi/2\cdot N$. Multiplying the 156 angle positions by 100 scan steps times 5 seconds gives the total measuring time, which is, in this case, a very long time of 21.7 hours. The resolution of the image, however, is quite satisfactory, e.g. the steel hooks for transportation can clearly be seen.

The image shown in fig. 4 is set up by 301x301 pixels and the total measuring time to collect the absorption data was 4.4 hours. Here, the number of angle positions was reduced to only 32. The quality of this image (resolution of the density distribution) is sufficient for the purposes mentioned above.

Fig. 5 gives an impression of the great influence of the number of angles on the image quality. The image shown is based on the data of only 16 angle positions and 100 scan steps (total measuring time 2.2 h).

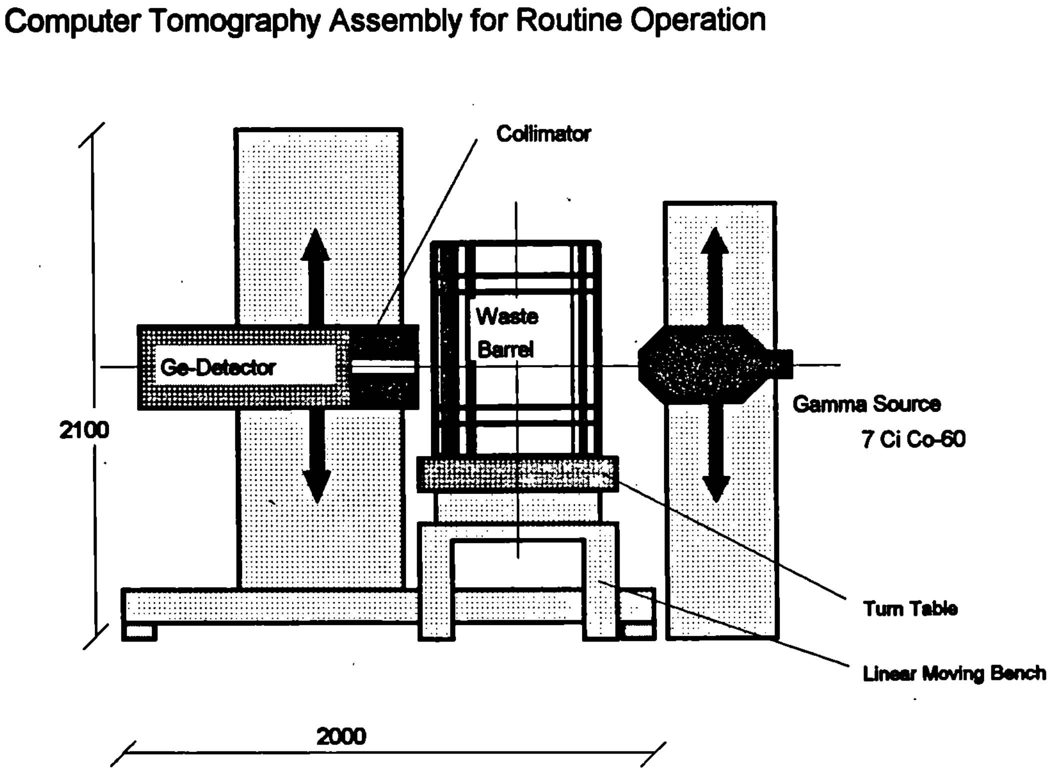

Computer Tomography Assembly for Routine Operation

Fig. 1: Tomography Assembly

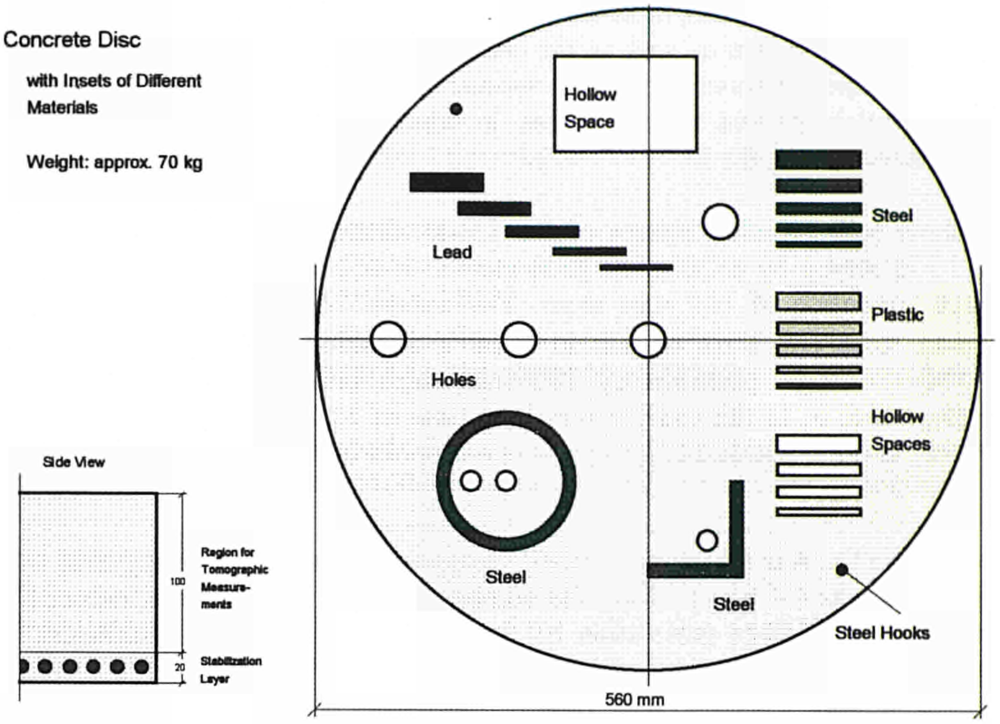


Fig. 2: Test Dummy

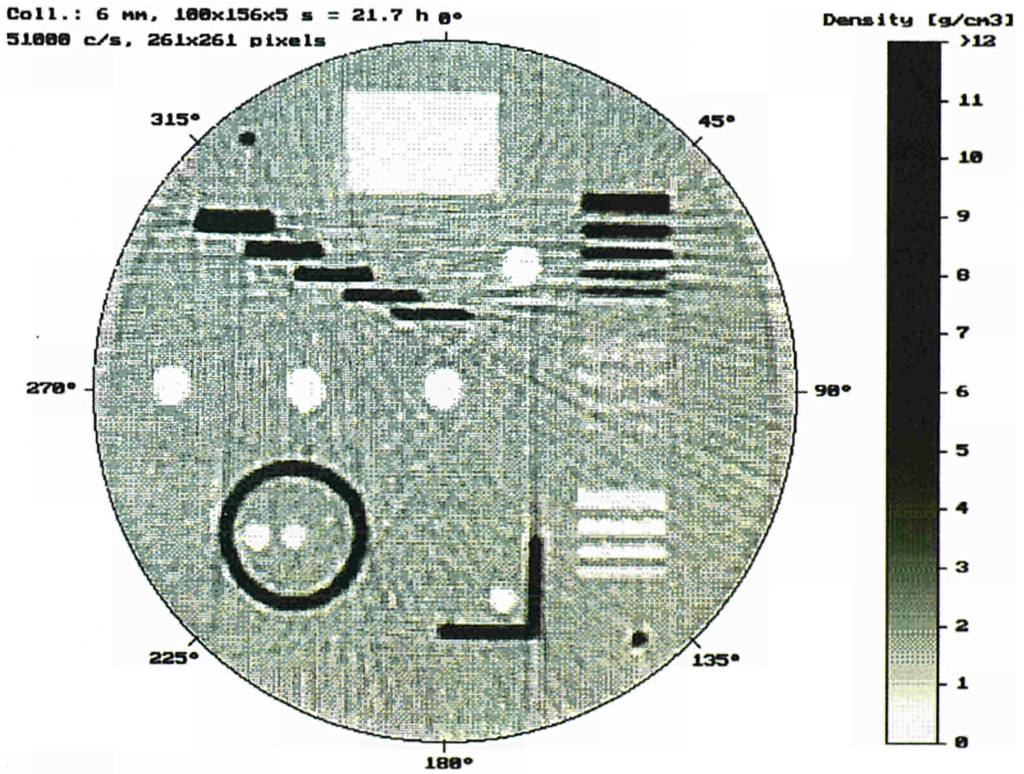


Fig. 3: High Resolution

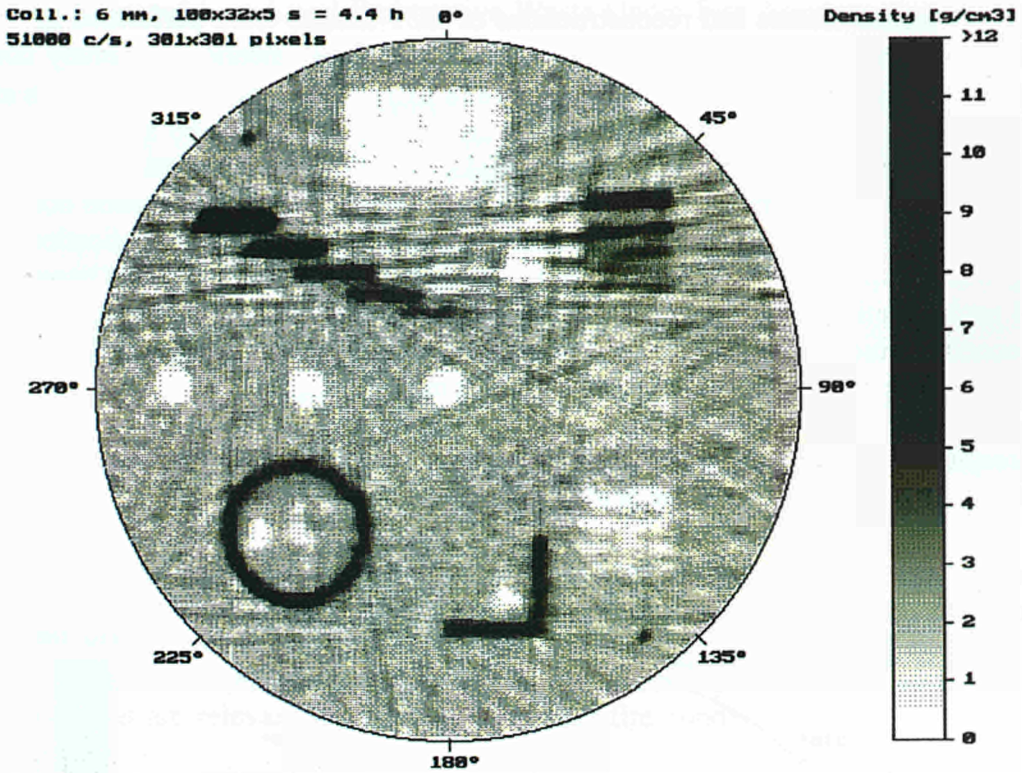


Fig. 4: Medium Resolution

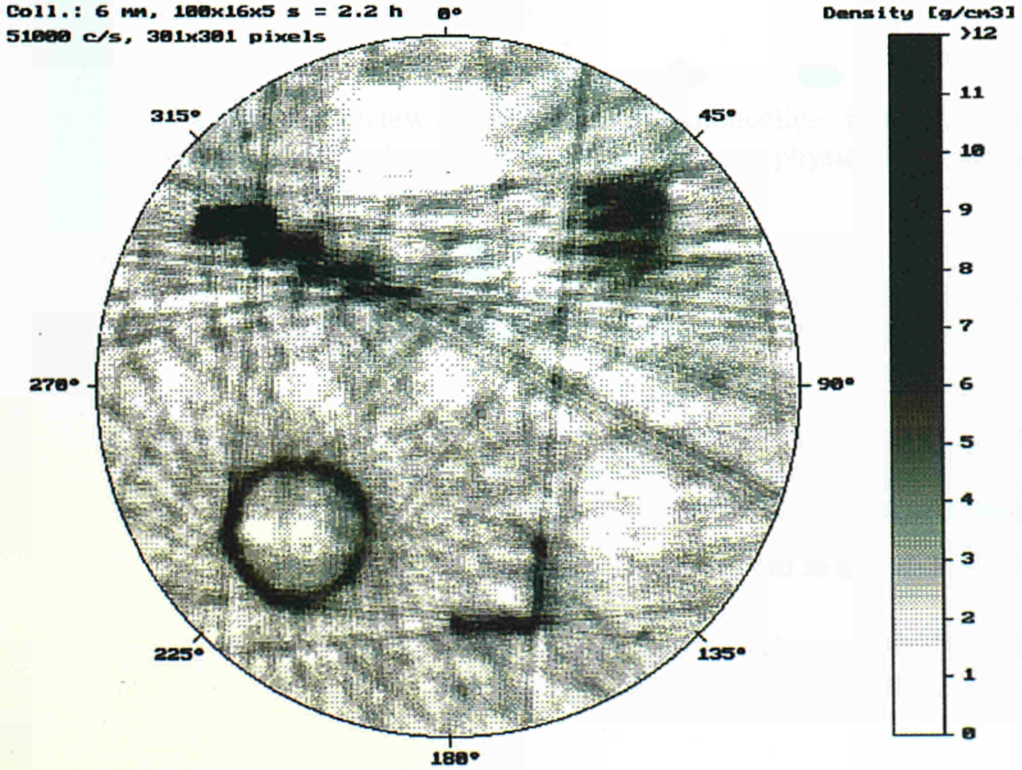


Fig. 5: Low Resolution

First ECT-measurements and reconstructions of ECT-images were performed in late January 94. Fig. 6 shows a reconstructed ECT-image of the above mentioned dummy containing 5 radioactive samples of 31 MBq Cs-137 each (838 µCi). These samples emit γ-rays at 662 keV within the observed plane. The transmission analysis using the Co-60 source, however, was carried out at the two well-known energy peaks of 1.173 and 1.333 MeV. Due to the fact, that the absorption coefficients are strongly energy dependent, the absorption coefficients had to be corrected in order to combine the transmission with the emission application. The image of fig. 6 is set up by a 127x127 pixels matrix (pixel size: 4.4 x 4.4 mm). It is based on the data of 64 angle positions, each consisting of 50 scan steps. The measuring time per step was set to 10 seconds, which gives a total measuring time of 8.9 hours, using one Ge-detector. The diameter of the collimator was chosen to be 15 mm.

The result is very satisfactory, because the sources shown by the image seem to have similar activities. This corresponds to the actual case.

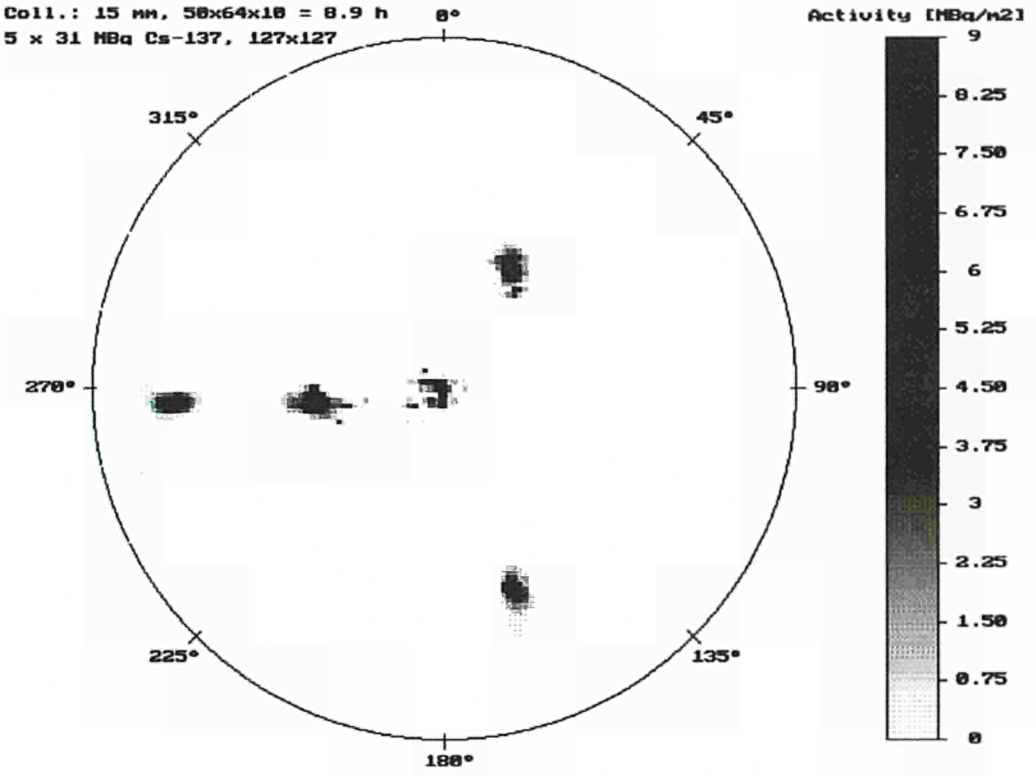


Fig. 6: ECT-Image of the Dummy Containing 5 Cs-137 Samples

Title: Behaviour of Low Level Radioactive Waste Under Fire Accident Conditions

Contractor:	AEA Technology (R.P. Bush - projet leader)
Contract No:	F12W/0014
Duration of Contract:	from 1st October 1991 to 31st March 1994
Period Covered:	1st January 1993 to 31st December 1993

A. OBJECTIVES AND SCOPE

The objective of the work undertaken within this project has been to provide information on the release of radionuclides from supercompacted low level waste (LLW) under fire accident conditions and to understand how these releases depend on the severity and characteristics of the fire accident. Mathematical models have been developed to predict the response of packaged LLW under various fire accident conditions.

Little information relevant to this topic was previously available. The approach to the project (based on large-scale inactive tests, mathematical modelling, and small-scale active experiments) was similar to that used in a previous study of immobilised intermediate level waste, but took account of the special properties of LLW and its constituents that are relevant to its behaviour under fire conditions.

B. WORK PROGRAMME

1.1 Objective

To obtain sufficient information to quantify the release of radionuclides from LLW under fire accident conditions, and to understand how these releases vary with the severity and characteristics of the fire accident.

1.2.1 Literature Review

To carry out a literature review on the release of radionuclides from LLW under fire accident conditions and related areas, such as the relevant physical and chemical properties of LLW, fire conditions etc.

1.2.2 Modelling Studies

To develop and validate mathematical models for the thermal behaviour of LLW, including heat and mass transfer, gas diffusion and combustion phenomena.

1.2.3 Large-scale Testing

To carry out large-scale thermal tests on simulated LLW in two stages: the first to provide a basis for the modelling and to define conditions for active experiments; and second, to validate the models and provide a basis for applying the results to a range of situations.

1.2.4 Small-scale Thermal Tests

To perform small-scale thermal tests to determine the releases of radionuclides from radioactive samples of LLW components, under conditions defined from the modelling work and large-scale tests.

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. State of Advancement

The project has now been completed as planned.

In the past year, the mathematical modelling work has been extended and refined. A model has been developed to simulate the behaviour of a single 'puck' of supercompacted waste exposed directly to a fire. Supporting measurements of physical properties have been completed. Factors affecting the spread of fire from puck to puck have been considered.

A second tranche of large-scale thermal tests has been completed on supercompacted 200 *l* drums of simulated LLW materials. Two materials were used: a mixture of equal weights of cellulose, polyethylene, polyvinyl chloride, latex and neoprene; and, cellulose containing a high metal content. Tests were conducted in an electrically heated oven at 300°C, 700°C and 1000°C. The temperature profiles generated, and the materials released, were studied.

Small-scale tests have been conducted with samples of the first of the mixed waste materials noted above, doped with selected radionuclides. Materials released at different temperatures were collected, and the fractions of each radionuclide released were measured.

Temperature profiles obtained from the mathematical models can be used in conjunction with the radioactivity release fractions to calculate the expected release of radioactivity from a known material under defined fire accident conditions.

2. Progress and Results

2.1 Literature Review

The main results of the literature review were presented in the 1992 Annual Report (EUR 15132 EN). It highlighted the fact that, at the start of the project, little was known about the behaviour of supercompacted LLW under fire accident conditions. The review provided useful information about the thermal behaviour of substances which are major combustible components of LLW.

2.2 Modelling Studies

Three aspects of fire behaviour needed to be addressed in the current study: heat transfer in an array of supercompacted pucks contained in a closed box; the pyrolysis of organic material in a puck exposed directly to fire and the associated heat and mass transfer; and the spread of fire from puck to puck. The first of these was addressed in the 1992 Annual Report.

The behaviour of a puck of supercompacted LLW directly exposed to a fire can be modelled by adapting the HOTDOG code originally developed for use with immobilised intermediate level waste. Changes in the physical state of LLW due to pyrolysis reactions have to be allowed for, as does the heat of such reactions. The transport of the gases formed can be modelled in the same way as that of water vapour in a cemented wasteform.

An analysis has been made of the spread of fire from puck to puck. This has proved difficult to model in detail, but it has been confirmed that fire-spread is unlikely to be an important phenomenon in fire accidents involving LLW.

2.3 Large-scale tests

Following completion of a first tranche of large-scale tests in 1992, a second tranche has been carried out in 1993.

Mixtures of key components of LLW were supercompacted in 200 *l* drums and heated in an electric oven. Two mixtures were used. One contained equal weights of cellulose, polyethylene, polyvinyl chloride, latex and neoprene; experiments with this material at 300°C, 700°C and 1000°C were designed to illustrate the effects of all important physical and chemical changes that can occur in heated LLW. The second mixture was cellulose with a high metal content, and was tested at 1000°C. This illustrated the effect of higher temperatures on an easily pyrolysed material in a matrix of high thermal conductivity.

The temperature profiles measured over time did not show any excursions due to rapid local reactions. The presence of cellulose led to a plateau at 100°C in the temperature profile, due to the evaporation and release of associated water. Analysis of volatile materials condensed from the oven tests has shown the presence of major products consistent with the known thermal behaviour of the waste components present. Samples of the pyrolysed residues from the large-scale tests have been used to measure physical properties (thermal capacity, thermal conductivity, permeability) required in the modelling calculations.

4. Small-scale active tests

The results of the large-scale tests and of the modelling studies were used to define conditions for a series of small-scale active tests. The same mixture of equal weights of the five major combustible components of LLW was used to make 1.5 *l* samples which were treated with selected radionuclides and supercompacted in cans to give 'mini-pucks'. These were heated to temperatures of 150°C, 450°C, 700°C and 1000°C. The released material was collected in traps, and analysed to measure the fractions of the various radionuclides released.

The results showed that even at 1000°C releases of actinides were very low. Releases of cobalt-60 and caesium-137 were higher, but less than 1% of the initial inventory. Ruthenium releases were in the range 1.5 to 2% at temperatures of 450°C and above.

The radiological consequences of these released fractions depend on the initial inventory and on the temperature distribution achieved in a particular fire accident. The data obtained, together with the mathematical models developed in this study, will enable releases from LLW under postulated fire accident conditions to be calculated.

TESTS FOR PROCESS CONTROL DURING TREATMENT OF LOW AND MEDIUM RADIOACTIVE WASTE IN PRACTISE

Contractor	:	KEMA Nederland B.V., KFA Jülich, Laborelec
Contract No.	:	F12W/CT90/0019
Duration of contact	:	January 1, 1991 to December 31, 1994
Period covered	:	January 1993 - December 1993
Project leader	:	H.A.W. Cornelissen (KEMA Nederland B.V., coordinator), R. Odoj (KFA), Mr. Roofthooft (Laborec)

A. OBJECTIVE AND SCOPE

Adequate management of radio-active waste that will be formed during operation of nuclear power stations, is an absolute necessity to warrant the protection of man and environment. Therefore the total waste treatment process from waste release up to interim/final storage has to be controlled. Continuous process control is preferable above verification just before storage because of its higher reliability, traceability and the possibility for corrections of the system.

This research project refers to the development of test methods which are necessary to control the process of conditioning of radioactive waste. The emphasis lies upon measurement techniques and operations.

On the basis of the international exchange of information between the partners recommendations will be formulated which respect to standard testing methods and procedures where specific quality systems can be based on.

There is also a close co-operation with CEA/CEN and Taylor Woodrow.

B. WORK PROGRAMME

B.1 Progress descriptions of waste treatment

B.2 Chemical characterization

B.3 Radiological qualification test methods

B.4 Mechanical and physical qualification tests

B.5 Validation of test methods and evaluation

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1 STATE OF ADVANCEMENT

In the laboratory α, β, γ spectroscopy was experimentally studied. Chemical characterisations were performed by means of selective electrodes and photometrical measurements. In order to follow the mechanical properties of cementated radwaste, especially viscosity and impedance test-methods proved to be appropriate if variations in composition are large. For smaller variations, the maturity method can be used as well.

Also a relation was found between water content and strength of cementated waste.

C.2 PROGRESS AND RESULTS

C.2-1 CHEMICAL TESTMETHODS

At the beginning of a cementation campaign a chemical characterisation of the components to be mixed should be performed. This is especially necessary for those components which could negatively influence the hardening process of the cement.

Two methods were chosen, namely the photometric method and the determination by means of selective electrodes. With respect to the photometric method a portable photometer is used. Test kits were available. To find out possible interferences, multi-element standard solutions were used additionally.

The results obtained clearly show that the linearity of the photometric method is fairly good for most of the species measured. An overview of the individual results can be found in table I. The results of our measurements indicate that accuracy as well as reproducibility are pretty good for photometry. The method applied therefore can be regarded as well suited for the determination of the so called cement poisons.

With regard to the restricted commercial availability of the method by means of selective electrodes only four types of ions could be examined: NO_3^-, Cl^-, Ca^{2+} and NH_4^+. All the results, the mean values and the deviations between the mean values and the exact quantities in the wastewater solution are mentioned in table II. Further the time needed for measuring each element amounts to about twenty minutes. From this it may be concluded that analyzing of chloride and nitrate by means of selective electrodes is quite well possible.

The accuracy is good and the speed of analyzing attractive. The deviation between the mean value of the calcium determinations and the actual wastewater concentration, however, was high (36%). This was caused by the interference of alkali ions, present in the wastewater.

With regard to ammonia the detection limit was determined and appeared to be 0.5 $mg\,l^{-1}$. The value is with respect to a possible interference with cement hardening quite low and therefore the determination of the ammonia concentration in wastewater by means of selective electrodes is possible as well.

The capability of ICP (Inductive Coupled Plasma) and IC (Ion Chromatography) was tested by Laborelec at the Doel power station. In the case of the ICP tests, the maximum error found, was 11.5%, in the case of IC the maximum error was 3%, with the exception of PO_4^- where the error proved to be 15.2%.

C.2-2 RADIOLOGICAL TESTS

α- and β- spectrometry

The work programme for α- spectrometrical determination contains the following aspects:

- sample preparation (chemical)
- sample amount
- procedures
- measurements
- instrument used
- results
- accuracy
- calibration

For β-spectrometrical determination of H-3 and Sr-89/90 the following steps were considered:

- sample preparation
- measurement procedure

γ-specrometry

With regard to the γ-spectrometry measurements KEMA provided Laborelec zirconium sand. The different nuclides were determined with the Canberra apparatus in the counting room of unit 1 and 2 at Doel. In table III the measured nuclides are given.

By KEMA a procedure is developed to assure that the measurements to waste packages are performed in such a way, that there will be no doubt about the quality of the results and on the other hand that operators will agree on the benefits of this procedure and subsequently execute their work according to this procedure. The procedure is given in a simplified block diagram with a brief explanation (table IV).

C. 2-3 MECHANICAL AND PHYSICAL TESTS

To insure that radwaste cementation remains immobilized after disposal, certain standards have been set; one such standard is compressive strength. The purpose of this project, was to determine whether the 7 day and 28 day compressive strength from radwaste cementation can be predicted during the mixing and early curing stages. Three methods were used for this project: maturity, rheology, and impedance.

Maturity is a temperature/time measurement, rheology is a shear stress/shear rate measurement and impedance is the opposition offered to the flow of alternating current. These three methods were employed on five different cemented radwaste concentrations with three different water-to-cement ratios; thus, a total of 15 different mix designs was considered.

The results of the maturity method did not fulfil all expectations. The results did not show the expected result that the higher the maturity value, the higher the strength. In fact, with the higher waste percentages the opposite was true. It was found that the higher the radwaste concentration was, the lower the curing temperature proved to be, which in fact causes a flaw in the maturity calculations. It was also shown that the maturity calculations do not take into effect the large changes in water-to-cement ratios.

The results of the rheology method were very good. The experiment showed that concrete is not a Newtonian liquid, but did follow the flow properties that conform to the Bigham plastic model. Therefore, using the rheology method, the compressive strength of cemented radwaste can be predicted. The only drawback to this method is that the method requires two constants too be determined. Trying to use this method to predict the compressive strenght of cemented radwaste may be too cumbersome. Also, it must be determined of this method is statistically viable by gathering more data. It is recommended that this method be continued in the laboratory environment until more data can be accumulated.

The results of the impedance method are very promising. The results showed a very good relationship between impedance and water-to-cement ratios. From the impedance and time figures it is clearly evident that a relationship can be developed between impedance and strength. The results from plotting strength and impedance show a high statistical accuracy for the data obtained. This method only needs one constant and that is a measured constant, where the rheology constants are derived from a linear relationship obtained by best fitting.

Another important note is that the results are obtainable 10 minutes after the addition of cement. Therefore, it is recommended that this method will be upscaled from a laboratory model and placed into use in the radwaste disposal industry.

To find a relation between the water content and the strength, five main waste percentages (between about 5% and 355) were developed with three to four different water to cement ratios. It was tried to find relations between mix composition parameters and compressive strength. The best parameter proved to be the ratio of cement and water plus waste. This relation is shown in figure 2. By linear regression the following equation was derived:

$$f'c\ (28d) = 41.7\ (c/(w+r)) - 17.3$$

In this equation c, w and r represent cement, water and waste content in mass %.

REFERENCES

KEMA 1993a. Tests for process control during treatment of low and medium radioactive waste In practice. Intermediate report 3 (period 93-01-01 - 93-06-30). KEMA report 20251-KET/R&B 93-4316, September 21, 1993.

KEMA 1993b. Methods to predict compressive strength for on-line quality control during radwaste cementation - experimental results. KEMA report 20251-KET/R&B 93-4300, September 14, 1993.

Table I Overview on photometrical determinations with single element standards and multi element standards and multi elements standards (KFA Jülich)

species	linearity range ppm	reproducibility measure at ppm	reproducibility in a multi el. standard measured at ppm	analysis time needed min
ammonia	0.2 - 2.7	2	n.dtd.	15
boron	0.02 - 0.5	0.5	0.5	20
calcium	10 - 2000	100	10	10
chloride	5 - 200	100	100	5
chromium	0.2 - 2	1.5	n.dtd.	20
magnesium	0.1 - 0.7	0.5	n.dtd.	20
nitrate	10 - 60	50	50	17
phosphate	2 - 10	6	10	12
sulfate	20 - 500	100	100	25

n.dtd. = not determined

Table II Determination of Cl^-; NO_3^- and Ca^{2+} in artificial, non-radioactive wastewater

	1	2	3	4	5	6	mean
Cl^-(g.l.$^{-1}$)	15.05	15.11	14.99	14.90	15.17	15.45	15.11
NO_3^-(g.l.$^{-1}$)	698	716	693	719	749	757	722
Ca^{2+}(mg.l^{-1})	999	973	1.078	1.099	1.099	1.165	1.069

	Cl^-	NO_3^-	Ca^{2+}
deviation (%)	1.2	0.4	36

Table III Analysis of nuclides

Nuclide	Bq/ml
Mn-54	0.111
Nb-95	0.131
Te-131	0.114
Bi-214	186
Pb-214	136
Th-234	7.25 (*)
U-235	2.4

(*) the value of Th-234 is calculated. It was indicated as Cd-109

Table IV Simplified block diagram of a quality procedure to control a gammaspectroscopy system

electronic control	The control of the electronics has only to be performed for those settlings, which are essential for the correct working of the HpGe-system
control of the ballistic deficit correction	The developed HpGe high count rate system incorporates a special spectroscopy amplifier which makes it possible to use shaping times of 0,25 μs. These short shaping times cause for extra disturbance in the photo peak. This disturbance van be corrected by adjusting a Ballistic Deficit Correction
control of energy calibration	Each standard gammaspectroscopy system is more or less sensitive for drift. This drift can cause errors in the reported activities and/or nuclides. The check of this calibration can easily be performed by measuring a special control source
efficiency control	To control the whole gammaspectroscopy system it is necessarily to measure the radioactivity with a special source. This source must contain gamma photons, which emit in the regions of interest. Important parameters of the system are: - total count rate of the source - FWHM (Full Width at Half Maximum), countrate, energy of the most important gamma photons.

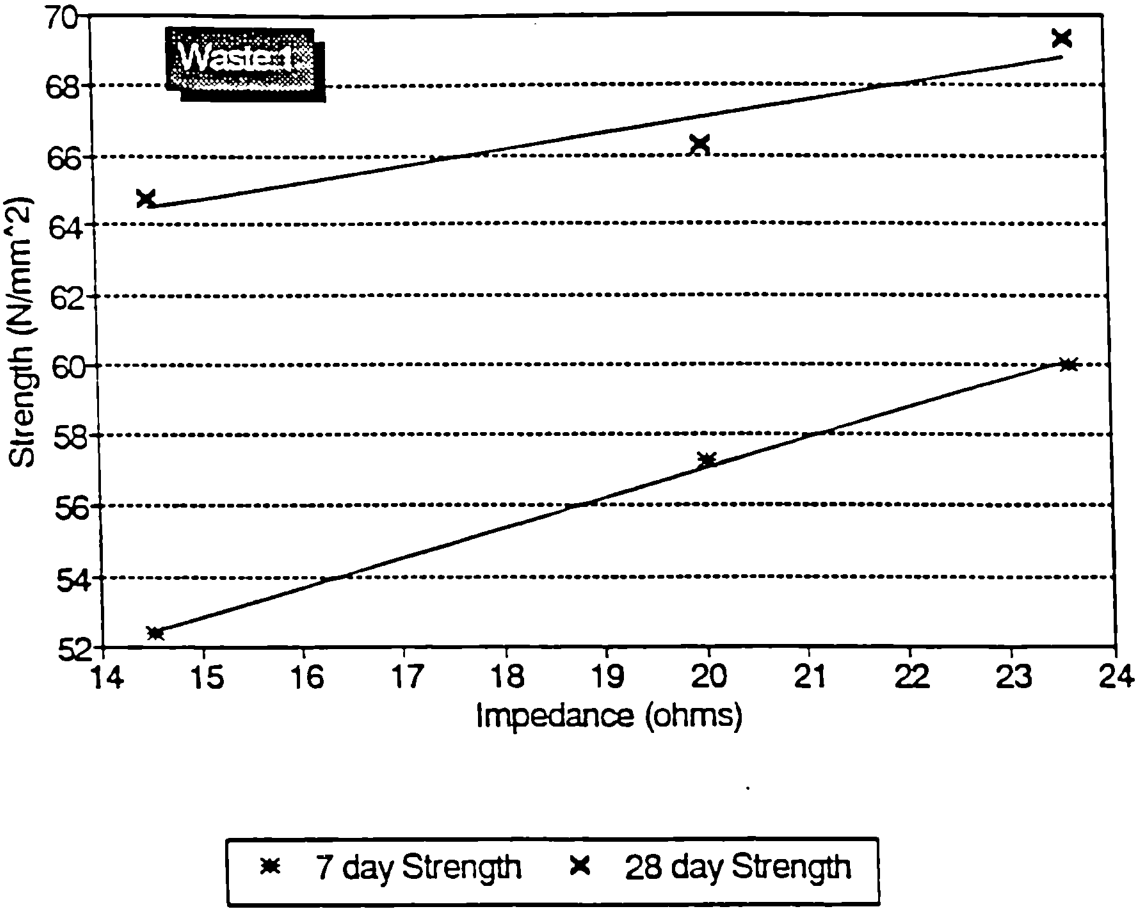


Figure I Strength versus impedance for waste 1

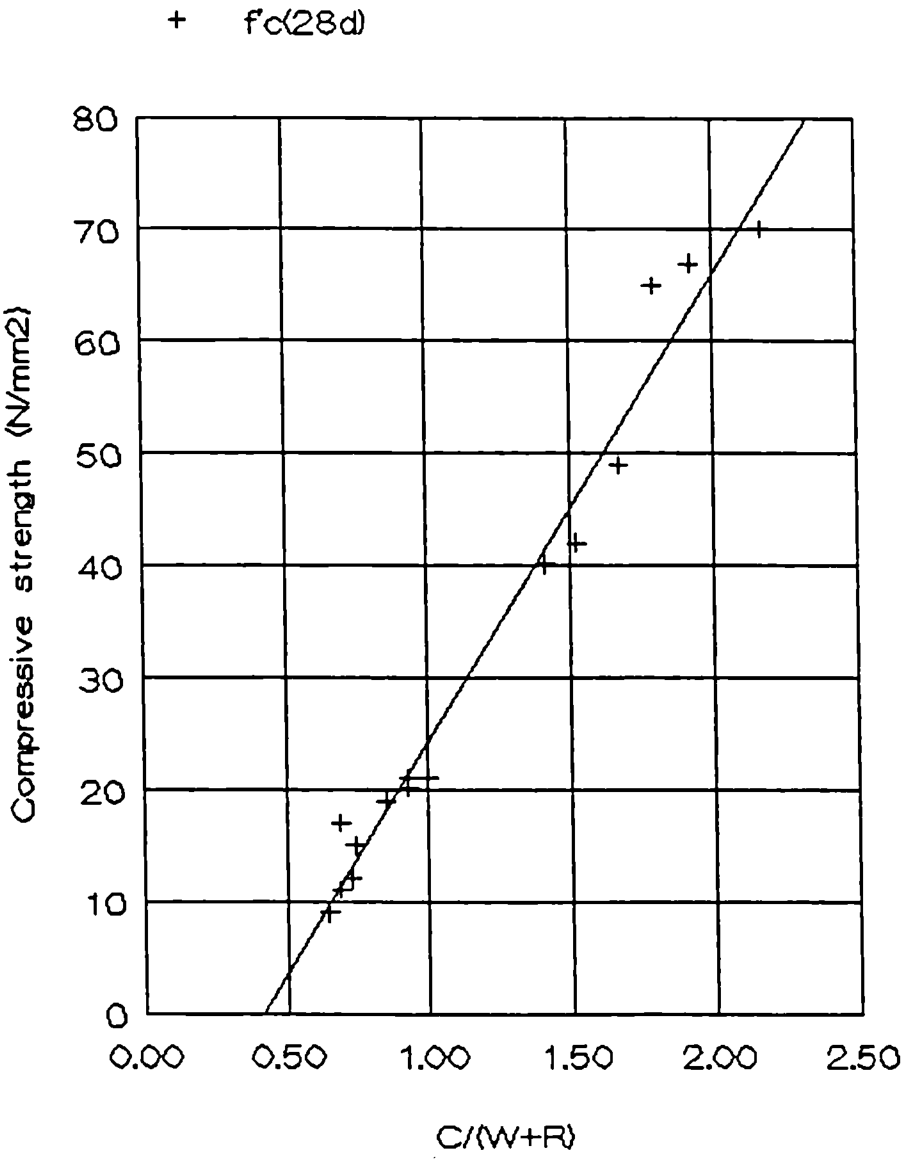


Figure 2 Compressive strength (28 days) versus cement to water waste ratio

Title: Establishment of non destructive or partially destructive test procedures for determining the characteristics of wastes containers
Contractor: CEA Cadarache - Dép. Entreposage - Stockage Déchets
Contract: FI2W-CT90-0021
Duration of contract: from 1.10.1991 to 30.09.1995
Period covered: 1.01.1993 to 31.12.1993
Project leader: J. MISRAKI ; Co-author: R. BOSSY

A. Objectives and Scopes

In the frame of the low and medium wastes package's characterization, this programme proposes to establish, examination procedures, leaning on acquired experiences about real packages.
One of the main objectives is to limit very hardest the destructive examinations, the non destructive examinations having the advantage not to cause secondary wastes.

B. Work programme

During the last year, we had published the two following technical files
B3 - Microorganisms Actions on embedded wastes (Bitumen matrix)
B4 - Water content measurement
as that was foreseen in the next planning:

PROGRAM	1992	1993	1994	1995
Agreement programme	---			
Procedures establishment	---	---	---	---
B1 : Sampling methods for analysis (alpha, beta, gamma)	---			
B2 : Gamma scanning on packages	---			
B3 : Microorganism actions on embedded wastes		---		
B4 : Water content measurement in embedded wastes		---		
B5 : Radiolysis gaz measurement			---	
B6 : Thermoluminescent dosimetry			---	

On the other hand we have going to establish a project of the fifth technical file relative to : "Radiolysis gaz measurement in embedded wastes".
Studies and Assays are going on with the specialized laboratory and we think to present this project in the next progress meeting in HARWELL on 16.03.94 to 18.03.94.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C1. Microorganisms actions on embedded wastes

Leaning on experiences effectued in the CEA/DCC/DESD/SEP laboratory, we have set up a technical file relative to the microorganisms actions on raw wastes embedded in bitumen matrix.

This test procedure is required by Fundamental Safety Rule (RFS III 2 f), relative to disposal of radwastes in deep geological formations.

After a study of the growing conditions on microorganisms in the site and possible degradation mechanisms for the various materials (organic and mineral material), it was observed that it is not possible to apply a single methodology to all the various matrix.

The application of the exisitng standards (ASTM G21 and G22 or ISO 846) cannot be used for each matrix. Therefore a selection will be made from:

- specific microorganisms adapted to degradation mechanisms,
- optimal culture medium,
- duration of test,
- test control after microorganisms exposition (visual examination, mechanical resistance, CO_2 release, or acid formation...)

The modification brought to the standards tests are very important, taking on account the different behaviour of various bitumen with the bacterial strain (positive or negative answers).

The detailled procedure (1) was presented to the members of Task 3 during the meeting held from 31.03.93 to 02.04.93 in SAN SEBASTIAN.

C2. Water content measurement

The moisture content of a waste package is one of the characteristic which had to be known, to appreciate the confinments power and package mechanical resistance.

The purpose of this technical file is to define a procedure for measuring the water content in embedded radwaste after a partially destructive tooling.

The device used is SOLO 40. The principle of the measurement carried out by this apparatus is the elastic diffusion of neutrons in a material. Also the package has been cored without water, an aluminium tube is put into the hole. The SOLO 40 probe is sent down in the tube and any measurements are carried out every 50 mm in depth from the bottom of the package. A repartition of moisture is also realized in the container. That is a kind of moisture scanning of the package. Comparative measurements of humidity carried out by this method and destructive test (sample dried at 120°c) shown that the results are comparable (10 to 15 %).

The detailled procedure (2) was presented to the members of Task 3 during the meeting held from 27.10.93 to 28.10.93 in ARNHEM (NL).

REFERENCES

(1) DCC/DESD/SECI BE93.094 - July 30th, 1993
Microorganisms actions on embedded wastes.

(2) DCC/DESD/SECI BE94. - January 1994
Water content measurement - Annual report 1993.

Title: Non-Destructive Examination of Nuclear Radioactive Waste packages by Advanced Radiometric Methods
Contractors: BAM Berlin, TU Munich, CEA CEN-Valrho
Contract n°: FI2W-CT90-0023
Duration of contract: from 1.09.1991 to 31.08.1995
Period covered: January - December 1993
Project leader: Dr. Peter Reimers

A. Objectives and Scope

NONDESTRUCTIVE EXAMINATION OF NUCLEAR WASTE PACKAGES BY ADVANCED RADIOMETRIC METHODS

The radiometric methods to be applied to the nondestructive examination of nuclear waste packages are computerized tomography (CT), digital radiography (DR), and microtomography (MCT). CT with Co-60 and linac radiation is established at BAM since more than five years. A new scanner particularly designed for waste drums was installed at TU Munich during the first months of 1992. It will be used for the work of this contract.

Computerized tomography (CT) offers the possibility to get information about the internal structure of waste containers. In many cases it is sufficient to make CT-measurements on selected parts of a package. Therefore, a fast method to get a survey image of the total package is very useful. As shown in the work before (CEC Report 1985-1989), digital radiography is such a NTD-method. The disadvantage is that with a one detector system the measuring time is much higher than for a CT measurement. DR with a CT-multidetector system gives a distortion of the geometry of the object. Part of this contract is the development of a new data acquisition programme that fulfils the following conditions:

- Measuring time lower than 10 min for a 200 l drum
- Correct geometrical projection and intensity calibration, probably by software correction
- Wide energy range (400 kV X-ray, Co-60, LINAC-12 MeV)

For high energy computed tomography (HECT) a new detector will be designed with improved dynamic range and fast read out time. After design and construction of the complete detector array the performance test will deliver information about spatial resolution, density resolution and limits of data readout time.

Three methods will be developed to improve the information from DR measurements:
- difference image formation
- filtering processes
- interactive image processing

The objective of the CEN-VALRHO work is the improved quality assurance of vitrified HLW packages. The purpose of this investigation is to develop a nonde-

structive tomographic examination method for vitrified waste packages.
The principal defects that occur during the fabrication of glass blocks are:

- cracks and cavities which increase the surface area exposed to leaching water
- molybdic inclusions which are water soluble.

The goal is to qualify and quantify those defects by a tomographic method.
The tomographic examination method will also be applied to estimate the water penetration into the glass block inside its canister, and the glass surface area actually in contact with the water. The consolidation effect of annealing the glass block to limit the degree of fracturation will be assessed using the same method.
The tomographic interpretations will be qualified by glass leach testing.

The objective of the work at TUM is the selection and application of destructive and nondestructive inspection methods for all kinds of LLW packagesc. It includes the use of computed tomography, digital radiography, gamma scanning, and destructive testing (sampling methods).

WORK PROGRAMME

The work programme comprises three main tasks correlated to the three partners:

BAM - digital radiography (DR), computerized tomography (CT), and micro computerized tomography (MCT)
CEA - quality control of HLW-glass blocks
TUM - quality control of LLW-containers

The nondestructive investigation work of BAM focuses on three groups of waste subjects: drums, glass canisters, and waste samples.
The work programme comprises the following topics:

- CT investigation of real LLW and MLW packages
- Study of fissuration of HLW glass blocks
- Evaluation of crack length and geometry by image processing
- Study of representative sampling procedures
- Micro-computerized tomography of core samples

The work programme of CEN-VALRHO has the following topics:

- fabrication of nonradioactive glass blocks
- definition of the tomographic examination procedure and the detection limits
- definition of the image analysis procedure using a "Pericolor" system, measurement of the length of the cracks on the images and estimation of the total internal surface to calculate the fracturation ratio
- quantification of the molybdic phase percentage
- experimental validation of the tomographic interpretation using the leaching method developed in the CEC contract n° FI 1W 182.

The contribution of the "Institut für Radiochemie, Technische Universität München "(TUM), consists of the selection of four 200 l drums with different categories of low level radioactive waste as they are produced in nuclear power plants or nuclear research centres, the use of computerized transmission tomography (TCT) for providing reliable information about the internal structure and composition of these waste containers, the application of destructive sampling techniques to two selected drums followed by preparation procedures suitable for subsequent chemical and radiochemical analyses, and the derivation of rules for representative sampling on the basis of the collected tomographic informations.
The time table for these tasks was updated and completed. Tab. 1 shows the actual situation. The work at TUM was started at 1st March 1992, and will be finished until 31st August 1994. In addition to the tomographic measurements, the application of gamma-scanning techniques was included in the work programme to extend the nondestructive tools and to provide additional data for an adequate characterization of the radioactive waste.
According to problems in transporting radioactive waste drums from Munich to Berlin, the order of the tomographic investigations at BAM and TUM has been inverted. All drums will be examined nondestructively at TUM before they are transferred to BAM.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

According to the time schedule four drums with radioactive waste have been measured at TU Munich and transported from Munich to BAM in April 1993. They were tomographically investigated at BAM and brought back to Munich in December. The control package "E" fabricated by CEN-VALRHO was investigated. Altogether 11 cross sectional images at various heights were measured.

Progress and results

C.1 New detectors for HECT

Due to thermal instability and rather high noise level of the old Linac-radiation detectors it is an objective of this contract to develop a new type of fast charge collecting detector.
The four most important design parameters of the new BAM data acquisition system were:

1. The system must accept signals from photodiodes (scintillation detectors) and photomultipliers (Cerenkov detectors) as well.

2. The system must integrate the signal produced by the 4 μs Linac pulse with 15 bit resolution.

3. The data processing system should be able to accept signals from at least 10 detectors.

4. Background and switching noise should be minimised.

The signal processing circuitry was designed and four prototype detectors are completed. They are now in the experimental testing procedure.

C.2 Investigation of Control Package E

CEN-VALRHO has produced a control package "E" in order to quantify the occuring defects and to determine the detection limits for each type of defect.
The internal structure of this "phantom" has already been described in the annual progress report 1992. It was investigated now using Linac-radiation and the new charge collecting detectors. All tomograms have the size 921x921 pixels with a resolution of 0.5 mm. The result gives quantitative values of the main parameters of the CT-system for the evaluation of 43 cm diameter glass canisters.

C.3 Evaluation of the internal surface

Three complementary investigation methods implemented to assess the degree of fracturation of a glass block were used to obtain results which have to be correlated. These methods are:

1) A nondestructive tomographic method based on stereological rules developed at BAM.

2) A measurement of the weight distribution of all the fragments constituting a fractured glass block performed at CEN-VALRHO.

3) Water leach tests - static and dynamic - to estimate the degree of fracturation based on the proportionality between the leached surface area and the leachate concentration of mobile elements released from the glass performed several times at CEN-VALRHO.

The aim of topic C.3 is to develop a nondestructive method for the quality assurance of sealed HLW packages.

Up today no test sample which had been submitted to all three tests is available. Therefore, the comparison was based on different glass canisters assuming a similar crack and fragment distribution. A comparison of all test methods applied to the same test sample will be done within this contract based on canisters produced by CEN-VALRHO.

Until now, for a HAW 35 canister the crack surface was determined to 6.66 m^2 using computerized tomography (cf. APR 1992). For the 3/200 and the 2/200 canister type RG 20 the total surface was determined to 15.76 m^2 and 15.06 m^2, respectively using method 2. (These and the following values were taken from final report FI 1W-0182). The comparison shows that computerized tomography is capable of detecting 42% - 44% of the cracks found by method 2) which is approximately the value obtained by dynamic leaching evaluating the leach rate of boron (7.06 m^2). For dynamic leaching based on the leach rate of silicon the surface obtained was only 2.92 m^2, for static leaching the values were closer to reality with 8.45 m^2 and 11.04 m^2 for silicon and boron, respectively.

C.4 Emission computerized tomography

The spatial distribution of the emitted activity in a radioactive waste package can be investigated by single photon emission computerized tomography (ECT). Here "single photon" indicates, that only photons from a gamma decay of the radionuclides contained in the waste are measured in contrast to the common "positron emission" technique. In principle, ECT data sets are measured and reconstructed the same way as TCT data. However, one has to take care of collimating problems and attenuation of the gamma photons on their way through the material.

We investigated a 50 l barrel of bituminized intermediate level waste (ILW) with a total activity of 3.9 GBq ^{60}Co and 68.9 Gbq ^{137}Cs. The ECT data were measured with a collimated GeLi gamma detector. A conventional MCA and two window discriminators were used to identify and extract the signals of either radionuclide separately, so that both of them could be measured at once.

First results consist of three digital emission radiographs and four ECT data sets. As an example we present in Figure 1 the emission radiographs. The used grey scale is not linear for reasons of contrast. By that one can see a structure that is in accordance with former transmission radiographs.

It is planned to investigate the effects of collimation and attenuation. Development of appropriate correction programs is in progress.

C.5 Tomographic investigation of TUM drums

For an interlaboratory comparison of results of TUM and BAM four 200 l drums (EG1 - EG4) were selected at TUM and first measured there (cf. Annual Progress Report 1992).

- Drum EG1 and EG2 with cemented evaporator bottoms from a nuclear power plant
- Drum EG3 with supercompacted mixed radioactive waste
- Drum EG4 with mixed radioactive waste from a research institute

Due to some technical difficulties with the LINAC and the time limited disposition of the drums at BAM the measurements were performed with a ^{60}Co radiation source. The tomograms were measured at the same positions as at TUM. As an example we present in Figure 2 a transmission radiograph and four tomograms of the drum EG1. A quantitative comparison of the results is in preparation.

C.6 Progress at TUM

Corresponding to the work programme, which was defined at the beginning of the project and updated during 1992, all nondestructive inspections of the four selected waste drums, i.e. gamma scanning (GS), digital radiography (DR) and computerized transmission tomography (TCT), were completed successfully at TU Munich in 1993. DR and TCT were also applied to the same packages at BAM in Berlin, in order to gather additional data and to compare both investigation techniques.
Since the LINAC was not available at BAM due to technical problems, the comparative study was carried out by means of a 70 Ci ^{60}Co radiation source.

Results of the gamma measurements using the GERNOD scanner showed that the scanning and data processing technique could be improved to give optimum informations about the gamma emitters not only in typical waste from nuclear power plants but also in waste from research institutes. The latter shows a completely different and large variety of matrix components and radioactive isotopes enclosed. An appropriate improvement of the GERNOD scanner was initiated and will be included in the work programme, if the available time is not exceeded.

The evaluation of the results obtained by nondestructive examinations comprises an appropriate combination of all processed transmission and emission data and is supposed to be finished in February 1994. It will provide the basis for the intended destructive sampling and radiochemical analysis of two of the four drums which will begin in March 1994. These two drums, containing cemented evaporator bottoms from a nuclear power plant (EG2) and mixed waste from a research institute (EG4) respectively, were already selected for the invasive inspection due to their interesting waste composition.

The setup of the sampling equipment was improved by a modified air filtering system which is able to sufficiently retain dust and aerosols being produced during the core drilling procedure.

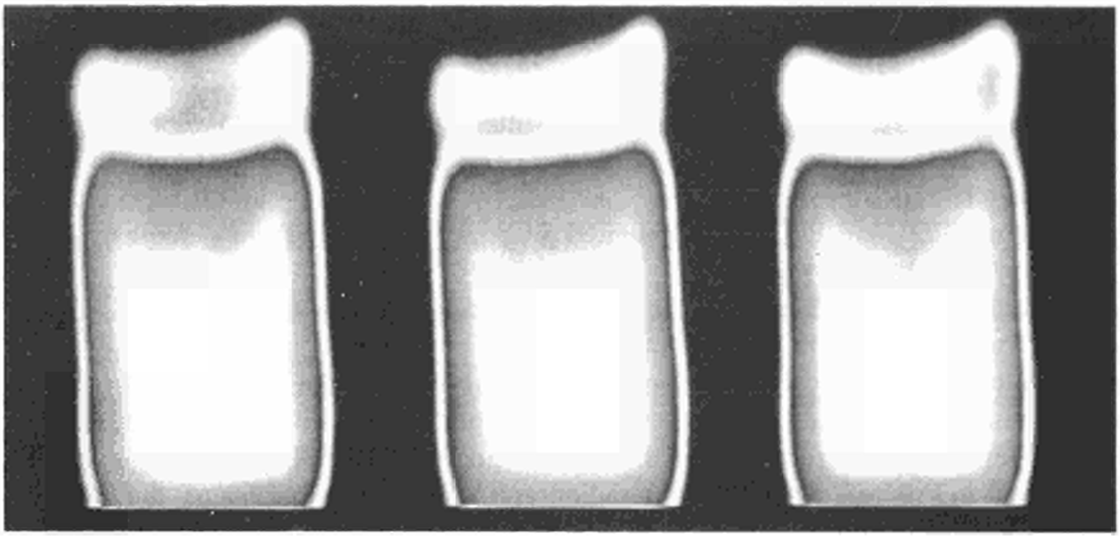


Figure 1: Digital emission radiographs of a 50 l bituminized ILW barrel

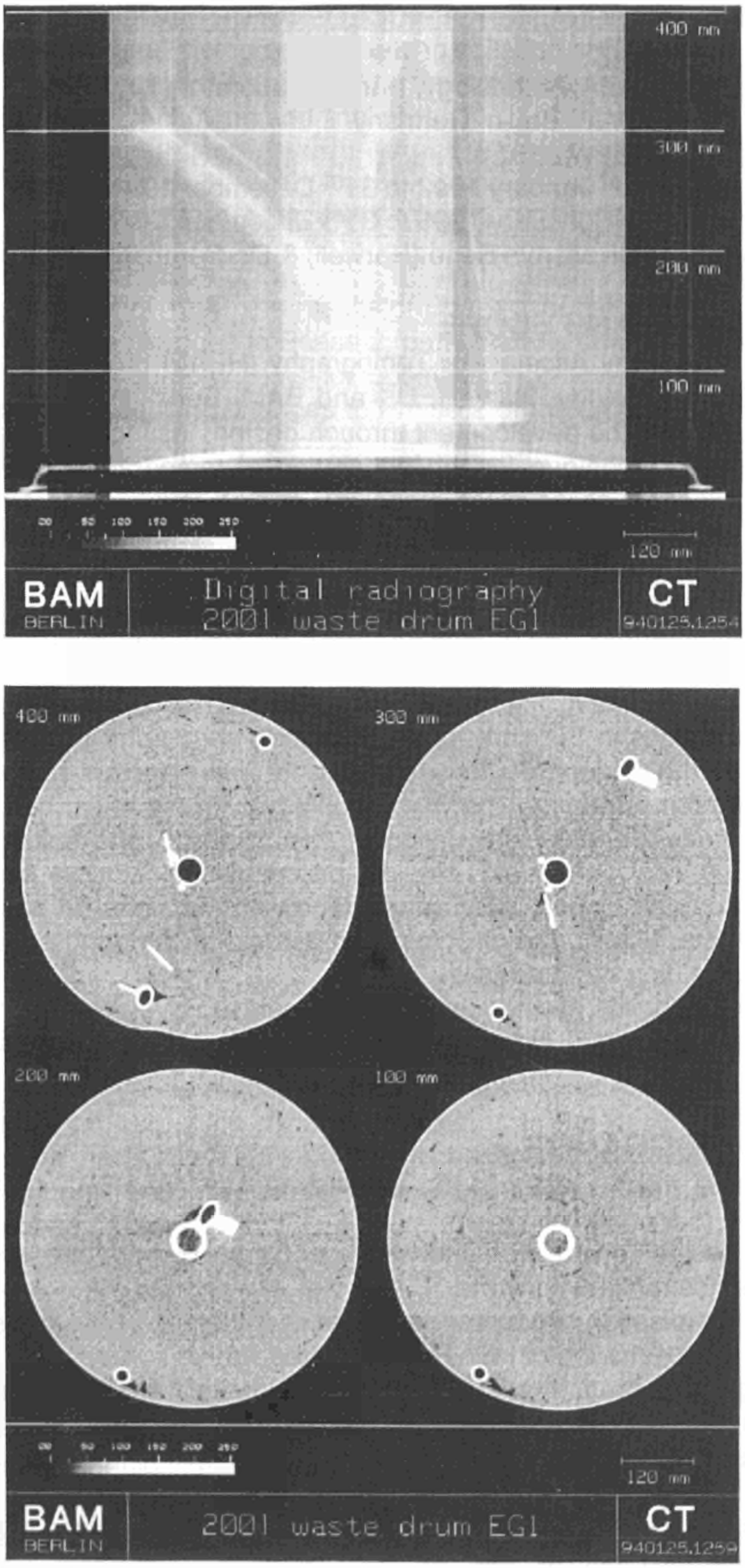


Figure 2: Digital radiograph and four tomograms of the EG1 drum

Title: **HIGH ENERGY ACCELERATOR TOMOGRAPHY (HEAT)**

Contractors: AEA Technology, Harwell Laboratory UK.
BAM, Berlin, Germany.
Contract no.: FI2W/0107
Duration.: 1st January 1992 to 31st December 1994.
Working period: 1st January 1993 to 31st December 1993.
Project leaders: Dr. Martyn Sené (Harwell) & Dr. Bernhard Illerhaus (BAM).

A. OBJECTIVES AND SCOPE

The High Energy Accelerator Tomography (HEAT) project is a collaboration between AEA Technology, Harwell, UK and BAM, Berlin, Germany. The primary goal of the project is the development through design, testing and demonstration of a non-destructive technique for the generation of tomographic images of highly radioactive objects such as glass monoliths of high level radioactive waste. The technique is based on the measurement of gamma-ray transmissions with electron bremsstrahlung from an electron linear accelerator as the photon source. The novel aspect of the technique is the use of Cerenkov counters for the detection of the transmitted gamma-rays. Such detectors have a gamma-ray energy response that exhibits a low energy threshold and a non-linear response up to gamma-ray energies of several MeV. The use of detectors with such a response has three potential advantages in the context of computed tomography of highly radioactive objects. Firstly the intrinsically low sensitivity of the detectors to the low energy portion of the bremsstrahlung spectrum should reduce the beam hardening effects which result from the rapid attenuation of this portion of the spectrum by waste packages. Secondly, it should provide discrimination against the low-energy background from the objects significantly improving the signal to background ratio in measurements. Finally, the discrimination against background should also relax the detector shielding requirements.

The project builds on the tomography expertise developed over a number of years at BAM and the expertise in detector design and operation in AEA Technology.

B. WORK PROGRAMME

There are three main phases in the development of the HEAT technique, each corresponding to a period of 1 year:

1. The design construction and testing of Cerenkov counters, collimators and a bremsstrahlung converter.
2. The optimisation of counter performance for tomographic measurements.
3. The demonstration of HEAT on simulated waste.

These three phases are further subdivided into a total of 11 work packages:

WP1. Design of Cerenkov detectors.
WP2. Construction of Cerenkov detectors.
WP3. Testing of Cerenkov detectors.
WP4. Design and manufacture of collimators and bremsstrahlung converter.
WP5. Tomography tests at BAM
WP6. Detector Modifications to optimise performance.

WP7. Modifications to BAM CT system for implementation of HEAT.
WP8. Construction of full detector array and installation at BAM.
WP9. Demonstration of HEAT at BAM with simulated waste.
WP10. Assessment of technique and final report.
WP11. Co-ordination of project.

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1 State of advancement

As reported at the end of 1992, the results of Phase 1 of the programme indicated the necessity for some changes in Phase 2, particularly a change in the location of the representative tomography tests for optimisation of the counter design from Harwell to BAM. The resulting changes to Phase 2 of the programme are reflected in changes to WP5-8 in section B above.

WP7, which was started at the end of last year is progressing well. In order to utilise the Cerenkov detectors with the BAM CT system it is necessary to integrate them with the data acquisition electronics. A new detector signal processing system has been developed which can accept inputs from both photomultipliers and the photodiodes used with the conventional detectors.

Whilst the data acquisition system was under development the first tests of the detector performance (WP5) were carried out at BAM at the beginning of March. Clean signals were observed from the detectors and a first indication of the reduced beam hardening effects expected from the detectors was observed. The tests also indicated that some modifications to the detectors were necessary if they were to perform well in the BAM CT system. The necessary changes to the detectors (WP6) have been made and the modified detectors were tested at BAM (WP5) with the modified data acquisition system during the last quarter of 1993. These tests, which included tomographic measurements of glass and steel test pieces, confirmed the suitability of the detectors for tomography measurements and demonstrated the operation of the new data acquisition system. Unfortunately, due to serious faults with the BAM radiography linac, it was not possible to complete the full set of tests by the end of 1993. As a result the final choice of the detector for use in the full detector array cannot yet be made. Following completion of the tests, expected by the end of January 1994, some minor modifications to the design of the detector light guides will be made and a full array of the chosen detectors will be constructed and used for demonstration measurements with simulated HLW glass monoliths in the final stage of the program

C.2 Modifications to BAM CT system

The four most important design parameters of the new BAM data acquisition system were:

1. The system should accept signals from photodiodes (scintillation detectors) and photomultipliers (Cerenkov detectors).
2. The system should integrate the signal produced by the 4µs Linac pulse with a 15 bit resolution.
3. The data processing system should be able to accept signals from at least 10 detectors.
4. Background and switching noise should be minimised.

The signal processing circuitry designed to satisfy these requirements is shown schematically in figure 1.

At the heart of the new system is the fast switching integrator IC AFC2101 (manufactured by Burr-Brown). In figure 1 this IC is shown with the components associated with a Cerenkov detector photomultiplier. In the case of the scintillation detectors the circuitry feeding the AFC2101 integrator is replaced by the a photodiode and preamplifier with offset compensation circuitry.

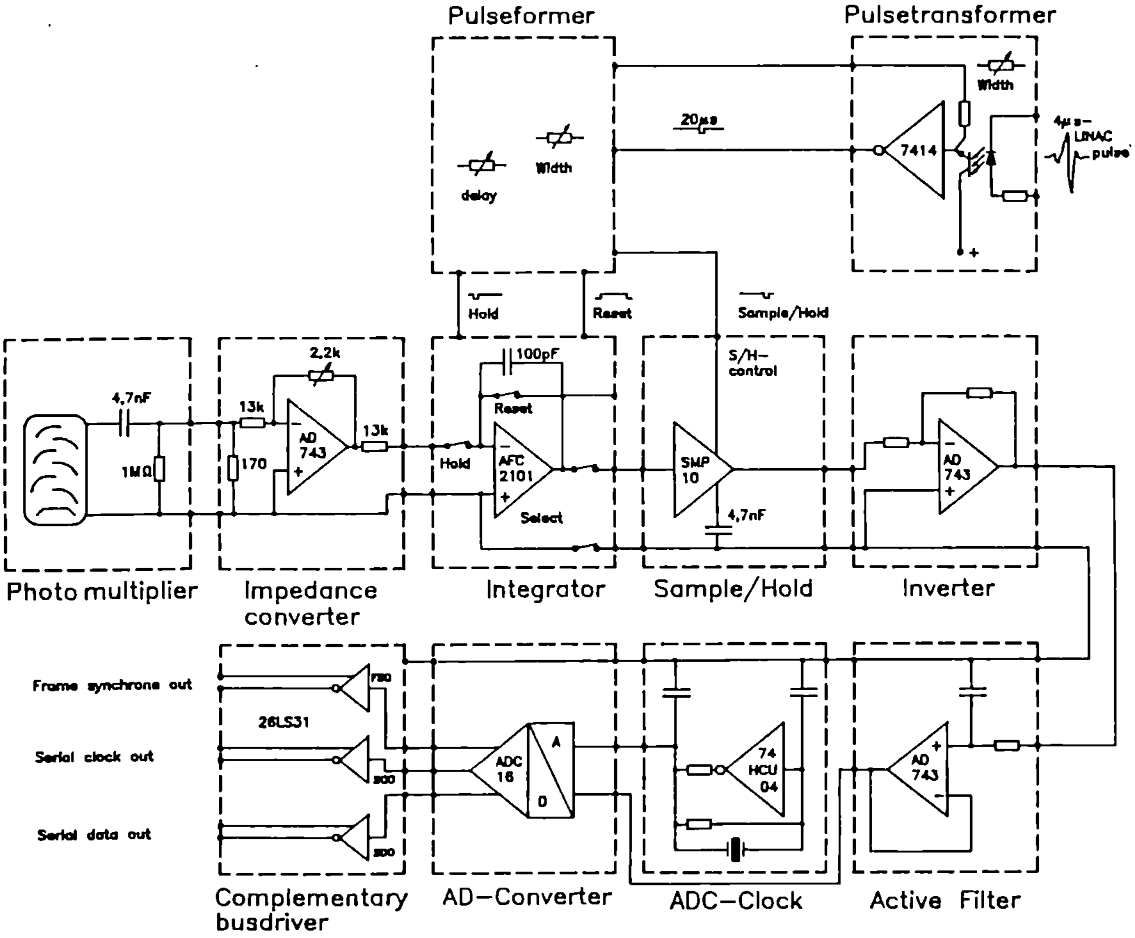


Figure 1: New signal processing circuitry.

At the start of each data acquisition cycle the "hold switch" of the integrator is closed with the Linac pulse. The "reset switch" (R) is opened synchronously and the signal from the detector integrated. At the end of the Linac pulse gate (6μs duration for the photomultiplier and 20μs duration for the photodiode), the "hold switch" is opened and the sample/hold amplifier starts to sample the integrator output. This "hold mode" continues for a period of 8μs.

An active low pass filter, connected in series with the sample/hold amplifier, transmits the integrated signal from the sample/hold amplifier to the ADC for data processing, but blocks switching transients. The ADC shown in figure 1 is a 16 bit device with MSB for the sign of the data. At present tests are being carried out with a superior replacement (type ADADC71JD) which has an internal clock and is gated and switched externally by time delayed pulses synchronised to the Linac pulse. Serial data from the ADC is transferred to the computer system by matched TTL circuits (26LS31) with complementary outputs and inputs. This arrangement ensures that external noise in the cables is averaged to zero.

Following conversion all switches are reset until the next Linac pulse (the Linac pulse repetition rate is 250Hz). The timing pulses for data acquisition are generated by a pulseforming circuit triggered by the Linac pulse. The timing sequence can be adjusted with the variable resistors shown in figure 1.

One of the most important features of this new signal processing system is that the integrator, sample/hold amplifier, filter and ADC for each detector are housed in a shielded enclosure with the detector on the CT scanner gantry. Only digital signals are transmitted from the Linac hall to the data acquisition computer system, thus minimising noise. A further reduction in noise is obtained by the fact that conversion of the analogue signal takes place between Linac pulses, minimising interference. Care must also be taken with the earthing arrangements for the detector and data acquisition system. This is especially the case with the Cerenkov detectors as these require an external HT supply for their photomultipliers.

Each detector has its own 2 MHz digital clock for transferring serial data to the micro-controller. The data transfer requires three different outputs: The Serial Clock Output (SCO), the Frame Synchronisation Output (FSO) and the Serial Data Output (SDO). The FSO and the SCO operate at 1/128 and 1/4, respectively, of the basic clock frequency.

The serial to parallel conversion of the data is performed by two conventional 8 bit converters (74LS595). Multiplexer units (74LS151) enable the data from each detector to be selected by an 8-bit microcontroller (80C145). Another logic unit, triggered by the FSO, the SCO and the microcontroller controls the correct sequence of picking up the data. The complete cycle of data transfer is synchronised to the Linac and the sample CNC via the micro-controller which is fed with timing signals from these two sources.

Finally a feedback system ensures accurate data transfer to the data acquisition computer. Taking into account the frequency of the SDO, the Linac pulses, the CNC pulses and the time required for data transfer and handshake it should be possible to connect up to 30 detectors to this new system.

C.3 First detector tests at BAM

The aims of the detector tests carried out in Phase 2 of the programme were to establish and optimise the performance of the detectors for CT measurements, primarily of HLW. Important features of the performance to be established were the linearity and dynamic range of the detectors under operating conditions expected in a CT scanner. A determination of the magnitude of beam hardening effects, which are directly related to the γ-ray energy threshold of the detectors is also valuable in assessing how such detectors will perform in actual CT measurements.

In order to establish these parameters the detectors were tested with the BAM CT scanner system. The first measurements were carried out at the beginning of March. For these measurements one additional water-based and one additional Aerogel-based prototype Cerenkov detector were constructed to act as reference detectors in the set-up shown schematically in figure 2.

The detector under test was placed behind a 0.8x6mm standard collimator and was shielded with lead. The second (reference) detector was placed in a similar lead

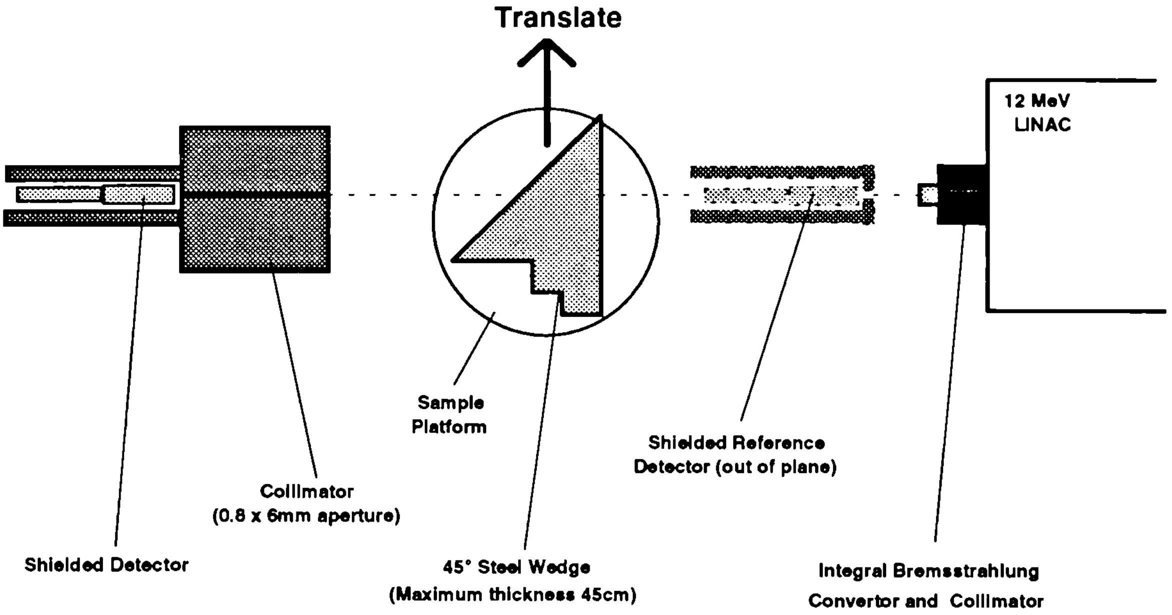


Figure 2: Schematic diagram of detector test configuration.

shield with a ~5x10mm aperture situated below the CT scanner plane. The detector signals were carried directly from the detectors via standard 50Ω coaxial cables to a digital storage oscilloscope outside the linac hall.

A specially fabricated steel wedge was placed on the CT scanner sample platform. Using the scanner sample control system the wedge could be moved as indicated in figure 2 so that the thickness of steel in the linac beam seen by the detector under test varied from 0 - 45 cm.

Clean pulses, faithfully reproducing the shape of the linac pulse, were observed for both types of detector. With minimal shielding (2cm of lead above and below the body of the detector and the photomultiplier) only signals originating from the collimated γ-ray beam were observed. With the collimator aperture closed, no signal from the detector could be observed above the level of noise. This level of shielding is significantly less than was required in tests on the Harwell linac. This is due to the significantly improved collimation of the bremsstrahlung beam from the BAM radiography linac.

Using the digital scope the stored detector pulses could be integrated to give the total detector response for each linac pulse. By varying the thickness of steel seen by the detector under test and normalising to the reference detector response to take account of variations in the linac output attenuation curves for steel were obtained for both water and Aerogel detectors and also for a photomultiplier tube decoupled from the Cerenkov medium. This last measurement was made by placing a light-tight foil between the photomultiplier and the Cerenkov medium.

The two most important features of the results obtained were the magnitude of the signal from the photomultiplier decoupled from the Cerenkov medium and the measured dynamic range of the two detector types. The significant contribution to the signal from the detectors that arises from the photomultiplier tube itself was observed in the detector tests carried out in Phase 1 of the programme, where it was shown that the signal derives almost exclusively from the photocathode region of the photomultiplier. Calculations using the electron/γ-ray transport code EGS4

[1], which was successfully used in Phase 1 of the programme to predict the Cerenkov light output of the detectors, suggest that the intrinsic response of the photomultiplier is dominated by Cerenkov light production in the 1.1 - 1.3mm thick borosilicate glass window in front of the photocathode. Due to the high refractive index (~1.5) of borosilicate glass the γ-ray energy threshold for the intrinsic response of the photomultiplier will be only 315keV. Any contributions from scintillation in the PMT glass window will have an even lower γ-ray energy threshold. In these well collimated and shielded tests the magnitude of the intrinsic response of the photomultiplier represented ~6% of the signal from the water detector and ~50% of the signal from the Aerogel detector. A signal of this magnitude would be unacceptable in the present application.

The dynamic range of the detectors measured in these tests was $\sim e^{5.5} \approx 250$ for the Aerogel detector and $>e^{7} \approx 1000$ for the water detector. The dynamic range of the water detector was already sufficient for CT measurements of HLW monoliths, which have attenuation factors of around 5 (factor of 150 attenuation), but the dynamic range of the Aerogel detector was barely adequate. However, the dynamic range in these measurements was primarily determined by the background noise generated in the long cable runs from the detectors to the digital storage oscilloscope, an effect that will not be present when the analogue signal processing stages of the data acquisition system are located on the CT scanner gantry with the detectors. This is important as the Aerogel detector, with its high γ-ray energy threshold of ~1.25MeV, is the favoured choice for the final detector array if a sufficient dynamic range can be achieved.

The differential of the attenuation curves represents the effective attenuation coefficient that would be derived from a CT measurement with these detectors as a function of thickness of steel. It is the variation in the effective attenuation coefficient with thickness that gives rise to the beam hardening artefacts in tomographic images. Examination of the attenuation curve for the water detector, which was least affected by the intrinsic response of the photomultiplier, clearly indicated a reduction in beam hardening effects in comparison with a previous measurement made at BAM with a $CdWO_4$ scintillation detector. It was expected that Aerogel detectors would show even greater improvement if they could be used.

C.4 Detector modifications

As described in section C.2 above, the results of tests at Harwell and BAM indicated a need to reduce the component of the detector signal resulting from the intrinsic response of the photomultipliers to γ-rays. One way to achieve this is to mount the photomultipliers so that the photocathode is not exposed to the direct collimated γ-ray beam by moving the photomultiplier from its original position directly behind the Cerenkov medium and providing some means of transporting the Cerenkov light to the new photocathode position. The simplest geometry which allows close packing of the modified detectors in a detector array is shown schematically in figure 3.

In this arrangement the photomultiplier is offset from its original position so that the direct collimated γ-ray beam, travelling along the central axis of the Cerenkov medium, does not strike any part of the photocathode. In the geometry adopted for the BAM CT system the optimum value for D is 25mm.

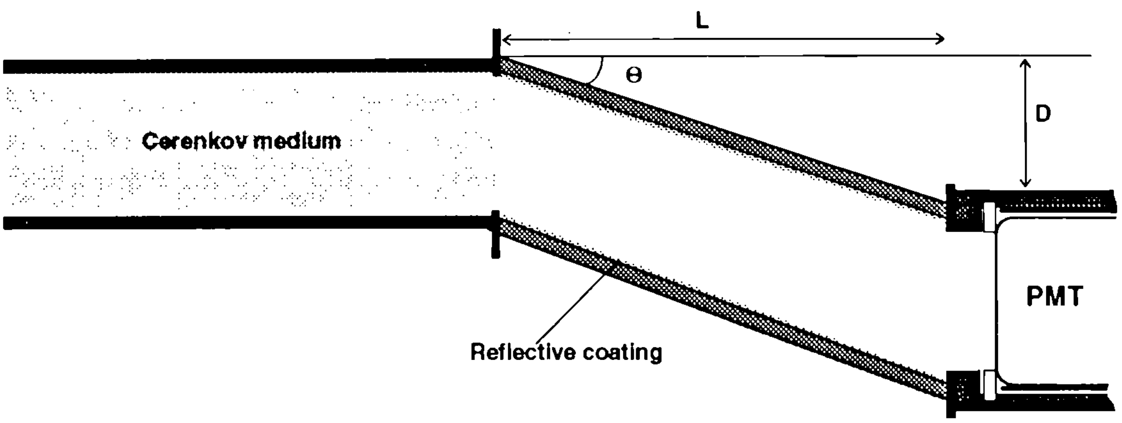


Figure 3: Schematic diagram of light guide from Cerenkov medium to photomultiplier. The photomultiplier offset D and the guide angle Θ determine the length of the guide L. In the case of the water detector the Cerenkov medium would fill the guide as well as the detector housing.

In order to select a value for the guide angle Θ (or equivalently the length L) calculations were carried out to estimate the light collection efficiency of both cylindrical and square section guides as a function of Θ for various values of the coefficient of reflection of the walls of the light guide. The end face of the Cerenkov medium was assumed to be a uniform and isotropic source of light emitting into a solid angle of 2π. Light was tracked using the 3D photon tracking routines from the Monte-Carlo code EGS4, with the loss on each reflection determined by the reflectivity of the walls and the angle of incidence of the light.
Various sizes of light guide were investigated and in all cases cylindrical guides performed better than square section guides. In the present case the choice of guide angle was a compromise between light collection efficiency and length of guide. Too long a guide would be impractical, particularly with regard to shielding. A guide angle of 0.3 radians was selected, resulting in a guide length of ~80mm.
The guides were electroplated on their inner surface with chromium. This has excellent reflection properties for blue light and is resistant to corrosion. This latter property is especially important in the case of the water detector as the water is in contact with the reflective coating. The inner surface of the water detector housing was also chromium-plated to improve light collection in this part of the detector.

C.5 Further detector tests at BAM

Following modifications of the detectors as outlined in section C3 above and production of prototype analogue signal processing modules for the data acquisition system, further tests were carried out at BAM during the last quarter of 1993. These tests utilised the BAM CT scanner in the same configuration as described in section C2 (see figure 2). In these tests, however, the use of the computer controlled data acquisition system enabled detailed scans of the steel wedge to be carried out under CNC control and tomographic measurements to be made of test samples. Unfortunately serious faults with the BAM linac have hampered completion of these tests.

Initial examination of the detector response indicated that, taking into account the fact that there was no longer any contribution to the signal from the photomultiplier, there had been a reduction in the detector output corresponding to a light guide collection efficiency of ~30%. This is a somewhat lower figure than had been expected. Further investigations of the surface treatment of the light guide are being carried out at present to see if its efficiency can be improved by improving the quality of the chromium-plating or by using polished steel or aluminium as the reflector. Tests of the light collection efficiency will be carried out off-line using a blue LED as the light source.

The following measurements were scheduled for the second series of tests, using the detectors with the BAM CT scanner:

i. One dimensional scan of steel wedge for Aerogel and Water Cerenkov detectors and for $CdWO_4$ scintillation detector.
ii. Tomographic measurements of small (~100mm ∅) cylinders of steel, glass and concrete.
iii. Demonstration tomographic measurement of simulated HLW glass monolith supplied by CEA/CEN Valrho (in connection with CEC contract FI2W-023). This test sample has the same outer dimensions as a commonly used high active waste cylinder and is filled with simulated waste glass. This test object has glass of various densities and a variable steel slit system embedded in it to enable density and spatial resolution of the tomographic images to be assessed.

The results of the first scans of the steel wedge are shown in figure 4. These results indicate a dynamic range of $\sim e^7 \approx 1100$ for both detectors, quite adequate for the present applications. Given the higher γ-ray energy threshold of the Aerogel detector these measurements suggest that this would be the best choice for the final detector array. However, the fact that the observed dynamic range of the two detectors is the same indicates that the limitation is the detector signal processing electronics and not the detector characteristics. Further improvements in the detector electronics to overcome this problem were made but a second set of measurements with the Cerenkov and $CdWO_4$ detectors could not be carried out due to the faults with the linac. However, a substantial reduction in beam hardening obtained with the Cerenkov detectors can already be seen in figure 5 which shows the effective attenuation coefficient as a function of thickness, determined from the differential of the first part of the attenuation curves in figure 4, compared with previous measurements made at BAM using the $CdWO_4$ scintillation detectors [2].

Finally figure 6 shows a tomogram of the simulated HLW glass block obtained with the Aerogel detector. Embedded pieces of glass with different densities are clearly shown as are various steel components related to the slit system (the slits themselves are not visible in this particular cross-section of the block). The striations across the whole image at various points are artefacts resulting from an intermittent fault on the BAM linac during the measurement and are not associated with the detector system. This measurement clearly demonstrates the practicality of making tomographic images of such objects with the Aerogel Cerenkov detector system. The detailed performance of the detector system in such measurements and their comparison with conventional scintillation detectors must await Phase 3 of the present program.

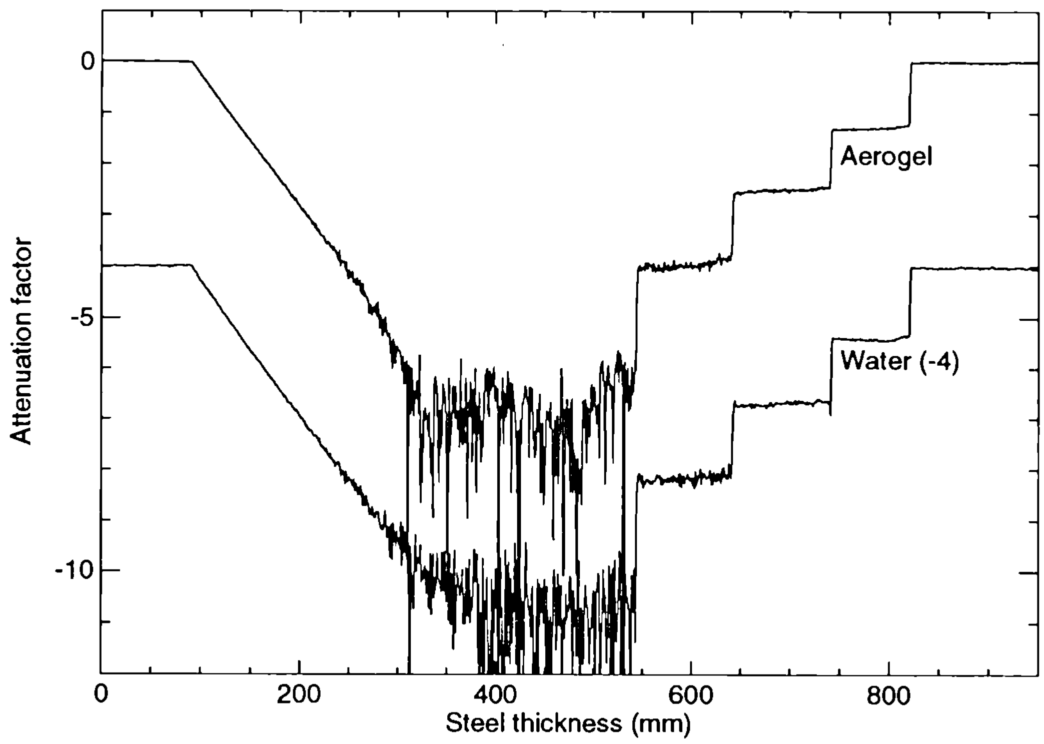


Figure 4: Attenuation factor as a function of position for scan across steel wedge using Aerogel and water Cerenkov detectors.

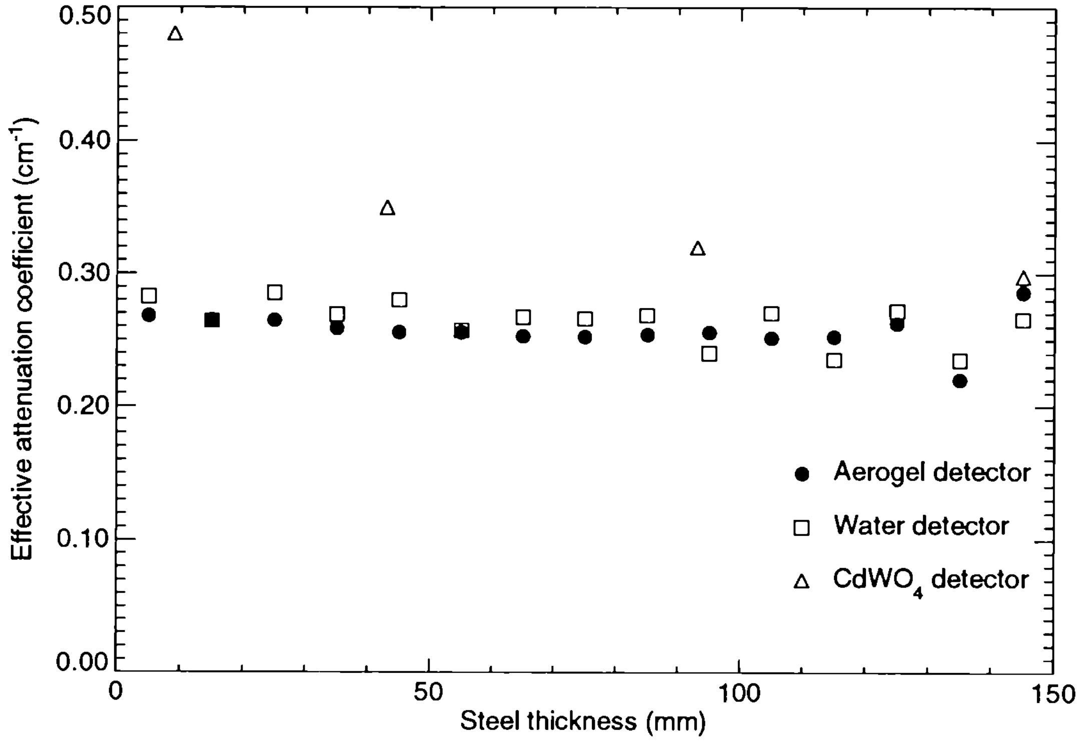


Figure 5: Effective attenuation coefficient of steel as a function of thickness derived from the first portion of the attenuation curves above, compared with previous measurements using $CdWO_4$ scintillation detectors [2].

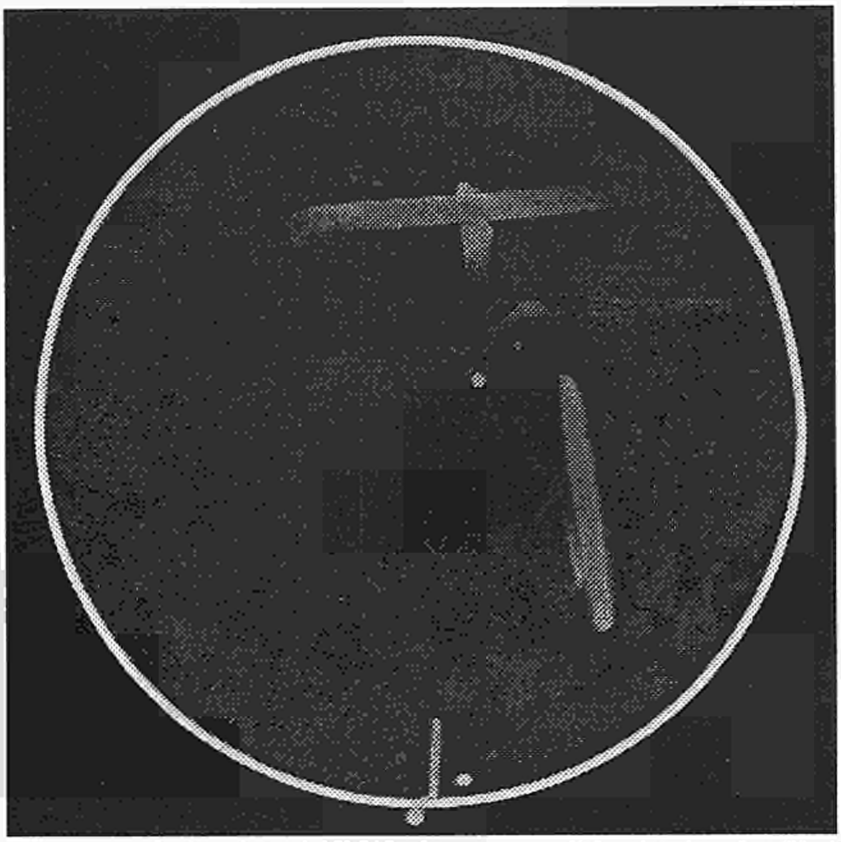


Figure 6: Tomogram of simulated HLW glass monolith obtained with the prototype Aerogel detector

C.4 Future Work

Although the final decision must await the completion of the second series of tests at BAM, it seems most likely that the Aerogel detector offers the best performance in the present application. Following modifications to the design of the detector housing to improve the light collection efficiency, 10 detectors (9 collimated detectors and one reference detector) will be assembled and tested together with ten channels of the data acquisition system and 9 of the new BAM collimators (described in last years report).

Once commissioned the system will be used to make detailed measurements of the simulated HLW glass monolith. The discrimination of the detector system against background radiation will be determined using a 2Ci ^{192}Ir and a 55Ci ^{60}Co source together with a high intensity X-ray tube. To simulate the high levels of radioactivity expected in HLW, the sources will be inserted into the glass block and/or placed close to the detector collimator system.

These measurements will be compared with measurements made with conventional $CdWO_4$ scintillation detectors

References

[1] W.R.Nelson, H.Hirayama and D.W.O.Rogers. Stanford Linear Accelerator Centre Report SLAC-265, UC-32 (1985).

[2] P.Reimers "Quality Assurance of Radioactive Waste Packages by Computerized Tomography". Final Report to CEC. Contract FI 1W - 0037/ FI 1W-0193 (1990).

Part A

Task 4

"Disposal of radioactive waste: Research to back up the development of underground repositories"

* List of contracts
* Introduction to Task 4

Topic 1	Research related to sites and their characterisation
Topic 2	Research on gas flow
Topic 3	Radionuclide migration in the geosphere
Topic 4	Modelling in the presence of uncertainty and management of data in non-homogeneous systems

TASK 4 - LIST OF CONTRACTS

Topic 1 Research related to sites and their characterisation

FI2W-CT90-0046	Simulation of the effect of long-term climatic change on groundwater flow and safety of geological disposal sites
FI2W-CT90-0049	Experiment of groundwater flow in a fracture for the validation of chemistry/hydromechanical transport coupled models for fractured media
FI2W-CT90-0050	Experiments in 600m borehole in the Asse II salt mine
FI2W-CT90-0051	Evaluation of a self-consistent approach to fractured crystalline rock characterisation
FI2W-CT91-0063	INTERCLAY II - A coordinated benchmark exercise on the rheology of clays
FI2W-CT91-0072	Methodology studies on sealing of boreholes
FI2W-CT91-0075	Paleoclimatological revision of climate evolution and environment in western mediterranean region
FI2W-CT91-0078	Water flow and solute convection through fractured rock
FI2W-CT91-0092	Geochemical validation of solute residence times: review and comparison for various geological environments
FI2W-CT91-0111	Decovalex Project: modelling of THM behaviour for fractured rock
FI2W-CT91-0113	Decovalex Project: modelling of THM behaviour for fractured rocks
FI2W-CT91-0115	Underground laboratory at Tournemire: groundwater flow tests in clayish material

Topic 2 Research on gas flow

FI2W-CT90-0048	Development of HLW-borehole sealing

TASK 4 - LIST OF CONTRACTS

FI2W-CT91-0064	The refinement of soil gas analysis as a geological investigative technique
FI2W-CT91-0076	MEGAS: modelling and experiments on gas migration in repository host rocks
FI2W-CT91-0093	Gas pressure build-up in radioactive waste disposal : hydraulic and mechanical effects
FI2W-CT91-0101	In-situ test on the permeability of salt for gas and brine

Topic 3 Radionuclide migration in the geosphere

FI2W-CT90-0039	Continuation of the migration experiments (laboratory and in-situ)
FI2W-CT90-0065	CHEMVAL-2. A coordinated research initiative for evaluating and enhancing chemical models used in radiological risk assessment
FI2W-CT91-0071	OKLO-Natural analogue for transport processes in a geological repository
FI2W--CT91-0079	Development of a model for radionuclide transport by colloids in the geosphere
FI2W-CT91-0080	Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment(El Berrocal)
FI2W-CT91-0081	Fundamental studies on the interaction of humic materials
FI2W-CT91-0082	Rock matrix diffusion as a mechanism for radionuclide retardation: natural radioelement migration in relation to the microfractrography and petrophysics of fractured crystalline rock
FI2W-CT91-0083	Effects of humic substances on the migration of radionuclides: complexation of actinides with humic substances in natural aquatic systems
FI2W-CT91-0084	Colloid migration in groundwaters: geochemical interactions of radionuclides with natural colloids
FI2W-CT91-0085	The role of colloids in the migration of radioelements

TASK 4 - LIST OF CONTRACTS

FI2W-CT91-0097	The role of colloids in the transport of radionuclides in geological media
FI2W-CT92-0121	Analysis of the geo-environmental conditions as morphological evolution factors of the sand clay series of Tiber basin and the Dunarobba fossil forest
FI2W-CT92-0122	CHEMVAL 2: Thermodynamic database

Topic 4 Modelling in the presence of uncertainty and management of data in non homogenous systems

FI2W-CT91-0088	The treatment of uncertainty in groundwater flow and solute transport modelling
FI2W-CT91-0089	Uncertainties in the modelling of migration
FI2W-CT91-0090	Unbiased guess, a concept to cope with fuzzy and random parameters
FI2W-CT91-0091	Review and development of methodologies for modelling with uncertainty and variability

INTRODUCTION TO TASK 4 - DISPOSAL OF RADIOACTIVE WASTE: RESEARCH TO BACK UP THE DEVELOPMENT OF UNDERGROUND REPOSITORIES

A. Objectives

The overall aim of Task 4 is to provide the theorical and experimental basis as well as data bases, concepts and/or models for understanding and testing the behaviour of potential host rocks (sedimentary, crystalline rocks, and evaporites) as natural isolation barriers in order to contribute to safety assessment of radioactive waste repositories in deep geological structures. The evaluation of the feasibility and safety of some design aspects of the construction and operation of underground repositories in different rock formations (clay, salt and granite) is also an objective of this work.

B. Research performed under the programme 1985-1989

The research areas covered were:

- development of measuring techniques for the detection and characterisation of fractures and faults in indurated clays;
- laboratory and in-situ tests to study the rheological behaviour of various host rocks, and benchmark exercises on the verification and partly "validation" of calculation tools for salt (project COSA) and clay (project INTERCLAY pilot phase);
- assessment of mechanical performance of metal containers (project COMPAS);
- mock-up and in-situ tests for emplacement and characterisation of candidate buffer and backfilling materials;
- radionuclide migration in the geosphere (project MIRAGE) including subprojects such as on the role of organic compounds, complexes and colloids (CoCo activities), on geochemical benchmark codes including the development of the thermodynamic database (CHEMVAL), and Natural Analogue studies (Natural Analogue Working Group, NAWG);
- study of the applicability of the fuzzy set theory for taking account of uncertainties in model parameters.

C. The present programme 1990-1994

The work to be carried out is subdivided into four topics:

Topic 1 : Research related to sites and their characterisation

This topic mainly deals with the calibration and intercomparison of adequate techniques for assuring relevant properties of groundwater chemistry and groundwater flow in fractured rock on selected reference sites, whereby investigations are undertaken

- in the underground laboratory at Tournemire (F) to evaluate the water flow through impermeable argillaceous formation by geological, hydrogeological and geotechnical investigations.

- at the Sellafield site (UK) to describe water flow and solute transport through fractured rock at the site and assess the feasibility of obtaining fracture flow data by suitable methods.

Studies are also carried out concerning:

- Rheology of clay, granite and salt, (i) to improve the understanding of large-scale rock mass behaviour through adequate laboratory or in-situ tests, (ii) to develop and test suitable calculation tools and (iii) to predict their material behaviour. Benchmark exercises are undertaken within the project INTERCLAY (rheology of clay) and the project DECOVALEX (on the thermo-hydro-mechanical properties of fractured crystalline rock)
- Geoforecasting studies to predict future climate changes and simulation of effects of climate change on groundwater flow conditions in the Netherlands during the last 500.000 years as well as Paleoclimatological revision during the last 2 million years in the Western Mediterranean regions.

Topic 2 : Research on gas flow

Various research efforts in the field of gas generation, gas release and migration through host (in particular clay and salt) were grouped together in a coordinated project PEGASUS (Project on the Effects of GAS in Underground Storage facilities for radioactive waste).

Topic 3 : Radionuclide migration in the geosphere

Research under this topic concentrates on international projects and subprojects already started in the 3rd programme like:

- studies of the role of colloids, organic substances and complexes (CoCo activities)
- migration experiments in clay and fractured crystalline rocks
- Natural Analogues: study of migration processes for the understanding of long-term behaviour of geological isolation systems (Oklo study, El Berrocal study and Dunarobba study)
- geochemical modelling of radionuclide migration and extension of the thermodynamic data base for use in transport models (CHEMVAL)

Topic 4 : Modelling in the presence of uncertainties and management of data in non-homogeneous systems

The overall objective of this topic is to study alternative methodologies and concepts for the modelling and handling of data in the presence of uncertainty in radionuclide transport modelling, whereas advanced studies are focused on:

- investigation of methodologies of the treatment of uncertainty with reference to modelling studies (e.g. fuzzy sets, expert judgement, information theory, etc.)
- treatment of uncertainties in radionuclide transport modelling
- methods of handling non-homogeneities (e.g. dispersion) at different scales in transport models.

Title : Simulation of the effects of long term climatic change on groundwater flow and the safety of geological disposal sites

Contractor : University of Edinburgh, Rijksinstituut voor Volksgezondheid en Milieuhygiene (RIVM), Rijks Geologische Dienst (RGD), Université de Paris-Sud, Université de Louvain-la-Neuve
Contract N° : FI2W-CT90-0046
Duration of contract : March 91 - August 94
Period covered : 1993
Project leader : G.S. Boulton (University of Edinburgh - Coordinator),
T. Leijnse (RIVM), E.F.M. de Mulder (RGD),
C. Martin (Université de Paris-Sud), A. Berger (Louvain-la-Neuve)

A. OBJECTIVES AND SCOPE

The project seeks to evaluate the role of climate change in controlling the flux of groundwater through zones which might be chosen as locations for deep disposal of radioactive waste, and to estimate potential future fluxes and their impacts in the area of the Netherlands and adjacent regions. The scope of the programme was as follows:

i) Development of a generic large-scale model of subglacial groundwater flow. This comprised an ice sheet model driven by a climate function related to Milankovitch insolation fluctuations; a sub-model designed to estimate the flux of meltwater across the ice/bed interface; determination of effective pressure fields in subglacial bedrock; a time dependent groundwater flow model.
ii) A geological model of the hydrology of the Netherlands and appropriate adjacent areas. This was to include palaeoclimatic and palaeoenvironmental reconstructions for the region.
iii) Application of the model to a transect running through the Netherlands. The model was to be applied to situations along the transect where tests of the model can be made using geochemical, geotechnical and other approaches.
iv) Development of a local sub-model to investigate the consequences of subglacial groundwater flow to subrosion of salt-domes. This was to include an evaluation of future subrosion.

B WORK PROGRAMME

i) Development of the ice sheet model. (Completed).
ii) Development of the subglacial groundwater flow model. (Completed).
iii) Testing the groundwater flow model. (Almost completed).
iv) Development of a subrosion model. (Completed).
v) Testing the subrosion model. (Under way).
vi) Hydrogeological model construction. (Completed).
vii) Reconstruction of patterns of past climatic change and extrapolation of future change as the climate drive for the glacier/groundwater models. (Completed).
viii) Simulation of past subglacial groundwater flow and its impacts. (Completed).
ix) Prediction of future subglacial groundwater fluxes. (Nearing completion).

C. PROGRESS OF WORK AND RESULTS OBTAINED

1.0 State of advancement.

The programme has been a great success so far. The programme is on schedule. All that was anticipated in the original proposal has been achieved, and a number of important results have been achieved which were not foreseen. The programme has yielded some fundamental scientific advances and important insights in the field of radioactive waste disposal. Some highlights of the last year's work are:

- Demonstration from the Muhlenrade borehole that isotopic profiles in aquitards do contain a record of recharge under varying climatic conditions.
- Validation of the model of subglacial melting model output and natural calibration of the melting rate using eskers as the (unexpected) means of validation.
- Demonstration of the power of our subglacial groundwater flow model in explaining features of European Geology such as the origin and locations of push moraines, the origin of species of hummocky moraine, the origin and location of liquifaction, loading and fracture structures.
- Demonstration, using the vertically-integrated groundwater flow model, of the varying geometry of areal groundwater flow directions and its potential to explain groundwater geochemical anomalies.
- Demonstration, using the subrosion model of the development of saline convection cells derived from salt diapirs, and their relation to climatic driving forces.

The results reported below reflect the work of G.S.Boulton, M.Broadgate, P.E.Caban, N.Dalgleish (Edinburgh); T. Leijnse, F. van Weert (RIVM); K.van Gijssel (RGD); C.Marlin, P.Ginidis (Paris-sud); M-F.Loutre, A.Dutrieux (Louvain la Neuve).

2.0 Progress and results

2.1 The past and future climate drive

The characterisation of past climate and the extrapolation of future climate are required to provide a drive for the subglacial groundwater model and to determine environmental boundary conditions (e.g. the presence/absence of permafrost).

a) Statistical Characterisation of Past and Future Climate Change.

The first aim of this work has been to model the relationships between long global climate records, shorter local records, and the orbital and insolation variations (Milankovitch cycles). We are then able to extrapolate the shorter records backwards (further into the past) and forwards (into the future).

Complex Demodulation is a statistical technique for extracting the changing amplitude and phase of the periods in data. Simultaneous analysis of the SPECMAP global record and the insolation record reveals coincident features which validate the technique of using orbital variations to force our predictions.

Linear Modelling has shown that it is possible to grasp the features of climate change, in particular the turning points. However, a linear model will never completely simulate the scale of changes and thus we have had to look at more advanced non-linear modelling techniques.

Non-linear Transformation Regression represents recent statistical methods which enable us to transform the regression variables and the response variable to give optimum correlation. By using the Milankovitch variables it has proved possible to model the SPECMAP curve very well, including the large scale glacial terminations (figure 1). Similar results for the shorter French pollen data show that we can now model the data we have and produce realistic future predictions and backwards extrapolations .

b) Stratigraphical data from Europe.

The statistically generated climates need to be correlated with stratigraphical evidence from Europe in order to be able to produce dated palaeoenvironmental bounary conditions for models which are compatible with the climate drive. Figure 2 shows a final version of the time/space diagram, which correlates the stratigraphical data from the model area for the period between the Holsteinian and the Holocene interglacials, aligned along the supraregional transect. These local, land-based data are compared with the continuous marine oxygen isotope stratigraphy to provide an absolute chronostratographic framework for palaeoenvironmental reconstructions. The sequence will be a basis for comparison with the hind-cast predictions of the Edinburgh-Group.

c) The potential impact of anthropogenic CO2 variations over the 5 kyr A.P.

The project has hitherto been exclusively concerned with the past and with "natural" futures, in which human impact on climate has been explicitly excluded. This has permitted us to evaluate a "baseline case". We now feel it appropriate to begin consideration of the impact of human impacts on possible futures. The approach of statistical extrapolation described above, cannot be used to evaluate a future for which there is no precedence. We have therefore begun to examine the impact of human-induced greenhouse scenarios.

A sectorially averaged 2D-LLN Northern Hemisphere climate model coupled to an ice-sheet/bedrock model has been used to test the sensitivity of the climate system to CO2 variations over the 5 kyr A.P. (Loutre, 1994).

Simulations of the climate system response to the future insolation and to different scenarios of atmospheric CO2 concentration indicate a global Northern Hemispheric warming related to the CO2 concentration increase.

This warming is more important in the highest latitudes because of a great albedo/temperature feedback. Moreover the consequence of an increase of CO2 concentration to the double of its present day value is the melting of the Greenland Ice-Sheet even if this high CO2 concentration (710 ppmv) is not maintained over all the time interval of the simulation. Nevertheless the melting is delayed when CO2 concentration is brought back to its present day value (350 ppmv).

Even if the hypothesis about future CO2 concentration may be questionable and even if the climate model used does not represent all the processes and feedbacks intervening in the climate system these experiments put forward the potential risks for the human society with respect to global warming and Greenland Ice-Sheet melting.

Given these primary results. new CO2 concentration scenarios for the future must be elaborated in order to get boundary estimates of the long term future climate variations.

2.2 Groundwater Modelling

Two principal models have been completed in this year. They are: a two-dimensional model along a transect from the core area of the European ice sheet to northern Belgium, which is designed to examine vertical and longitudinal changes in groundwater flow and time-dependent changes; a vertically-integrated model designed to examine areal patterns of groundwater flow under different environmental and climatic conditions. It was not originally envisaged that a vertically integrated model would be developed. It has added considerably to our understanding.

a) The transect model

The 'ice-sheet head limited' groundwater model described in previous reports has been further extended to consider the role of the permafrost distribution associated with the ice-sheet margin on the nature of groundwater flow. In particular, the hypothesis that the presence of permafrost will radically alter the nature of the subglacial material properties through the presence of very low effective pressures in pore waters has been examined.

Permafrost thicknesses and extents have been predicted by the ice-sheet model. Following the work of the RIVM in previous reports, permafrost has been incorporated into the groundwater flow model as a no-flow boundary condition, rather than as regions of zero conductivity. This assumption would break down were the maximum thickness of permafrost penetration (<150 m) to be greater than the thickness of the upper aquifer: the permafrost zone would 'pinch out' the upper aquifer, and hence completely inhibit flow in the upper aquifer, and drive water through the clay aquitard. This only occurs where the aquifer thins towards the south-eastern end of the transect, however; here the pinching out of the aquifer occurs naturally as part of the geology of the transect.

There are two major rivers that cross the transect, the Rhine and the Elbe. These rivers would both melt holes in the permafrost, allowing groundwater to escape (if hydraulically feasible). The Elbe has been assumed to have been dammed as the ice-sheet advances over its course; the Rhine, draining a much larger area, is much more likely to have persisted through time. As the ice-sheet advances over the course of the Rhine, its course is assumed to have been diverted in front of the ice-sheet margin. In both cases, permafrost holes have been included in the model as a one-element wide hole of zero head.

Figure 3 presents effective pressures and groundwater trajectories for span c1, melt model 3: an intermediate melt rate model at close to the glacial maximum. The presence of permafrost causes a region of negative effective pressure beneath and just to the front of the ice-sheet margin. This feature is present at the same location relative to the ice-sheet through all time, except for the periods where the ice-sheet margin is just above the zero datum - the boundary between the Scandinavin bedrock and Dutch/German basin sections of the transect. This has glacio-tectonic effects, for example the low effective pressure in the material at the glacier margin is likely to be highly deformable; this could be transported to form push morraines. The region of zero effective pressure beneath the ice-sheet is also likely to indicate the region of tunnel (esker) formation. The concentration of flow within the small holes caused by the Rhine (and to a lesser extent the Elbe) may also lead to glacio-tectonic phenomena - for example deformation structures due to the highly localised expulsion of water.

b) The vertically integrated groundwater model

The vertically integrated model computes the geohydrological response of the west european aquifer system to various paleogeographical situations comprising the advancing and retreating of the Saalian glacier.

The geohydrological model consists of a good permeable upper aquifer separated from a lower aquifer (permeability is about two orders in magnitude less then in the upper aquifer) by a thick clayey aquitard. In this model the flow is assumed to be horizontal in the aquifers and vertical in the aquitard There is an interaction between the groundwater system and the surface water system comprising seas, lakes and rivers. When the hydraulic head in the aquifer beneath such a body of water exceeds the water level within the body, groundwater will drain out of the groundwater system. When this head is less, surface water will infiltrate into the groundwater system. The infiltration of the subglacial meltwater is dependent on the hydraulic head in the aquifers. Meltwater will infiltrate when the hydraulic head in the aquifer beneath the icesheet is less then the surface elevation. The meltwater will flow out of the aquifer when the heads exceed this elevation. This relationship prevents the hydraulic head exceeding the surface elevation of the icesheet causing an incorrect physical situation. A number of six different paleogeographical situations with various spatial distributions of icesheet, seas, lakes, river patterns and zones of permafrost have been simulated. These are the paleogeographical situations such as are thought to have existed at the times of 156, 152, 147 and 140 thousand years before present during the Saalian glacial period.

The general observations of the hydrogeological responses are as follows:

* The hydraulic heads beneath the ice sheet seem to follow the icesheet surface elevation. In most zones the heads are even much less than the elevation implying that most of the subglacial groundwater can be dissipitated easily. Groundwater heads in the lower aquifer are higher than in the upper aquifer (the difference is about 100 meters).

* The hydraulic gradients are large in these situations. On one side the heads are being kept extremely low by the relatively low sea levels (minus 100 meters) and on the other side they are kept high by the glaciers. Due to these large gradients high groundwater velocities develop, especially in zones where the upper aquifer is pinching out (these velocities go up to 400 m per year).

* In most subglacial areas the total amount of meltwater is able to infiltrate in the aquifer system. Partial infiltation of the meltwater or even outgoing flux of meltwater appear in areas of

very low transmissivity, in areas where the aquitard is outcropping and in areas where there is convergent groundwater flow when the British and Scandinavian icesheet lobes are colliding.
* Seas, lakes and rivers are the most controlling drainage possibilities for the groundwater (approximately 90 % of the outgoing water.

Figure 4 shows the groundwater flow vectors (velocities in m/yr) for 147ka.

2.3 The subrosion model and calculation of subrosion rates

Subrosion rates have been calculated for a salt dome structure in the lower part of the aquifer system. Simulations were carried out in a vertical cross section, 40 km wide. Figure 5 shows the geometry of the model domain with the position of the clay layer and the deep salt dome structure indicated. The thickness of the system is approximately 4 km. The salt dome is part of the modelled domain, but the permeability is set to zero, such that it does not contribute to the flow and transport in the system. Boundary conditions at the side- and top-boundaries were obtained by interpolation from the results of the large transect model run by the Edinburgh group.

The subrosion model used in the simulations grossly overestimates the subrosion rates. The salt concentration on the surface of the salt dome boundary was prescribed at the maximum (saturated brine) value. From the salt mass balance equation, the total amount of salt that has to dissolve to maintain the salt concentration on the salt dome boundary can be calculated. From the rock salt density and the area of the salt dome surface, the subrosion rate (mm/yr) can be obtained. Initial conditions for all simulations were fresh water in the system. As a consequence, the subrosion rates in the early stages of the simulations will be very high.

Six different simulations have been carried out so far: for three different basal melting rates and for two different glacier positions. Subrosion rates for the six different situations turned out to be identical, decresing to less than 1 mm/yr after a period of 23,000 years and stiil decreasing. Figure 5 shows the salt concentration distribution in the system after 10,000 years. Analysis of the velocity field in the lower aquifer showed that the average velocity induced by the boundary conditions is at least one order of magnitude lower than the velocity induced by the influx of salt at the salt dome boundary and the resulting density gradients. This would explain the fact that the subrosion rates are identical for all scenarios.

In the next period, the same type of calculations will be carried out for a shallow salt dome that pierces the Tertiary clay. From an analysis of the velocity in the upper aquifer it can be expected that for the shallow salt dome the subrosion rates will be much more dependent on the boundary conditions.

2.4 Model Testing

Testing of models during the last year has concentrated on three issues:

a) Eskers along the line of the transect.

Parameter studies on the ice sheet model have suggested a range of possible basal melting rates, from 0 to 85mm per year maximum. This melt represents water which will be injected into groundwater. Long-established glaciological theory suggests that any water flowing at the ice/bed interface will tend to be discharged in subglacial tunnels, and that such tunnels will leave eskers on glacier retreat.

Where however an ice sheet flows from a low to a high transmissivity bedrock sequence, meltwater which has hitherto been forced to flow at the ice/rock interface because of low bedrock transmissivity, will be able to drain entirely through the bed. As a consequence, no tunnels and no eskers will form in this zone. The transmissivity of the bed at the point where eskers disappear will be a measure of subglacial meltwater discharge and therefore of melting rate. Moreover this transission would be suppressed if significant surface melt were to reach the bed.

This work therefore permits us to estimate the basal melt from the last European ice sheet and therefore the meltwater available to recharge groundwater. We conclude that maximum melting rates were about 30mm per year.

b) Geochemistry of the Muhlenrade borehole.

The Muhlenrade borehole was drilled from the internal resources of the group provided by RGD. Its objective was to establish whether the 100m thick Tertiary clays, sandwiched between sand formations which we believe to have carried geochemically-distinctive glacial meltwaters, have retained that distinctive signature. Laboratory analyses were undertaken as follows:

- oxygen isotopes on porewater
- deuterium on porewater
- mineralogy from X-ray diffractometry
- measurements of water loss with temperature
- electical conductivity in lixiviation experiments

The results (Table 1) show apparent diffusion profiles through the clays from isotopically light water in the middle to isotopically heavier water at the margins and in the adjacent sands. The isotopic results plot on the meteoric water line, and indicate that there has been no secondary process, such as evaporation, at work. The results are consistent with a general climatic warming since deglaciation.

The final part of the analysis will consist of extraction of the remaining porewater with liquid nitrogen, and lixiviation of all samples for Bromine/chlorine and Lithium/sodium ratios.

c) Salinity distribution in the lower aquifer (Mesozoic) in the Netherlands.

The distribution of salinity within the upper and lower aquifers in the Netherlands is currently being investigated as test for the subrosion model.

2.5 Geological data aquisition and management.

a) Geological boundary conditions for the subrosion model.

The geometry of a selected salt diapir in the northeastern part of the Netherlands, and its overburden, has been incorporated into the supra-regional transect for subrosion modelling by the RIVM-group. Two situations have been considered: one with the top of the salt structure piercing through the aquitard of the Tertiary clay layers and one with a salt structure below this aquitard.

b) Geological setting for the Muhlenrade test-borehole.

The regional geology and groundwater patterns of the area surrounding the Muhlenrade test-borehole, drilled in 1993, has been investigated and prepared for publication together with the results of the geochemical analysis of the clay porewaters (Paris-Group).

c) GIS development. .

A solid framework for the efficient storage and manipulation of the geological data has been developed for the glacial geomorphological and sea level data sets for the development of past reconstructions. The value of a good data model providing an efficient database with reliable data cannot be underestimated, and, although the time and effort inolved in such a development is huge, once in place it supports any future project requiring such data, aswell as the provision of reliable data for the current project. Within this framework procedures for data input, manipulation and output have been established and software has been developed for implementation of these procedures and also for investigatory analysis.

3.0 List of Publications and Presentations

3.1 Refereed papers:

BOULTON, G.S., PUNKARI,M., CABAN,P.E., and WALLROTH,T. (in press) Eskers, subglacial groundwater flow and deduction of subglacial melting rates and water discharges from former ice sheets. Journal of Glaciology

BOULTON, G.S., SLOT, A.F.M., BLESSING, G., GLASBERGEN, P., LEIJNSE, T. and VAN GIJSSEL, K. 1993. Deep circulation of groundwater in overpressured subglacial aquifers and its geological consequences. Quaternary Science Reviews, 12, 1-7.

BOULTON, G.S. and DOBBIE, K. 1993. Consolidation of sediments by glaciers: relations between sediment geotechnics, soft-bed glacier dynamics and subglacial groundwater flow. Journal of Glaciology.

BOULTON, G.S. and PAYNE, A. 1993. Simulation of the European ice sheet through the last glacial cycle and prediction of future glaciation. Technical Report 93-14. Svensk Karnbranslehantering AB, 1-38.

3.2 Oral Presentations

International Geological Congress (Kyoto) - Predicting the future of geological sites for deep disposal of radioactive waste.

International Union for Quaternary Research (Beijing) - Extrapolation of future from past global change in the context of radiactive waste disposal.

International Geomorphological Congress (Canada) - Validating models of ice sheet dynamics.

Several presentations at Universities and research institutes on issues related to the programme.

4.0 Figure and Table Captions

Figure 1 Modelled climate over the last 200ka derived from non-linear analysis of the Milankovitch insolation curve. The solid line shows the statistically reconstructed SPECMAP curve and the dotted line the actual SPECMAP curve. This excellent fit gives us confidence in our hindcasts and forecasts of climate based on Milankovitch.

Figure 2. Time/space diagram showing the stratigraphic correlations between late-Quaternary stratigraphic elements in Europe, compared to the SPECMAP curve.

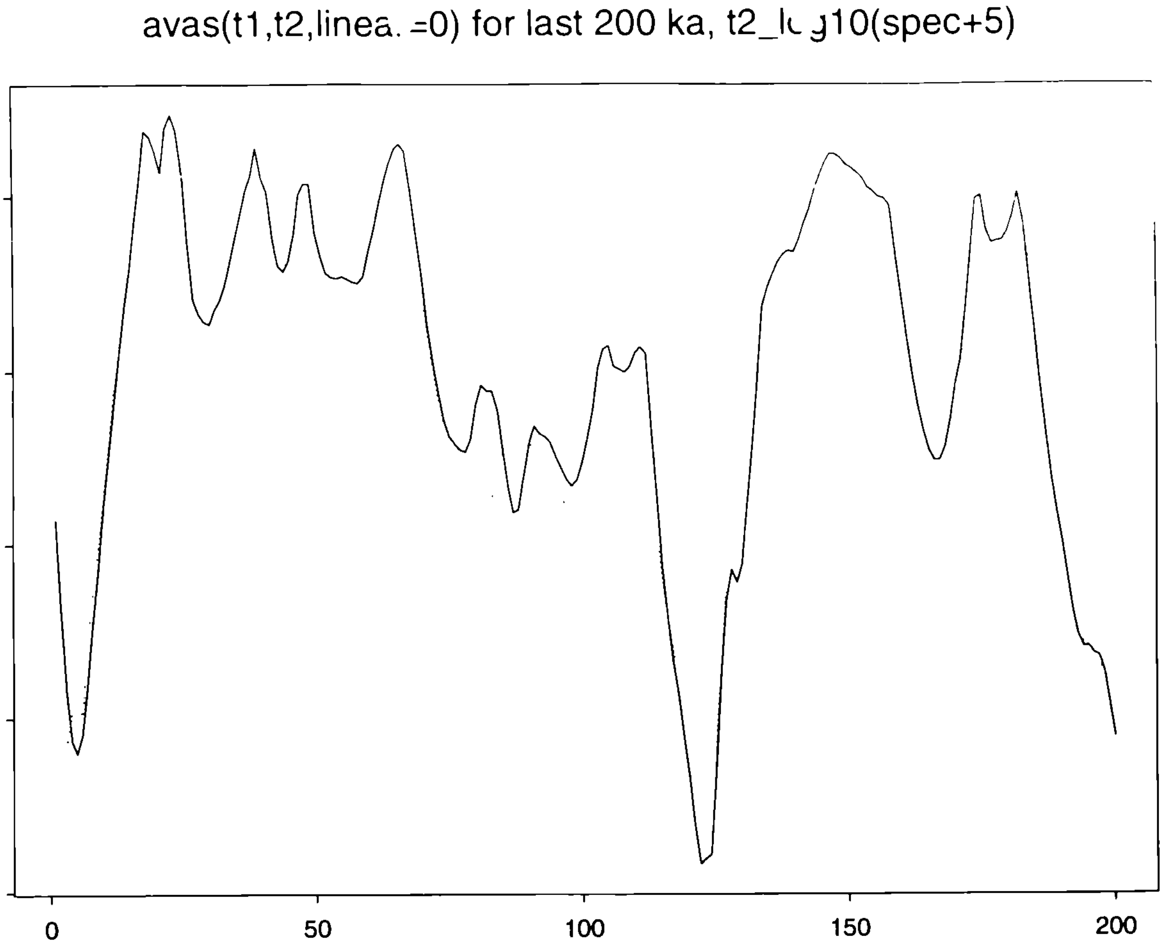
Figure 3. Effective pressures and groundwater trajectories for span c1 and melt model 3 along the transect.

Figure 4 Groundwater flow vectors in the upper aquifer, computed using the vertically integrated model for 147ka.

Figure 5. Salt concentration distribution in the lower aquifer after 10,000 years of model run predicted by the subrosion model. The expansion of saline groundwater away from the salt dome is controlled by a large scale density-driven convection cell.

Table 1. Geochemical results from the Muhlenrade borehole.

Figure 1

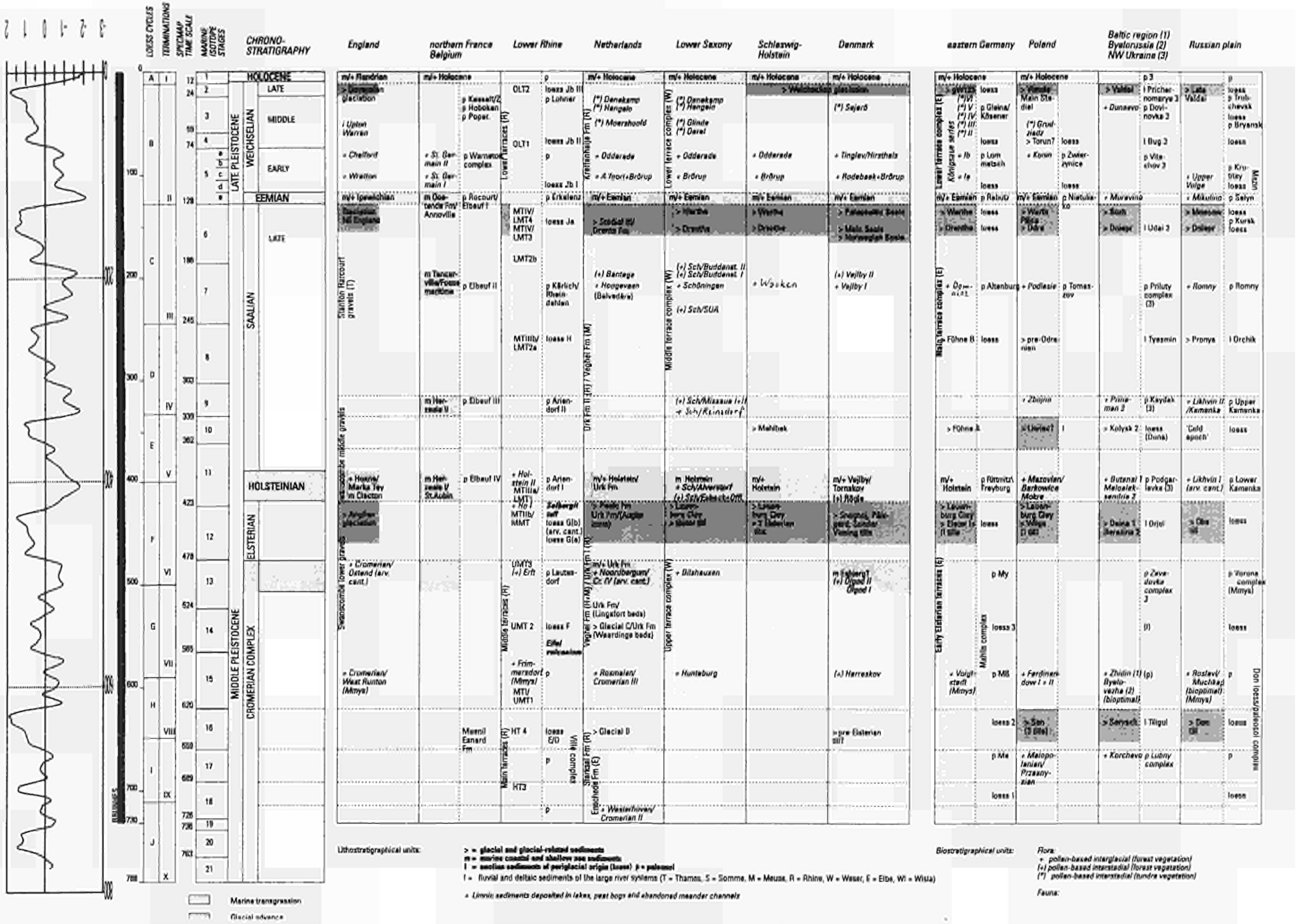


avas(t1,t2,linear=0) for last 200 ka, t2_log10(spec+5)

Ref MU / 93 /	Depth (m)	Sample weight (g)	% water (weight)	Oxygen-18 (‰ vs SMOW)	Deuterium (‰ vs SMOW)
1	20-21	*	*	*	*
2	22,5-23,5	51,4	17,1	-8,13	-62,5
3	24-25	49,4	18,1	-8,53	-62,9
4	26-27	61,8	18,9	-8,57	-59,9
5	28-29	45,3	18,1	-8,62	-65,6
6	30-31	64,0	18,9	-8,31	-58,1
7	35-36	58,1	17,4	-9,24	-63,8
8	40-41	33,9	18,9	-9,88	-65,5
9	45-46	32,5	23,1	-8,70	-62,9
10	50-51	26,6	19,9	-10,14	-72,2
11	55-56	30,6	19,6	-10,43	-68.5
12	60-61	25,8	25,8	-9,62	-69,4
13	65-66	31,5	25,9	-8,84	-59,7
14	70-71	29,5	20,0	-9,46	(-40)
15	75-76	41,7	18,7	-9,11	-70,5
16	80-81	26,7	24,7	-9,32	-71,4
17	85-86	*	*	*	*
18	90-91	49,6	19,2	-9,02	-65,2
19	94-95	76,2	18,9	-7,81	-56,2

Table 1

Tentative correlation of Middle and Late Pleistocene stratigraphy in Northwest and Central Europe and the marine isotope stages (version 1)



Lithostratigraphical units:

> = glacial and glacial-related sediments
m = marine coastal and shallow sea sediments
l = aeolian sediments of periglacial origin (loess) p = paleosol
f = fluvial and deltaic sediments of the large river systems (T = Thames, S = Somme, M = Meuse, R = Rhine, W = Weser, E = Elbe, Wi = Wisla)

+ Limnic sediments deposited in lakes, peat bogs and abandoned meander channels

Biostratigraphical units:

Flora:
+ pollen-based interglacial (forest vegetation)
(+) pollen-based interstadial (forest vegetation)
(*) pollen-based interstadial (tundra vegetation)

Fauna:

Figure 2

Figure 3

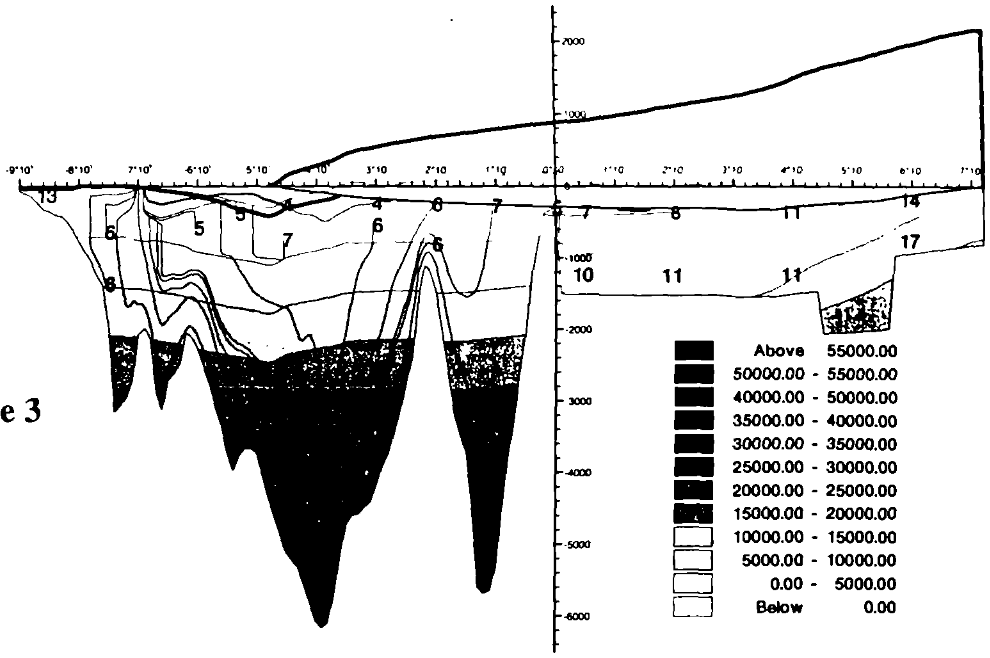


Figure 4

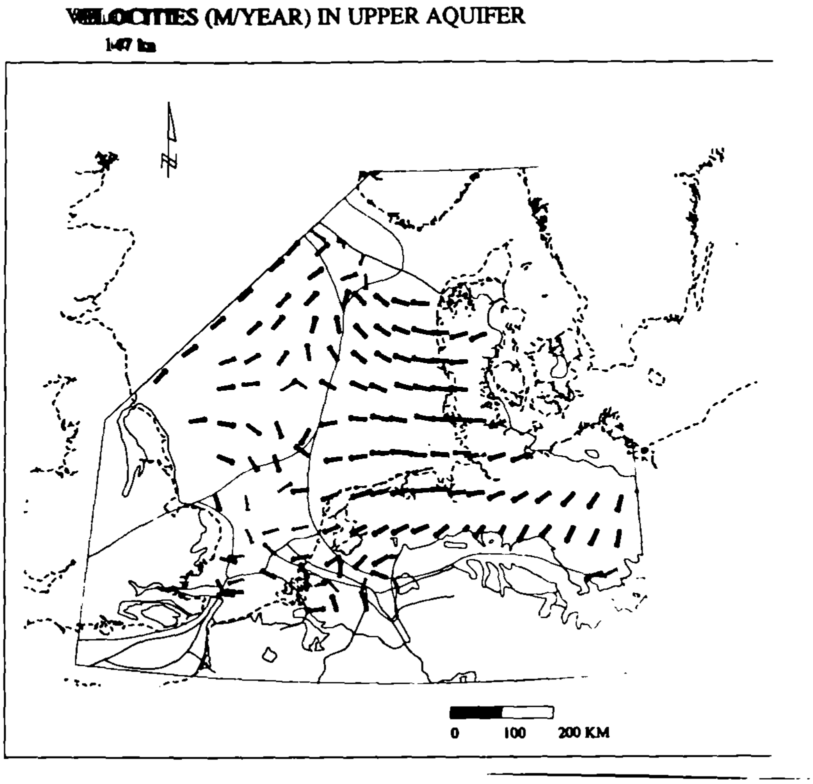
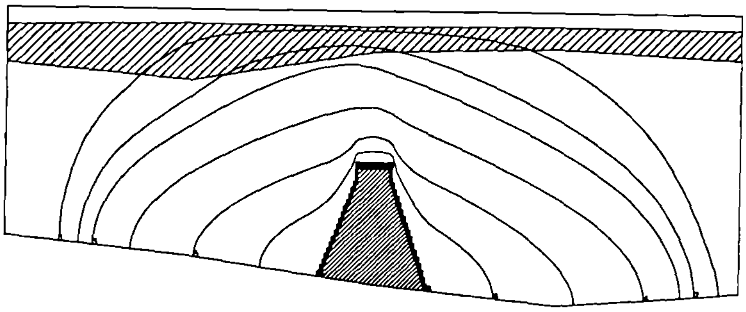


Figure 5



Salt concentration distribution after 10 000 years

Contours are 1%, 5%, 10%, 25%, 50% and 75% of maximum

Title: EXPERIMENT OF GROUNDWATER FLOW IN A FRACTURE FOR THE VALIDATION OF CHEMISTRY/HYDROMECHANICAL TRANSPORT OF COUPLED MODELS FOR FRACTURED MEDIA
Contractor: BRGM
Contract No: F12W-CT90-0049
Duration of contract: from 01/01/1991 to 12/31/1994
Period covered: from 01/01/1993 to 12/31/1993
Project Leader: S. GENTIER

A. OBJECTIVES AND SCOPE

This project is a circumstantial study in laboratory concerning the relationship between the morphology, the flow and the chemical reactions water-rock in the fracture. The objective is the achievement of an experiment designed for the validation of chemistry-hydromechanical transport of coupled models which integrate explicitly the morphology of the voids of the fracture and its variations.

The morphology of a natural fracture in a granite will be studied from profiles recorded on each side of the fracture and from the casting of the voids. The flow channels will be determined from the morphology of the voids and from radial flow experiments. The petrology of each side of the fracture will be studied. All these data will permit the choice of some little fields on the sides of the fracture about which the microroughness will be analyzed.

After this preliminar phase, radial flow tests will be performed on the fracture. The tests will be realized at various levels of normal stress and in temperature. During the tests, the chemistry of the water entering and exiting of the fracture will be determined. At the end of each experiment, the morphology of the fracture will be examined again.

B. WORK PROGRAMME

The scheduled successive phases for the achievement of the works are:

- Design, fitting of the prototype of testing equipment and qualification tests.
- Choice of the sample and initial caracterization of the fracture.
- Tests of percolation (3 or 4 tests acccording to the necessary duration for each percolation).
- Presentation and interpretation of the results.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

By the end of this year, the state of advancement is the following:

- The qualification tests of the prototype are achieved.
- A simulation of percolation has been performed with a replica in concrete.
- An explorative stage has been carried out to inventory the various devices for microroughness used in the industrie. The microrugosimeter RANK TAYLOR HOBSON has been selected.
- The initial petrographical description of the fracture plane has been carried out.

Progress and results

1. Qualification tests of the prototype and simulation test

Each constitutive part of the percolation cell has been tested separatly, after that, the complete one bas been tested.

A simulation of percolation has been performed with a replica in concrete. For an injection pressure of 0.6 MPa, the loading of the fracture induces a clear variation of the recovered fluid in each compartment of the tank. The anisotropy of the flow in this fracture is clearly shown. There is a delay (approximatively 30 s) between the beginning of the test and the fluid recovering (Fig. 1).

2. Selection of a microrugosimeter

Characterization of the fracture walls before and after the percolation test needs the use of a microrugosimeter.

First, a specification sheet has been written and then an explorative stage has been carried out in order to inventory the various devices used in the industry for microroughness.

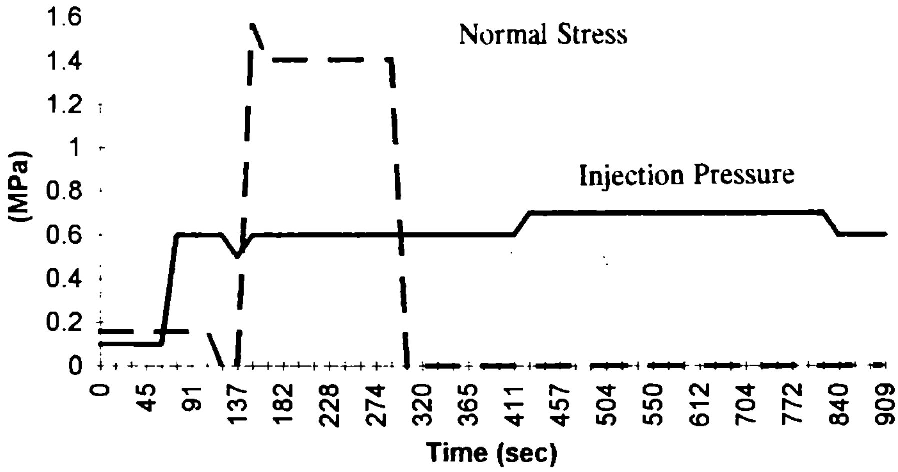
This was needed because of numerous aspects of the study, such as the volume and the weight of samples, very large heterogeneity of the fractures wall's surface...

The microrugosimeter of RANK TAYLOR HOBSON has been selected as answering the best to the specification sheet. This is a modular system and many requirement can be programmed (parameters of measurement, and analysis, results presentation).

Test have been performed successfully on two granite samples presenting smooth surfaces and dissolution surfaces.

3. Petrographic description of the fracture plane

The initial petrographic description of the fracture plane was carried out successfully (fig. 2), same thing with the study of the distribution of biotitic areas (Fig. 3) and the analysis of their volumic



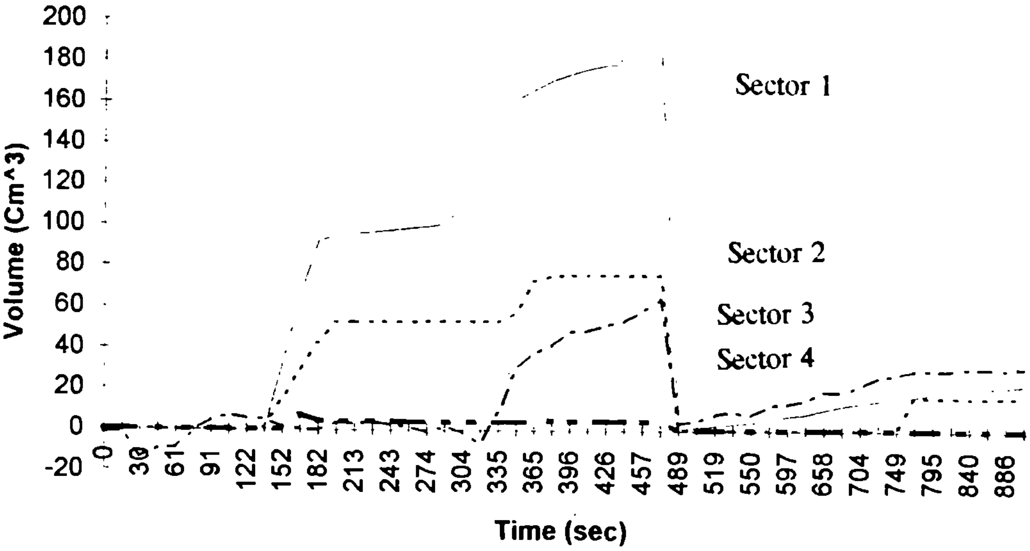


Figure 1 - Percolation test with a replica in concrete.

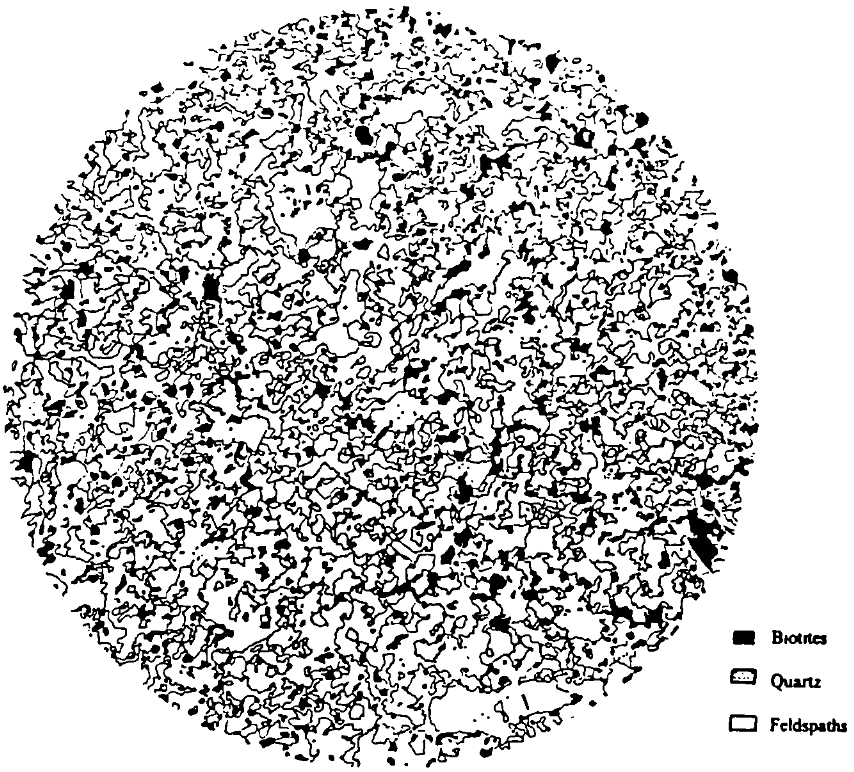


Figure 2 - Reduced Petrographic map of a fracture plane.

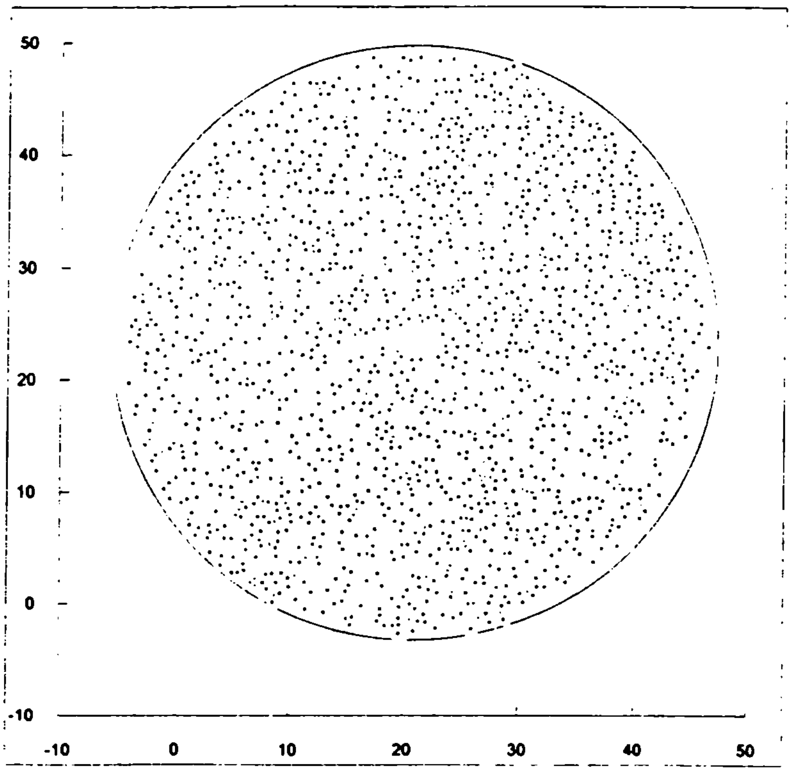


Figure 3 - Gravity centers map of biotitic areas

distribution in three perpendicular directions. This petrographical map could be compared with the morphology, the channel network and the chemical evolution of the percolated fluids.

Title: Experiments in a 600 m borehole in the Asse II salt mine.
Contractor: ECN
Contract no: FI2W/0050
Duration of contract: January 1991 to December 1993
Period covered: January 1993 to December 1993
Project leader: J. J. Heijdra

A. *OBJECTIVES AND SCOPE*

In order to assess the safety of disposal of radioactive waste in salt formations, models for the thermo-mechanical behaviour of rock salt that have been developed in previous programmes have to be verified by in-situ experiments. It has been proven by the COSA project that computations based on laboratory scale experiments do not accurately predict the in-situ measurements.

In this research programme the following in-situ measurements are carried out in the Asse II salt mine in Germany with measuring equipment developed in a previous programme under contract number FI1W/0084:

1. Determination of in-situ elastic behaviour of salt and convergence measurements at the bottom of the borehole with different pressures. The measurements will be carried out with the Variable Pressure Device (VPD) in the available 300 m hole.
2. Free convergence measurements of the salt wall at five depths in a borehole, i.e. at different salt pressures as soon as a 600 m deep borehole becomes available.

The experimental results obtained will be available to predict the behaviour of salt deposits and will give essential information to be used in safety assessment of disposal facilities for radioactive waste in rock salt, especially in the field of elastic behaviour and pressure dependency of creep.

B. *WORK PROGRAMME*

The tasks which need to be preformed during the contract period are:

1. Maintenance of installed equipment:
   Including the maintenance of the hardware and software required for remote instrument control and data transmission between the Asse salt mine and the ECN in Petten.
2. Execution of the experimental programme:
   The VPD measurements require that parameters (pressures) are changed and thus require local operation. The convergence measuring devices have to be installed in the borehole before measuring and removed afterwards.
3. Data collection and interpretation of the results:
   The automatically collected experimental data will be validated and interpreted.
4. Evaluation of experimental results:
   Consequences for the models used for the description of thermo-mechanical behaviour of rock salt resulting from the measurements will be evaluated taking into account the measurements performed in previous programmes.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

The drilling of a 600 m borehole suffered from technical problems. These problems where not caused by the great depth itself and hence can be considered as start-up problems in the use of a completely new developed drilling device. In the last months of the reporting period the drilling advance has been considerably and it can be considered probable that in the first quarter of 1994 a 600 metre deep borehole will be available. All actions have been postponed until the availability of a suitable hole will be guarantied.

As soon as a suitable hole is available the measurements can proceed. Extension of the contract will be requested.

Title: EVALUATION OF A SELF-CONSISTENT APPROACH TO FRACTURED CRYSTALLINE ROCK CHARACTERIZATION

Contractor: Golder Associates (UK) Ltd
Contract No: F12W/0051
Duration of Contract: From June 1991 to June 1994
Period Covered: January 1993 to December 1993
Project Leader: M. Brightman

A. OBJECTIVES AND SCOPE

The aims of the project are:

(i) to assess the errors in predictions of a nuclide migration in fractured crystalline rocks resulting from the application of inappropriate interpretation techniques;
(ii) to assess the impact of the "partial flow dimension" approach on the results derived from hydrogeological testing; and
(iii) to develop a methodology for constructing fracture network models to incorporate field flow dimensional information directly.

B. WORK PROGRAMME

The project has been subdivided into the following five tasks:

(1) to provide a literature review of the impact of the application of "partial flow dimension" interpretation on hydrogeological tests in fractured crystalline rocks;
(2) to evaluate, present and assess the effect of "dimensional" interpretation on some existing data sets;
(3) to simulate "dimensional" results within a fracture network model;
(4) to assess the available methods by which "dimensional" results would be incorporated explicitly into a fracture network model; and
(5) to demonstrate the effect of cylindrical flow assumptions on the output from a transport version of the fracture network model, when compared to results analyzed using the actual "partial flow dimension".

C. PROGRESS OF WORK AND RESULTS TO DATE

State of Advancement

The work carried out during 1993 was concentrated on Tasks (3), (4) and (5).

Task (3): The FracMan package has been further used to simulate packer tests in fracture networks and partial dimensional behaviour has always been observed, various interpretation techniques have been compared; difficulties associated with the conventional interpretation method have been highlighted; using the same fracture networks, different test conditions have also been simulated to examine whether the dimensional behaviour is a fracture network intrinsic property. This task is completed.

Task (4): The relationship between fracture geometry and flow dimension has been examined in detail so that the flow dimension information determined from field testing data can be incorporated into discrete fracture network realizations. Both planar and rough fractures have been considered. In order to achieve this, the original generalized radial flow theory was extended and a new in-house well test interpretation package, FLOWDIM, has been developed. The concept of space-filling problem in fractured rocks has been introduced. This task still requires the building of a "library" to relate flow dimension with different fracture network configurations.

Task (5): Through 14 solute transport simulations with their flow dimensions ranging from 1 to 3, the influence of different flow dimensions on solute transport breakthrough curves in both planar and rough fractures has been studied. This task is completed.

Progress and Results

C1. Tasks 1 and 2: Review and Data Analysis - completed and reported in 1991 and 1992

C2. Task 3: Fracture Network Simulations

In addition to one simulation reported in 1992, two more fracture networks were generated, one has two times higher fracture intensity than the other. Synthetic hydraulic tests were then conducted within these fracture networks. In both cases, the initial flow dimensions were very close to 2.0 (cylindrical radial flow) and late time flow dimensions were less than 2.0 (sub-radial flow): 1.0 and 1.7. Detailed interconnection analysis of these networks revealed that the late time flow dimension is closely related to fracture interconnectivity. The same synthetic data sets were also analyzed using conventional interpretation technique by assuming flow dimension = 2.0. For Early time data sets, the interpreted transmissivity values were fairly close to the input in simulations, but not as good as partial dimensional interpretations. In addition, conventional interpretations always lead to high skin factors which did not exist for synthetic test data. Using the same fracture network, different flow rates in constant-rate test simulations lead to the same flow dimension and interpreted hydrogeological properties; constant-head and constant-rate test simulations also lead to the same flow dimension. Therefore, flow dimension is essentially a geometrical property of the fracture network in the vicinity of a **given** packer test interval and is independent of rate effects or of the test type.

C3. Task 4: Incorporation of Dimensional Data in Fracture Network Modelling

This is the key issue of this project: incorporate dimensional information into discrete fracture network modelling, serving as the self-consistent simulator. This implies two aspects: (1) to obtain better fracture hydraulic property values based on the partial dimensional interpretation technique; and (2) to use the inferred flow dimension itself to condition fracture network realization. The first requires a new well test interpretation package, so FLOWDIM was developed; the second requires the relationship between fracture geometrical configuration and its corresponding flow dimension. Seven known geometry fractures were generated and packer tests were simulated. FLOWDIM interpretation results are listed in Table 1. The matched flow dimensions were exactly as expected for the given fracture geometries. After introducing the space-filling-parameter which measures the conductive fracture intensity in the vicinity of the testing section, the fracture transmissivity values can be recovered from FLOWDIM interpretation of the synthetic testing data. Conventional interpretations using Interpret 2^{TM} have also been carried out for some of the simulations and their values are also quoted in Table 1 in parentheses. It can be seen that if flow dimension is 2.0, the two analyses lead to the same transmissivity values, but for flow dimension different from 2.0, there are quite significant differences in the derived transmissivity values. These exercises demonstrate that flow dimension is uniquely related to the conductive section area as a function of flowing path r. The derived flow dimension, together with inferred space-filling parameter, fracture size and fracture orientation (by other means), we can realistically construct a self-consistent local conductive fracture network in the vicinity of a testing section. This information should be used to condition large regional fracture network realizations.

We also studied water flow in rough fractures and its interpretation. Figure 1 shows the in-plane transmissivity distribution of one of the nine fractures we generated using roughness fractal models. Figure 2 shows a synthetic transient hydraulic testing response carried out with the source section located at the centre of the region. Interpretation using partial dimension approach (FLOWDIM) leads to realistic local transmissivity; the inferred flow dimension of 1.5 at early time and 2.4 at late time reflects perfectly well the conductive area variation in the radial direction of the synthetic testing.

The partial dimensional interpretation technique is based on the generalized radial flow model presented by Barker (Water Resources Research, 1988). We have extended the theory to include hydraulic property variations in the radial direction of a testing (in addition to flowing area variation). The extended model shares identical form as the fractal reservoir model used in the oil industry which was developed from flow through fractal objects. Therefore, quite extensive studies from oil industry and their conclusions can be brought in characterization of fractured rocks in the context of nuclear waste disposal. One of the significant conclusions is that late time flow dimension reflects the fractal dimension of the underlying flowing structure. This information can be directly used to condition fracture network realizations if we can obtain the stabilized late time flow dimension in field hydraulic tests.

Table 1 Summary of the interpretation results of the known geometry fracture simulations with and without considering the space-filling parameter

Simulated Fracture Geometry	Partial Dimensional Interpretation			Corrected Values with S.F.P.		
	Matched Flow Dimen.	Interval transm. (m^2/s)	Storativity	S.F.P.	Interval transm. (m^2/s)	Storativity
[1] Narrow Horizontal	1.0	$1.93 x 10^{-8}$	$2.57 x 10^{-6}$	1.3094	$1.474 x 10^{-8}$	$1.965 x 10^{-6}$
[2] Horizontal with arc length $\propto$ $[distance]^{1/2}$	1.5	$1.623 x 10^{-9}$ $(1.63 x 10^{-10})$	$2.76 x 10^{-6}$	1/12	$1.948 x 10^{-8}$ $(1.96 x 10^{-9})$	$3.308 x 10^{-5}$
[3] Large Horizontal	2.0	$1.048 x 10^{-8}$ $(1.06 x 10^{-8})$	$4.90 x 10^{-7}$	1.0	$1.048 x 10^{-8}$ $(1.06 x 10^{-8})$	$4.90 x 10^{-7}$
A Quarter of [3]	2.0	$2.694 x 10^{-9}$	$8.91 x 10^{-7}$	1/4	$1.078 x 10^{-8}$	$3.563 x 10^{-6}$
[4] Horizontal with arc length $\propto$ $[distance]^{3/2}$	2.5	$2.59 x 10^{-10}$	$1.5 x 10^{-6}$	1/24	$0.621 x 10^{-8}$	$3.59 x 10^{-5}$
[5] Vertical constant height	1.0	$2.321 x 10^{-7}$ $(3.55 x 10^{-10})$	$4.74 x 10^{-5}$	20	$1.161 x 10^{-8}$ $(1.78 x 10^{-11})$	$2.371 x 10^{-6}$
Half Height of [5]	1.0	$1.283 x 10^{-7}$	$2.28 x 10^{-5}$	10	$1.283 x 10^{-8}$	$2.28 x 10^{-6}$

Note: (1) input fracture transmissivity = 10^{-8} m^2/s; fracture storativity = 10^{-6}

(2) values in parentheses are from conventional interpretation using Interpret 2™

C4. Task 5: Impact of the Dimensional Approach on Transport Simulations

A literature survey on solute transport modelling algorithms for discrete fracture networks has been carried out and the algorithm used in FracMan/MAFIC package is validated. 14 solute transport simulations have been conducted. It is concluded that the impact of flow dimension on the solute transport is to provide a tool for better interpretation of fracture properties; there is no clear relation being found between the breakthrough characteristics and flow dimension. Rather, the breakthrough characteristics are closely related to fracture roughness. Combining the transient hydraulic test interpretation using the partial dimensional technique and tracer migration experiment interpretation techniques will provide a "fuller picture" about natural fractures. Figure 3 shows the particle breakthrough curves in the nine rough fractures simulated.

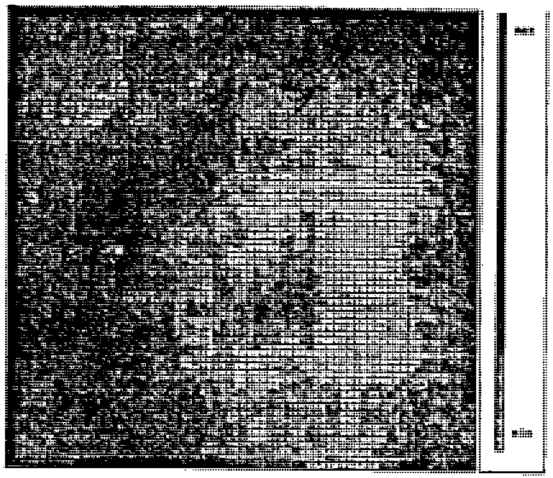


Fig. 1: Transmissivity distribution of rough fracture R253 (roughness fractal dimension 2.5)

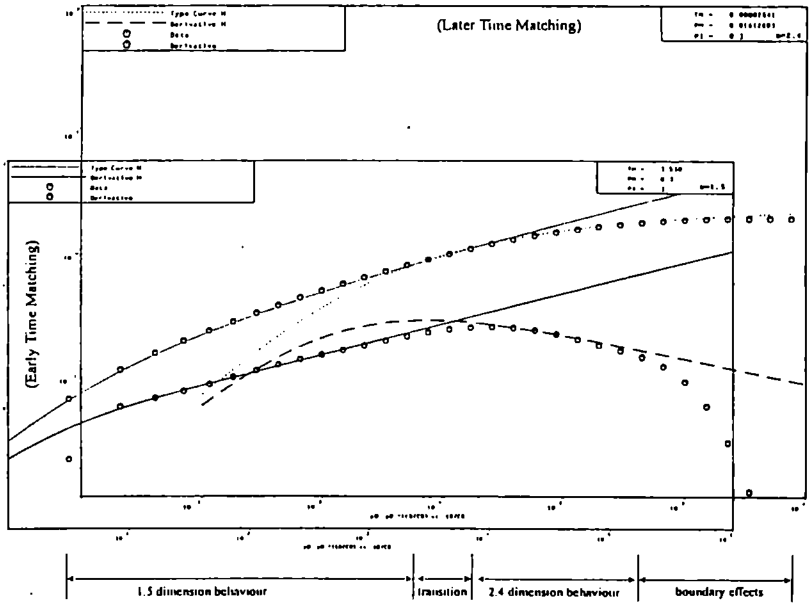


Fig. 2: FLOWDIM type curve matching of Fracture R253 synthetic test data

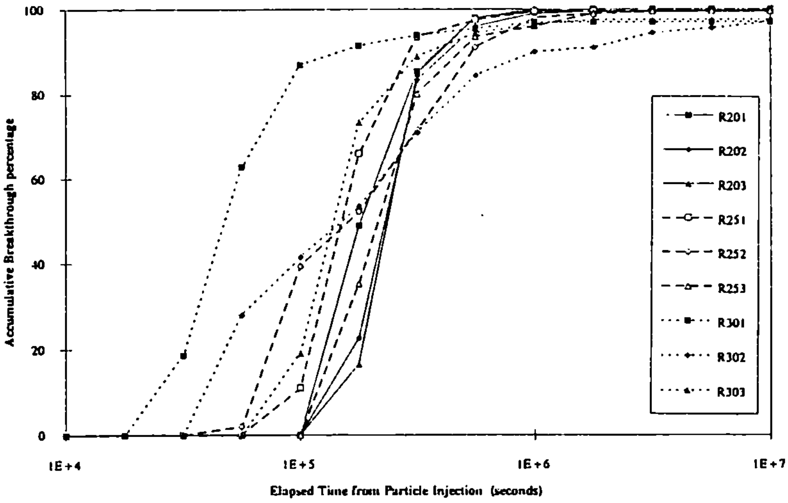


Fig. 3 Accumulative breakthrough particle fraction curves of the nine rough fractures.

INTERCLAY II - A Coordinated Benchmark Exercise in the Rheology of Clays

Contractor:	WS Atkins Engineering Sciences
Contract No:	F1 2W-CT91-0063
Contract Period:	June 1991 - May 1994 (36 months)
Project Leader:	N.C. Knowles

A. Objectives and Scope

INTERCLAY II is a coordinated benchmark exercise dealing with the numerical prediction of the rheology of clays. Its broad objectives are to improve confidence in long term predictions of geomechanical behaviour of clay in situations relevant to the underground disposal of radio-active waste. Eleven organisations are participating; in addition BNFL and ENRESA are providing sponsorship and have 'observer' status (Table I). A small Steering Committee comprising the coordinator, GCG and SCK provide the technical leadership.

B. Work Programme

There are 3 principal stages.

In Stage 1 the basic ability of popularly used models and the computer codes which contain them are briefly reviewed. The review comprises a comparison of the theoretical capabilities of the codes and their performance on 4 simple, somewhat hypothetical problems.

In Stage 2 laboratory tests on reconstituted clays provide the basis for two computational benchmark problems. Participants are asked to replicate the measured laboratory behaviour as far as possible, in their calculations.

In Stage 3 "in-situ" behaviour is modelled. Sources of well validated in-situ behaviour are relatively scarce and a specially designed heater test is currently in progress at SCK's Mol research facility. Precise details of the actual in-situ behaviour have been withheld from participants so that their predictions are "blind".

In each stage, the work programme is broadly as follows:

1. The coordinator prepares discussion documents, in cooperation with the Steering Committee, and circulates them to the participants for comment.
2. Participants in plenary meetings discuss and agree details of suitable benchmark problems to be solved.
3. The coordinator prepares and circulates detailed specifications of agreed problems.
4. The participants solve specified benchmark problems to the best of their ability using appropriate codes. The Coordinator collects and compiles results and other data from participants and prepares draft reports.
5. Results and overall progress are assessed in plenary meetings at intervals of approximately 6 months.
6. The Coordinator prepares and issues final definitive reports taking account of participants' comments.

C. Progress of Work

The chronological progress to date in terms of key events is set out in Table II. Two day plenary meetings of all participants were held in Epsom (4/5 July 1991) /1/, Mol (20/21 January 1992) /2/, Fontainebleau (7/8 September 1992) /3/, Bergamo (29/30 March 1993) /4/ and Madrid (17/19 November 1993) /5/. The Steering Committee has met periodically and in addition has maintained regular contact by telephone and fax, in order to progress necessary activities.

The achievements to date are best addressed stage by stage:

Stage 1 is now complete and four benchmark problems have been successfully addressed. All are hypothetical problems and serve as verification tests of the computer codes used ("verification" in this sense is defined as demonstrating that the mathematical formulation of the problem is correctly implemented and solved by the program. It says nothing about whether the mathematical formulation correctly replicates the real physical situation). The broad technical capabilities of the codes used by the various participants have also been reviewed in this stage and an attempt has been made to collate authoritative sources of data for Boom clay /6/.

The four benchmarks are:

1.1 an axisymmetric 1-D approximation of a cylindrical (i.e. tunnel) excavation under isothermal and isotropic conditions /7/.

1.2 a two-dimensional, axisymmetric approximation of the progressive excavation of a cylindrical tunnel in clay, again under isotropic and isothermal conditions /7/. (The approximations implied in 1.1 and 1 .2 are relevant to deep repositories in clay - e.g. Mol).

1.3 a plane-strain representation of the somewhat idealised construction operation and post-closure stages of a shallow 'lined trench' repository founded on clay /8/. (This was based on the Drigg LLW disposal facility operated by BNFL in the UK).

1.4 problem 1.1 extended to include a centrally located heat source /8/.

In all cases interest centres on the ability of the various conceptual models (and the codes in which they are implemented) to predict steady state behaviour. To provide a proper basis on which to assess these verification problems the "physics" was fully defined - i.e. the loading, boundary conditions, material models and the numerical values of the parameters were all given. It was intended that the only variation between the participants' models would be code-specific (e.g. in the detail of the numerical discretisation or solution procedure used). Various popularly used constitutive models were defined in terms of both effective and total stress with data parameters selected to provide equivalent behaviour wherever possible. (The data relates to Boom clay for benchmark 1.1, 1.2 and 1.4 and to the Drigg site for 1.3, although in the latter case it was found that despite extensive geotechnical surveys the existing information was not in a form suitable for numerical models).

The results of Stage 1 /9/ broadly demonstrated that verification of computer codes is no longer a major issue (i.e. all codes were capable of predicting the same behaviour, given identical descriptions of the problem). Some differences were observed but these have been satisfactorily resolved following discussion and subsequent investigation. (In this respect two further smaller scale problems were posed to investigate aspects of problems 1.3 and 1.4).

In Stage 2, two benchmarks based on laboratory-scale tests have been tackled. In both cases it has been necessary to compromise from the ideal basis of a set of tests in which the behaviour is fully quantified, self-consistent and moreover unfamiliar to participants. A search, carried out concurrently with Stage 1, highlighted the paucity of any authoritative data from suitable tests.

Benchmark 2.1 is based around tests on kaolin carried out at Cambridge University some years ago /10,11/. Three sets of heated triaxial tests on cylindrical samples were available, the first two of which were undrained and the third drained. Experimental results were available for temperature and pore pressure at two locations within the sample. As few additional material data were available, participants were asked to calculate the temperature and pore pressure changes at the two locations observed in the first two experiments. They were then asked to 'back-fit' their constitutive models to achieve adequate agreement with these experimental results and subsequently predict the results for Experiment 3. Thus they were to use the first two experiments to 'validate' their models prior to calculating the response of Experiment 3 thereby retaining an element of 'blind prediction'.

For the two undrained experiments, good agreement with the experimental results for temperature profile was achieved but much wider variation was seen in the pore pressure results. Nevertheless the predicted results for the drained test (Experiment 3) were in good agreement with each other and with the experimental results for temperature profile, but the predictions of pore pressure were consistently lower than the measured values. This latter effect can be explained by the use of the two undrained tests as the principal means of validation: the undrained tests were not sufficiently sensitive to parameters such as permeability.

Benchmark 2.2, is based on experimental work commissioned by the INTERCLAY II project performed at ISMES in Bergamo, Italy /12,13/. The experiments comprise a series of heated hollow cylinder tests supported by triaxial tests on Boom clay from the -223 level at Mol. As in Benchmark 2.1, some element of blind prediction is included in the specification: participants were asked to predict the results of the hollow cylinder tests based on the triaxial test data. They were then issued with the results for the hollow cylinder tests to enable 'back-fitting' and some investigation of the effects of parametric variations.

In comparison with Stage 1, the second stage benchmarks are more complex, both in the idealisation of the experimental arrangements and in selection and tuning of the constitutive model. This complexity is reflected in the scatter in the results, which although still within acceptable bounds, highlights the need for further work to fully understand the differences. The inevitably small scale of the laboratory tests also tends to exaggerate effects such as non-heterogeneity of material (relative to in-situ measurements). It is clear that in developing and tuning constitutive models, the stress path followed in the supporting laboratory tests needs to be designed with sound appreciation of the effects of anisotropy.

The Stage 3 benchmarks use the ATLAS in-situ heater tests at the Mol facility in Belgium. These tests were designed specifically for the project and comprise a 20m long, l90mm diameter, horizontal lined borehole containing electrical resistance heaters with two smaller diameter boreholes, containing pressure and temperature sensors, in the same horizontal plane. Design and installation were satisfactorily completed by July 1992 /14/, although some sensors were inadvertently damaged during installation and the full implications of this damage have not yet been assessed. The heating phase of the tests started in July 1993 and is presently in progress.

The specification for Benchmark 3 was discussed at the Madrid plenary meeting and subsequently finalised. The benchmark consists of a 2D analysis in the plane of the boreholes. Boundary and initial conditions are prescribed based on the in-situ stresses in the clay mass and the conditions in the gallery prior to drilling. Participants are asked to model the history of the test, including construction of the main borehole and the effects of this construction on the surrounding clay, followed by heating of the clay and its subsequent thermal response /15/. The initial results will be reported in April, 1994.

References

/1/ INTERCLAY II Minutes of plenary meeting, Epsom, 4/5 July 1991, WS Atkins Engineering Sciences.

/2/ INTERCLAY II Minutes of plenary meeting, Mol, 20/21 January 1992, WS Atkins Engineering Sciences.

/3/ INTERCLAY II Minutes of plenary meeting, Fontainebleau, 7/8 September 1992, WS Atkins Science & Technology.

/4/ INTERCLAY II Minutes of plenary meeting, Bergamo, 29/30 March 1993, WS Atkins Science & Technology.

/5/ INTERCLAY II Minutes of plenary meeting, Madrid, 17/19 November 1993, WS Atkins Science & Technology.

/6/ INTERCLAY II - Properties of Boom Clay - Bibliography GCG (London), August 1992.

/7/ INTERCLAY II - Specification of Benchmarks 1 & 2, October 1991, WS Atkins Engineering Sciences.

/8/ INTERCLAY II - Specification of Benchmarks 3 & 4, February 1992, WS Atkins Engineering Sciences.

/9/ CEC INTERCLAY II project - Report on Stage 1, WS Atkins Science & Technology, January 1993. (To be published as an EUR Series Report)

/10/ Savvidou, C. and Britto, A.M., 'Thermally Induced Effects in Saturated Clay', Proceedings of the International Workshop on Thermo-mechanics of Clays and Clay Barriers, Seriate (Bergamo), Italy, October 20 - 22, 1993.

/11/ INTERCLAY II - Specification of Benchmark 2.1, October 1992, WS Atkins Science & Technology.

/12/ Baldi, G., Borsetto, M. and Pellegrini, R., 'Medium Scale Laboratory Tests for the Interpretation of the Thermo-mechanical Properties of Clays', Proceedings of the International Workshop on Thermo-mechanics of Clays and Clay Barriers, Seriate (Bergamo), Italy, October 20 - 22, 1993.

/13/ INTERCLAY II - Specification of Benchmark 2.2, May 1993, WS Atkins Science & Technology

/14/ CEC Benchmark INTERCLAY II - Installation Report of the ATLAS Equipment, November 1992, SCK/CEN.

/15/ INTERCLAY II - Specification of Benchmark 3.1, December 1993, WS Atkins Science & Technology

Table I - INTERCLAY II Participants

Coordinator:	WS Atkins	(UK)	)
	GCG	(UK)	) Steering Committee
	SCK/CEN	(B)	)
	BRGM	(F)	
	CEA	(F)	
	EMP	(F)	
	ETSIM	(S)	
	G.3S	(F)	
	GEODESIGN	(B)	
	ISMES	(I)	
	LGC	(B)	
	BNFL	(UK)	) Observer
	ENRESA	(S)	) Observer

Table II Summary of Interclay II Key Events

Date	Event	Purpose
June, 1991	Steering Committee Meeting, Braunschweig	Discussion of possibilities for Benchmarks 1.1 to 1.4
July, 1991	Plenary Meeting, Epsom	Selection of Benchmarks
August, 1991	Draft specification for Benchmarks 1.1 and 1.2 issued	
September, 1991	Specification frozen - results required 31/12/91	
January, 1992	Plenary Meeting, Mol	Discussion of Benchmark results. Specification of Benchmarks 1.3 and 1.4.
February, 1992	Draft specification for Benchmarks 1.3 and 1.4 issued	
March, 1992	Specification frozen - results required 31/7/92	
June 1992	Installation of ATLAS Tests at Mol completed	
September, 1992	Plenary Meeting, Fontainebleau	Discussion of Benchmark results. Specification of Benchmark 2.1. Experimental tests for Benchmark 2.2 commissioned at ISMES.
October, 1992	Specification of further studies on 1.3 and 1.4 issued. Specification for Benchmark 2.1 issued.	
November, 1992	Specification frozen - results required by 31/12/92	
March, 1993	Plenary Meeting, Bergamo	Discussion of Benchmark results. Specification of Benchmark 2.2. Discussion of Stage 1 Report
May, 1993	Specification for Benchmark 2.2 issued	
May, 1993	Specification frozen - results for 'blind prediction' required by 14/7/93	
July 1993	Heating phase of ATLAS tests started	
November, 1993	Plenary Meeting, Madrid	Discussion of Benchmark results. Specification of Benchmarks 3.1 and 3.2.
December, 1993	Specification for Benchmarks 3.1 and 3.2 issued	

Title: SEALING OF BOREHOLES IN CRYSTALLINE ROCKS
Contractor: BRGM, SIF BACHY, MOTT MACDONALD
Contract No: F12W - CT 91-0072
Duration of contract: from 1/10/1991 to 30/09/1995
Period covered: 1993
Project leader : J.-F. OUVRY (BRGM - Coordinator)
F. DUFOURNET-BOURGEOIS (SIF BACHY)
L.M. LAKE (MOTT MACDONALD)

A. OBJECTIVES OF THE PROJECT

The objective of the study is the theoretical design and practical implementation of an in situ borehole-sealing technique that is applicable to fractured crystalline rock, as well as its subsequent implementation. The sealing or backfilling of boreholes in, or around, sites for the disposal of radioactive waste, is usually done with compacted bentonite, bentonite slurry or cement slurry. It is proposed to design a special product that combines a bitumen emulsion with clay and other substances. A fracture identified in crystalline rock will be selected for injection testing. The fracture aperture, measured in drill cores, will be studied in the laboratory and the data will be processed statistically. Tests with water will enable the study of the hydraulic behaviour of the fracture, before and after slurry injection, to define the efficiency of the method.

The contract combines the experience of several partners, including BRGM (F), the SIF BACHY Company (F) and MOTT MACDONALD Civil Ltd (UK).

B. WORK PROGRAMME

- Literature survey and assessment of earlier work.
- Laboratory tests for optimizing the grout component concentrations.
- In situ tests of the fracture (geophysics, water injection), and laboratory work (definition of the fracture aperture on core samples).
- Grout injection into the fracture, geophysical estimation of its penetration, and evaluation of the injection by means of sample studies and water tests.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of progress

By October 1993, the progress of the work phases that began in October 1991 was as follows:

- The literature survey concerning the concept of resealing boreholes in the context of an underground laboratory is completed.
- Research into the components of the mineral and hydrocarbon phases of the sealant was continued. Laboratory analysis of the various preselected materials made it possible to define the components and their relative proportions for the experimental grout. During this phase, a laboratory device was developed for testing the injectability of the selected mixtures.
- At the experimental site, the fractures were sampled and studied morphologically. At the same time a series of in situ tests were carried out to determine the hydraulic behaviour of the rock and a geophysical radar (Georadar) reconnaissance provided additional information on the in situ rock structure.
- Finally, the selected grout was tested during an in situ injection programme.

Progress and results

Fracture study of the granite by georadar

Georadar uses the reflection of electromagnetic waves to investigate the upper levels of the subsurface. A transmitter sends brief impulses (a few nanoseconds) of electromagnetic energy into the ground, and these are reflected by anomalies such as a contact between two materials of different composition or the presence of a fracture. The signal is then captured by a receiver, amplified, developed, and finally transformed into an electric current.

An on-site Georadar programme was carried out in order to provide a complete tomographic survey within the area delimited by the four boreholes. The transmitter and receiver were placed in two different boreholes, then progressively moved one at a time within the boreholes. Figure 1 shows the principle of tomography and Figure 2 shows an unprocessed record obtained between boreholes S1 and S3, where the transmitter was placed in S1 and the receiver was moved within S3. The direct path between S1 and S3 shows up clearly (it is the shortest and the first to arrive at the receiver), as do multiple coherent forms that reflect the presence of the anomalies being sought.

A second programme, to be carried out after the in situ injection programme, should make it possible to assess the penetration of the slurry and the quality of the injection.

Characteristics of the crystalline rock to be treated - study of the fracture morphology

To reconstruct the initial characteristics of the rock (i.e. before it was disturbed by the reconnaissance drilling) it is necessary to acquire a good knowledge of the rock structure. This is done through petrographic and structural studies on oriented borehole cores, complemented by geophysical logs, and it enables one to assign the various joints and fractures to specific families characterized by a strike and a dip.

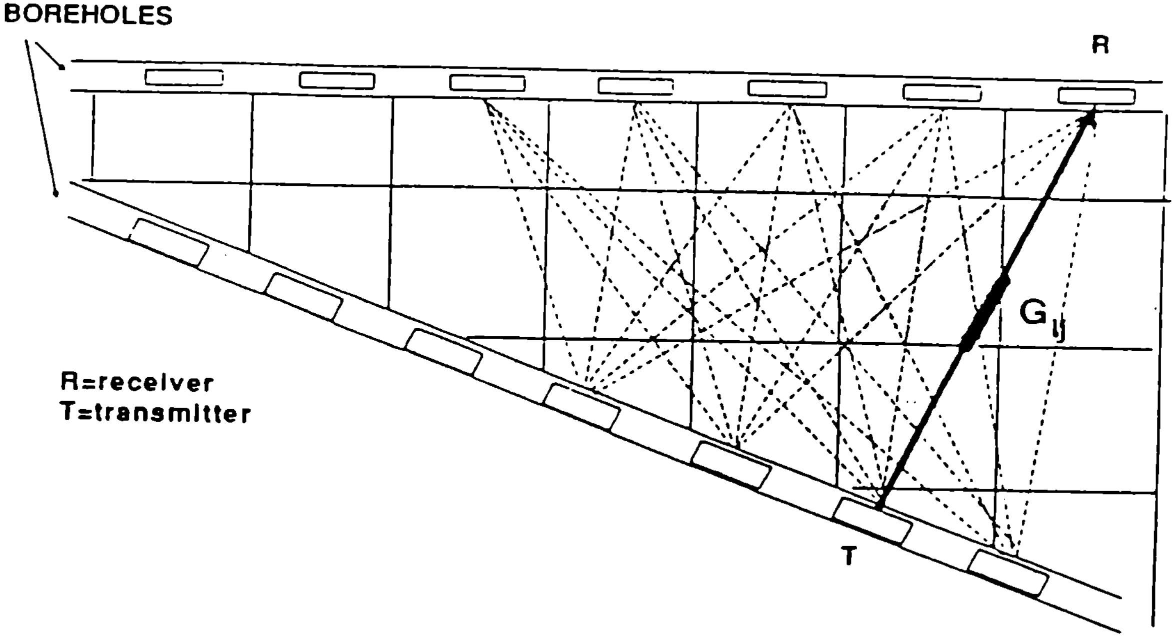


Figure 1 - Example of tomography between two boreholes.

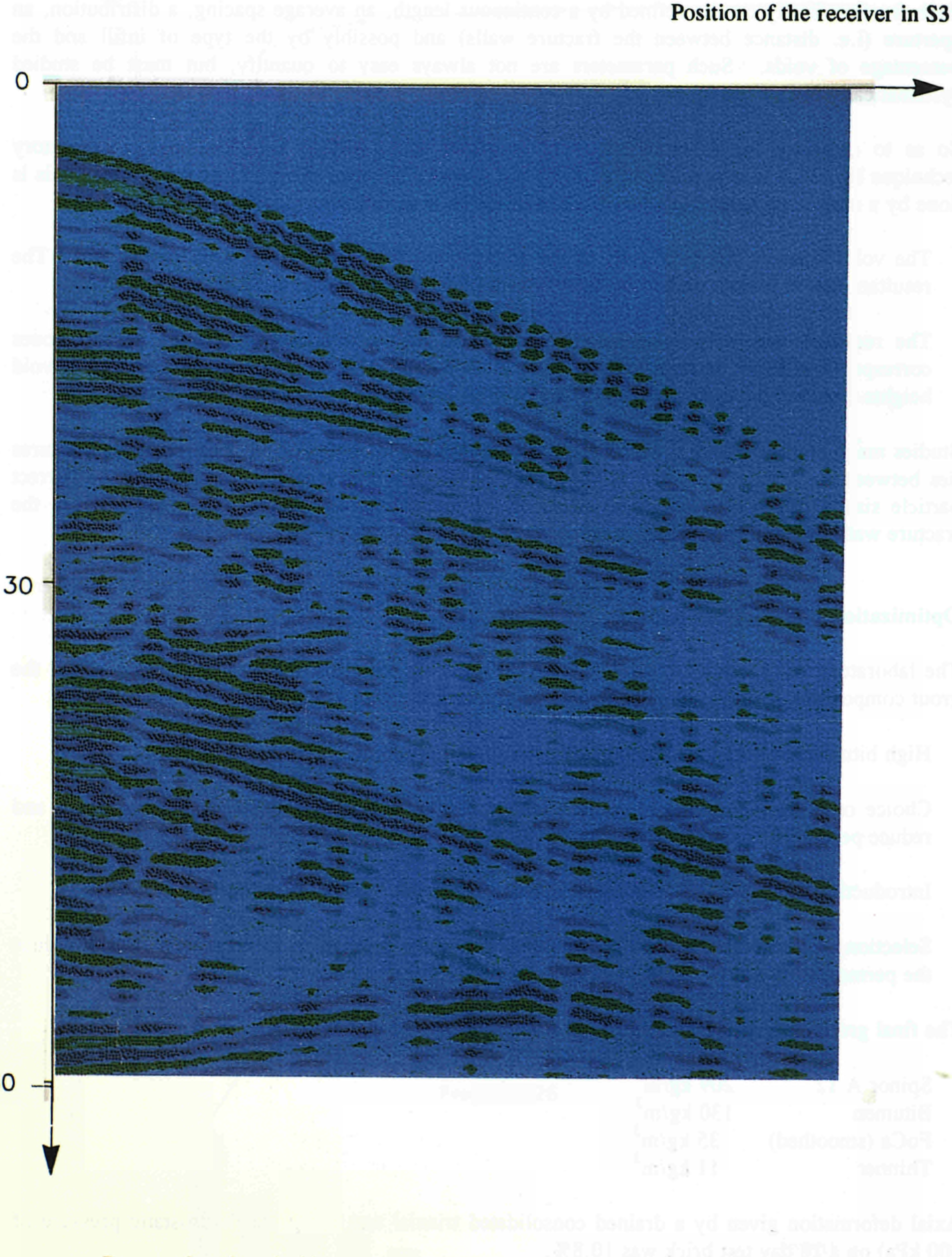


Figure 2 - Unprocessed record obtained between boreholes S1 (containing the transmitter) and S3 (in which the receiver was placed at different depths between 1 and 4 m).

Each fracture family can be defined by a continuous length, an average spacing, a distribution, an aperture (i.e. distance between the fracture walls) and possibly by the type of infill and the percentage of voids. Such parameters are not always easy to quantify, but must be studied systematically in any sealing project.

So as to complete the characterization of fractured rock, BRGM has developed a laboratory technique by which it is possible to quantify the aperture between two walls of a fracture. This is done by a method of moulding, the principle of which is as follows:

- The voids between the two walls of the fracture are filled with a coloured silica resin. The resultant mould is then studied by light transmission and the image digitized with a camera.

- The required data is revealed by the grey levels of the obtained image, the darkest zones corresponding to the largest voids. Figure 3 shows the distribution, after processing, of void heights obtained for three sampled fractures (F24 - F26).

Studies made on the various fractures have shown that the thickness of the most common fractures lies between 0.10 and 0.35 mm. A knowledge of this factor is essential for selecting the correct particle size of the constituent components of the injection grout so that the voids between the fracture walls are correctly filled.

Optimization of the injection grout

The laboratory work carried out by SIF BACHY during 1993 has made it possible to adjust the grout composition so as to achieve the desired properties:

- High bitumen content for its important deformation properties.

- Choice of a minimum cement content (about 200 kg/m^3) to provide mechanical strength and reduce permeability.

- Introduction of a relatively high mineral content (cement + clay) to reduce permeability.

- Selection of a second ultra-fine cement to improve the mechanical strength and further reduce the permeability; i.e. SPINOR A 12 (Ciments d'Origny).

The final grout composition that has been selected is:

Spinor A 12	209 kg/m^3
Bitumen	130 kg/m^3
FoCa (smoothed)	35 kg/m^3
Thinner	11 kg/m^3

Axial deformation given by a drained consolidated triaxial test to failure (hydrostatic pressure of 300 kPa) on a 28 day test brick was 10.8%.

The permeability coefficient measured at the same time was 2.9 x 10^{-9} m/s. Considering the continued curing of the grout, this very low value should decrease even further with time.

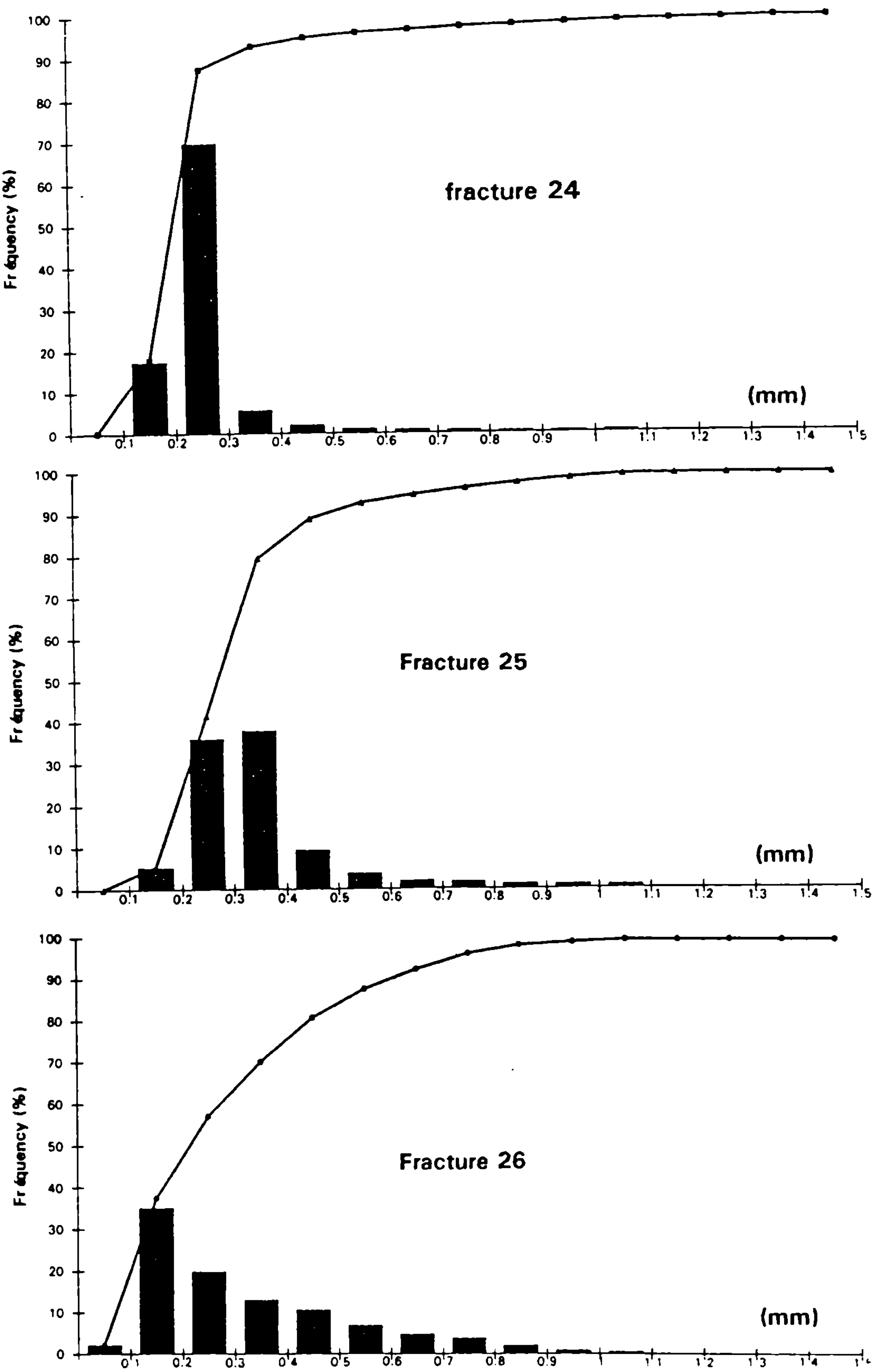


Figure 3 - Distribution of void heights in fractures 24, 25 and 26.

Adaptation of the grout to the fracture openings

The morphological study has shown that the fracture openings to be injected are very narrow, with a void aperture mainly between 0.1 and 0.3 mm.

The adaptability of the grout to such a "thin" environment will depend principally on its liquid state characteristics, and its aptitude for retaining these during the injection phase; i.e.:

- capacity to retain homogeneity under pressure,
- viscoplastic type rheological behaviour favourable for injecting thin fractures,
- good penetration power, which is also dependent on the particle size of the components in suspension. It is essential that the particle size of the solid phase in the grout is compatible with the fracture openings.

The selected grout satisfies all these requirements:

- It is stable (2% shrinkage after 2 hours) and has a low drying coefficient (filtrate: 100 ml at 30 min under 0.7 MPa).

- It has a viscoplastic type behaviour (5 MPa.s for a flow threshold of 0.4 Pa).

- The initial particle size distribution of the FoCa bentonite (d_{100} = 26 μm) needed to be filtered so as to eliminate the >10 μm fraction (see Figure 4). The other components of the mixture contain no element larger than 12 μm.

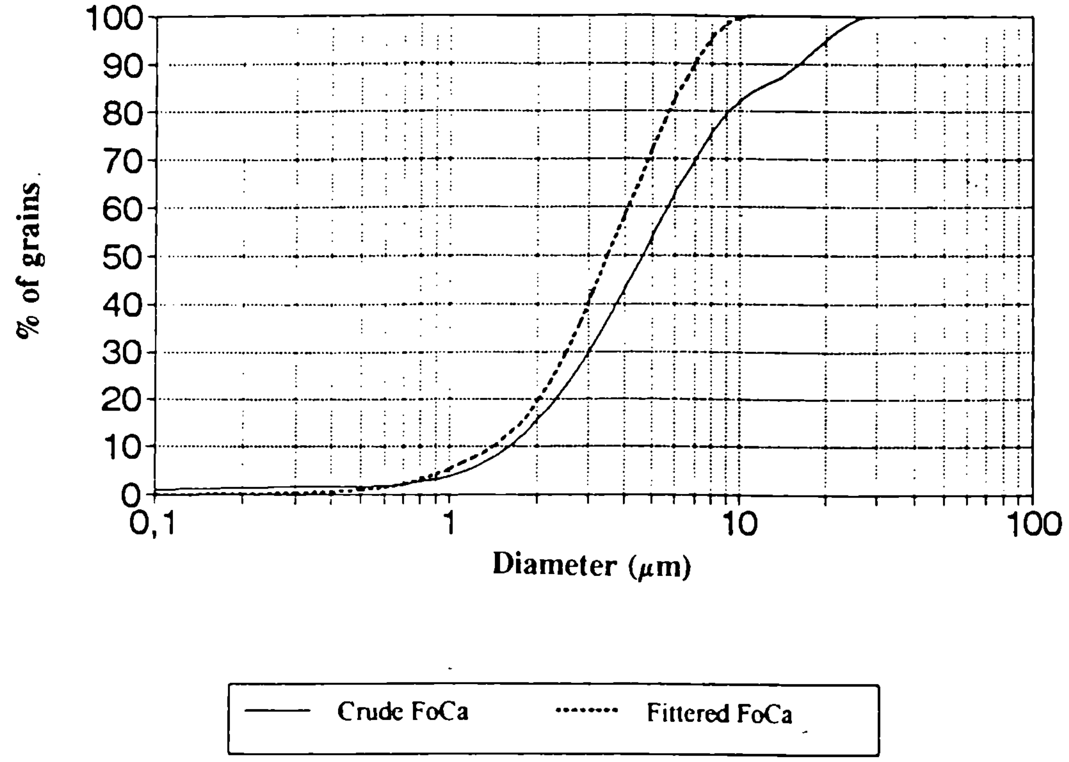


Figure 4 - FoCa bentonite cumulative particle size curves.

In situ injection programme

Principle:

In situ injection was carried out from 18 to 21 October 1993 using the configuration shown in Figure 5. The grout was injected by a pneumatic piston pump which can operate at a given constant pressure. The injection pressure and flow rates were measured at the borehole collar, and the surrounding boreholes were equipped with sensors to record possible over-pressure caused by the injection.

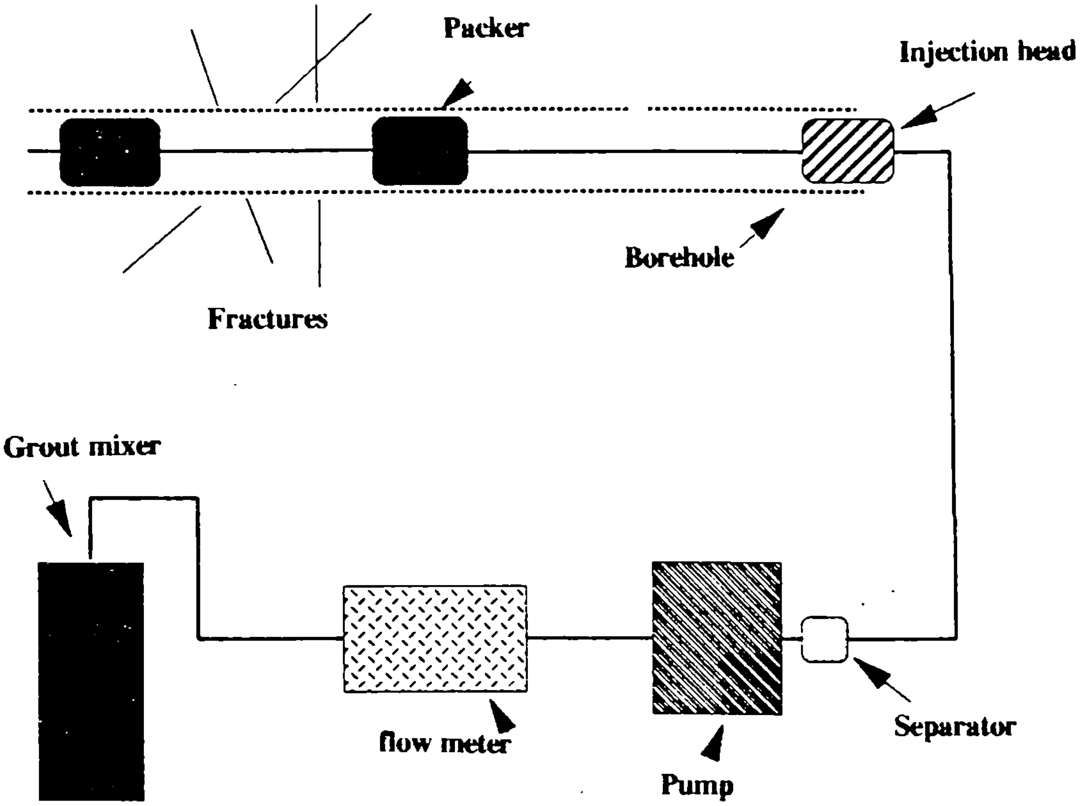


Figure 5 - Diagram of the injection unit.

The grout was prepared in a practical for field use "manufacturing unit".

Injection of the central borehole (S2) fractures

Before injecting the grout, each of the boreholes was cleaned and saturated with circulating water for about 12 hours at 0.6 MPa pressure.

During a first trial, the section of the borehole intersecting fractures F24, F25, F26 and F27 was isolated with a double packer then injected. Figure 6 shows the pressures and flow rates throughout the injection. The injection pressure was fixed at about 2 MPa in the first instance and later at 4 MPa. The total volume of grout injected was 14.5 l.

In a second trial, the double packer was replaced by a simple packer and the borehole injected in sections of 1 m.

Finally the borehole was cleaned with water.

Injection of the surrounding boreholes S1, S3 and S4

The three boreholes were injected using the same method as for borehole S2, i.e. at 1 m intervals with a single packer. The boreholes were then cleaned with water.

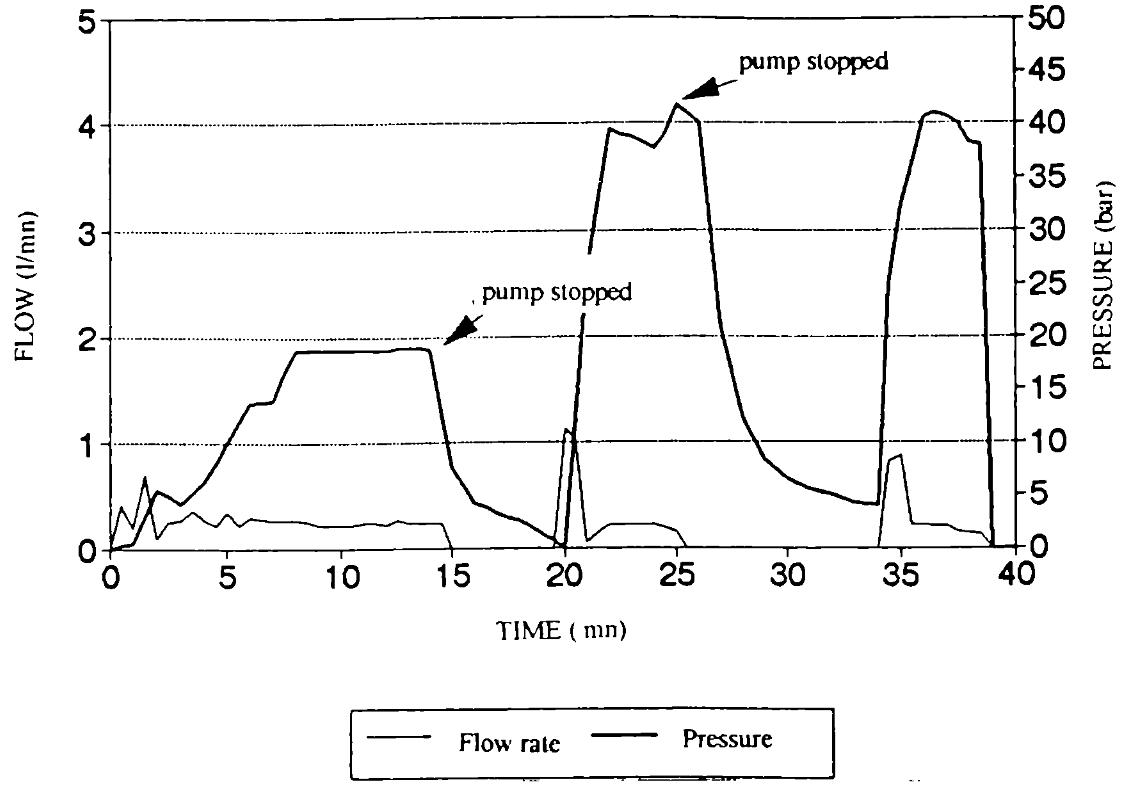


Figure 6 - Injection of borehole S2.

DUFOURNET-BOURGEOIS F., OUVRY J.F., Traitment des forages de reconnaissance autour ou au droit d'un site potentiel de stockage. Symposium International GEOCONFINE, 8-11 June 1993, Arnould, Barres and Corne (eds.), A.A. Balkema.

DUFOURNET-BOURGEOIS F., OUVRY, J.F., Sealing of exploration boreholes in and around a potential radioactive waste disposal site. First workshop on design and construction of deep repositories. 30-31 March 1993, Bäckblon and Svemar (eds.), Swedish Nuclear Fuel and Waste Management Co., SKB.

GANDAIS M., DUFOURNET-BOURGEOIS F., ESNAUT A., OUVRY J.F., Scellement de forages sur les sites de stockages de dechets radioactifs. First International Congress on Environmental Geotechnics, Edmonton, Canada, 10-15 July 1994 (to be published).

Title: Paleoclimatological Revision of Climate Evolution and Environment in Western Mediterranean Regions.
Contractor: ENRESA
Contract N° : FI2W-CT91-0075
Duration of Contract : June 91 - May 95
Period covered : From January to December 1993
Project leader : C. Bajos (ENRESA - Coordinator), P. Peaudecerf (BRGM) and D. Barettino (ITGE)

A. OBJECTIVES AND SCOPE

To evaluate the security of a high level waste repository it is necessary to determine how future climate changes will affect the safety of the repository. The magnitude and likelihood of these changes can be inferred from the study of past climate changes. However, up to date, little data is available about past climate evolution in Spain and other Western Mediterranean countries. This project is concerned with the study of climatological changes occurred during the last 2 million years in the Western Mediterranean regions, which will be of importance for developing scenarios for the safety analysis of a high level repository in Spain. Even though the techniques to be used in the study will provide information with different time scales, special emphasis will be placed on climate changes during the last 1000 years.

The project is being carried out by ENRESA as the main contractor and BRGM as an associated contractor. Work about climate evolution in Spain has been subcontracted to the Instituto Tecnológico y Minero de España (ITGE). BRGM is responsible for the review of past climate data from Southern France, Italy and North of Morocco and for the development of scenarios.

B. WORK PROGRAMME

The project has been subdivided into the following tasks:

Task 1) a) Synthesis of the environment in Spain over the last two million years: D. Barettino (ITGE) and T. Torres (ETSIMM).
b) Paleoenvironmental evolution during the Quaternary in the context of Europe and Western Mediterranean regions: B. Defaut, P. Peaudecerf (BRGM).

Task 2) Paleoclimatic and environmental study of Quaternary deposits in the River Tajo Valley. A. Pérez (CSIC) and D. Barettino (ITGE).

Task 3) Study and dating of travertines in Spain as a paleoclimatic and paleoenvironmental index. T. Torres (ETSIMM) and D. Barettino (ITGE).

Task 4) Climatic reconstruction of the last thousand years in Spain on the basis of dendrochronological series: J. Creus (CSIC), L. A. Fernández (INIA) and D. Barettino (ITGE).

Task 5) Paleoenvironmental reconstruction and construction of future evolution scenarios. P. Peaudecerf, G. Farjanel, M. Garcín (BRGM).

C. PROGRESS OF WORK

State of advancement.

The problems caused by the delay in signing the collaboration agreements between ITGE and the specialists contracted to carry out Tasks 2-4 and by the delay in the transfer of funds have now been solved. In spite of these problems, Task 1 has been completed and Task 5 is going according to the original schedule. The new completion date for Tasks 2 and 3 is November 1994. This will make it possible to carry out an additional fieldwork campaign during the Spring and Summer of 1994. The timetable for Task 4 has not been modified because although the fieldwork foreseen for 1993 has been reduced, laboratory work has progressed at a faster pace than expected.

Progress and results.

Task 1: Synthesis of the environment in Spain over the last two million years.

This task has now been completed. The report on "Paleoenvironmental evolution during the Quaternary in the context of Europe and Western Mediterranean regions", prepared by BRGM (B. Defaut and P. Peaudecerf) was completed and sent to the CEC in June 1993. The report contains 83 pages , including 29 figures and 2 appendices. An original methodology has been used for this summary, consisting of linking, wherever possible, the different external geodynamic phenomena to the associated bioclime, in order to provide the reader with a tread connecting the different phenomena considered and serving as a common denominator.

The "Synthesis of the environment in Spain over the last two million years", compiled by D. Barettino (ITGE) and T. Torres (ETSIMM), has been completed during the last semester of 1993. The final document contains 473 pages and includes 110 figures and tables. The structure of the report consists of a series of subject-specific chapters written by specialists from different universities and public research organizations. It begins with a chapter dedicated to establishing and outlining the general chronological framework. Following this there are six major headings describing the evolution of the following aspects over the last two million years: sedimentation and morphogenesis, edaphic formations, neotectonics and vulcanism, the biosphere, mankind, exploitation of the land and climate.

Task 2: Paleoclimatic and environmental study of Quaternary deposits in the Tajo Valley.

The three field sites selected within the Tajo River Valley are shown in Figure 1. Work accomplished at each site is described below:

- Talavera de la Reina Area: The geomorphological mapping of an area measuring 500 km^2 has now been completed at a scale of 1:50,000. Work has now begun on sedimentological analysis and sampling on terraces and deposits from lateral sources. The edaphocatena has been completed through the surveying of 24 new profiles in new testing pits with 92 soil samples taken. Twenty four testing pits were sampled every 10 cm. for paleomagnetic studies. This type of studies give an indication on the amount and types of iron oxides (magnetite, hematites, goethite, etc.) formed during the genesis of the soils which could be a potentially good paleoenvironmental indicator. Other samples were taken oriented, with a view to determining magnetic polarity and the direction of the magnetic components responsible for magnetization. Several archaeological deposits, from the Lower Palaeolithic found in the area, are currently under study.

- Toledo Area: About 70-80% of the 300 km^2 area has been mapped and stratigraphic and sedimentological work has begun on the sector of the Valley located downstream from the city of Toledo. The most interesting edaphic sequence has been found in the Valdelobos sandpit, with a series of paleosoils from the Upper Pleistocene. Prospecting for vertebrates has provided good indications. Fossil remains have been found in two of the 11 locations sampled. Sampling for palynology studies has given excellent results. For the first time in these areas of the Tajo River there is the possibility of having pollinic sequences from the Upper and Middle Pleistocene.

- Fuentidueña de Tajo Area: Systematic reconnaissance and geomorphological mapping were initiated during the months of September and October. This work included sampling of sediments for prospecting of vertebrates at 5 locations.

Task 3: Study and dating of travertines in Spain as a paleoclimatic and paleoenvironmental index.

Work has progressed fundamentally in four of the selected areas: the karstic area of El Reguerillo and the travertinic areas of Río Blanco, Priego and Bañolas. In addition, visits have been made to the following caves for paleontological sampling: Troskaeta (Ataun, Guipuzcoa), Santa Isabel (Arnero, Vizcaya), Pasada (Gueriezo, Vizcaya) and Picos de Europa area. (Figure 2). The current status of the work and the results obtained may be summarized as follows:

- Cueva del Reguerillo and Karst of the Cerro de la Oliva: Seven samples have been taken for dating by means of the Electrospin Resonance method (ESR), and fifteen for dating with the Amino Acid Racemisation (AAR) method. Even though the results of these dating methods are still pending, some conclusions can be drawn from the interpretation of the information collected in this area:

  From a paleoenvironmental point of view, the deposits located on the first level of the Reguerillo Cave, (Figure 3) indicate a decrease in the volume of water flowing through until finally the river Lozoya ceased to flow into the Reguerillo Cave. The important process of settling that then occurred may be related to drainage of the karstified massif whose local base level progressively sunk. The speleothemes correspond to deposits laid down during warm wet periods with periods of drought interrupting their growth. Later the infiltration in the karstified massif increased but without any important increase in the level of surface flows, until finally there is an important increase in flow causing at least two paleofloods.

  With the information currently available, it may be stated that the fluviokarstic deposits of the Pontón de la Oliva initiated sometime between the normal Gauss Magnetozone and the reverse Matuyama Magnetozone, at topostratigraphic position of +145 m above the present Lozoya river bed. Between the Lower and Middle Pleistocene they were located at topostratigraphic position of +40 m. (dated with fauna). This leads to the conclusion that at the end of the Pliocene, fluvial incision had already been initiated and that the Lozoya river bed descended 100 metres in 1 million years.

- Priego Area (Cuenca): The fieldwork and the isotopic analysis has now been completed. Work is now being carried out on interpretation of all these data. There are seven levels of terraces, the lowest one was formed during the late Würm-Holocene, and the next terrace in the Eem (Riss-Würm interglacial). Five samples have been taken for AAR dating and six for dating by means of ESR techniques.

- Río Blanco Area (Soria): Both the fieldwork and the isotopic analysis of 95 samples have now been completed, the results of the latter now being available. Work is now being carried out on correlation between the isotopic data with the environmental interpretation derived from field sedimentology and analysis of seventy thin sections. The first palynological analyses have been received. Two samples have been taken for AAR dating and seven for dating by means of ESR.

- Bañolas Area (Gerona): The fieldwork has now been completed. Three hundred samples have been collected from one borehole (130,000 BP-present), one hundred of which have been sent for isotopic analysis. Three samples were taken for AAR dating and seven more for dating by means of ESR. Dr. David Brusi of the University of Tarragona has joined the project and has provided columns and samples of the area from his recently submitted Doctorate Thesis, from which twenty-two samples have been taken for isotopic analysis.

- Other Areas: Several sites with remains of Ursidae have been visited to collect samples for ESR dating, (Troskaeta, Santa Isabel and La Pasada). One hundred samples have been sent for dentine carbon and oxygen isotope analysis.

Task 4: Climatic reconstruction of the last thousand years in Spain on the basis of dendrochronological series.

Figure 4 shows the spatial distribution and current situation of each of the available chronological series, and reflects the larger number of synchronized chronologies at both local and regional level. In total there are 13 series now ready for standardization and continuation of the reconstruction process.

Up to date, the data collected indicates that the most significant variables as regards to the relationship between climate and growth are: in the North-Western area (Rogueira), the Summer temperatures (June to September) tend to be most significant, while in the central mountain chain (Navacerrada and Cuenca) the most significant variables are Spring and Summer rains. In the area of the Iberian massif (Soria) both variables are outstanding, with Summer rainfall and Autumn temperatures being those with the greatest influence.

Task 5: Paleoenvironmental reconstruction and construction of future evolution scenarios.

One of the objectives of this task is the paleoenvironmental reconstruction of a paleosite during the last 120,000 years. The paleosite chosen is located in the Tajo River Basin, near the Jarama River (Figure 1). Expect, an expert system developed by BRGM, is being used for this purpose.

The methodology used in the reconstitution is as follows: 1) Identification of the relevant geological phenomena that have acted at the paleosite during the last 120,000 years. 2) Conceptual model. 3) System simulation. 4) Model calibration. Up to date, phases 1 and 2 are almost completed and phase 3 has just begun.

The most relevant geological phenomena considered at the paleosite are:

- On a large scale the phenomena considered are sea level fluctuations caused by freezing and melting of glaciers worldwide and annual mean temperature variations.
- On a regional scale, the Jarama River, a Tajo River tributary, appears to have had an important role in the morphogenesis and evolution of water courses. In addition, the Jarama River is a discharge zone. All these factors have weighed heavily in the consideration of the geologic phenomena at the paleosite, some of which are shown schematically in Figure 5.

List of Publications.

Torres, T., Cobo, R., Hoyos, M. Mansilla, H., Soler, V. y Coello, F.J. (1993): "Sedimentología, magnetoestratigrafía e isotopía de los depósitos fuvliokársticos de la Cueva del Reguerillo (Patones, Madrid). Interpretación paleoambiental". Comunicación presentada en la XV Sesión Científica de la Sociedad Geológica de España (Octubre 1993).

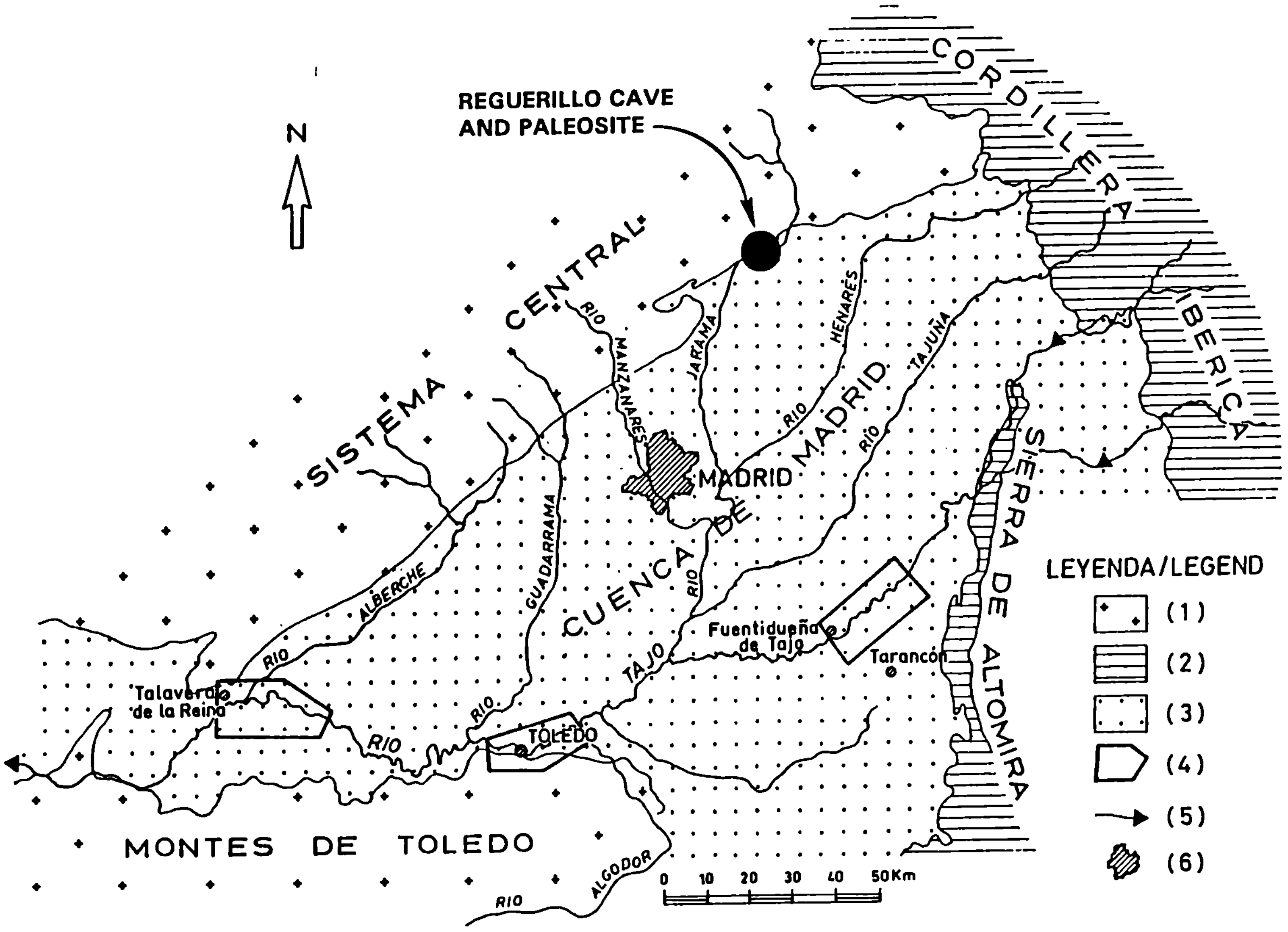
Torres, T., Cobo, R., García Cortés, A., Hoyos, M., García Alonso, P. (1993): "Cronoestratigrafía de los depósitos fluviokársticos del Cerro de la Oliva (Patones, Madrid)". Comunicación presentada en la XV Sesión Científica de la Sociedad Geológica de España (Octubre 1993).

Torres, T. y Guerrero, P. (1993): "Análisis multivariante de la morfología de los metapodos de los osos espeloides del Pleistoceno Ibérico: Ursus denningeri VON REICHENAU y Ursus spelaeus ROSENMÜLLER - HEINROTH". 9as Jornadas de la Sociedad Española de Paleontología.

Cobo, R. y Torres, T. (1993): "El Programa Eliequi de dibujo de elipses equiprobables. Aplicación biométrica al material de oso de la Cueva R-27 del Karst del Cerro de la Oliva (Torrelaguna, Madrid, España Central)". 9as Jornadas de la Sociedad Española de Paleontología.

Defaut, B. and Peaudecerf, P. (1993): "Paleoenvironmental evolution during the Quaternary in the context of Europe and Western Mediterranean Regions".

Barettino, D. and Torres, T. (1993): "Synthesis of the environment in Spain over the last two million years".



Areas de trabajo en el Valle del Río Tajo. LEYENDA. (1) Precámbrico y Paleozoico, (2) Mesozoico, (3) Cenozoico, (4) Zonas Seleccionadas, (5) Ríos Perennes, (6) Núcleos urbanos.

LEGEND. (1) Precambrian and Paleozoic, (2) Mesozoic, (3) Cenozoic, (4) Areas of Quaternary fields works in Tajo River Valley, (5) Perennial Rivers, (6) Towns.

Figure 1. Field sites for Task 2. Paleosite and Reguerillo Cave locations

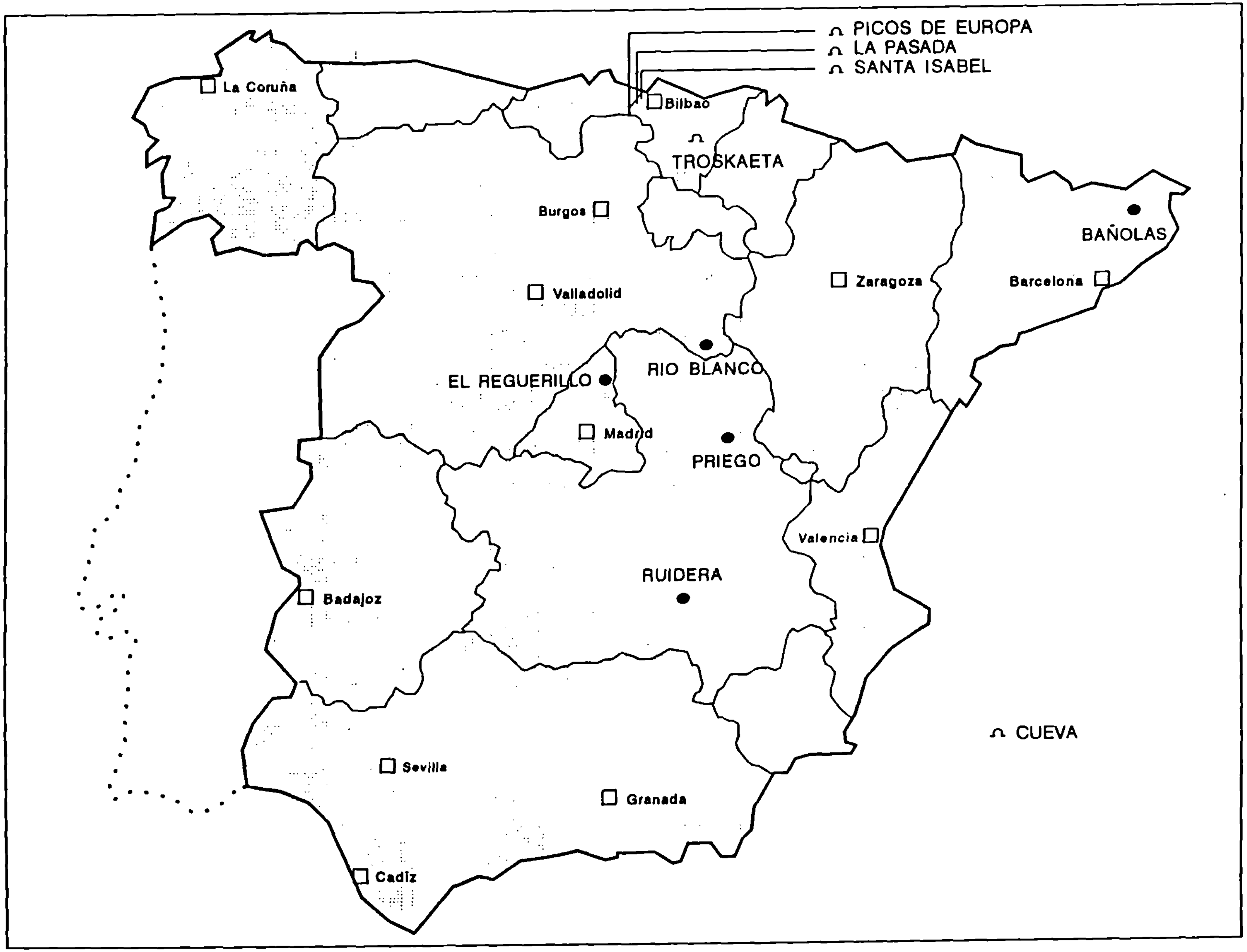
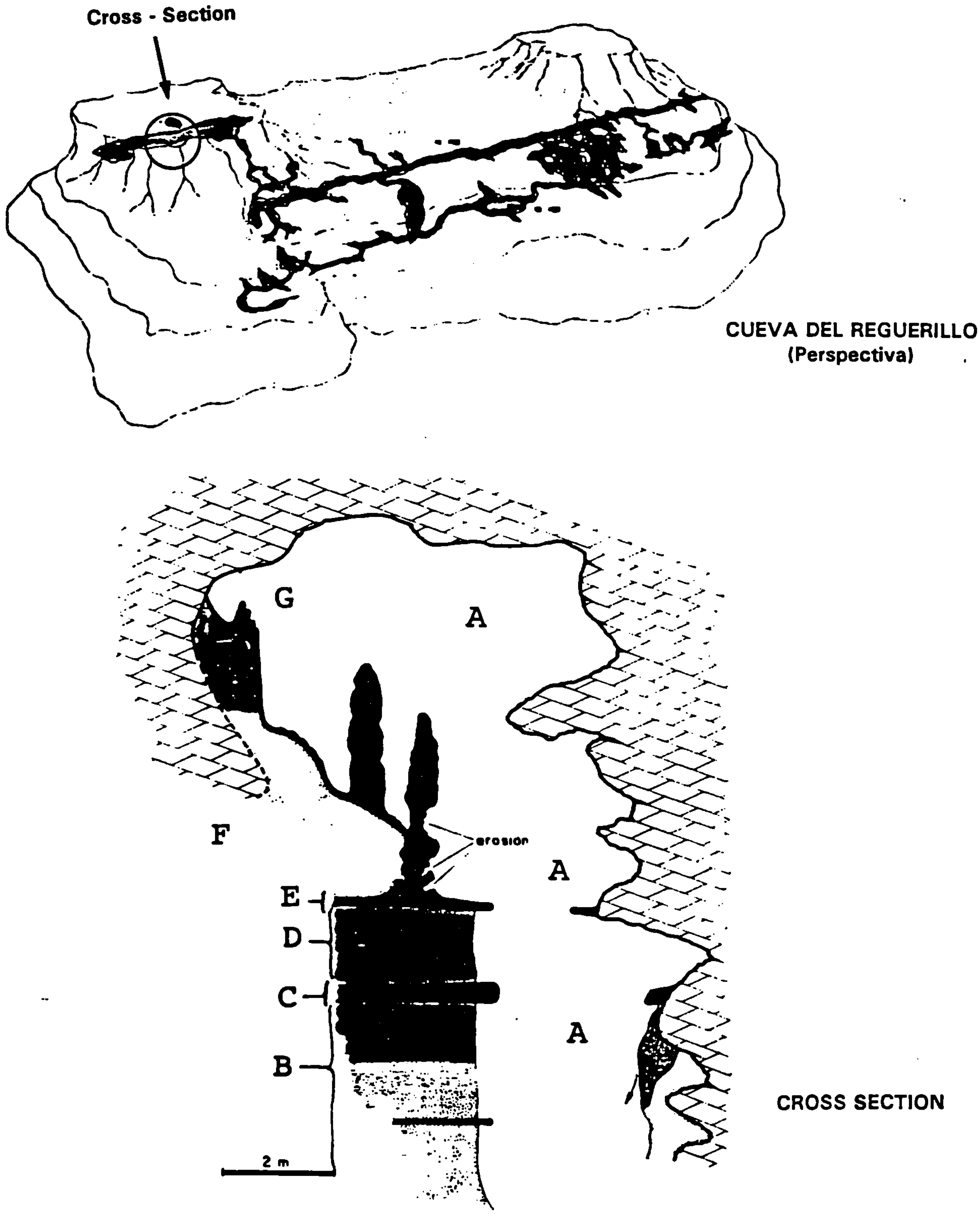
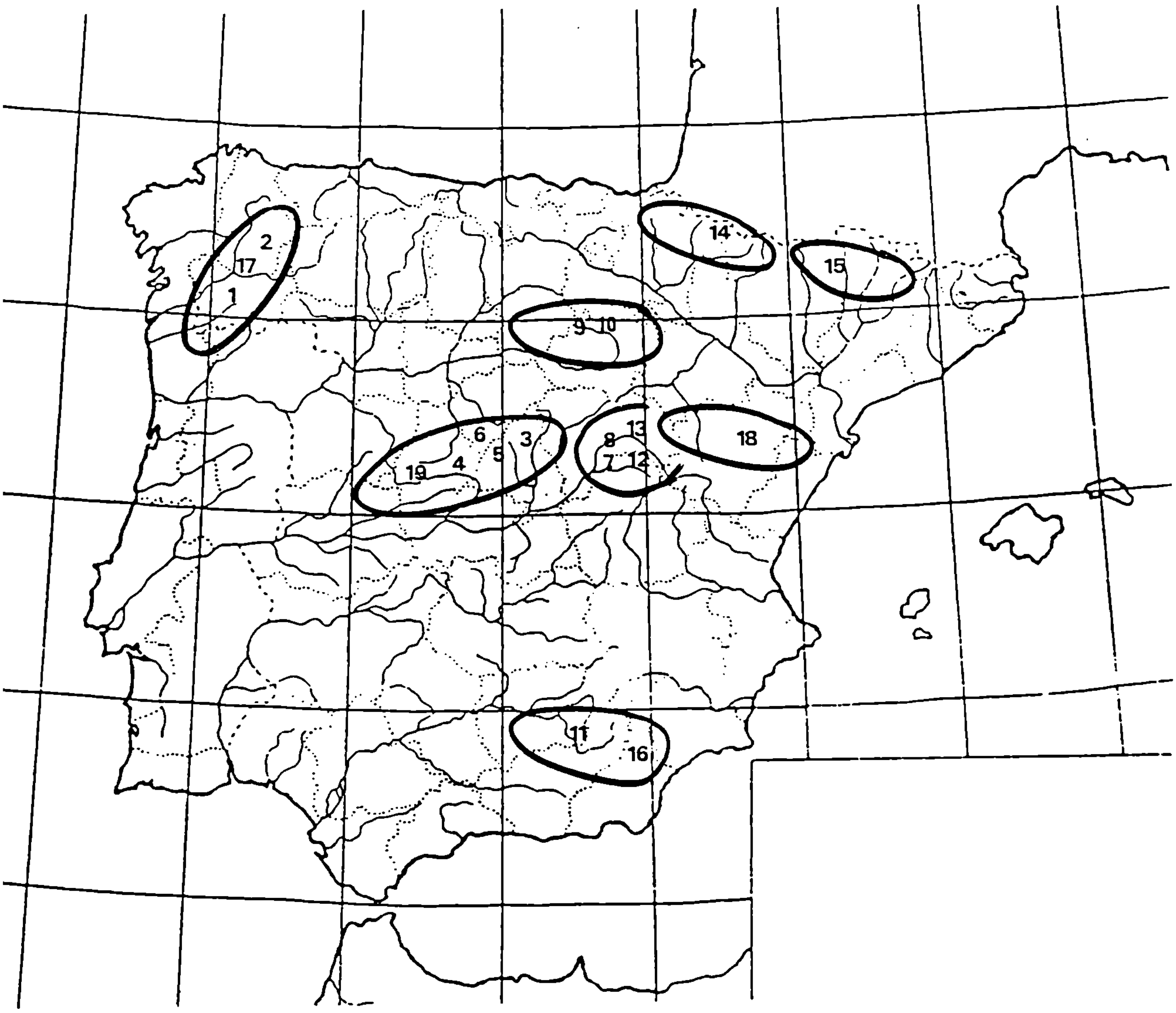


Figure 2. Field sites for Task 3.



A: Karst development during the late Cenozoic, under "covered karst" conditions and phreatic functioning. B: First karst deactivation and almost immediate capture of "Paleo Lozoya River". Karst functioned under vadose conditions. Allochthonous deposits. Upper Pliocene. C: Sedimentation break (stalagmitic floor) containing Plio-Pleistocene boundary (Matuyama inverse). D: Local reactivation of this part of the karst under vadose and autochthonous conditions. E: Thick stalagmitic floor (stalagmites too). F: Large fluviokarstic (allochthonous) reactivation, older stalagmites were eroded. G: Latest stalagmitic deposition after general retouching of preceding cave infill.

Figure 3. Reguerillo Cave. Cross section.



Synchronized Chronologies

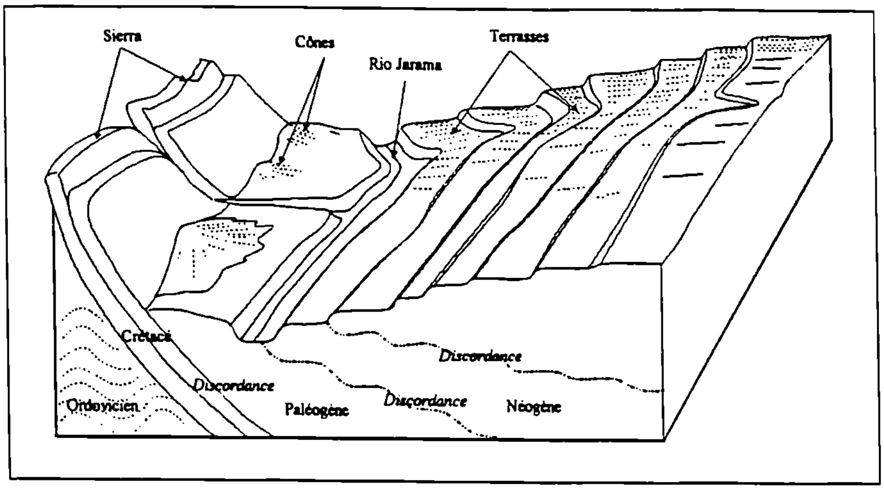
1. Invernadeiro. 2. Ancares. 3. Peñahorcada. 4. Riscopol
5. La Peñota-Molinos. 6. Sietepicos. 7. Torretón.
8. Tierramuerta. 9. Covaleda. 10. Vinuesa. 11. Cazorla.
17. Rogueira. 18. Peñarroya.

Chronologies to be Synchronized

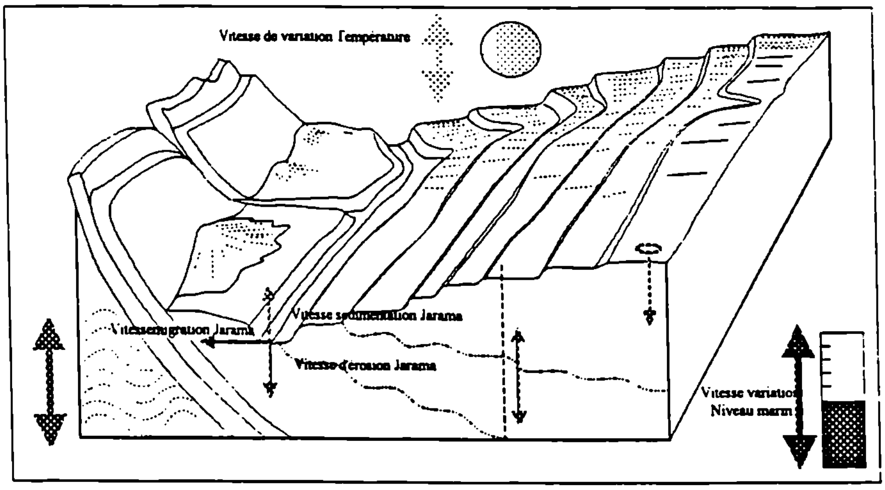
12. Alto Tajo. 13. Boquerón. 14. Larra.
15. Aigües Tortes. 16. Filabres. 19. Andrinal.

Figure 4. Field sites for Task 4.

Schéma géologique et morphologique du paléosite



Vitesses des phénomènes



Position des phénomènes et des variables pris en compte

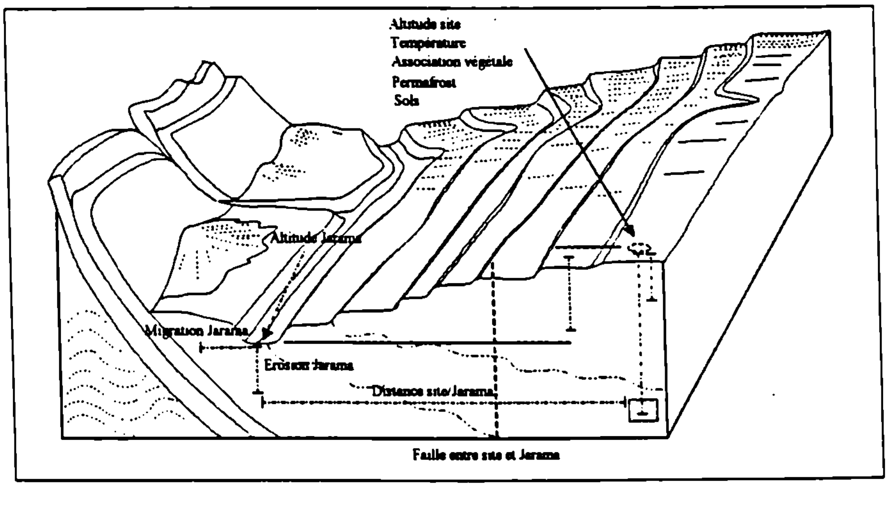


Figure 5. Conceptual model of Paleosite.

WATER FLOW AND SOLUTE CONVECTION THROUGH FRACTURED ROCK

Contractor: United Kingdom Nirex Ltd
Contract No: F12W/0078
Duration of Contract : February 92 - December 93
Period covered : January to December 1993
Project leader . Ms A K Littleboy

A. OBJECTIVES AND SCOPE

The scope of this project is to show that the experimental and theoretical methods, which have been developed for field measurements at research sites in Cornwall and for long term prediction of water flow and radionuclide transport in fractured rocks, can be used at Sellafield to investigate the suitability of this site for waste disposal.

The objectives are

- to quantify the extent to which water movements through the fractured basement rocks at Sellafield occur by flow through large numbers of small fractures amenable to statistical description, as opposed to permeation throughout the bulk of the rock and/or flow through only a few large faults;
- in the case of flow through many small fractures, to prove that the fracture data for both flow and transport required for site assessment can be obtained by the methods developed for Nirex at the Cornish research sites;
- to provide at an early stage in the work at Sellafield, experience and guidance in the use of these methods in the site investigation.

B. WORK PROGRAMME

1. Drill core and hole logs will be examined to determine the depths, orientations and average spacing of fractures expected to take flow.
2. Double packers with a spacing less than this average will be used to make steady flow measurements contiguously down the hole.
3. If only a few (<1 in 3) tests give measurable flows, it will be assumed that most of the flows will have been into single fractures and the packer spacing will be accepted as suitable. If more tests give flows, the spacing will be reduced, if possible until the foregoing condition is satisfied.
4. Assuming that most flows are in single fractures, tests to determine the distribution of fracture conductivities as accurately as practical will then be made.
5. These data will be used in the stochastic, discrete fracture flow code NAPSAC to predict flows into long pressurised lengths of the hole with many fractures.
6. Corresponding measurements with double packers will be made to prove these predictions.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

A testing methodology for the transmissivity of fractures in the Sellafield basement rocks has been proposed and independently reviewed for suitability against the requirements to provide input data for the NAPSAC fracture network code. It is anticipated that the necessary fieldwork will be carried out in 1994.

Progress and results

The first task has been to define a methodology for determining the transmissivity of individual fractures in the Borrowdale Volcanics Group basement rocks at Sellafield, with the objective of providing input hydrogeological data for the stochastic fracture network code NAPSAC, which is to be used in the long-term prediction of water flow and radionuclide transport. This will be an essential input to the assessment of the performance of a waste repository at Sellafield. The NAPSAC code has been under development for a number of years, and has been extensively tested at the Cornish research sites.

A methodology considered appropriate to testing the Sellafield basement rocks has been proposed, and has been independently reviewed. Two possible packer systems have been proposed, one a development of the wireline double packer system used at the Cornish site, the other a basically similar commercially-available system. The review has compared these in terms of their likely suitability and costs, together with general operational factors including sheathing of cables and hydraulic lines, and the importance of commissioning the tool under appropriate conditions. The review has considered the choice of borehole in which the work might be carried out.

Whichever system is chosen, the programme will involve isolating each fracture in the selected borehole individually by means of the double packer system. It is envisaged that the system will be configured with a constant length test zone throughout the programme. Based on currently-available data on fracture spacings, a test zone of approximately one metre is proposed, the packer system to be located such that the fracture to be tested is in the middle of the zone.

The details of the test procedure are dependent on the design of packer system, not yet finalised, and on the actual transmissivities found. In general, the methodology for determining lower transmissivities, quantitatively down to 10^{-11} m^2s^{-1}, and qualitatively down to 10^{-12} m^2s^{-1}, is the pulse test, in which the pressure in the test zone is instantaneously raised or lowered, and the pressure decay then monitored as a function of time. At transmissivities greater than 10^{-9} m^2s^{-1}, where leakage to the formation would become significant during application of the pulse, a constant rate of injection or withdrawal technique is used.

The major flowing fractures in the Sellafield BVG have transmissivities up to 10^{-6} m^2s^{-1}, but for this programme the interest is in fractures carrying lower flows, 10^{-8} m^2s^{-1} and below. The prime purpose of the review has been to consider the suitability of the test techniques and procedures for the measurement of fractures of these transmissivities, in particular those at the low end of the range, down to 10^{-11} m^2s^{-1} and below. This will determine the strategy defining the borehole conditions and equipment that are required.

The delay in initiating the fieldwork has arisen from the need for sufficient assurance that the equipment specification and choice of borehole would be appropriate to the task. An extension to the contract to the end of 1994 has been requested, which should allow a generous contingency against any further delays in conducting the fieldwork.

GEOCHEMICAL VALIDATION OF SOLUTE RESIDENCE TIMES: REVIEW AND COMPARISON FOR VARIOUS GEOLOGICAL ENVIRONMENTS

Contractor	:	United Kingdom Nirex Limited and NERC.BGS
Contract N°	:	F12W/0092
Duration of contract	:	from 1 April 1992 to 31 March 1995
Period covered	:	January 93 - December 93
Project leader	:	Dr P J Hooker (UK Nirex - Coordinator) Dr R Metcalfe (NERC.BGS)

A. OBJECTIVES AND SCOPE

The scope of the project is to assess the uses of geochemical and isotopic techniques in the estimation of groundwater movements over the long time-scales appropriate to the disposal of radioactive waste in various and 'reference' hydrogeological environments. The objectives are:

- to compile relevant geochemical data for various European hydrogeological environments from different sources;
- to review the validity of these data under the various hydrogeological and geochemical conditions and their consistency with hydrodynamic information. The review will highlight the contrasts between the geological and hydrological histories of the various European locations (e.g. structure, tectonics, permeabilities, climate etc);
- to assess the concept of 'reference' hydrogeological environments to illustrate principles, features and limitations of groundwater residence time estimations;
- to identify specific data needs, 'gaps' and uncertainties.

B. WORK PROGRAMME

1. Review of the literature for methods and data for estimating solute and groundwater residence times in various hydrogeological environments.
2. Discussions and collaboration with appropriate European research groups concerned with radioactive waste repository investigations and groundwater tracer techniques.
3. Gaining new data from measurements in European laboratories on samples from (a) investigations being carried out by UK Nirex Ltd., if available, and (b) other appropriate groundwater systems.
4. Reporting on the different stages of work as they are completed. The expected reports comprise two review reports, a progress report on new data and a final report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

In 1993, the work programme has mainly been focused on completing the review of the scientific basis of each geochemical and isotope method used for estimating groundwater residence times. The first review report on methodologies has been submitted for approvals. It outlines for each method the systematics and assumptions, the sampling techniques and precautions, the analytical procedures, the applications and interpretation and limitations. The necessity for an integrated strategy of estimating groundwater residence times for a hydrogeological system associated with a geological site for radioactive waste disposal is evident from the review. A library search for relevant papers in the literature produced about 350 references which have been entered into a database in Endnote^{TM}. A printout forms an appendix to the first review report. In 1994 a second review report will be produced on a selected number of hydrogeological case studies involving different rock types. This will include a review study of the Triassic clastic aquifers in the Paris Basin by BRGM. A study of sediment pore waters from Wast Water lake near Sellafiel ' was initiated as a sub-project.

Progress and results

1. Review of the literature for methods and data

A report has been produced in draft, and is awaiting final approvals. It is the first in a series of reports which together are aimed at assessing the uses of geochemical and isotopic techniques in the estimation of groundwater movements over the long time scales appropriate to the disposal of radioactive wastes. The aim of this report is to begin this assessment by reviewing all the various methods which are available for estimating the residence times at a variety of temporal scales. The approach has been to evaluate the concept of 'solute residence times' and then to review published work on each of the chemical and isotopic systems which may be used in estimating such times. During this process a bibliographical database has been maintained and this is presented as an appendix to the report. It includes 350 references entered into a database in Endnote^{TM}.

The concept of solute residence time links the concentration of a solute in an aquifer to the rate of solute input to, and removal from, that aquifer. The duration of solute residence is dependent upon the nature of the solute, with conservative solutes such as chloride having longer relative residence times than the more reactive solutes which are sorbed or precipitated from the groundwater. Therefore, there is no 'system' residence time and it is necessary to evaluate residence times for as many of the solutes present in a groundwater as possible in order to interpret the history of that water and ultimately to estimate a time since it entered the rock system of interest.

The various methods available for estimating solute residence times may be divided into two groups: 1. those which allow estimates of absolute times; and 2. those which are of indirect value in estimating residence times and which allow estimations of relative residence times. The applicability of a given method is in turn dependent upon the nature of the solute, with methods of the first type being applicable only to solutes which have a known and invariant time-dependent property such as radioactive decay, associated with them. Methods of the second type are applicable where the general nature of the processes controlling addition or removal of a solute to or from a groundwater are known, but where the rates of these processes are not predictable. For example, in silicate aquifers Cl is relatively unreactive and hence conservative, so that it will tend to have a longer residence time than Na, which may interact significantly with silicates during processes such as the albitisation of feldspars and cation exchange with clays. Additionally, there is a group of techniques which are of intermediate character, in that they allow limits to be placed on residence times but not absolute numerical values. For instance, the use of tritium falls into this category since the presence of tritium abundances greater than c. 25 TR (tritium ratio) indicates a groundwater 'age' of less than c. 30 years.

The report is divided into sections, each of which reviews the principles, applications and limitations associated with estimating the residence times of solute components in one chemical system. The techniques which may be used to estimate absolute residence times are considered first, followed by techniques which are more qualitative. Thus, radioactive isotopes are considered initially, with those which are produced predominantly in the atmosphere (^{3}C,^{14}C, ^{36}Cl, ^{129}I) being considered before those which are produced predominantly in the subsurface (^{4}He, ^{78}Sr, U-series). Techniques which employ noble gases make use of isotopes which fall in both of these categories and are considered in between techniques which use atmosphere-generated and subsurface-generated isotopes.

The qualitative techniques are divided into those which employ stable isotopes (^{16}O, ^{18}O, ^{1}H, ^{2}H, ^{10}B, ^{11}B, ^{12}C and ^{13}C) and those which employ a solute property such as solubility (Cl, CFCs etc). The use of oxygen and hydrogen isotopes is of special significance since the concentrations of these in a groundwater solution are dominated by their abundances in the solvent (water). Therefore, a study of these isotopes in addition to the various solute parameters often enables a relationship to be established between the origins of the water and the residence times of its solutes.

The review concludes that an integrated interpretation of all available physical and chemical data for a given groundwater is necessary in order to estimate the residence times of solutes and the 'age' of a groundwater. Furthermore, there is no 'best' method by which to estimate a groundwater 'age' and all available methods must be applied together. However, for any given study some methods will give more appropriate 'ages' than others, although the relative merits of the different dating techniques will depend upon the particular groundwater-rock system which is under investigation and the nature of the problem being addressed. For these reasons it is perhaps more appropriate to develop groundwater dating strategies rather than groundwater dating methods.

In 1993, a second review task was initiated dealing with data from a selected number of hydrogeological case studies involving different rock types. Some case studies have already been described e.g. the Chalk system in southern England, the Lincolnshire Limestone of eastern England and the fractured crystalline hydrogeologies at Stripa, Sweden, and Carnmenellis granite in Cornwall, and sites in norther Switzerland, Canada and the USA.

2. Collaboration with appropriate European groups.

Dr J M Matray (BRGM Orleans) has been commissioned to produce a review of the Upper Triassic clastic aquifers of the Paris Basin. There are parallels with the Sherwood Sandstone aquifers in the UK. This complements the second UK review task referred to above.

3. Gaining new data.

The proposal to sample and analyse the pore waters of lake sediments from Wast Water, near Sellafield in England, in order to confirm the process of groundwater feed into the sediments from the underlying granite rocks has been approved and permissions have been granted for appropriate sediment cores to be collected from Wast Water. New measurements on the pore waters in 1994 should illuminate the nature of the groundwaters from the granitic basement; these same waters may be present in the zone of the proposed deep repository nearby.

4. Reporting.

The first review has been submitted for approvals to print. The second review report on case histories in different and mainly European hydrogeologies is in preparation for submission in 1994.

List of publications

M B Crawford, W G Darling, P J Hooker and R Metcalfe (in press). Geochemical validation of solute residence times: a review of the scientific basis for dating groundwaters. British Geological Survey Technical Report WE/93/4.

Title:	DECOVALEX project: modelling of thermo-hydro-mechanical behaviour for granite rocks
Contractor:	CEA/IPSN
Contract n°:	FI.2W-0111
Duration of contract:	3 years (from January 1st, 1992 to December 31st, 1994)
Period covered:	1993 (2nd year of contract)
Project Leader:	J.Cl. GROS, CEA/IPSN

A. *OBJECTIVES AND SCOPE*

The objective of DECOVALEX project, (international co-operative project for the DEvelopment of COupled models and their VAlidation against EXperiments in nuclear waste isolation), is to increase the understanding of the various coupled thermo-hydro-mechanical processes of importance for radionuclides release and transport, from a repository to the biosphere and how they can be described by mathematical models.

This project has launched in 1991 by the Swedish Nuclear Power Inspectorate (SKI), and include nine funding organizations and one funding party, (CEC).

The work presented in this report concerns the 1st phase and part of the 2nd phase of the international DECOVALEX project.

The DECOVALEX project is composed in its first phase, (October, 1991 to September, 1992) of two bench mark-tests and one test-case. The first bench mark-test, (BMT.1) is a far-field study of a fractured rock mass, the second one is a near-field study of a reduced number of fractures, (BMT.2), and the test-case study the real behaviour of a single fracture, (TC.1).

In its second phase, (October, 1992 to September, 1993), the project is composed of one bench mark-test and two test-cases. The bench mark-test is a near-field study of a very fractured rock mass, (BMT.3), the two test-cases respectively concern the behaviour of a single fracture, (continuation of TC.1) and the thermo-hydro-mechanical experiment of Fanay-Augères, (TC.2, phases 2 and 3).

Results presented in this report concern the first bench mark-test BMT.1 "Far-field model", the second test-case (TC.2) "Fanay-Augères THM experiment", and a short exercise: "Booker & Savvidou's analytic solution" prepared by AECB, Canada.

B. *WORK PROGRAMME*

1- Bench mark-test n°1 (BMT.1) "Far-field THM model":

This bench mark-test is proposed by M. Durin, (CEA/DMT, France) and by H. Baroudi, (INERIS, France). This two-dimensional bench mark test is designed to simulate the THM processes in a large jointed rock mass with a repository located at a depth of about 500 meters. The objective of this test is to examine the thermal, hydraulic and mechanical effects of the repository on its far-field environment.

The model measures 3000mx1000m. The rock mass is made of an elastic rock cut into numerous blocks by two sets of orthogonal fractures, (figure n°1). A non uniform hydraulic head is imposed on the lateral boundaries and at the bottom. The heat flux from the repository is assumed to decrease exponentially with time.

A constant initial temperature is specified within the model, including the top surface.

The better approach to model the fractured rock mass is to represent each of the fractures: this is the discrete approach. One method has used within this approach: the Finite Element Method (FEM) in which the blocks are discretized by means of standard continuum finite elements, and the discontinuities by means of joint. A purely quasi-static version of the equilibrium equations is used for the mechanical aspects.

Three computer codes based on the discrete approach, and developed by the Ecole Nationale Supérieure des Mines de Paris, were tested:

- CHEF, to thermal analysis,
- HYDREF, to hydraulic analysis,
- VIPLEF, (visco-plastic model), to mechanical analysis and couplings.

These three codes were developed by the Ecole Nationale Supérieure des Mines de Paris.
A joint-element taking into account both a thermo-hydraulic approach by a quadratic estimation of the density, the viscosity and the temperature of the fluid, and a hydro-mechanical approach by a quadratic estimation of the joint aperture, was added to the HYDREF code.
The final report of the bench mark-test n° 1 was issued in June, 1993.

2- Fanay-Augères THM experiment, (TC.2)
This experiment has been carried out by the CEA/IPSN, from 1985 to 1988, with the financial support of the CEC. This is the CEA/IPSN proposed test-case n°2 (TC.2) for phases 2 and 3 of the DECOVALEX project.
The aim of this experiment was to study the effects of the heating on fractured and unsatured granite rock mass, and to validate and improve computer codes. The laboratory was located 100m below surface in the Fanay-Augères uranium mine worked by COGEMA.
Rock mass investigated for the experiment, comprised a volume of granite 10mx10mx5m thick serving as the base of the experimental laboratory, (figure n°2).
The work programme of TC.2 is as follows:

- development of tridimensional hydro-mechanical joint taking into account the thermal variations of the rock environment. The discontinuities are modeled using special joint finite elements,
- determination of principal characteristics of fractures for joint modeling,
- geometric definition of discontinuities allowing mesh of fractures by finite elements method: geometry, aperture, roughness, mechanical parameters of fractures,
- hydraulic description of fractures: channelling and connecting,
- thermo-hydrological coupling taking into account heat transfer by convection,
- search of tension behaviour laws in compression and in shearing taking into account the displacement of the rock matrix,
- search of the connection between stress-strain and mechanical aperture - hydraulic aperture for mechanical behaviour modeling.

3- Modeling of thermo-hydro-mechanical coupled phenomenon in continuum medium: Booker & Savvidou's analytic solution.

- Development of a new coupling methodology for modeling consolidation phenomenon, in saturated porous medium,
- Validation of coupling between three codes, (CHEF, HYDREF, VIPLEF).

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

- *State of advancement*

1- Bench mark-test n°1 (BMT.1): "Far-field THM model"
We chose to model the rock mass by a discrete approach, i.e. by representing all the blocks and the discontinuities.
Three two-dimensional finite element codes were used by the Ecole Nationale Supérieure des Mines de Paris, (ENSMP) for the BMT.1.
The following hypothesis have been made:

- the blocks are impervious (zero porosity and zero permeability), and the water is flowing only in the discontinuities of the rock,
- convective heat transfer in the discontinuities is neglected,
- the discontinuities are modeled using special finite elements joint,
- for the mechanical behaviour, the joint opening can be positive or zero, but never negative.

Blocks are not allowed to interpenetrate.
This bench mark-test finished in 1993. Publication of the results, in the" International Journal of Rock Mechanics and Mining Sciences & Geomechanical abstract", is in progress. The aim of this paper is to compare the results obtained by two approaches in modeling the THM response of the fractured rock mass: the discrete approach and the continuum one.

2- Fanay-Augères T.H.M. experiment (TC.2)
Most of the time used for this study was dedicated to the hydraulic description of fractures and to the development of tridimensional hydro-mechanical joint taking into account the thermal variations of the rock. This test-case will be carried out in 1994.

3- Modeling of thermo-hydro-mechanical coupled phenomenon in continuum medium: Booker & Savvidou's analytic solution.
The aim is to develop a coupling methodology for modeling consolidation phenomenon in infinite and elastic saturated porous medium, around heating cylinder. This exercise was carried on the second half-year 1993.

- ***Progress and results***

1- Bench mark-test n°1 (BMT.1): "Far-field THM model"
The study of the BMT.1, modeling by discrete medium allows to distinguish three zones:

- above disposal: shearing along joint facing at 60°; normal aperture and sometimes important aperture of fractures facing at 150°,
-near disposal: dilation of blocks and closing of joints during the first 100 years, then return to normal conditions with little fluid flow.
- the other parts of the model have continuum medium behaviour with no influence on the water flows.

The most important influence of the disposal on the host-rock takes place in the 430m between the disposal and the surface. Important perturbations are observed: displacements, stresses variations, increase of permeability between the storage and the surface. The influence of disposal on the rock brings about serious damage as far as 500 years. After 500 years, the heat anomaly will be smaller and also less localized.
Figures n° 2, 3 and 4, show some results of this exercise.
The thermo-hydro-mechanical coupling shows the critical influence of hydraulic effects which drastically increases strains and fluid flows, and the irreversible perturbations near the disposal zone.
The bench mark-test n°1 (BMT.1) has shown the importance of joints on the rock mass behaviour, with regard to the mechanical effects, (rock blocks rotation, moving locking, important aperture of joints...), and with regard to the hydraulic effects, (flow perturbations around the disposal zone, flow cancelling in some joints by rotation and closing of blocks...).
The introduction of a joint element in blocks finite elements calculations, was proved efficient
Some restrictions for discrete approach appears:

- the numerous joints induce a long time of calculations,
- the joints hydraulic model where the flow is a fonction of cubic aperture induce a great variation of flow for a little aperture variation of fracture.
- in the bidimensional model, the fractures system is prolonged indefinitely in the third dimension. It's necessary to use a three dimensional model to have a more realistic approach.

2- Fanay-Augères T.H.M. experiment, (TC.2)
Most of the time used for this study was dedicated to the development of tridimensional hydraulic joint to take into account the connecting of fractures system and the initial shape of deforming blocks.
The principal idea is to uncouple thermical calculations as in the BMT.1 exercise.
The essential thermal phenomenon is the wastes disposal heating. Convection is neglected.
The objective of the study is to resolve a tridimensional problem by hydro-mechanical coupling in joint, taking into account the temperature, with regard on mechanical phenomenon, (modification of rock characteristics, thermal behaviour), and with regard on hydraulic phenomenon, (modification of water characteristics).
We mean to do calculations as follows:

- temperature calculations,
- displacements and stresses calculation to infer the hydraulic aperture of the fractures,
- flows and pressures calculation,
-stresses modifications caused by the introduction of pressure in the joints,
- looping of the calculations as far as results stabilization.

3- Modeling of thermo-hydro-mechanical coupled phenomenon in continuum medium: Booker & Savvidou's analytic solution.
The three bidimensional codes, VIPLEF, HYDREF and CHEF, based on the finite elements method, can be associated for a thermo-hydro-mechanical calculation in a saturated porous medium. If the temperatures story is known, the hydro-mechanical coupling is completely carried out: effect of pore pressure on stresses and effect of stresses on water drainage out of the saturated medium.

This coupling is possible by an iterative process between HYDREF and VIPLEF. This process converge rapidly and give good results which are compared with an other well known analytic solution.

List of publications

DECOVALEX
Memorandum - 3rd Meeting of the Steering Committee, Berkeley (USA), March 10, 1993.

DECOVALEX
Memorandum - 4th Meeting of the Steering Committee, Tokyo (Japon), October 28, 1993.

DECOVALEX
Memorandum - 2nd Workshop, Berkeley (USA), March 8-9, 1993.

DECOVALEX
Memorandum - 3rd Workshop, Tokai (Japon), October 26-28, 1993.

J.C. GROS (1992)
DECOVALEX - Phase III (TC.2): Fanay-Augères Thermo-Hydro-Mechanical (T.H.M.) experiment - Test-Case n° 2. Rapport SERGD 92/43.

A. BOUGNOUX, G. VOUILLE & J.C.GROS (1993)
Modélisation du comportement thermo-hydro-mécanique d'un massif granitique - participation au projet DECOVALEX. Rapport d'avancement n° 3 (1er semestre 1993). Rapport SERGD 93/58.

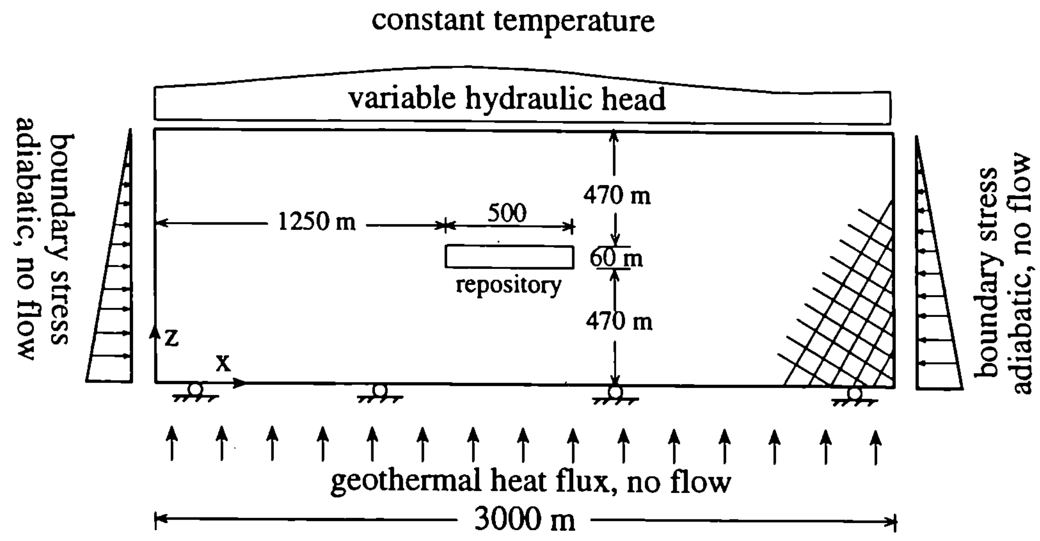


Figure 1: DECOVALEX - Far-field THM model (BMT.1): model geometry, fracture sets and boundary conditions

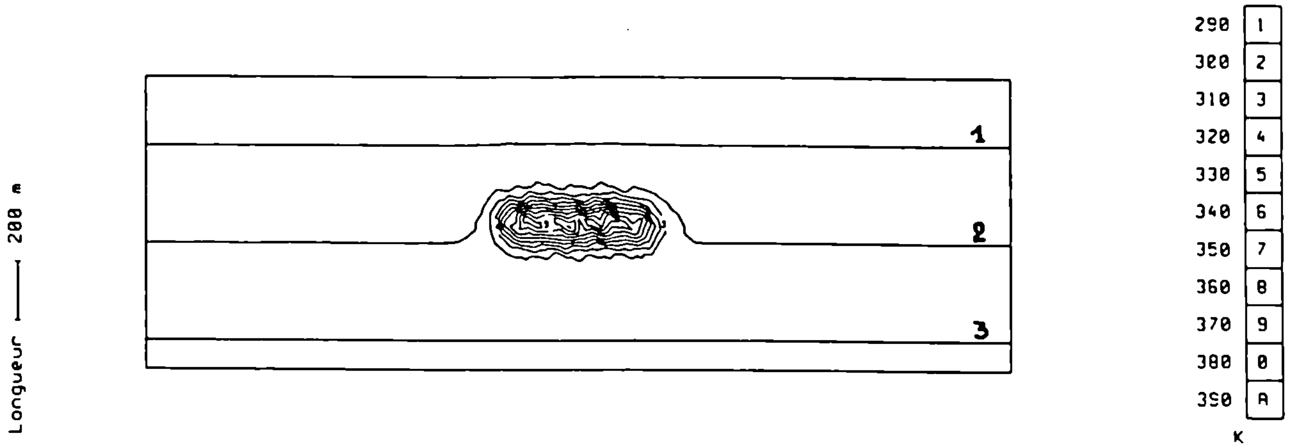


Figure 2: DECOVALEX - Far-field model - d = 100 m
Isothermal contours - Time t = 50 years - T max. = 392 °K

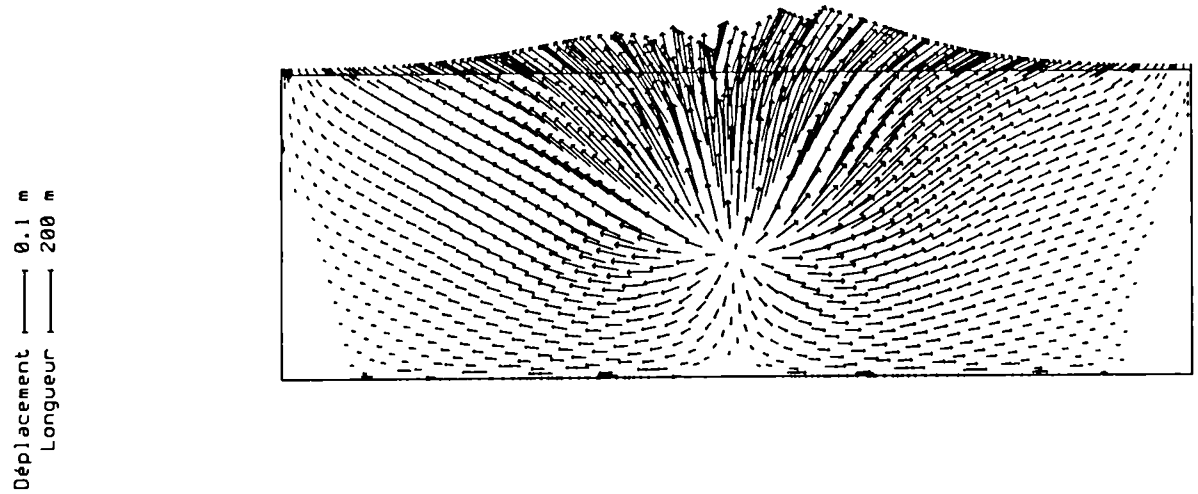


Figure 3: DECOVALEX - Far-field model - d = 100 m
Displacement vectors - Time t = 200 years - D max = 141.03 mm

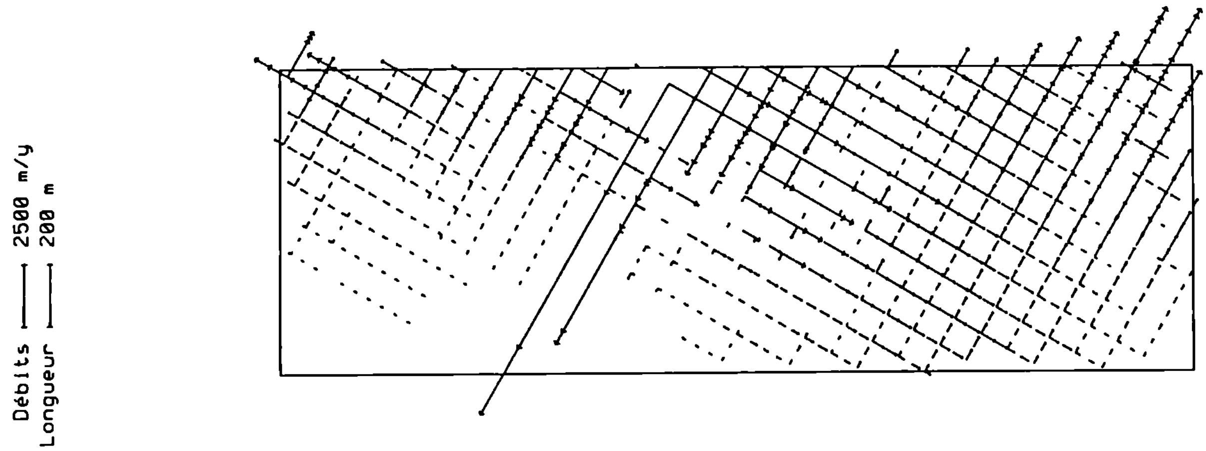


Figure 4: DECOVALEX - Far-field model - d = 100 m
Flow velocity - Time t = 150 years - V max = 15563.42 m/y

Title : Participation to the International cooperative project for the DEvelopment of COupled models and their VALidation against EXperiments in nuclear waste isolation - "**DECOVALEX**"

Contractors :
(1) Agence Nationale pour le gestion des Déchets RAdioactifs (**ANDRA**) - France -
(2) Commissariat à l'Energie Atomique (**CEA**)
Direction des réacteurs Nucléaires - Département de Mécanique et Technologie
- Service d'Etudes Mécaniques et Thermiques - France -
(3) INERIS
Groupe Géotechnique et Atmosphère Industrielle - Laboratoire de Mécanique des Terrains - Ecole des Mines de Nancy - France -
(4) United Kingdom Atomic Energy Authority (**AEA**)
Theorical Studies Department - AEA Decommissioning and Radwaste
Harwell Laboratories - United Kingdom -

Contract n° : FI2W-CT-91-113

Duration of contract : November 1991 to October 1994

Period covered : 1993

Project leaders : F. PLAS (ANDRA: Coordinator), M. DURIN (CEA),
H. BAROUDI (INERIS), A.H. HERBERT (AEA D&R)

A/OBJECTIVES AND SCOPE

Hydro-Thermo-Mechanical processes in jointed rock is very difficult task to treat but may be of importance in nuclear waste performance assessment. This called for an international cooperation in peer review for code developers, to develop a data base and to provide bench-mark tests and test cases of HTM processes. So DECOVALEX was born as an international coordinated project for three years (1991-1994) dealing with the study of coupled hydro-thermo-mechanical modelling processes in fracturated rock and associated computer codes /1//2/. The objectives of DECOVALEX are listed below.

- To support the development of codes for THM modeling.
- To investigate and apply suitable algorithmes for THM modeling.
- To investigate the capabilities of different codes to describe recent laboratory experiments and to perform code verification.
- To compare theory and model calculations with results recent field experiments.

The aim of the CEC contract FI2W-CT-91-113 is the participation of European research teams to the international DECOVALEX project. In order to increase the understanding of the various coupled THM processes in fractured hard rocks, three laboratories developing specific modeling concept are collaborating for this contract with the coordination of ANDRA:

- ▸ CEA/DMT using the equivalent porous media modeling concept with CASTEM/TRIO codes,
- ▸ INERIS using the discrete block network modeling approach with UDEC code,
- ▸ AEA D&R using the discrete fracture network modeling approach with NAPSAC code.

B/WORK PROGRAM

The DECOVALEX programme is composed for the following main phases:

Phase I (October 1991 - # march 1993)

Three exercices were defined: **(1)** Bench-Mark Test 1, called "Far field model" proposed by CEA/DMT and INERIS, **(2)** Bench-Mark Test 2, called "Multiple fracture model" proposed by AECL (Canada), and **(3)** Test Case 1, called "Coupled Stress-Flow model" proposed by NGI (Norway) /2/.

Phase II (# march 1993 - October 1993)

Two exercices were defined: **(1)** Test Case 2.1 as a revision of Test Case 1 of phase I and **(2)** Bench-Mark Test 3, called "Near field model" proposed by ANDRA, CEA, INERIS, AEA R&D and NGI /2//3//4/.

BMT3 is to simulate the processes in a fractured rock mass and improve the modelling approach to be applied to a tunnel above a heater in a repository. Three sequences are distinguished : Sequence 1 : Initial hydromechanical equilibrium, Sequence 2 : Excavation of a tunnel. back to a new hydromechanical equilibrium, Sequence 3 : Thermal loading while the tunnel is opened. The tunnel is located at 500 meters depth. The model measures 50 m x 50 m around the tunnel. The initial fracture network comes from Stripa data and contains more than six thousand discontinuities (figures 1 and 2).

Each research team involved may use any approach (continuum, discontinuum, other...) and make any simplification needed to solve the problem. But the modeling process must be clearly defined.

Phase III (# November 1993 - December 1994)

C/ PROGRESS OF THE WORK AND OBTAINED RESULTS

State of advancement

Two DECOVALEX workshops were taking place in 1993 : 2nd workshop on march 1993 at Laurence Berkeley Laboratory, Berkeley, United States /3//4/, and 3rd workshop on october 1993 at PNC Tokai works and Tokio, Japan /5//6/.

The phase I of DECOVALEX is now closed and CEA/DMT treated the BMT1 while INERIS treated the BMT1 and the BMT2. The final report of phase I was available in june 1993 /2/, but all the results and the first comparisons were presented and discussed at Berkeley. At this occasion it was decided to produce synthesis of each exercice for a special issue of International Journal of Rock Mechanics. These synthesis will have to be done by the research teams who defined the exercice. CEA/DMT was designed as the responsable for the BMT1.

The phase II of DECOVALEX started on march 1993. An officicial dead line is provided on october 1993 but some works will probably continue on 1994. For this phase CEA, INERIS and AEA R&D are only treating the BMT3.

Exercices for phase III were presented and discussed in Japan. They include: TC2 (Fannay-Augère Field test) proposed by CEA/IPSN, TC3 (BIG-BEN experiment) proposed by PNC, TC4 (Triaxial Test of jointed rock cores) proposed by STUC, TC5 (Direct shear - flow test) proposed by NRC and TC6 (Borehole injection test) proposed by KTH/SKI. INERIS, CEA/DMT and AEA R&D declared intentions to study respectively TC2 and TC6. No decision regarding CEA and INERIS was made in 1993.

Progress and Results

Phase I

All the results obtained with the original reference boundary conditions were presented at Berkeley. First comparisons revealed that in fact it was difficult to compare properly the results because all the teams didn't use similar boundary conditions. In particularly School of Mines of Paris changed the hydraulical heads at the top of the model in order to avoid a effect of Archimede upward thrust on blocks. By the way basic comparison of models and codes (numerical methods) appeared insuffisant and had to be studied thoroughly. That's why it was decided to define new hydraulic boundary conditions that could be acceptable by all the modeling approach and then to make new computations, only for the case of 100 meters fracture spacing.

The new modeling results were presented in Japan. Except those of Hazama research team (Japan) all computations are consistent and already give same orders of magnitude for temperatures, stresses and displacements. The comparison of hydraulic heads and water fluxes is more difficult. Studies are still going on and a first synthesis is provided at the beginning of 1994.

Phase II

a- CEA/DMT /8/

As CEA has done previously for the BMT1 Benchmark test, this team used a continuum approach, but one that is based on a fully coupled set of hydromechanical equations, taking into account the mechanical effects of pressure variations and the hydraulic effects of stress variations, among other processes. The coupled continuum equations can be summarily described as a combination of Darcy's law, and Biot's poro-elasticity equations, and classical conservation equations. The constitutive laws are being cast in their most general anisotropic form. The continuum coefficients to be used in the constitutive laws are determined based on a homogenization approach specifically developped for fractured rocks, an adaptation from *Oda 1986*, and other works.

CEA analysed the discrete fracture network data, and the resulting equivalent permeability tensor (scale dependence and spatial variability). As regards to teh REV scale, the 'Representative Elementary Volume' may be a square no smaller than 15 x 15 m. *At the scale of the domain*, the equivalent hydro-mechanical coefficients are necessarly constant in space. *Indeed the equivalent medium is mechanically non-orthotropic and hydraulically anisotropic.*

Then two basic simulations at the scale of the domain have been considered, both with spatially constant material properties:

(1) The case of an isotropic material of reference, not formally homogenized;

(2) The case of a non-isotropic, non-orthotropic material, with equivalent tensorial coefficients calculated by homogeneization at the domain scale (50 m scale).

When results of case (1) were compared with results of case (2) for the excavation phase, the effects of anisotropy of the rock-mass were clearly seen on the pore pressure distributions (figure 3). These effects are less pronounced on the displacements and still less on the stresses. The thermo-mechanical sequence, and the results themselves, are qualitatively similar to those for isotropic case, especially in terms of time evolution. However as in the excavation phase, the values of tunnel convergence obtained for the anisotropic case are significantly different from the isotropic case.

The modeling results are qualitatively similar to those of the others teams except for the tunnel inflows witch are greater (figure 4). So the following main topics will be addressed in future work:

- Correction of homogenization formulae for better representation of crack interaction ans crack connectivity, both hydraulically and mechanically.

- Numerical modeling of a heterogeneous anisotropic elastic medium, choosing a 5 m homogenization scale, in particularly around the tunnel.

- Comparison of the equivalent continuum properties with those obtained by other methods (UDEC...).

b- INERIS /8/

Due to the large number of fractures, UDEC obliged to simplify the network. Two zones were defined: a first zone, A, near the tunnel (20 x 20 around the origine) with the real fracture network and a second zone, B, with a two arbitrary sets of perpendicular fractures. Indeed in order to have a transition zone between the simplified network and the reference network, zone B was divised in two parts B1 and B2 with different fracture spacing, 2.5 metres and 5 meters (figure 5).

However for the zone A, two options were considered following the case that all the fractures with an hydraulic aperture below 3 μm were included or not.

For the zones B1 and B2 the Singh's relations has been used to determine the equivalent properties of the blocs (Young modulus, Poisson coefficient, fracture apertures). Some tests had been realized before with UDEC in order to evaluate the equivalent mechanical properties of the intact "fractured" rock-mass. It was found that the equivalent rock-mass could be considered as isotropic with a Young modulus reducing by a factor 3.

Despite the decrease of the number of fractures, INERIS found numerical problems to reach the new hydro-mechanical equilibrium in the sequence n°2. This led to reduce the time step but the computation time exceeded fifteen days. Indeed computation is still going on and any results can't be presented in 1993.

In order to avoid the numerical problems and obtain "short" computation times, INERIS would like later to use a new scheme developped by Cundall for the transient flow computation.

c- AEA R&D /8/

A discrete fracture network approach has been used by the AEA Technology team; The NAPSAC fracture network code has been used to model flow in the network after excavation of the tunnel up to equilibrium.

First the equilibrium flow field was calculated. An analytical solution was then used to evaluate the change of stress field imposed by the excavation of the tunnel (The Kirsh 2D linear elastic solution), and two stress-aperture (transmitivity) couplings were applied resulting in fractures opening and closing around the tunnel. The effect of using these differents stress models or no stress model at all the fracture properties of the network was fully investigate by comparing histograms of aperture and network aperture plots. The subsequent effect this has on the flow field was studied comparing graphs of tunnel inflow against time. *The mechanical effect of changes in pore pressure on the properties of the network and the thermal effects on the network were not modelled.*

The horizontal pressure profiles clearly showed that flow througth the two sides of the network was not symetric and that this was a feature of this particular realisation of the network (figure 6). The first coupling provided no great change in the flow field. The second coupling had a major impact on the network properties around the tunnel ans on the flow field. It resulted in the tunnel inflow decreasing by half. Despite the effect on the flow field, it was shown that for all the stress models used the timescales associated with the flow field were the same and these are in good agreement with those observed for experiments carried out at Stripa (figure 7).

AEA also studied different approaches to simplify the fracture network without consideration of hydro-mechanical effects. Effect of aperture distribution, symetry assumption and cut-off length were studied. The results showed that simplification of the model by deleting all fractures less than 2 meters reduces the inflow to the tunnel by one order of magnitude due to less well connected fracture network.

The works of AEA R&D on the BMT3 are now closed.

List of references

/1/ DECOVALEX Memorandum - 1st meeting of Steering Committee at Hotel Mercure, Paris, France - October 28, 1991.

/2/ DECOVALEX - Mathematical Models of Coupled T-H-M Processes for Nuclear Waste Repositories - Report of Phase I -
L. Jing, J. Rutqvist, O. Stephansson, C-F. Tsang, F. Kautsky
SKI Technical Report 93:31

/3/ DECOVALEX Memorandum - 3rd meeting of Steering Committee at Laurence Berkeley Laboratory,San Francisco, USA - March 10, 1993

/4/ DECOVALEX Memorandum - 4st meeting of Steering Committee at PNC Head Office, Tokio, Japan - October 29, 1993

/5/ DECOVALEX Memorandum - 2nd workshop at Laurence Berkeley Laboratory, San Francisco, USA - March 8-10, 1993

/6/ DECOVALEX Memorandum - 3rd workshop at PNC Tokai Works, Mito, Japan - October 26-28, 1993

/7/ DECOVALEX - 2nd Progress Report - CCE Contract n°FI2W-CT91-113, Rapport ANDRA 694 RP AND 92.003, May 1993

/8/ DECOVALEX - 3rd Progress Report - CCE Contract n°FI2W-CT91-113, October 1993

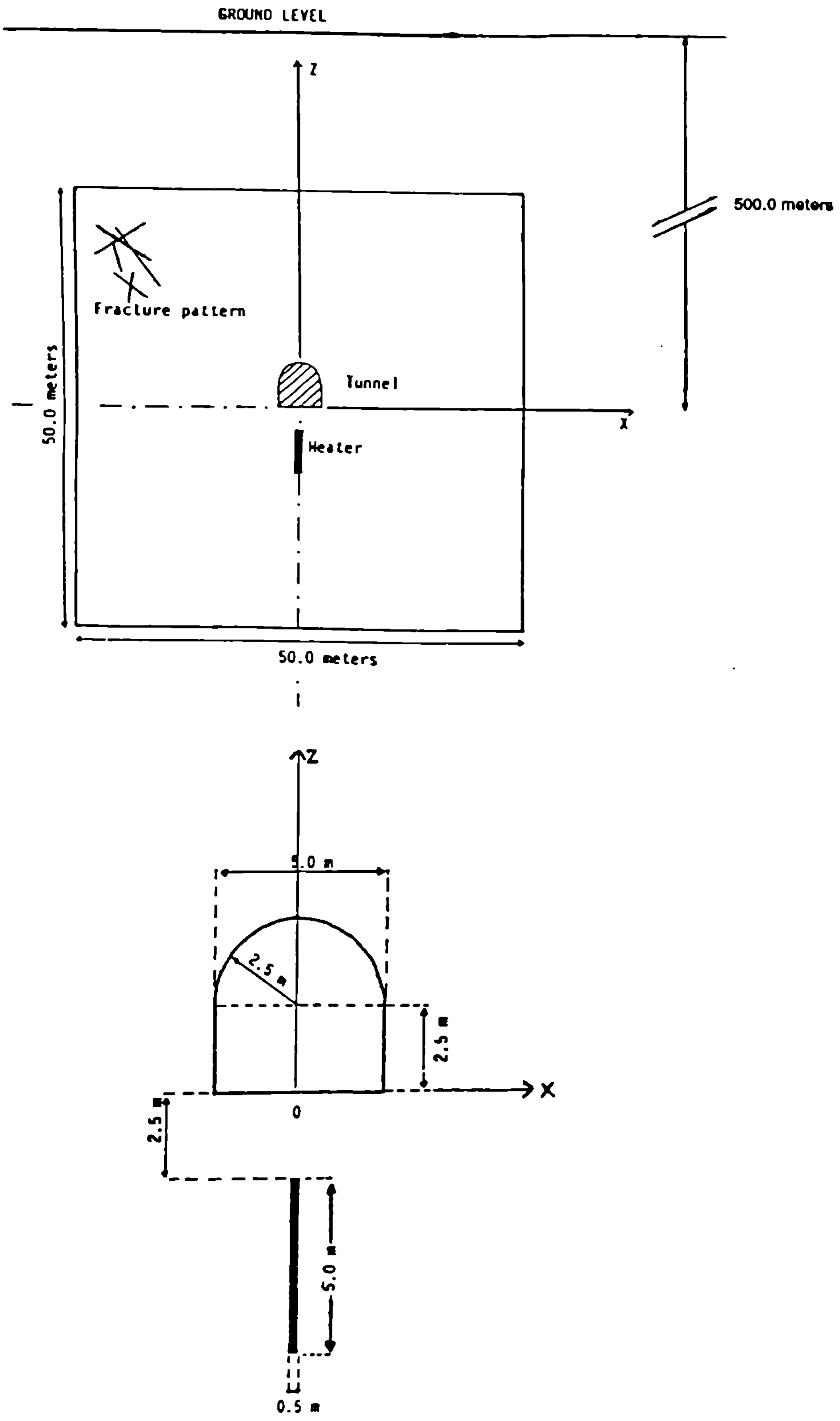


Figure 1 - The geometry, dimensions and coordinate system of the Near Field Repository model with a tunnel

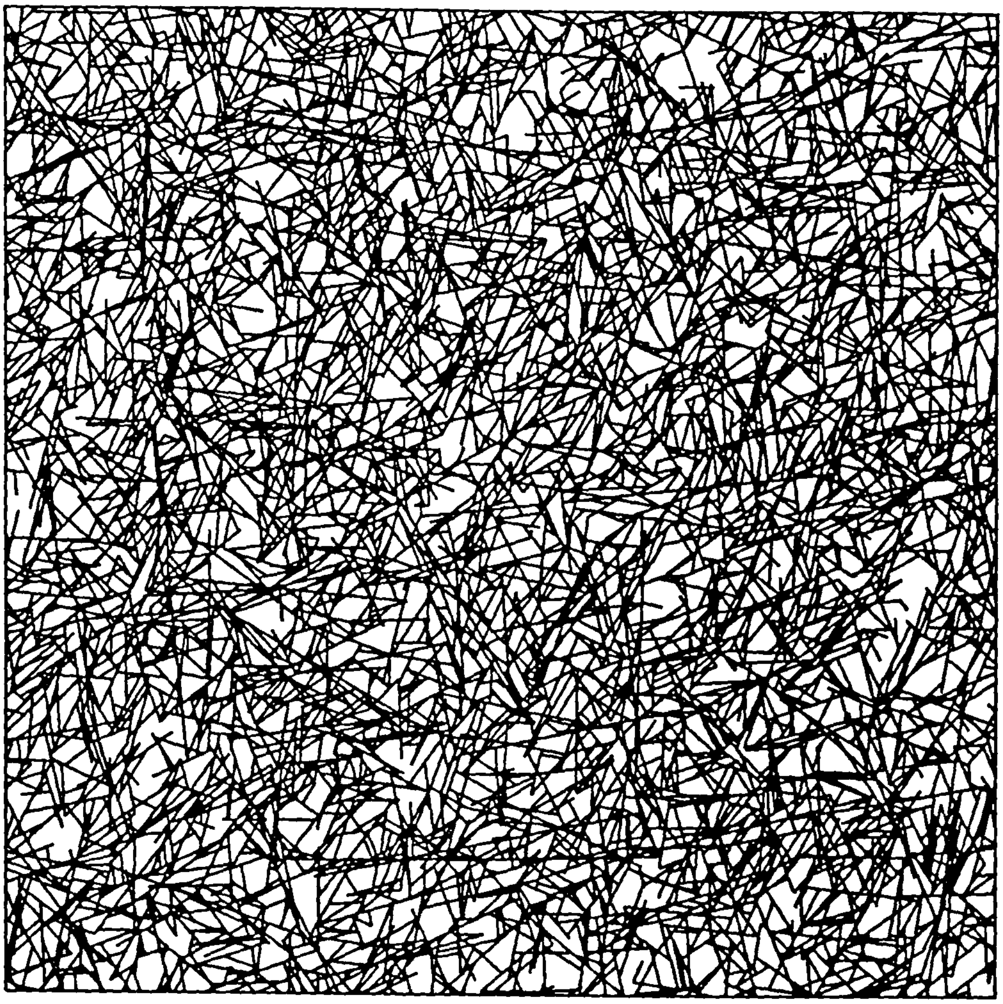


Figure 2 - The reference network of the BMT3

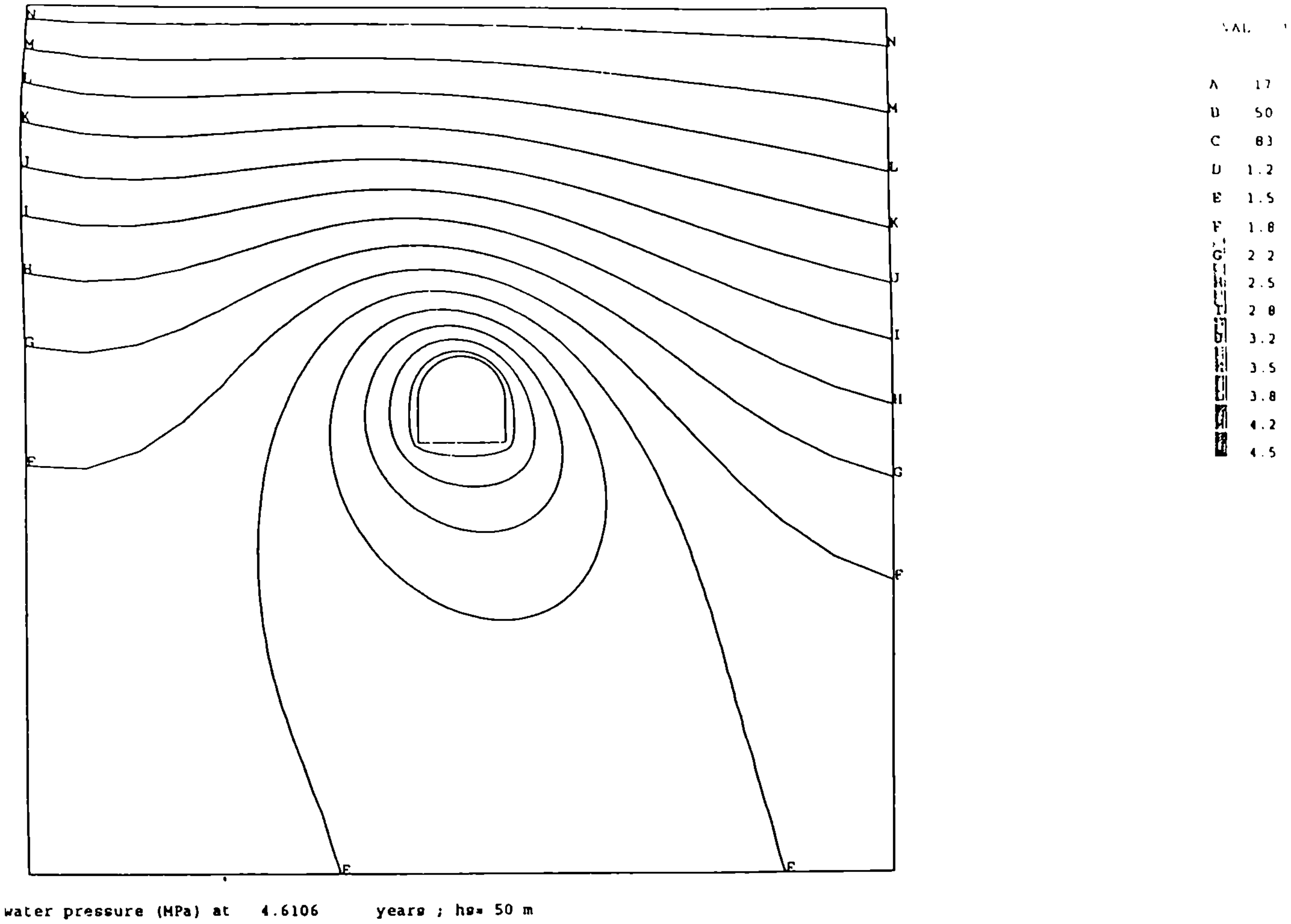


Figure 3 - BMT3 CEA/DMT results : water pressure (MPa) at 1 year for sequence n°2 with the anisotropic case

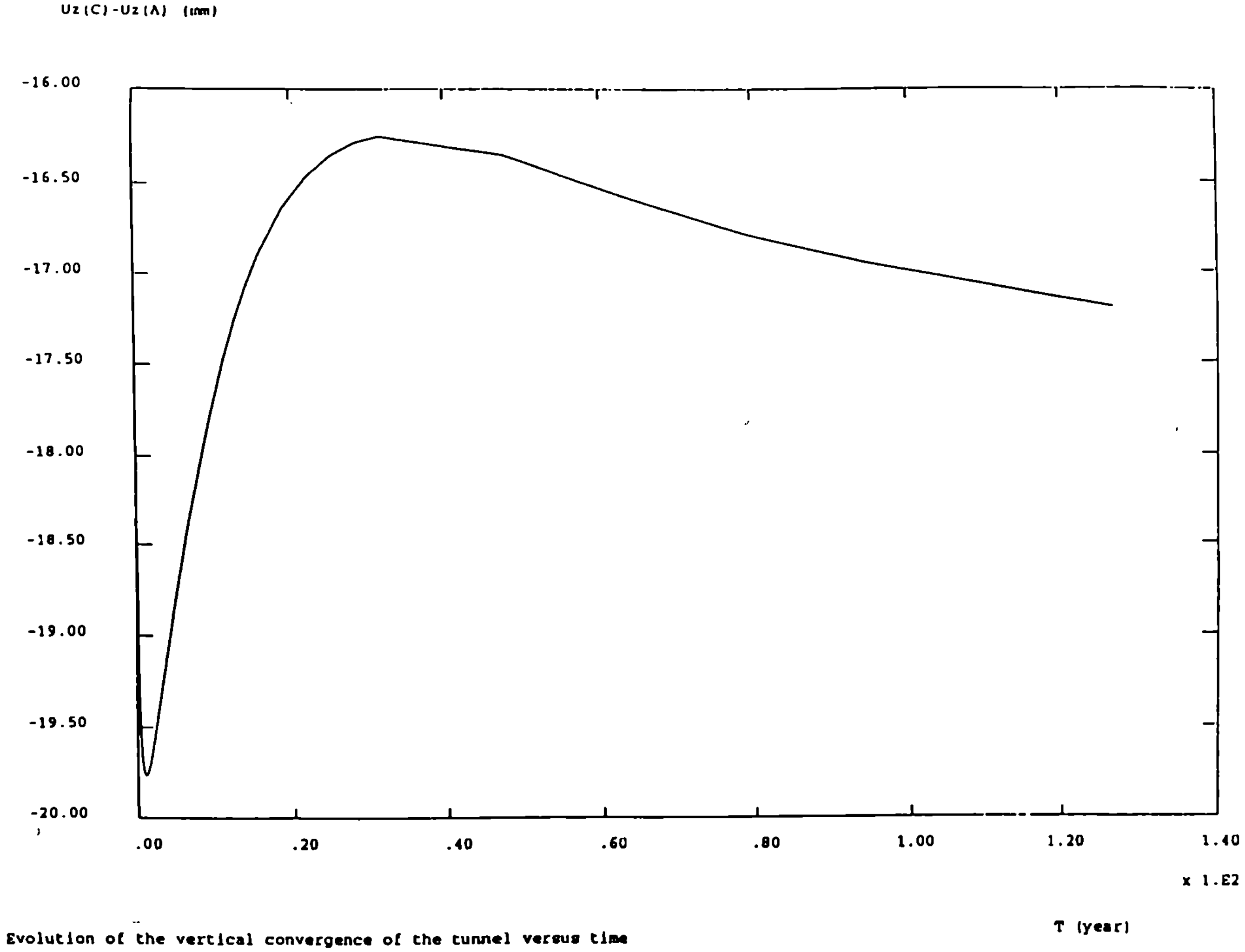


Figure 4 - BMT3 CEA/DMT results : Evolution of the water flux across the tunnel surface versus time for the sequence n°2 with the anisotropic case

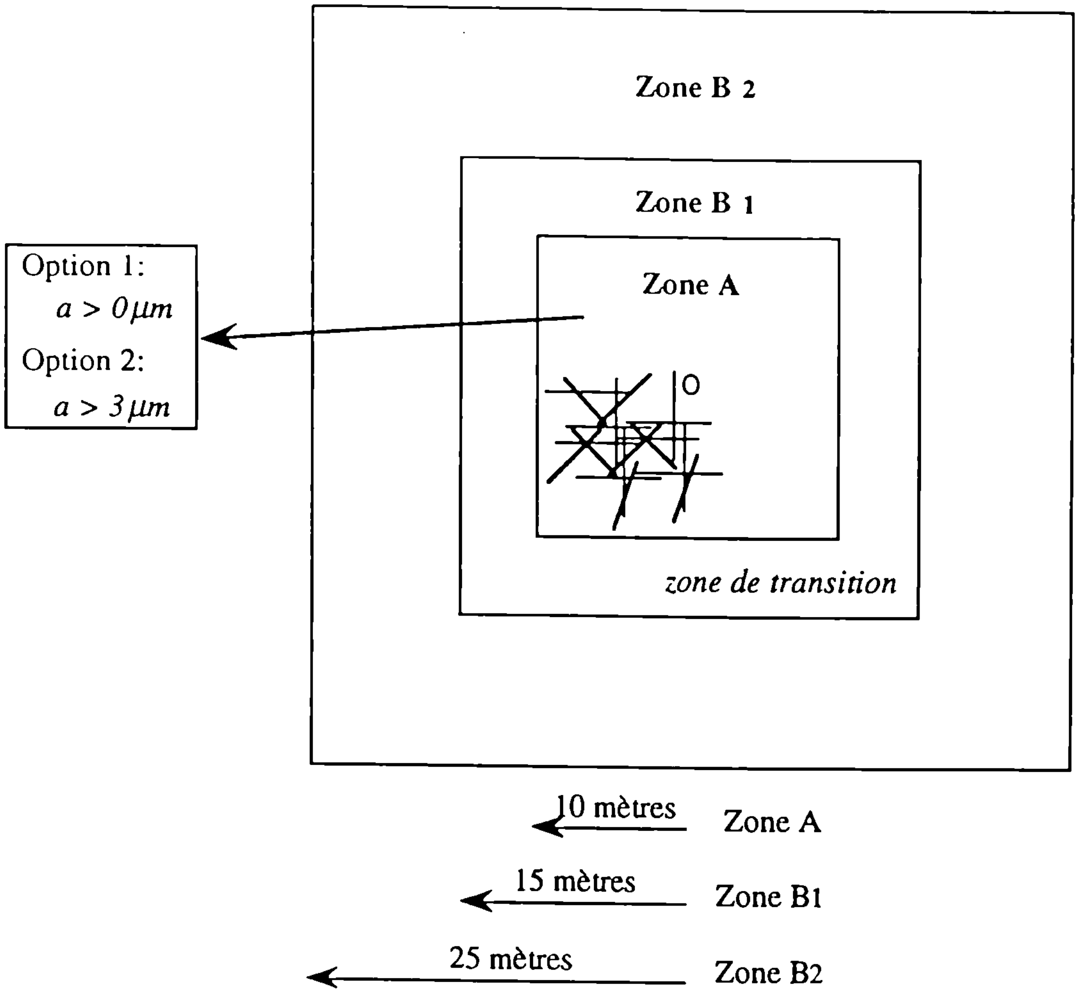


Figure 5 - BMT3 INERIS : Scheme of the simplified network

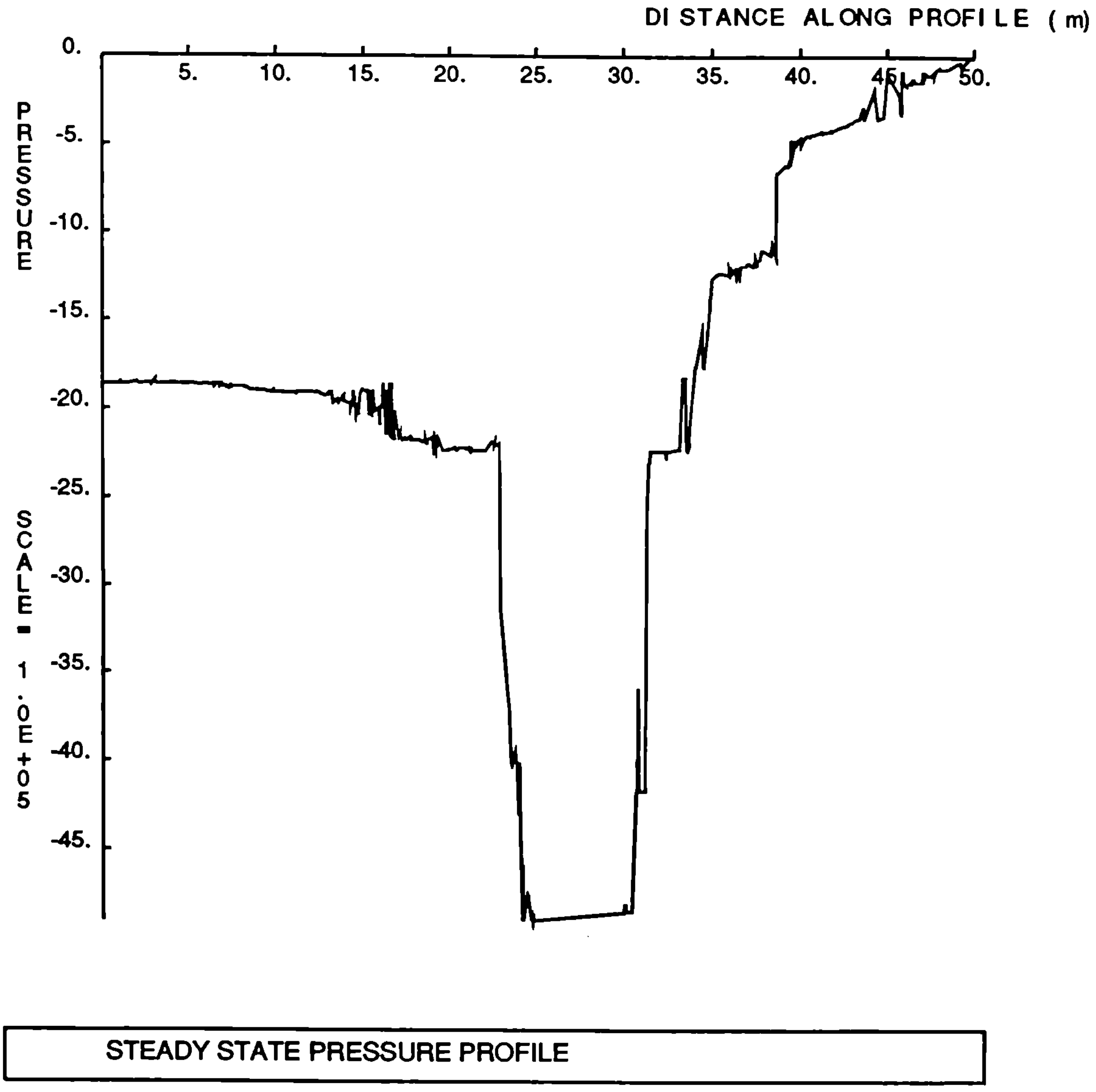


Figure 6 - BMT3 AEA R&D : Steady state pressure profile along the horizontal line I for the sequence n°2

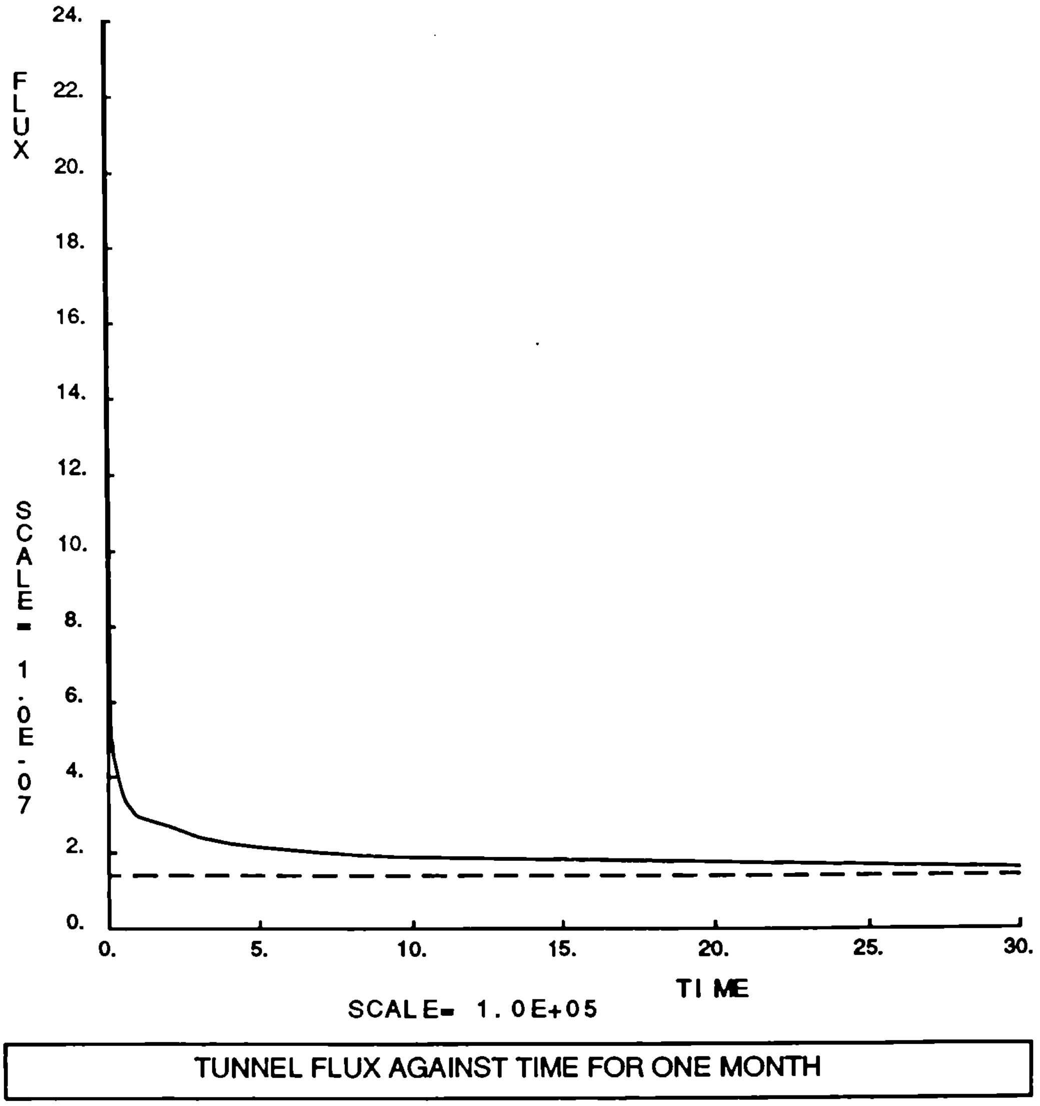


Figure 7 - Tunnel flux against time for no-stress model

Title : Underground laboratory at Tournemire : groundwater flow tests in clayish material
Contractor : C.E.A. / IPSN
Contract N° : F12W/0115
Duration of contract : from januarv 1. 1992 to december 31, 1994
Periode covered January - December 1993
Project Leader : André Barbreau

A. OBJECTIVE AND SCOPE

The Institut de Protection et de Sûreté Nucléaire (Département de Protection de l'Environnement et des Installations) of the Commissariat à l'Energie Atomique is developing, in the framework of its R and D safety programs, in situ research concerning the confining properties of geological formations.

In situ research work concerning argillaceous formations has been started at the end of 1990. The selected site is a hundred years old given up railway tunnel, 1885 meters long, in the close vicinity of the village of TOURNEMIRE, in the South of France. This tunnel, crosses a 200 m thick toarcian clay formation; the overlying limestone layers are 270 meters thick, so the geotechnical and hydrogeological conditions can be considered as representative of those of a deep repository.

The research program concerns hydrogeological properties of clay in order to determine the characteristics of water flow through the clay formation.
and more particularly, it intends also to develop new methods, apparatuses and devices, for the investigation of very low permeability medium and to perform modelling.

B. WORK PROGRAM :

The Tournemire program includes :

General geological and hydrogeological investigation of the site
Drilling operations in the tunnel
Detailed structural study
Preliminary modelling
Isotopic studies
Laboratory study of core samples

C. PROGRESS OF WORK AND OBTAINED RESULTS :

1. General geological and hydrogeological investigations

A general geological survey of the area has been carried out to precise the geological environment around the tunnel : it has mainly included a detailed geological mapping and the determination of the main hydrological et hydrogeological features of the area.

The geological formations near the site are constituted by sub-tabular sedimentary layers of the lower and middle Jurassic period. The stratigraphic formations involved in the Tournemire environment are the following:

Hettangian: limestones and dolomites (200 m)
Carixian: limestones with interbedded marls (45 m)
Domerian: marls and clay (argilites) (40 m)
Toarcian: marls and clay (argilites) (200 m)
Aalenian: limestones (with interbedded clay) (60 m)
Bajocian and Bathonian: massive limestones and, in upper Bathonian, dolomites (430 m). Above the tunnel, this serie is about 200 m thick. This formation constitutes the "Causses" table.

The springs and draining lines connected with the different aquifers, in the region, have been investigated to precise the main hydrogeological features.

The prevailing lower limestone formations of Hettangian and Carixian contain the general lower regional aquifer below the domerian and toarcian argilites of very low permeability. At the place of the tunnel, the aquifer of these limestones is in charge below the domerian and toarcian clay and its head is roughly located at mid-height inside the Toarcian formation.

The limestone layers from Aalenian up to upper Bathonian are the reservoir for the upper regional aquifer. At Tournemire, this aquifer lies in the lower part of the Aalenian and should feed the toarcian clay just below.

The water flow through the toarcian argilites, which could behave hydraulically as a semi-permeable medium, is supposed to be vertical downwards.

The tunnel, in the longest part, is inside the Toarcian formation of which the dip is weak (5%).

At 1700 m from the south entrance, the tunnel crosses a big fault that brings into contact Toarcian argilites and Hettangian limestone, producing a spring in the tunnel at this place.

2. The 1990-1991 drilling operations

After the first geological and hydrological survey, it has been decided to carry out boreholes to get additional and more precise information on the depth, lithology, statigraphy and hydrology of the geological layers around the LEMI.

Six boreholes (5 vertical downwards and 1 vertical upwards) have been drilled, respectively 231 m (DC) 169 m (CD), 144 m (DI), 118 m (DM), 30 m (DS), and 65m (CA) long, with demineralized water to allow isotopic analysis. The most part of these boreholes has been cored.

Four boreholes have been equipped with the ground water monitoring system, the B.A.T. filter tip, which is designed to allow pressure measurement and water sampling in low permeability rocks. One of the B.A.T. filter tips has been set at the top of the domerian formation (CD), constituted also of clay, which is just below the toarcian clay, and three other B.A.T. filter tips have been located at different levels of the toarcian clay (DI, DM, DS), to get information on the hydraulic gradient.

The downwards 230 m long borehole (DC) had the aim to investigate the hydrology of the carixian limestone, underlying the domerian clay and the upwards 65 m long borehole (CA) had the aim to investigate the aquifer of the lower aalenian formation overlying the toarcian clay. These two boreholes are equipped with a pressure gauge respectively set in carixian and aalenian limestones.

Data provided by these different pressure measurement devices were permanently recorded and sent to IPSN by a computer teletransmission system. So, the aquifer head at different levels and its evolution in time can be continuously monitored.

Many permeability tests at different levels have been performed (mainly pulse tests) as well as geophysical loggings : natural gamma, gamma gamma, acoustic log, and neutron log. The results of the permeability tests show that the permeability of the two toarcian and domerian clay formations is very low, between 10^{-11} and 10^{-13} m/s. The permeability of the calcareous carixian and aalenian formations is substantially higher : the Carixian has a permeability of about 10^{-8} m/s and the Aalenian of about 10^{-6} m/s.

The aquifer heads, in the carixian and in the aalenian limestones tally with the values that could be deduced from the hydrogeological regional and local system data (springs, draining lines, etc...). It has not been possible up to now to determine the actual head in the argilite formations because of the very long period to reach the steady state after the perturbation induced by the drilling operation resulting from the very low permeability of this kind of rock. Pressure data obtained from B.A.T. measurement look in discrepancy with the values that could be deduced from the flow model set up to give a first approach of the groundwater circulation in the Toarcian.

Dilatometer tests have also been carried out in the Toarcian : the argilites look very stiff.

3. Detailed structural study

A detailed structural study has been performed, based on observations in quarries and on core samples. Three states of stress have been identified: a N-S Pyrenean compression (Eocene), an E-W extension (Oligocene), and an Alpine compression. Limestone formations are extensively fractured; in toarcian clay, some faults have been observed but are filled in by calcite.

4. Preliminary modelling

On the basis of the first available data, a first flow model into the clay has been performed at the beginning of 1992, to be used for the conception of the following programs and in particular for precising the characteristics of the new drift contemplated for carrying out the scale effect experiment. Its objectives were:

- to get an opinion on the duration of the transient state after the excavation of the drift ;
- to evaluate the possible rate of discharge of water in the draft itself ;
- to get an order of magnitude of the transfer time in the geological formations to constitute a framework for the interpretation of the geochemical and isotopic studies.

The two main results are:

- the transient period to reach the steady state after a significant perturbation is very long (several years). This means that the different tests which will be performed in the argilites should be interpreted in transient state ;
- the value of the ground water head at different levels in the Toarcian is close to the value of the topographic level at this point. Combined with the very low permeability of the rock, it means that the flow discharge rate by drainage that can be anticipated, even in a drift 100 m long, will be very low (below 10 cm^3/h).

5. Isotopic study

It is possible to get information on the age of the ground water by using natural radio-isotopes such as ^{14}C, ^{36}Cl, ^{129}I, and the ratio U/Th. In other respects, stable isotopes ^{13}C, ^{18}O and ^{2}H can provide information on the origin of water: for example, the presence of meteoric or connate water.

Unfortunately, in the case of Tournemire argilites, the difficulty for extracting pore water from the cores has jeopardised up to now the possibility for performing an exhaustive research program regarding the natural isotopes. By the time being, it has been only possible to extract pore water by distillation, which has limited the investigations to ^{18}O and ^{2}H for the liquid. So, a valuable dating of pore water has not been possible nowadays.

In these conditions, it is difficult to get a good representation of the groundwater transfer in the argilites. However, the first investigations on the liquid phase extracted by distillation from cores of CD and CA boreholes give some information (cf. Fig.(1)):

- a peak in the concentration in ^{18}O and ^{2}H (distillation) has been observed nearby the tunnel, produced probably by the influence of the tunnel on the saturation of the rock (evaporation) ;

- an other peak has been observed in the fist analyses at -60 m; more recent analyses raise some controversy on this result: the peak at -60 m may be interpreted either as a mixing in meteoric and connate water resulting probably of diffusion phenomena or as an artefact.

As far as the solid phase is concerned, the content of ^{13}C and ^{18}O in the fracture minerals shows that the "mixing" hypothesis is possible; the measurement of ^{14}C content in fracture carbonate minerals indicates that no ground water significant circulation has occurred in the toarcian argilites since at least about 20,000 years.

These preliminary results have of course to be precise and confirmed by other studies.

6. Laboratory study of core samples

Laboratory study has been performed on sixteen argilite samples coming from the CD borehole. Mineralogical and petrographical investigation by XR diffractometry has provided the mineralogical composition of the clay, which is mainly composed of 40-50 % of clay minerals (40-50 %) such as mica, kaolinite illite and interstratified clay mineral close to illite, about 10 to 30 % of carbonates (dolomite, and siderite and mainly calcite), 10 to 15 % of quartz, and in some samples, a few samples, a few amount of chlorite, and pyrite.

The water content, very low, is from 1 to 3%. Porosity is referred to a diameter of pores lower to 0.02 µm. Hydraulic conductivity is between 10^{-13} m/s and 10^{-14} m/s.

Geomechanical testing shows that the seismic wave velocity of toarcian argilites in laboratory samples is high (approximately from 3,000 m/s to 4,000 m/s for P waves and 1,500 to 2,200 m/s for S waves. The Young's modulus (E) is between 10,000 and 15,000 MPa and the Poisson's ratio is between 0.15 and 0.20.

7. Conclusion at the present stage of the program

The geological and hydrogeological conditions of the environment of the LEMI are well known, by the time being, but the properties of the argilites as they have been described, are such that the determination of fluid pressure and fluid transfers through this type of rock, by in situ experiments, is very difficult. One of the most important point is the pore access diameter in clay which influence strongly the modalities of ground water flow. This means that it is now untimely to carry out a scale effect experiment by ventilation test in a drift as it was initially forecast for the second phase of the program. Additional laboratory studies and new in situ experiments of a more pertinent conception are needed for precising the actual fluid movement in the Toarcian.

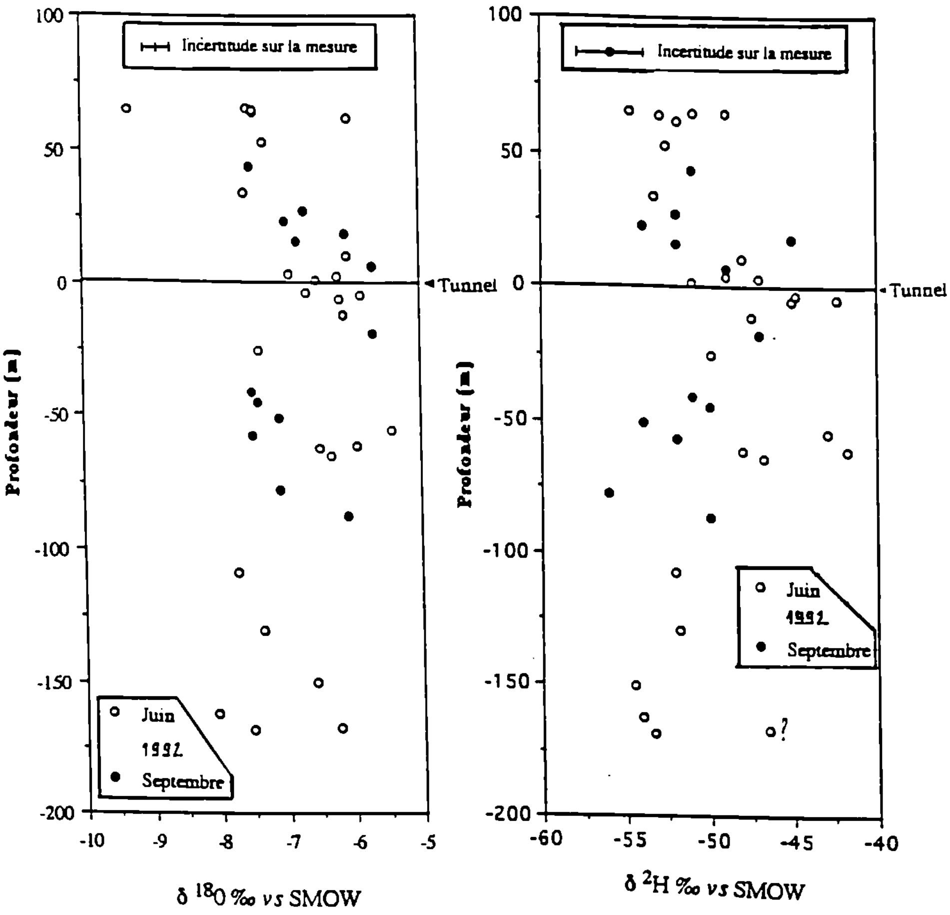


Figure 1 - Variations of ^{18}O and ^{2}H concentration (from distillation) versus depth

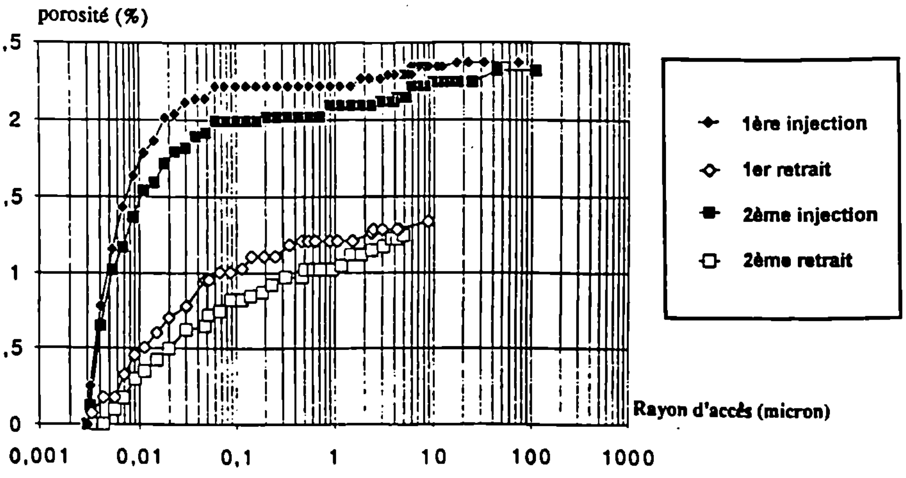


Figure 2 - Porosimetric curves from sample n°14

DEVELOPMENT OF BOREHOLE SEALS FOR HIGH-LEVEL RADIOACTIVE WASTE (THE DEBORA-PROJECT)

Contractors: GSF-Institut für Tieflagerung (IfT), Braunschweig, Germany
Stichting Energieonderzoek Centrum Nederland (ECN), Petten, The Netherlands
Contract No.: FI2W-CT90-0048
Duration of Contract: January 1991 - December 1994
Period covered: January 1993 - December 1993
Project Leaders: T. Rothfuchs, J. Prij

A. OBJECTIVES AND SCOPE

The overall objective of a nuclear repository is to protect man and his environment against ionizing radiation from radioactive waste emplaced in this underground repository.

According to section 45 of the German Radiation Protection Ordinance the individual dose to man, caused by radionuclides passing out of the repository, is to be limited to 0.3 mSv/year. In order to achieve this objective within the multiple barrier system of the repository, suitable sealing systems like borehole seals, drift seals and shaft seals are to be developed.

The objective of the DEBORA-project is the "Development of Borehole Seals for High-Level Radioactive Waste".

The DEBORA-project consists of two phases. During the first phase (1991 - 1994) a test plan for a subsequent in situ verification test will be developed in form of a desk study. This study will include an evaluation of literature, a performance of model calculations, and discussions of experts to identify the requirements for and the tasks of HAW-borehole seals under normal repository conditions. Altered repository conditions will be considered at a later stage of the project.

During the second phase, to be started in 1995, in situ tests will be performed and the sealing techniques elaborated during the first phase will be verified.

B. WORK PROGRAMME

B.1 Compilation of the technical boundary conditions important for the design of HAW-borehole seals
B.2 Definition of the tasks of HAW-borehole seals
B.3 Analysis of events affecting the design of the borehole seal
B.4 Performance of model calculations
B.5 Elaboration of sealing techniques
B.6 Development of an in situ test plan

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

After the completion of items 1 and 2 of the work programme (see APR 1991 and APR 1992) emphasis was given to the analysis of events affecting the design of HAW borehole seals. This work comprises the evaluation of literature and, as for as possible, the performance of model calculations in order to estimate the conditions of state in and around borehole seals. In this regard fluids which will be released into the borehole and their generation mechanisms have been summarized. Corrosion of steel as packaging material has been studied in the literature and the amount of hydrogen resulting from corrosion and from radiolysis of released fluids have been estimated in order to obtain input data for the calculation of the borehole gas pressure.

Concerning the elaboration of sealing techniques (item 5) the literature studies were continued and the material data of bentonite were evaluated in regard of the suitability of bentonite as a sealing material.

Progress and results

1. Compilation of the technical boundary conditions important for the design of HAW-borehole seals

A compilation of the technical boundary conditions was already reported in (GSF-ECN, 1992). According to the german disposal concept data about the geometrical arrangement of a HAW repository and about the waste canisters were compiled.

2. Definition of the tasks of HAW-borehole seals

The work performed in this regard consisted in a review and compilation of legal requirements to be considered inside and outside a nuclear repository. The respective information was reported in (GSF-ECN, 1992).

3. Analysis of events affecting the design of the borehole seal

In the past years the importance of the waste emplacement tempo, the release of fluids from the rock mass and the generation of fluids by corrosion of the waste canisters and by radiolysis of fluids was analysed.

During the report period most emphasis was given to the analysis of the thermomechanical load on the borehole seal and to the determination of the gas pressure inside a disposal borehole.

3.1 Thermomechanical analysis

The thermomechanical load consists of the stresses, deformations, and temperatures caused by the heat generation of the HAW disposed in the borehole and by the stress redistribution caused by the excavation of the gallery. The waste induced loads depend on the amount of waste, the tempo of the waste emplacement and the heat load. The gallery induced loading depends on the dimension and shape of the gallery, the rock pressure, and the creep properties of the rock salt.

Numerical analyses have been performed to determine the significance of all relevant parameters with respect to the influence on the loading. Having identified the most sensitive aspects one can concentrate on these items for further research in this project.

3.1.1 Interaction of the gallery and the borehole

A three-dimensional model has been made for the structural analyses of the upper part of the borehole drilled from the floor of a gallery (GSF-ECN, 1993a). The results show that the radial deformation of the upper 20 m of the borehole are significantly disturbed by the presence of the gallery. This is elucidated in Fig. 1 where the radial deformation of the borehole wall, after 7 years of creep, is presented as a function of the distance from the gallery floor. The circumferential position along the perimeter of the borehole is given with the angle theta. Theta is zero in the plane normal to the gallery direction while theta is 90° in the plane in the gallery direction. Due to the actual stress state in this part of the model the borehole deformation slightly deviates from the rotational symmetry. It can be seen that due to the interaction the radial deformation deviates from the radial deformation in an undisturbed borehole. At the gallery floor the radial deformation is about half of the value for the undisturbed borehole. About 5 m below the floor the radial deformation reaches an extreme value, about twice the deformation in an undisturbed borehole. At a depth of 20 to 30 m below the gallery the distortion almost disappears.

It must be concluded that due to the stress redistribution around the gallery the borehole convergence is significantly enlarged except in the upper meters below the gallery. This enlarged convergence has to be taken into account in an accurate analysis of the mechanical behaviour of the seal which will be located in this region.

3.1.2 The thermomechanical behaviour of an entire borehole

The analyses have been made for a borehole without any backfill to study the free convergence and for a borehole having backfill in the annulus between the containers and the borehole wall to study the compaction behaviour of the backfill.

The main goal of the analyses of the entire borehole is to obtain a detailed description of the convergence behaviour of boreholes immediately after the radioactive waste has been placed. The convergence behaviour is needed to determine boundary conditions for filling strategies of the borehole and they also determine the period in which the gap between the containers and the borehole wall can be considered to be open. Another aim of the analysis is the compaction of the backfill which gives the necessary input for the permeability needed in the gas transport calculations.

The models for the temperature and structural analyses have been described in the semi-annual progress reports. It must be noted that for the analyses an axisymmetric unit cell has been used with an external radius of 25 m. This model represents the extreme conditions in an infinetely extended field with boreholes.

To evaluate the sensitivity the interim storage has been varied, three values have been used: 0 years, 31 years and 40 years. The interim storage period of 31 years has been determined in such a way that the maximum temperature to be reached in the salt does not exceed 200 °C. In the analyses it has been assumed that the boreholes are filled instantaneously.

The maximum temperatures and the time after which these temperatures are reached are tabulated in Table 1 for each interim storage period. In all cases the maximum temperatures are reached at the centre of the heat sources.

The maximum temperatures at the borehole wall during the entire loading history are presented in Fig. 2. It appears that the temperatures are only little rised the first 10 m beneath the gallery floor. In the heated area the curves are symmetric with respect to the centre of the heat source apart from a small effect due to the geothermal gradient.

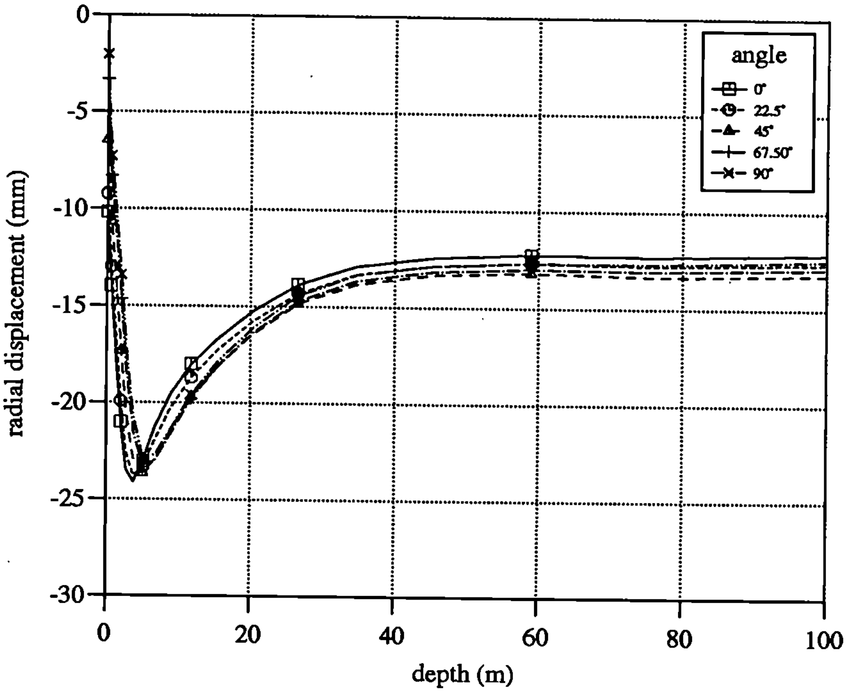


Fig. 1: Radial deformation of the borehole after 7 years of free convergence

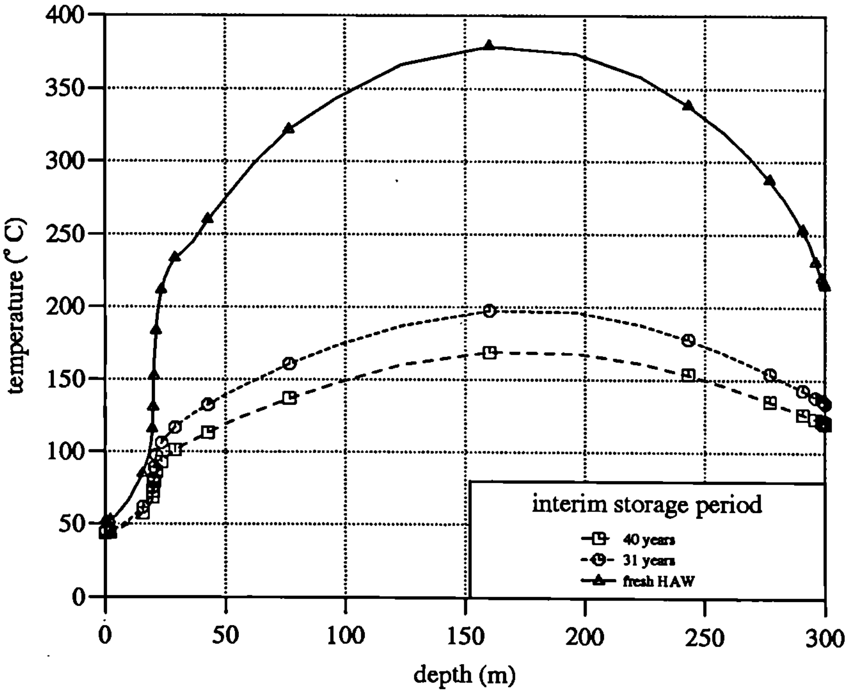


Fig. 2: Maximum temperature along the borehole wall during the entire loading history for each interim storage period.

Table 1: Maximum salt temperatures for each interim storage period

Interim storage period (years)	Temperature (°C)	Depth (m)
0	379	160
31	197	160
40	169	160

Another representative result of the analyses is given in Fig. 3 where the evolution of the temperature of the borehole wall is presented. The resulting free convergences are summarized in Fig. 4 where the time to fill the initial radial gap of 8.5 cm is presented as a function of the distance from the gallery floor. In the cold area, say the first 25 m beneath the gallery floor, the deformation rates are very small and the time needed to fill the gap exceeds the period for which calculation results are available. At distances more than 290 m below the gallery floor an edge effect is visible, which is caused by the presence of the borehole bottom. The numerical results correspond with the experiment with the Heated Free Convergence Probe in the 300 m borehole (Prij et al., 1986).

To analyse the compaction behaviour of the backfill in the annulus, a model is used which was developed in the framework of the safety study PROSA (Prij et al., 1993a) for the nuclide transport calculations. In the model the borehole convergence and backfill compaction are coupled. Details of this convergence/compaction model are described by Prij et al., 1993b. The experimental basis for the convergence model is formed by the convergence measurements performed in the Asse. The experimental basis for the compaction is formed by the laboratory experiments in Utrecht (Spiers et al., 1989) where the effects of brine pressure p_{br}, external pressure, temperature, volumetric strain, porosity, grain size and moisture content have been determined. The present model explicitly accounts for the constitutive parameters of the backfill.

The interaction of the convergence and compaction is given by the fact that at each point in time the convergence rate K must be equal to the compaction rate β. At each point in time the internal borehole pressure p_i has iteratively be derived from the equation:

$$K(p_r - p_i(t) = \beta(p_i(t) - p_{br}(t))$$

with p_r being the rock pressure.

To assess the accuracy of the new model the results have been compared with finite element models of different repository relevant in-situ situations. It appears that a good correspondence exists between the finite element models and the convergence/compaction models used in the safety study PROSA (Prij, J. et al., 1993a).

The model has been applied to predict the compaction behaviour of the crushed salt in the annulus between the waste container and the borehole wall. Typical results are given in the Fig. 5 where the evolution of the porosity of the backfill is presented for various interim storage periods. An initial backfill porosity of 0.3 was selected. It appears that the porosity drops rather slow in the area close to the upper canister at a depth of 20 m below the gallery floor, as well as close to the bottom of the borehole. The differences in the area between 30 m and 287 m depth are limited and are mainly caused by the geothermal gradient and by the rock pressure.

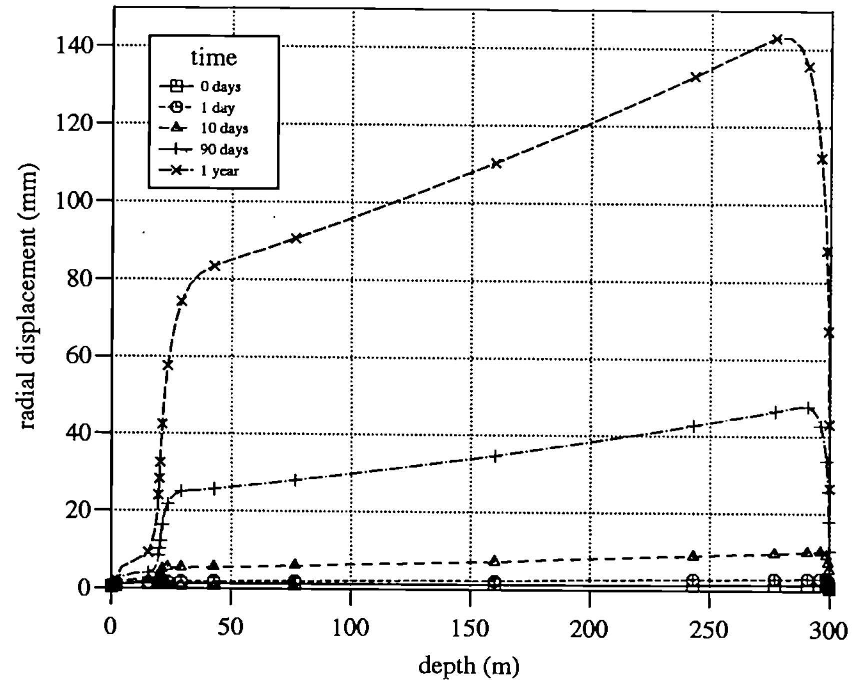


Fig. 3: Distribution of the temperature along the borehole at various time points. (Interim storage period is 31 years).

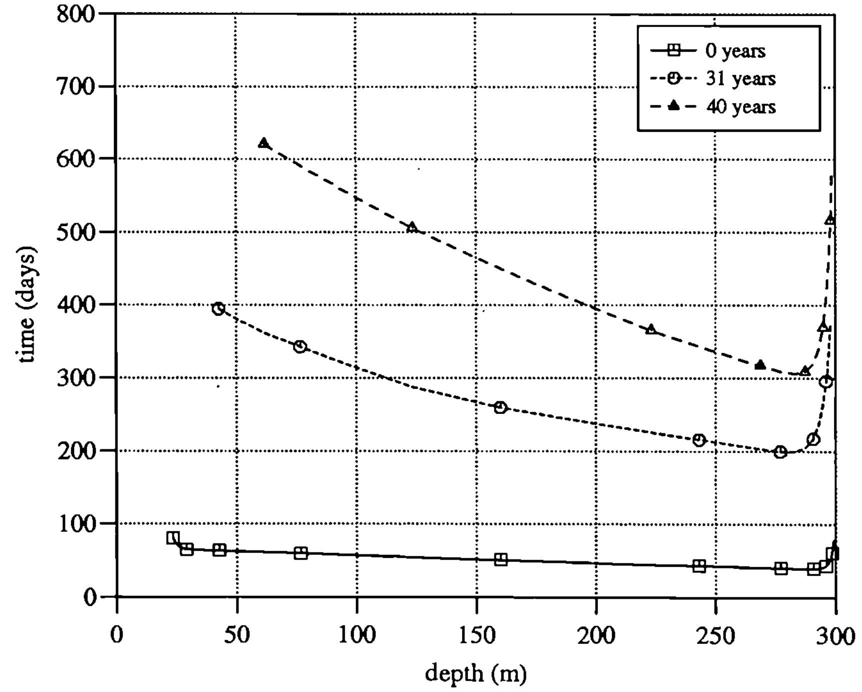


Fig. 4: Time needed to reach a radial displacement of 8.5 cm.

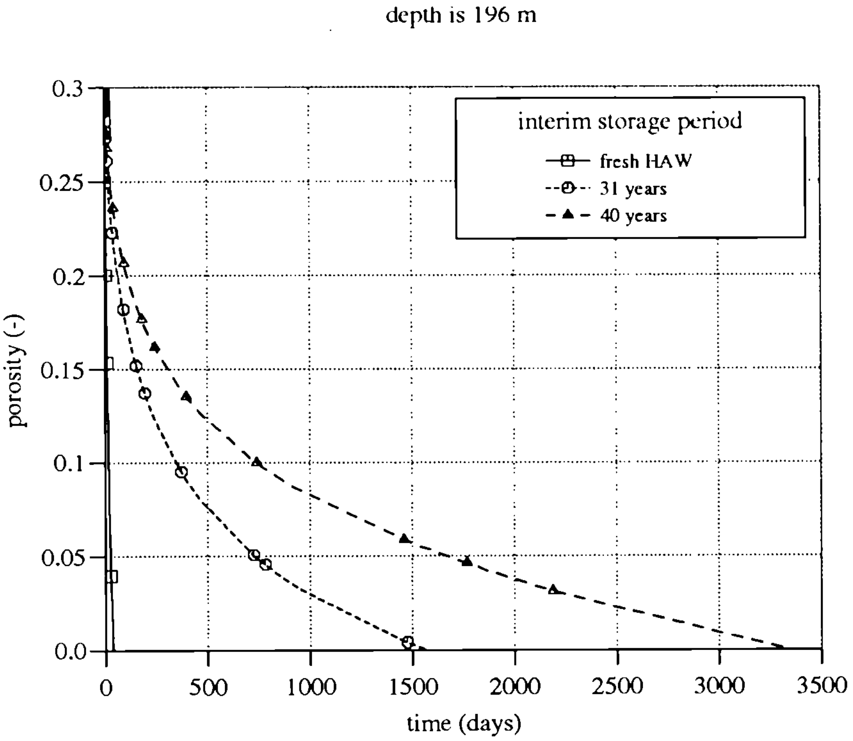


Figure 5 Porosity of the crushed salt in the borehole at a depth of 196 m for various interim storage periods.

3.2 Determination of the gas pressure inside a HAW disposal borehole

In previous reports (e. g. GSF-ECN, 1993a) calculations of water release into the borehole and the resulting production of hydrogen have been presented. These are the most important fluids regarding the gas pressure inside the borehole. Results have been obtained for a reference borehole of 300 m depth but can be transferred to other borehole depths as well. The determined fluid production rates are important input parameters for the ongoing geohydraulic calculations.

In a first step an analytical solution for a simplified case was used to determine the gas pressure inside the borehole. In this case the gas pressure in the borehole is estimated on the basis of the hydrogen production only. The contribution of the water vapour was neglected because the maximum value of which amounts to only 1.5 MPa. The results, however, are relevant in case of much higher permeability of the seal than that of the surrounding salt. Because of the neglection of the disturbed zones in the salt around the borehole and the gallery the results can be considered as upper estimations.

Because of the simplifications described above and in order to consider the real geometry of the problem numerical calculations will be performed in the future.

Figure 6 displays a sketch of the case considered. Inside the borehole the conditions of state are the unknown gas pressure p_2 and the temperature T_2, the mass production rate of hydrogen is denoted by j and the temperature dependent dynamic viscosity of hydrogen by η. The surrounding salt is considered to be impermeable and the flow of H_2 through the seal will be taken into account using the ideal gas equation of state. The seal is characterized by its permeability k, its length l and the cross section a. In the gallery the fixed conditions of state are the pressure p_1 and the temperature T_1. In the isothermal case T_1 and T_2 are identical, in the non-

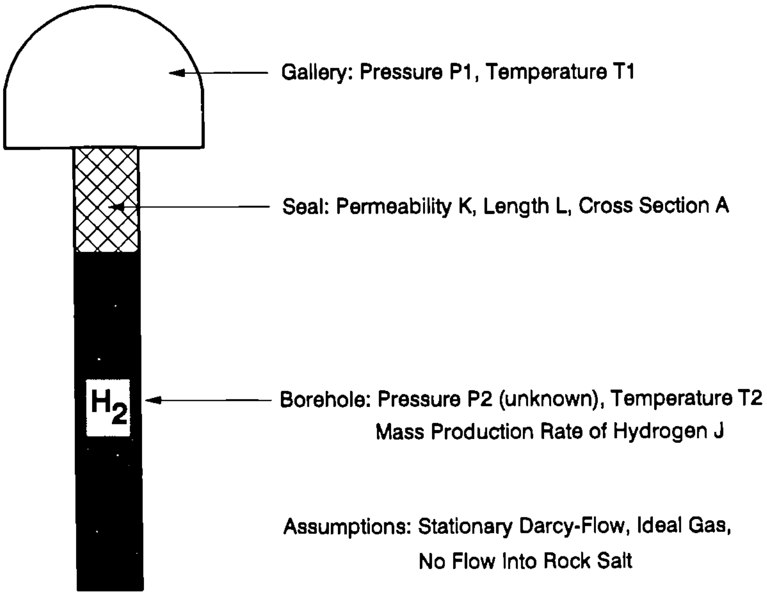


Fig. 6: Sketch of the simple model used for the estimation of gas pressure in the borehole.

isothermal case a linear variation of temperature across the seal is assumed.

For stationary conditions Darcy's law for compressible fluids relates the mass production rate and the pressures as following:

$$p_2 = [l \cdot \eta \cdot R \cdot j \cdot (T_1 + T_2)/(k \cdot a \cdot m) + p_1^2]^{0.5}$$

R denotes the universal gas constant and m the molecular weight of hydrogen.

A value of 10 kg/a H_2 for Pollux-canisters and a value of 0.5 kg/a for HAW-canisters has been chosen for the mass production rate j. The difference arises from different surface rates of steel corrosion and different dose rates of the waste (compare GSF-ECN, 1993a).

The temperature was varied in different ways. A value of 200 °C for T_1 and T_2 will be choosen as an upper value in the whole model and a value of 50 °C as a lower value for isothermal conditions. The pressure in the gallery will be taken as 0.101 MPa. A summary of the input data is given in Table 2.

Figure 7 displays as an example the results for the chosen range of production rates of hydrogen and isothermal conditions of 200 °C and 50 °C. The difference in temperature causes significant differences of about 50 % in gas pressure and, as expected, the different production rates cause even higher differences. For tight seals around 1.E-18 m^2 permeability, up to 8 MPa are determined in case of the low production rate, up to 35 MPa in case of the high production rate.

The simple model is relevant in case of a seal permeability which is significantly higher than that of the surrounding rock salt. The permeability around the gallery will be in the range from 1.0E-16 m^2 to 1.0E-20 m^2 as indicated by measurements in the dam project in the Asse

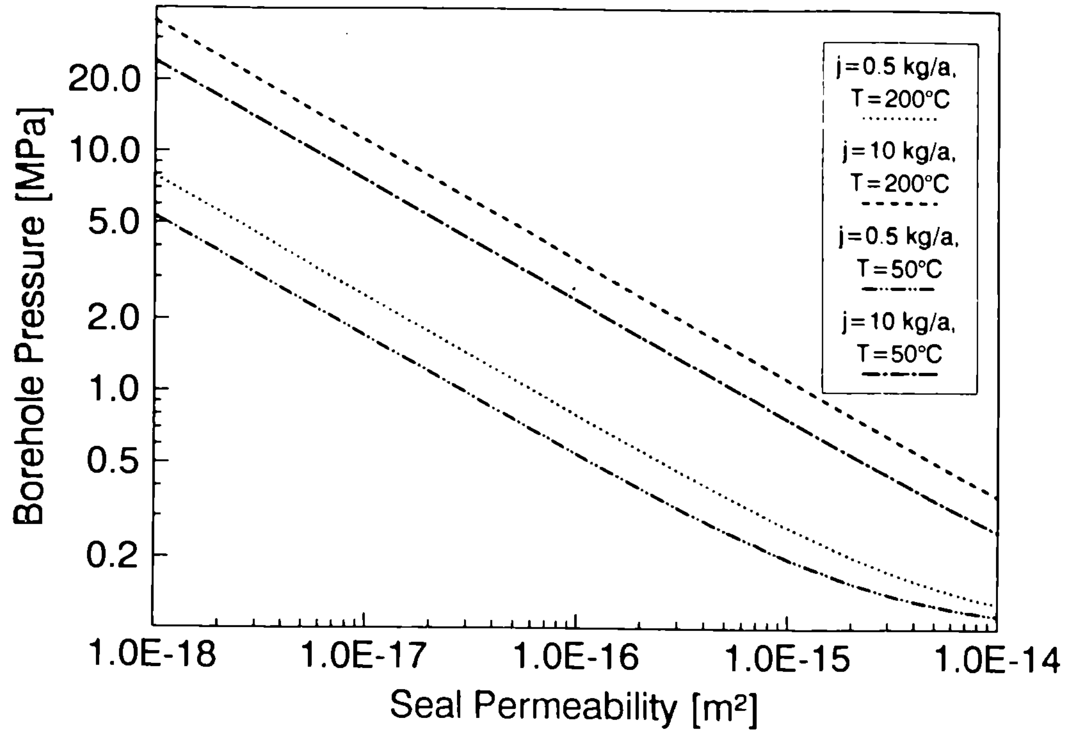


Fig. 7: Gas pressure in the borehole as a function of seal permeability for different values of hydrogen production (0.5 kg/a for HAW Cogema and 10 kg/a for Pollux) and different values of temperature (200 °C and 50 °C, isothermal), seal length 20 m.

Table 2: List of input data for calculation of gas pressure in the borehole

Parameter, Quantity	Value, Range	Dimension
Seal properties		
permeability k	1.E-18 - 1.E-14	m^2
length l	10, 20, 30, 40	m
cross sectional area a	0.283	m^2
Gas properties H_2		
dynamic viscosity η	(0.03·T+8.)·1.E-6	Pa·s, T in °C
molecular weight m	0.002	kg/mol
gas constant R	8.314	J/K/mol
mass production rate j	0.5, 10	kg/year
Conditions of state		
drift pressure p_1	0.101	MPa
temperature T_1,T_2	200 (isothermal), 50 (isothermal), T_2 = 200 and T_1 = 50 (non-isothermal)	°C

mine. Permeability of the intact rock salt is around 1.0E-21 m^2. If the values of the disturbed zone around the gallery are transferred to the zone around the borehole, the results presented above can be considered as relevant up to around 1.0E-16 m^2 for the permeability of the seal. In case of lower values of seal permeability the results are too high and have to be considered as upper estimates. In this regard 20 MPa borehole pressure or even higher does not seem to be realistic but maximum pressures from 1 MPa up to 5 MPa may be reached (relating to the low and high production rate).

3.3 Radionuclide release from HAW-boreholes under normal and altered repository conditions

The release of radionuclides out of the HAW-borehole has been studied in literature. An evaluation of the results of the SAM-safety analysis (GSF-IfT, 1991) revealed that for normal repository conditions no release is to be expected. Evaluation of scenarios of altered repository conditions imply that the amount of brine inflow into the borehole from undetected brine pockets has a more important influence on the radionuclide release than the permeability of the borehole seal. From these studies it can be concluded that an initial seal permeability of 1.0E-13 m^2 might be sufficient in regard of a radionuclide release.

3.4 Evaluation of literature on the properties of candidate sealing materials

The relevant properties of bentonite as a potential sealing material have been compiled after an intensive search in the literature and can be used for designing and modeling purposes. The material data are summarized in (GSF-ECN, 1993).

References

GSF-IfT, 1991: Systemanalyse Mischkonzept, Technischer Anhang 7, Analyse der Langzeitsicherheit von Endlagerkonzepten für wärmeerzeugende radioaktive Abfälle, GSF-Institut für Tieflagerung

GSF-ECN, 1993a: The DEBORA-Project, Progress Report July - December 1992, Joint Report of GSF-Institut für Tieflagerung and Energy Research Foundation Netherlands - ECN, Abteilungsbericht IfT 1/93

GSF-ECN, 1993b: The DEBORA-Project, Progress Report January - June 1993, Joint Report of GSF-Institut für Tieflagerung and Energy Research Foundation Netherlands - ECN, Abteilungsbericht IfT 4/93

Prij, J., Jansen, D., Klerks, W., Luyten, B., de Ruiter, A., Vons, L. H., 1986: Measurements in the 300 metre deep dry-drilled borehole and feasibility study on the dry-drilling of a 600 metre deep borehole in the Asse salt mine, EUR 10737 EN

Prij, J. et al., 1993a: Probabilistic safety assessment PROSA, final report, ECN/RIVM/RGD August 1993

Prij, J., John, J., Heijdra, B. A., van den Horn, 1993b: Convergence and compaction of backfilled openings in rock salt, Proceedings of the 3rd Conference on The Mechanical Behavior of Salt, September 1993, Paris

Spiers, C. J., Peach, C. J., Brzesowsky, R. H., Schutjens, P. M. T. M., Liezenberg, J. L., Zwart, H. J., 1989: Long-term rheological and transport properties of dry and wet salt rocks, EUR 11848

Title: The refinement of soil gas analysis as a geological investigative technique
Contractor: Università "La Sapienza", Rome (Italy)
Contract N°: FI2W-CT91-0064
Duration of contract: from April 1991 to March 1994
Period covered: 1993
Project Leader: S. Lombardi

A. *OBJECTIVES AND SCOPE*

The present research project consists of a multidisciplinary study aimed to refine a set of geological investigation methods for the assessment of the safety of sites for operation such as radioactive waste repositories, with high potential for environmental hazard.

The studies are based on the integration of sampling and analyses of soil gases with other investigation techniques. Previous soil gas surveys performed by the participants have demonstrated that the soil gas method has great potential for tracing buried faults and fractures in clayey terrains and has a great flexibility. It is possible in fact to carry out surveys along profiles and/or according regular grids at different scales, i.e. with sampling densities in the range of one to a hundred samples per square kilometre.

The main objectives of the research are:

- the implementation of the analytical and sampling techniques of the soil gas method;
- the study of soil gases as fault tracers and of gas migration within soil and fractured zones by means of in situ tests;
- the comparison (and calibration) of the soil gas approach with other methods in order to test both the soil gas method and different lithotypes as natural barriers to gas migration;
- the creation of a data base in order to give mathematical models on gas generation and migration. The co-participants in the research with Rome University are: ISMES, Italy; Exeter University, U.K., and INTERA Sciences, U.K., as subcontractor of Rome University.

B. *WORK PROGRAMME*

The present work has been subdivided into seven tasks:

Task 1- Selecting areas in Italian subsiding sedimentary basins as test sites for the soil-gas and geophysical surveys. Laboratory equipment testing and setting up.
Task 2 - Sampling and analysis of soil gas (Rome and Exeter Universities).
Task 3 - Comparison between Rome and Exeter soil gas data.
Task 4 - Study of soil gas variations with depth, using shallow boreholes ranging from 5 to 10 meters (Rome University).
Task 5 - Execution of in situ tests by injection of gases into the soil and subsequent sampling and analysis (Rome University).
Task 6 - Geomorphological and structural research as support to the study of fracture and fault systems (Rome University). Geophysical, geotechnical and pedological studies in order to identify the main geological features and to characterise the soil and subsoil of the study areas (ISMES).
Task 7 - Statistical and mathematical analysis of the distribution of soil gases upon the data collected in the surveys conducted by Rome and Exeter Universities. This task will be carried out with the help of Intera Sciences.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In 1993 the research focused on a further development of tasks 2 and 6 and on starting task 5. The soil gas data-base has been furtherly amplified (1219 samples have been collected so far) and significant results have been obtained by the gas injection test.
In particular the following works have been performed:
- regional (Rome University) and detailed (Exeter University) soil-gas surveys, mesostructural and photogeologic studies (Rome University) in the Ofanto Basin;
- a comparison between soil-gas results obtained by different scale sampling (Rome University): two detailed soil-gas surveys were performed in the Site 2 of the Siena Basin;
- a gas injection test to study the gas movement through faulted clayey rocks (Rome and Exeter Universities);
- a geophysical investigation to select the fault in clay for the gas injection test and geotechnical analyses to assess the main characteristics of the clayey rocks (ISMES).

As experienced in all the areas surveyed so far, i.e. Piano d'Asco, Pisticci, S.Vittorino valley, Siena basin (1992 annual report), Ofanto basin and Siena basin (present report), the clay sequence, in spite of its great thickness, plasticity and low intrinsic permeability, if fractured, does not form an impermeable barrier to naturally occurring gases. The rapid ascent by advection of geogas through fractured rocks, i.e. carrier gas flowing in form of microbubbles (through ground water) or in form of free gas-phase flow (in dry conditions) and transporting trace elements (Rn, He), seems to be the most likely way in which the described soil-gas anomalies originate. Finally, the data obtained by the gas injection test provided new informations on the gas bearing properties of fractured clays.

Progress and results

UNIVERSITY OF ROME (S. Lombardi, G. Etiope, M.Guerra)

Soil-gas, mesostructural and photogeologic studies in the Ofanto basin

The Ofanto Valley is mainly filled with overconsolidated clayey sediments in which several sandy gravels horizons occur. The whole sequence shows a maximum outcropping thick of about 600 meters. The pre-pliocenic substratum is a complex flysch sequence of orogenic clayey rocks and limestones. Structural lineaments have been marked by recent geological surveys only on strathigraphic and morphological bases . In order to confirm the presence of such tectonic elements and to assess the fracturing status of the clays a regional soil-gas sampling, fracture field analysis and photogeologic study were performed. 110 soil-gas samples were collected using a sampling density of 1 sample per square kilometre (regional sampling).
Photogeologic analysis was performed using 1:33000 scale photos and consisted of identification and selection of lineaments, genetically associated with structural discontinuities, on the basis of their morphological characteristics. All linear elements with topographical expression (such as scarps, valley-floors, water courses etc.) have been marked on the aerial photographs. The total range of lineaments that may be fracture-associated have been transferred from the photos to a small-scale map. The information thus obtained has been successively completed with a check in the field.
Fracture field analysis was performed getting 18 stations including a total of 581 measured elements. Because the number of faults was not enough for a statistical analysis, only extension joints have been computed. Rocks potentially subjected to landslides or recognised as olistolites have not been considered. Structural data (azimuth and dip) have been grafically and statistically processed for each station using plane projection on the Schimdt net. All the surveys were carried out within an area of about 120 square km, from Andretta town at west and Fiumara di Atella at east, where pliocenic and pleistocenic clayey deposits outcrop.
Helium and radon statistics are summarized in Table I. About 19% He, 27% Rn and 13% CO_2 values have concentrations above the mean value plus 1/2 standard deviation (i.e. 80 ppb of He, 22 Bq/l of Rn and 2.4 % of CO_2). As usual such values are considered anomalous. Figure 1 shows the distribution of He, Rn and CO_2 concentrations. All three gases show an elongated

anomaly N45E oriented and placed in the central part of the valley, but greatest CO_2 values occur south of Calitri town. Other sharp linear trends occur in the neighbourhood of Andretta and in the southeastern part of the surveyed area. Figures 2 and 3 show statistical distribution of brittle deformations and photolineaments respectively. In the last one only lineaments occurring within zones of soil-gas anomalies were considered: five areas are so marked and for each of them a ray diagram was plotted. In the same manner mesostructural stations within each soil-gas anomalous area are clustered so that the rose diagrams at the bottom of Figure 2 are obtained. A good congruence comes out from the comparison between soil-gas lineaments, photolineaments and fracturing trends as follows:

- Stations 1, 2 and 3 show a preferential fracturing trend N10W (about N-S) coinciding with the direction of the He and Rn contour lines (N5E). More precisely the anomaly pattern is represented by a flex, i.e. a sudden decrease of gas concentration from east to west. This decrease suggests an unexpected change of rock permeability, probably because of a N-S tectonic contact between two lithotypes having different rheologic behaviour, occurring in the area, i.e. arenaceous-conglomerate sequence (eastward) and clays (westward). Photolineament direction in the area n° 1 well agrees with both fracturing and isoanomaly direction. Field observations identified a system of N-S morphological stairs that may be fault linked.
- The group including stations 5, 6, 7, 8 and 18 shows a sharp trend N50E coinciding with the He, Rn and CO_2 linear anomalies (N45E) in the central part of the valley. In this area greatest values of helium (up to 402 ppb) and radon (up to 97.31 Bq/l) occur. Even in this case the photolineament direction (N40E) coincides with previous data as showed in diagram of the area n°2. In this sector stratigraphic evidence suggests the occurrence of two great antiapenninic faults.
- The diagram referring to mesostructural stations n° 15, 16 and 17 shows a preferential fracturing trend N55E coinciding with the direction of Rn anomalies in the western area of Rapone. Such an antiapenninic component is also reported by the photolineament diagram of the area n°5 and it is also suggested by regional tectonic features occurring just south of the Ofanto basin (for example the "S.Fele-Vulture Line" reported by small-scale geological maps).

The main conclusion is that the clayey sequence of Ofanto basin is affected by a great fracturing. Soil gas analyses indicate that vertical migration of deep seated gases occurs through fractured and/or faulted zones, whose presence is supported by both photogeological and fracture field data. Further surveys are planned using detailed samplings in order to develop the presented results.

Soil-gas surveys at site 2 (Siena basin): comparison between results from different scale sampling

To recognize the sensitivity of the soil gas method for tracing faults, a comparison between soil gas results obtained in the same area at different scales of sampling has been done. During summer 1993 two different scale surveys were performed in Siena Basin at Pieve di Pacina i.e. Site 2 (Figures 4a and 4b). Site 2 is placed 8 km north-easting respect Site 1, along the great fault system known as Arbia Line (see 3rd progress report for details).
At Site 2 gas sampling was executed in accordance with two different dimensioned regular grids with square meshes. The larger one (in the following referred to as Site 2) covers an area 4 km^2 wide and has meshes with side 200 m long. The closer grid (in the following referred to as Site 2bis), placed in the core of the larger grid, covers an area of 0.16 km^2 and has a point to point distance of 50 m.

Descriptive statistics of soil-gas results are reported in Table II (data from Site 1 are shown for comparison as well). Values above the mean plus 1/2 standard deviation are considered anomalous. The distribution of the gases are plotted in Figures 5, 6 and 7.

Results from Site 2 show that both higher Rn and CO_2 concentrations (Figures 5 and 7) are linearly distributed in the central sector of the investigated area, corresponding with the Malena river valley. Furthermore such linear anomalies seem to follow the Malena river in its change of direction; this change is likely induced by tectonic as revealed by a photogeological analysis and field check.

On the contrary major helium concentrations were found in the south-east side of the scanned area (Figure 6). Few anomalous (positive) points occur in the valley. Everywhere in the central sector of site 2, crossed by the Malena river, helium values are negative except for few isolate and scattered points where values exceed atmospheric reference by 200 ppb.

The excellent agreement between Rn and CO_2 distribution is visible from both the results of Site 2 and Site 2bis: major concentrations of both gases were found just in the talweg of the valley. The absence of helium anomalies in the central sector of the valley is confirmed by the more detailed sampling grid of Site 2bis, where no anomalous ridges or trends were detected.

From these results three main conclusions can be drawn:

a) Results from the two different scale sampling show an appreciable congruence; it can be observed for all three gases. In particular as Rn as CO_2 anomalies show, from the comparison of the two scales, the same trends in the same locations, but a better resolution of the anomaly size and shape appears from the more detailed sampling (Site 2bis). Furthermore, also the absence of helium positive anomalies comes out from both maps.

b) The excellent agreement (the spatial association) between Rn and CO_2 distribution, which is shown in both different sampling surveys, suggests that CO_2 may act as a carrier gas for Rn which, because of its very low concentration, cannot move by itself /1/.

c) No sensible time-variations of soil-gas concentrations appeared during the time-gap between the two surveys (about two weeks); even if the variation of the climatic factors (mainly soil moisture, atmospheric pressure, soil and air temperature) affected punctually soil gas values, the statistically derived gas distributions was unchanged.

UNIVERSITY OF EXETER (G.A. Duddridge, P. Grainger)

Soil-gas traverses in the Ofanto basin

The results of soil-gas traverses in the Ofanto valley have proved less discerning than earlier surveys such as that undertaken in the Siena Basin, where overall soil gas values were higher and anomalies more pronounced. In the Ofanto Basin concentrations were closer to background variations, that is changes due to soil moisture content/permeability, sampling and analitycal errors. Average ΔHe values from the area were only 21 ppb which is close to the ± error of readings from the helium analyser chart output. This coupled with a maximum ΔHe value of just 110 ppb left little that could be positively identified as fault or fracture related. Similarly average CO_2 was only 0.49% whereas on moist grassland in Britain a value of 2% is typical. Radon was more informative with the average of total Rn being 102 cpm or about 20 Bq/l. The highest count was 519 cpm and each traverse showed a maximum above 200 cpm.

The low soil gas values of He, Rn and CO_2 were particularly a feature of the faulted area tested to the south of Andretta. A possible explanation of this is that at the topographic level tested the lithology consists of gravel/boulder horizons rather than clay. It is likely that they would permit lateral gas flow, so reducing and spreading the peaks of any anomalies.

Nevertheless, for Rn there were isolated high values, for example the highest ^{220}Rn recorded by the University of Exeter was 339 cpm (total Rn 519 cpm) and this was located 1km south west of Andretta. On the east-west traverse 4 (Figure 8b), half a kilometre south of Andretta, sample site -160 m, above average 75 ppb ΔHe was matched by 224 cpm of ^{222}Rn and 3.45% of CO_2. At site 380 m on traverse 4 ^{220}Rn was relatively high at 196 cpm, but ΔHe was only 25 ppb. The traverse crossed a fault scarp, downthrow on the western side, at the 220 m point. However, there appears to be no evidence of enhanced soil gas concentrations at this point.

Valleys in the neighbourhood of Calitri, believed to be fault guided, showed some evidence of anomalous soil gases. Traverse 2 from east of Calitri (Figure 8a) showed a broad ^{222}Rn anomaly, peaking at 189 cpm, 140 m to the west of the river bed. A further test traverse, 500 m up the valley to the north, showed ΔHe up to 110 ppb over a 150 m wide zone in the valley bottom.

ROME AND EXETER UNIVERSITIES (G.A. Duddridge, G. Etiope, P. Grainger, M. Guerra, S. Lombardi)

Gas injection experiment

A gas injection test has been planned in order to examine the movement of a discrete gas phase (helium) within saturated, porous and faulted clayey rocks. An inclined borehole for gas injection was used; it was drilled close to a fault marked by geophysical data.

The location of the test is shown in Figure 9 and the geometry of the borehole-fault system is shown in Figure 10.

Prior to the helium injection, a He and CO_2 soil gas survey was performed to establish background values in the field. Gas sampling and analysis were performed according to the procedure adopted by Exeter University (see previous reports).

A sampling grid was pegged out and labelled. Its geometry and orientation are represented in Figure 9. Each grid point was 10 m apart. The greatest concentration of sampling and analyses was centered over the inferred position of the fault as established by the geophysics. The principal monitoring points established for the duration of the experiment were along two SSE to NNW traverses and along the fault.

The results of background survey are reported in Figure 9 as contour plots. On the same figure, results from the network of grid points to the north of the Malena river, as surveyed in 1992, are also presented.

The background survey showed that, except for one sample point where the ΔHe value was recorded at 458 ppb above atmospheric reference, the natural ΔHe values in soil gases ranged between 0 and 100 ppb. CO_2 values reached a maximun of 4.88%.

The gas injection procedure arrangements consisted of a 9000 litre capacity helium cylinder fed via a gauge panel to the gas injection point at the bottom of a packered borehole. A single type packer (1 m long, 63.3 mm diameter rubber sleeve) was used. The packer was lowered to a 20 m below ground level, just above the screened borehole section. Repeated measurements assessed the water table at 7.1 m below ground surface

The packer was inflated up to a pressure of 8 bars using an air compressor. A little over 3000 litres of He were injected in 45 minutes, with an injection pressure of about 2.4 bars (see 5th report for details).

After the gas injection the same grid used for background survey was daily monitored, from June 18th (the injection day) to July 3rd, by Exeter University and twice a week up to July 28th by Rome University. Each group was using its own but similar techniques (see previous reports).

A graph concentration of the variation of ΔHe versus time during injection test is shown in Figure 11. It was position 4-4 (see Figure 9) that began to reveal high ΔHe starting with 161 ppb, 2 days after the injection. Daily increases then took values to: 238, 391, 2795, 8159, 15640, 22240, 36182, 47955 and 54584 by the 29th June. Up to this time it was thought that gas could be emitted at other points along the fault and possibly elsewhere. Surrounding positions within 10 m did not respond to the injected gas revealing only values considered to be background. Time was spent during the upward passage of gas at position 4-4 in checking all other points in the field plus other points to the north of the Malena river. From this date, the pattern of gases was explored in more detail, firstly by establishing sample points at 5 m and then when this gave higher He values at the 2.5 m distance. The highest value of recorded ΔHe was 477020 ppb at 3.5 m west of position 4-4, 92 times more than atmospheric level. Heavy rain then disrupted the daily monitoring for 24 hours and from 3rd July 1993 sites around 4-4 were monitored on selected days to 28th July by the University of Rome.

In the ligth of such results the main observations can be summarized as follows:

- The injection of gas at 2.4 bars, about 20 m below the ground, produced an advective movement of gas, mainly through saturated sediments, towards the surface, i.e. a gas migration in a two phase system occurred. This means that displacement of groundwater and/or a gas micro-bubble stream took place. Considering a break through time of 36 hours ± 12 hours (as suggested by the curve of Figure 11) the gas reached a velocity along the fault path of 0.015 cm/sec (± 0.003 cm/sec).

- The high soil gas values of He appeared over the fault at the minimum distance from the subsurface injection point and were confined to one small 200 sqm circular area. Beyond this area, even over the fault, no high values of ΔHe above background were recorded.
- The concentration in the soil, in this small area, of injected He indicates transport to the surface via a channel. The contrast in values over distance of a few metres shows that the channel must have been similarly narrow. The pattern of decreasing soil gas ΔHe values around the centre of the highest concentration (3.5 m west of position 4,4) may be considered as an halo of dispersion occurring just in the soil which cause a funnel-shaped distribution in 3 dimensions.

It is concluded that when a relatively high pressure occurs within fractured clayey rocks, gas can migrate quickly upwards following channels of enhanced permeability. Faults in clay are not totally gas tight, but at some points may yeld preferential paths, even if narrow, for gas escape. This has already been suggested from observations of naturally occurring soil gas anomalies over faults in clay.

ISMES (F. Gera, V. Chiantore, R. Pensieri)

Geophysical surveys in the Siena basin

The study area is Site 2 (northern sector of the Siena basin) in the Malena River valley. The geophysical investigations have been located after an accurate topographic survey.

During November 1992 ISMES carried out the following surveys:

- 2 High Resolution Reflection Seismic Lines (SI-01-92, SI-02-92);
- 3 Vertical Electrical Soundings (VES01, VES02, VES03);
- 2 Horizontal Electrical Soundings (along SI-01-92, along SI-02-93).

The high resolution reflection seismic survey has been aimed at evaluating the usefulness of the method to reveal the presence of small dislocations to be related with the results of soil gas measurements.

The geoelectrical survey has been carried out to define the main characteristics of the geological formations: thickness, presence of main sedimentary discontinuities, etc..

Considerations about seismic sections

On both lines SI-01-92 and SI-02-92 the presence of two marked horizons has been identified. The first horizon is located at the depth of 70-100 m from the field plane; the second horizon is located at the depth of 130-180 m from the field plane.

On line SI-01-92 the presence of a fault is evident on the vertical of the geophone point 163. On line SI-02-92 a fault is evident on the vertical position of geophone point 174. Further inferred faults seem to be present on the seismic sections.

Geoelectrical reconnaissance

The resistivity values measured with the resistivity profiles are of the same order of those measured with VES; the values range between 25 Ohm/m and 40 Ohm/m. Further, there is a difference on the average resistance among the shallow sediments located in the northern side and those in the southern side of Malena river. They could indicate the presence of zones with different characteristics.

VES02 and VES03 have pointed out the presence of a thick low resistance layer at the depth of about 180 m from the field plane (Figures 12 and 13). To date, VES01 has not been used for interpretation.

In addition, during May-June 1993, a more detailed geophysical survey was performed in the same area (site 2) to achieve more precise information on the location of faults. On such informations the site for the gas injection test was selected.

Laboratory determinations

Geotechnical, pedological, mineralogical determinations have been carried out on samples collected both in the Siena and Irpinia areas in order to define preliminarly the main characteristics of the superficial and (at Poggio Bonelli) deep sediments.

The samples under investigation have been identified according to the area and the points of collection (and the date) as follows:

a) SIENA 92, L01/L02: 5 shallow disturbed samples;
b) IRPINIA 92, A1/A2/A3/A4/A5: 5 shallow disturbed samples;
c) SIENA 93, drilling: 2 deep undisturbed samples.

From the physico-mechanical and chemico-mineralogical points of view, the main obtained results are the following.

Superficial samples

- those collected in Irpinia (near Andretta viilage) are quite variable in granulometric composition but quite homogeneous as far as chemical and mineralogical characteristics are concerned (Tab. 1a);

- those coming from the Siena area (Poggio Bonelli) are sandy-silty (or silty-sandy), showing only minor variations in granulometric composition.

Deep samples from the poggio bonelli borehole

SAMPLE 1 (depth 10.10 - 10.30)

Sandy silt with clay (AGI classification); liquid limit 32%; plastic index 15%; classification (according to Casagrande) "inorganic clay, medium plasticity"; maximum preconsolidation strain: about 1.5 MPa. The determination of the overconsolidation ratio has not been possible in absence of information about the depth of the water table.

SAMPLE 2 (depth 21.70 - 21.90)

Silty sand with clay and a few of gravel; no Atterberg limits determination due to the limited amount of fine grain material; the oedometric curve, typical of a quite disturbed material, did not allow the definition of the maximum preconsolidation strain.

It is worth to note that the bulk density of each sample has been determined by taking measurements of weight, height and diameter of the trimmed specimens prepared for the oedometric and permeability tests. The mean values of the determinations carried out on each sample are: 20.43 kN/m^3 (sample 1) and 20.57 kN/m^3 (sample 2).

The specific gravity, related to water density (20°C) and expressed as a pure number, has been determined by using a pycnometer and an appropriate amount of overdried soil. Two independent tests have been performed for each sample and the results presented are the mean values: 2.73 (sample 1) and 2.71 (sample 2).

In addition, the two samples coming from the borehole at Site 2 (depths about 10.20 m and 21.80 m) show very similar composition of clay minerals even if the clay content of the deepest is subordinated. A triaxial permeability test (on the first sample, depth 10.20 m) indicates a very limited water conductivity of the silty formation (k=4E-10 m/s).

The results of the pedological determinations are still under study; preliminarly, it is possible to anticipate that variations in both the characteristics and chemical contents are not negligible.

REFERENCES

/1/ ETIOPE G., LOMBARDI S. (1993): Soil gases as fault tracers in clay basins: a case history in the Siena Basin (Cenral Italy)- Proceedings of 2nd C.I.G.G., Besancon 5/9 Jul. 1993, for conference papers

TABLES

***Table I Ofanto Basin* (1 sample/km^2)**

GAS	Mean	St.Dev.	Max.Val.	Min.Val.	Count
ΔHe (ppb)	19	131	402	-509	110
^{222}Rn (Bq/l)	16.93	17.24	97.31	0.74	110
CO_2 (%)	1.33	2.10	15.51	0.13	106

Table II Siena Basin

(Site n°1 - Acqua Borra- 25 samples/km^2)

GAS	Mean	St. Dev.	Min.	Max.	Count
ΔHe (ppb)	0	126	-460	626	195
^{222}Rn (Bq/l)	14.17	18.87	0	100.64	195
CO_2 (%)	2.77	4.72	0.30	58.25	195

(Site n°2 - Pieve di Pacina - 25 samples/km^2)

GAS	Mean	St. Dev.	Min.	Max.	Count
ΔHe (ppb)	-21	216	-772	998	121
^{222}Rn (Bq/l)	29	23.91	0	123.58	121
CO_2 (%)	3.04	2.31	0.03	10.15	121

(Site n°2bis - Pieve di Pacina - 400 samples/km^2)

GAS	Mean	St. Dev.	Min.	Max.	Count
ΔHe (ppb)	-62	201	-688	998	81
^{222}Rn (Bq/l)	23.88	16.63	0	71.78	81
CO_2 (%)	2.58	1.96	0.13	9.8	81

CAPTIONS

Figure 1 - Sketch-maps of soil gas distribution in the Ofanto Basin

Figure 2 - Fracture field analisys in the Ofanto Basin

Figure 3 - Photo-lineament map from the Ofanto Basin

Figure 4a,b - Location and geometry of sampling grids in Siena Basin

Figure 5a,b - Rn distribution in soil-gas from two different scale samplings

Figure 6a,b - ΔHe distribution in soil-gas from two different scale samplings

Figure 7a,b - CO_2 distribution in soil-gas from two different scale samplings

Figure 8a,b - He/Rn values from (a) traverse 2 - Calitri and (b) traverse 4a,b,c - Andretta

Figure 9 - Location of gas injection test site and background helium values

Figure 10 - Stratigraphic sequence and geometry of the borehole-fault system

Figure 11 - Helium variations during injection test

Figure 12 - Resistivity profiles SI-01-92 and SI-02-92, V.E.S. 02 and V.E.S. 03

Figure 13 - Line SI-02-92: geological interpretative section

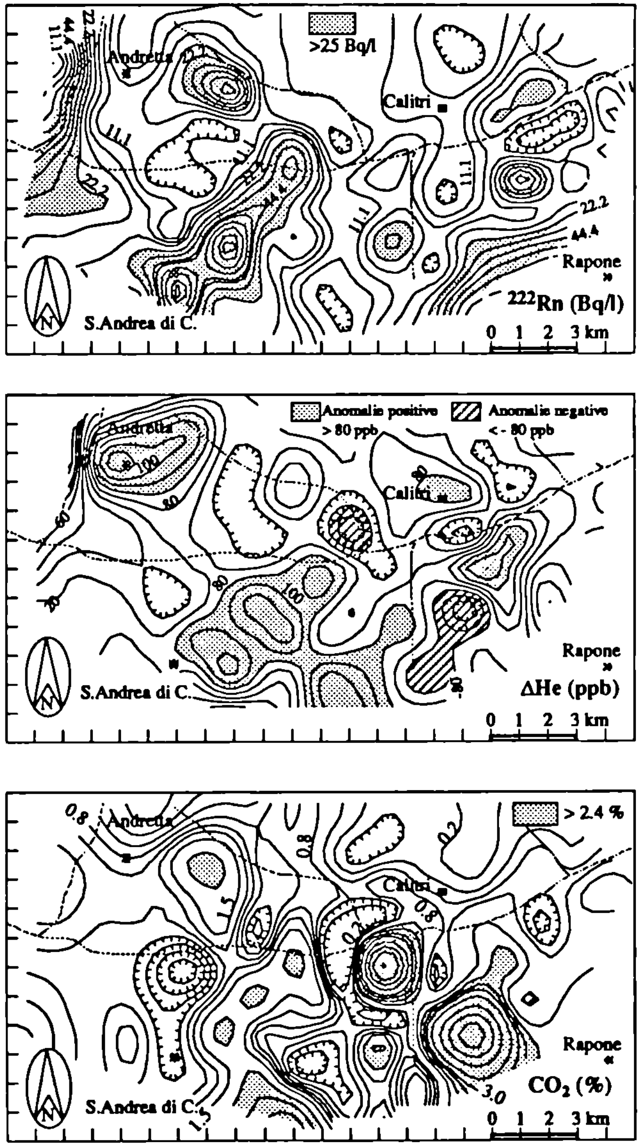


Fig. 1

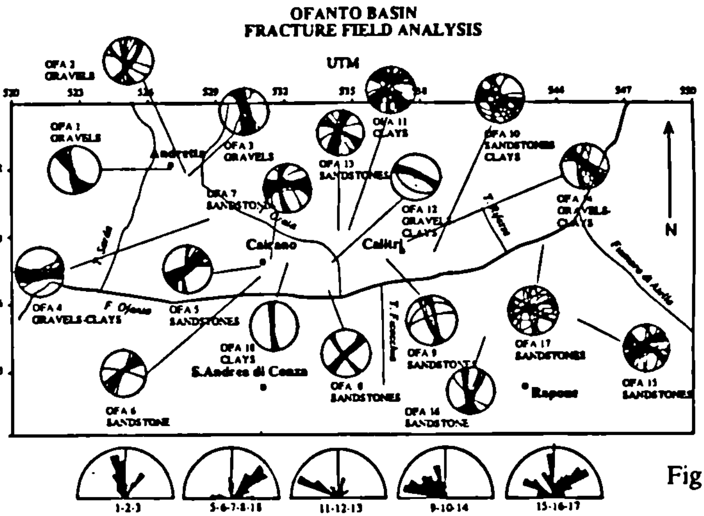


Fig. 2

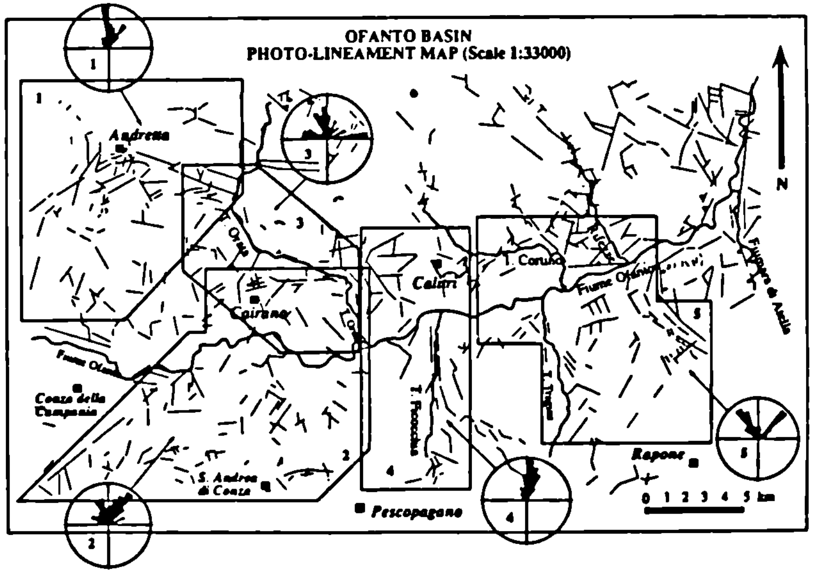


Fig. 3

Fig. 4a

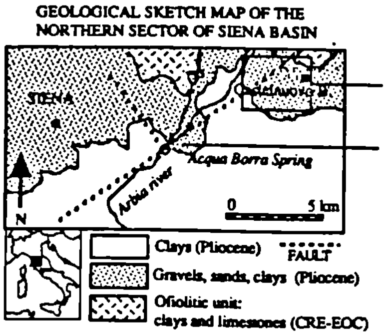


Fig. 4b

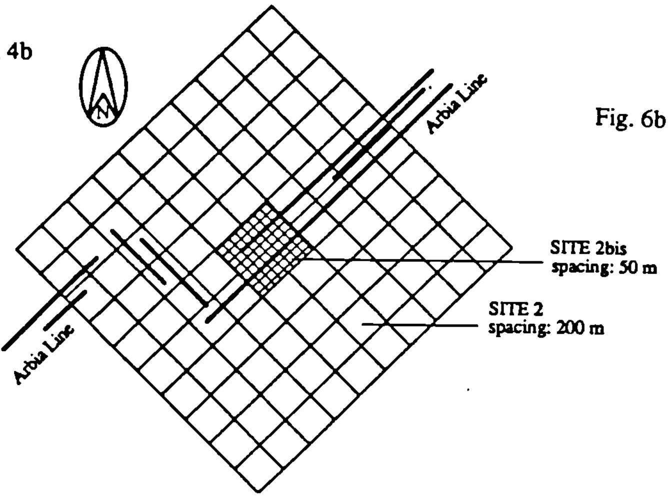


Fig. 5a

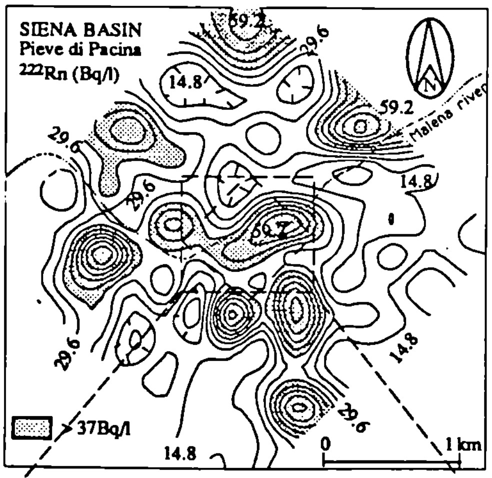


Fig. 5b

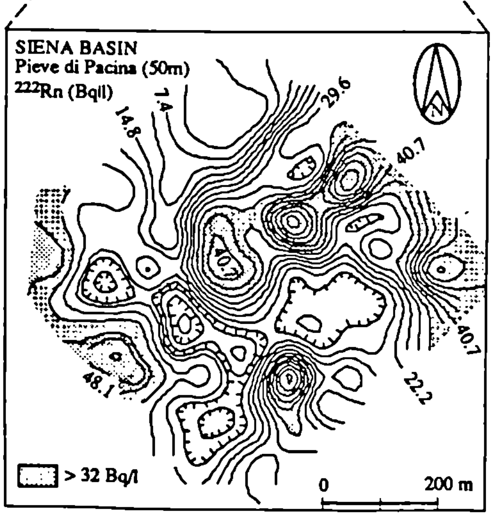


Fig. 6a

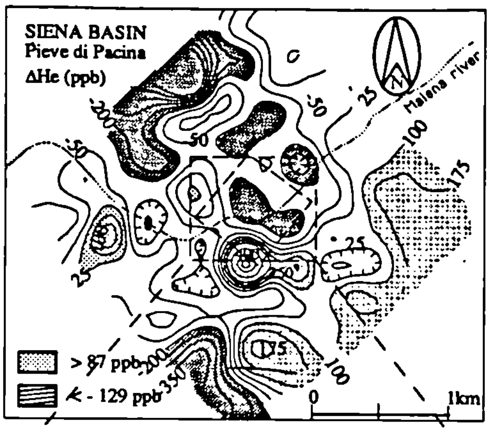


Fig. 6b

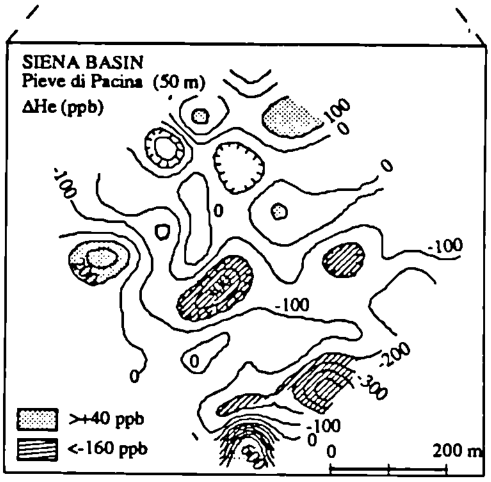


Fig. 7a

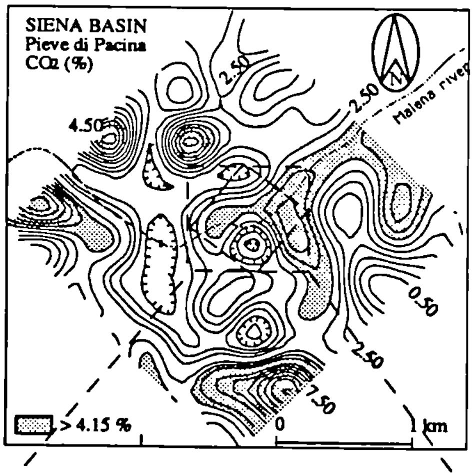


Fig. 7b

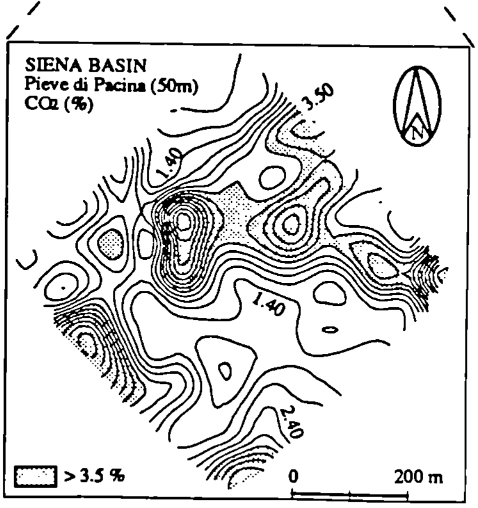


Fig. 8a

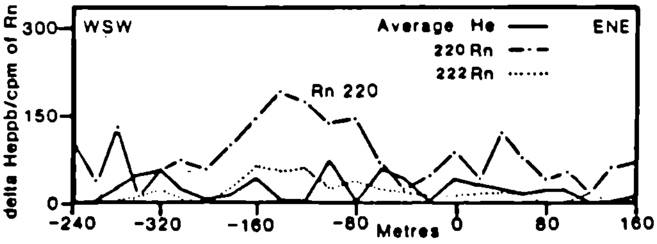
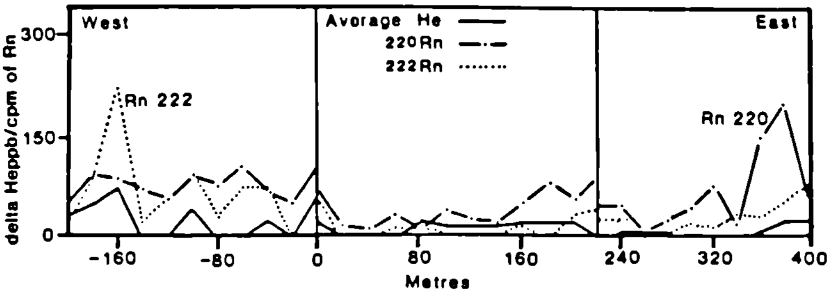


Fig. 8b



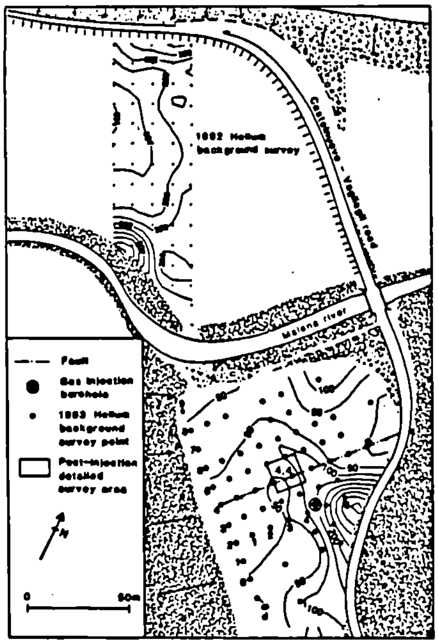


Fig. 9

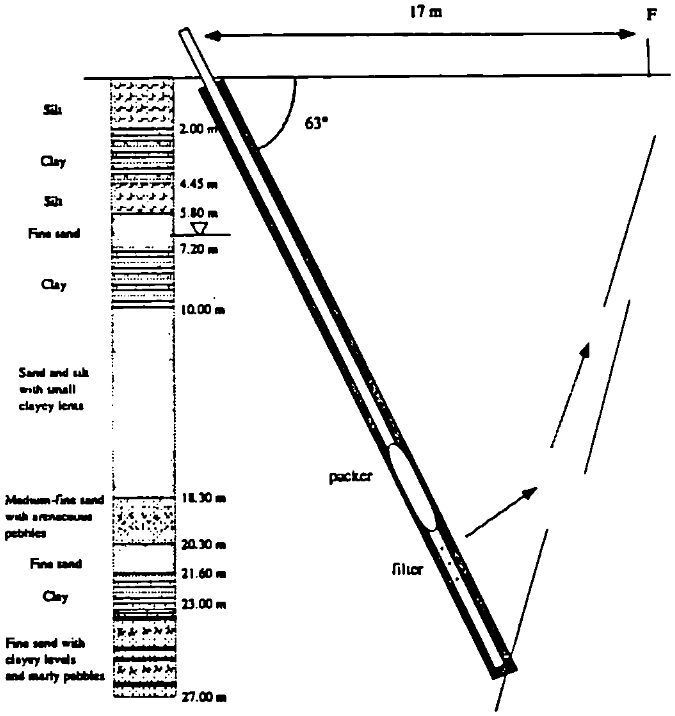


Fig. 10

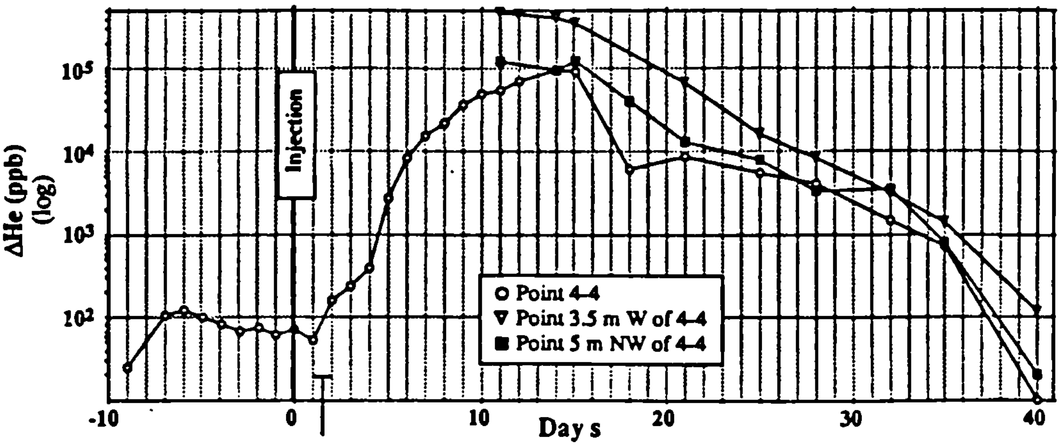


Fig. 11

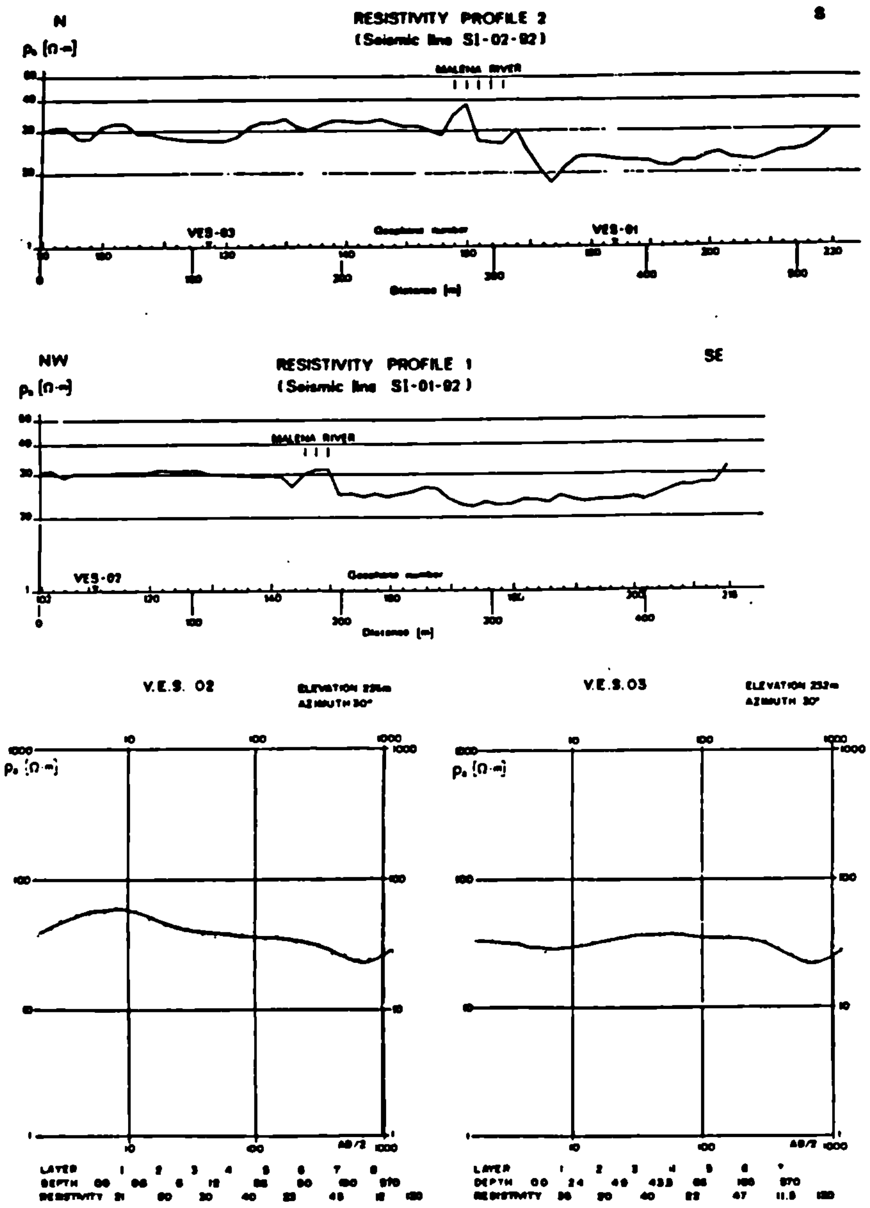

N
RESISTIVITY PROFILE 2
(Seismic line SI-02-92)
S
MALENA RIVER
VES-03
Geophone number
VES-01
Distance (m)
NW
RESISTIVITY PROFILE 1
(Seismic line SI-01-92)
SE
MALENA RIVER
VES-07
Geophone number
Distance (m)
V.E.S. 02
V.E.S. 03
ELEVATION
AZIMUTH 30°
AB/2
LAYER
DEPTH
RESISTIVITY

Fig. 12

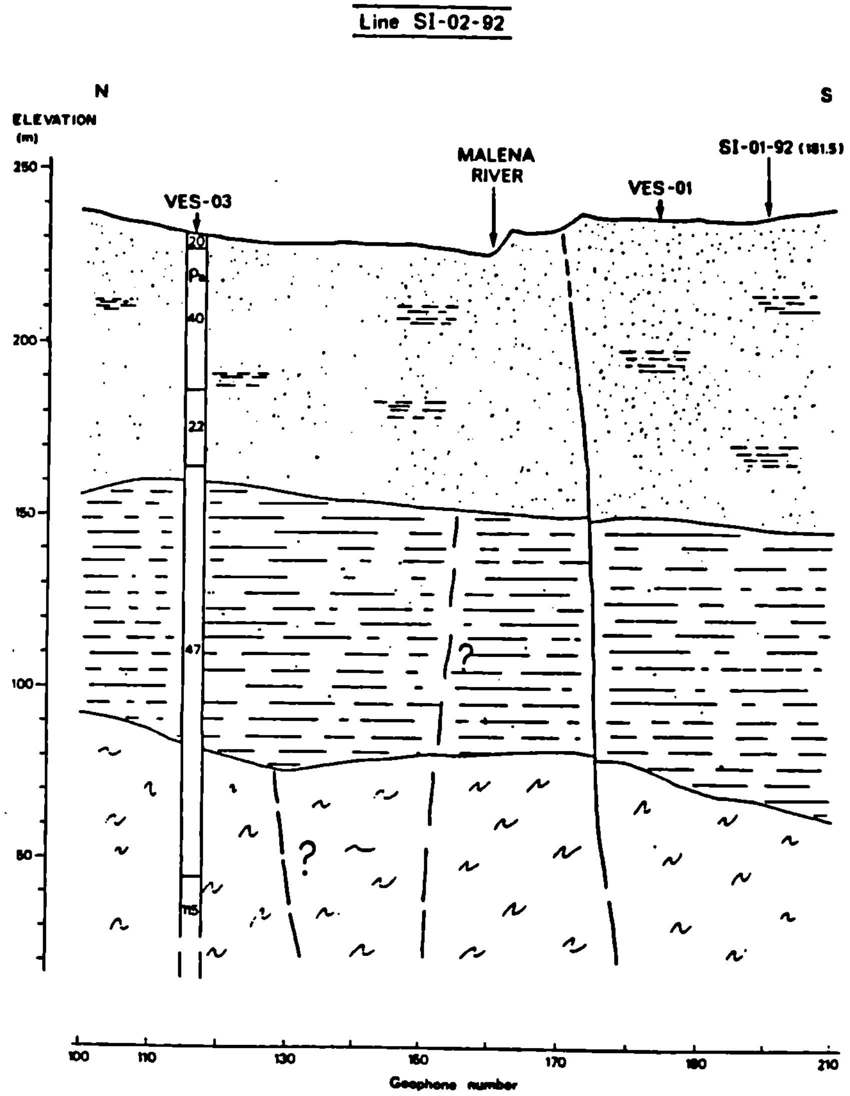

Line SI-02-92
N
S
ELEVATION (m)
250
200
150
100
50
VES-03
MALENA RIVER
VES-01
SI-01-92 (181.5)
20
ρ_a
40
22
47
115
?
?
100
110
130
150
170
180
210
Geophone number

Fig. 13

Title : MEGAS : Modelling and Experiments on GAS migration in repository host rocks
Contractors : SCK/CEN, INTERA, BGS, ISMES
Contract N° : FI2W-CT91-0076
Duration of contract : from 01-03 91 to 28-02 94
Period covered : January to December 1993
Project leader : G. Volkaert (coordinator), M. Impey (INTERA), P. Hooker (BGS), V. Fioravante (ISMES)

A. OBJECTIVES AND SCOPE

For the option of a deep geological disposal facility several potential sources of gases were identified : i.e. the anaerobic corrosion of iron, degradation of organic materials, the gas present as such in the waste packages. Of those gases hydrogen is certainly the gas which can be released in the potentially largest amount. For the safety evaluation of a repository, it is necessary to know the effects of gasses on the host rock.

The primary objective of the MEGAS project is to understand the consequences of gas generation in a clay host rock. The final objective of this project will be to validate a gas migration model and to confirm our understanding using an in situ gas injection experiment.

B. WORK PROGRAMME

1. Chemical reaction and diffusion experiments

The reaction capacity of hydrogen with Boom clay observed in previous experiments will be further investigated by determining the intrinsic reaction rate, the reaction capacity and the diffusion coefficient.

2. Geotechnical experiments : uniaxial

In these experiments the gas permeability (two-phase flow) and the gas breakthrough pressure will be determined.

3. Geotechnical experiments : triaxial

The goal of these experiments will be to define the conditions under which preferential pathways for gas migration might develop and to examine bubble growth and migration. Triaxial experiments will also be performed at elevated temperature.

4. In situ experiments

These will be performed in the HADES underground research facility (Mol, Belgium).

5. Modelling

The following approaches will be utilized : modelling the dynamics of bubble flow and modelling two phase flow. The laboratory experiments will be used to validate and, possibly, calibrate a basic two phase flow model.

Within this project INTERA will perform the main modelling work. The SCK/CEN will be responsible for the gas reaction, diffusion, uniaxial flow and in situ experiments. BGS will perform geotechnically based triaxial gas flow experiments. ISMES will perform experiments at higher temperature.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

1. Chemical reaction and diffusion experiments

The new improved reactor was tested and two reaction experiments were performed in it.

An in-diffusion test was performed using copper seals. The diffusion leak was reduced but is still not negligible. Therefore two completely welded through-diffusion cells were developed. The first results obtained with this cell type are promising.

2. Geotechnical experiments : uniaxial

X-ray tomography was applied to measure in a non-destructive manner the saturation profile during gas breakthrough. The gas breakthrough experiments were continued and refined. A first gas breakthrough experiment on a clay core under controlled vertical stress was started.

3. Geotechnical experiments : triaxial

1D and radial (needle injection) gas flow experiments were performed on clay plugs under isostatic confinement conditions. Both constant gas flux as constant gas pressure conditions were applied. Needle gas injection experiments at higher temperature up to 80 °C have been performed on Pontida and Boom clay.

4. In situ experiments

Preliminary in situ gas injection experiments were performed using the multi screen piezometer installed in 1986 at the bottom of the shaft.

The equilibration of the hydrostatic pressures on the four piezometers for the new in situ gas injection experiment was further followed. A hydraulic test was performed to measure the hydraulic conductivity and storage coefficient. Due to the slow pressure equilibration, the start of the gas injection was delayed until end January 1994.

5. Modelling

The two phase flow code TOPAZ was applied to simulate the results of two laboratory gas injection experiments.

The TOPAZ code has been further refined to study the effect of gas pressure on the porosity, the hydraulic conductivity and the time needed to reach a steady state gas flux.

Progress and results

1 Chemical reaction and diffusion experiments

The new reactor is now operational and was tested by performing two blank tests with pure water under a hydrogen atmosphere. No other significant phenomenon than the dissolution of H_2 in water occurred. A H_2-clay slurry reaction was started in September 1993 and is still going on. The observed hydrogen reaction has a constant rate of about 10^{-8} mole H_2/day.g clay. The total actual hydrogen consumption is 1.12 µmol/g clay.

The fifth in-diffusion experiment carried out with a soft copper ring placed at the bottom flange gave a better result regarding the hydrogen leak, which was reduced by a factor two compared to the former system. Nevertheless, hydrogen continues to escape by diffusion through the piston's Buna O-rings.

A first through-diffusion experiment was performed. In this experiment, at one side of the clay core a constant hydrogen pressure is applied while initially the pressure at the other side is equal to the equilibrium water vapour pressure. The quantity of hydrogen diffused through the core is determined by measuring the pressure increase at the outlet side. This side is completely sealed by welding so that leaks can be excluded. The value of the diffusion coefficient D derived from the first through-experiment is in the same range as for the in-diffusion experiments, but ηR and thus ηRD are an order of magnitude lower.

2 Geotechnical experiments: uniaxial

The three gas breakthrough experiments installed at the University of Ghent have been finalised. The goal of these experiments is to measure non - destructively the change in saturation of a clay core caused by gas flow. X-ray tomography was applied to determine density changes in the clay cores. By calibration we have shown that a change in radiological density of 10.1 H.U. (Hounsfield units) corresponds to a change in water content of 1 volume %. This is equivalent to 2.5 % change in saturation. After gas injection through core 23B7K3 a decrease in mean radiological density of 19 H.U. corresponding to a 5 % decrease in saturation was observed. In the two other experiments the change in saturation was negligible. These results correspond well with those obtained by destructive analysis.

Two experimental set-ups for the study of gas flow on clay cores under controlled vertical stress have been constructed. With this equipment the influence of the vertical stress on the gas flow parameters will be studied. Two experiments were started. The hydraulic conductivities before and after applying 4.4 MPa vertical stress were measured. Gas injection has been started and is still ongoing on the first experiment. End January 1994 gas injection on the second experiment will start.

3 Geotechnical experiments: triaxial

Figure 1 shows a simplified scheme of the "flow-through" apparatus developed by BGS for the MEGAS Project. The apparatus comprises 5 main components: (a) a sample assembly, (b) a pressure vessel rated at 35 MPa together with its associated pressure control equipment, (c) a fluid injection system, (d) a back pressure system and (e) a microcomputer-based data acquisition system. Total stress σ has been shown to be an important parameter in determining the behaviour during gas injection. Therefore a key feature of the design is that the sample is subjected to an isotropic total stress σ, which is maintained constant during the course of a test. By applying a fixed back pressure P_w, the sample can be consolidated at the onset of testing under predetermined effective stress conditions ($\sigma_{eff} = \sigma - P_w$) so that the initial porosity is as close as possible to its in situ value.

Control of the injection flux is achieved using a stepper-motor driven syringe pump. The fluid injected into the 49 mm diameter by 49 mm long cylindrical test sample can be either water-saturated helium or a synthetic ground water solution with chemistry matched to the "bulk interstitial pore water" of the clay. In normal use the injection pump is set up for constant flow-rate control, with flow-rates typically in the range 5-50 μl per hour. Back pressure P_w is controlled at the outgoing end of the sample using a second syringe pump which is also capable of continuously monitoring the volume of effluent.

A typical test sequence for a sample of clay consists of the following stages: (a) resaturation and consolidation at in situ effective stress ($\sigma_{eff} \approx 2.2$ MPa), (b) intrinsic permeability determination at a number of (volumetric) water flow-rates, (c) re-equilibration, and (d) gas injection at a number of gas flow-rates.

Figure 2 shows a typical result of a gas injection test under constant inflow conditions and constant outlet pressure. The inlet pressure builds up until gas breakthrough occurs. At this point there is a small but sharp drop in the inlet pressure. The gas outflow is not continuous but seems to occur in small "bursts". When the inflow rate decreases, the inlet pressure decreases while the outflow continues be it at a lower flow rate. This means that after gas breakthrough, gas flow can occur at a lower pressure than the breakthrough pressure.

The measured gas flow rates and breakthrough pressures are of the same magnitude as those obtained from the uniaxial experiments on Boom clay.

ISMES has further modified the internals of the HITEP triaxial apparatus so that now gas can be injected through a hollow needle perforated over its whole length (see Fig. 3). Before gas injection the samples are consolidated at a given vertical stress. The consolidations were performed under k_0 conditions i.e. no radial deformations allowed. Experiments have been performed on Pontida and Boom clay. In total 44 experiments were performed with this experimental setup. In these experiments, different consolidation stresses, different degrees of saturation and temperatures between 20 °C and 80 °C were applied.

For both clay types it was shown that with increasing consolidation stress and/or increasing degree of saturation, the gas breakthrough pressure increases and the gas flow rate decreases. As shown in Figure 4, an increase in temperature at constant consolidation stress leads to an increase in gas breakthrough pressure.

4 In situ experiments

Preliminary in situ gas injection experiments using helium were performed in a vertical piezonest installed under the shaft on the 18-12-1986 (see Fig. 5). Since end 1986 the hydrostatic pressures on this piezonest were followed and have shown that there is no direct hydraulic connection between neighbouring filters.

First gas was injected through filter 6 at 2.25 MPa. After only two days a sharp pressure rise in filter 7 occurred indicating gas breakthrough. Gas injection was stopped in filter 7 and was started again in filter 9. First gas was injected during 1 month at 2.17 MPa and no breakthrough occurred. Then the gas pressure was increased to 2.25 MPa and after about one week the gas created a connection with filter 8. Two weeks later a connection with filter 7 was created and then quickly with all the other filters.

As the initial hydrostatic pressure in filter 9 was 1.6 MPa, gas breakthrough occurred at only 0.6 MPa overpressure which is much lower than in the laboratory experiments i.e. at least 1.2 MPa. The most probable explanation for the observed phenomena is the disturbance of the local geomechanical stress field due to the installation of the piezonest.

Figure 6 shows the hydrostatic pressures measured on the new gas injection experiment installed last year. A hydraulic test was performed to measure the local hydraulic parameters around the four piezometers. In this test water was allowed to flow out of one of the filters of the central piezometer and the pressure drop in the other filters was determined. The following hydraulic parameters were obtained:

storage coefficient = $8.07\ 10^{-6}\ m^{-1}$

horizontal hydraulic conductivity = $5.17\ 10^{-12}\ ms^{-1}$

vertical hydraulic conductivity = $2.35\ 10^{-12}\ ms^{-1}$.

These values are within the expected range for natural Boom clay.

5 Two-phase flow modelling

A series of calculations were performed, using the TOPAZ two-phase flow code, for comparison with the results of gas injection experiments performed by SCK•CEN on cores 23B5.5k2 and 23B4.5.

The results obtained with the TOPAZ code appear to be in reasonable agreement with the experimental measurements of saturation profile for core 23B5.5K2. For core 23B4.5 however the calculated result is a few percent higher throughout the core. The error with experimental measurements may be 1-2 %.

The correspondence between measured and calculated gas fluxes is also variable. Closest agreement is obtained for core 23B4.5, using the lower estimate capillary pressure curve. All flux results obtained with TOPAZ are lower than the measured values, suggesting that the measured hydraulic conductivity and relative permeability curves used in the calculations may have to be modified to more accurately reflect the flow of gas in the cores. The calculated times needed to reach steady state flow was much larger than the observed equilibration times. It should be noted that the calculated fluxes are in good agreement with the analytic prediction for gas flow through an unsaturated medium. Thus it may be that the order of magnitude difference in the gas flux for the core 23B5.5k2 is a result of flow conditions not matching the Darcy two-phase flow model assumed in TOPAZ : one possibility is the existence of preferential pathways for the gas in the core.

The TOPAZ code has been further refined to include the effects of rock compressibility on the gas flow. It has been shown that these effects might explain the observed equilibration times.

4. Conclusion

At low gas pressures, hydrogen is only transported by diffusion. The reaction capacity of undisturbed Boom clay is negligible and even the reaction capacity of oxidized clay seems to be very limited. At higher pressures, two phase flow occurs. It was experimentally shown that only a small fraction of the pore water is displaced by the gas. An increase in temperature has the same result on gas flow as an increase in effective vertical stress i.e. an increase in breakthrough pressure and a reduction in flow rate.

In case of two phase flow the TOPAZ code simulates rather well the gas flow rate and the saturation profile. Once the gas pressure annihilates the effective stress, preferential pathways are created and a much larger gas flow is observed.

The MEGAS project will further be focused on the determination of the conditions under which two phase flow prevails and those under which preferential pathways are created.

List of publications

/1/ G. Volckaert, P. De Cannière, L. Ortiz, M. Put
Experiments on gas migration in the Boom Clay.
SMIRT-12 Post-conference seminar N°10
ETH, Zurich, Switserland, 23-24 augustus 1993

/2/ G. Volckaert, M. Put, L. Ortiz, P. De Cannière, S. Horseman,
J. Harrington, V. Fioravante, M. Impey, K. Worgan
MEGAS - Modelling and experiments on gas migration in repository host rocks.
Pegasus meeting 3 to 4 june 1993 GCS Köln

/3/ G. Volckaert, M. Put, P. De Cannière, K. Bateman, J. Harrington,
V. Fioravante, M. Impey, K. Worgan
MEGAS - Modelling and experiments on gas migration in repository host rocks.
Annual Progress Report 1992
Contract N°FI2W-CT91-0076
Ed.: SCK•CEN R-2938

/4/ K. Worgan, M. Impey, G. Volckaert, P. De Preter
Modelling gas migration experiments in repository host rocks for the MEGAS project.
High Level Radioactive Waste Management.
Proceedings of the fourth annual international conference
Las Vegas, Nevada, April 26-30, 1993
Published by ANS, ASLE, Vol. 1, 1993, pp. 387-391

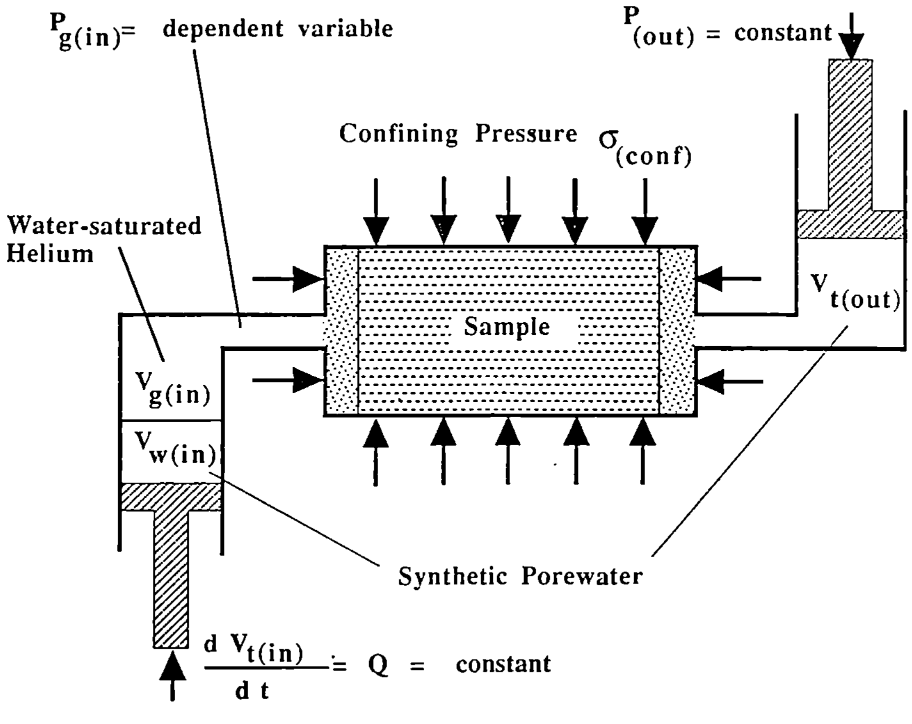


Figure 1 : Simplified scheme of the "flow through" apparatus developped by BGS

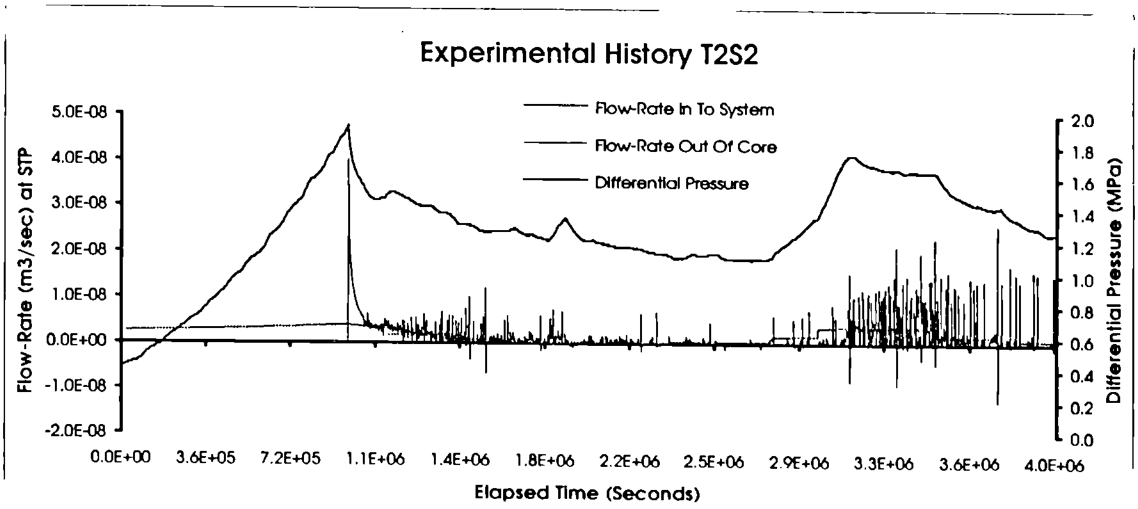


Figure 2: Mass-flow and pressure history sample 2

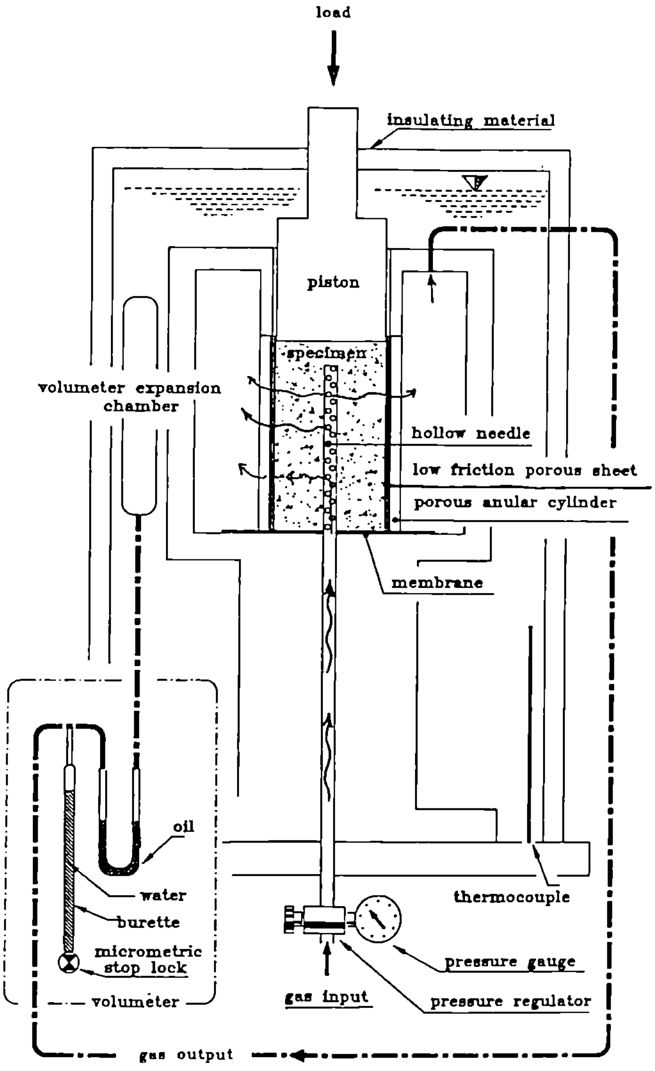


Figure 3: Design of the new needle gas injection system

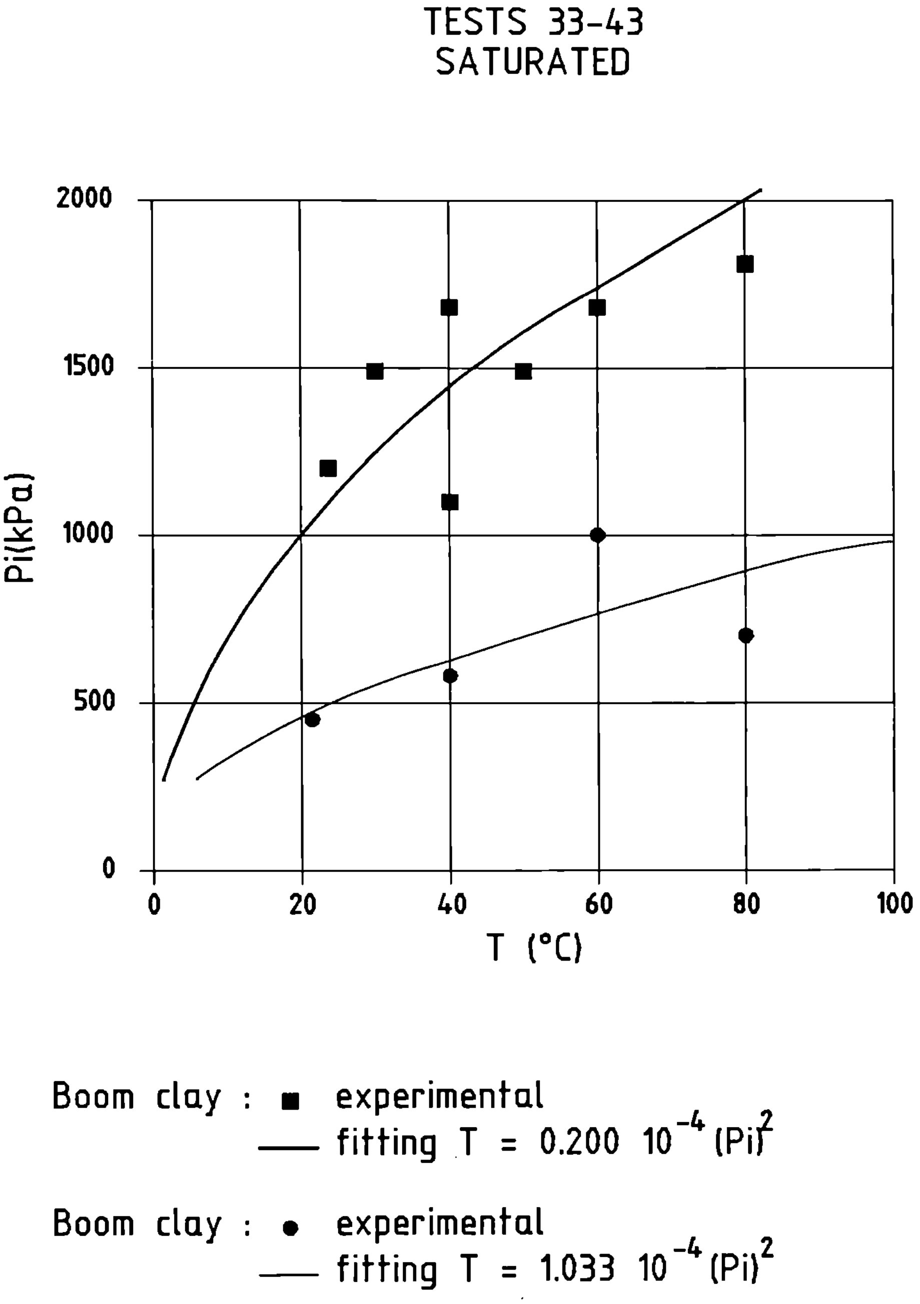


Figure 4: Gas break-through pressure as function of time

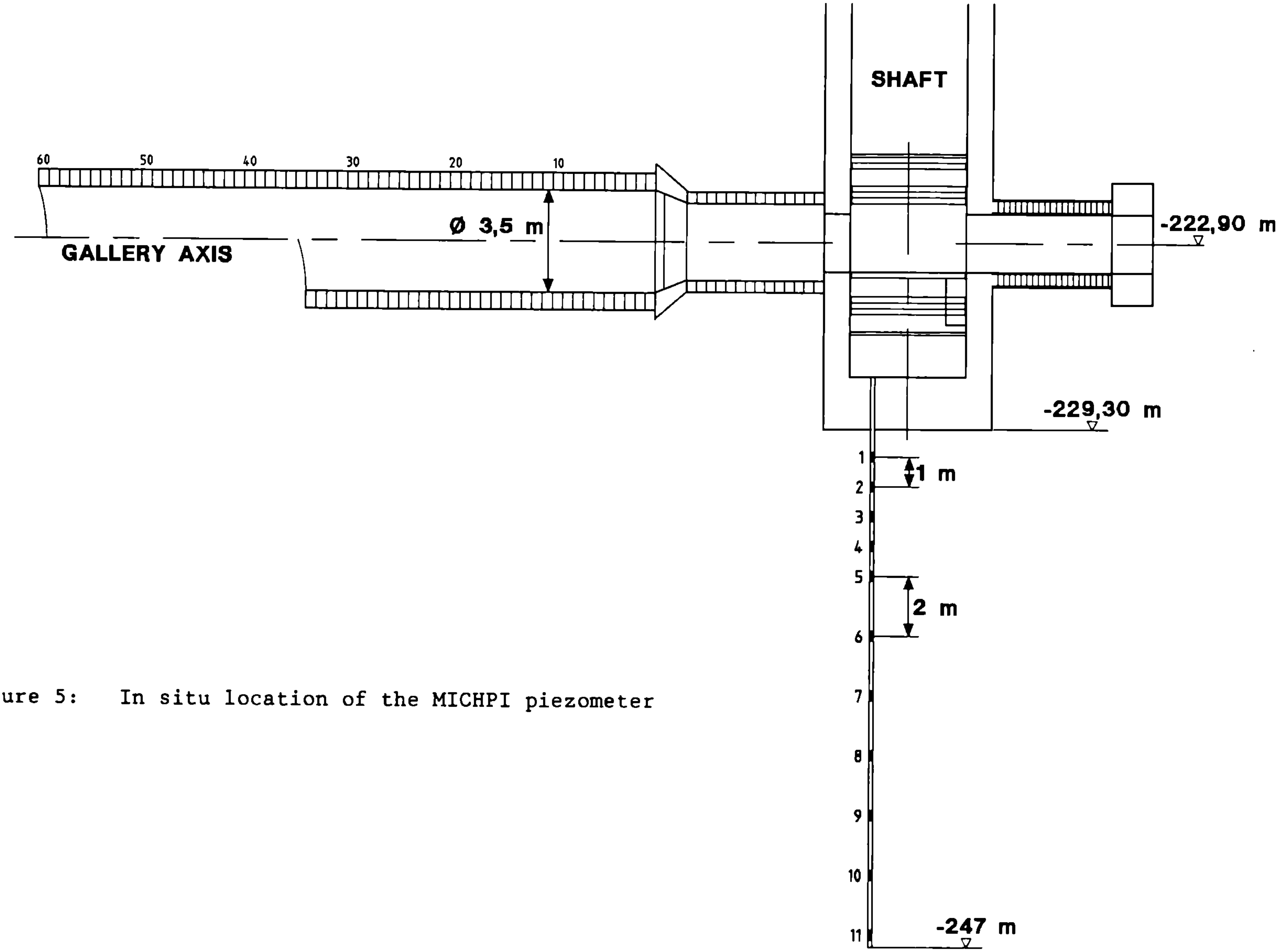


Figure 5: In situ location of the MICHPI piezometer

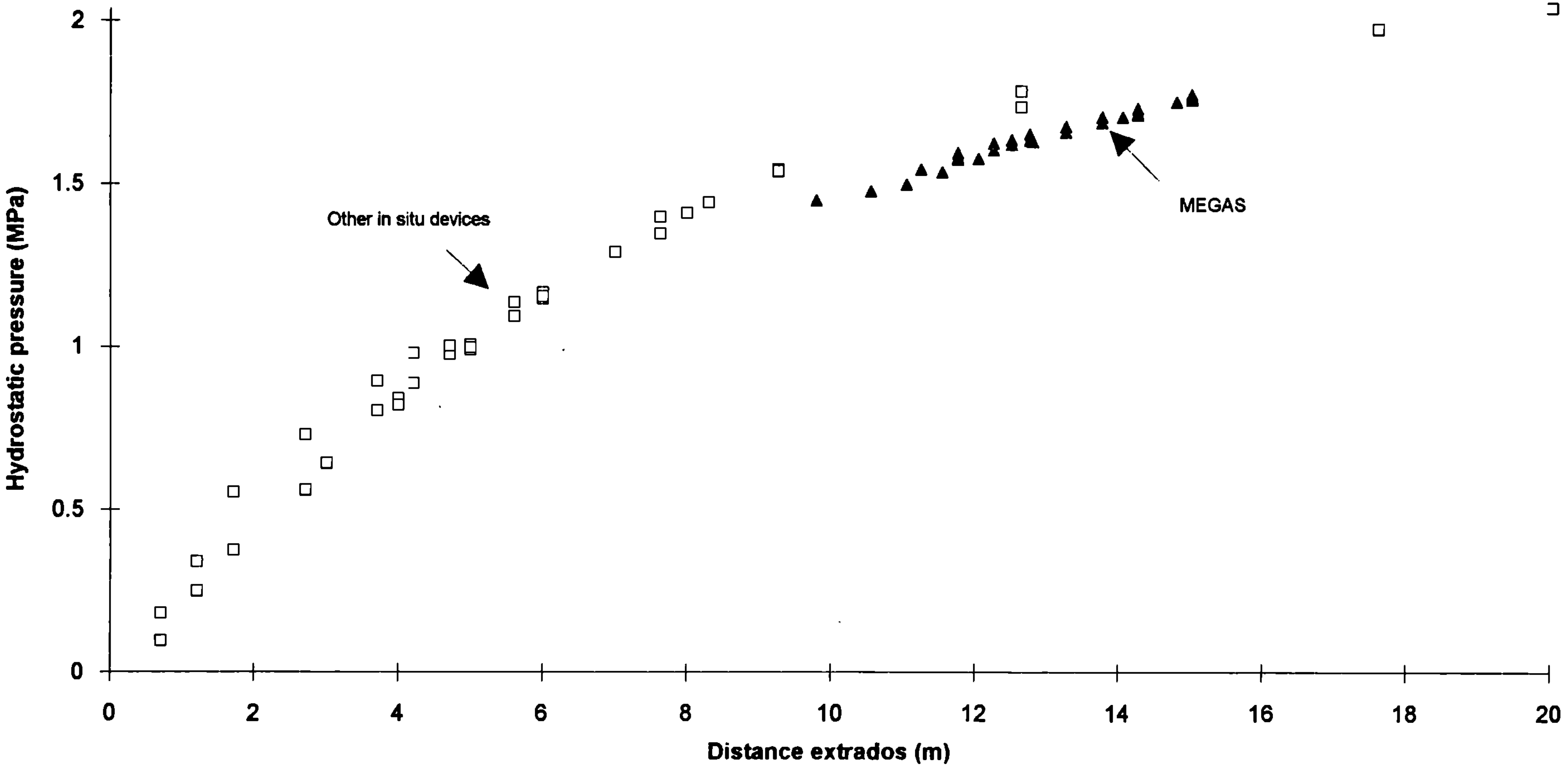


Figure 5: Pore water pressure profile in the MEGAS in situ experiment versus other earlier installed in situ devices.

Title:	Gas Pressure Build-up in Radioactive Waste Disposal and Mechanical Effects
Contractor:	GEOSTOCK - France
Contract number:	FI2W/CT-91-0093
Duration of contract:	July 1991 - January 1995
Period covered:	January 1993 - December 1993
Project leader:	T. Manai

A. OBJECTIVES AND SCOPES

The specific aim of this study is to evaluate the consequence of gas generation from a radioactive waste repository. The evaluation will be carried out in terms of gas migration in the backfill and the host rock and in terms of mechanical effects.

The phenomenology of physical process involved in gas transport will be reviewed; then some selected numerical codes taking into account two phase flow will be presented, the gas pressure build-up will be simulated for different designs of repositories, different host rock characteristics using numerical two phase flow models such as reservoir simulations used in the oil industry.

The mechanical modelling using new theoretical development for fracture initiation and propagation through the bifurcation theories will be carried out with the cooperation of the French Institute of Petroleum (IFP).

B. WORK PROGRAMME

The work is divided into work packages (WP):

WP1:	is dedicated to the phenomenology review: inventory of two phase flow phenomenology applied to gas migration from a radioactive wastes repository.
WP2:	Laboratory experiment: limited number of investigations on some representative host rock core samples.
WP3:	Two phase flow modelling.
WP4:	Mechanical developments modelling: theoretical works for the elaboration of a new criterion for fracture initiation and propagation
WP5:	Risk of gas generation
WP6:	Final report and conclusions

C. PROGRESS OF WORK AND RESULTS OBTAINED

C.1. State of advancements

The main activity of the last year (1993) is essentially dedicated to new developments of WP4, i.e. the implementation and the extension of the 3D model bifurcation, in the computer in order to achieve the criterion of fracture initiation and propagation and evaluation model parameter with experimental data.

By the end of 1993, the situation is:

WP1	completed in 1991
WP2	to be completed (mid 1994)
WP3	completed in 1991 (first part)
WP4	2D Modelling completed 1992
	3D Modelling completed 1993
WP5	to be completed (1994)
WP6	to be completed (end of 1994)

C.2. Progress and results

C.2.1. Summary model description

The equation of state which describes the relationship between strain and displacement is derived from the thermodynamic potential W (ε, D) by:

$$\sigma_{ij} = \frac{\partial W(\varepsilon, D)}{\partial \varepsilon_{ij}}$$

The endamagement tensor D is derived from

$$D = d(S)\ n \otimes n$$

where $d(S) = \frac{\Sigma a_i^3}{\overline{V}} \quad ; \quad 0 \le d(S) \le 1$

a_i is the radius of the microcrack
$\overline{V}$ is the total volume
n is the normal of surface crack
d(S) is interpreted as the density of microcracks

The initiation and propagation of the microcrack is described by the discontinuities of normal vector in the point detected and the initial criterion is:

$$\boxed{\det(n.L.n) = 0}$$

The expression of the thermodynamic potential formula is:

$$W(\varepsilon, D) = g.\mathrm{tr}(\varepsilon.D) + \frac{1}{2}\lambda \mathrm{tr}(\varepsilon)^2 + \mu \mathrm{tr}(\varepsilon.\varepsilon) + \alpha.\mathrm{tr}(\varepsilon).\mathrm{tr}(\varepsilon D) + 2\beta \mathrm{tr}(\varepsilon.\varepsilon.D)$$

ν, μ are the classical lamé coefficient defining the strain energy for non damaged isotropic solid, α and β are elastic coefficients related to damage induced modification of the strain energy function and g is a constant relevant to damage induced residual stresses (fig. 1).

C.2.2. Elastic damage response and damage growth

The thermodynamic forces related to D are given by:

$$F^D = \frac{\partial W(\varepsilon, D)}{\partial D} = F^{D1} + F^{D2}$$

F^{D1} = residual stress term

F^{D2} = reversible damage

The damage growth is supposed to be time-independent and progressive one.

The damage growth criterion is:

$$F(F^D - F^{D2} - F^{D1}, D) = 0$$

This new criterion has been developed previously in 2D (in 1992), and now the whole model is working in 3D.

C.2.3. Model parameters evaluation

An example of experimental vs model stress-strain curve for Vosges sandstone under confining pressure of -50 MPa has been used to evaluate model parameters.
The set of material parameters adopted further in the localization analyses is as follows (fig. 2):

ν = 14141 MPa

μ = 7954 MPa

α = 19000 MPa

β = 14280 MPa

g = -179 MPa

A global procedure of evaluating model parameters in 3D has been achieved and the comparison between the classical triaxial loading test has been accomplished and good agreement has been observed between the model result and the experiment.

C.2.4. Tests

Several tests have been done in the final version of the model (i.e. in 3D, fig. 3) and reveal the complexity of geometrical configurations of localization surfaces and completeness of related discontinuity modes when the three-dimensionality is admitted.
At the same time, these tests analyses how the efficiency of this new criterion of initiation and propagation of microcrack in the solid.

A specific algorithm has been written to implement this method because of the multiple solution found locally.

D. FURTHER ACTIONS

The 1994 year will be dedicated to the achievement of WP_2, end of WP_3, WP_5 and WP_6.

The experimental study on some representative rock samples will allow to evaluate:

- threshold pressure,
- capillary pressure,
- relative permeability.

The result of this experimental testing will be used to achieve the calculation of two phases flow modelling and to evaluate the risk of gas migration in repository.

The experiment will be done with the collaboration of BEICIP laboratory.

Experimental set up and some results will be present at PEGASUS meeting.

At the end of this year, a global report will be generated.

E. COMMENTS

The working programme modification leads to the difficulties for implementing the 2D and 3D of numerical codes because of the non standard techniques involved:

- modified finite element method taking into account discontinuities and anisotropic response,
- multiple solution involved in the detection criterion,
- testing procedure of the 2D and 3D bifurcation model.

On the other hand, a representative host rock samples from radioactive repository was difficult to obtain.

Now the work package No. 4 was achieved and the whole results is presented as a PhD work at the middle of this year.

1992 has been dedicated to the model investigation in two dimensional and some tests.

1993 has been dedicated to model implementation and extension in three dimensional localization, the implementation of the model is quite difficult but successful. No further theoretical work will be carried out in this year.

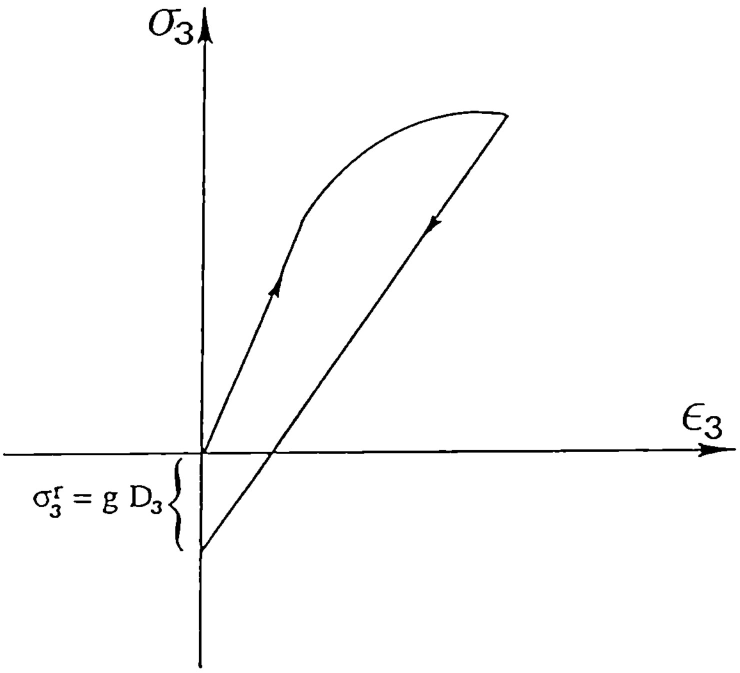


Fig. 1. Typical stress-strain behaviour according to the model

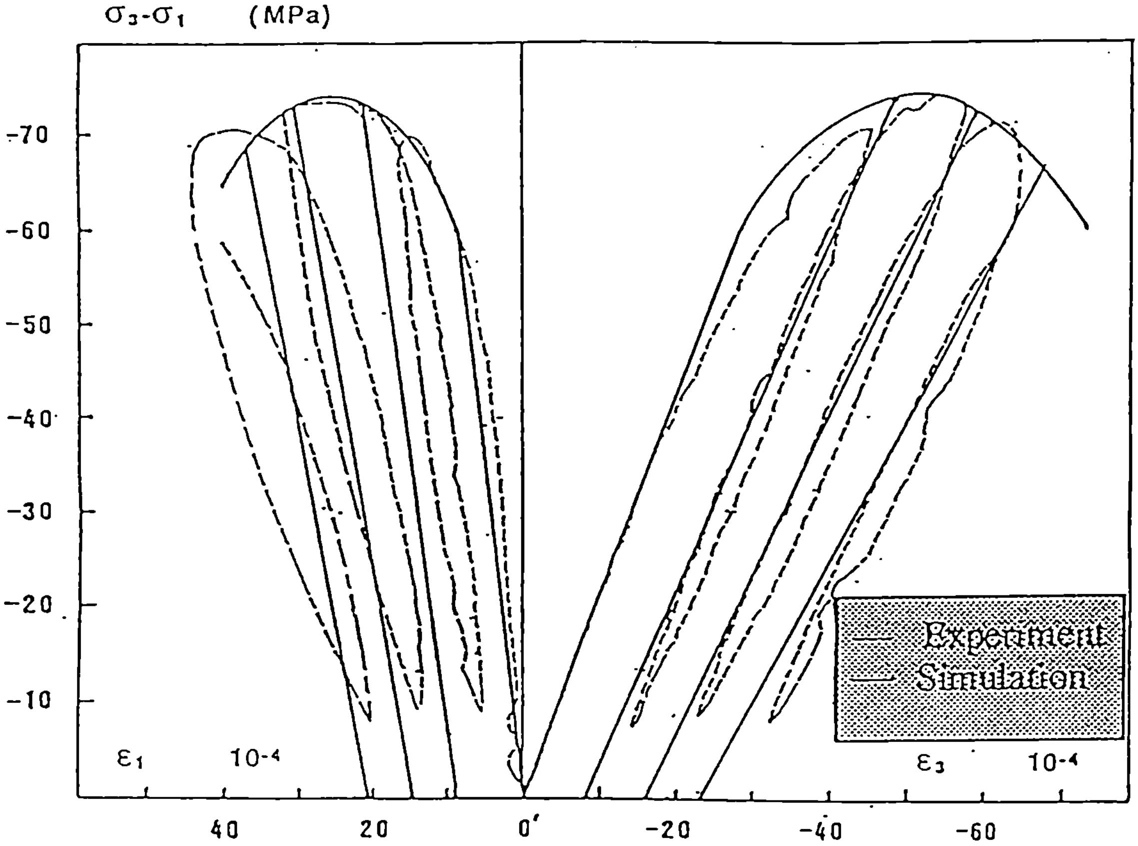


Fig. 2. Comparison with experimental result

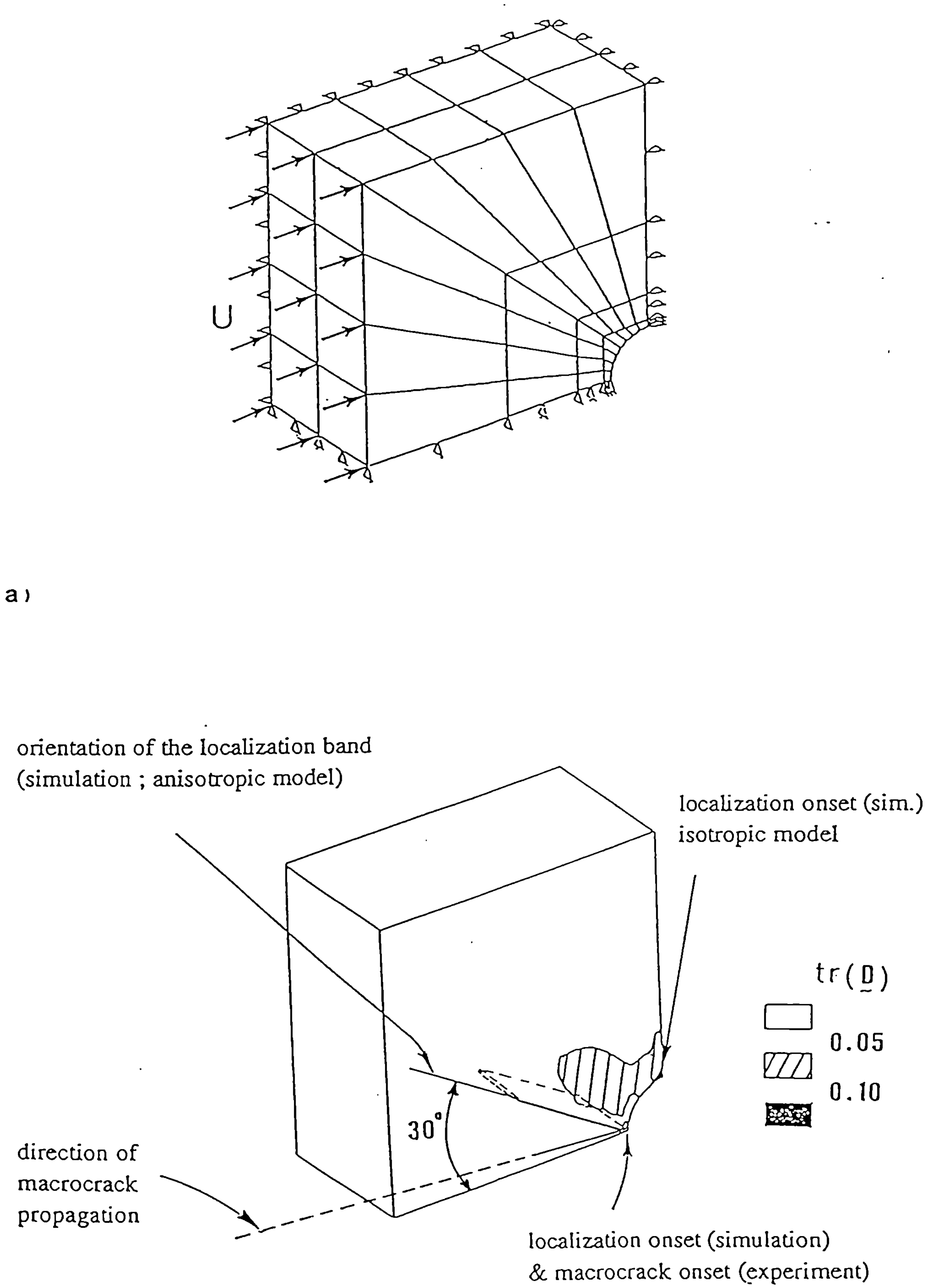


Fig. 3. Simulation of 3D case

Title : Salt permeability in situ test (Amélie Mine France)
Contractor : CEA/ANDRA - Fontenay aux Roses (F)
Contract N° : F12W-CT91-0101
Duration of contract : January 92 - June 95
Period covered : January - December 1993
Project leader : J.F. Laurens

A / OBJECTIVES AND SCOPE

The purpose of the in situ test that will be performed in MDPA mines is to measure the gas permeability of a rock salt bed previously submitted to a brine percolation.

This is of major importance for predicting the becoming of the gases present in the repository (gases coming from radiolysis, corrosion, bacteriological activity, trapped air...).

The experiment is planed to include two tests in separate boreholes at Amelie underground facilities.

As the measured quantities will be very low, the choice of experimental parameters will allow to eliminate or minimize or quantify all the underisable effects in order to facilitate the datas interpretation.

The scientific interpretation of the results will be made by the G.3S.

B / WORK PROGRAM

The initial work program was :

1 - Prefeasability tests in order to validate the experimental device (tightness of the borehole system, accuracy of the measurements).

2 - Pilot test in borehole n° 1, with brine, increasing the pressure up to fracture the rocksalt.

3 - Test in borehole n° 2 including :

- measurement of gas permeability ;
- injection of brine and measurement of brine permeability ;
- emptying of the borehole and measurement of gas permeability.

Due to the result of the cost evaluation and of the prefeasability tests, it has been decided in 93 to reduce the work program in order to stay within the financial limits of the contract.

The second part of this program consisting in a pilot test with the aim of fracturing the rocksalt is cancelled. Only one borehole will be used for all the test including fracturing of the rocksalt.

C / PROGRESS OF WORK AND OBTAINED RESULTS

- the specifications of the test site and of the experimental device have been defined,
- the technical procedures of the test have been written,
- the test site and the borehole have been done in Amélie mine,
- all the parts of the experimental device have been ordered.

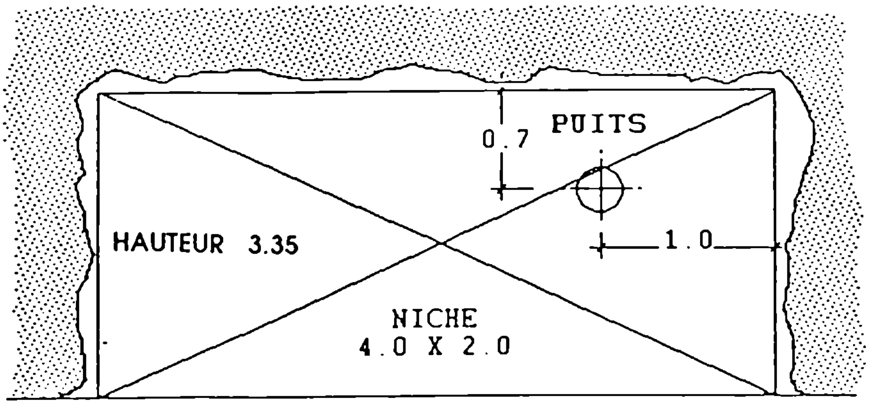
1 - SPECIFICATIONS OF THE TEST SITE

1.1 Dimension of the test site

The test site is located in an existing gallery "voie au mur JOSEPH". Its dimensions are :

length : 4.0 m
width : 2.0 m
height : 3.35 m.

It will include all the experimental devices and the borehole.

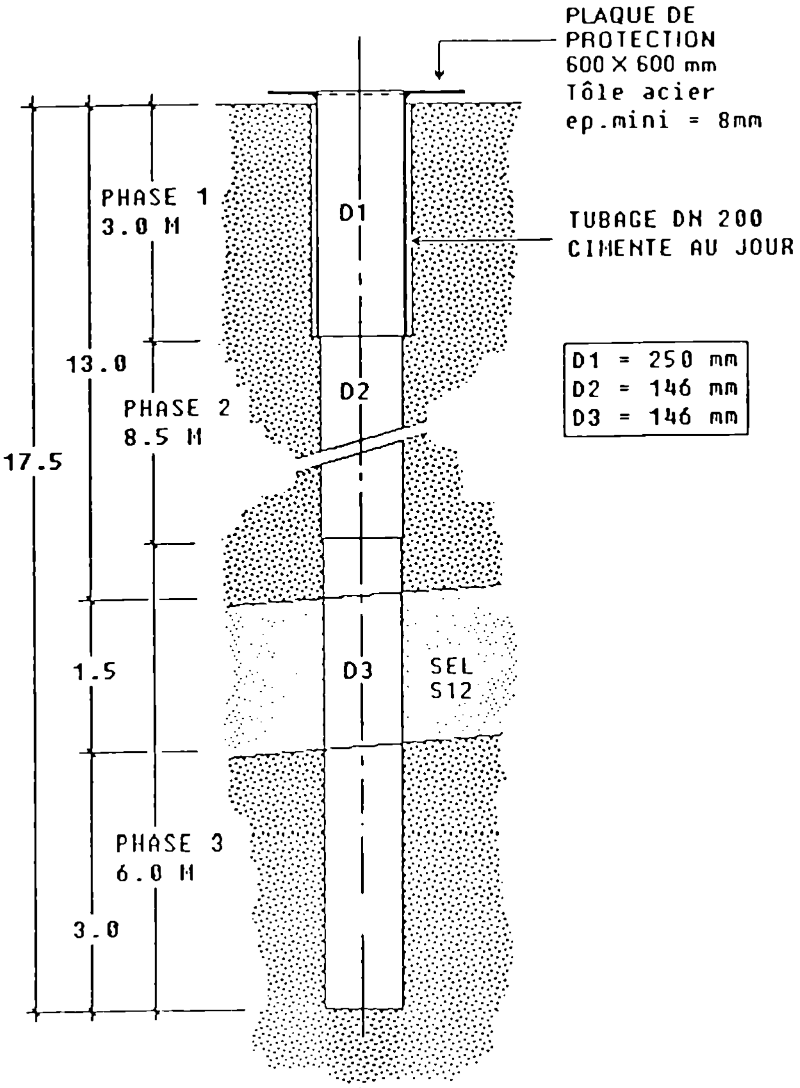


GALERIE EXISTANTE
VOIE AU MUR JOSEPH

1.2 Borehole specifications

The borehole length is 17.5 m. Its diameter 146 mm in the lower part. Only the last 6 meters are cored.

At the top of the borehole a casing is sealed to the rock. The quality of the borehole wall must be very good in order to ensure a perfect gas and brine tightness of the packers system. This finality will be controlled by endoscopy.



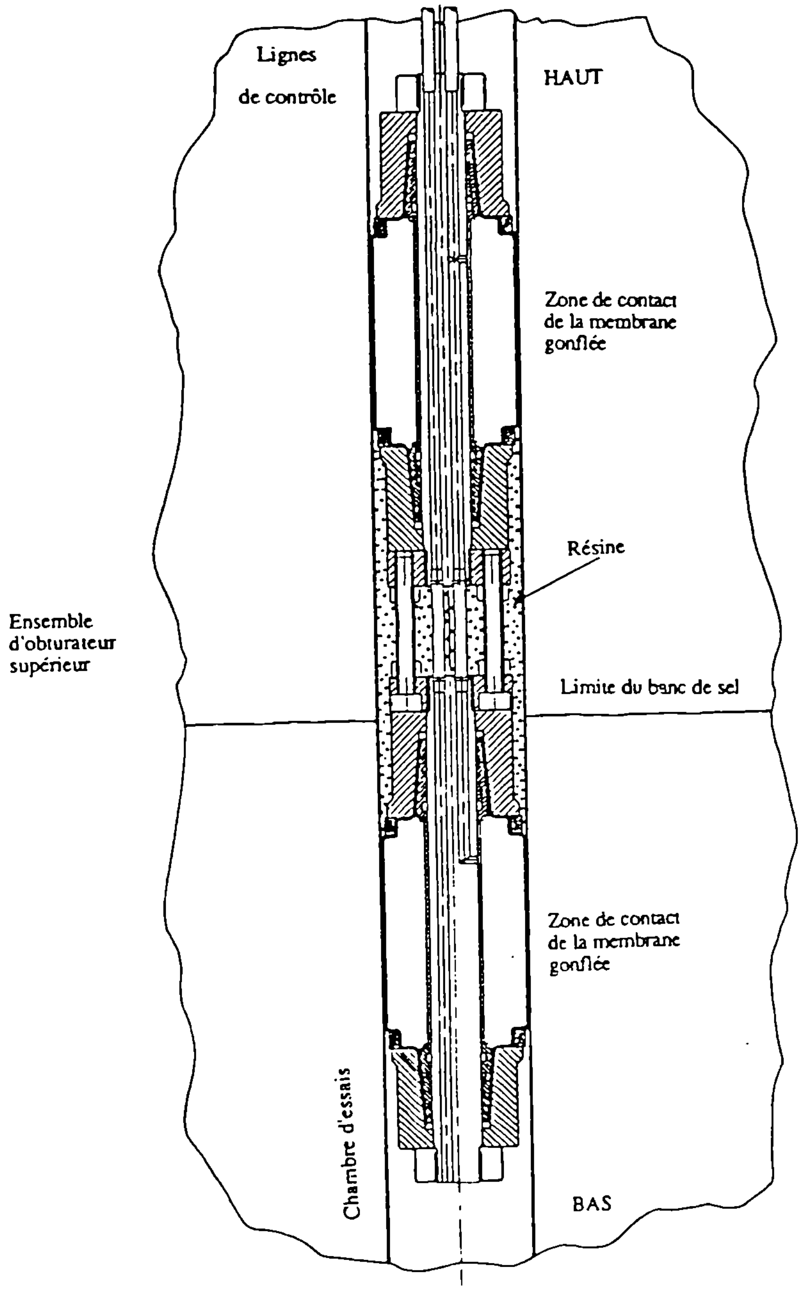
· SPECIFICATIONS OF THE EXPERIMENTAL DEVICE

2.1 Shutter system

The length of the experimental chamber will be defined after the endoscopy of the borehole (~ 0.85 m). The tightness of the chamber will be realised by two double packers systems.

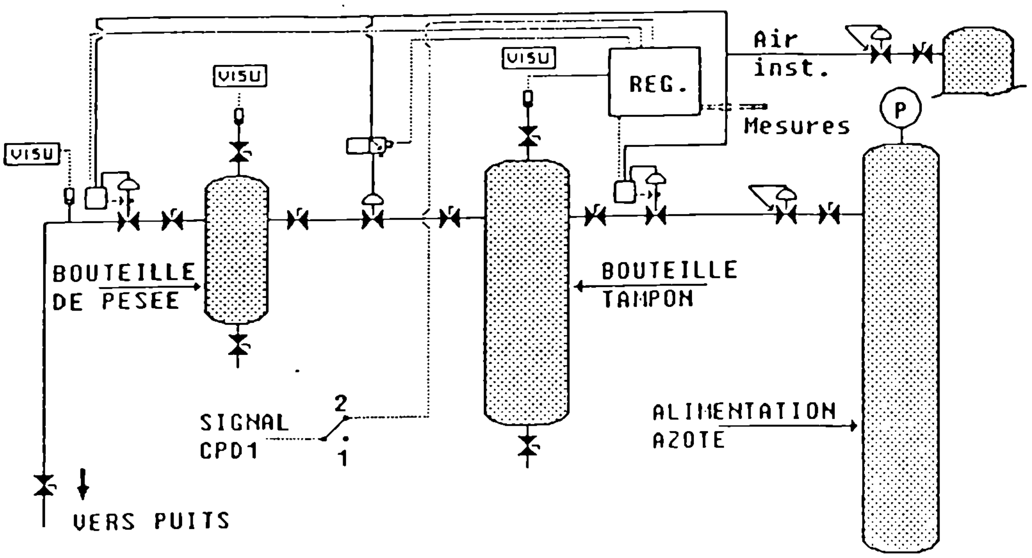
Each system will be 1 m long including to inflatable packers 0.2 m long separated by a 0.6 m long chamber that will be injected with a special polymeric resin.

Eight injection or control pipes will connect this system to the top of the borehole.



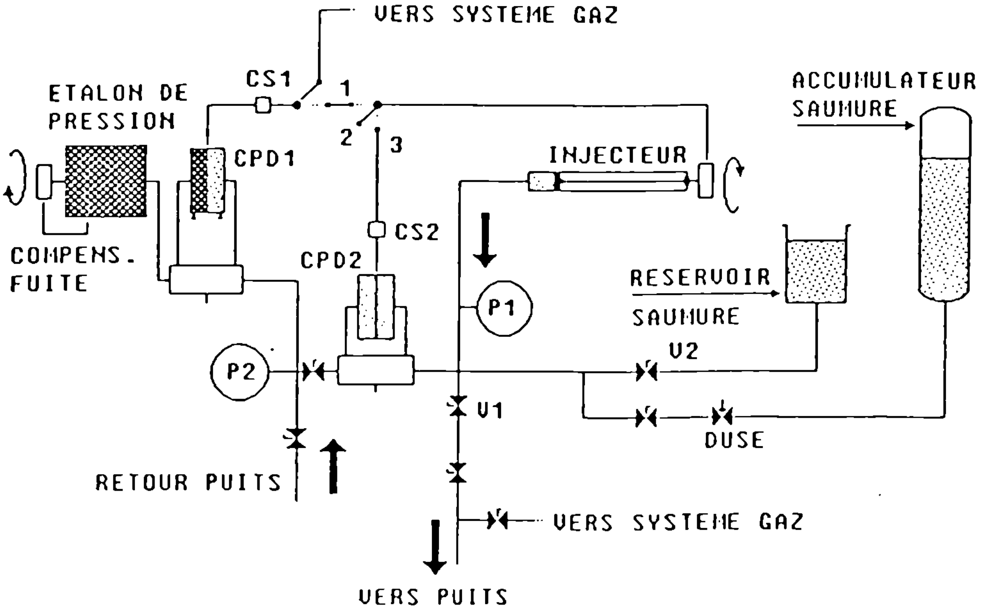
2.2 Gas injection system

A reference pressure will be given by a device using a dead weight. The difference between the pressure of the chamber and the reference pressure will allow gas injection until equilibrium is found. The amount of injected gas will be calculated knowing the loss of pressure of a buffer bottle. The precision of the pressure will be 0.01 MPa.



2.3 Brine injection system

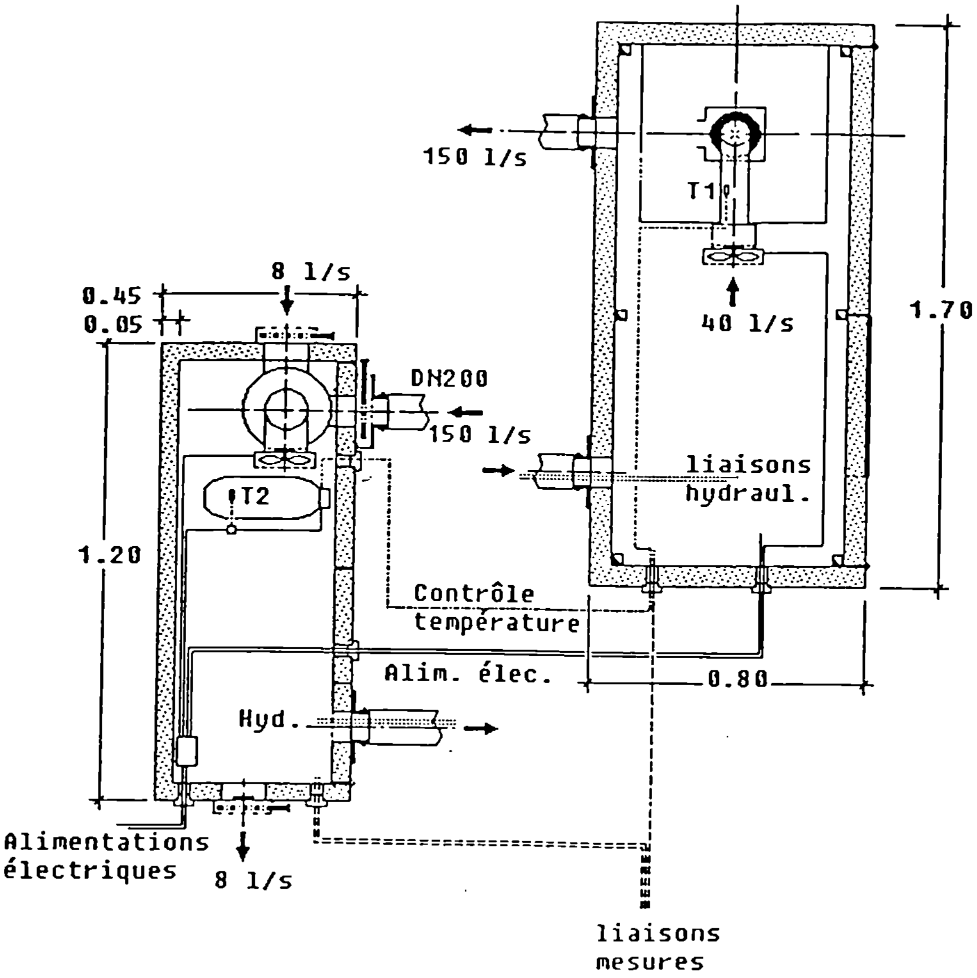
The injector is a piston whose movement is driven continuously by the difference of pressure between the reference and the chamber. The maximum brine flux will be 500 mm^3 / mn, the minimum 0.1 mm^3/ mn.



2.4 Thermal regulation system

All the injection system (surface, borehole) will work at the temperature of the chamber (≈ 36°C) in order to prevent all the undesirable effects (cristallization, creeping...).

For that purpose, a ventilation system with two fans and electric heaters will be built.



2.5 Data aquisition system

All the datas of the test will be collected by a data logger connected to the SELTICA system (already used for the "SEL BROYE" and "CPPS" test) that will send them daily to Palaiseau near Paris.

WORKS DONE

The test site has been dug in September. The borehole has been cored in December. Two endoscopies had to be done in order to be sure of the quality of the wall and of the position of the marnoanhydritic layers limiting the length of the shutters.

Title : Continuation of the migration experiments in Boom clay (laboratoy and in situ)

Contractor : ONDRAF/NIRAS, Brussels, Belgium

Contract N° : FI2W/0039

Duration of contract : September 1991 - Augustus 1995

Period covered : January 1993 - December 1993

Project leader : J. Van Miegroet.

A. OBJECTIVES AND SCOPE.

As the PAGIS /1/ and PACOMA /2/ safety studies have indicated, the migration of the critical radionuclides in the Boom clay is one of the key factors in the overall HLW disposal concept in Belgium. For this reason this programme aims at identifying the relevant migration mechanisms and at quantifying the migration parameters for these radionuclides.
The programme, a continuation of ongoing research, involves both percolation and diffusion experiments in the laboratory and in situ (underground lab).
The experimental work is performed by CEN/SCK.

B. WORK PROGRAMME.

1. Migration experiments in the lab.
   For a selected list of critical (^{14}C, ^{99}Tc, ^{129}I, ^{135}Cs, ^{237}Np) and possibly critical radionuclides (^{79}Se, ^{93}Zr, ^{107}Pd, U-, Am- and Cm-isotopes) as well as for dissolved organic molecules migration experiments in clay cores will be executed.

2. In situ migration experiments.
   In situ migration tests with HTO (tritiated water) and ^{134}Cs were started previously and are regularly monitored.
   Additional tests with Am, Tc and HTO are planned.

C. PROGRESS OF WORK AND OBTAINED RESULTS.

STATE OF ADVANCEMENT.

1. Lab-experiments.

One flow-through experiment, in which the simultaneous migration of HTO, HCO_3^- and I^- was followed, confirmed earlier results.
The experimental data of 4 migration tests with selenium have been analysed and interpreted. Also, new experimental results were obtained for uranium (2 tests) and europium (4 tests).

2. In-situ experiments.

New experimental results have become available for the three large scale in situ tests: two with I^- and one with HTO. For the HTO migration experiment, which is running since January 1988, the results encompass a migration distance of 2 meters. All the experimental data are compared to model calculations.

PROGRESS AND RESULTS.

1. Lab-experiments.

The obtained results for the flow-through experiment in which the simultaneous migration of HTO, I^- and HCO_3^- was followed are given in Table 1. The results of the earlier reported mixed HCO_3^-/I^- flow-through tests are also given for comparison.

Mean ηR and D values for HCO_3^- derived from these data are :

$\eta R = 0.12$ ($\pm$ 0.04)

$D = 1.9\ 10^{-10}$ ($\pm$ 0.8) $m^2.s^{-1}$

$\eta RD = 1.9\ 10^{-11}$ ($\pm$ 0.4) $m^2.s^{-1}$

The obvious conclusion is that, just as I^-, HCO_3^- is not retarded by sorption and that as a result of anion exclusion the diffusion accessible porosity η is $\pm$ 3 times less than for HTO .

The experimental data of the four Se migration experiments (two diffusion and two percolation tests) have been interpreted. In these tests a ^{75}Se labelled clay slice or filter was contacted with non-labelled clay cores. A solubility limited ^{75}Se source term had to be assumed in order to be able to accurately describe the obtained migration profiles. The calculated parameter values are summarized in Table 2. C_b refers to the calculated Se bulk concentration in the source at the end of the experiment.

As the pore solution concentration $C = C_b/\eta R$ and as we know the specific activity of the ^{75}Se label, we can calculate the Se solubility in the Boom clay slice, yielding the range 6.10^{-9}-6.10^{-10}M. Values for the retardation factor R, and consequently for the distribution coefficient K_d, could be derived from the migration experiments making use of the semi-empirical Bruggeman equation ηRD ($m^2.s^{-1}$) = $6.84\ 10^{-10}$ x $(\eta)^{1.5}$ /3/. K_d values of 0.032 and 0.13 $m^3.kg^{-1}$ have been derived, which tend to be slightly lower than K_d values obtained in batch sorption experiments (0.1-1.0 $m^3.kg^{-1}$).

The results of two U percolation experiments are given in Table 3. Similar to the Se migration tests a solubility limited source term had to be assumed. The calculated U-solubilities range between 10^{-6} and 10^{-7}M.

Four migration experiments with Eu have been terminated. These diffusion experiments only yielded D values (Table 4).

A pronounced influence of the reconsolidation pressure can be observed, in contrast to earlier observations for Sr /4/. It is evident that this decreasing apparent diffusion coefficient D for increasing reconsolidation pressures cannot solely be ascribed to a decreasing diffusion accessible porosity. Pore geometrical changes (tortuosity, constrictivity) seem to be at least equally important.

In-situ experiments.

The updated experimental results and the calculated predictions for the large scale HTO migration experiment in the CP1 piezometer are given in Figure 1. As can be seen form this figure, the first experimental data for the filters at a 2m distance from the injection filter are available. The agreement between experimental measurements and model predictions remains excellent. This figure also shows that this experiment can still be followed for several years.

A second large scale in-situ migration experiment studies the ^{125}I migration in one vertically and one horizontally oriented piezometer. The results for the vertical and the horizontal piezometer are given in Figures 2 and 3 respectively. The migration parameter values used in the predictive calculations are given in Table 5. The observed difference between the experimental and calculated values for filters nr. 7 are probably due to a mass balance disturbance as a result of the pore water sampling. This will be checked.

LIST OF PUBLICATIONS

- M.J. PUT and P. DE CANNIERE (1993)
  Migration behaviour of ^{14}C labelled bicarbonate, HTO and ^{131}I in Boom clay.
  Paper presented at the Migration 1993 Conference - Charleston (USA).

REFERENCES

/1/ PAGIS - Disposal in clay formations (Ed. by J. Marivoet), CEC report EUR 11776 EN (1988)

/2/ PACOMA - Performance assessment of the geological disposal of medium-level and alpha waste in a clay formation in Belgium (J. Marivoet and Th. Zeevaert), CEC report EUR 13042 EN (1991)

/3/ HENRION P.N., PUT M.J. and VAN GOMPEL M. (1991)
The influence of compaction on the diffusion on non-sorbed species in Boom clay
Radioactive Waste Management and the Nuclear Fuel Cycle, 16 (1) 1-14

/4/ DE PRETER P., PUT M., DE CANNIERE P. and MOORS H. (1992)
Migration of radionuclides in Boom clay.
State-of-the-art-report. June 1992
NIROND 92-07

Table 1 : Results of the flow-through diffusion tests with HCO_3, I and HTO on reconsolidated clay plugs

Test no.	Species	$P_{consolidation}$ (MPa)	ηR (-)	D ($m^2.s^{-1}$)	ηRD ($m^2.s^{-1}$)
1	HCO_3^-	4.41	0.18	7.5×10^{-11}	1.4×10^{11}
2	HCO_3^- I^-	2.00 2.00	0.12 0.10	1.5×10^{-10} 3.7×10^{-10}	1.8×10^{-11} 3.7×10^{-11}
3	HCO_3^- I^-	2.00 2.00	0.10 0.12	1.8×10^{-10} 3.5×10^{-10}	1.8×10^{-11} 4.2×10^{-11}
4	HCO_3^- I^-	1.98 1.98	0.11 0.11	2.2×10^{-10} 4.3×10^{-10}	2.4×10^{-11} 4.7×10^{-11}
5	HCO_3^- I^- HTO	2.00 2.00 2.00	0.07 0.08 0.29	3.0×10^{-10} 5.3×10^{-10} 6.2×10^{-10}	2.2×10^{-11} 4.2×10^{-11} 1.8×10^{-10}

Table 2 : Results of the ^{75}Se migration experiments

Test	ηR (-)	D ($m^2.s^{-1}$)	ηRD ($m^2.s^{-1}$)	C_b ($Bq.ml^{-1}$)
1	-	1.2×10^{-13}	-	1610
2	-	2.1×10^{-13}	-	122
3	54	1.9×10^{-13}	1.0×10^{-11}	849
4	215	1.3×10^{-13}	2.8×10^{-11}	11.300

Table 3 : Results of the two ^{233}U percolation experiments

Test	ηR (-)	D ($m^2.s^{-1}$)	ηRD ($m^2.s^{-1}$)	C_b ($Bq.ml^{-1}$)
1	14.4	4.3×10^{-13}	6.1×10^{-12}	1200
2	155	5.8×10^{-14}	8.9×10^{-12}	2200

Table 4 : Results of the diffusion experiments with ^{152}Eu

Test	Run time (y)	$P_{consolidation}$ (MPa)	D ($m^2.s^{-1}$)
1	4.15	0.8	$1.6\ 10^{-15}$
2	4.36	4.5	$6.2\ 10^{-16}$
3	4.49	4.5	$6.3\ 10^{-16}$
4	4.39	4.5	$2.6\ 10^{-16}$

Table 5 I^- parameter values used in the predictive calculations

Parameter	Value
D_{hor} ($m^2.s^{-1}$)	$2.65x10^{-10}$
D_{vert} ($m^2.s^{-1}$)	$1.4x10^{-10}$
η (-)	0.15
R (-)	1
$(V_d)_{vert}$ ($m.s^{-1}$) (*)	$1.6x10^{-11}$
$(V_d)_{horiz}$ ($m.s^{-1}$) (+)	$7.6x10^{-11}$

(*) Darcy velocity for the vertical piezonest ; water flow towards the gallery.

(+) Darcy velocity for the horizontal piezonest ; water flow towards the gallery.

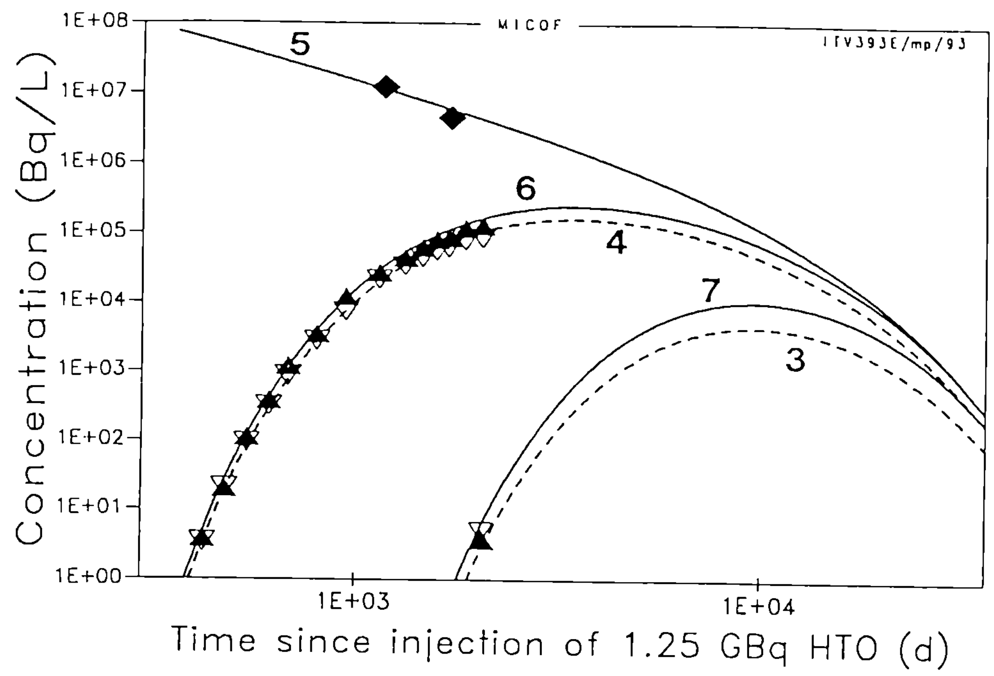


Figure 1 : HTO concentration evolution in the Boom clay interstitial liquid for the filters 3 to 7. Symbols refer to experimental measurements and curves to model predictions. Results are given for the injection filter nr. 5 and for the filters at distance of 1 m (nr. 4 and 6) and 2 m (nr. 3 and 7) from the injection filter.

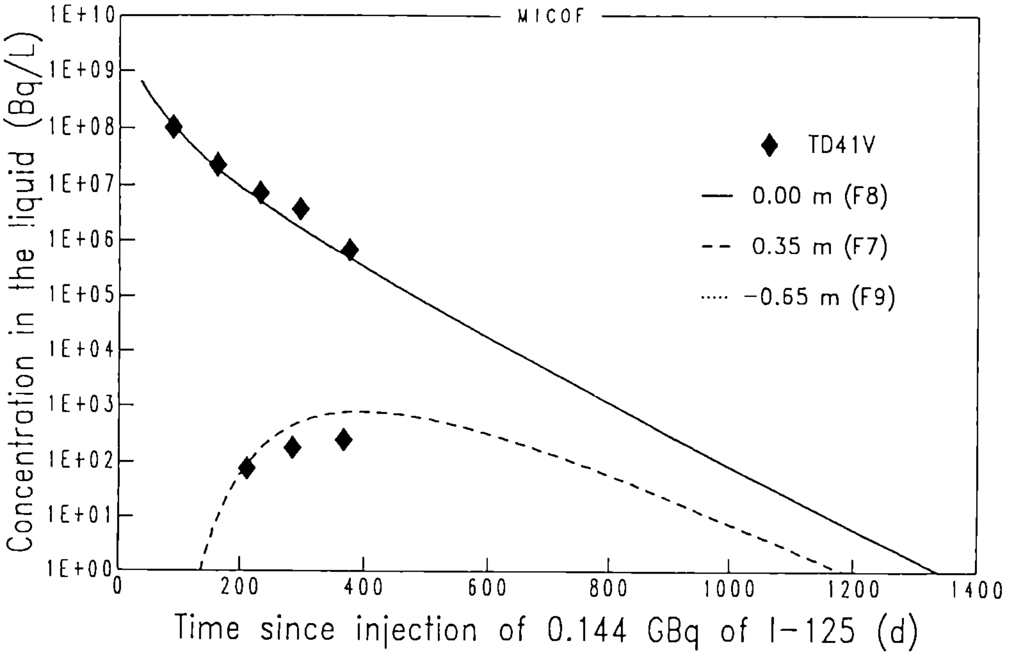


Figure 2 : ^{125}I concentration evolution for the filters 8 (injection filter) and 7 (at 0.35 m) of the vertically oriented piezonest. Symbols refer to experimental measurements and curves to model predictions.

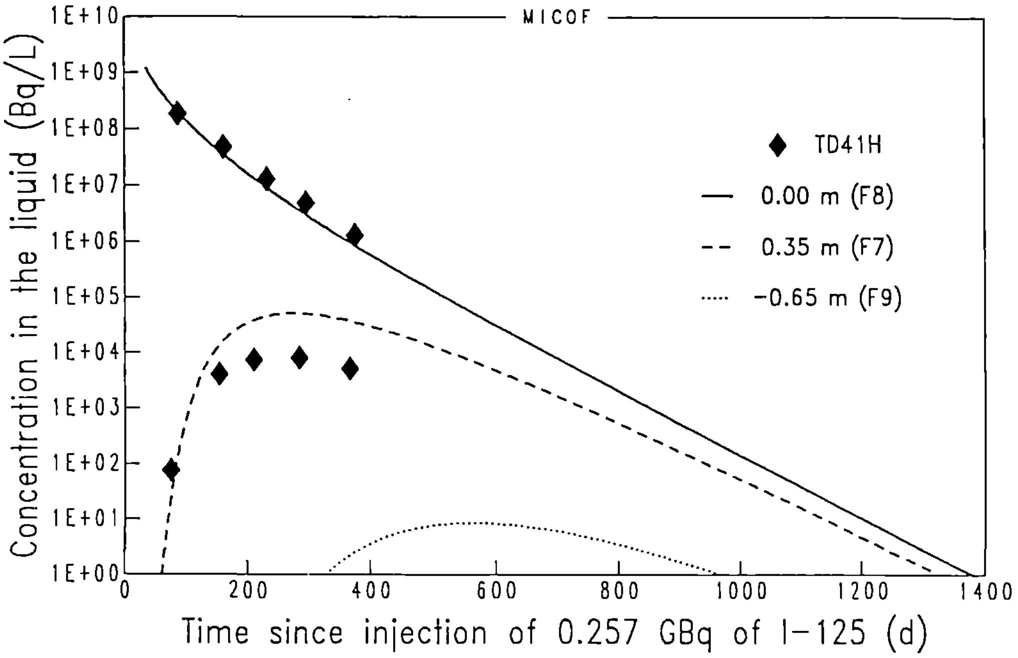


Figure 3 : ^{125}I concentration evolution for the filters 8 (injection filter) and 7 (at 0.35 m) of the horizontally oriented piezonest. Symbols refer to experimental measurements and curves to model predictions.

CHEMVAL2: A COORDINATED RESEARCH INITIATIVE FOR EVALUATING AND ENHANCING CHEMICAL MODELS USED IN RADIOLOGICAL RISK ASSESSMENT

Contractor/Coordinator:	WS Atkins Environment, Epsom, UK
Contract No:	F12W/0065
Duration of Contract:	May 1991 - October 1994
Period Covered:	January 1993 - December 1993
Project Leader:	D Read

A. OBJECTIVES AND SCOPE

The international CHEMVAL Project, initiated in 1987, has been assessing the validity of computer-based models used to describe the geochemistry of radioactive waste disposal systems. The original project /1/2/3/ was concerned, primarily, with the verification of equilibrium models though a number of attempts were made at a priori predictive validation. CHEMVAL2 aims to build on this earlier study by targeting specific areas shown to be of particular concern in radiological assessment. Eighteen organisations in nine countries currently participate in CHEMVAL and, of these, seven have direct responsibility for technical coordination, as outlined below:

a) Temperature Effects: BRGM/ANDRA, France (R Fabriol, T Merceron)
b) Ionic Strength Effects: GSF-IfH, Germany (H Lang)
c) Organic Complexation: LUT/WS Atkins, UK (P Warwick, D Read)
d) Sorption Processes: AEA Harwell/BGS, UK (C Tweed, M Crawford)
e) Co-precipitation: MBT/ENRESA, Spain (J Bruno)
f) Coupled Modelling: EMP/CEA, France (Ph Jamet, D Stammose)

B. WORK PROGRAMME

1. Definition and initiation of programme, production of status reviews.
2. Execution of research programmes for each technical area encompassing data review, model development, code verification and model validation.
3. Comparison with experimental studies and reporting.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

During 1993, the tasks identified in the CHEMVAL2 status review /4/ have been undertaken and a programme of experimental and numerical investigations is in progress. Results presented at the 3rd Plenary Meeting (Stockholm) and 4th Plenary Meeting (Oberschleißheim) have been analysed and subsequently issued as progress reports /5/6/.

In addition the need for continued development and maintenance of a standardised thermodynamic database, both within this project, and for studies of radioactive waste management in general, has been recognised and is being undertaken in parallel with the CHEMVAL2 programme under the related CEC Contract F12W/CT92/0122.

Progress and Results

The structure of the CHEMVAL2 Project is shown in Figure 1. WS Atkins together with the two main funding organisations, CEC and HMIP, provide a secretariat acting as a contact point for the technical coordinators. The role of WS Atkins encompasses organisation of meetings, preparation of reports and dissemination of data in addition to modelling and review activities. Progress within each research area is summarised below.

a) Temperature Effects

Owing to the imcompleteness of data describing the heat capacity of many species as a function of temperature, a modified form of the classic Van't Hoff relationship has been adopted to account for temperature induced changes in equilibrium stability constants. The activity coefficient of ions in solution also varies with temperature and a modification of the Davies equation has been proposed by BRGM/ANDRA. This incorporates a fourth order polynomial expression for the Davies 'A' parameter enabling calculations to be made in the range 0-200°C. In order to implement and test these ideas, modifications were made to existing codes and comparisons made against a set of verification tests performed by participants using alternative numerical methods. The results of these tests are in close agreement. As expected, the results depart from reality where the change in heat capacity is significant over the temperature range studied, pointing the way for future experimental work.

A set of "validation" tests has been issued based on the "Dogger" limestone reservoir of the Paris Basin and involves the prediction of saturation indices for named minerals and the precipitation-dissolution of iron over a range of temperatures. The results of these tests will be analysed early in 1994.

b) Ionic Strength Effects

The CHEMVAL thermodynamic database developed in Phase 1 of this project (1987-1990), accounts for the activity coefficient (γ) using a modified form of the Davies equation /7/ intended for applications where the total salinity does not exceed 0.3 mol

dm^{-3}. A review of alternative methods, conducted by GSF-IfH, demonstrates that specific interaction methods (SIT) including the Pitzer approach /8/ extend the prediction of γ well above the maximum salinity of 1 mol dm^{-3} intended for this work. The SIT approach as recommended by the OECD/NEA /9/ is favoured over the Pitzer method due to its relative simplicity and the paucity of data from which Pitzer coefficients can be obtained.

The relative capability of the different approaches to predicting experimental activity data was illustrated using modelling results obtained at WS Atkins. The calculated activity correction coefficients in 1:1 (Na, Cl) and 2:1 (Ca, Cl_2) electrolytes compare well with experimental data published by Robinson and Stokes /10/ Figure 2. Compilation of SIT coefficients for incorporation into the CHEMVAL database is in progress. Where no published data are available, recourse will be made to estimated values, based on chemical analogy (ie ionic radius and charge) for the purposes of model testing.

c) Organic Complexation

The problems associated with quantifying complexation of trace elements by high molecular weight organic matter were highlighted during the original CHEMVAL Project /2/. The theoretical basis for most extant models is weak and few if any have a real predictive capability. Essentially, CHEMVAL2 is aiming to develop a practical modelling approach which can be independently tested and, further, be used in conjunction with conventional inorganic speciation models. The work is being coordinated jointly by LUT and WS Atkins. Following a review of the literature /4/, three approaches have been advanced as meriting more detailed consideration; the simple ligand-binding model of Sposito and Mattigod /11/, as incorporated in the GEOCHEM code, the continuous distribution (statistical) approach of Perdue and Lytle /12/, and the electrostatic site-binding models of Tipping and Falck /13/14/. Both of these electrostatic models have been incorporated within the PHREEQE code /15/.

In order to identify which modelling approach, if any, possesses advantages over the remainder, experimental data obtained at LUT, using High Performance Size Exclusion Chromatography (HPSEC) for the binding of Ni on humic material, have been used to test the four models. Each modelling approach predicted greater Ni binding than was observed experimentally and considerable variability existed in the predictions. This is thought to be due in part to the HPSEC method resulting in lower measured concentrations than those obtained by ion exchange. The results of this work are still being assessed.

d) Sorption Processes

The objectives of work on sorption processes within CHEMVAL2 are to compare the various models which have been incorporated into geochemical speciation codes and to assess their usefulness for simulating observed behaviour in the laboratory and in the field.

Following analysis of the results of the verification and validation test cases completed earlier in the project, it is evident that two conventions exist for the treatment of the activity coefficient (γ) for sorbed species. In the first, the activity of surface species is set to unity, whereas for the latter the activity coefficient section of the equation is omitted and the correction for chemical potential is incorporated into the electrostatic term. This accounts, in part, for variations between the wide range of models which were used to fit the experimental data.

Model validation concentrates on two systems; the sorption of uranium onto Clashach sandstone (based on experimental data from UKAEA Winfrith) and the sorption of nickel onto silica (experiments at BGS). Nickel was chosen as this work is complementary to the organic complexation studies at LUT.

e) Co-precipitation

Solubility limits based on equilibrium precipitation - dissolution are used to establish source term concentrations for radiological assessment and also to estimate maximum concentrations of radioelements in geological media. Calculations based on pure solid phases may be grossly in error, however, as trace elements in nature tend to occur as substituted "impurities" in mineral phases. The aim of work within CHEMVAL2, coordinated by MBT/ENRESA is to develop viable models of trace element coprecipitation with ubiquitous minerals such as calcite and amorphous iron oxides /4/.

Experimental work at the Polytechnical University of Catalonia (UPC) has demonstrated that in the coprecipitation of uranium and iron hydroxides from solution, the distribution of uranium is uniform in the solid phase. This strongly suggests incorporation of uranium in these solids is the result of co-precipitation as opposed to surface adsorption. Further examination by x-ray diffraction shows that they do not experience any structural changes over ageing periods of 1 year. Modelling of this system has yielded results in close agreement with the experimental findings at low aqueous uranium concentrations, but shows increasing discrepancies as concentrations increase. Further test cases involving the solubility of Sr in seawater and the co-precipitation of Np, Pu and Am with iron hydroxide are currently under review.

f) Coupled Chemical-Transport Processes

The results of six verification test cases proposed by the coordinators, CEA/EMP, have been analysed /6/ and show close agreement between the participants in the overwhelming majority of cases.

Validation of the coupled chemical transport models has concentrated on laboratory studies commissioned at AEA Winfrith and CEA Grenoble. These are column experiments, the former examining uranium transport through intact sandstone cores whilst the latter is an ion exchange study of Cs and Sr migration through columns of packed sediments. Results have been received from a number of participants although in most cases this work is still on-going. A second validation phase is currently under development based on experimental data from BGS, which investigates the dissolution of anorthite/quartz and precipitation of lanmonite. This will be discussed at the 5th Plenary Meeting in Barcelona, March 1994.

g) Database Activities

The majority of the unreviewed data in version 4.0 of the CHEMVAL Database for aqueous species have now been traced to source literature and reviewed. Redox couples were not reviewed previously owing to uncertainties that exist in measurement, although review work will be completed before the release of version 5.0. Thermodynamic data has been collated for Cu, Ni, Co, As, Cd and REE. So far, additional data for approximately 250 aqueous reactions and the dissolution of approximately 70 solids have been identified. Data for As are to be released with version 5.0 of the CHEMVAL Database. It is intended that another version will be released prior to the end of the project containing enthalpy data collected at BRGM.

REFERENCES

/1/ READ, D. and BROYD, T.W., CHEMVAL Project. Report on Stage 1: Verification of Speciation Models. CEC Report EUR 12237 EN. 364p (1989).

/2/ READ, D. (ed), CHEMVAL Project. Report on Stage 2: Application of Speciation Models to Laboratory and Field Data Sets. CEC Report EUR 13124 EN. 229p (1990).

/3/ READ, D. (ed), CHEMVAL Project. Report on Stages 3 and 4: Testing of Coupled Chemical Transport Models. CEC Report EUR 13675 EN. 234p (1991).

/4/ READ, D. (ed), CHEMVAL2 Project: Status Review of CHEMVAL2 Technical Areas June 1992 Report UK DoE/HMIP/RR/93.014. 236p (1992).

/5/ READ, D. (ed), CHEMVAL2 Project: 3rd progress report covering the period June 1992 - December 1992. 26p (1992).

/6/ READ, D. (ed), CHEMVAL2 Project: 4th progress report covering the period December 1992 - June 1993. 28p (1993).

/7/ DAVIES, C.W. Ion association. Butterworths, London (1962).

/8/ PITZER, K.S. Thermodynamics of electrolytes: Theoretical basis and general equations. J. Phys. Chem. 77 268p (1973).

/9/ GRENTHE, I., FUGER, J., KONINGS, R.J.M., LEMIRE, R.J., MULLER, A.B., NGUYEN-TRUNG, C. and WANNER, H. Chemical thermodynamics of uranium. OECD-NEA, North Holland (1992).

/10/ ROBINSON R.A. and STOKES, R.H. Electrolyte Solutions: The measurement and interpretation of conductance, chemical potential and diffusion in solutions of simple electrolytes, 2nd ed., Butterworths, London (1959).

/11/ SPOSITO, G. and MATTIGOD, S.V. Dept. Soil Sci. Report, Keerney Foundation of Soil Science, Univ. California (1980).

/12/ PERDUE, E.M. and LYTLE, C.R. Environ. Sci. Technol. 17 p654-660 (1983).

/13/ TIPPING, E. et al. Environ. Sci. Technol. 24 p1700-1705 (1990).

/14/ FALCK, W.E. BGS Tech. Report WE/88/49 (1988).

/15/ PARKHURST, D.L., THORSTENSON, D. and PLUMMER, L.N. PHREEQE: A computer program for geochemical calculations. U.S. Geol. Survey: Water Res. Investigations. 96 (1980).

PUBLICATIONS

BRUNO, J., de PABLO, J., DURO, L. and FIGUEROLA, E. Experimental study of the U(VI)-Fe(OH)$_3$ coprecipitation equilibria: The application of the conditional solubility constant concept. In: Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere: MIGRATION '93, USDOE, CEC, IAEA (1993).

SIMS, R.J., LAWLESS, T.A., BENNETT, D. and READ, D Uranium migration through intact sandstone - effects of pollutant concentration, competition and organic complexation. In: Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere: MIGRATION '93, USDOE, CEC, IAEA (1993).

SCOTT de MARTINVILLE, E., CHUPEAU, J., STIETEL, A., PFIFFER, M., TOULHOAT, P. and PITSCH, H. Development and validation of a 3D coupled transport chemistry code for the radwaste disposals performance assessment. In: Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere: MIGRATION '93, USDOE, CEC, IAEA (1993).

WARWICK, P., HALL, A., TIPPING, E. and READ, D. A comparative study employing three different interpretive models to investigate the complexation properties of humic and fulvic acids. In: Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere: MIGRATION '93, USDOE, CEC, IAEA (1993).

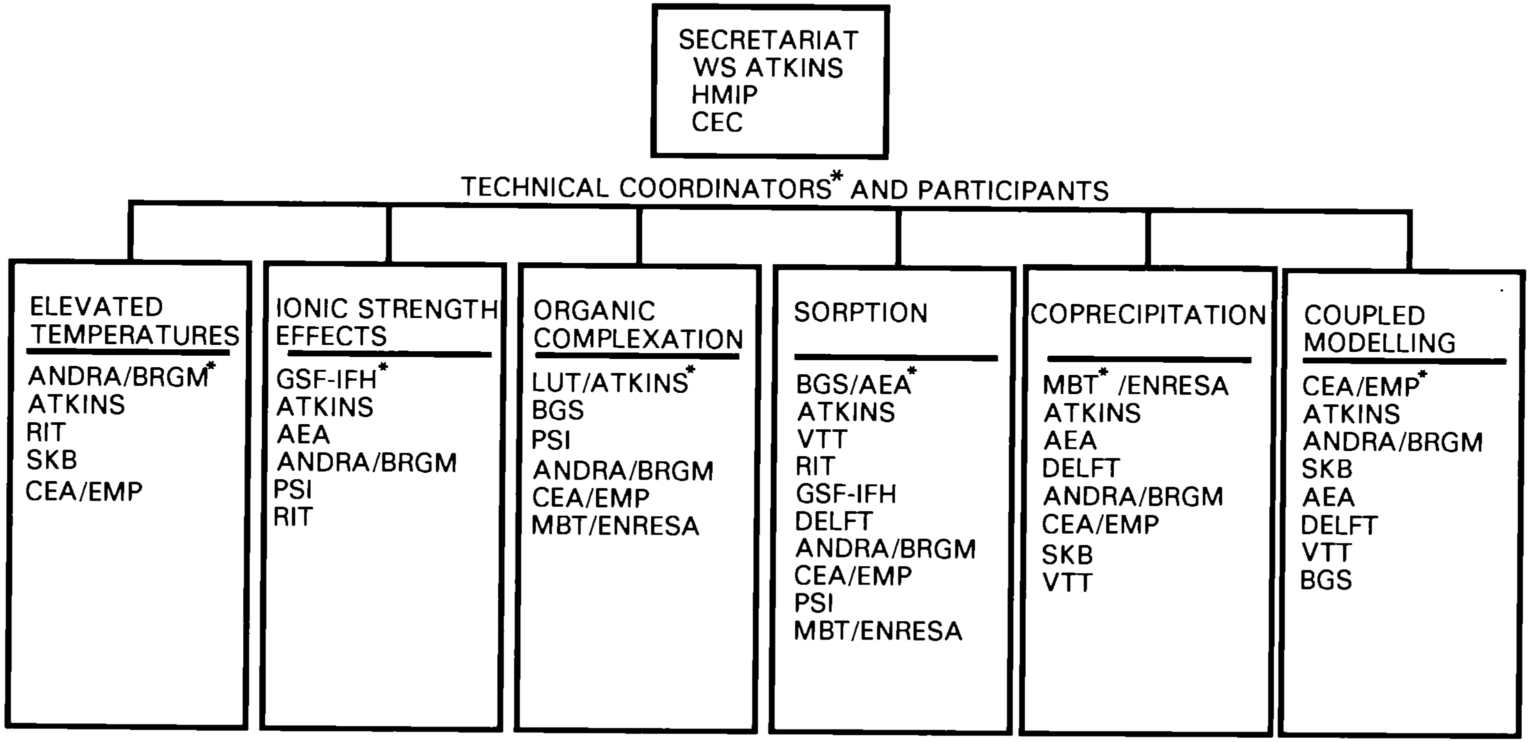


Figure 1. Organisation of the CHEMVAL 2 Project

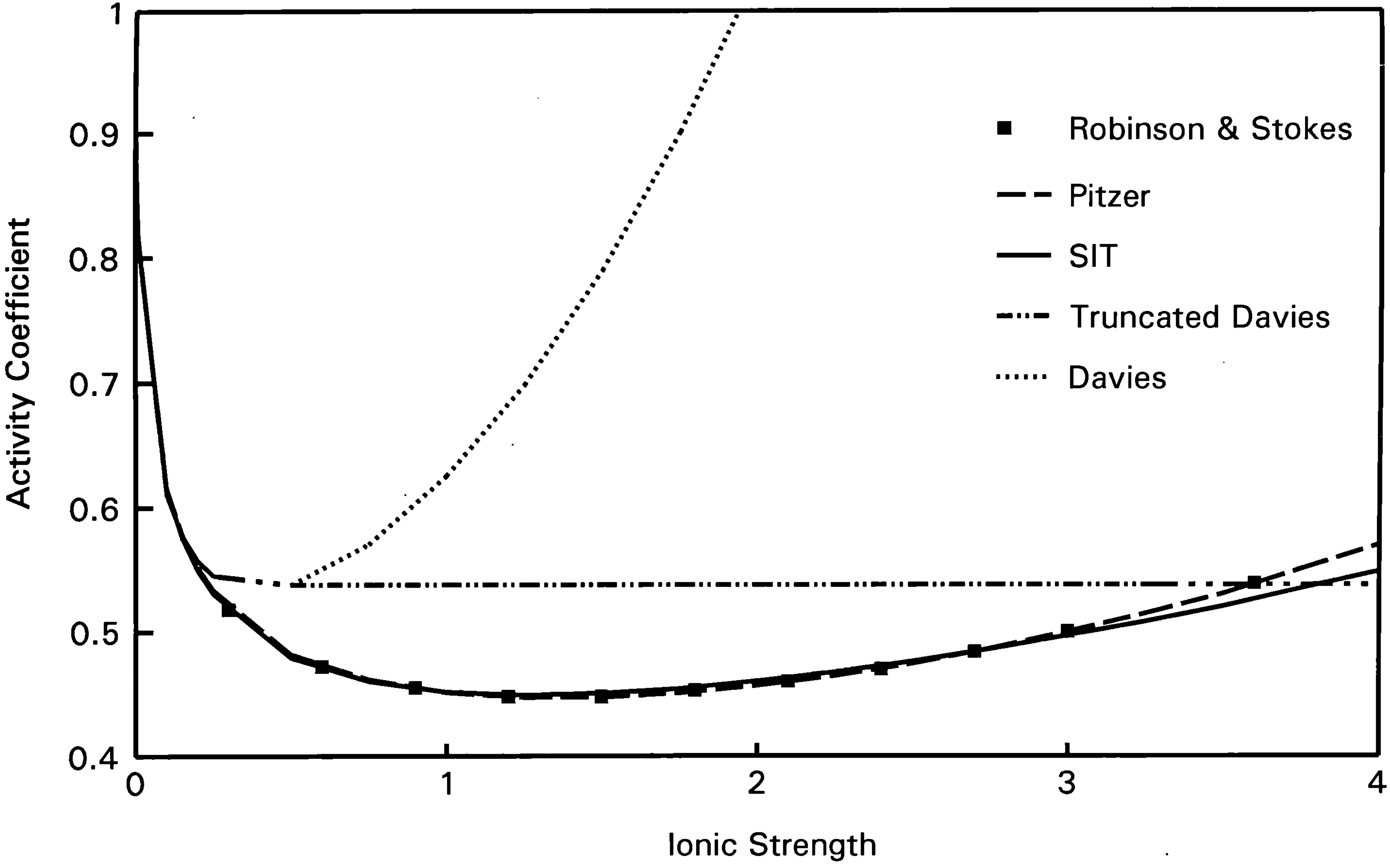


Figure 2. Activity coefficients for CaCl2 solutions calculated by different ionic strength correction methods

Title : Oklo, natural analogue for transfer processes in a geological repository

Contractor : C.E.A./ I.P.S.N.

Contract : FI 2 W CT 0071

Duration of contract : 4 years (January 1st, 1991 to December 31st, 1994)

Period : 1993 (3rd year of contract)

Project leader & task-coordinators:
General : P.-L. Blanc,
Source term : Ph. Holliger,
Ancient migrations : F. Gauthier-Lafaye,
Recent migrations : E. Ledoux, P. Toulhoat,
Integrated modelling : E. Ledoux.

A.- OBJECTIVE AND SCOPE

The nuclear phenomenon of Oklo (Gabon) is the only natural case of fission products being stored in a geologic environment for a significant period of time (two billion years). Therefore, the Oklo uranium deposit is a good example for the study of natural analogy with deep radioactive waste disposal, specially radionuclide mass transfer processes to the surface. However the peculiarities of this uranium ore deposit imply a thorough assessment of the radionuclides and daughters as well as ancient and recent geochemistry and hydrodynamics.

B.- WORK PROGRAM

This program involves several different tasks :

1°- *In situ* sampling, in close collaboration with the mining company (C.O.M.U.F., COMPAGNIE DES MINES D' URANIUM DE FRANCEVILLE, Mounana, Gabon). To this part of the program can be added the collecting of new data on the general setting of the Oklo mining area and deposits.

2°- Study and characterisation of the source term (mostly in CEA laboratories).

3°- Studies on the geochemical systems ruling the migrations can in turn be divided into : studies on the ancient migrations, contemporaneous to the rock diagenesis, to the nuclear reactions and to the general geological history of the basin, and on the recent to present migrations (tertiary to present?).

3.A.- The studies of the ancient migrations will encompass several subjects, and imply collaboration between CEA laboratories and other institutions :

3.A.a.- CEA laboratories (DCC/DSD/SECTION DE GEOCHIMIE) cooperate with all other institutions in the program to assess the petrography and elemental chemistry of the deposits.

3.A.b.- The retention properties of the clays towards radionuclides is the main topic of the investigations of the CENTRE DE GEOCHIMIE DE LA SURFACE (CNRS, Strasbourg).

3.A.c.- The contribution of CREGU (CENTRE DE RECHERCHES SUR LA GEOLOGIE DES MATIERES PREMIERES MINERALES ET ENERGETIQUES, formerly "DE L'URANIUM", Nancy) is to investigate the thermal history of the deposits in and around the reactor zones. The CRPG (CENTRE DE RECHERCHE EN PETROGRAPHIE ET GEOCHIMIE, CNRS, Nancy) collaborates with them to the modelling of heat transfer.

3.A.d.- Reconstructing the chemical characteristics of the hydrothermal fluids which left their chemical imprint in tracer mineral when they were circulated through the deposits has been undertaken by the CENTRE DE GEOLOGIE GENERALE ET MINIERE of the ECOLE NATIONALE SUPERIEURE DES MINES DE PARIS (ENSMP, Fontainebleau).

3.B.- The study of the recent migrations also imply collaborations between CEA laboratories and other institutions :

3.B.a.- The CENTRE D'INFORMATIQUE GEOLOGIQUE (ENSMP, Fontainebleau) is responsible for the understanding of the hydrogeological conditions.

3.B.b.- The SECTION DE GEOCHIMIE of CEA/DCC/DSD is in charge of the hydrochemistry.
(Conterra A.B. on behalf of SKB from Sweden collaborates to part 3.B., particularly on the Bangombé area.)

4°- Modelling : Part of the modelling will take place in each laboratory involved, but the final integrated hydrodynamical-geochemical models will be the responsibility of ENSMP and CEA/IPSN.

C- PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

At the close of the analytical period of this program, we can summarise the advancement of work as follows :

*Task 1, **field sampling**, is now finished : the only opportunities for solid rock sampling during 1993 were provided by the hydrogeology & hydrochemistry field missions.*

*Task 2, **source term studies** : the analytical phase is finished for R.Z. 10 and 13. The next step for these R.Z. is to obtain a general balance of fissiogenic materials. The analyses of the more recent samples from the BA 145 R.Z. have been completed and will provide the necessary source term to the hydrochemistry part of the program there.*

*Task 3.A, **Ancient migrations** : a wealth of data has already been obtained on the general petrography and geochemistry of the reactor zones, on the reactor-clay and on the reconstruction of the fluids. New results have been obtained on fluid inclusions. The results of the fission tracks studies are still lacking, and so are the environmental isotopes analyses on clay minerals.*

*Task 3.B, **Recent migrations**, is very much linked to **task 4, Integrated modelling**. The water samples needed for the hydrochemical and isotopic analyses have been collected late February and March 1993. A complete description and understanding of groundwater* *chemical evolution in Okelobondo and Bangombé conceming major elements behaviour, redox control and uranium behaviour has been obtained. The next step of these tasks is the integration of hydrology and hydrochemistry in a general model.*

Progress and results

1°- FIELD SURVEY, SAMPLING, AND GEOLOGICAL SETTING

The Oklo uranium ore body lies on the south-western margin of the precambrian sedimentary basin of Franceville.

The uranium deposits are sedimentary, in a sandstone layer 3 to 6 meters thick, at the top of the conglomerate and sandstone basal formation (FA) of the Francevillian series (Palaeoproterozoic). They are overlain by the mudstones, shales, dolomites and organic-rich shales ("ampélites") of the FB formation : the early diagenesis of the clays in these levels has been dated at 2.065 Ga by the Sm/Nd radiochronometer.

The uranium originates from erosion of the Chaillu granitic basement to the South-west, the age of which was already known from Ru/Sr and K/Ar dating and ranges from 2.680 to 2.696 Ga., and maybe also from the leaching of overlying volcanic ashes interbedded in the FB levels. The uranium precipitated in hydraulic fracturation corridors, at a reduction front determined by the presence of mature organic matter, probably at the same time as the early diagenesis of the clay minerals took place.

There is at present no specific mining of the remaining reactors, as there is no market for depleted uranium. The accessibility to the reactors has thus decreased during the course of our program as follows :

- Reactor 10, is situated in the center of the bearing, 70 to 80 m North of the dolerite dyke, downhill from the quarry, between the 120 and 150 m elevations (slices D65 to D81). It has been estimated to about 300 tonnes of depleted uranium, of which 40 % have already been taken. In February 1992, a new circulation drift has been mined into the lower levels of this reactor (D81). The trace of borehole SF 29 and the lower closure of the reactor have been directly observed and extensively sampled. Unfortunately, owing to the structural conditions, it has been necessary to wall out this drift soon afterwards.

- Reactor 13 was also situated downhill from the quarry, but about 35 m to the South of the dolerite dyke, at an elevation of 230 to 218 m. Very little of this reactor, if any at all, may remain at level SD 38.

- Reactor 16 was discovered in may 1991, in slice D75N, *i.e.* at mid-level of reactor n°10, but about 150 m to the North. No indication of the presence of a reactor was known there previously. As drift D75N was intended for ventilation, an easy access to the reactor was kept for some times, but this is not the case any longer.

- The "OK 84" reactor lies 500 m to the South-east of the quarry, at an elevation of about 60 m. Several drifts come close to it, but none did actually cut through it up to now. The hydrology drilling campaign has provided a new opportunity for sampling anew this zone during the autumn of 1992.

- The "Bangombé" (rather than "Bagombé") reactor is located a few kilometres to the South-east of the town of Moanda, itself 20 kilometres South of Mounana and the Oklo deposit. This reactor is very shallow, as the "reactor facies" lies less than 12 meters from surface. The hydrology campaign there also provided new cores through this zone.

2°- THE SOURCE-TERM

The main characteristics of reactor zones 10 and 13 from the time of the reactions to the present have been investigated in 1991-1992 :

- the age of the nuclear reactions in R.Z 10 has been measured accurately to 1970 Mega-annum (Ma). This age fits perfectly to the one derived from the fission products ; it makes it possible to recalculate an uranium-235 enrichment ratio at the time of divergency of 3.68 %, *i.e.* five times the present value ;
- the uranium grains in the so-called "sandstone reactor" in R.Z. 10 have remarkably preserved their fission products and original isotopic composition. The same applies to the uraninite grains in R.Z. 13, despite complete loss of their radiogenic lead 750 Ma ago. In these samples we find an excellent *in situ* correlation between the uranium depletion and the neodymium, samarium, zirconium and thorium amount.
- Metallic aggregates containing fission platinoïd elements (gold, rhodium and palladium) to which lead, bismuth, antimony, tellurium, arsenic and sulphur are associated, have been observed in the silica and in the joints of some uranium oxide grains.

New results have been obtained on the Ba 145 reactor zone : In the core of the reactor, uranium oxide corresponds mainly to very large grains of cubic uraninite, with crenated edges evidencing secondary alteration. Galena is not present in the reactor core. Despite the weathering of the site, it has been possible to put into evidence the rather weak uranium isotopic depletion for this isolated reactor ($^{235}U/^{238}U = 0.005902$; $\tau = 0.488\ 10^{21}$ n/cm^2). In the reactor core, the ages obtained from the uranium to neodymium, uranium to samarium and uranium to thorium ratios are consistent, and point to the same age as in the reactor zones Oklo proper : 1.97 ± 0.05 billion years. The present thickness of the uranium enriched layer (only 5 cm) cannot justify criticality, and despite the fact that uranium isotopic ratios appeared normal in shales and sandstones within contact from the reactor, one anomalous value has been recorded in the weathering profile, 5.5 m above the reactor, thus evidencing present migration of depleted U from the reactor core.

3.A.- THE GEOCHEMICAL SYSTEMS : ANCIENT MIGRATIONS

3.A.a.- PETROGRAPHY AND ELEMENTAL CHEMISTRY

The rock facies observed in and around the deep reactor zones are similar to those known from the previously studied reactor zones. However they exhibit some peculiar features, such as a high mechanical coherency, related to the absence of supergene weathering. The same differences are now found with the shallow Bangombé "Ba 145" zone.

The sandstones surrounding the reactors are made up of detrital mineral grains (quartz, biotite little feldspar and accessory minerals, mainly zircon, uranium oxides, sphene and organic matter). These sandstones were deposited as layers (or lenses) with thickness ranging from a few centimetres to the meter, and the grains ranges from fine sand to conglomerate. The clay fraction is made of ferrous chlorite and illite, and calcite may be present as fissure infillings. In Bangombé, chlorite disappears from the levels closest to the surface (6.52 to 10.25 m) while low amounts of kaolinite and metahalloysite are found. The levels above circa 8 m. show goethite accumulation, marking the major redox front , above which the local brown to rubefied pelites result from supergene weathering.

The "reactor-clay" facies generally surrounds the reactor proper. In this facies, magnesian chlorite is interspersed with corroded quartz grains and less-soluble primary minerals (zircon, sphene, uranium oxides). Some secondary minerals develop at the expense of primary accessory minerals : coffinite, cryptocristalline zircon, sphene and variable amount of apatite. Organic matter is generally present in close vicinity of the reactor-clay and reactor-core facies. In Bangombé, where ferralitic alteration is superimposed, red (ferrous) oxydes are present at every level.

In the "reactor-core" facies, the main mineral phases are uraninite and magnesian chlorite. In the shallow Ba 145 reactor, hematite and iron hydroxides are present together with titanium oxides, separated from uraninite by a rim of illite.

All these facies can be run through by fissures, with a width ranging from micrometers to a few millimetres. They are generally filled with fibrous calcite (probably dissolved at Bangombé).

Silica accounts for 95 % of the total rock in the sandstones, and decreases drastically towards the reactor-core facies. This is interpreted as the result of silica dissolution by the intense hydrothermal circulation triggered by the heat from the nuclear reactions. The other major elements, Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, MnO, and TiO_2, clearly increase from the sandstone to the reactor. These elements are clearly linked to the phyllitic component of the different facies, either primary or secondary. A good correlation between CaO and CO_2 shows that they are linked together as carbonate.

The trace elements can have two origins : some come from the initial sandstones (accessory phase and clay fraction) : apart from uranium, the sandstone contain Ba, Sc, Ga, Sr, V, Zn, and Zr. The second possible origin is the formation of trace elements in the course of the nuclear reactions and radioactive decay. This is the case not only for Zr, Nb, Ba, Nd, Sm, Eu and Gd, but also for Pb, Ru, Ag, Cd and Te. All trace elements have much higher concentrations in the reactors than in the surroundings.

3.A.b.- RETENTION BY CLAYS

The finding of a sample enriched in uranium-235 in reactor zone 10 has demonstrated the existence of two different processes of nuclide retention by clay minerals :

the first one is subcontemporaneous to the nuclear reactions , and involves the direct trapping of the radioelement (plutonium) into the crystal lattice of hydrothermal chlorite. A very low amount of total uranium seems to be the determinant factor to make it possible to detect the uranium-235 enrichment resulting from the decay of the plutonium.;

The second of these processes is sorbtion of depleted uranium removed from the reactor zone onto the surface of clay particles, and can have taken place during any hydrothermal phase, later than the nuclear reaction. The amount of uranium trapped by the second process is much the highest, but it remains by far more mobile.

New observations in Bangombé seemed at first to indicate that no remobilisation of depleted uranium had taken place from the reactor, as the isotopic composition of the uranium in the over- and underlying shales and sandstones is normal.

However as the thickness of the uranium rich layer and the total uranium amount are unsufficient to explain criticity at any time, and as depleted uranium has been found in the farthest sample to the reactor in borehole BAX03 (6.52m from surface, 5.5m above the reactor) we have to assume that the normal or subnormal ratios in most argillaceous samples reflect large removal and secondary input of normal uranium from the ore surrounding the reactor zone.

The minimum distance for Rare Earth Elements displacement is the same as for depleted uranium, though the evolution curves of neodymium, samarium and europium contents are not correlated, indicating chemical fractionnation of the REE during displacement.

3.A.c.- THERMAL HISTORY OF THE REACTOR ZONES

Mineralogical and petrologic observations on samples from the Oklo natural fission zones show that the secondary mineral paragenesis is different at the border and the core of reactors. At the border, the presence of minium (Pb_30_4) and hematite indicates that their formation took place under oxidising conditions. The existence of free oxygen and hydrogen in the gas bubble of fluid inclusions trapped in nearby quartz crystals also suggests oxidising conditions because hydrogen is inert at low temperatures whereas oxygen is very reactive. In the core of the reactor, native lead, galena and coffinite indicate a reducing environment during their formation. This zonation can reasonably be attributed to oxidising and reducing species produced by the radiolysis of water and organic matter.

In order to better understand the hydrothermal circulations around reaction zones, a microthermometric study on fluid inclusions from authigenic quartz, apatite and calcite crystals is presented. The fluids so investigated are distributed into three types :

- The regional diagenetic fluids yelded melting temperatures of -2 to -6° C, (3 to 8 % NaCl wt equ.), and temperature of homogenisation of 160 to 200° C.

- The fluids associated to circulation around the reactors (fissures infillings) gave melting temperatures of -10 to -15° C (14 to 24 % NaCl wt equ.) and homogenisation temperatures of 110 to 150 °C in calcite or 190 to 270 °C in apatite grains.

- Nearest to reactor 10, in the nourishment zone of quartz grains within contact of the reactor-clay, melting temperatures of -6 to -10 °C (9 to 14 % NaCl wt equ.) and homogenisation temperatures from 280 °C up to 480 °C have been observed.

In addition, low salinity fluid at temperatures 200-250°C occurs at 50 meters from the dolerite. For the first time, it is possible that the fluid related to the dolerite intrusion is observed.

The meaning of this evolution is as such : in quartz, the reactor fluid of low salinity has been heated to more than 400°C. In apatite, the temperature is lower but the salinity has increased and finally in calcite, the temperature is about 120°C and the salinity is high.

3.A.d.- RECONSTRUCTION OF ANCIENT FLUIDS

During hydrothermal circulation, mineral precipitation occurs either at the walls of open cracks, as vein lining, or as isolated crystals within percolated rocks. Authigenic minerals act as traps for trace elements in solution, thus supplying efficient concentration mechanism for elements specific to the mineral species considered. Apatite [$Ca_5(PO_4)_3F$], and sulphides [galena (PbS) and pyrite (FeS_2)] are efficient geochemical traps for REE, and for Ag, As, Sb and Mo, respectively.

Several fluids or fluid stages have been identified, and mixing processes between some of these have been argumented, on the basis of heterogeneous mineral populations in some samples. By contrast, some samples, though close from each other, have shown quite different mineral populations, and have thus been in contact with quite different fluids, without any evidence for interaction : this suggest a rather large time-span between the circulation of these fluids, and may help in assessing the relative time of sealing of the permeability/porosity of the different facies or levels under investigation.

However the correspondance between the thermal and chemical observations is good, as four hydrothermal circulation stages have also been inferred :

an initial stage (or fluid), related to the reworking of the sedimentary metal stock present in the FA sandstone formation, and showing no relation to the reactor zones, has been recognised ;

one fluid at least appears directly related to the nuclear reactions 1.97 Ga ago : this fluid seems to have had a very low content in most elements, except in fission products, as shown by the light rare earth elements (L.R.E.E.) content of the associated apatites.;

Another fluid apparently contributed to the dilution of the fluids escaping from the reactor zones ;

At least one stage is very late in the history of the deposit, and is related to the dolerite intrusion around 750 Ma ago.

3.B.- THE PRESENT MASS-TRANSFERS

3.B.a.- HYDROGEOLOGY

An extensive drilling program, set down in 1991 and during the first half of 1992, has been mainly conducted during field missions from September 1992 to September 1993. Two sites are being investigated :

- a deep reactor zone at Okélobondo, allowing study of elemental transfers at a 500 m scale, through a highly heterogeneous sedimentary sequence ; preliminary modelling indicated that the zone is submitted to an upward (discharging) groundwater flow from deep geological formations, increasing the odds to sample waters having been in contact with a reactor zone.
- a shallow reactor zone at Bangombé, in a well defined flow system in a less heterogeneous geological situation, featuring supergene alteration.

At Okélobondo, the piezometric levels (hydraulic heads are around 375-380 m in the discharge area, and around 435 m in the recharge area. The data in the surficial piezometers are in accordance with the preliminary modelling, while the deeper ones show the influence of the mining activities.

At Bangombé, piezometric observations show that, upstream from the experimental trench, the free water table is about 15 m below ground surface, while it is just level with the surface below this trench. The change in heads from the dry to the rainy season have remained minor during the observation period.

On both sites hydraulic tests have been performed in order to assess the hydraulic conductivity of the stratigraphic units of concern.

The preliminary modelling had shown the need to complete the drilling program to collect new data to constrain the conceptual models. The next step will be a successive integration of the new data : physical and chemical parameters, and will be followed by the radionuclide transport modelling.

3.B.b.- HYDROGEOCHEMISTRY

During the previous years, the use of depleted uranium as a natural tracer of the reaction zones in the present groundwaters has been investigated, as uranium is soluble in oxidising environment and as the $^{235}U/^{238}U$ ratio is the clearest and most conservative tracer of nuclear reactions. Two preliminary groundwaters samples from Okélobondo and from borehole Ba 145, the initial borehole by which a reactor zone was discovered at Bangombé, have shown significant deviation from natural uranium isotopic composition.

The samples needed for the hydrochemical and isotopic analyses of the waters, necessary to the validation of the hydrogeological diagrammatic model proposed and to the development of the hydrodynamical model, have been collected late February and March 1993.

The groundwaters evolution can be evaluated with reference to two major phenomena, which are :

- the progressive acquisition of solutes by water-rock interaction, and the following reequilibration with secondary minerals ;
- the lithological redox conditions, which are generally controlled by an equilibrium between Fe II (dissolved) and Fe III.

On these ground the waters in the Oklo-Okélobondo area can be split into three type, as follows :

- shallow waters from the alterites have a low pH and a low bicarbonate content, low total dissolved sulphur, but a high CO_2 content caused by biological activity, and a high tritium content.
- intermediate waters from the upper pelites and complexes show intermediate pH and alkalinity, together with a high silica content due to intense leaching, an increasing total dissolved sulphur content with pH, intermediate tritium content, and a tendency to equilibrium with carbonate minerals, in carbonate rich aquifers (dolomitic complexes) ;
- confined waters as found in the deep pelites and Okélobondo mine have high pH, high alkalinity, high total dissolved sulphur, low tritium content and a tendency towards equilibrium with secondary alumino-silicate minerals and are in equlibrium with carbonates. however the waters from the OK 84 reactor zone show a very high tritium content, so high that the possibility of *in situ* tritium production is now under investigation, rather than any recent water contamination.

The redox control in the areas under investigation is anomalous, the Eh values are not correlated to depth and confinment : the most reducing waters are found in the aquifers in organic matter bearing aquifers.

Preliminary results on the stable environmental isotopes allow a similar splitting of the Okélobondo groundwaters into three sets :

- surface waters have the higest heavy isotopes content and their main recharge is of local origin, at present time,
- the deeper and more eastern waters are depleted, indicating either recharge under cooler climatic conditions or recharge from an area at a higher altitude and a longer transit time,
- sample from the "complexes" and from the western part of the area show isotopic compositions close to the global meteoric water line, and may represent either shorter aquifer pathways from lower altitude recharge areas, or mixing of the two end-members already defined.

In Bangombé it is also possible to discriminate between waters recharged high above on the Bangombé plateau and shallow waters with local recharge. The calculated (from total inorganic dissolved carbon ^{14}C data) mean transit time for the COMILOG plateau waters is 5000 ± 300 years. The buffering of the redox conditions by organic matter appears intense in the reactor zone there, preventing uranium migration.

Thus, a complete description and understanding of groundwater chemical evolution in Okelobondo and Bangombé concerning major elements behaviour, redox control and uranium behaviour has been obtained. The good agreement between hydrology and hydrochemistry has to be noted. The next step of the task is the integration of hydrology and hydrochemistry in a general model.

List of publications

BLANC P.-L. & A.-M. CHAPUIS (1993) : Oklo, analogue naturel de stockage de déchets radioactifs. Contrat FI 2W-CT91-0071, Rapport d'avancement du 1er janvier au 30 juin 1992, SERGD 93/04, 66 p., 36 fig.

BLANC, P.-L. (1992) : Oklo as a natural analogue for radionuclide transfer processes in a waste geological repository : present status of the program. 5TH CEC NATURAL ANALOGUE WORKING GROUP MEETING AND ALLIGATOR RIVER ANALOGUE PROJECT FINAL WORKSHOP. 5-9th October, Toledo, Spain (to be published in the EUR-SERIES).

BROS R. (1993b). Géochimie isotopique (Sm-Nd, Rb-Sr, Kr-Ar, U) des argiles du bassin protérozoïque de Franceville et des réacteurs d'Oklo (Gabon). Thèse Univ. Strasbourg, 12 février 1993, 154 p. + annexe.

BROS, R., L. Turpin, F. Gauthier-Lafaye, Ph. Holliger & P. Stille (1993) : Occurence of naturally enriched ^{235}U. The implications for plutonium behaviour in a natural environment. Geochim. Cosmochim. Acta, Vol. 57, 1351-1356.

CARPENA J. & A. V. WALTER (1993) : Histoire thermique des zones de réaction d'Oklo : première phase - test de faisabilité des datations traces de fission, caractérisation des apatites. Rapport d'avancement 1992, 4 p.,3 Pl.

CHAPUIS, A.M. & P.-L. BLANC, (1993) Oklo, natural analogue for transfer processes in a geological repository : contract FI 2W CT91 0071, an overview. Oklo Working Group Meeting, *in* Proceedinge of the 2nd joint C.E.C.-CE.A. progress meeting, Brussels, 6-7 avril 1992, EUR 14877 EN, pp. 9-16.

CHAPUIS, A.-M. & P.-L. BLANC, (1993) : Oklo, natural analogue for transfer processes in a geological repository : present status of the program. Migration of radionuclides in the geosphere (MIRAGE project-3rd phase). Proc. of prog. meet, Brussels, 9-10th april 1992, EUR 14690 EN, pp. 137-142 .

GURBAN, I., E. Ledoux, M. Poncey, J. Smellie & A. Winberg (1992) : Etude de l'analogue naturel d'Oklo. Aménagement hydrogéologique du site d'Oklo : Champs expérimentaux de Bagombé et Okélobondo. Rapport ENSMP/CIG LMD/93/1, 18 p., 22 fig., 1 ann.

GURBAN, I., E. Ledoux, H. Peycelon, L. Raimbault, R. Guérin, P. Toulhoat, D. Louvat, J. Smellie & A. Winberg (1993) : Caractérisation des migrations à distance des zones de réaction. Rapport ENSMP/CIG - CEA/DCC/DSD/SCS - Conterra AB, juillet 1993, 50 p., 11 tab., 51 fig.

HIDAKA H., Ph. Holliger & A. Masuda (1993) : Evidence of fissiogenic Cs estimated from Ba isotopic deviations in a Oklo natural reactor zone. Earth and Planet. Sci. Lett., 114, 391-396.

HOLLIGER, Ph. (1993) : Oklo-Terme source : paramètres nucléaires. Etude isotopique et topographique de la zone de réaction 10. Rapport d'avancement 1992 DCC/DSD/SCS 93/96, 18 p.,12 Pl. & fig., 1 ann.

HOLLIGER, Ph. & P. LANDAIS (1993). Organic matter and uraninite from the Oklo natural fission reactors : Natural analogue of radioactive bitumen and UO^2 irradiated fuel. CEC contract ann. report 1992, DSD-93/84, 29 p., 8 pl.

MENET-DRESSAYRE C & M.-T. MENAGER (1993) : Migration élementaire des produits de fission, des actinides transuraniens et de leurs descendants autour des réacteurs nucléaires naturels d'Oklo (Gabon). Rapport DCC/SCS/SGC/LGS, 12 p., 2 fig.

E. MOINY, M. Piboule & J. Amossé (1993) Compte-rendu d'activités, 1er semestre 1993. 35 p., 8 pl.

OKLO WORKING GROUP (1993) : Proceedings, 2nd joint CEC-CEA prog. meeting, Brussels, 6-7 avril 1992, EUR 14877 EN.

OKLO WORKING GROUP (1994) : Proceedings, 3rd joint CEC-CEA prog. meeting, Brussels, 11-12th octobre, (to be published in the EUR-series).

PEYCELON H. (1992) : Suivi des travaux miniers et échantillonnage : Mission de septembre 1990 à décembre 1991. Rapport CEA/IPSN, 62 p., repris *in* BLANC & CHAPUIS (1993), Annexe.

RAIMBAULT L. & H. PEYCELON (1993) : Reconstruction des paléocirculations fluides : géochimie des minéraux pièges. Rapport d'avancement ENSMP/CGGM, 18 p., 2 Tab.

ROYER, J.-J. & C. LE CARLIER DE VESLUD (1993) : Modelling heat and fluid transfers during natural nuclear reaction in the Oklo uranium deposit (Gabon). Oklo Working Group Meeting, *in* Proceedings of the 3rd joint C.E.C.-CE.A. progress meeting, Brussels, 11-12 octobre 1993, EUR series à paraître & contrat C.C.E-C.E.A.-CREGU, Rapport d'avancement 1er semestre 1993, annexe CNRS/CRPG, 14 p.

ROYER, J.-J., C. Le Carlier & L. Florès (1992) : Modélisation des transferts thermiques et fluides autour d'un réacteur naturel de fission (Oklo, Gabon). Rapport d'avancement CNRS/CRPG, 51 p.

SAVARY V. & M. PAGEL (1993) Détermination de l'histoire thermique et chimique dans et autour des zones de réactions nucléaires naturelles du gisement d'Oklo (Gabon). Contrat C.C.E-C.E.A.-CREGU, Rapport annuel 1992, 23 p.

SAVARY V. & M. PAGEL (1993) Redox conditions and thermal history in reactors 10 and 16. Oklo Working Group Meeting, *in* Proceedinge of the 3rd joint C.E.C.-CE.A. progress meeting, Brussels, 11-12 octobre 1993, EUR series à paraître & contrat C.C.E-C.E.A.-CREGU, Rapport d'avancement 1er semestre 1993, 12 p. & ann.

TOULHOAT P., J.-P. Gallien & P. L'Hénoret (1993) : Far field hydrogeochemistry in the Oklo reactor area (Gabon).Oklo Working Group Meeting, Proceedings of the 2nd joint CEC-CEA Progress Meeting, Brussels, 6-7 April 1992, EUR 14877 EN, pp. 137-148.

TOULHOAT P., J.-P. Gallien, D Louvat, V. Moulin, P. L'Hénoret, R. Guérin, E. Ledoux, I. Gurban, J. Smellie & A. Winberg (1993) : Present-time migration around the Oklo natural reactor. Evidence of uranium isotopic anomalies in groundwaters close to reaction zones. Migration 93, Charlestown, Dec. 13th-17th, 1993, 19 p.

WINBERG, A. & J. SMELLIE (1993) : Preliminary reporting of CEA/EMP & SKB actvities at Bangombé performed during September-December 1992. Rapport Conterra AB SKB, 12 p.

WINBERG, A. & J. SMELLIE (1993) : Bagombé area, descriptive geological and hydrogeological model : a working document prepared for CEC/ CEA/ SKB Oklo analogue study. Rapport SKB/Conterra AB juin 1993, 7 p, 9 pl.

DEVELOPMENT OF A MODEL FOR RADIONUCLIDE TRANSPORT BY COLLOIDS IN GEOSPHERE.

Contractors	ARMINES / INTAKTA / RIVM / CNRS-LSGC / ENRESA
Contract n°	FI2W - CT91 - 0079
Duration of the contract	from 01/10/91 to 30/09/95
Period covered	01/10/93 - 31/12/93
Project leader	E. LEDOUX

A. OBJECTIVES AND SCOPE

The objective is the development of mathematical models for radionuclide migration from underground repositories for radioactive waste to the accessible environment by colloids in groundwater. The model development is to be supported by migration experiments in laboratory, its validity will be evaluated against field data.

The model must be able to interprete laboratory and field experiments, and also to be included in geosphere transport code for safety assessment. For this reason a serie of codes, from detailed to simplified, must be developed and validated successively, at different scales.

B. WORK PROGRAMME

1 Literature survey.

2 Formulation of a first conceptual model. Screening of phenomena to be included in the model by performing simple calculations of test cases.

3 Planning of laboratory migration experiments with a simplified fixed solid phase. Research of optimal experimental conditions with the help of task2.

4 Laboratory migration experiments focusing on the study of mechanisms for advection-dispersion of particles, on the interaction between particles and fixed solid phase, and agglomeration and sedimentation of particles.

5 Formulation of a second conceptual model, computer programming, numerical verification of the computer code and tests against the laboratory experiments (task 4 and 6).

6 Planning and performing laboratory experiments using field material as fixed solid phase. Verification of the relevance of the second conceptual model. Compilation of a field data base for model verification.

7 Development of a model for simulating field experiments. Application of this computer code to field experiments and to the compiled data base.

8 Development of a colloid migration model for performance assessment. Application of the code to some relevant performance assessment scenarios.

9 Project management.

C. PROGRESS OF WORK AND OBTAINED RESULTS

STATE OF ADVANCEMENT

The scientific work carried out during year 1993 is based on experiments : definition, execution of experiments to be used to validate the codes. This also leaded to improvment of the models developed during the previous work periods, and to first tests of these codes against laboratory experiments (task 5). Within this frame, the activities of the partners have been the following :

- Partner 01 (ARMINES [F]) introduced the concepts of a microscopic approach, focusing on the colloid-medium interface.

- Partner 02 (INTAKTA [F]) tested the accuracy of the code TRUMP to describe the colloidal behaviour within the case of fractured media. The parameters involved have been listed.

- Partner 03 (RIVM [NL]) focused on the kinetics of colloid metal interaction, based on literature. The colloid transport module of COLTRAP had been tested against laboratory experiments.

- Partner 04 (LSGC/CNRS, [F]) worked with batch and column experiments, using natural porous media (Entraigues sand).

- Partner 05 (ENRESA - CIEMAT, [SP]) provided information about columns experiments performed with El Berrocal granite and groundwater.

More details about this work can be found in the third and fourth progress reports of the project.

1. LABORATORY EXPERIMENTS - POROUS MEDIA

During the first period of this project, laboratory experiments involved porous medium modeled with glass bead packs; it has been extended to a natural porous media (Entraigues sand). Latex particles are used as colloids and strontium as an analogue for radionuclides. The usual experimental set-up has been used for column experiments.

Injection flow rate has been chosen as low as possible (velocity close to 2 mm/mn). The diameter of the colloidal particles was 0.21µm to avoid mechanical retention at the inlet and outlet of the column. The concentration of the latex solution was 100 mg/l ; columns were conditioned in pure water and particles introduced as a step input until the signal at the outlet was constant and equal to the optical density of the inlet signal. The column was then washed with pure water. The influence of three parameters on the transport of colloids was tested: pH at low velocity, flow rate at the inlet, and ionic strength. The characteristics of the column and the chromatographic conditions are given in the following tables.

length	7.35 cm
diameter	0.9 cm
volume	4.676 cm^3
mass of sand	6.521 g
outer volume	0.3134 cm^3

characteristics of the column

pore volume Vp	2.156 cm^3
number of mixing cells	200
porosity ε	0.461
Cationic Exchange Capacity	0.2 µeq/g of sand

chromatographic conditions

Some of the main results are presented in this section.

Effect of pH

The effect of pH related to the ionic strength has been studied at a low flow rate (0.064 ml/mn ≈ 2.18 mm/mn). First a solution at pH 8.8 was injected, then after washing up the column, a solution of pH 6 was injected. Breakthrough curves are given on figure 1.

It can be seen that the curves are symmetrical and that the value $C/C_0 = 1$ is reached at 1.1 V/V_p. In fact, the phenomenon usually observed is a filtration of latex particles through natural or artificial porous medium [*Rodier*, 1993], it means that the initial latex concentration value (C_0) is reached after a very long time. In our experiment no filtration occurs. The values of the "outlet" time of latex particles in pore volume units are 0.794 at pH 6 and 0.87 at pH 8.8. We observe that the velocity of the colloids passing through the porous medium is greater than that of the molecular tracer NaCl. This is probably due to the hydrodynamic chromatographic effect. Due to their size, the particles are excluded from the slow flow components of the velocity profile in the pores of the bed and pass through the system more rapidly than the carrier fluid which has access to all the pore space. We may conclude that at low flow rates an increase of pH related to an increase of ionic strength does cause any retention of latex in the porous medium.

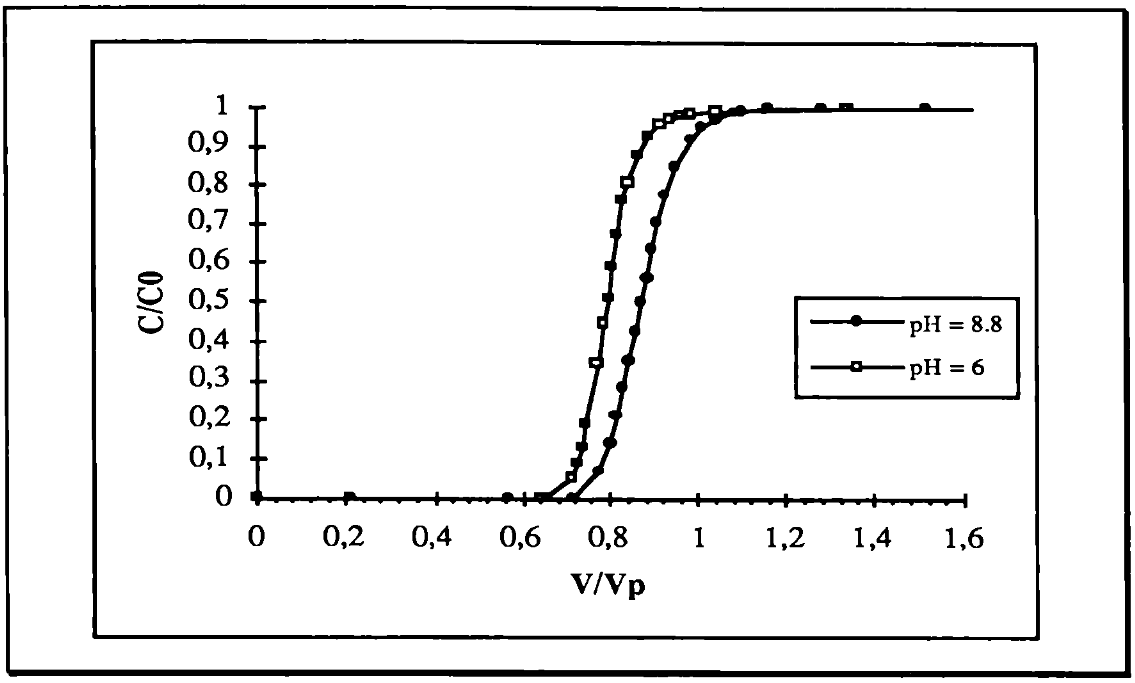


Figure 1 *Breakthrough curves of latex particles (0.21µm) under different pH and ionic strengths : ionic strength=10^{-4} M for pH =6 and 3.10^{-4} M for pH = 8.8 - flow rate =0.064 ml/mn .*

Effect of the ionic strength

The solutions are injected at a low velocity: 0.064 ml/mn at 10^{-4} M and 10^{-2} M of NaCl; 0.0726 ml/mn for 10^{-3} M of NaCl. A pH of 6 is used for all the three solutions. Figure 2 shows that the retention of the colloids increases with the ionic strength: 0.795 V_p at 10^{-4} M, 1.9 V_p at 10^{-3} M and 2.85 V_p at 10^{-2} M. The breakthrough curves are not so symmetrical and the two last injections show a more marked dispersion. The observed retardation could be explained by the D.L.V.O. theory. The thickness of the double layer around the particles of sand and around the latex particles decreases with an increase of the ionic strength, in this case the latex will be "caught" in the secondary minimum in the interaction profile between the particles and the sand surface. This sort of retention would be a function of the distance between the latex particle and the surface of sand at a specific ionic strength. The fact that the phenomenon is reversible and that we can recover the latex by washing the column tends to support this explanation.

In conclusion, the main results concerning the behaviour of the latex can be resumed as follows: in column experiments, even in repulsive conditions it is possible to obtain a retention of the latex at specific values of ionic strength. In these experimental conditions, the retention time of latex can be predicted if the ionic strength in the medium is known. The experiments presented here will have to be completed by pre-conditioning the column and washing after the injection of latex with a solution at the same ionic strength as the latex solution.

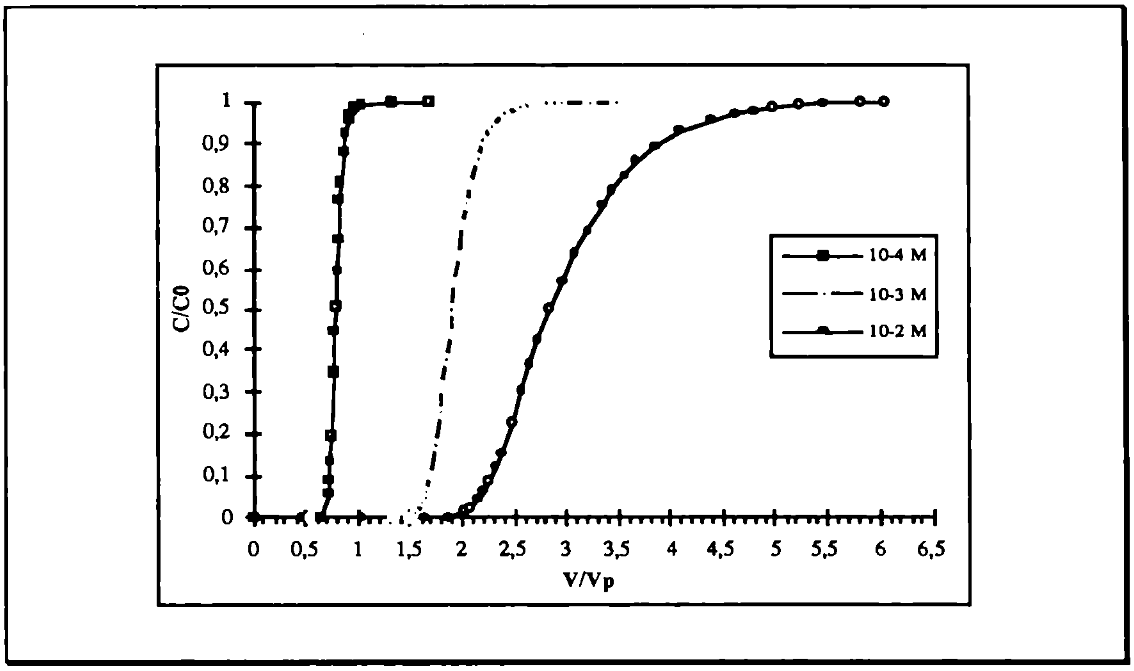


Figure 2 *Breakthrough curves of latex particles (0.21 μm) - pH=6 -- flow rate = 0.064 ml/mn for 10^{-4} M and 10^{-2} M; 0.0726 ml/mn for 10^{-3} M .*

2. COLUMN EXPERIMENTS - GRANITIC MATERIALS

The aim of these experiences has been to determine the hydrodynamic characteristics of the two columns selected to perform migration studies of colloidal particles through a fractured rock system. The choice of columns of fractured granite instead of weathered or compacted granite columns is due to the fact that for granitic rocks at high depths, the most significant component of groundwater flow transpasses a network of interconnected open fractures. The flow through whole rock or cemented fractures would be almost negligible when compared with this fracture flow. The experiments were performed with fresh granitic rock from the "El Berrocal" Experimental Station. It presents an important fracture that will be the most significant feature that will control the groundwater flow through the columns.

Both columns present a subparallel fracture dipping with an angle ~ 85°. The fracture is closed, meaning with this that there is no evidence of actual groundwater flow through it. It presents a fracture coating consisting mainly of weathering products, such as phyllosilicates like chlorite or smectite and carbonated coatings. In all cases the coatings are very scarce and the fracture can be considered as a clean surface for the water flows that have been used in the experiments, always in the range of about 1 fracture volume (10 ml) per hour.

Some of the main features observed after analysing the breakthrough curves of both columns for the tracers used are the following : Column 1 presents a higher fracture volume of about 17 ml while in the case of Column 2 this volume is much smaller, about 8 ml. For both columns it is observed that an increase in the flow velocity through the columns means a sharper peak, with a tail dispersion decreasing as it increases the flow rate. In the case of Column 2 there are only data available for two velocities, 0.1 and 0.2 ml/min, but other experiences with higher flow rates have been recently performed.

The work in progress does not yet allow to obtain the true image of what it is happening inside this two fractured columns. What is observed is that the flow along the fracture path is of the laminar type and that an increase in flow rate results in a decrease of the diffusion of the tracer species. In all cases the recovery measured is not of 100% but this is probably due to counting errors.

3. MICROSCOPIC APPROACH : CHESS

The code CHESS [*Van der Lee J*, 1993] is devoted to microscopical scale. It has been developed to calculate CHemical Equilibrium Speciation with Surfaces, using an approach which is applicable to inorganic and organic colloids and surfaces in general, and has been refined during the last work period. Its major characteristics are :

- speciation according to a thermodynamic database
- precipitation/dissolution
- surface complexation
- electrostatic correction (double layer assumption)
- different site-affinities per surface
- different surfaces per system

This code is used to calculate the speciation spectrum (e.g. it provides the predominant species of the radionuclides under investigation for a given background chemistry) and the colloidal electrical charge and surface potential, which appears to be a dominant parameter in colloid-medium interaction processes.

In order to develop this code, existing modelling studies have been carefully examined [*van der Lee J. et al.* 1992, 1993], and three possible approaches have been identified. Then, a partly deterministic, partly probabilistic attachment model has been built. It is first applicable to a one-dimensional transport equation which can be used easily to test laboratory column experiments.

During this work period, this code has been validated against laboratory experiments which have been performed either within our project or within linked projects (MIRAGE - CoCoClub) ; batch experiments and column experiments have been satisfactorily simulated.

4. MACROSCOPIC APPROACHES

4.1 COLTRAP

The one-dimensional model developed during the last period of work, describing the transport radionuclide through a "saturated porous medium - groundwater - colloid system" with stationary groundwater flow has been tested against experimental results coming from either literature or experiments performed within the project. Furthermore the kinetics of colloid-metal interaction has been surveyed.

Four experiments performed at LSGC in Nancy with a given diameter of latex particles, two ionic strengths and two flow velocities were selected to test the code. The results used were the breakthrough curves corresponding to an inlet of a latex step through a column of glass beads.

The interaction between colloids and solid phase is described by a kinetic association/dissociation expression. The mass balance equations for the respective mobile and immobile colloids are the following :

$$\frac{\partial C^c}{\partial t} + \frac{(1-n)\rho_s}{n_c}\frac{\partial S^c}{\partial t} + v_c\frac{\partial C^c}{\partial x} = \frac{\partial}{\partial x}\left(D_c\frac{\partial C^c}{\partial x}\right) \quad ; \quad \frac{\partial S^c}{\partial t} = \frac{n_c}{(1-n)\rho_s}K_A C^c - K_D S^c$$

where C^c is the number of mobile colloids per unit volume of water available for colloids, D_c the diffusion/dispersion coefficient of colloids, K_A the association rate of colloids with solid surface, K_D the dissociation rate of colloids from solid surface, n the porosity, n_c the porosity available for colloids, S^c the number of immobile colloids per unit mass of solid phase, v the mean interstitial velocity of water, v_c the mean interstitial velocity of water, available for colloids, and ρ_s the density of solid phase.

Three fitting parameters considered were dispersivity, association and dissociation rate constants (fitting is done by trial and error). Experimental and model simulation results have been found to be correct for two velocities (the effect of changing velocity is accounted for by the kinetic association/dissociation expression),and two ionic strength values.

For the cases tested, it can be concluded that the experimental data can be fitted reasonably well using COLTRAP. At both ionic strengths, the value of the association rate of colloids with solid surface remained, as expected, constant with decreasing velocity. However, the value of dissociation rate of colloids from solid surface had to be changed. Consequently, the results seem to indicate that colloid association is a kinetic process. The experimental data could not be fitted without considering dissociation.

4.2 TRUMP

The code **TRUMP,** developed by the Lawrence Berkeley Laboratory and Department of Mineral Sciences and Mineral Engineering within the University of California [*Narashiman et al.* 1986] is our basis for the implementation of a module to represent the colloid migration within fractured or porous medium. Last year, the case of a porous medium was studied, this year, we worked onto a fractured medium model.

The code TRUMP allows different configuration to describe different levels of complexity for the considered system. The case of the transport of both solute and colloid-bound radionuclides in a monodimensional fracture has been studied, considering two configurations :

- A single column configuration : solute and colloids-bound radionuclides are in the same node net. This kind of configuration has already been described and tested with an other code by *Grindrod and Worth* [1990]. A limit of this approach is that it only allows to calculate *instantaneous equilibrium* between solutes and colloids.

- A double column configuration which aims to overtake the limit mentioned above. Therefore, the fracture is represented by two columns, that is two parallel node nets : one describing the mobile fluid (and the dissolved radionuclides) in the fracture ; the other describing the mobile colloids (and the colloid-bound radionuclides). A term of flux of radionuclides is considered between the two node nets; it depends on a "kinetic" constant and on the concentrations of both solute and colloid-bound radionuclides; this term describes the kinetics of the sorption and desorption reactions of radionuclides to and from colloids.

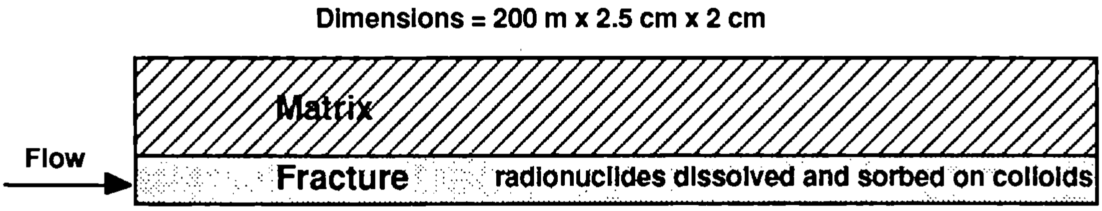


Figure 3 *Single column configuration.*

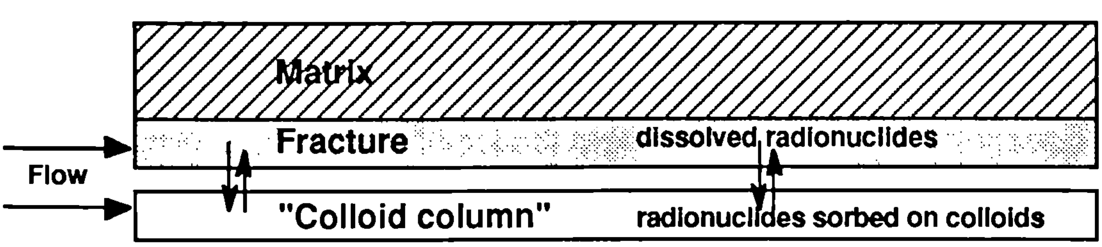


Figure 4 *Double column configuration.*

The phenomena taken into account for radionuclides are transport by convection dispersion and diffusion, matrix diffusion, reversible sorption on fracture wall, reversible sorption on mobile colloids, and transport by colloids, and the phenomena taken into account for colloids are transport of mobile colloids by convection dispersion and diffusion.

The first hypothesis made for simple tests are the following : constant concentration and constant velocity of colloids in time and space and no retention of colloids on fracture walls; these hypothesis can be modified without changing the code TRUMP. The specific hypothesis made are instantaneous equilibrium between solute and colloids for the single column configuration and delayed equilibrium between solute and colloids for the double column configuration.

It has then been demonstrated that, using specific parameters, the simulation of migration of radionuclides by colloids is possible with TRUMP using configuration either where solutes and colloids are in the same node net or where there is one column of nodes representing the dissolved radionuclides and an other one representing the radionuclides sorbed on colloids.

The specific interest of the two columns configuration is that it allows to simulate delayed sorption equilibrium between radionuclide and colloids. It has been verified to give the same results as the single column configuration when instantaneous equilibrium is assumed.

Selected references

GRINDROD P. and WORTH D.J., Radionuclide and colloid migration in fractured rock: model calculations. Technical report 91:11, SKI, Stockholm, June 1990.

NARASIMHAN T.N. , WHITE A.F. AND TOKUNAGA T. : Groundwater contamination from an inactive uranium mill tailings pile. 2. Application of a dynamic mixing model. Water Resources Research, vol. 22, n°13, pp 1820-1834, dec. 1986.

NERETNIEKS I. AND RASMUSON A. : An approach to modelling radionuclide migration in a medium with strongly varying velocity and block sizes along the flow path. Water Resources Research, vol. 20, n°12, pp 1823-1836, dec. 1984.

VAN DER LEE J. Complexation of metals and amphoteric organic colloids: interim state of modelling. Centre d'Informatique Géologique et d'Hydrogéologie Mathématique, Ecole des Mines de Paris, Fontainebleau, France. (1992)

VAN DER LEE J., LEDOUX E., AND DE MARSILY G., Modeling of colloidal uranium transport in a fractured medium. Journal of Hydrology, 139:135-158, 1992.

WIMMER H., KIM J.I., KLENZE R. A direct speciation of Cm(III) in Natural aquatic systems by time resolved laser-induced fluorescence spectroscopy. Radiochemica Acta 58/59 p.165-171 (1992)

List of publications (project - 1993)

HARMAND B., HERNANDEZ A., VAN DER LEE J., SARDIN M., VINSOT A., VAN DE WEERD H., Development of a model for radionuclide transport by colloids in the geosphere, Fourth six-monthly progress report. CEC contract FI2W-CT91-0079, Oct 93.

RODIER E., Le passage et la rétention de particules colloidales dans un milieu poreux, PhD Thesis, Institut national polytechnique de Lorraine (1993).

VAN DER LEE J, CHESS, another speciation and surface complexation computer code. Technical Report LHM/RD/93/39, CIG, Ecole des Mines de Paris, Fontainebleau, France, June 1993.

VAN DER LEE J., DE MARSILY G. AND LEDOUX E., Are colloids important for transport rate assessment of radionuclides ? A microscopic modeling approach. In High Level Radioactive Waste Management, Proceedings of the fourth annual international conference, pages 646-652, Las Vegas, Nevada, April 1993. American Nuclear Society, Inc.

Title: CHARACTERIZATION AND VALIDATION OF NATURAL RADIONUCLIDE MIGRATION PROCESSES UNDER REAL CONDITIONS ON A FISSURED GRANITIC ENVIRONMENT.

Contractor: ENRESA (Coordinator)/CIEMAT, CIMNE, AEA, BGS and CEA/IPSN
Contract n°: FI2W-CT91-0080
Duration of contract: March 1991 - February 1995

Period covered: January 1993 to December 1993
Project leader: Pedro Hernán (ENRESA) **Task leaders:** Carmen Marín (CIEMAT), Luis Pérez del Villar (CIEMAT), Jordi Guimerà. (CIMNE/UPC).

A. OBJECTIVES AND SCOPE

The objective of the project is the characterisation of natural radionuclide (U, Th, and their decay products) migration processes in a fractured granitic environment and validation of models describing these processes.

In situ studies are being developed at the "El Berrocal" site, a post-tectonic batholith, taking into account:

- The characteristics of the rock fissures and discontinuities
- The hydrodynamic and hydrogeological conditions, and
- The variation of the physico-chemical characteristics with depth.

In parallel to these in situ activities, a series of laboratory experiments are underway to study the same phenomena under controlled conditions.

Finally, the identified processes are being modelled and the models validated.

The project is managed and co-ordinated by ENRESA (Spain), with the technical assistance of Intera Environmental Division (United Kingdom). Participating organisations include CIEMAT (Spain), CIMNE (Spain), CEA/IPSN-Cadarache (France), AEA Technology (United Kingdom) and BGS (United Kingdom). Partial funding is provided by the CEC-Brussels. JRC/CEC-Ispra co-operates with the Project participants. The Project is scheduled to run for four years, in two-year phases. Phase 1 was initiated on 1st March 1991 and finished the 28th February 1993. Phase 2 begun the 1st of March 1993 and will run up to the 28th of February 1995, this second Phase is the subject of this contract.

B. WORK PROGRAMME

I. Characterization of the physical environment: Geotectonic characterisation from the surface. Underground characterisation from boreholes. Geochemical and petrographic fissural filling studies. Litho-structural model of the site. These last two, are comprised from the beginning of Phase 2, in the following section.

II. Geochemical characterisation: Hydrogeochemistry (physicochemical and ionic phases). Groundwater colloidal phases studies (sampling, characterisation and transport). Groundwater mixing and circulation patterns. Fissure filling characterization. Hydrothermal and weathering transformations.

III. Migration studies: Natural radionuclide distribution. Mobilization/retention processes (laboratory). In situ migration experiments

IV. Hydrogeological characterisation: Assessment of borehole conditions. Design and construct wireline straddle packer testing system. Transmissivity and head measurements. Define numerical models. Design and perform cross-hole interference tests in selected fractured zones.

V. Modelling studies: Development of a computer code (flow and transport, 2-D fractures in 3-D medium). Prediction of uncertainties caused by spatial heterogeneity. Flow and solute transport in a single fracture.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

It is intended to provide here a global and updated overview of the current Project status.To give, in the first place, a general idea of the variety of the work in progress, we refer to Table I in which all activities are shown indicating the participants involvement. Regarding original planning and subsequent modifications, it is relevant to indicate that Phase 2, formerly conceived as a confirmation of preliminary geochemical and hydrogeological modelling intended to be performed in Phase 1, resulted, due to administrative constraints, in a continuum with Phase 1. Another modification to previously stated work has been the creation of four task groups, namely; structural, hydrogeology, geochemistry and tracer test, which have aided the work progress.The creation of these task groups coincided with the commencement of Phase 2.

Abstracted highlights about the current status, include the construction of a detailed geological frame for the El Berrocal batholite that has allowed the formation of a quite complete 3-D Structural Model, to which hydrogeological and geochemical features of the site can be related. Regarding work progress, hydrogeology has experienced more difficulties than others in obtaining reliable data, partially due to the fact of being somehow subordinate to hydrogeochemistry, in terms of Project priorities given on site. Nevertheless a consistent amount of data it is already available and a final interpretation will be soon realised.

Geochemistry is in an advanced state of development regarding both solid phase and water chemistry.An extensive study has been performed on the mineralogy and geochemistry of the rock matrix and fissure fillings with an accent on the U behaviour for each of the magmatic and alteration events of El Berrocal batholite. As regards Hydrogeochemistry more than 200 samples have already been taken and analyzed. Data were sufficient to establish a classification of El Berrocal groundwaters into seven types Notwithstanding this, data from depths below 300 m. are still missing. Geochemical and hydrogeological data are being incorporated in a Database specifically designed and constructed for the Project. Currently information from a range of study areas is gathered to define conditions for an in situ tracer test which is planned to begin by the first of June 1994.

Progress and Results

Within this section, a more detailed description of the work in progress is given according to the subjects included in section B, which largely coincides with the working groups division. Before considering the updated thematic information it is convenient to indicate that the global objective indicated in section A is intended to be fulfilled by means of the working groups whose specific sub-objectives are:

Structural WG. Development of the 3-D Structural Model of the site.

Geochemistry WG. To establish the Geochemical Model integrating litho and hydrogeochemistry of the Site. Modelling the minor and trace elements behaviour according to the geochemical conditions of the Site.

Hydrogeology WG. To develop the Groundwater Flow Model of the site.

Tracer Test WG. To study the radionuclide behaviour in the granitic media (at laboratory scale), and to design, perform and model, the mass transport in the fractured granite (at a real scale between boreholes).

It is also important to present here, as a foreword for the whole series of activities, the status of the boreholes performed both in Phase 1, and in the previous Phase 0. In this Preliminary study (1988-1990), two 60-m-deep boreholes were drilled in the gallery at distances of 13 m (borehole S-1) and 20 m (borehole S-7) from the quartz dyke, and a 30-m-long subhorizontal borehole (S-2) was drilled at the end of the gallery. Seven further shallow boreholes were drilled in the gallery (S-3, S-6, S-8, S-10) and two deeper boreholes (S-11 and S-12) 150 m to the south of the gallery. During Phase One seven more boreholes were drilled (S-13 to S-19), all of them considerably deeper than those of the preliminary phase and all sited to the north (uphill) of the entrance to the gallery. Borehole location can be seen in Figure 1.

Finally it is convenient to indicate that some of the activities referred to here that were initiated at the beginning of Phase 2, constitute extensions in addition to the work covered in the scope of the EC Project. These are basically the three following themes: **(i)** The use and interpretation of Isotopic data (other than U/Th series disequilibrium), **(ii)** the Blind Predictive Modelling Exercise and **(iii)** the implementation of a Hydrogeochemical and Hydrogeological Database.

I. Characterisation of the Physical Environment.

A detailed structural mapping exercise have been performed with the aim of integrating local structures within a regional context. This has allowed a better interpretation of the fracturing significance mainly regarding hydraulic behaviour.

Up to now a series of fracture sets have been defined according to their relative age, /23/:

N 50-60 **N 110** N 75-80 **N-S** N 35 **N 15** N 150

Those in black, are considered to be the most important directions regarding development and probable influence in the hydrogeological system.

The kinematic interpretation has been carried out combining different scales, going from the regional scale to the local one. The characterisation of the single faults has been based on their geometry and presence or absence of kinematic indications such us grooves, steps, associated veins, and internal structures of the quartz veins. The fracture families identified at El Berrocal consistently fit with an offset, or extensional zone, developed between two large regional faults in the Sistema Central. The extensional regime is identified in the field by banded and orbicular structures, fillings of cavities and quartz growth perpendicular to the walls of the quartz veins. The regional tectonic model considers El Berrocal to be a pluton situated in a tension megafracture.

Preliminary extrapolation of surface data to boreholes (core visual observations and televiewer data), has allowed a preliminary 3-D structural model to be established. Although this model is continuously being updated it already shows the main structural features and being in an advanced state of construction by the end of 1993. It is intended to incorporate the structural model into the hydrogeological interpretation. The detailed work has centred on three different locations that constitute candidate sites for the tracer tests performance.

II. Geochemical Characterisation.

II.1 Introduction

This area of activity as a whole, is a basic one within the Project. Three main inter-related fields integrate geochemistry: Lithogeochemistry, Hydrogeochemistry and Geochemical modelling.

The topics considered by lithogeochemistry are the reconstruction of the geochemical episodes of the El Berrocal Granite, with a special emphasis on hydrothermal and weathering processes, and the characterisation of fissure infillings.

As regards hydrogeochemistry, the main parts of the work performed have been:

(i) sampling, in which a great effort has been made to gain a maximum degree of representativity and quality of the samples.

(ii) the chemistry of the water components (physico-chemical, ionic and colloidal phases).

(iii) the definition and distribution of the hydrogeochemical facies.

(iv) the study of the water-rock interaction processes.

(v) the identification of origins, sinks and pathways for U-series transport and

(vi) a contribution in defining fracture zones for deep cross-hole migration test.

There are two areas of geochemical modelling, the first is the construction of a geochemical model (as a further integration of the lithogeochemical and hydrogeochemical models, both already in an advanced state of realization), and second a blind predictive geochemical modelling exercise which is being carried out in parallel by four different teams.

II.2 Lithogeochemistry.

The end of Phase 1, has meant a turning point regarding geochemistry of the solid phase, since a model was established, /27/, that incorporates a global understanding of the petrogenesis which in a very concise fashion can be summarised as:

The El Berrocal facies is **SiO_2 rich** (74-75%), **peraluminous** (13-14%), **hypocalcic** (± 0.5%), and **PO_2 rich**, regarding major chemistry. As regards trace elements the low Ba and Sr, and high Rb, confirm this granite as being highly evolved and enriched in incompatible elements such us U, Li and Sn. The U/Th higher than 2 and regarding [U], a 60% of the total, as Uraninite.

Schematically the main geochemical features linked to the petrogenesis are:

1. Intrusion: A radiometric Rb-Sr age (bulk rock) of 300 ± 1 m.y. and regarding uranium, **the granite is clearly U fertile and it is the primary source for U.**

2. Deuteric alteration: An age for this phase of 289 ± 1 m.y. (also Rb-Sr dated but in mineral separates). **Partial oxidation of U minerals ⇒ 1st U mobilization.**

3. Hydrothermal alteration: Contemporary with late Hercynian fracturing, produced a **destabilization of accessory minerals ⇒ 2nd U mobilization.**

4. Quartz vein tectonics and U mineralization: **Evolution of U-rich solutions precipitating in pitchblende N-110-E fractures ⇒ 3rd and most important U mobilization.**

5. Weathering: Current water-rock system. **The mobilized U is adsorbed onto Fe-Mn oxy-hydroxides and precipitated as Autunite and Torbernite. ⇒ Latest period of U-mobilization.**

II.3 Fracture fillings

Also within the period contemplated in this summary, the fracture mineralogy has been studied in detail /26/. To this respect it can be said that the mineralogical associations are very constant, and they appear to be independent of the orientation of fractures. Kaolinite seems to be the best indicator of currently hydraulically active fractures. These studies have recently been focused on the U mineralogy /7/, /12/. The amount and detail of data regarding this item will help to the final water-rock interaction studies that should continue with U disequilibrium studies on bulk samples and on sequential leachates and separated U minerals in spite of the difficulties associated with the very fine grained mineral assemblages. Nevertheless some observations lead to preliminary statements in the sense that Uranium in the system has limited mobility, being readily retained by precipitation and adsorption.

II.4 Hydrogeochemistry

Up to now, seven types of waters have been distinguished /14/, that correspond to seven different stages of evolution of recently percolated waters (**Figure 1**). No information is available, from S-16 below 300 mbgl, but it is intended to be obtained from February to June 1994. The differences in water composition are mainly due to the geological features (relative position to the dyke) and depth of percolation. These factors give rise to variations in:

- **major chemistry:** calcic-sulphated in shallow waters to calcic-bicarbonated in deeper ones. A neutralizing effect, with depth, of the shallow oxidizing waters of recent meteoric origin.

- **U contents:** much lower concentration in waters percolating the rock to the South of the dyke.

- **pH and Eh:** Apart from local anomalies, that can be found very close to the mineralisation, generally the conditions tend to be more basic and reducing with depth.

The main chemical and physico-chemical characteristics of the seven types of waters, are given in table II.

II.5 U series disequilibrium

A component of the geochemical work already mentioned refers to **Uranium series disequilibrium studies** /3/, which acts as a direct method for understanding water-rock interaction. These studies are in progress and definitive conclusions cannot yet be established. Nevertheless the latest water analysis indicate that waters are in disequilibrium in favour of ^{234}U, with respect to ^{238}U. Something which is coherent with the nature of the El Berrocal groundwaters. To this respect $^{234}U/^{238}U$ activity ratios range from 1.1 corresponding to surface/near-surface waters, to 1.7-2.8 corresponding to more mature deeper ones. Earlier studies performed in solid samples (4 different kinds of fracture infillings) had given a variety of results (close to unity in most of the samples, higher than 1, in some others and finally below 1 in the rest). These results may reflect the fact that it was not always possible to obtain paired solid and groundwater samples from the same hydraulically active fracture. Paired samples have now been obtained and analyzed from (from S-13 and S-16 boreholes) but their application to the one-dimensional mass-balance model under development is so far limited, further groundwater and solid samples must be analyzed in order to obtain solid and liquid data into consistent pairs to feed the SUDDEN code being developed at AEA, and thus to model the rock/water interaction involving U series radionuclides. This model should lead to the calculation of:

- The sorption-desorption and precipitation rate constants.
- Effective retardation factors for U and Th, and
- The evaluation of the time scales involved. (Some preliminary calculations indicate that the rock water interaction time, ranges from 28 years in S-7 to 800 years in S-15 at ~ 110 mbgl).

II.6 Colloids

Only sampling has been covered within this period. An important part of the work will be completed during 1994, provided by the samples obtained during 1993; (S-13, between 64-78 m., S-14 93-96 m and 213-218 m, S-1/S-7 39-42 m.) and some others which are currently in progress. The main contributions of the former work, are the following, /17/: The concentration of colloids is in the order of 10^{10} particles per litre in oxidizing waters, decreasing to 10^8 in reducing ones. The size varies between 208 and 342 nm. Regarding composition they are mainly inorganic (clay minerals, silica, Fe and Al oxy-hydroxides). Finally with respect to U, 88% of the total Uranium is associated with true solution and the remaining 12% with the particulate phase. It can be said that colloids are not an important vehicle for U transport at El Berrocal.

II.7 Testing of Down-hole Probes

A parallel study but one that will be integrated within the whole frame of the Project is the **Testing of downhole lab-probes** /24/. The conceptual basis for their application resides on the uncertainties associated with conventional groundwater sampling methods, regarding perturbation of local flows, introduction of allocthony from intensive pumping, etc. Use of the downhole probes would limit these problems by means of "in situ" measurements. All the tests have been performed in borehole S-17 entirely devoted, during the first phase of the Project, to the probe tests. It is foreseen to apply the same techniques in borehole S-19, both boreholes will be also sampled by the standard methods,used elsewhere at El Berrocal, enabling a comparison and mutual validation of conventional procedures (sampling and analyses) and the use of downhole probes.

The lab-probes utilized at El Berrocal have been:

- **Autolab:** for diffusion tests on site.
- **Chromatolab:** to concentrate and analyze trace elements using resina adsorbers.
- **Foralab:** for performance of very small scale migration tests.

The global results are satisfactory regarding implementation and validation of the equipment. Thematic results are too detailed for this report, and only recently published and will now be discussed and integrated in the global context of the Project.

II.8 Blind Predictive Geochemical Modelling

The objective of the exercise, is twofold:

- To contribute to the understanding of the system, and
- To try and predict the behaviour of some trace elements, given the major elements concentrations.

The trace elements, considered in the blind predictive exercise, are:

As Ba Cr Cu Mo Ni Pb Se Th U V Zn and **Mn**

The exercise integrates two consecutive stages of blind modelling and a final phase of interpretation and integration within the global frame of activities. The first stage of blind predictive modelling will takes place early next year with a meeting to integrate the participants results.

III Migration Studies

Within this field there are two areas of study: **Laboratory sorption and diffusion studies** and **in situ Tracer Tests.**

III.1 Laboratory studies.

The objective is to deduce and quantify Retention Mechanisms. Five series of experiments (batch and column) have been performed, based on five different kinds of samples from El Berrocal; ground granite (125 μm mesh), mineral separates, fracture coating minerals, ground granite (< 1mm) and granite columns. /1/, /10/, /15/.

The radionuclides employed have been: ^{75}Se, ^{137}Cs and ^{60}Co. Different experimental conditions have been obtained through variations in size fraction, concentration and pH.

Some results of the work in progress indicate that smaller size fractions give higher K_d values, being relatively little affected by concentration. On the contrary pH effects are significant, generally the higher pH, the higher K_d.

III.2 In situ Tracer tests.

These have been carried out with the aim of identifying those mechanisms controlling radionuclide migration at El Berrocal. Two tracer tests were completed during Phase 1 of the Project both sited in the same location (between S-1 and S-7 boreholes). The major involvement has been that of JRC/Ispra team.

Tracer test One:

After laboratory tests, ^{79}Br was selected as the most suitable tracer. The experiment was carried out between boreholes S-1 and S-7 sited at the access gallery. The physico-chemical environment was characterised with the IDRONAUT probe and the major fractures intersections located by means of; visual televiewer, pumping and IDRONAUT records. The final configuration for the test was: injection through borehole S-7 between packers sited at 35 and 40 mbgl and inlet of the sampling pump at 37 m, the recovery in borehole S-1 with the main pump at 51 mbgl. A difficulty was the impossibility of maintaining a constant hydraulic gradient due to the unavoidable cuts of electric power overnight. **Results:** /17/ The tracer arrived at the three sampling points at 25 to 28 hours after injection, the concentration peak occurring some 50 hours after injection. A tentative interpretation of the breakthrough data suggest, a storage coefficient of 1.5. 10^{-3} and a transmissivity of 2. 10^{-6} m^2/s.

Tracer Test two:

The **main differences compared to Tracer Test One**, were the following:/19/

- both, injection and recovery were performed in packed-off sections.
- Tracers: ^{79}Br plus KI (allowing monitoring in real time).
- Preliminary pumping tests were performed in order to adjust the pumping rate so as to attain a steady state regime.
- Transducers to monitor heads were incorporated between packers.
- Recirculation pumps connected to surface equipment allowing:
    - Injection and recovery of the tracer
    - Homogenization of the tracer-groundwater mixture
    - measurement of tracer concentration, and
    - Access to the packed-off sections.

The results attained during Phase I, were different to expected. The duration of the test was 118 hours, nearly twice than foreseen. At the end of the sampling 85% of the tracer (IK) had disappeared from the injection point, but only half of the tracer had arrived at the recovery point. The work to be performed during Phase 2 envisages the completion of this second tracer test, regarding the mass spectrometric analyses of the ^{79}Br tracer breakthrough and calculation of the hydrological parameters.

Future Work

It is foreseen the fulfilment of two more tracer tests: One between boreholes S-11 and S-12 and the other, either in (S-2, S-13, S-15) or in (S-14, S-16, S-18) sets. Information of different kind is getting together for defining the performance of both experiments. The first one of these two tracer tests will be carried out between February and May 1994, and the second is intended to be initiated by the 1st of June.

IV Hydrogeological Characterisation

IV.1 Introduction

The main areas of activity regarding this area of study have been:

- The determination of transmissivity and head measurements.
- Monitoring of the water level evolution in boreholes.
- Construction of conceptual and numerical models.
- Designing and performance of cross-hole interference tests in selected fracture zones.
- A hydroclimatic study and a Water Sites Inventory, both currently in progress.

It is convenient to indicate that when trying to make compatible the obtaining of hydrogeological data with hydrogeochemical sampling, some difficulties arise that can influence the yield of work on site.

IV.2 Current Progress

Regarding the hydroclimatic study, the current situation shows that there is a clear response between rainfall and discharges within periods of a few weeks both for the gallery and some springs. The water Sites Inventory has been extended to cover information of regional scale, by the end of the reported period it is about to be finished.

Recently hydrogeological testing in boreholes has been centred in two sets preselected for further performance of tracer tests. A first set of vertical boreholes (S-14, S-16, S-18) and a second one, conformed by the horizontal borehole S-2 and the inclined ones S-13 and S-15.

In the first set. Single hole testing has been completed only in borehole S-14. A large flowing feature was identified in this borehole at a depth of 92 to 96 mbgl. This was used as an input to test for cross-hole responses in the other boreholes. A clear cross-hole response was noted in borehole S-18 but the depth has not yet been established. The responses in borehole S-16 are difficult to determine because of the low water level in this borehole.

Single hole testing of borehole S-16 has been partially completed in the lower part of the borehole. Initial hydraulic conductivity measurements are:

Zone	K
150-194 mbgl	$< 1 \times 10^{-11}$ m/s.
223-267 mbgl	2×10^{-8} m/s.
455-499 mbgl	4×10^{-10} m/s.

These zones will be retested when hydrogeological work resumes in borehole S-16.

In the second one. Modelling work been done on the cross-hole data obtained from performing a slug test in borehole S-2. The use of an homogeneous model appeared to show that there were scale effects, *i.e.* that there was an apparent increase in hydraulic conductivity with increasing volume of water used in the test. Testing of S-2 showed clearly that most of the water flow from this borehole comes from one fracture located at its end. For the cross-hole test, borehole S-2 was divided into three sections using packers and sections of boreholes S-13 and S-15 were also packed-off. It was found that the response in borehole S-15 was from above the packed-off section (above 67 mgbl) while in borehole S-13 similar responses were obtained in the bottom of the borehole and in a packed-off section at 62 to 66 mbgl. This suggests some hydraulic connection around the packer.

In global terms the results obtained till now from the hydrogeological work can be expressed as follows: There is a predominance of a low permeability sections, the flow being constrained to a few major pathways. The most important control for the local hydrogeology at the site is the mineralised quartz vein. Finally regarding cross hole connections, their existence has been proved but they have not yet been quantified.

IV.3 Conceptual Model

El Berrocal is clearly sited in a recharge area, and the flow is topographically controlled with a main downwards vertical component /2/. At a regional scale can be considered as homogeneous but at the local scale groundwater flow is heterogeneous. In fact at this scale, flow is strongly perturbed by geological features, namely fractures and the vein, making 3-D modelling necessary. Complementary alternative conceptual models have been proposed regarding the quartz vein´s hydrogeological role, taking into account the relative hydraulic conductivities of the dyke itself and the enclosing rock, together with the possibility of a downwards connection to a discharge zone.

V. Code development

This is a further activity which is connected to the previous four, whose objectives are: 1) developing a stochastic formulation for flow and transport in fractured media by superimposing a two-dimensional medium (high permeability fracture zones) onto a three-dimensional continuum and 2) implementing the formulation in a computer code able to analyze real cases. To meet these objectives four different tasks have been defined: flow and solute transport inversion, flow and solute transport through isolated fractures, flow and solute transport through a network of fractures and finally hydrogeological modelling. While the three first are essentially development work the last is mainly the application of the codes to El Berrocal site.

The work performed during 1993, in the different tasks has been:

Modelling flow and transport inversion. The selection of a tridimensional network generator suitable for the Project needs. Input data pre-processor and output data post-processor of TRANSIN-III results. Finally the strength of theoretical basis for the TRANSIN-II code, has been the object of a Thesis which covered the analysis of the basic theory, including the problems of the direct solver, the inverse solver and the stability and identiafibility problems. It was also studied its possibilities in a broad spectrum of real and synthetic cases.

Flow and transport through isolated fractures. New formulations (discretization of flow domain into blocks and upscaling). Scale effects in transmissivity. Several simulations with different types of correlation structures, results are compared to give insight on the kind of structures that can lead to important scale effects in nature, connectivity turning out to be a very important factor.In the same context, part of the work has been devoted to find fields with a better representation of the real connectivity. It has been finished and tested a simulation algorithm (CONECTIV) capable of generating transmissivity fields with enhancement of high regional connectivity, in such a way that high values have a different correlation structure that low ones. Directional effects in convergent flow. The work done to this respect has been focused on directional effects in porosity and dispersivity in an heterogeneous medium with anisotropic correlation structure.

REFERENCES:

External

/1/ GARCIA GUTIERREZ, M. Studies of transport phenomena in granitic columns. *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration'93), Charleston, 12-17 December 1993. Proceedings in press. Abstracts pp 68.*

/2/ GUIMERA, J., CARRERA, J., HOLMES, D., RIVAS, P., TALLOS, A., BAJOS, C. Preliminary analysis of the hydrogeology of El Berrocal experimental site. *Congress of the International Association of Hydrogeology, Oslo, 28-31 June 1993. Proceedings pp 225-238.*

/3/ HERNANDEZ BENITEZ, A., HASLER, S., IVANOVICH, M. Uranium series isotopic analysis of fracture infill materials from El Berrocal granitic batholith. *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission products in the Geosphere (Migration'93), Charleston, 12-17 December 1993. Proceedings in press. Abstract pp 109.*

/4/ MARIN, C. Porosity analysis of the granitic rocks from El Berrocal pluton. *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission products in the Geosphere (Migration'93), Charleston, 12-17 December 1993. Proceedings in press. Abstract pp 74.*

/5/ MILLER, W.M., RIVAS, P., PEREZ DEL VILLAR, L., GOMEZ, P., DE LA CRUZ, B., HERNAN, P., CARRERA, J.,GUIMERA, J., HOLMES, D., IVANOVICH, M., AVOGADRO, A., VINSON, J.M., BRUNO, J. The International El Berrocal Project: site characterization and radionuclide mobility around a fractured granite-hosted uranium orebody. *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission products in the Geosphere (Migration'93), Charleston, 12-17 December 1993. Proceedings in press. Abstract pp 113.*

/6/ MONTOTO, M., MENAGER, M.T., RODRIGUEZ-REY, A., MENENDEZ, B., MARTINEZ NISTAL, A., FERNANDEZ-MERAYO, N. Microfractography of granites and its implication in uranium transfer phenomena in rock matrix: application to El Berrocal experimental site, Spain. *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission products in the Geosphere (Migration'93), Charleston, 12-17 December 1993. Proceedings in press. Abstract pp 34.*

/7/ PEREZ DEL VILLAR, L., DE LA CRUZ, B., PARDILLO, J., COZAR, J.S. Cálculo de la distribución mineralógica del Uranio y Torio en el granito sano del plutón de El Berrocal (Sierra de Gredos, Provincia de Toledo. *Bol. Soc. Esp. Mineralogía, 15, 1.992 pp 123-136*

/8/ PEREZ DEL VILLAR, L., DE LA CRUZ, B., COZAR, J.S., PARDILLO, J., GOMEZ, P., TURRERO, M.J., RIVAS, P. The clayey fissural fillings associated with N100-110 o E fractures at El Berrocal Uranium mine (Sierra de Gredos, Spain): Characterization, genesis and retention capacity of radioactive and other elements. *Estudios geológicos (in press).*

/9/ PEREZ DEL VILLAR, L., DE LA CRUZ, B., PARDILLO, J., PELAYO, M., RIVAS, P. ASTUDILLO. J. El sistema granito-mineralización de Uranio de El Berrocal como análogo natural de un enterramiento de residuos radiactivos. *Estudios geológicos (in press).*

/10/ PEREZ DEL VILLAR, L., DE LA CRUZ, B., PARDILLO, J., PELAYO, M., RIVAS, P. Los procesos geoquímicos análogos en el sistema granito-mineralización de Uranio de El Berrocal (Sierra de Gredos, Provincia de Toledo. *Primeras Jornadas de I+D en la gestión de residuos radiactivos, Tomo II, pp 45-60. ENRESA, 1993.*

/11/ PEREZ DEL VILLAR, L., SANZ, H.G., QUEJIDO, A.J., LALLENA, P.P., FERNANDEZ-DIAZ, M., PARDILLO, J. Datación absoluta del plutón granítico de El Berrocal por el método Rb-Sr (Sierra de Gredos, España). *Rev. Soc. Geol. España.*

/12/ PEREZ DEL VILLAR, L., MENAGER, M.T., DE LA CRUZ, B., PARDILLO, J. Uranium distribution in relation to the mineralogical and geochemical characteristics of the El Berrocal granite - an experimental site, Spain. *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission products in the Geosphere (Migration'93), Charleston, 12-17 December 1993. Proceedings in press. Abstract pp 114.*

/13/ RIVAS, P., PEREZ DEL VILLAR, L., DE LA CRUZ, B., GOMEZ, P., TURRERO, M.J., HERNANDEZ, A., MARIN, C., PELAYO, M., PARDILLO, J. El Proyecto Berrocal. *Fifth Spanish Geochemistry Congress, Soria, 21-24 September 1993. Proceedings in press.*

/14/ RIVAS, P., DE LA CRUZ, B. Estudios integrales de migración de radionucleidos en condiciones reales: proyecto Berrocal. *Geological Society of Spain Conference on the Geochemical Processes in the Deep Geological Storage of High-level radioactive Wastes, Madrid, 11-12 February 1993. Proceedings in press.*

/15/ TURRERO, M.J., GOMEZ, P., PEREZ DEL VILLAR, L., MOULIN, V., MAGONTHIER, M.C., MENAGER, M.T. Relation between colloids and geological environment: Application to the El Berrocal granitic site (Spain). *Sent to Applied Geochemistry.*

/16/ YLLERA DE LLANO, A., AVOGADRO, A., BIDOGLIO, G. Effect of chemistry on flow and selenium transport in fractured granite. *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission products in the*

Geosphere (Migration'93), Charleston, 12-17 December 1993. Proceedings in press. Abstract pp 62.

Internal

/17/ EL BERROCAL PROJECT. Phase One Summary Report (march 1991 - February 1993) [Topical Report TR-20]. pp 126.

/18/ CARRERA, J., SAMPER, J., GUIMERA, J., SANCHEZ-VILA, X., MEDINA, A., GALARZA, G., CANDELA, L. Flow and Transport Modelling. *El Berrocal Project Fourth Six Monthly Progress Report. pp 379-419.*

/19/ D'ALESSANDRO, M., MOUSTY, F. Second Cross-Hole Migration Test With Conservative Tracers. *El Berrocal Project Fourth Six Monthly Progress Report. pp 420-447.*

/20/ GOMEZ, P., TURRERO, M.J., MINGARRO, M., TEJEDOR, E., COLLADO, P. First Approach to the Hydrogeochemical Model. *El Berrocal Project Fourth Six Monthly Progress Report. pp 159-200.*

/21/ GUTIERREZ, M.G., SALAMANCA, E., ZUECO, J.L., BENITEZ, A.H. Sorption-Desorption Processes and Column Migration Experiments. *El Berrocal Project Fourth Six Monthly Progress Report. pp 307-332.*

/22/ IVANOVICH, M., HASLER, S., HERNANDEZ, A. Geochemical Characterization and Migration Studies. *El Berrocal Project Fourth Six Monthly Progress Report. pp 333-355.*

/23/ MARIN, C. Analysis of the Fracture Systems Identified in Borehole 16. *El Berrocal Project Fourth Six Monthly Progress Report. pp 201-226.*

/24/ MARIN, C. Porosity Analysis of the Granitic Rocks From El Berrocal. *El Berrocal Project Fourth Six Monthly Progress Report. pp 227-251.*

/25/ PARDILLO, J., PELAYO, M., FERNANDEZ, A.M., DE LA CRUZ, B., PEREZ DEL VILLAR, L. Mineralogical and Geochemical Study of the Reference Granite Intersected by Borehole 16. *El Berrocal Project Fourth Six Monthly Progress Report. pp 274-290.*

/26/ PELAYO, M., PARDILLO, J., FERNANDEZ, A.M., DE LA CRUZ, B., PEREZ DEL VILLAR, L. Mineralogy of the Fracture Infill materials From Boreholes 13, 14, 15 and 16. *El Berrocal Project Fourth Six Monthly Progress Report. pp 252-273.*

/27/ PEREZ DEL VILLAR, L., DE LA CRUZ, B., PARDILLO, J. PELAYO, M., TURRERO, M. J. GOMEZ, P., RIVAS, P. Preliminary Lithogeochemical Model of the El Berrocal Site (S. Gredos, Spain). *El Berrocal Project Fourth Six Monthly Progress Report. pp 101-158.*

/28/ ROGERS, S.F., HOLMES, D.C., WARD, R.S., BAILEY, D.E. Hydrogeological Activities and Progress. *El Berrocal Project Fourth Six Monthly Progress Report. pp 356-378.*

/29/ TALLOS, A., LOMBA, L., GIMENO, M.J., ORTIZ, L. Borehole Survey: Variations in Piezometric Levels, Results and Discussion. *El Berrocal Project Fourth Six Monthly Progress Report. pp 45-100.*

/30/ VINSON, J.M., FERNANDEZ, J.M., TILLARD, S. Down-Hole Tool Development. *El Berrocal Project Fourth Six Monthly Progress Report. pp 448-453.*

DISTRIBUTION OF ROLES	CIEMAT	CIMNE	BGS	AEA	CEA	ISPRA	MBT	CSIC
Geological mapping	●							
Structural geology	●							
Mineralogy	●							
Rock Chemistry	●							
Hydro-Chemistry	●		◉	◉	◉			
Colloids	●			◉	◉			
Isotopes	■			◉				▣
U-Th disequilibria	◉			●				
Geochemical modelling	▣	▣		▣			■	
On-site hydrogeology	◉	◉	●					
Hydrogeological modelling		●	◉					
Laboratory migration experiments	◉					◉		
"In Situ" migration experiments	▣	■	▣			◉		
Global modelling	■	■	▣	▣	▣	▣		

◉ Phase I and II
● Phase I and II, main participant
▣ Phase II only
■ Phase II only, main participant

Table 1 DISTRIBUTION OF ROLES

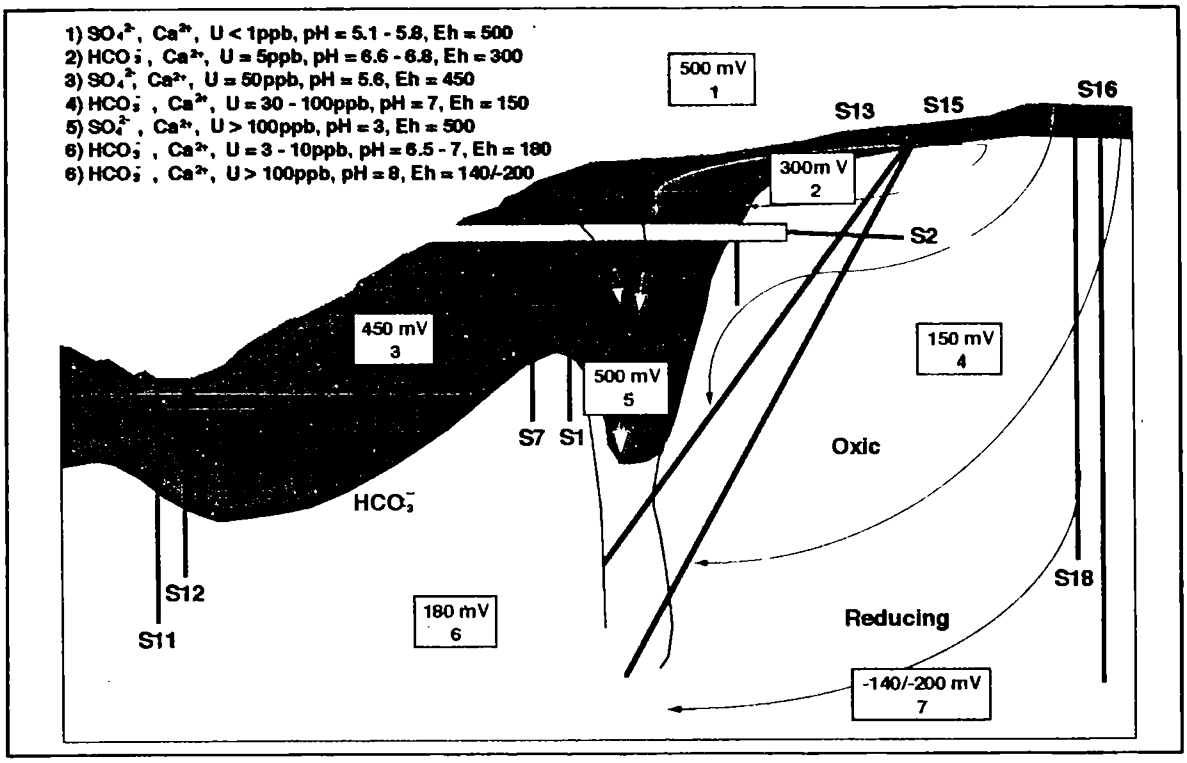


Figure 1. HYDROGEOCHEMICAL ZONES.

Title: Fundamental studies on the interaction of humic substances
Contractor: National Environmental Research Institute
Contract N°: FI2W/0081
Duration: from 01-06-1991 to 30-05-1994
Period covered: 01-01-1993 - 31-12-1993
Project Leader: Lars Carlsen

A *OBJECTIVES AND SCOPE*

The overall objective of the project is to covalently label humic materials with a radionuclide (eg C-14, H-3, I-125) in order to use the labelled material during investigations of their interactions in

(a) complexation reactions with cations (eg Eu, Sn, Co, Ni) and cation competition reactions (eg with Na, Ca)

(b) sorption of humic and humic complexes onto solid surfaces and

(c) precipitation/dissolution behaviour of humic material.

The radionuclidic labelled humic material will provide information on the presence of the complexed radionuclide as well as information on the "free" humic material.

The project is carried out by a collaborate effort of the National Environmental Research Institute (DK) and Loughborough University of Technology (UK).

B *WORK PROGRAMME*

The project is subdivided into three phases:

Phase 1: Preparation of labelled humic materials:
a) Preparation of C-14-labelled humic material from C-14-labelled phenol or C-14-labelled methylamine.
b) Preparation of iodine-labelled humic materials.
Phase 2: Characterisation of the labelled humic material:
a) Determination of the acidity, functional group capacity and size distribution of the non-labelled and labelled humic materials.
b) Determination of the europium binding capacity of the non-labelled and labelled humic materials.
Phase 3: Studies on the aqueous and solid surface chemistry of the labelled humic material
a) Investigation and determination of the associating capacities of the labelled humic material with radionuclides of interest (eg Ni, Sn, Co).
b) Investigation of solid surface sorption using columns filled with sand.

C PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Humic and fulvic acids are present in nearly all environmental waters and because they are known to form water soluble complexes with metals and some anthropogenic organics materials they may be important transport agents for environmental pollutants. Studies of the interactions of humic materials with these pollutants and their transport behaviour is more easily facilitated if the humic material is covalently labelled with a suitable radionuclide. During the year 1993 successful radiolabelling of humic materials with ^{125}I, a gamma emitter and with ^{14}C, a beta emitter and the characterisation of the radiolabelled humic material have been accomplished.

The project is sub-divided into three phases:

Phase 1: Preparation of labelled humic materials:

Phase 2: Characterisation of the labelled humic material:

Phase 3: Studies on the aqueous and solid surface chemistry of the labelled humic material:

Phases 1 and 2 are completed and Phase 3 is ongoing.

Progress and results

1. Phase 1

Experimental details can be found in references 1, 2, 4 and 5.

Radioiodination of humic materials is readily achieved by reacting the humic material with $^{125}I^-$ in the presence of the mild oxidising agent chloramine-T. An apparent 100% incorporation of the label is achieved but the resulting radiolabelled material is not very stable and the ^{125}I readily dissociates from the humic material producing free ^{125}I. Stability of the labelled material is achieved by addition of a reducing agent, such as sodium metabisulphate which eliminates the non-covalently bonded iodine from the humic material. The yield of the radioiodinated product is generally found to be of the order of 20%. In early preparations, separation of free ^{125}I from the humic bound ^{125}I was achieved using size exclusion chromatography but the use of this technique restricts the volume of reaction mixture that can be separated to a few mls. Later preparations used dialysis for separations. The stability of the radioiodinated humic was determined by passing the radioiodinated humic through columns of sand and faction collecting the eluant. The percentage of free^{125}I and humic bound ^{125}I in each eluant fraction can then be determined using size exclusion chromatography. The stability of the radioiodinated humic material was found to be excellent.

^{14}C incorporation into humic material is achieved by reacting 1-ethyl-3-dimethylaminopropyl carbodiimide with humic material in the presence of ^{14}C-methylamine. Separation of the radiolabelled humic material from the reaction mixture is not necessary because of the small quantities of reactants used in the reaction mixture which ensures that free reactant is not present at the end of the reaction. The yield of radiolabelled material is therefore 100%. The stability of the radiolabelled humic material was found to be excellent after passage through a column packed with sand.

^{14}C can also be incorporated into humic materials by reacting the material with ^{14}C labelled phenol in the presence of horseradish peroxidase and hydrogen peroxide. Separation of the enzyme from the reaction mixture is easily achieved if insoluble enzyme is used in the reaction mixture. Although it was found that ^{14}C-phenol was incorporated into humic material, the production of ^{14}C-polyphenol, and the consequent difficulty of separating this from the labelled humic material, means that ^{14}C-phenol labelling was abandoned.

Table 1 Results from Phase 1 of the project

	^{125}I-Ha (Gamma)	^{14}C-Methyl-Ha (Beta)	^{14}C-Phenol-Ha (Beta)
Labelling	Successful	Successful	Problems polyphenol
% Yield Radiochemical	~20%	~100%	?
Stability (Gel and Sand)	Good	Good	Good
Specific Activity (not maximum)	50 kBq mg-1	50 kBq mg-1 (0.5% COO Occpn.)	50kBq mg-1
Separation	Size Excl Chr	Not necessary	Insoluble Enzyme

2. Phase 2

If radiolabelled humic materials are to be used in investigations of their properties, their reactions with metal and organic pollutants and in their transport properties, radiolabelling must not significantly change the inherent characteristics of the humic material. Experimental details can be found in reference 3.

2.1 Ultrafiltration

^{14}C labelled humic material, in 0.05 M NaCl, pH 6.5, was prepared to give 0.5% COOH occupancy (3). The 14C labelled humic material was filtered through AMICON filters of nominal cut-off 100000, 30000, 10000, 5000, 1000 and 500 daltons using an AMICON 8050 Ultrafiltration system. The ^{14}C activity of each filtrate was determined by liquid scintillation counting in a LKB 1215 rackbeta using Ecoscint A scintillator cocktail. The percentage of humic material in the filtrates could then be calculated from the ^{14}C activity. A similar solution containing unlabelled sodium humate was filtered and the uv absorption at 254 nm determined for each filtrate. The percentage of humate in each filtrate was then calculated from the absorbances of each solution (assuming that the absorptivity of the humic material is independent of size of humic material). The results of the characterisation of the humic material before and after radiolabelling are shown in the following table 2.

Table 2 Size distribution of Sodium Humate before and after radiolabelling

	Unlabelled Sodium Humate % in filtrate	Labelled Sodium Humate % in filtrate
<100 000	89.6	65.5
<30 000	47.2	46.8
<10 000	21.6	27.5
<5000	18.4	18.1
<1000	5.1	6.2
<500	2.3	2.4

From the above results it can be seen that although the percentage of sodium humate smaller than 100 000 daltons has decreased after labelling, probably due to some cross linking of humate producing a higher proportion of humate above 100 000 daltons, the percentage of humate < 30 000, < 10 000 etc remain fairly constant. Similar results were obtained when the humic material was labelled with ^{125}I.

2.2 Metal Uptake

Radioiodinated humate was prepared and samples of the solution were spiked with ^{63}Ni and ^{152}Eu. The reaction mixture was separated by size exclusion chromatography and 91% of the ^{63}Ni and 81% of the ^{152}Eu was found to be associated with the humic material. The reactions were repeated using unlabelled sodium humate and 78% of Ni and 58% of Eu were found to be associated with the humate material. Thus an increase of 13% bound Ni and 23% bound Eu was found after radiolabelling the humic material. An increase of 8% bound Eu was found after labelling the humic material with ^{14}C- methylamine.

2.3 Metal Recovery From Sand Columns

The recovery of the labelled material that had been reacted with europium was investigated by passing the metal-labelled complex through 15cm columns packed with sand and eluting the columns with synthetic groundwater. When radioiodinated humic-Eu complex was passed through the column, 17.8 % of the Eu and 60% of the ^{125}I was recovered from the column. These values compare with 66% of recovered ^{125}I when radioiodinated humate was injected into the column by itself and 62% of ^{152}Eu when a complex of ^{152}Eu-humate was injected into the column by itself. Similarly, 25% of 152Eu was recovered when ^{14}C-Ha-^{152}Eu was injected onto the column and 43% of 152Eu-Ha and 60% of ^{14}C-Ha was recovered when ^{14}C-Ha-^{152}Eu and ^{14}C-Ha were separately injected into the column. These results show that metal recovery from the sand column is decreased after radiolabelling the humate. It is therefore recommended that in future experiments, a mixture of radiolabelled humate and radioactive metal-humate complex is injected into columns in order to study the transport behaviour of the humic material and the metal.

2.4 UV Studies

The absorbances of solutions of sodium humate, ^{14}C labelled humate and 125I labelled humate were measured at 265nm, 365nm, 465nm and 665nm and the E2/E3 and E4/E6 ratios calculated. The results showed that the ratios calculated from the ^{14}C labelled humate and ^{125}I labelled humate were the same as those calculated for the unlabelled sodium humate solution.

2.5 Fluorescence

Fluorescence measurements on solutions of sodium humate, ^{14}C labelled humate and ^{125}I labelled humate were made on an Hitachi F-4000 fluorescence spectrophotometer set at an excitation wavelength of 355 nm and an emission wavelength of 460 nm. The results showed that the fluorescence intensity of the radiolabelled humate solutions were not significantly different to the fluorescence intensity of an unlabelled humate solution.

2.6 DEAE Cellulose Extraction

DEAE cellulose was prepared by stirring 10 g of the cellulose in 0.5 M HCl for one hour. The cellulose was then washed with water until the washings were neutral. The cellulose was then placed into 0.5 M NaOH and stirred for one hour. The cellulose was again washed with water until neutral the washings were neutral. The cellulose was then stored in 0.05 M NaCl.

The absorbance of a solution of sodium humate was measured at 254nm. DEAE cellulose was then added to the solution and the mixture allowed to stand. The mixture was then filtered and the absorption at 254nm of the filtrate was measured. The percentage of sodium humate removed by the DEAE cellulose was then calculated form the absorbance measurements. The investigation was repeated using 125I labelled humate and 14C labelled humate. The results showed that there was no significant difference between the percentages of radiolabelled humic extracted and non-labelled humic extracted.

The results of the characterisation are shown in table 3.

Table 3 Results of characterisation study

	^{125}I-Ha	^{14}C-M-HA
Ultrafiltration	No Change	No Change
Metal Uptake	^{63}Ni No change ^{152}Eu No change	No Change ^{152}Eu No change
Metal Recovery (Sand)	^{63}Ni No Change ^{152}Eu Change	^{63}Ni No Change ^{152}Eu Change
UV E2/E3	No Change	No Change
UV E4/E6	No Change	No Change
Fluorescence	No Change	No Change
DEAE Extraction		
Control	65%	59%
Sample	62%	51%

3. Phase 3

The transport of radiolabelled humate, and complexes of metal-radiolabelled humate, have been investigated using 15cm long glass columns packed with sand taken from the Drigg site in Cumbria, UK. The columns were eluted with synthetic groundwater of similar chemical composition to that found at the Drigg site. Two types of investigations were conducted; flooding experiments in which the column was continually eluted with synthetic groundwater containing either radiolabelled humate or metal-radiolabelled humate complex or, injection experiments, in which a solution containing the radiolabelled humate or metal-radiolabelled humate complex was injected onto the column from a 1ml injection loop. For the flooding experiments a flowrate of 10 mL h-1 was used whereas for the injection experiments a flowrate of 40 mL h-1 was used. In each set of experiments, the eluant was fraction collected in order to determine the activity in each fraction and therefore permit the calculation of the percentage of radioactivity recovered from the column. The speciation of the radioactivity in each the fraction could also be determined by using size exclusion chromatography.

References

1. ^{14}C and ^{125}I labelling of humic material for use in environmental studies.
P. Warwick, L. Carlsen, A. Randall, R. Zhao and P. Lassen.
Chemistry and Ecology, 8, 65-80 (1993).

2. Radio-labelled Humic Materials in Migration Studies.
L. Carlsen, P. Warwick, P. Lassen and A. Randall.
Submitted to Symposium V, Scientific Basis for Scientific Basis for Nuclear Waste Management XVI, eds C.G. Interrante and R.T. Pabalan, Materials Research Society, Pittsburgh, USA, 811-816, 1993.

3. Radioactive labelling and characterisation of humic materials.
Lassen, P., Carlsen, L.,Warwick, P. and Randall, A.
Environmental International.
In Press.

4. Labelling of humic material by enzymatically mediated incorporation of ^{14}C-phenol.
P. Warwick, A. Randall, P. Lassen and L. Carlsen.
Environmental Science and Technology.
Submitted for publication.

5. Radio-labelled humic and fulvic acids: A new approach to studies on environmental fate of pollutants.
L. Carlsen, P. Lassen, P. Warwick and A. Randall.
Proceedings of the 6th International Meeting of the International Humic Substances Society. Monopli, Bari, Italy, September 1992. Elsevier, Amsterdam.

List of publications

1) Lars Carlsen, Pia Lassen, Peter Warwick and Amanda Randall, *Radio-labelled humic materials in migration studies*, in: Scientific Basis for Nuclear Waste Management XVI, C.G. Interrante and R.T. Pabalan, eds., Materials Research Society, Pittsburgh, 1993, pp. 811-816

2) Peter Warwick, Lars Carlsen Amanda Randall, Rui Zhao and Pia Lassen, *^{14}C and ^{125}I labelling of humic material for use in environmental studies*, Chem.Ecol. **8** (1993) 182-186

3) P. Lassen, L. Carlsen, P. Warwick, A. Randall and R. Zhao, *Radioactive labelling and characterization of humic materials*, Environ. Int. **20** (1994) 127-134

4) Lars Carlsen, Pia Lassen, Peter Warwick and Amanda Randall, *Radio-labelled humic- and fulvic acids: A new approach to studies on environmental fate of pollutants*, Proc. 6th Int. Meeting of the Int. Humic Substances Society (Monopoli (Bari), Italy), sept., 1992, Elsevier, Amsterdam,in press

5) Amanda Randall, Pia Lassen, Peter Warwick and Lars Carlsen, *Labelling of humic material by enzymatically mediated incorporation of ^{14}C-phenol*, submitted for publication

6) L. Carlsen, P. Warwick, P. Lassen and A. Randall, *Studies on humic acid labelling (2)*, submitted for publication (presented at the Mirage Plenary Meeting, Brussels, Oct. 1993)

7) Amanda Randall, Peter Warwick, Pia Lassen, Lars Carlsen and Peter Grindrod *On the mobility of metal-humic species through sand columns*, submitted for publication (presented at the Migration '93 Conference, Charleston, SC, Dec. 1993)

ROCK MATRIX DIFFUSION AS A MECHANISM FOR RADIONUCLIDE RETARDATION: NATURAL RADIOELEMENT MIGRATION IN RELATION TO THE MICROFRACTOGRAPHY AND PETROPHYSICS OF FRACTURED CRYSTALLINE ROCK

Contractors:	University of Exeter (UK), University of Oviedo (E), Commissariat àl'Energie Atomique, Fontenay-aux-Roses (F), University of Liverpool (UK), University of Franche-Comté, Besançon (F), University of Oxford (UK).
Contract No.:	FI2W-CT91-0082.
Duration of contract:	01.03.91 - 31.12.94.
Period covered:	01.01.93 - 31.12.93.
Project Leaders:	M. J. Heath (Exeter), M. Montoto (Oviedo).

A. OBJECTIVES AND SCOPE.

Rock matrix diffusion is an important element in radionuclide migration models: diffusion from water-conducting fractures into the rock matrix provides a potentially important mechanism for the retardation of nuclides migrating from a repository. Recent studies of crystalline rocks have shown, however, that free diffusion of nuclides from fractures into the rock matrix does not always take place and that very little of the rock adjacent to fractures may be available for diffusion.

Although mathematical models describing diffusion have been developed in the past, they have never been furnished with complete physical and chemical data from actual sites. The aims of the study are: (1) to observe evidence of past diffusion of uranium and its daughters from fractures into the rock adjacent to fractures; (2) to relate observed diffusion phenomena to the physical properties of the rock; (3) to construct physicochemical profiles across fractures and into the adjacent rock to allow complete characterisation of past diffusion and assess the potential for future diffusion; and (4) to develop a mathematical diffusion model that can be validated by reference to geological evidence and be incorporated reliably into overall radionuclide migration models.

B. WORK PROGRAMME.

(1) Determination of rock properties and examination of evidence for past diffusion in a series of rock slices at distance of up to 50 cm from hydrogeologically-active fractures;
(2) Quantitative petrophysical analysis and the determination of key physical properties (accessible porosity, dry density, void index, kinetic water behaviour, dynamic properties);
(3) Quantitative microstructural analysis using optical, fluorescence, acoustic and confocal laser microscopy, digital image processing and stereological techniques;
(4) Geochemical analysis (major elements, iron chemistry, uranium and thorium Rare Earth Elements, selected trace elements);
(5) Uranium disequilibrium studies by alpha spectrometry;
(6) Uranium microcartography by autoradiographic, fission track and SEM/EDX techniques;
(7) The development of a mathematical diffusion model based upon real geological/geochemical data.

C. PROGRESS OF WORK AND OBTAINED RESULTS.

State of advancement.

The study is being focused on granite cores obtained from the El Berrocal field site in Spain. The analysis of three cores has been completed during the year; four additional cores are at different stages of preparation and analysis. The work undertaken can be described under the following headings:

1. Field sampling, sample preparation and distribution (Oviedo, Exeter);
2. Petrophysical characterisation (Oviedo, Besançon, Oxford);
3. Uranium microcartography (CEA Fontenay-aux-Roses, Exeter);
4. Uranium series investigations (Exeter, Harwell);
5. Geochemistry (Exeter, CEA Fontenay-aux-Roses);
6. Uranium series diffusion modelling (Liverpool).

Complete profiles have been determined for three of the cores studied (EB4, EB5, EB6) while data for another three (EB7, EB8, EB9) are still being obtained; two further cores (EB10, EB11) are undergoing non-destructive testing and sample preparation.

Progress and results.

1. Field sampling, sample preparation and sample distribution.

A total of eight cores have been provided by the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) from boreholes S-14 and S-16 (Table I).

TABLE I.

Sample number	Borehole number	Depth (m)
EB5	S-14	161.07 - 161.18
EB6	S-14	119.90 - 120.50
EB7	S-14	227.60 - 227.73
EB11	S-14	215.35 - 215.45
EB4	S-16	37.85 - 38.24
EB8	S-16	327.40 - 327.65
EB9	S-16	468.50 - 468.85
EB10	S-16	481.70 - 482.00

TABLE I. Borehole core samples, El Berrocal.

Additionally, oriented cores, 42 mm in diameter and about 150 mm long, have been obtained from three locations inside the mine gallery. These cores have been drilled into fracture surfaces for study under confocal laser microscopy in order to relate the microcrack network to the fracture. Additional work has been carried out on block samples from the mine gallery.

To facilitate the cutting of cores, it was originally intended to select core samples with fractures orientated approximately perpendicular to the core axis (e.g. EB4, EB5). It soon became clear, however, that the most important fractures hydrogeologically are sub-vertical and, therefore, steeply dipping in the cores from vertical boreholes. In order to interpret the results of the study, it is necessary to relate the data obtained from the rock to the geochemistry of the water flowing through the fractures, so hydrogeologically-active fractures have been selected. The cutting procedures have, therefore, been modified so that the rock adjacent to these steeply dipping fractures can be analysed.

2. Petrophysical characterisation of the El Berrocal granite.

Different studies have been carried out to characterise petrophysically the rock matrix and to determine petrophysical profiles for each core in relation to distance from the fracture. Before cutting, each core has been subjected to non-destructive testing in Oviedo using ultrasonic techniques to determine any possible anisotropy in the rock matrix. Following core cutting, a series of petrophysical parameters have been determined on rock slices obtained at different distances from the fracture.

Porosity has been determined in Besançon by mercury porosimetry which allows an accurate evaluation of the range of pore dimensions along the accessible cracks in the rock. In order to understand the water dynamics in the rock matrix, a series of elemental physical properties (open porosity, void index, and water content after two days, five days and under saturation) have been determined in Oviedo, along with the following petrographic components and parameters of petrophysical significance: volume percentage of minerals (Vv), specific surface of grains (Sv grains), mineral affinity, specific surface of microcracks (Sv cracks), and microcrack orientation. The best results have been obtained by applying different microscopy techniques to the same thin section, combining the information obtained by polarising light, fluorescence, confocal laser scanning, acoustic and scanning electron microscopy, the latter coupled with energy dispersive X-ray analysis. The petrographic components thus observed have been mapped and quantified using stereology and digital image analysis of the images obtained.

The application of confocal laser microscopy to the three-dimensional fractographic analysis of the rock matrix has continued to be developed in Oviedo, with special interest in the relationship between microfractures and the rock-forming minerals and fissure orientation. Acoustic microscopy has been used in Oxford to quantify the weathering of feldspar crystals at grain level; the study has also attempted to evaluate possible anisotropies in small volumes of the rock matrix.

NDT Characterisation

Non-destructive testing using ultrasonic techniques is carried out on all sample cores prior to cutting in order to detect possible anisotropies in the rock and for microstructural characterisation. The velocity of longitudinal waves (Vp) and the flight time have been measured in each core at increasing distances from the fracture surface and parallel to it. The cores described here (EB8 and EB9) have sub-vertical fracture surfaces, so the 'virtual' slices are the same shape but each is 10 mm further from the fracture. Four directions (45° from each other) have been measured for each 'slice'. The values for each direction versus distance from the fracture are plotted for core EB8 in Figure 1, where it can be appreciated that there is no significant variation of Vp with distance from the fracture. Figure 2 shows the results for core EB9, which show fairly constant values of Vp with distance from the fracture. These measurements, parallel to the fracture surface, show differences in Vp of around 4% which, in practice, can be interpreted in terms of the petrophysical isotropy of Cores EB8 and EB9.

Physical properties

Selected physical properties (open porosity, void index, water content after two days, water content after 5 days and saturation water content) have been measured following ASTM and ISRM standard methods. These physical properties have been evaluated in the different 10 mm slices obtained by cutting parallel to the fracture. The results for cores EB5 and EB6 are presented in Figures 3 and 4, respectively. It can be observed that the value of each parameter plotted decreases with increasing distance from the fracture. The results show that this variation with distance from the fracture varies from property to property and from core to core.

Mercury porosimetry

Mercury porosimetry has been carried out at the Laboratoire de Microanalyses Nucléaires of the University of Franche-Comté, Besançon, in order to characterise and quantify the rock porosity. Cylindrical granite cores (diameter 24 mm; height 10 mm) were sampled from parallel slices (10 mm thick), cut perpendicular to the main fracture. Two series of eleven cores have been obtained from EB5 and two series of 5 cores and one of 4 cores from EB6. The mean porosity values of cores EB5 and EB6 are in the range 0.86 - 1.30% for EB5 and 0.76 - 1.08% for EB6. The pattern of variation with distance from the fracture is similar to that shown by porosity values obtained by water absorption, though the values obtained by mercury porosimetry for EB5 are a little higher.

Confocal laser microscopy

Fluorescein-impregnated 'thin' sections, mainly 180 µm thick, have been studied under confocal laser scanning microscopy using a "LEICA CLSM". Experience has shown that, under normal instrumental conditions, microfractographic information can be obtained to a depth of 170 µm in thin sections. The CLSM has the ability to obtain 'virtual' sections of the rock at given depths (Z); thus, correlative images corresponding to different Z values in the thin section can be obtained, and any other information coming from upper or lower Z values can be ignored.

All the results obtained so far prove the unique usefulness of CLSM in characterising the microcrack network of fissured rocks. This technique has been shown to be the most appropriate for observing and evaluating the open rock microfractography of El Berrocal granite; that is, the interconnected fissure network that would allow the migration of water and radionuclides through the intact rock.

Stereological and digital image processing data

Digital image analysis and stereological techniques have been applied to images obtained under different microscopy techniques using 'vertical' thin sections from a block of El Berrocal granite. These techniques have been set up for the quantification and characterisation of selected parameters from images obtained by different microscopy techniques and have provided detailed information on the relationship between the different petrographic parameters. The following parameters have been evaluated:

i) Mineral grains:

Mineral	Vv (%)	Sv (mm^{-1})	V^* (mm^3)
Q	30 (31)	2.57 (2.34)	4.35
Feld	63 (62)	6.42 (5.57)	2.05
Mica	7 (7)	0.61 (0.49)	2.14

( ) data from image analysis in brackets
Vv: Volume percentage of each mineralogical component
Sv: Specific surface of each mineralogical component
V^*: Mean star volume of each mineralogical component

ii) Fissures:

Mineral	D	Sv (mm^{-1})			σ_2		
		Q	Feld	Mica	Q	Feld	Mica
Q	1.076	0.53	1.10	0.17	1.2	0.8	1.7
Feld	1.081		2.19	0.24		1.2	0.5
Mica	1.080			0.04			3.5

D fissures = 1.180 (image analysis)

D: Fractal dimension of grain boundaries (image analysis)
Sv: Specific surface of the contacts between phases (image analysis)
σ_2: Mineral Affinity (image analysis data in brackets)

Fissure thickness has been determined by stereological procedures (Fig. 5).

iii) Microcrack network:

The following microcrack network parameters have been evaluated from image analysis data:

Sv (total) = 7.50 mm^{-1}
Sv (intergranular) = 3.80 mm^{-1}
Sv (intragranular) = 4.41 mm^{-1}

Sv (intragranular in Q) = 0.68 mm^{-1}
Sv (intragranular in M) = 0.10 mm^{-1}
Sv (intragranular in F) = 3.63 mm^{-1}

Sv (inter-QQ) = 0.15 mm^{-1}
Sv (inter-QM) = 0.56 mm^{-1}
Sv (inter-MM) = 0.02 mm^{-1}
Sv (inter-QF) = 0.91 mm^{-1}
Sv (inter-FM) = 0.15 mm^{-1}
Sv (inter-FF) = 2.02 mm^{-1}

3. Uranium microcartography: fission track analysis and alpha-autoradiography.

The microdistribution of uranium within the El Berrocal granite has been mapped using fission track analysis (CEA Fontenay-aux-Roses) and alpha-autoradiography (Exeter) in order to understand better the migration behaviour of uranium in the rock and identify migration pathways. Uncovered thin sections, 30 µm thick, cut perpendicular to the fracture surface, have been prepared from granite cores so that variation in the microdistribution of uranium with distance from the fracture can be observed.

The analysis of fission tracks produced following neutron irradiation of ^{235}U allows precise determination of the location of uranium in a sample. Fission track analysis of core EB4 shows three major modes of uranium distribution:

(1) point sources showing very dense clusters of tracks associated with uranium-bearing accessory minerals ('resistate uranium');

(2) zones with scattered sources associated with the uranium enclosed within major primary or secondary phases; this dispersed uranium can be mobilised during alteration processes;

(3) inter- and intra-granular linear zones corresponding to uranium situated in microfissures, cleavages, grain boundaries etc.; this fraction of the uranium is the most easily mobilised; in EB4, a good correlation exists between the linear track distributions and iron oxyhydroxide microfracture fillings.

Qualitative evaluation of the track density shows that (1) there is a fairly heterogeneous distribution of the uranium-bearing accessory phases; (2) there is a fairly homogeneous distribution of the scattered tracks; and (3) there is a strong increase in the density of linear track features close to the fracture.

The images obtained by alpha-autoradiography show the same pattern of uranium distribution as the fission track images, though the exposure period is longer and the track densities obtained lower.

4. Uranium series investigations.

Uranium series disequilibrium studies have been carried out in Exeter, supported under sub-contract by the Isotope Geoscience Laboratory, Harwell. These investigations have focused on the key activity ratios $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ in a series of rock slices taken from each sample core. Results are shown in Figures 6 to 8 (error bars omitted for clarity - for further details see Heath et al. 1993).

Uranium series profile, Core EB4

Results from core EB4 show that the rock immediately adjacent to the fracture has a high $^{234}U/^{238}U$ isotopic ratio, falling rapidly to values nearer equilibrium within 25 mm of the fracture (Fig. 6). The fracture surface also shows an enrichment in radium. Both the ^{238}U and ^{226}Ra profiles appear to have a diffusional shape, though the radium profile is a little erratic. The $^{234}U/^{238}U$ activity ratio data are also consistent with a diffusional origin for the profile. The $^{230}Th/^{234}U$ activity ratio in this profile is close to unity within one standard deviation.

Uranium series profile, Core EB5

The isotopic profile for EB5 shows an elevated $^{234}U/^{238}U$ activity ratio of 1.85 on the fracture surface; the rest of the profile is fairly flat with activity ratios near unity (Fig. 7). This ^{234}U enrichment indicates geologically-recent uranium deposition, though the chemical data show uranium concentrations to be fairly constant throughout the profile. The $^{230}Th/^{234}U$ activity of 0.85 at the fracture surface is consistent with recent uranium deposition.

Uranium series profile, Core EB6

The EB6 profile is very interesting in that there is a severe ^{234}U depletion throughout the 60 mm profile studied, with $^{234}U/^{238}U$ activity ratios as low as 0.34 and $^{230}Th/^{234}U$ activity ratios as high as 2.52 (Fig. 8). These data suggest strong leaching of uranium from the rock adjacent to this hydrogeologically-active fracture. This contrasts with the chemical uranium data which show a uranium enrichment on the fracture surface, with U concentrations of 35 ppm. These data suggest an older uranium deposition on the fracture surface followed by a geologically-recent leaching of uranium from the entire profile.

5. Geochemistry.

Major and trace element geochemistry has been determined in Exeter and Fontenay-aux-Roses on a series of rock slices taken from each core.

Uranium and thorium

The uranium concentration profile for sample EB4 shows that mobilisation of this element has taken place close to the fracture surface (Fig. 6), there being an enrichment immediately adjacent to the fracture where concentrations of 27 ppm are observed. In contrast to the results from sample EB4, the geochemical uranium data for sample EB5 show no significant uranium enrichment on the fracture surface (Fig. 7), although the isotopic data do suggest that there has been some surface deposition of uranium. Core EB6 shows uranium enrichment on the fracture surface where the U concentration is 35 ppm (Fig. 8). This enrichment does not extend beyond the fracture surface itself. The chemical uranium profile for EB6 contrasts strongly with the isotopic data which indicate very recent uranium leaching throughout the profile. Thorium does not show any mobilisation in any of the profiles studied to date (Figs. 6, 7, 8).

Iron chemistry

Of particular importance in the geochemical work being undertaken is the iron chemistry, as the iron oxidation and uranium geochemistry appear to be closely correlated in the profiles examined. Results from EB4 show an increase in iron oxidation in the 20 mm or so immediately adjacent to the fracture with fairly constant levels for the rest of the profile studied (Fig. 6). There is a slight enrichment in total iron on the fracture surface. The iron oxidation profile correlates well with the uranium profile suggesting that the redox conditions exercise a strong control over uranium mobility in the near-fracture environment. In samples EB5 and EB6, taken from greater depth in the rock mass, the iron oxidation levels are much lower, there being a slight reduction on the fracture surface in EB5 where there is also geologically-recent uranium deposition (Fig. 7). In sample EB6, there is a slight but insignificant increase in iron oxidation on the fracture surface where there is a chemical uranium enrichment (Fig. 8). The isotopic data for EB6 reveal extreme ^{234}U depletion due to leaching of uranium from the entire 60 mm profile studied, but there appears to be no correlation here with iron chemistry; indeed, iron oxidation levels appear to be low and comparable with the 'unoxidised' part of the EB4 profile.

6. Uranium diffusion modelling.

The data obtained in these studies are providing the input for a mathematical diffusion model being developed in Liverpool. The intention is to model the uranium concentration and uranium isotopic activity ratios with distance from the fracture for comparison with the observed profile data in order to describe the processes observed and estimate values of the solid/solution exchange coefficient, Kd, and effective diffusivities.

Assumptions and model

The main basis of the diffusion model consists of the following elements:

(1) migration of ^{234}U and ^{238}U from a fracture into the rock wall by matrix diffusion;

(2) retardation of the uranium by absorption, characterised by a linear absorption (partition) coefficient which is assumed to be reversible.

The simulations of this model are based upon the observation that fracture profile data from a number of fractures studied show enrichment of uranium at the fracture face decreasing rapidly with distance into the rock. It seems, however, that the simulated $^{234}U/^{238}U$ activity ratios do not vary with distance from the fracture in a way that matches the actual data. Early simulations have shown that:

(1) Uranium concentrations alone can be simulated without much difficulty; these lead to estimated 'long-term' values of Kd in line with upper estimates (0.1 to 10 m^3/kg) from laboratory batch and other experiments;

(2) Neither $^{234}U/^{238}U$ nor $^{230}Th/^{234}U$ activity ratios can be simulated with any confidence by assuming simple diffusion and sorption processes alone.

Identification of processes affecting fracture profiles

Matrix diffusion is the process thought to be dominant in the transfer of radionuclides from fracture water into the rock matrix adjacent to fractures. It has two components, the physical diffusion of the chemical species through the connected porosity of the rock, and the chemical exchange interactions of the species in solution with the minerals in contact with the pore fluids. Processes other than diffusion and retardation are also in operation which can bring about uranium enrichment or depletion. In order to identify which processes result in uranium enrichment and cause isotopic disequilibrium, and which of these can be interpreted as having affected these profiles, the following should be noted:

(1) Uranium enrichment in the fracture zone (usually 0 - 4 cm) results either from uranium-enriched fracture water (the model presented here) or, less likely, by transfer of uranium from the interior of the rock;

(2) ^{234}U is more mobile that its parent ^{238}U because it recoils from alpha-particle emission, occupies damaged lattice sites and can be leached more easily that ^{238}U. $^{234}U/^{238}U$ values less than unity are common in weathered granite as are values greater than unity in groundwater;

(3) If uranium is removed from a given volume of rock, the $^{230}Th/^{234}U$ ratio is expected to be greater than unity; ^{230}Th is immobile in groundwater since it is readily hydrolysed;

(4) Uranium is readily sorbed by iron oxyhydroxides;

(5) In granite, the uranium is contained either within resistate minerals, such as zircon and sphene, or in intergranular positions (as shown by the fission track and autoradiographic studies); the latter is more mobile and is often shown to be secondary (e.g. in altered biotite).

El Berrocal fracture profiles

The data obtained from El Berrocal cores EB4, EB5 and EB6 demonstrate the difficulty of establishing a model that is widely applicable to the many profiles that are now being obtained. Each profile has its own characteristics, having evolved in a different geochemical environment. The presence of apparently contradictory evidence is not uncommon, as each profile has been produced by a long and complex history. In core EB6 (Fig. 8), for example, uranium enrichment on the fracture surface appears to have been followed by leaching of uranium, the latter having produced the very low $^{234}U/^{238}U$ activity ratios observed. More data and profiles are needed before any widely applicable model can be developed.

List of publications.

HEATH. M. J., MONTOTO, M., et al. (1993). Rock matrix diffusion as a mechanism for radionuclide retardation: natural radioelement migration in relation to the microfractography and petrophysics of fractured crystalline rock. Phase 1 Interim Report, March 1991 - February 1993. Report to CEC, July 1993.

MÉNAGER, M. T., HEATH, M. J., IVANOVICH, M., MONTJOTIN, C., BARILLON, R., CAMP, J. and HASLER, S. E. (1993). Migration of uranium from uranium-mineralised fractures into the rock matrix in granite: implications for radionuclide transport around a radioactive waste repository. 4th Int. Conf. on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration '93), Charleston, USA, 12-17 December 1993.

MONTOTO, M., MÉNAGER, M. T., RODGIGUEZ REY, A., MENENDEZ, B. and A. MARTINEZ NISTAL (1993). Microfractography of granites and its implication in uranium transfer phenomena in rock matrix: application to the El Berrocal experimental site, Spain. 4th Int. Conf. on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration '93), Charleston, USA, 12-17 December 1993.

PÉREZ DEL VILLAR, L., MÉNAGER, M. T., DE LA CRUZ, B. and PARDILLO, J. (1993): Uranium distribution in relation to the mineralogical and geochemical characteristics of the El Berrocal granite - an experimental site, Spain. 4th Int. Conf. on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration '93), Charleston, USA, 12-17 December 1993.

LATHAM, A. G. (1993). Diffusion-sorption modelling of natural U in weathered granite fractures: potential and problems. 4th Int. Conf. on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere (Migration '93), Charleston, USA, 12-17 December 1993.

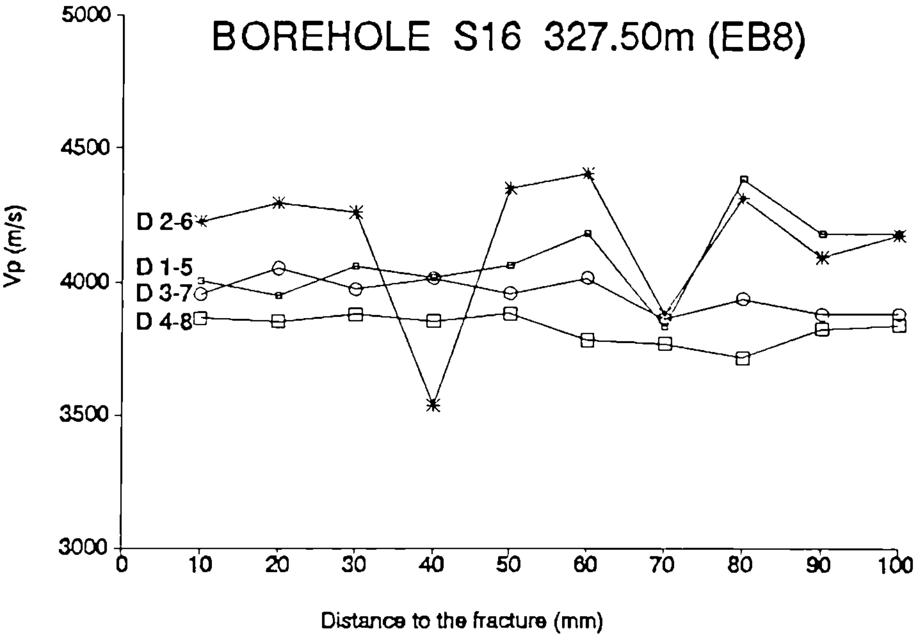


Figure 1. Longitudinal wave velocity (Vp) profiles, Core EB8.

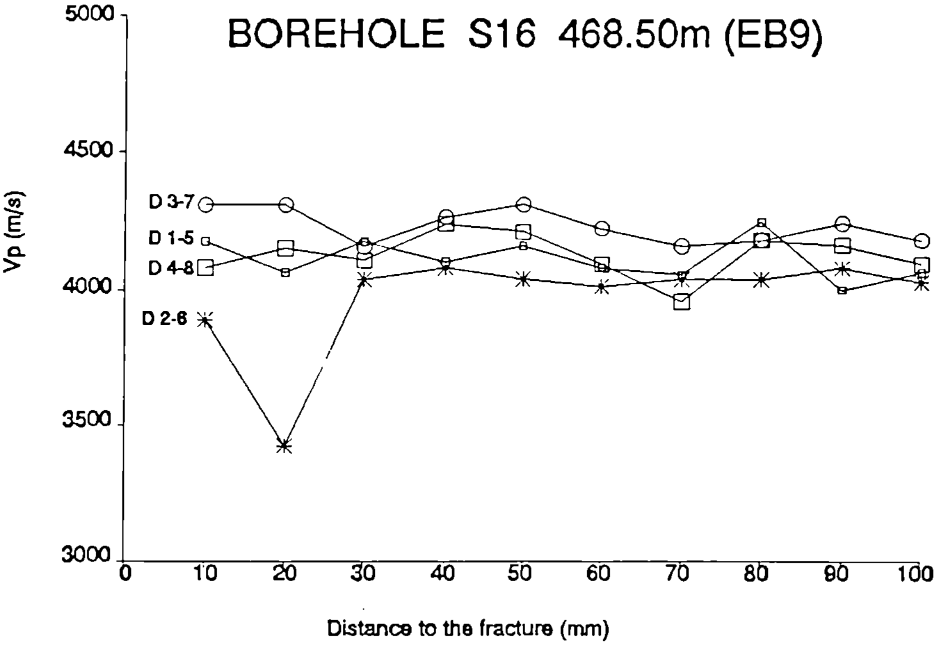


Figure 2. Longitudinal wave velocity (Vp) profiles, Core EB9.

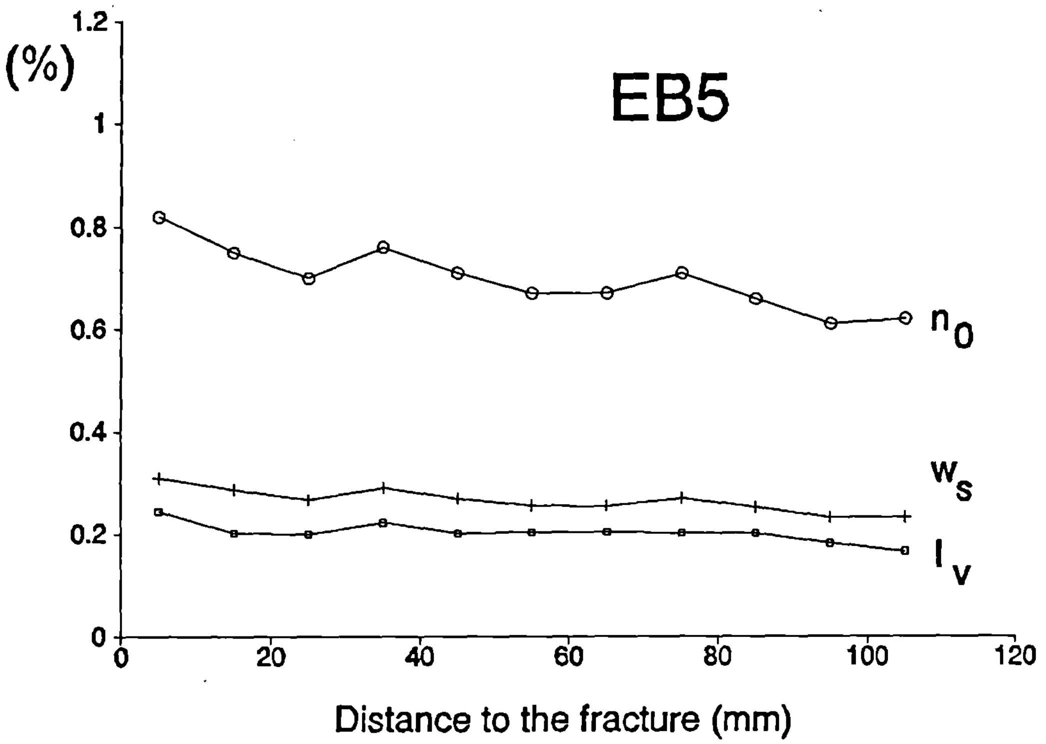


Figure 3. Physical property profiles, Core EB5. n_0 = open porosity Iv = void index; Ws = saturation water content.

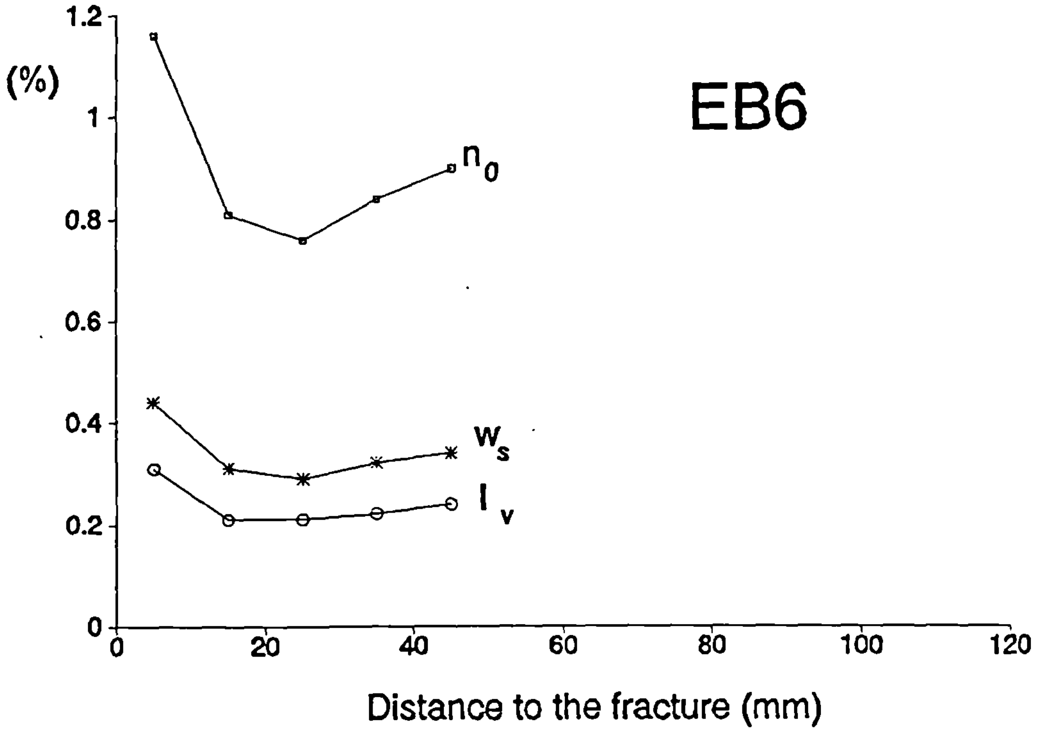


Figure 4. Physical property profiles, Core EB6. n_0 = open porosity Iv = void index; Ws = saturation water content.

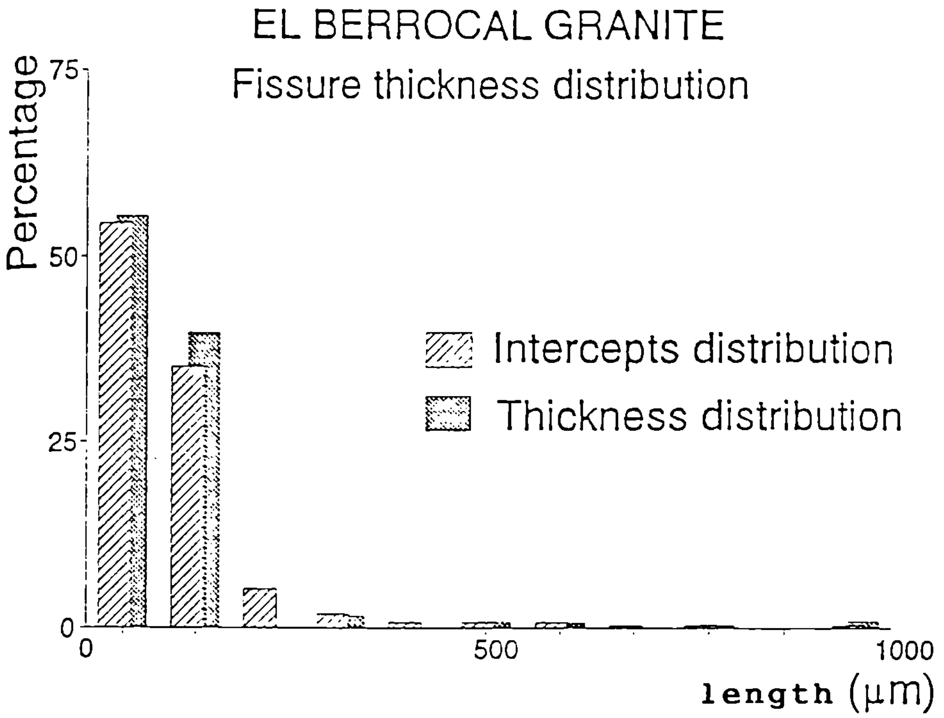
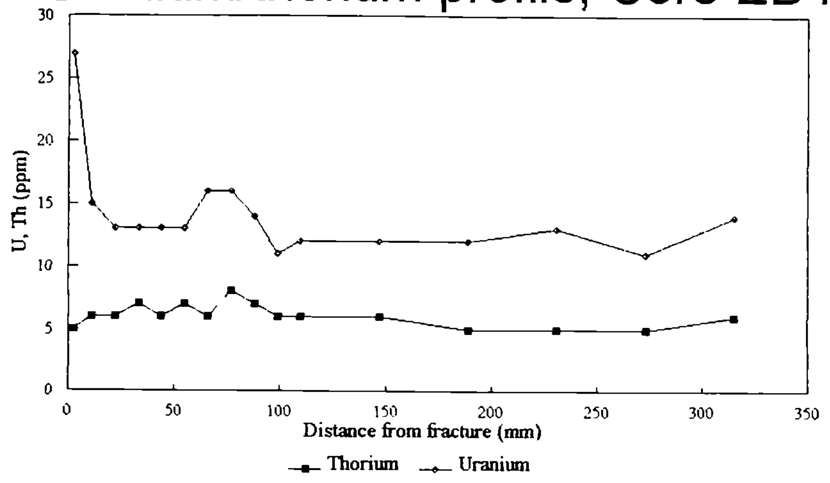
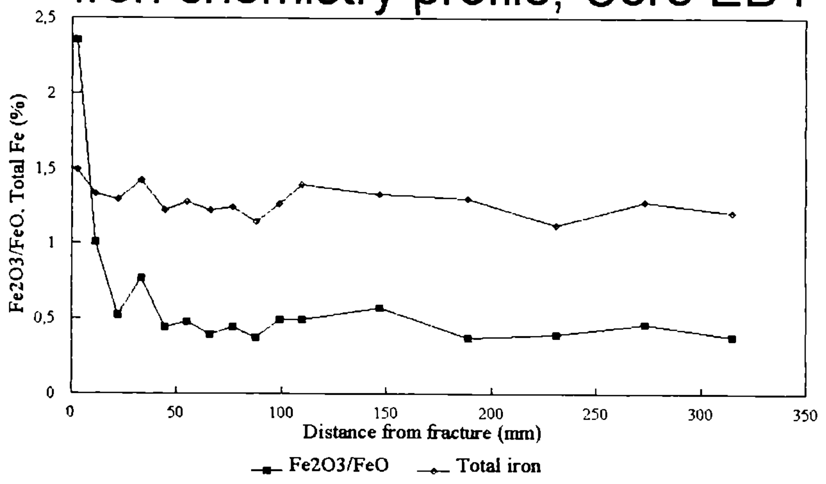


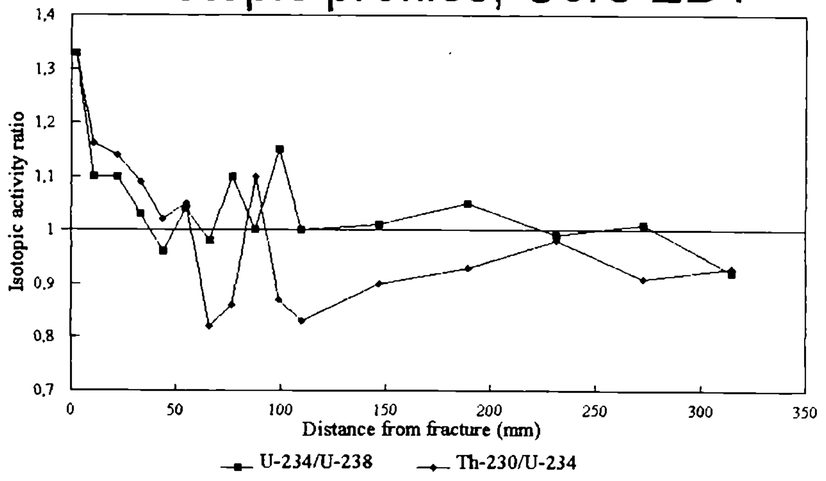
Figure 5. Fissure thickness distribution of El Berrocal granite (block collected from mine gallery).



Uranium/thorium profile, Core EB4

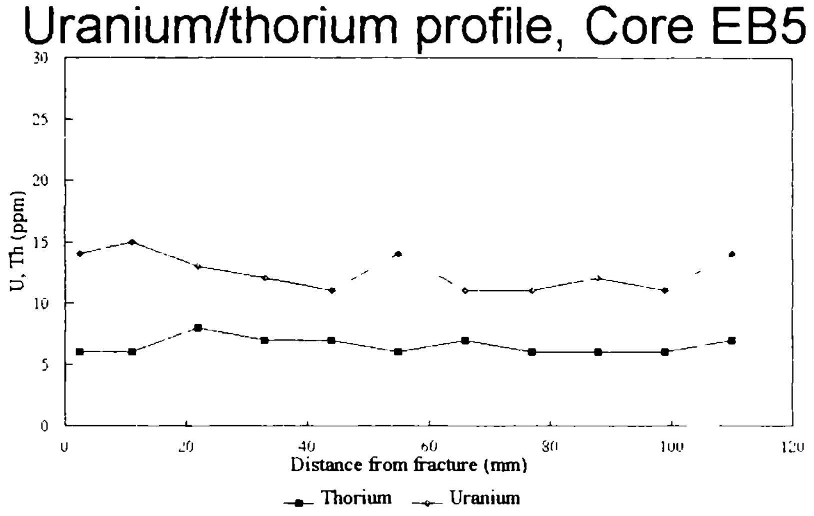


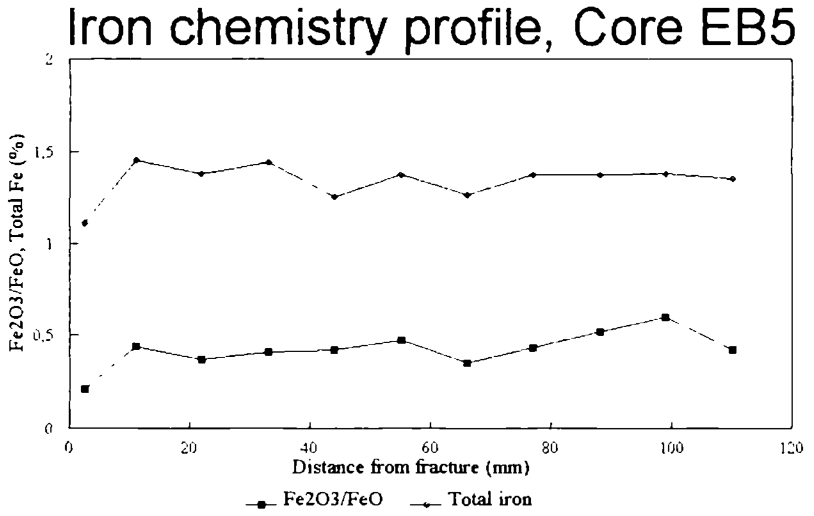
Iron chemistry profile, Core EB4



Isotopic profiles, Core EB4

Figure 6. Geochemical and isotopic profiles, Core EB4.





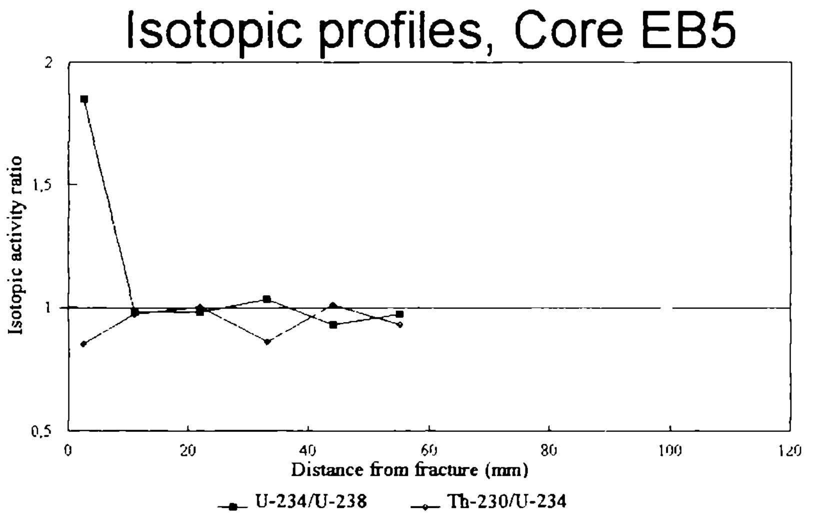
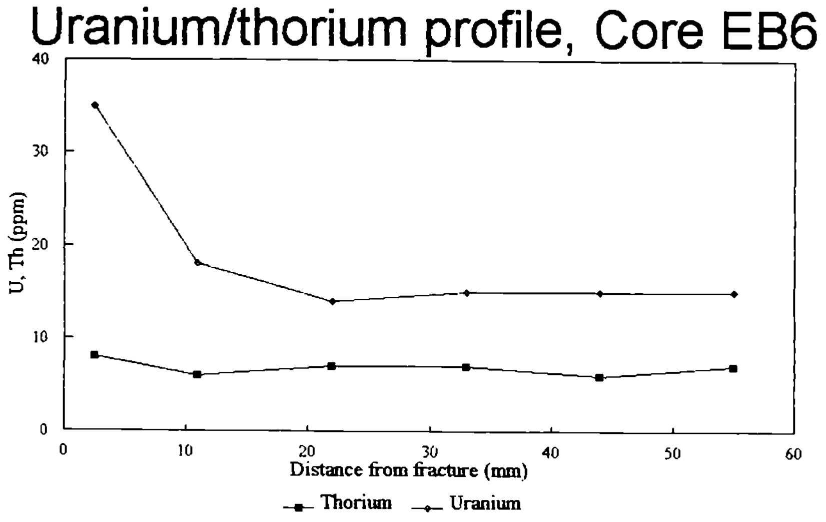
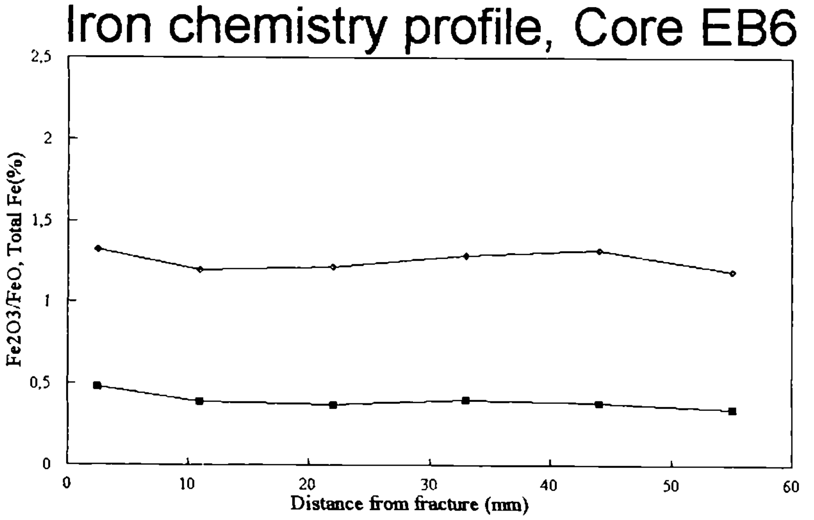


Figure 7. Geochemical and isotopic profiles, Core EB5.


Uranium/thorium profile, Core EB6


Iron chemistry profile, Core EB6

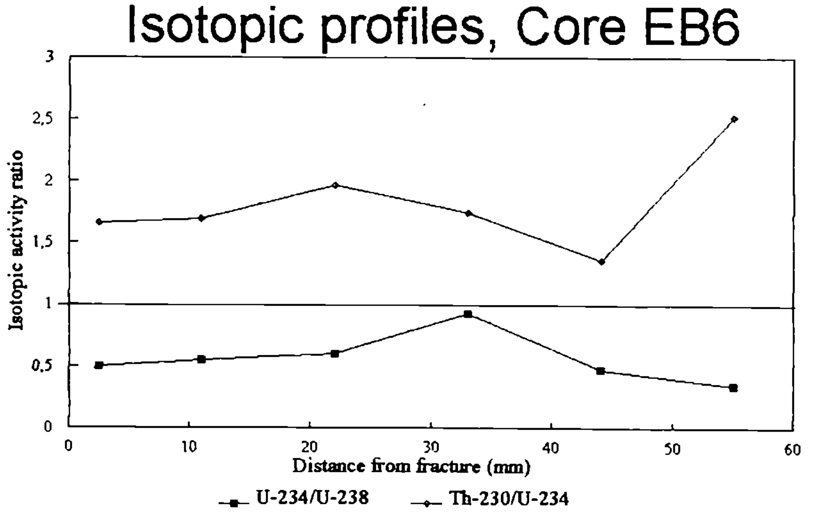

Isotopic profiles, Core EB6

Figure 8. Geochemical and isotopic profiles, Core EB6

Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances

Contractor:	Institut für Radiochemie, Technische Universität München
Contract N°:	FI 2W-CT91-0083
Duration of the contract:	July 1991 - June 1994
Period covered:	January 1993 - December 1993
Project leader:	J.I. Kim, G. Buckau

A. *OBJECTIVES AND SCOPE*

The aim of the present research programme is to study the complexation behaviour of actinide ions with humic substances in natural aquifer systems and hence to quantify the effect of humic substances on the actinide migration. Aquatic humic substances commonly found in all groundwaters in different concentrations have a strong tendency towards complexation with actinide ions. This is one of the major geochemical reactions but hitherto least quantified. Therefore, the effect of humic substances on the actinide migration is poorly understood. In the present research programme the complexation of actinide ions with humic substances will be described thermodynamically. This description will be based on a model being as simple as possible to allow an easy introduction of the resulting reaction constants into geochemical modelling of the actinide migration. This programme is a continuation of the activities of the COCO group in the second phase of the CEC-MIRAGE project.

The laboratories participated in the research programme are:

TUM:	Technische Universität München (coordinator: J.I. Kim, G. Buckau)
CEA-FAR:	Centre d'Energie Atomique, Fontenay-aux-Roses (V. Moulin)
UM:	Universität Mainz (N. Trautmann)
KUL:	Katolieke Universiteit Leuven (A. Maes)
JRC-Ispra:	Joint Research Centre, Ispra (G. Bidoglio)

In this period of the programme no working contribution of JRC-Ispra is given.

B. *WORK PROGRAMME*

The programme consists of the following three main tasks:

Task 1: Complexation reactions of actinide ions with well characterized reference and site-specific humic and fulvic acids

Task 2: Competition reactions with major cations in natural groundwaters

Task 3: Validation of the complexation data in natural aquatic systems by comparison of calculation with spectroscopic experiment

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

In this report period a number of methodical developments are in progress. The effective ligand concentration is one of the important parameters for the evaluation of the metal ion complexation behaviour of bulk polyelectrolytes like humic or fulvic acids. Studies by KUL and TUM show that the effective ligand concentration of humic acid is related to the protonation of the ion exchanging groups. For a precise evaluation of the complexation reaction, however, a direct measurement of the effective ligand capacity under given experimental conditions is neccessary. The humate complexation has been studied for pentavalent neptunium (UM), hexavalent uranium (TUM) and trivalent lanthanide ions (CEA, UM and KUL) under different experimental conditions. The pH is varied between 3.0 and 9.0, the ionic strength between 0.01 and 0.1 M with metal ion concentrations between 10^{-13} and 10^{-5} mol/L. Competition of Al^{3+}, $[Co(NH_3)_6]^{3+}$, Ca^{2+}, Cu^{2+}, Fe^{2+} and Na^+ on the Eu humate interaction is investigated by KUL. CEA-FAR has studied the influence of temperature on the Dy(III) humate complexation as well as the Dy(III) complexation with EDTA for the purpose of comparison. Studies by KUL on the influence of different competing ligands show that in such a ternary system (metal ion, humic acid and competing ligand) mixed complexes are generated.

Progress and results

1 Complexation reaction of actinide ions with reference and site specific humic acids.

1.1 Humic substances

For the present study, humic and fulvic acids from three different sites and a commercial humic acid from Aldrich Co. are used. They were purified, protonated and characterized previously [1-4]. The commercial product is included as a reference material for the purpose of intercomparison. These products are named as follows:

Gohy-573 HA:	Humic acid from Gorleben (FRG)
Gohy-573 FA:	Fulvic acid from Gorleben (FRG)
Fanay-Augeres HA:	Humic Acid from Fanay Augeres (F)
Fanay-Augeres FA:	Fulvic Acid from Fanay Augeres (F)
Boom-Clay HA:	Humic acid from Boom Clay (B)
Boom-Clay FA:	Fulvic acid from Boom Clay (B)
Aldrich HA(I):	Humic acid from Aldrich Co. (Commercial)

The participating laboratories have agreed upon the introduction of additional batches of the reference humic acid, since the original amount purchased was not sufficient to meet with growing experimental demands. KUL and UM prepared batches of Aldrich HA: KUL (Aldrich HA(II)) and UM (Aldrich HA(III)). KUL has furthermore purified and characterized humic acid from Podzol B as an additional product for comparison. Methods of isolation and purification of humic substances as well as the results of characterization are described elsewhere [1-4].

For interpretation of the complexation behaviour, the proton exchange capacity of each humic substance is of main importance. The proton exchange capacities of the studied humic substances determined by different groups using pH-titration are:

	Proton exchange capacity (in meq/g)			
	TUM	CEA-FAR	KUL	JRC-Ispra
Aldrich HA(I)	5.43 ± 0.16	6.0 ± 0.5	2.7/3.9[1)]	5.24
Aldrich HA(II)	4.18 ± 0.15		4.38 ± 0.07	
Aldrich HA(III)	4.61 ± 0.11			
Gohy-573 HA	5.38 ± 0.20	5.2/5.2	3.5/4.5[1)]	
Gohy-573 FA	5.70 ± 0.09			
Fanay-Augeres HA	1.85 ± 0.05	3.4 ± 0.2		
Fanay-Augeres FA	6.93 ± 0.06	5.7		
Boom-Clay HA	4.22 ± 0.02			
Boom-Clay FA			To be investigated	
Podzol-B HA			5.4	

1): pH=7/10

1.2 Experimental techniques

TUM

Time resolved laser fluorescence spectroscopy (TRLFS) [5], anion exchange chromatography and ultrafiltration are applied for the study of the U(VI) humate complexation in the μmolar concentration range of both reactants. The anion exchange chromatography is performed with "Analytichem Bond Elute Strong Exchanging Resin" column from Varian on which the polyanionic humic acid and the uranyl humate complex are sorbed whereas the non-complexed uranyl cation remains in solution. Speciation by TRLFS is done by excitation of the uranyl ion followed by peak deconvolution of the emission bands from the non-complexed UO_2^{2+} ion and UO_2-humate. By time gating the high humic acid fluorescence background is discriminated. Ultrafiltration separates colloidal humic acid and the uranyl humate complex from the non-complexed uranyl ion by their size differences.

CEA-FAR

TRLFS [6] is applied for the study of the EDTA complexation of Dy(III) using a fixed excitation wavelength of 355 nm. By energy transfer from EDTA to the complexed Dy(III) ion, the Dy-EDTA complex is selectively quantified by its emission at 576 nm. The temperature effect on the Dy humate complexation is also studied by this method.

UM

A three step-laser-resonance-ionization mass spectroscopy system (RIMS) [7] is used for the detection of actinides down to the femtomolar concentration range. This detection system is coupled with two different experimental methods for the separation of the non-complexed ions from their humate complex. The separation techniques are cation and anion exchange chromatography. The first technique uses Biorad 50W X 8 cation exchanger to separate the free Sm^{3+} ion from the solution. Anion exchange chromatography is performed with DEAE Sephadex A-25 where the humic acid and humate complex is sorbed whereas the non-complexed NpO_2^+ is left in solution.

KUL

Two different experimental methods are used for the study of the Eu-humate complexation and competition with different cations. The cation exchange technique has been used by KUL over several years [8,9]. The second experimental method is the dialysis technique by which involved Eu(III) species are separated by their size difference. By both experimental techniques the influence of different competing ligands (diglycolic acid, iminodiacetic acid and acetylacetone as well as hydroxide and carbonate ions) on the Eu-humate complexation is also studied.

1.3 Results of the complexation study

TUM

The humate complexation of the hexavalent uranyl ion with Gohy-573 HA is investigated at pH 4.0 and an ionic strength of 0.1 M . The uranyl ion concentration varies over two orders of magnitude from 0.1 to 10 µmol/L in order to allow precise determination of the loading capacity under given experimental conditions as well as to examine whether the degree of loading of the humate ligand influences the complexation behaviour. By the anion exchange chromatography technique, the non-complexed uranyl cation is found to elute without retention whereas the humate complex is sorbed quantatively. For TRLFS, reference emission spectra of the non-complexed UO_2^{2+} ion and the uranyl humate are used for quantification by peak deconvolution. Using ultrafiltration, the free metal ion is separated from the colloidal humate complex by their size difference. The comparable results are obtained by the three experimental methods.

The loading of the humic acid by the uranyl ion is varied from approximately 16 percent to a level of saturation (96%). The reaction mechanism is shown to be a charge neutralization process namely two proton exchanging sites by one uranyl ion. This reaction mechanism has also previously been shown to govern the humate complexation of tri- and pentavalent actinide ions [10-14]. Taking the loading capacity into account no influence on the complexation constant with the degree of loading of the humate ligand is observed. The complexation constant of U(VI) for Gohy-573 humic acid is found to be: logß= 6.16 ± 0.13.

CEA-FAR

The complexation of Dy(III) with EDTA is investigated at pH 3.5, 5.0 and 7.0 at a constant ionic strength of 0.1 M. EDTA is chosen as a possible model ligand for comparison. At a constant Dy(III) concentration its fluorescence intensity is measured varying the EDTA concentration. Evaluation of experimental results is based on analyzing the resulting fluorescence titration curve [15]. For this investigation the Dy(III) concentrations are either 1 or 10 μmol/L.

The effective EDTA ligand concentration, expressed as the complexation capacity, is found to be dependent on pH. For the complexation reaction it is assumed that only a 1:1 complex is formed. The complexation constants evaluated taking the complexation capacity into account are found to be independent of pH. In contrary to previous results by CEA-FAR as well as JRC-Ispra [16-18] on the actinide(III) and lanthanide(III) humate interaction no influence of the metal ion concentration on the EDTA complexation constant is found. Investigations with other model ligands are in progress.

The temperature effect on the humate complexation of Dy(III) in trace concentrations is studied by experiments at 20, 35 and 50°C. No significant difference between the results at these three temperatures is observed. The investigations will be continued at higher Dy(III) concentrations for verification at higher loading of the humic acid.

UM

The complexation of Np(V) at a concentration of approximately 10^{-13} mol/L with Aldrich humic acid is studied. From pH 4.0 to pH 7.0 the humic acid concentration is varied between 20 mg/L and 80 mg/L (appr. 0.1 to 0.4 meq/L) at a constant ionic strength of 0.01 M.

Over the investigated experimental range a mean value for the stoichiometry factor of 1.4±0.1 is found. Due to the low metal ion concentration, a saturation of the humic acid ligand by the NpO_2^+ ion is not approached and therefore, the loading capacity cannot be evaluated. With no correction for the pH dependent loading capacity of the humate ligand with the neptonyl ion an "apparent Np(V) humate complexation constant" is described by the following relation:

$$\log\beta^* = (0.24 \pm 0.02) \times \mathrm{pH} + (2.54 \pm 0.11)$$

Previous results by UM using electrophoretic ion focusing technique for species separation gave slightly higher values[19]. Correction of the present values for the influence of the loading capacity by published data from TUM [14], a pH independent complexation constant is obtained:

$$\log\beta = 5.12 \pm 0.13$$

The Sm(III) complexation with Aldrich humic acid is studied at pH 3.0, 3.5, 4.0, 5.0 and 6.0 at an ionic strength of 0.1 M. The humic acid concentration is 50 mg/L which corresponds to approximately 250 µeq/L or 80 µmol HA(III)/L whereas the Sm(III) concentration is only approximately 1 nmol/L. Speciation is done by evaluation of the distribution of Sm(III) between solution and the cation exchanger Biorad 50W X 8.

Over the entire experimental range a 1:1 stoichiometry is found. With increasing pH the concentration of the non-complexed Sm^{3+} ion decreases. From pH 3 to 6 the amount of Sm(III) humate complex increases from 43% to 88%. Due to the low Sm(III) concentration compared to humic acid, saturation of the humate ligand is not approached and the loading capacity cannot be evaluated. Assuming a loading capacity of 100 % an "apparent Sm(III) humate complexation constant" is found to increase from $\log\beta^*=3.99\pm0.02$ at pH 3.0 to $\log\beta^*=5.0\pm0.1$ at pH 6.0. Correction for the effective humate ligand concentration dependency by the loading capacity of humic acid with Am(III) from the investigations of TUM [20] the Sm(III) humate complexation becomes independent of pH:

$$\log\beta = 5.08 \pm 0.09$$

KUL

The generation of mixed complexes in the ternary system metal ion, humic acid and competing ligand is investigated by cation exchange and dialysis. The dialysis method makes use of the size difference between the colloidal humic acid and non-complexed metal ions as well as competing ligands. Experiments are performed at ionic strength of 0.1 M with a Eu(III) concentration of approximately 10^{-7} mol/L. The competing ligands are acetylacetone, diglycolic acid, iminodiacetic acid as well as carbonate and hydroxide ions.

Above a certain critical concentration of a competing ligand, an increase of the interaction strength with humic acid is observed. The critical concentration decreases with increasing the interaction strength of a given ligand. The results are interpreted as a generation of mixed complexes. Several mixed complexes are considered. Experimental data with competing ligand concentratrion well beyond their critical concentrations are examined for the stoichiometry by analysis of the relation:

$$Eu^{3+} + HA(I) + nL <=> EuL_nHA(I) \qquad (1)$$

For L being acetylacetone, diglycolic acid, iminodiacetic acid, and the carbonate ion the nearest integer number for the n value is 2 (1.76±0.28). Therefore, KUL suggests to describe the ternary system Eu^{3+}, humic acid and ligand L by the following two reactions:

$$Eu^{3+} + HA(III) <=> EuHA(III) \qquad (2)$$

$$Eu^{3+} + 2L + HA(I) <=> EuL_2HA(I) \qquad (3)$$

for which on a common basis for the humate ligand of HA(III) the observed (or experimental) complexation constant $\log\beta_{exp.}$ is written as:

$$\log\beta_{exp.} = \log\beta_1 + \log\beta_{mix\,2,1} + 2 \times \log[L] + \log 3 \qquad (4)$$

where $\log\beta_1$ refers to reaction (2), "$\log\beta_{mix\,2,1} + 2 \times \log[L]$" refers to reaction (3) and log 3 accounts for the two different expressions of the humate ligand concentration (HA(I) and HA(III)) in reactions (2) and (3).

$\log\beta_1 = 6.88$ [21] and $\log\beta_{mix\,2,1}$ for different ligand are measured to be:

	Ligand	$\log\beta_{mix\,2,1}$	standard deviation
1	AA^-	15.44	0.43
2	DGA^{2-}	16.33	0.46
3	IDA^{2-}	18.14	0.49
4	CO_3^{2-}	17.97	0.58
5	OH^-	18.00	0.36

Ligands: 1; Acetylacetone, 2; Diglycolic acid, 3; Iminodiacetic acid,

For the complexation study an overwiev of the present results is given as follows:

	M(III)		M(V)	M(VI)	Dependency of logß on	
	Non-hydrol. range	Hydrol. range			pH, I, origin of HA	[M]
TUM	x		x	x	No	No
CEA	x		x		No	Yes
UM	x		x			No1)
KUL	x	x			No	No
JRC-Ispra	x					Yes2)

1): Np(V): Results at ≈10^{-14} mol/L comparable to ≈10^{-4} mol/L (TUM [14]);

2): Eu(III) and Tb(III); [17] and [18]

2 Competition reactions with cations in natural groundwaters

KUL

Studies on the competition effect of different cations on the Eu(III) humate complexation are conducted at pH 5.4, 6.0 and 9.0 at a constant ionic strength of 0.1 M by cation exchange and dialysis techniques. The concentrations of competing cations are varied keeping the Eu(III) concentration constant at 10^{-6} mol/L. The competition reaction is found to deviate from a simple ion exchange process on a single type of humate ligand sites. Therefore, results are interpreted assuming two different types of exchange sites with different interaction strength towards different complexing cations. The competition strength of the different cations studied is found to increase with the strength of their humate complexation:

$$Cu^{2+} > Al^{3+} > Fe^{2+} > Ca^{2+} > [Co(NH_3)_6]^{3+} > Na^+$$

These and previous results (see table below) verifies that the competition effect is mainly governed by the relative complexation strength between the studied actinide ions and the competing metal ion.

Summary of previous results of the competition study;

	Competition effect of		
	Ca(II) on		Cr(III) on
	M(III)	M(V)	M(III)
CEA	minor		
UM		important	
KUL	minor		
JRC-Ispra			≈equal strength

3 Validation of the results in natural aquatic systems by comparison of calculation with spectroscopic experiment

Work on this task is in progress.

Literature

[1] Kim, J.I., Buckau, G., Klenze, R., Rhee, D.S. and Wimmer, H.: Characterization and Complexation of Humic Acids, CEC report EUR 13181, (1991)

[2] Moulin, V., Billon, A., Theyssier, M. and Dellis, Th.: Study of the Interactions between Organic Matter and Transuranic Elements, Final report 1986-1989, Commissariat a l'Energie Atomique, Fontenay-aux-Roses.

[3] Carlsen, L.: Characterization of Humic Acids, CEC report EUR 12784, (1990)

[4] Kim, J.I., Buckau, G., Li, G.H., Duschner, H. and Psarros, N.: Characterization of Humic and Fulvic Acids from Gorleben Groundwater, Fresenius J. Anal. Chem., **338**, 245, (1990)

[5] Klenze, R., Kim, J.I. and Wimmer, H.: Speciation of Aquatic Actinide Ions by Pulsed Laser Spectroscopy, Radiochimica Acta, **52/53**, 97-103 (1991)

[6] Moulin, C., Decambox, P., Mauchien, Moulin, V and Theyssier, M.: On the Use of Laser-Induced Time-Resolved Spectrofluorometry for Interaction Studies Between Organic Matter and Actinides: Application to Curium, Radiochimica Acta, **52/53**, 119-25 (1991)

[7] Ruster, W., Ames, F., Kluge, H.-J., Otten, E.-W., Rehklau, D., Scheerer, F., Herrmann, G., Muehlbeck, C., Riegel, J., Rimke, H., Sattelberger, P. and Trautmann, N.: A Resonance Ionization Mass Spectrometer as an Analytical Instrument for Trace Analysis, Nucl. Instr. Meth. Phys. Res., **A281**, 547 (1989)

[8] Maes, A., De Brabandere, J. and Cremers, A.: A Modified Schubert Method for the Measurement of the Stability of Europium Complexation in Alkaline Conditions, Radiochimica Acta, **44/45**, 51-7 (1988)

[9] Maes, A., De Brabandere, J. and Cremers, A.: Complexation of Europium(3+) and Americium(3+) with Humic Substances, Radiochimica Acta, **52/53**, 41-7 (1991)

[10] Buckau, G., Kim, J.I., Klenze, R., Rhee, D.S. and Wimmer, H.: A Comparative Study of the Fulvate Complexation of Trivalent Transuranium Ions, Radiochimica Acta, **57**, 105-111 (1992)

[11] Kim, J.I., Rhee, D.S. and Buckau, G.: Complexation of Am(III) with Humic Acids of different Origin, Radiochimica Acta, **52/53**, 49-55 (1991)

[12] Kim, J.I., Wimmer, H. and Klenze, R.: A Study of Curium(III) Humate Complexation by Time Resolved Laser Fluorescence Spectroscopy, Radiochimica Acta, **54**(1), 35-41 (1991)

[13] Kim, J.I., Buckau, G., Bryant, E. and Klenze, R.: Complexation of Americium(III) with Humic Acid, Radiochimica Acta, **48**, 135-43 (1989)

[14] Kim, J.I. and Sekine, T.: Complexation of Neptunium(V) with Humic Acid, Radiochimica Acta, **55**, 187-192, (1991)

[15] Decambox, P., Mauchien, P., Moulin, C., Moulin, V. and Tits, J.: Complexation of Lanthanides and Actinides with Humic Acids, in: Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances, Eds.: J.I. Kim and G. Buckau, Report RCM 00392, TU München, February 1992.

[16] Moulin, V., Tits, J., Decambox, P. and Moulin, C.: Complexation of Lanthanides and Actinides with Humic Acids, in: Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances (Third progress report), Eds.: J.I. Kim and G. Buckau, Report RCM 00593, TU München, March 1993.

[17] Bidoglio, G., Omenetto, N. and Robouch, P.: Kinetic Studies of Lanthanide Interactions with Humic Substances by Time Resolved Laser Fluorescence, Radiochimica Acta, **52/53**, 57-63, (1991)

[18] Bidoglio, G., Grenthe, I., Qi, P., Robouch, P. and Omenetto, N.: Complexation of Eu and Tb with Fulvic Acids as Studied by Time Resolved Laser Fluorescence, Talanta, **38(9)**, 999-1008, (1991)

[19] Marquardt, C., Franz, C., Herrmann, G and Trautmann, N.: The Behaviour of Neptunium(V) and Samarium(III) in Humic Acid Solutions at Very Low Concentrations, in: Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances (Third progress report), Eds.: J.I. Kim and G. Buckau, Report RCM 00593, TU München, March 1993.

[20] Kim, J.I., Rhee, D.S. and Buckau, G.: The Complexation of Trivalent Actinide Ions with Humic and Fulvic Acids, in: Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances (Third progress report), Eds.: J.I. Kim and G. Buckau, Report RCM 00593, TU München, March 1993.

[21] Dierckx, A., Vancluysen, J. and Maes, A.: Contribution by KUL (Appendix 4), in: Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances, Eds.: J.I. Kim and G. Buckau, Report RCM 00392, TU München, February 1992.

COLLOID MIGRATION IN GROUNDWATERS: GEOCHEMICAL INTERACTIONS OF RADIONUCLIDES WITH NATURAL COLLOIDS

Contractor:	Institut für Radiochemie, Technische Universität München
Contract N°:	FI2W/0084
Duration of contract:	May 1991 - April 1994
Period covered:	January 1993 - December 1993
Project Leader:	J.I. Kim, B. Delakowitz

A. *OBJECTIVES AND SCOPE*

The aim of the joint research programme is to determine the significance of groundwater colloids in far field radionuclide migration. The characterization, quantification and theoretical interpretation of colloid-borne transport phenomena of radionuclides in selected Gorleben aquifer systems are the main objectives of the present research programme. Gorleben aquifer systems are chosen because they are well characterized in terms of their hydrological and geological properties and because they contain substantial amounts of colloids of different chemical compositions as well as considerable quantities of chemical homologues and natural analogues of radionuclides, e.g. M(III), M(IV), M(VI), and Th and U decay series. The research tasks are investigated jointly by the four laboratories (listed below) in close coordination of experimental capacities of each laboratory.

TUM:	Technische Universität München, F.R.G. (coordinator: J.I. Kim, B. Delakowitz)
AEA:	AEA Technology, Harwell, U.K. (M. Ivanovich)
GSF:	Gesellschaft für Strahlen- und Umweltforschung, München, F.R.G. (P. Fritz)
Atkins:	W.S. Atkins Engineering Sciences, London, U.K. (D. Read)

B. *WORK PROGRAMME*

1 Sampling of groundwaters, colloids and sediments under well controlled conditions (TUM, AEA, GSF)

2 Characterization of colloids, groundwaters and sediments (TUM, AEA, GSF)

3 Generation of pseudocolloids of radionuclides ($Z \geq 3^+$): Am(Eu) for M(III), Pu(Th) for M(IV), Np for M(V), U for M(VI); (TUM)

4 Transport process study by scaled column experiments (TUM, GSF, AEA, Atkins)

5 Synthesis and theoretical interpretation (Atkins ES)

6 Liaison with related studies within the MIRAGE programme (e.g. calculation tool)

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

For the present study, groundwater samples and sediments were collected from four boreholes that penetrate the geologically and chemically heterogeneous Gorleben aquifers. The sampled groundwaters were submitted to parallel ultrafiltration using filters of different pore sizes to estimate the size and quantity of natural colloids present. Groundwaters, colloids and sediments have been characterized for their chemical composition and physical properties. The actinide ions of M(III), M(IV) and M(VI) are found to be strongly sorbed on the aquatic colloids rich in humic substances (termed humic colloids). Sorption preferentially occurs on humic colloids with a size range between 100 nm down to about 1 nm. The sorption and desorption of the actinide ions onto and from the aquatic humic colloids are reversible with respect to the pH variation.

The results from the column experiments with trivalent ^{152}Eu and ^{241}Am and tetra/pentavalent ^{237}Np/^{233}Pa indicate that in groundwater rich in humic colloids a substantial part of injected lanthanide and actinide ions appears mobile through generation of actinide pseudocolloids. The recovery of the injected lanthanide and actinide ion concentration is > 63 %, while being dependent on the groundwater flow velocity through the column. The retardation factor of the mobile portion of lanthanide and actinide ions is close to 1, indicating that the migration of the mobile lanthanide and actinide ions through the column is comparable to that of ^{3}HHO and $^{82}Br^{-}$. This may be explained by the fact that the lanthanide and actinide ions introduced in the groundwater are stabilized through sorption onto humic colloids, which migrate through the sediment column with negligible interaction. The migration behaviour of humic colloids through the column may be explained by size exclusion as well as anion repulsion.

Progress and results

1 Sampling of groundwaters, colloids and sediments

Groundwater and colloids were collected anaerobically (N_2 + 1% CO_2) from selected aquifer systems from the geological site foreseen for the future German nuclear waste repository at Gorleben [1]. The sampling procedure is explained in detail in the six-monthly progress reports to the present research programme [2]. Sediments were collected from drill cores, corresponding to sampled boreholes.

2 Characterization of groundwaters, colloids and sediments

2.1 Experimental techniques

Analytical methods and laboratory techniques employed for the characterization of groundwaters, colloids and sediments are described in the recent progress report to the present research programme [2].

2.2 Chemical composition of groundwater and colloids

The physical characteristics, partly measured in the field, and the chemical compositions determined in groundwaters of boreholes Gohy 572, Gohy 611, Gohy 573 and Gohy 2227 are varying due to their different aquifer conditions [1]. The salinity, given as an electrical conductivity ($\mu S\ cm^{-1}$), generally increases with the aquifer depth and, as expected, the highest salinity among the four groundwaters is found in the one (Gohy 2227) nearest to the salt dome surface. High DOC concentrations are found in Gohy 573 and Gohy 2227. These boreholes are intersecting stratigraphic intercalations of lignite within the sampled aquifers. There is no correlation between the salinity and DOC concentration. DOC in the groundwaters, separated and characterized according to a known procedure [3] is observed as a composite of humic and fulvic acids which are loaded with various metal ions and behave as colloids. For this reason they are named "humic colloids". Ultrafiltration of the four groundwaters Gohy 572, Gohy 573, Gohy 611 and Gohy 2227 using a flat bed filter system with a variety of nominal filter pore sizes from 1000 nm down to about 1 nm was carried out at TUM. Analytical results of filtrates are given in the 3rd progress report [2]. Concentrations of DOC in the filtrates show a gradual decrease with decreasing the pore size of filters. At the smallest pore size of about 1 nm, between 91.2% (Gohy 2227) and 95.7% (Gohy 573) of DOC are filtered, whereas the measured values for DOC in the filtrates at 1000 nm, 450 nm and 100 nm are almost identical. From these data and according to the results obtained from the earlier work [1, 4], it is apparent that the predominant amount of humic colloids is found in the size range less than 100 nm down to about 1 nm. It is known from the earlier work [1, 4] that trace elements of higher oxidation state are, in general, preferentially associated with humic colloids. Between 87.9% - 99.6% of REE and other trace elements (Th, U, Hf, Zr) in the groundwaters Gohy 573 and Gohy 2227 are filtered at the smallest pore size of about 1 nm, suggesting that main portions of these trace elements are associated with humic colloids. This is supported by U/Th studies carried out at AEA Harwell.

Colloids fractionated by ultrafiltration at different pore sizes from 400 nm down to about 1 nm are analysed by neutron activation analysis (NAA) at TUM and the analytical values given in the 3rd progress report [2]. The metal ions, Ca, Sr and Ba, are associated with humic colloids in a relatively large portion. In the colloid fraction filtered at 1 nm, as an average, 61.4 ± 6.5 % of the total concentration is found for each divalent ion in the groundwater. The mole fraction of the divalent ions loaded on humic colloids changes from groundwater to groundwater, depending on their total concentration and the amount of DOC [3]. The trace metal ions of higher oxidation state (≥3+) are strongly associated with humic colloids. In groundwater Gohy 2227 the filtration at about 1 nm pore size shows an average (92.9 ± 11.5)% of these ions being bound on thus filtered colloids. Trace ions associated with humic colloids are the trivalent rare earth elements (REE; 94.4 ± 9.2 %), tetravalent Zr, Hf, Th (98.2 ± 14.5) %, pentavalent Ta (87.7 %) and hexavalent U (73.7 %). The trivalent Fe follows the same tendency. In Gorleben groundwaters with relatively large amount of humic substances, generally more than 80 % of metal ions of higher oxidation state (≥3+) are sorbed on colloids collected on 1 nm filters [1, 3, 4].

2.3 Chemical and mineralogical compositions of sediments

The chemical compositions of the sediment samples from drill cores taken from boreholes Gohy 573, Gohy 611 and Gohy 2227 show marked differences in concentrations of SiO_2, Al_2O_3, Fe_2O_3 and K_2O, the main components of quartz, feldspar and clay minerals. This is supported by mineralogical studies. The lowermost lignite found in borehole Gohy 573 is overlaid by relatively pure quartz-sand, whereas the lignite in borehole Gohy 2227 is covered by sediments with a higher portion of clay (marl). In the case of borehole Gohy 573, concentrations of lanthanides and other metal ions in the lignite are ten times higher than those of the quartz-sand. This is not the case for borehole Gohy 2227, where the lanthanides and other elements are equally distributed between lignite and overlying sand and marl. Differences might be accounted for the different sorption behaviour of the overlying sediments owing to varying clay content. Another reason could be different sources for the lignites found in drill cores of the two boreholes Gohy 573 and Gohy 2227. The high concentrations of humic colloids in the groundwater samples Gohy 573 and Gohy 2227 are probably related to the glacial lignite intercalations.

2.4 Colloid size distribution and population quantification

Particle counting by photocorrelation spectroscopy (PCS) at AEA for unfiltered groundwaters from boreholes Gohy 573 and Gohy 2227 indicates that particle populations are different among these samples. Colloid investigation by TEM and SEM-EDX and quantification of colloidal particle concentrations in various filter fractions by laser induced photoacoustic detection of light scattering (PALS) have been carried out at TUM. Results are partly reported in the 3rd progress report [2].

2.5 Isotope studies

Determination of the isotopes ^{2}H, ^{3}H, ^{13}C, ^{14}C and ^{18}O has been carried out at GSF in groundwater samples of the boreholes Gohy 201, 611, 612, 572, 573 and 2227. ^{14}C and ^{13}C were measured in the humic acid (HA) and fulvic acid (FA) DOC fraction. In groundwater samples of the boreholes Gohy 201, 611 and 2227, the isotopes ^{34}S and ^{18}O were also measured on dissolved SO_4. From the results obtained at GSF it may be assumed that the FA has originated from near-surface material (soil), whereas the HA fraction originated from organic matter of older sediments (lignite). However, this assumption needs further verification.

2.6 Study of U/Th-decay series disequilibrium

Surface characterization of some drill core samples from boreholes Gohy 573 and Gohy 2227 have indicated that solid/solution exchange processes are taking place [2]. However, the U series disequilibrium data obtained to date by AEA are ambiguous in terms of the humic colloid provenance and the source of their natural actinide loads. Thus, for example, total sand samples $^{234}U/^{238}U$ activity ratios are all close to unity indicating little exchange with groundwaters; the lignite total sample, on the other hand, indicate U uptake. The solid phase distributions of U and Th indicate significant components of total U and Th residing in the original phase of the lignite samples in contrast to sand samples where the residual mineral phases contain most U and Th. From the U/Th isotope ratios found in the surface phases of the solids it has been inferred that active radionuclide exchange is taking place in these aquifers. The question of colloid provenance and the origin of the colloid borne actinides in the Gorleben aquifer has been adressed through the U series disequilibrium data. Although the conclusions are somewhat ambiguous, it is possible that the humic colloids present in groundwater Gohy 573 and Gohy 2227 have different isotopic histories and possibly different sources, other than local lignite [2].

3 Generation of pseudocolloids of radionuclides

Actinide ions with a variety of oxidation states (≥3+) are in general unstable in groundwater at neutral pH, besides a dioxoactinyl ion of pentavalent state [5], because of their strong tendency towards the hydrolysis reaction [6]. For this reason, they are easily sorbed on aquatic colloids through either complexation or ion exchange reaction [7, 8]. The generation of such colloids, termed actinide "pseudocolloids", may lead to an apparent solubility of a given actinide being much higher than its thermodynamically available solubility [9]. For this reason, the generation of actinide pseudocolloids may facilitate the migration, or eventually the retardation, of these elements in a given aquifer system. Task 3 of the present study adresses the mechanisms that may lead to the generation of actinide pseudocolloids in the selected groundwaters. The main intention is to investigate how actinide pseudocolloids are generated in groundwaters rich in humic substances. The generation of actinide pseudocolloids by sorption of actinide ions on groundwater colloids is studied at TUM with actinide ions of three important oxidation states (trivalent, tetravalent and pentavalent) [2]. The study of the hexavalent ion is confined to the behaviour of the naturally occuring uranyl ion in the groundwaters. Results of sorption/desorption experiments carried out so far with the trivalent ^{241}Am and ^{244}Cm and the tetravalent $^{232/234}$Th in humic substance rich groundwaters from the Gorleben aquifers are reported in detail in the 3rd progress report to the present research programme [2]. The $^{241}Am^{3+}$, $^{244}Cm^{3+}$ and the $^{232/34}Th^{4+}$ ions introduced in the original groundwaters are found to be sorbed quantitatively on humic colloids. The sorption and desorption behaviour is depending on the pH.

4 Transport process in the column experiment

The aquatic transport of lanthanide and actinide ions through a sediment matrix may be retarded by various sorption reactions such as ion exchange, matrix diffusion and diffusion into micropores of the sediment [10]. Knowledge of the retardation factor and the total recovery of an injected tracer ion enables the assessment and quantitative description of its migration behaviour through a sediment-groundwater column. The column experiment is performed for ^{152}Eu, ^{241}Am, ^{237}Np and ^{233}Pa in the presence of natural humic colloids. Data obtained from the column experiment are used to test either an organic complexation model and a coupled chemical transport model developed in the frame of this study [11] which may assist in predicting retardation or mobility of colloid bound lanthanide and actinide ions in aquifer systems rich in humic substances.

Hydraulic properties

Prior to the migration experiment with the lanthanide or actinide ions under investigation, the hydraulic properties of each column are characterized carefully and stable experimental conditions are maintained. The effective porosities determined by eight different experiments at both TUM and GSF [2,11] appear consistent. The mean value is found to be $n_{eff} = 0.330 \pm 0.014$.

Trivalent ions: ^{152}Eu

The breakthrough characteristics of the trivalent ^{152}Eu ion allow the assessment of the migration behaviour of trivalent actinide ions, since the europium ion can be regarded as a chemical homologe to trivalent actinide ions. The Eu tracer introduced in the groundwater (5×10^{-5} mol L^{-1}) is quantitatively sorbed on humic colloids and 70% of the ^{152}Eu concentration injected into the column is recovered. The ^{152}Eu is eluted from the column at a retardation factor of $Rf = 1.0$, indicating that 70% of the injected ^{152}Eu concentration is transported without sorption, at the same flow rate as $^{82}Br^-$ [2, 11].

The Eu tracer experiment is repeated at different flow velocities in order to examine the influence of the groundwater flow rate on the Eu migration behaviour. The filtration velocities applied (Table 1) correspond closely to groundwater velocities observed in Gorleben aquifer systems, between < 1 m a^{-1} and 48 m a^{-1} [12]. The sorption parameters (retardation factor and recovery rate) determined for individual experiments are listed in Table 1. At the lowest flow rate of $v_f = 5.2 \times 10^{-5}$ cm s^{-1} (corresponding to 16 m a^{-1}) only 64.3 % of the injected ^{152}Eu concentration is found in eluates and the rest 35.7 % remains sorbed on the column. At a rather high velocity of $v_f = 1.2 \times 10^{-3}$ cm s^{-1} (corresponding to 378 m a^{-1}), 91.6% Eu is recovered. The fact suggests that the flow rate of groundwater has a direct influence on the recovery of a colloid borne tracer ion migrating through the column. The retardation factors for the mobile portion of ^{152}Eu tracer at different v_f, however, are almost identical (0.90, 0.98, 1.02). The colloid size distribution determined by ultrafiltration of the ^{152}Eu traced groundwater remains the same both in the injected water and in the eluate, in the size range between 2 nm and 100 nm in diameter, indicating little interaction of the colloids with the Pleistocene sand.

Table 1: ^{152}Eu tracer experiments at different filtration velocities

Column	Flow velocity v_f (cm s^{-1})	Flow velocity v_f (m a^{-1})	Recovery W (%)	Retardation factor R_f
EG 1-25	5.2×10^{-5}	16.4	64.3	0.90
EG 1-24	2.1×10^{-4}	66.2	71.2	0.98
EG 1-27	1.2×10^{-3}	378	91.6	1.02

Trivalent ions: ^{241}Am

Am in the groundwater is quantitatively sorbed on humic colloids [2, 4]. The humic acid concentration in groundwater, estimated on the basis of proton exchangeable functional groups [13, 14] is approximatly 7.8×10^{-4} eq L^{-1} and the CO_3^{2-} concentration under 1 % CO_2 partial pressure at pH 7.6 is calculated to be 6.6×10^{-5} mol L^{-1}. The first complexation constants of Am(III) with the ligand anions: OH^-, CO_3^{2-} and humic acid are known to be log $\beta = 6.3$ [15], 6.22 [16] and 6.44 [17], respectively. A combination of both sets of data suggests that the predominant species in the groundwater at pH 7.6 would be the Am(III) humate. Fig. 1 shows both the breakthrough and recovery curves of ^{241}Am as well as the breakthrough curve of $^{82}Br^-$. 75% Am injected at a flow velocity $v_f = 2.4 \times 10^{-4}$ cm s^{-1} passes through the column at a velocity similar to that of the ideal tracer (R_f = 1.12). The result suggests that the Am^{3+} ion is stabilized by sorption onto humic colloids which suppress its interaction with the column sand. At a lower Am concentration (1.8 x

10^{-6} mol L^{-1}) nearly the same result is obtained with a retardation factor $R_f = 1.04$ and 68 % recovery. The size distribution of Am pseudocolloids is determined in the input groundwater as well as in different eluate fractions. Almost no change in size distribution of Am pseudocolloids occurs during their passage through the column. The Am pseudocolloids are found in the size smaller than 200 nm.

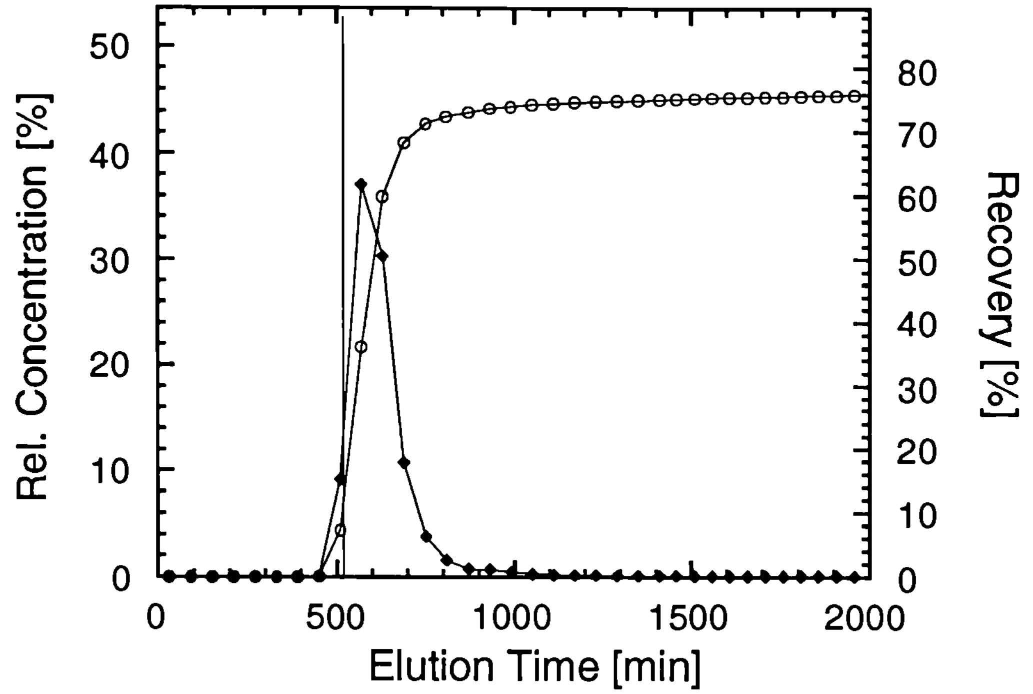


Figure 1: Am column experiment: Breakthrough curve ($^{82}Br^-$) and recovery for $^{82}Br^-$ and $^{241}Am(III)$.

Tetra- and pentavalent ions: ^{237}Np

The results of the migration experiment carried out with the pentavalent ^{237}Np ion indicate that a large quantity of Np has undergone reduction to Np(IV) during equilibration with humic colloids. After an equilibration time of 20 days approximately 27% of Np in solution is still present in the pentavalent oxidation state as NpO_2^+, Np(V)-monocarbonate and Np(V)-humate. The remaining 73% can be attributed to the tetravalent Np(IV). The neptunium reduction phenomenon is studied in detail elsewhere [11, 18]. As expected, the tetravalent Np is strongly bound on humic colloids and its migration through the sand column is directly influenced by the mobility of humic colloids. The sorption of the NpO_2^+ ion on humic colloids, however, is shown to be negligibly small [19]. The recovery of Np in the column experiment at a flow velocity $v_f = 2.5 \times 10^{-4}$ cm s^{-1} is 63%, which is somewhat lower than the values for Am and Eu. This may be explained by the relatively large non-colloid bound portion of Np compared to that of Am and Eu. The retardation of the mobile Np is calculated to be $R_f = 0.94$. This indicates that the migration of the mobile portion is similar to that of $^{82}Br^-$.

5 Synthesis and theoretical interpretation

The overall objective is to develop a model capable of simulating complexation between natural organics and heavy metals, in conjunction with transport in groundwater systems. Three organic complexation models [20, 21] based on an electrostatic description of the humic surface have been selected for development. The Rigid Sphere and Surface models [20] have been enhanced and incorporated into the coupled chemical transport code, CHEMTARD [22], by WS Atkins. This phase of work has been verified successfully by inter-code comparison with corresponding models in the static equilibrium code, PHREEQE [23]. A third model, Model V [21] has also incorporated into PHREEQE. Currently this phase of model development is undergoing testing. Data from the column experiments are being analysed into a form suitable for modelling purposes. However, no data for the surface properties of the heterogeneous column matrix or the organic colloids are available from these experiments. Consequently an extensive literature survey has been carried out to identify suitable data for optimisation, with emphasis on the interaction of Am with inorganic and organic surfaces. The results of this review process made by WS Atkins are summarised in the following description of the supporting modelling studies.

a) Speciation of Americium in groundwater from Gohy 2227

Speciation calculations using PHREEQE [23] and the CHEMVAL database [24] have been carried out to identify the most important species present ($AmCO_3^+$, Am^{3+}) which could participate in adsorption process.

b) Derivation of intrinsic binding constants for Am on silicia

Using protonation/deprotonation data [25] and surface area data [26] collated as part of the literature survey, intrinsic binding constants have been derivated from experimental data [27] to describe the binding of Am on a silica surface. This has involved fitting the sorption profile over a range of pH values, using the data optimisation code FITEQL [28], for the following reactions:

$SOH + AmCO_3^+ - H^+ = SO - AmCO_3$ log K - 2.9
$SOH + Am^{3+} - H^+ = SO - Am^{2+}$ log K - 4.4

c) Organic complexation of americium

The complexation of americium with humic material has been simulated using the Flat Surface model in PHREEQE [20]. The results of this study suggest that under the experimental conditions of the column tests and in the absence of other surfaces, approximately 80% of the americium will bind to the humic material.

On the basis of the code refinement and the data optimisation described above, modelling studies using CHEMTARD are now being carried out to simulate the transport of americium through the Gorleben glacial sands with sorption on both the organic colloids and the inorganic matrix.

Summary of work in progress

Task 4: Transport process study by scaled column experiments

- Assessment of migration behaviour (break-through characteristics) of the tetravalent $^{232/234}$Th(IV) and the ^{233}U(VI) in the column experiment with groundwater Gohy 2227 (TUM),

Task 5: Synthesis and theoretical interpretation

- carrying out a priori testing of the model against column experiment data,
- testing the validity of the local equilibrium assumption in the context of organic complexation reactions.

List of publications

[1] Dearlove, J.P.L., Longworth, G., Ivanovich, M., Kim, J.I., Delakowitz, B., Zeh, P.: A Study of Groundwater-Colloids and their Geochemical Interaction with Natural Radionuclides in Gorleben Aquifer Systems, Radiochim. Acta **52/53,** 83 (1991)

[2] Kim, J.I., Delakowitz, B., Zeh, P., Probst, T., Lin, X., Ehrlicher, U., Schauer, C.: Colloid Migration in Groundwaters: Geochemical Interactions of Radionuclides with Natural Colloids, CEC-Contract FI2W/0084, 3rd Progress Report, Institut für Radiochemie, Technische Universiät München, RCM **00293** (February 1993).

[3] Buckau, G.: Komplexierung von Americium (III) mit Huminstoffen in natürlichen Grundwässern, Inaugural Dissertation, Freie Universität Berlin (1991).

[4] Kim, J.I., Zeh, P., Delakowitz, B.: Chemical Interactions of Actinide Ions with Groundwater Colloids in Gorleben Aquifer Systems, Radiochim. Acta **58/59,** 147-154 (1992).

[5] Neck, V., Kanellakopulos, B., Kim, J.I.: Solubility and Hydrolysis Behaviour of Neptunium (V), Radiochim. Acta **56,** 25 (1992).

[6] Kim, J.I.: Chemical Behaviour of Transuranic Elements in Natural Aquatic Systems, In: Handbook on the Physics and Chemistry of the Actinides, eds. A.I. Freeman and C. Keller, Elsevier Science Publ. B.V., 1986, Chap. 8.

[7] Moulin, V., Robouch, P., Vitorge, P., Allard, B.: Spectrophotometric Study of the Interaction between Americium (II) and Humic Materials, Inorg. Chim. Acta **140,** 303 (1987).

[8] Kim, J.I., Buckau, G., Rommel, H., Sohnius, B.: The Migration Behaviour of Transuranium Elements in Gorleben Aquifer Systems: Colloid Generation and Retention Process, Mat. Res. Soc. Symp. Proc. **127,** 849 (1989).

[9] Kim, J.I.: Actinide Colloid Generation in Groundwater, Radiochim. Acta **52/53**, 71 (1991).

[10] Klotz, D., Lang, H.: Experimentelle Untersuchungen zur Migration ausgewählter Radionuklide im Deckgebirge des Endlagerortes Gorleben, Untersuchungsprogramm IV. Teil III: Durchlaufsäulen-Versuche zur Bestimmung dynamischer Sorptionsdaten ausgewählter Radionuklide in Sedimenten aus den Schächten des Bergwerkes Gorleben. GSF-Bericht **20/92**, GSF-Forschungszentrum für Umwelt und Gesundheit, Neuherberg, 98 - 129 (1992).

[11] Kim, J.I., Delakowitz, B., Zeh, P., Probst, T., Lin, X., Ehrlicher, U., Schauer, C.: Colloid Migration in Groundwaters: Geochemical Interactions of Radionuclides with Natural Colloids, CEC-Contract FI2W/0084, 4th Progress Report, Institut für Radiochemie, Technische Universiät München, RCM **00793** (August 1993).

[12] Bundesamt für Strahlenschutz, BfS: Fortschreibung des Zusammenfassenden Zwischenberichtes über bisherige Ergebnisse der Standortuntersuchung Gorleben vom Mai 1983, **ET-2/90**, Bundesamt für Strahlenschutz, Fachbereich Nukleare Entsorgung und Transport, Salzgitter, 161 - 173 (1990).

[13] Kim, J. I., Buckau, G., Li, G. H., Duschner, H., Psarros, N.: Characterization of Humic and Fulvic Acids from Gorleben Groundwater, Fresenius, J. Anal. Chem. **338**, 245 (1990).

[14] Kim, J. I., Buckau, G., Klenze, R., Rhee, D. S., Wimmer, H.: Characterization and Complexation of Humic Acids, CEC-Report EUR **13181** EN, Brussels, 5 (1991).

[15] Stadler, S., Kim, J. I.: Hydrolysis Reactions of Am(III) and Am(IV), Radiochim. Acta **44/45**, 39 (1988).

[16] Meinrath, G., Kim, J. I.: The Carbonate Complexation of the Am(III) Ion, Radiochim. Acta **52/53**, 29 - 34 (1991).

[17] Kim, J. I., Rhee, D. S., Buckau, G.: Complexation of Am(III) with Humic Acids of Different Origin, Radiochim. Acta **52/53**, 49 - 55 (1991).

[18] Zeh, P., Kim, J. I.: Reduction of Neptunium(V) in Humic Rich Groundwaters, Radiochim Acta (in progress).

[19] Kim, J. I., Sekine, T.: Complexation of Np(V) with Humic Acid, Radiochim. Acta **55**, 187 (1991).

[20] Falck, W.E.: Two Modified Versions of the Speciation Code PHREEQE for Modelling Macromolecule-proton/cation Interaction. Br. Geol. Surv. Tech. Rep. **WE/89/57** (1989).

[21] Tipping, E., Hurley, M.A.: A Unifying Model of Cation Binding by Humic Substances. Geochem. Cosmochim. Acta **56**, 2627-3641 (1992).

[22] Bennett, D.G., Liew, S.K., Mawbey, C.M., Read, D.: CHEMTARD Version 3.0: Theoretical Overview. UK Dept. of Environment Report No. **DOE/HMIP/RR/92.036** (1992).

[23] Parkhurst, D.L., Thorstenson, D.C., Plummer, L.N.: PHREEQE - A Computer Program for Geochemical Calculations. US Geol. Surv., Water-Resources Investigations 80-96 (1985).

[24] Chandratillake, M., Falck, W.E., Read, D.: CHEMVAL Project. Guide to the CHEMVAL Thermodynamic Data Base, UK DoE/HMIP/RR92.094 (1992).

[25] Brady, P.V.: Silica Surface Chemistry at Elevated Temperatures, Geochem. Cosmochim. Acta **56**, 2941 (1992).

Title: The role of colloids in the migration of radioelements.
Contractor: Risø National Laboratory, Denmark.
Contract N°:FI2W/0085.
Duration of contract: 1/4 1991 to 1/4 1994.
Period covered: 1/1 1993 to 31/12 1993
Project leader: B. Skytte Jensen

A. OBJECTIVES AND SCOPE

The objective of the present investigation is to quantify the behavior of colloids (humic acids) under varying chemical conditions. The aim is to derive thermodynamically based expressions, which may be used for modelling their interactions with pore-water constituents in natural systems.

B. WORK PROGRAMME

To collect useful information on humic acid behavior, which can support the present investigation.

To study and quantify flocculation processes, which are induced by the addition of polyvalent cations in competition with other ions present.

To follow the distribution of trace elements (R.E.) between flocculate and solution.

As a tentative model for the thermodynamic interpretation of the experimental data the humic acids will be modelled as finely dispersed ion-exchangers with a possible limited miscibility of surface phases.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The experimental work, which has been presented previously, has resulted in a series of 4x6 matrices containing data on concentrations of soluble humic acid, calcium, sodium, lanthanum, europium and erbium as well as pH and E4/E6 data obtained in experiments in which calcium chloride and sodium chloride were added in varying amounts.
The aim of the study is to identify mathematical expressions relating these data to the conditions imposed on the system, ultimatively to be able to derive equations useful for predictive modelling.

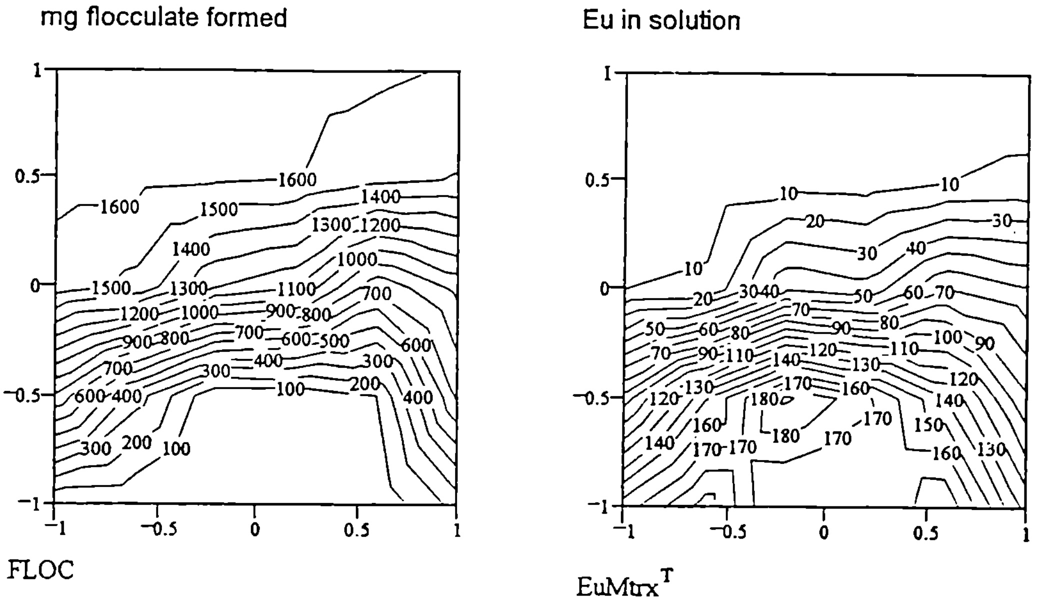
A priori the speciation of humic acid interacting with added salts is expected to be rather complicated both in the soluble and the flocculated state. Not alone the flocculate must be expected to possess ion-exchange properties, but because of their size, the soluble humic acids will also be expected to associate strongly with available cations in ion-exchange like reactions.

The experiments have therefore, as described previously, been designed such as to reveal possible interferences between the proton and the cations Na+ and Ca++ added in macro amounts. In addition the fate of some lanthanides added in trace amounts i.e. of the order of 100-200 ppb, simultaneously with the addition of sodium and calcium has been studied.
It is obvious, that we are facing many experimental and also theoretical difficulties in the search for quantitative relations between the multitude of possible parameters considered. Apart from unavoidable random errors several more systematic errors may obscure or distort the measurements.

Whereas the pH values in the supernatant after a centrifugation from the flocculate could readily be measured, the free sodium or calcium concentrations could not be determined potentiometrically, because the sodium - and calcium electrodes behaved erratically in the humate solutions. Only the total concentrations of these ions not bound to the flocculate could be determined by standard analytical techniques. The amounts of humate in solution could be determined by with a reasonable precision by U/V-spectroscopy although the spectra changed slightly during the flocculation process.

The data for mg. humate in solution show a pattern almost identical with those for the three lanthanides in solution. This can only be the case, if the lanthanides are strongly bound to the humic acid both in solution or in the flocculate.
In fig. 1 a and b are shown examples of niveaucurves calculated from the somewhat meager data available for mg. humate flocculate and for europium in solution.

Figure 1a,b.



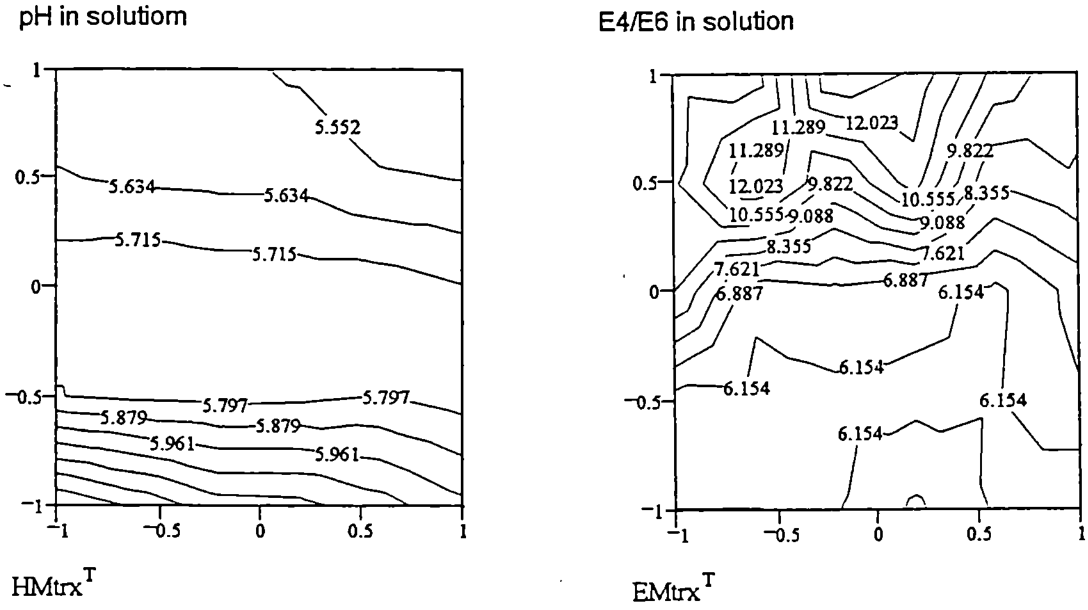
mg flocculate formed

Eu in solution

An interesting observation is, that the flocculation induced by the addition of calcium chloride seems to be reversed by the addition of modest concentrations of sodium chloride in contradiction with the commonly accepted postulate, that flocculation is favored by an increase in ionic strength. This 'abnormal' behavior indicates, that the humate species in solution are not highly charged or even almost neutral, and that the partaking in reactions with added reagents occur mainly via exchange of ions.

This conclusion is supported by independent measurements performed in other connections, in which have been proved that anionic species with charges less than or equal to -3 tend to associate so strongly with counter ions that neutralization reactions beyond that stage have the character of ion-exchange.

Figure 2 a,b.



pH in solutiom

E4/E6 in solution

From these curves are observed, that a region of the pH-pattern show only very small changes in pH with added calcium- and sodium salts. By comparison with the diagram for humate flocculated in fig. 1 is seen, that the "constancy" of pH coincide with the region where the major part of the flocculation reaction occurs. This indicates, that flocculation is mainly governed by exchange of sodium with calcium according to the following reaction scheme:

Eqn. 1

$$n*HuNa_x+y*Ca^{2+}=(Hu)_nCa_yNa_{nx-2y}+2yNa^+$$

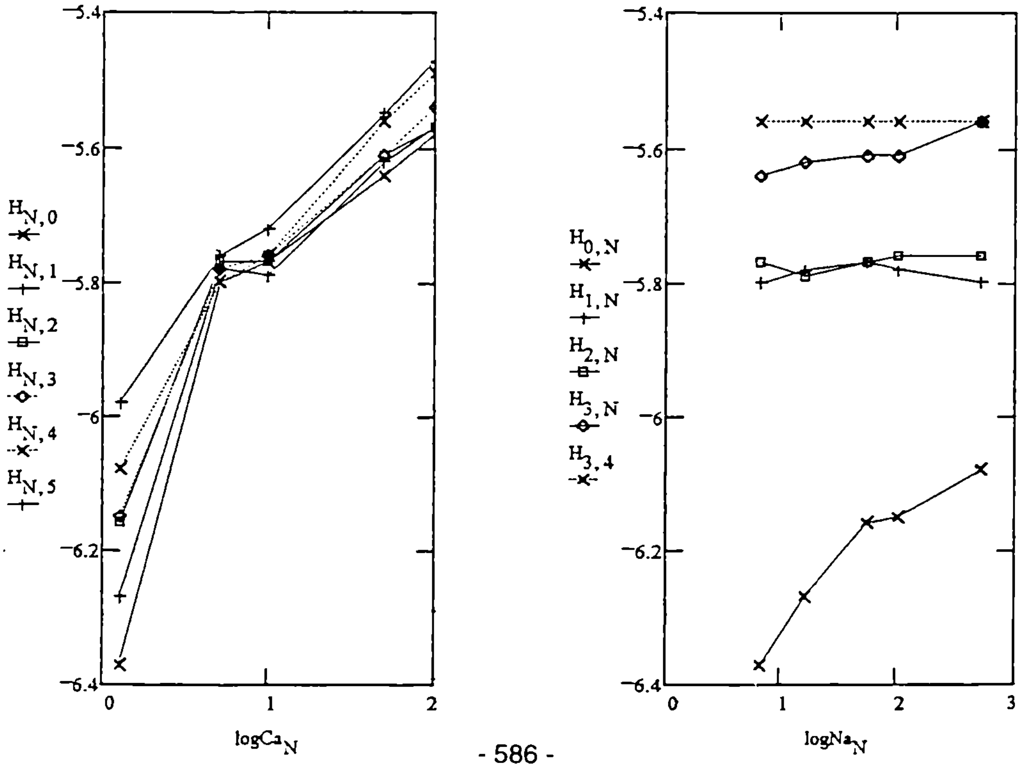
The pH pattern beyond the flocculation displays a slight pH change indicating that the the primary flocculate may contain minor amounts of residual protons, which are exchanged when additional sodium or calcium ions are added.

The E4/E6 ratios, which are displayed in fig. 2, are ratios of the absorbances measured on solutions of humic acids at two wavelengths. For a given type of humic acid, it has been found, that when the ratio is small, the moleweight is large and vice versa, but the number cannot be used as a general quantitative measure of size of different samples.
The data presented indicate that the flocculate is primarily formed from the larger humate species, but with increasing calcium concentrations, smaller species are also precipitated. There is no obvious indication of the formation of soluble aggregates or polymers before the onset of flocculation.

A standard procedure for identifying the stoichiometry of chemical reactions is to plot the logarithm of the concentration of one species against the logarithm of the concentration of a probable reactant. The limiting slopes at low concentrations will indicate the ratio between the number of moles of the reactant in the product to the monomer. In the case of the formation of a precipitate, which can be considered as an infinite polymer, the slope should be infinite at the onset of flocculation.
The basis for this analysis is easily derived by taking the logarithm of the law-of-mass-action expressions, which, however, are only valid for data obtained at equilibrium. In fig. 3 are shown the plots of log(H) versus log(Catot) and log(Natot). Unfortunately it was not possible to measure the free Ca and Na concentrations directly, but because the amounts of the added cations which are bound to the flocculate are rather small, the curves presented can be used as fair approximations to the more correct expressions.

Figure 3 a,b.

log(H) as a function of log(Ca-tot) and log(Na-tot)



From fig. 3a is found a limiting slope of appr. one at the lowest sodium concentration. The slope is gradually diminished when the sodium concentrations are increased merging into the slope of zero, where the curves almost coincide.
It is here noted, that too few experimental points are available allowing for a precise quantitative definition of the shape of the curves.
Tentatively the following reaction scheme may "explain" the first rise which is observed.

Eqn.2

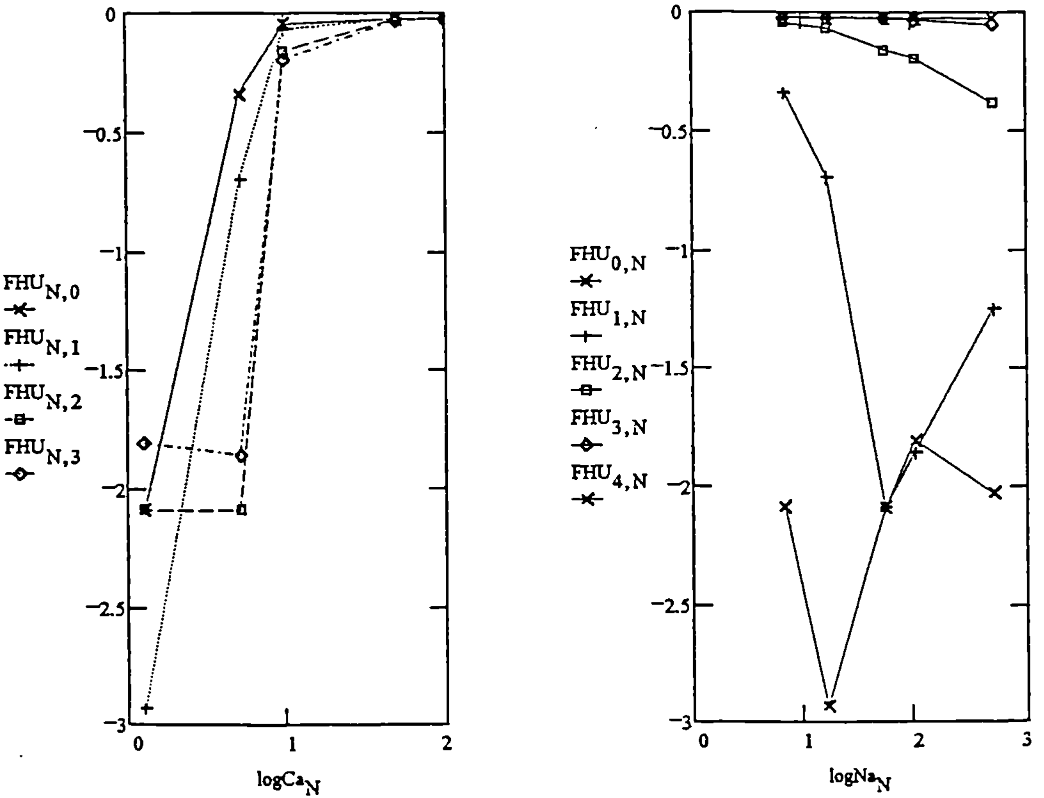
$$HuNa_xH_y + Ca^{2+} = HuNa_{x-z}H_{y-(1-z)} + zNa^+ + (2-z)H^+$$

where z varies from 1(0 ?) to 2.

In fig. 3b is observed a slight increase in free protons with increase in sodium concentrations when the calcium concentrations are small, but else very small changes. This could be explained as being due to proton-sodium ion exchange on soluble humic acids at low calcium concentrations and a calcium-sodium ion exchange during flocculation as the reverse of eqn.1. The observed dissolution of a flocculate by the addtion of modest amounts of sodium chloride does in fact demand an equilibrium reaction of this type, in which a soluble sodium-humate "complex" is formed.

Figure 4 a,b.

log(fract. humate flocculated) as a function of log(ppm Ca-tot) and log(ppm Na-tot).



In figs. 4a,b the effects of varying concentrations of calcium and sodium concentrations on the formation of a flocculate are shown.

A couple of the curves in fig. 4a indicate the very steep increase expected in an equilibrium transition from a soluble to a precipitated species. It is expected, that with more closely spaced data it should be possible to characterise the flocculation process both with regard to the effect of sodium concentrations and the total humic acid present.

The curves in fig.4b confirm the observation, that the flocculate tend to redissolve when increasing amounts of sodium chloride is added. For the two lowest calcium concentrations there is an indication of the formation of a sodium enriched flocculate.

CONCLUSIONS.

Although it is premature to elaborate on a model describing humic acid behavior, the observations made indicate, that it is governed by equilibrium reactions and thus should be amenable to purely thermodynamic modelling.
However, to be able to characterise the reactions more data are needed especially with smaller concentration steps between the experimental conditions and also with varying humic acid concentrations.

A feasible model might describe the flocculate as solid solutions of HHu, NaHu and $CaHu_2$ into eachother in equilibrium with as yet non-characterised soluble "complexes" with humic acid.
A simple model along these lines is at present being tested.

THE ROLE OF COLLOIDS IN THE TRANSPORT OF RADIONUCLIDES IN GEOLOGICAL MEDIA

Contractors:	CEA (F), CIEMAT (E), CNRS (F), GERMETRAD (F), GSF (D), INFM (I), INTERA (GB), NRI (CZ)
Contract n°:	FI2W/0097
Duration of contract:	from October 1, 1991 to December 31, 1994
Period covered:	January - December 1993
Project Leaders:	V. Moulin, P. Rivas, JC. Dran, J. Piéri, H. Lang, G. Della Mea, P. Grindrod, V. Balek

A. OBJECTIVES AND SCOPE

The main objective of this programme is to understand how colloids could influence the migration behaviour of radionuclides in geological formations. This is being achieved firstly, by identifying the *retention mechanisms* of colloids and pseudocolloids on mineral surfaces by static and dynamic experiments, and secondly by investigating the formation of pseudocolloids. These studies will provide an insight into retention mechanisms and there upon validate retardation parameters used in *transport models,* which will be developed to predict colloid transport under conditions relevant to geological disposals. Moreover, this research is focused on *model systems* (surfaces, colloids) selected from studies carried out on the El Berrocal site (Spain).

Two types of experiments are planned, depending on whether well-characterised colloidal solutions interact with mineral surfaces (as monoliths), allowing the solid-liquid phase analysis (batch tests), or powdered materials (batch and column tests). For the study of pseudocolloid formation, sorption experiments (batch tests) with radionuclides are conducted either with model inorganic colloidal suspensions or with mineral monoliths as macroscopic surfaces of colloids. Dynamic experiments are performed using well-defined packing of both synthetic and natural minerals (major constituents of granite, such as those found at "El Berrocal"). Moreover, a particular attention is devoted to the *organic coatings* (under static and dynamic conditions). These studies will provide data directly usable by migration models. These models are developed to predict colloid transport under conditions relevant to geological disposals.

B. WORK PROGRAMME

B.1. Colloid properties
B.1.1. Colloid characterisation
B.1.2. Application to a site
B.2. Sorption mechanisms
B.2.1. Pseudocolloid formation: association of radioelements with colloids
B.2.2. Interaction of colloids and pseudocolloids on mineral surfaces
B.3. Transport mechanisms
B.3.1. Transport experiments in model systems without organic coatings
B3.2. Transport experiments in model systems with organic coatings
B.4. Modelling

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The main emphasis of work in this period (Jan-Dec 93) has involved:

- the characterisation of natural colloids from El Berrocal groundwaters (more or less oxidised conditions) in relation with their geological and geochemical environment, with a particular interest to their stability;

- the interaction of actinides with colloidal suspensions through static experiments and radiochemical analysis (formation of pseudocolloids); the effect of pH, ionic strength, the presence of competing cations has been particularly studied in the case of systems constituted by silica colloids and americium/uranium;

- the interaction of colloidal and pseudocolloidal suspensions with mineral surfaces through static experiments and ion beam analysis with a particular attention to the reversibility and the surface coverage;

- the transport behaviour of radioelements and colloids within model porous media through column experiments; the influence of organic coatings has been specially investigated;

- the development of a theoretical model to account for the transport of colloids in geological media which will be validated by means of the present experimental data.

Progress and results

1. Colloid properties: Application to a site, "El Berrocal" (Spain) (CIEMAT, CEA)[1]

The characterisation of the colloids from El Berrocal groundwaters has been performed for different types of groundwaters (with more or less oxidising conditions: S1,S2,S7) with a particular attention to their origin and the mechanisms involved in their generation. Their main characteristics identified by several methods (electronic microscopy, photon correlation spectroscopy, micro-analysis X) are the following:

- silica colloids occur in all the waters as well as aluminosilicates,
- the colloids from the bicarbonate hydrofacies (S2 and S7) groundwaters are composed of carbonate phases,
- the less oxidised groundwater (S7) contains colloids mainly composed of sulphur phases,
- the less oxidised groundwater (S7) exhibits a higher content of colloids.

With respect to these characteristics, the role of the different components of the system such as the mineralogical composition of the bedrock (granite, clayey materials from fracture fillings) and the physico-chemical conditions has been identified in order to identify their contribution in the nature of colloids occurring in the groundwaters of the "El Berrocal" site. In addition, one focused our interest on the mechanisms involved in the colloid generation. From a general point of view, the colloidal phases identified in the three types of groundwaters here studied are mainly formed by condensation

---

[1] This working task on the "El Berrocal site" leads to have strong interactions with another CEC contract "Matrix Rock Diffusion" (FI2W-CT91-0082) coordinated by Exeter University (Dr Heath).

processes linked to the bedrock properties and physico-chemical conditions. The only distinctive feature between groundwaters is the higher proportion of colloids in the less oxidised groundwater. Analyses are in progress in order to investigate the relation between colloid content and conditions of oxido-reduction.

The stability of these natural colloids as well as of those generated by the clayey materials constituting is strongly dependent of pH, particularly n the acidic pH-range. Further studies are in progress for the ionic strength.

2. Sorption mechanisms (CEA, CNRS, GSF, INFM)

The main aim of this working phase is to determine the retention mechanisms of colloids and pseudocolloids (association of radionuclides with colloids) on mineral surfaces which induces to study firstly the formation of pseudocolloids and secondly the interaction of model colloids (true, pseudo) with mineral surfaces. In this part, model systems are used for

* *the colloidal suspensions*: either representative of those identified in "El Berrocal" ground waters with respect to their composition, or representative of specific charges or sizes

* *the mineral surfaces*: representative of the constituents of the granitic geological barrier.

Formation of peudocolloids[2] (CEA, CNRS, GSF, INFM)

Two complementary batch tests are performed within this task:

1) sorption experiments with fine particle suspensions and radionuclides or chemical analogues and use of radiochemical analysis of the liquid phase (CEA,GSF)

2) sorption experiments with mineral monoliths (considered as macroscopic surfaces of fine particles) and heavy elements and use of Rutherford Backscattering Spectrometry (RBS) for the analysis of the solid surface (CEA, CNRS, INFM).

The scavenging properties of model colloids (silica, clays) towards trivalent (Am, Nd) and hexavalent cations (U) have been studied by these two approaches (colloids, monoliths) which show a good agreement. Retention mechanisms have been proposed to describe the sorption of Am (III) and U (VI) on silica and mica particle suspensions through the use of the surface complexation model (in its non-electrostatic form). In both cases, no effect of calcium as competing cation has been observed on the cation retention on colloid or monolith surface in the concentration range found in natural waters (below 0.001 M). Moreover, through the study of the monolith systems, the surface coverage of the cation is less than one monolayer (0.1 - 0.2).

The reversibility of cation sorption onto colloids with respect to pH appears dependent on the conditions (in particular ionic strength, particle concentration, cation concentration). In the case of the cation-monolith system, the sorption of the cation does not exhibit a complete reversibility with respect to the solution composition (such a cautious statement is due to the uncertainty of the measurements at low cation concentration).

A particular attention is now devoted to the role of humic substances in the retention behaviour of cations on mineral surfaces (either colloids or monoliths).

---

[2] In the framework of this working task, a collaboration with another CEC contract "Development of a model for radionuclide transport by colloids in geosphere" (FI2W-CT91-0079) coordinated by ARMINES (Dr Ledoux) becomes effective.

Interaction (retention) of colloids and pseudocolloids with mineral surfaces (CEA, CNRS,INFM)

The interaction of colloids (true or pseudo) with mineral surfaces (as monoliths) is studied by batch tests on model systems (colloids, monoliths, cations) by using Rutherford Backscattering Spectrometry (RBS) for the analysis of the surface. This technique allows to determine the quantity of the heavy element fixed (in atoms/cm^2) as well as the depth distribution.

For this working task, different items are studied:

- the influence of the characteristics of the components as the size and the charge of the colloids and the charge and the composition of mineral surfaces;
- the effect of addition order of the constituents (simultaneously or sequentially);
- the influence of physico-chemical parameters: pH, ionic strength;
- the reversibility (with respect to solution composition);
- the influence of organic coatings on mineral surfaces (see section 3.).

Different systems have been investigated such as i) binary systems (monolith, colloid) ii) ternary systems (monolith, colloid, cation or monolith, colloid1, colloid2). The monoliths are either silica (untreated, prehydrated), mica or hematite; the colloids either CeO_2 (50nm), Fe_2O_3 (hematite, 100nm), SiO_2 (80 nm) or ThO_2 (5 nm); the ions either Nd (III) or U (VI).

The main features arising from the study of the binary systems are:

a) Effect of colloid concentration (0.5 - 100 ppm): for all systems there is an increase of the amount sorbed up to about 0.1-0.2 monolayer (figure 1); the surface coverage is always less than one monolayer;

b) Effect of ionic strength (0.001-0.1 M): no clear trend is observed, likely due to the instability of colloidal suspensions;

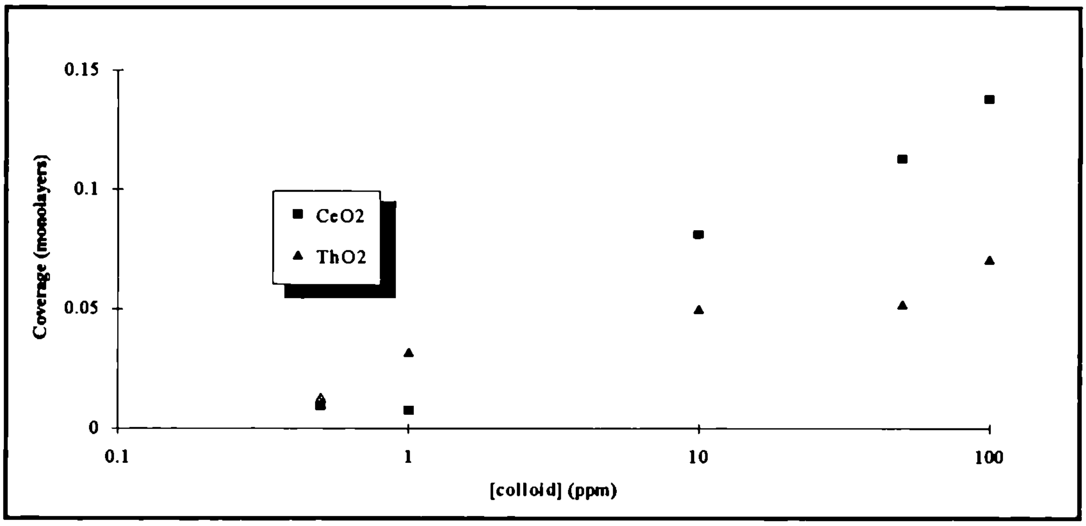


Figure 1: Surface coverage (in terms of monolayer) as a function of colloid concentration for the systems constituted by ceria or thoria colloids and silica surfaces (pH ~5; $NaClO_4$ 0.001 M)

c) Effect of pH (3-8): a marked increase of sorption on silica or mica surfaces with pH for thoria colloids is noticed whereas an irregular variation for ceria colloids;

d) Effect of the type of monolith and of surface pretreatment: no marked influence is seen;

e) Response to reversibility test (up to 7 days): for all systems, the sorption mostly appears irreversible (with respect to solution composition) whatever the solution parameters.

From a general viewpoint, it also appears that the colloid sorption is a surficial process.

The effect of the order of sequential addition of reactants (ternary systems constituted by the monolith, colloids 1 and 2) is noticeable with the following observation: the presence of a carrier colloid (silica or hematite) reduces the sorption of heavy elements (in the form of ceria or thoria colloids), whereas a layer of presorbed colloids favours the fixation of heavy elements.

The future prospects will concern i) experimental improvements (use of a complementary analytical technique to avoid heterogeneity problems; test of a new experimental procedure to evaluate the influence of colloid sedimentation) ii) the influence of physico-chemical parameters such as other colloidal and pseudocolloidal suspensions, the effect of organic coatings and the reversibility study with respect to pH and other solution characteristics and iii) shift from pure model systems to more realistic ones (use of granitic groundwater of "El Berrocal" site or use of whole rock samples of "El Berrocal" site).

In the framework of the static experiments, a particular attention is devoted to the changes occurring on solid surfaces (colloid, monolith) during sorption processes through the use of the Radon Emanation Method (REM: labelling with Th228 and measurement of release rate of radon) developed by the NRI (Nuclear Research Institute). This method permits to investigate rapid changes on the solids and at the interfaces and brings information on the retention dynamic (i.e. kinetics). The same systems as those studied in the project are under investigation.

3. Transport mechanisms (GSF, GERMETRAD)

The main goals of this part is to determine the transport mechanisms of colloids as well as the role of colloids on the transport of radioelements through well defined materials (column experiments). In particular, the contribution of filtration effects as well as sorption effects has to be identified. For this purpose, flow-through column tests on model systems are carried out as a function of:

- the colloid characteristics (size, charge)
- the water chemistry (typical boundary conditions)
- the hydrodynamic factors (flow-rate)

A particular attention is devoted to the role of the organic coatings.

Transport experiments in model systems in the absence of organics (GSF)

These transport experiments which are investigated to infer the colloid and pseudocolloid transport in porous media are carried out in small columns packed with stable monodisperse materials (either glass beads or quartz sand). In order to achieve the objectives, batch (determination of sorption and desorption coefficients) and column tests are performed in parallel in order to better understand the sorption and transport mechanisms of colloids (true or pseudo).

The main characteristics of these column packings (with different granulometries) have been determined, in particular their ion-exchange capacity, their surface area and their pore volume and pore size distribution (table 2). Before handling colloids and pseudocolloids, breakthrough curves of radionuclides (tracers such as ^{36}Cl; ions such as ^{85}Sr, ^{45}Ca, ^{22}Na; potential colloids such as ^{144}Ce, ^{152}Eu) have been obtained on these model columns with different mobile phases (NaCl 0.01 M, $CaCl_2$ 0.01 M, ammonium formate 0.01 M, synthetic "El Berrocal" water (borehole S1): pH 6.8; I=0.0012; cations: Ca,Mg,Na,K; anions: Cl,SO_4,HCO_3). In particular, through these flow-through column tests, the importance of isotope- and ion-exchange mechanisms has been quantified showing a very small contribution of the isotopic effects compared to the ionic exchange effects.

As the main properties of the colloidal systems are linked to their charge, the electrostatic surface charges of the colloids under investigation (ceria, silica, iron oxides) have to be determined. In addition, latex particles (fluorescent) are also used in order to stress important features. Streaming potential studies have thus been performed qualitatively and quantitatively using a special streaming current technique. Under the conditions of the synthetic groundwater, negatively charged colloids are occurring for silica and latex particles, whereas ceria colloids are found to be positively charged.

The first transport experiments dealing with these colloids (ceria and silica) have shown that they are quantitatively filtered within the first 5cm of the column packing. This effect could not be explained by a filtration caused by the pore size of the column bed which is about 100 times bigger than the size of the colloids. Electrostatic interactions between colloids and filter bed are thus assumed to exist. Further experiments are under progress with these systems.

The use of fluorescent latex spheres (negatively charged) in the flow-through column tests has allowed to show that no retardation (or scarcely) occurs (the batch tests have shown very low affinity of these entities for the packing materials) but a very low recovery of particles (27 % to 1 % according to their sizes) is observed (figure 2). These experiments illustrate the importance of filtration effects in colloid transport phenomena.

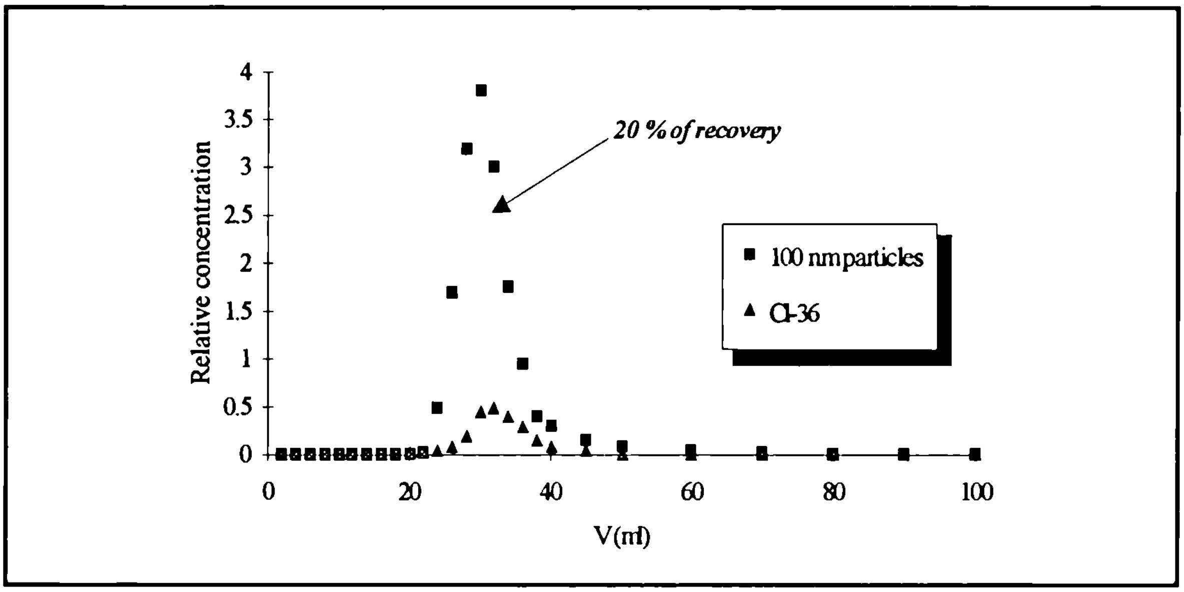


Figure 2: Flow-through column tests performed with tracer (Cl) and 100 nm particles. Column packing: glass beads (0.8-0.11 mm); column dimension: 2.5 cm of diameter and 14.5 cm of length; elution with synthetic water (1 ml/h).

The percent of particle recovery is indicated: 20 % for 100 nm particles, 0 % for 200 nm particles.

Transport experiments in model systems in the presence of organic coatings (GERMETRAD)

The effect of organic coatings on the transport of radionuclides (in the ionic, colloidal or pseudocolloidal form) is evaluated through dynamic experiments performed with columns filled with silica beads covered with humic acids. A novel procedure has been developed in order to link the organic molecules (through covalent bonding) on the well-defined packing particles of silica. Hence stable "humic acid columns" are realised. Moreover this procedure is applied to coat humic substances on the monoliths used in the section 2.B. Sorption experiments are under progress with these samples.

The procedure followed in these dynamic experiments is illustrated on figure 3.

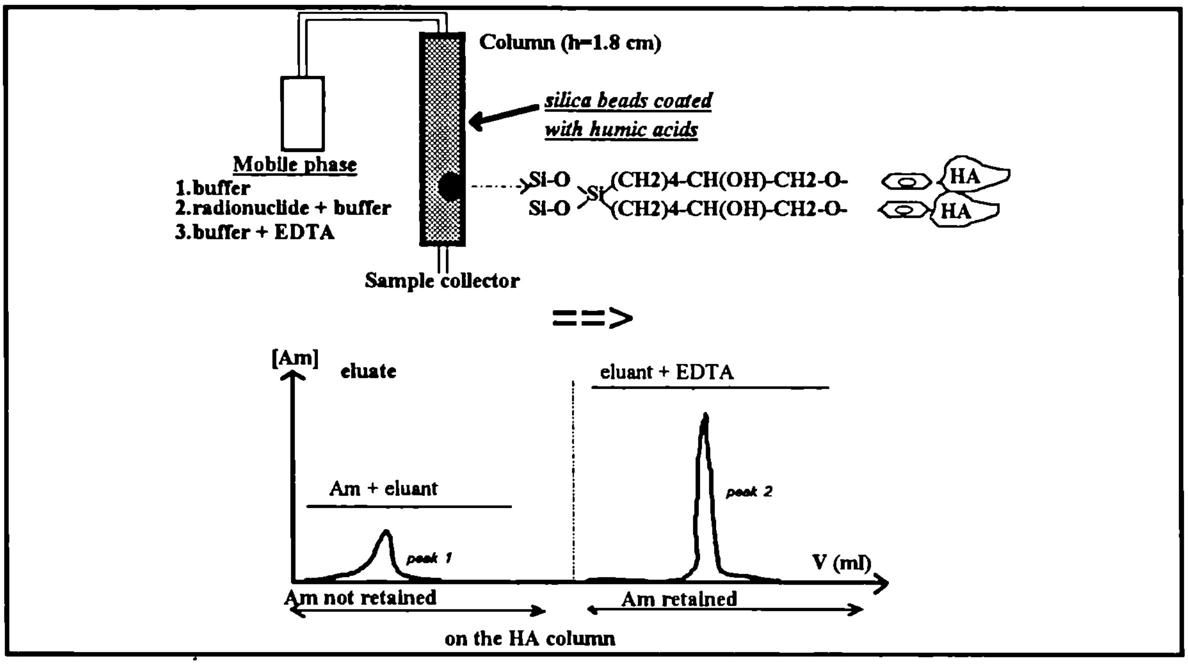


Figure 3: Schematic representation of the procedure followed in the dynamic experiment with organic coatings

The affinity of a radionuclide such as americium for the "humic acid" (HA) column has been determined in various medium (phosphate and carbonate buffers) at different flow-rates. The main features arising from the present studies are:

a) a great effect of flow-rate according to pH on the Am recovery: the binding of americium for the "HA column" decreases with increasing the flow-rate in phosphate buffer; at low flow-rate (5 ml/h) only 10% of americium is eluted at pH 7.5 and pH 8;
b) the importance of Am speciation on the Am elution curve: a large retardation of Am on the "HA column" at acidic pH is observed, whereas a decrease of binding with increasing pH (pH 7.5 to 8.7) is noticed; in this pH range hydrolysed and carbonate species are occurring. In order to underline the importance of the nature of Am species, experiments have been performed at pH 8 under argon atmosphere showing a higher retention of hydrolysed species than carbonate complexes (figure 4). In carbonate medium (pH 8.2), americium presents a relatively low affinity for the "HA column" whatever the flow-rate, except at low flow-rate (5 ml/h) where 50% of americium is retained on the "HA column".

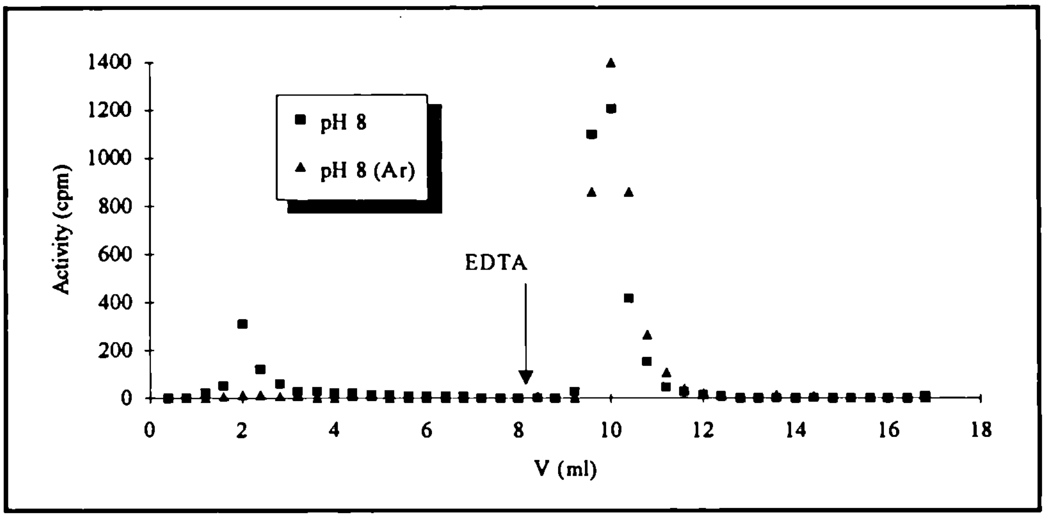


Figure 4: Am elution curves on the "HA column" at pH 8 (under Ar atmosphere or not); 3 ml/h; phosphate buffer; Am activity injected: 3700 cpm

Parallel experiments with pure silica as the packing material have also been carried out in order to underline the effect of the organic coatings. Moreover, studies with Am as a pseudocolloid will be also performed as well as studies with other radionuclides.

These studies show that carbonatation and hydrolysis reactions could compete with the formation of organic complexes in specific conditions. However, it appears that at neutral-alkaline pH (7-8) and a low flow-rate, organic complexes could occur in a relatively high proportion. These results are particularly important because of the lack of data on Am speciation in this pH range in the presence of carbonate, hydroxide and organic ligands.

4. Modelling (INTERA)

The modelling of colloid transport through fractured and porous media has been developed so as to provide:

- an initial review and discussion of theoretical and experimental issues from the transport modelling perspective;
- calculations of elution rates and dispersivities which could be generalised and calibrated by the experimental data;
- a consideration of the microscopic models useful in characterising dynamic processes prior to the derivation of microscopic migration parameters.

As a result of this initial phase, it is suggested that wherever possible simultaneous elution curves for both colloids and a non-sorbing tracer should be obtained. The principle is that the tracer breakthrough and dispersion embodies fundamental information regarding the flow path geometry and flow regime, and that the *relative* behaviour of the colloids to that of such a tracer will be robust for similar columns (rather than the absolute properties). It was also concluded that capture surface geometry is likely to have a large impact on the capture and dispersion of colloids, yet remains largely uncertain. Hence there is a need initially to focus on well characterised stream tubes or packed media.

It has been considered a range of process models for colloid media interactions. These terms are considered in both static and dynamic situations. Generally it is the aim to formulate a range of candidate processes and consider what support there is for each one from the experimental behaviour obtained within the project. Key processes, that is those which are not shown to be invalid or inappropriate, can be included in migration models, along side the considerations of flow rates and dispersion rates made during the earlier part of this project. The retardation processes under consideration are :

a) linear instantaneous adsorption partition ;
b) first order kinetic adsorption/desorption ;
c) diffusion into stagnant water within the medium or rock matrix (this characterises the tails of breakthrough curves, as $t^{-3/2}$, when present).

The mathematical models can be derived in a number of ways, so here "adsorption" can be taken to be either or both physical and chemical retention and release of colloids. These processes can be surimposed (since they are linear) and hence a composite model will be used to analyse the transport data available from the GERMETRAD humic column experiments.

Colloid-media interactions may be non-linear though, being effectively limited to partial monolayer coverage of surfaces by either steric repulsion due to previously immobilised colloids, or a limited distribution to active sorption sites. Since there is growing evidence of partial monolayer formation within the monolith experiments (see section 2), we have modelled this mechanism. The resulting non-linear terms controlling either dynamic or fast (instantaneous) monolayer formation, result in a non-linear migration model. Nevertheless we have shown that these equations are amenable to direct analysis, and obtained estimates for frontal propagation which could be used to model column experiments or else to verify non-linear model solvers.

The modelling component of this project is in three distinct parts :

(i) colloid migration processes - effective flow rates, dispersivities, relative to tracer migration;
(ii) colloid-media interaction - retardation mechanisms;
(iii) colloid-radioelement interactions.

To date (i) is complete, (ii) is ongoing and will be completed and (iii) will be covered during the final year of the project, relying on the static experimental data obtained within this programme.

LIST OF PUBLICATIONS

Dran J.C., Della Mea G., Moulin V., Petit J.-C. and Rigato V., Interaction of pseudocolloids with mineral surfaces: the fate of the scavenged cation. Radiochimica Acta, submitted (1993) Presented at Migr ation 93 Conference (USA, December 1993)

Gomez P., Turrero M.J., Moulin V. and Magonthier M.C., Characterization of natural colloids in groundwaters of "El Berrocal" (Spain). 7th International Symposium on Water Rock Interaction WRI-7, Proceedings, Kharaka & Maest (Eds) Balkema, Rotterdam, pp 797-800 (1992)

Della Mea G., Dran J.C., Moulin V., Petit J.C. , Ramsay J.D.F. and Theyssier M., Scavenging properties of inorganic colloids toward heavy elements, Radiochim. Acta 58/59, 219-223 (1992)

Moulin V., Labonne N., Theyssier M., Vilarem J.P., Magonthier M.C., Ménager M.T., Dran J.C., Milcent M.C., Durand JP., Goudard F., Bioret A., Piéri J., Della Mea G., Wolfrum C., Gomez P., Turrero M.J., Rivas P., Perez del Villar L., Grindrod P., Edwards M., The role of colloids in the transport of radionuclides in geological media. RT DSD/92.74 (2nd progress report CCE 0097) (1992)

Moulin V., Labonne N., Theyssier M., Vilarem J.P.., Dran J.C., Milcent M.C., Durand JP., Goudard F., Bioret A., Piéri J., Della Mea G., Lang H., Gomez P., Turrero M.J., Perez del Villar L., Rivas P., Grindrod P., Edwards M. and Thomas R., The role of colloids in the transport of radionuclides in geological media. RT DSD/93.98 (3rd progress report CCE 0097) (1993)

Grindrod P., Brown R.C. and Gealy N.D., Colloid migration and dispersion within saturated media: a modelling perspective, Draft, Intera Technical Report I2421-1(1992)

Grindrod P.,Edwards M. and Higgo J., Validation of processes governing colloid migration. To be submitted.(1993) Presented at Migration 93 Conference (USA, December 1993)

Title: Analysis of the geoenvironmental conditions as morphological evolution factors of the sand-clay series of the Tiberine Valley and the Dunarobba forest preservation
Contractor: Dipartimento di Scienze della Terra - Università di Roma "La Sapienza"
Contract N°: FI2W/0121
Duration of Contract: from August 1992 to January 1995
Period covered: January 1993 - December 1993
Coordinator: Giovanni Valentini (Università degli Studi "La Sapienza")
Leaders: Pierluigi Ambrosetti (Università degli Studi di Perugia), Dr. Peter Grainger (University of Exeter)

A. *OBJECTIVES AND SCOPE*

Based on the large presence of fossil trunks in the alluvial deposits of the Tiber basin outcropping near Todi, Umbertide and Dunarobba villages (Umbria region, Central Italy), the proponents of the present research believed worth of interest to study such geological environment that may be considered as a "natural analogue". In particular, Dunarobba Forest site represents a large and rare data source and natural laboratory in order to achieve further informations about geological formations as potential nuclear waste repositories. The research's principal aim is the definition of the geological, hydrogeological and geochemical processes which allowed the preservation of the vegetable matter in Dunarobba area. The definition of the processes which led to the lignitification of coevi deposits is important as a term of comparison and in order to better interpret the whole environmental evolution as well. In order to study and to analyze the most influential parameters which could have been affecting the geochemical processes which allowed the organic matter to be preserved from the forest formation until now, it is necessary to reconstruct the present environmental scenario and, based on the analysis of probable evolution indicators, to understand the past ones, with particular reference to the geochemical conditions.

The following topics have been considered of basic importance:
a) the acquisition of the geological, tectonic and hydrogeological boundary conditions;
b) the definition, in the area of Dunarobba Forest, of the whole stratigraphic sequence along with the structural, hydrogeological and geochemical conditions, the mineralogical and petrographical features, the permeability as regards to endogenetic gases, density and water natural content of rock bodies and finally the stress and drainage conditions inside the soil masses;
c) the reconstruction of the past geomorphological conditions underwent by the continental deposits and the present geomorphological framework.

In order to achieve an exhaustive definition of the most of factors which allowed the described environment to be preserved, it has been realized a partnership among Rome University (I), Perugia University (I) and Exeter E.R.C. (U.K.).

B. *WORK PROGRAMME*

About the reconstruction of the present and past environmental scenarios it is necessary to define:
1) - the basin boundary conditions, the lythostratigraphy of the alluvial deposits and the principal fault systems in order to scan the evolution of the Tiberine Valley environmental scenarios from the forest formation until Present;
2) - the hydrogeological scenario with reference to the geometry of the aquifers, the groundwater flow networks and the phreatic water geochemistry;
3) - the spatial distribution of the inorganic and organic matter in the solid phase and of the liquid phase in the interstitial space of the Tiberine depositional sequences with particular reference to the mineralogical, petrographical, geochemical and physical characters;

4) - the consolidation state of the fine grained sequences as an indicator of the drainage conditions inside the studied deposits;
5) - the fossil trunks boundary geochemical conditions and the geochemistry of the organic matter (both well preserved trunks and lignite deposits) with particular reference to the interactions between organic (wood) and inorganic (clay) matter.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1.1 Basin geometric boundary conditions

The application of gravimetric methodologies, which are consistent with the large differences of density values between the alluvial deposits and the carbonatic substratum, allowed a preliminary reconstruction of the tridimensional geometry of the plio-pleistocenic basin.
The map of Bouguer's anomalies[1] shows a clear thickening of the isoanomalies in the limestone and marly-limestone outcrop areas with higher values in the western border of the basin. The presence of a clear gravimetric low, having a N-S trend south of the Naja stream and a NW-SE trend north of it, is fundamental in defining the geometry of the basin (fig. 2). Close to the Dunarobba village area, the isoanomalies put in evidence a relative gravimetric low. The geological models based on such gravimetric surveys may be summarized in the following way (fig. 3a and 3b):

1) thicknesses of the plio-pleistocenic sediments greater in the northern part of the area (up to 2300 m) and significant decreases toward the southern end, probably connected with the presence of a threshold, which could have allowed the formation of local basins;

2) calcareous bedrock dislocations given by dip-slip faults having throws up to hundreds of meters and which reach also the plio-pleistocenic units;

3) lower thickness of the plio-pleistocenic deposits toward the western and eastern margins of the basin; these are greater in the southern part of the area where, close to the Dunarobba forest, it is possible to recognize a satellite basin which could have been separated for a certain period from the principal one; in this area the maximum thickness of alluvial deposits is about 120 m.

These informations have been very useful for planning the drilling of a deep borehole in the Dunarobba area to better ascertain the palustrine and lacustrine deposits lythostratigraphic characters along their whole length; here, the contact between the calcareous bedrock (marly-limestones) and the alluvial deposits is 116.5 m below the ground level.

1.2 Lythostratigraphic characters of the Tiberine Valley's depositional sequences

The geological surveys and the boreholes drilled at different depths, between 30 and 121 m (fig. 4), allowed a first reconstruction of the lythostratigraphical sequences in the area. Based on the boreholes' stratigraphies (fig. 5 shows the stratigraphy of the S6 borehole as the most representative of the deposits which sorround the trunks) the sequences are prevailingly given by clays and silts with interbeddings of coarser deposits (sands and gravels) that are more frequent and thicker toward the top of the local series, where the trunks outcrop. A large number of lignite levels, at different stratigraphic heights, are interbedded in the lacustrine and palustrine sequences.

Previous deep seated investigations, carried out by boreholes drilled in the central and southern areas of the tiberine basin, give us further informations about the time variations in the depositional conditions in the whole basin which are now represented by clay-silt sequences with interbeddings of coarser sediments (sands and gravels) and lignite and peat levels.

---

[1] It has been carried out a gravimetric survey based on 286 measure points scattered on an area 180 km^2 wide which is delimited by the Amelia Mts. at the western margin, the Todi-Massa Martana lineament at the northern one, the Martani Mts. at the eastern one and Castel Todino village at the southern one.

Based on the analyses of the cores recovered during the borehole drilling, the sedimentological study of the lythostratigraphic sequences in the Dunarobba forest area allowed us to recognize depositional facies variations, that are summarized in the following way:

116.5 - 111 m on the marly-limestone substratum there are swampy facies deposits which are given by clay silt sequences and by a lignite level;

111 - 35 m lacustrine environment, represented by clay deposits interbedded by sandy-silty levels having sedimentary structures that testify a basin depth greater than 10 m.

35 - 0 m transition environment from lacustrine to palustrine; the progressive change from lacustrine conditions to emersion ones is represented by lacustrine and palustrine lythofacies alternances and the emersion phases are marked by pedogenized levels (hydromorphic paleosoils) whose characters show very high sedimentation rates which led to a rapid trunks buring.

At the top of this transitional environment, where the Dunarobba forest developed, conditions of submersion occurred and a flooded plain can be recognized. The progressive filling up of this submerged area is evidenced by the sediemntray sequence which clearly shows a decreasing in the grain size characters and thickness of the coarser deposits upwards, until the area emerges and a paleosoil overlined by a lignite bed is formed. Although the area eventually returns under water level, the lacustrine basin which settles in, does not show any evidence of clastic contribution because of morphological and/or climatic reasons. The deposits in which the forest of Dunarobba is contained would thus correspond to a coastal depositional subenvironment on the margins of a lacustrine system.

1.3 Analysis of tectonic discontinuities by regional soil-gas survey

Reconstructions of the principal tectonic discontinuities inside the fluvio-lacustrine sequences and on the Tiberine basin's borders come from first results about soil gas anomalies (He, CO_2 and Rn) based on a regional survey[2].

This study can contribute to the definition of:

- the network of gas bearing fractures that could represent potential paths for water movement as well;
- active faults whose movement possibly influenced the environmental scenario evolution of the Dunarobba area.

The connected elaborations, depicted in fig. 6 and tab. 1, suggest that a significant occurrence of endogenetic gas ascent, as expected, is along enhanced permeability paths located at the boundaries of the basin, where the main regional border fault systems are known. Major Rn and He anomalies lie on the eastern and south-western boundaries of the basin forming lineaments oriented respectively N-S and N45W. The first group of anomalies could be related to the boundary fault system (Acquasparta fault) between the basin and the Martani Mts, the second one coincides with the geologic limit between clays and marls in the Castel dell'Aquila area. Nevertheless, a SW-NE oriented linear gas anomaly crosses the basin from Castel dell'Aquila area; it is marked by all three gases, in good agreement with gravimetric and geological surveys which already suggested the presence of an important transversal tectonic element in this area. Secondary soil-gas lineaments cross Dunarobba and Montecastrilli (N45W) and the area south of Montecastrilli. Spotty anomalies occur north of Montenero and in correspondance with the carbonates-clays limit in the north-western part of the investigated area.These preliminary results show that even if background values of endogenetic gases in soil are quite low, some gas ascent phenomena occur inside the basin as well; therefore clays, locally, do not act as barrier for naturally occurring gases.

Further information about tectonic discontinuities are based on self-potential geoelectrical investigations, specifically performed in order to study the ground water flow conditions inside the tiberine alluvial sequences along the Dunarobba-Furapane scanline. They will be discussed in the following section.

---

[2] They have been collected about 100 soil-gas samples randomly distributed in the investigated area.

2. Geometries of the aquifers and of the hydrodynamic network and chemistry of the interstitial-phreatic waters

The groundwater flow network inside and around the tiberine alluvial sequences has been investigated by the self potential assessment, whose spatial variations are linked to specific oriented flows as a function of the deep structural setting. The two performed tomographies (fig. 7) give us indications about the water circulation both in a wide range of depth (0-10 km) and in a greater detail (0-1 km). Figures 8 and 9 represent the map of self potential anomalies map and the section of self potential gradients which have been necessary to construct the tomographies. The two tomographies respectively show:

a) an undulated geometry of the isolines in the whole right-hand positive portion of the large scale dipolar field that testify a prevailing ascending or discending flow between the carbonatic substratum and the alluvial deposits; the presence of an intruding shallow positive nucleus, distorting the otherwise regular pattern of the negative portion of the regional field, very closed to the Dunarobba forest area (fig. 10);

b) a very clear dipole field with a clear inclined elongated shape, centered at a depth of about 3 km b.g.l. and dipping eastward to a depth of more than 5 km; such a dipole field could likely be associated with a large scale tectonic discotinuity surface (fig. 11).

Furthermore, the high resolution dipole-dipole tomographic approach gives information about the presence of fine grained (sands and clays) sequences in the Dunarobba forest containing deposits. The DD pseudo-section is characterized by quite low resistivity values, in good agreement with the borehole data and allow to better define the spatial extension of the sand-clay deposits sorrounding the trunks; it puts also in evidence a horst-like resistivity structure that probably corresponds to the threshold pointed out by the gravimetric survey and that may be responsible for a groundwater vertical flow (fig.12).

Even though the hydrogeological data analyses are still in progress, it is possible to recognize, especially in the area of Dunarobba forest, remarkable aquifers in the sandy-clayey beds which are scarcely interconnected. With particular reference to the area of Dunarobba forest, where there are neither springs nor wells, based on the borehole drillings have been pointed out the presence of four confined aquifers whose water discharges range from 5.2 to 30 l/min. Further data will be obtained in the next months and results will be presented in the next reports.

According to this work plan, in the Dunarobba forest area, it has been defined the groundwater-flow network; it is influenced by the sandy-gravelly beds inside the clay sequences. Specific information regarding this comes from the field measurements of hydraulic parameters during the drillings, from the γ-ray logging and from the first chemico-isotopical analyses that have been until now carried out.

3. Characteristics of the inorganic and organic matter in the solid phase and of the liquid phase in the interstitial space along the sedimentary sequence in the Dunarobba area

Analyses carried out on the recovered cores pointed out significant variations of the grain size distribution, of the specific weigths and of the mineralogical and petrographical characters in relation to the stratigraphic level, as a consequence of the facies etheropies. As regards the analyzed samples[3] the grain size distributions are characterized by the prevailing silty and clayey fractions, whereas mineralogical analyses pointed out the presence of illite and smectite like minerals in the clay fraction; the Atterberg limits and the colloidal activity of the finer fraction are in good agreement with these results and assume values that are generally assigned to illitic clays (fig. 13). Chemical and isotopic

---

[3] They have been analyzed 35 samples collected along the vertical sequence from 2 m b.g.l. to 95 m b.g.l..

analyses pointed out both high carbonatic contents (between 8 and 20%) and Th & U concentrations of 5 and 2 ppm respectively in the studied sequences. Based on such information it should be possible to define the geochemical conditions which were acting during the sedimentation of the deposits that contain the Dunarobba Forest.

Specific analyses will allow to reconstruct the radionuclide migration processes, from the organic matter to the sorrounding sediments. These analyses have been started on soil samples recovered close to the vegetable matters.

In order to reconstruct the environmental scenario, with specific reference to the chemico-isotopical characters, investigations on the interstitial waters both at the boundaries of the trunks and in lower/upper stratigraphic levels have been started. They are carried out on clay samples recovered from boreholes drilled at the boundaries of the fossil trunks and they shall give further information about the paleoenvironmental conditions and about the interactions with the circulating waters.

4. Permeability assessment and analysis of the consolidation states of the fine grained deposits

Based on oedometer tests, the values of the consolidation coefficients have been assessed for the silty-clayey levels; they range from 2.67E-7 to 6.33E-8 m^2/s that suggest very low hydraulic conductivities (tab. 2) with respect to fluid migration in the finer grain deposits which behave as a barrier.

Information about the consolidation states of the silty-clayey beds comes from in situ measurements and laboratory oedometer tests respectively carried out on cores and undisturbed samples. The first ones give indications about the trends of the moisture contents and of the undrained strength parameters along the vertical sequences (see fig. 5). The second ones allow to assess the unit weigth volumes and the void ratios of the silt-clayey levels and their variations versus the distance from the ground level. The assessment of the consolidation states assumed by the finer deposits, show along the vertical sequence (especially from 0 m to 30 m b.g.l.) an alternance of beds having different consolidation ratios which is probably related to periodic phases of submersion and emersion; this is in good agreement with the paleoenvironmental reconstructions based on the sedimentological and stratigraphical analyses (section 2.2.). The knowledge about the presence of overconsolidated and normally consolidated levels gives important indications about the drainage conditions inside the alluvial sequences, as the overconsolidated levels have already come to an equilibrium state with regards to the physical interactions between solid skeleton and liquid phase.

Further investigations about the viscous behaviour of the soil system in the silty-clayey levels have been started, with particular reference to the secondary consolidation processes. The obtained results will be compared with the detailed lythostratigraphical sequence in order to have other informations about the interactions between the interstitial waters and the phreatic ones as an important influential parameter which might affect the isolation conditions of the sediments sorrounding the vegetable matter.

5. Fossil trunks boundary conditions

Once defined the environmental boundary conditions, the U/Th disequilibrium pattern analyses have been started on more than 24 samples recovered close to the wood-clay interface; they are based on alpha-spectrometry in order to assess the radionuclide diffusion processes whose definition will give indications about the geochemical evolution at the trunk boundaries.

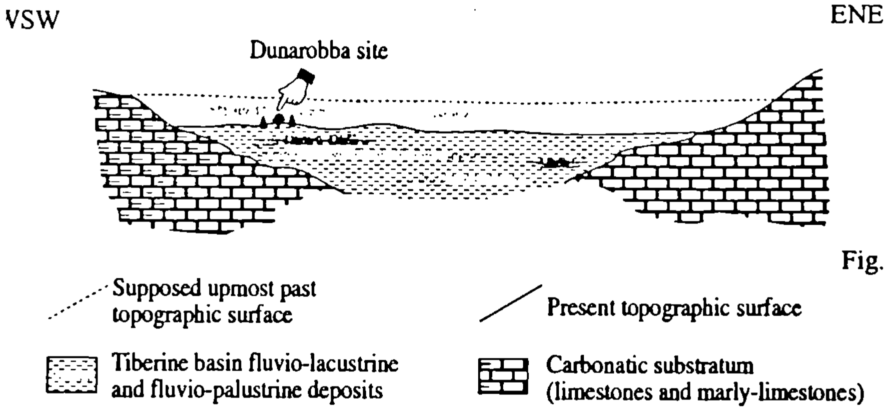


Fig. 1 - Tiber Valley hypothetical section, E-W oriented.

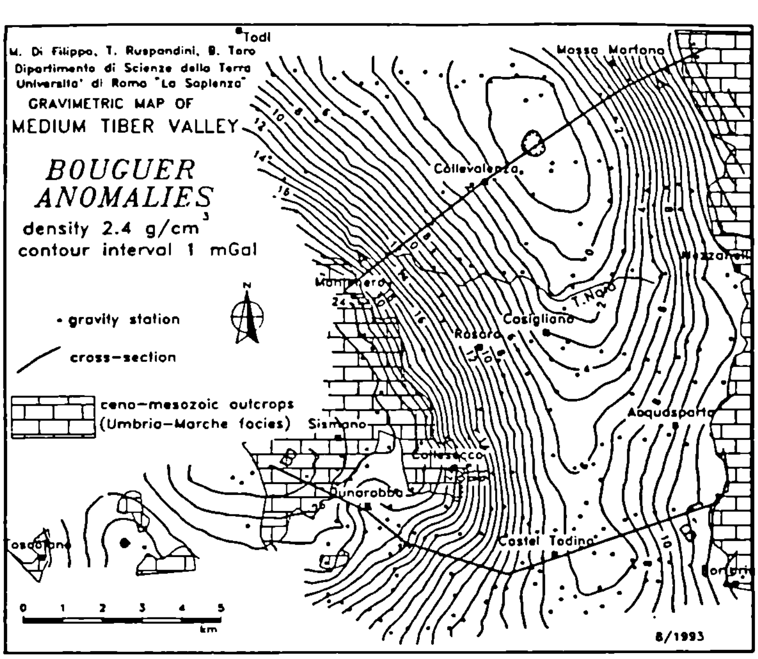


Fig. 2 - Bouguer anomalies map in the investigated area.

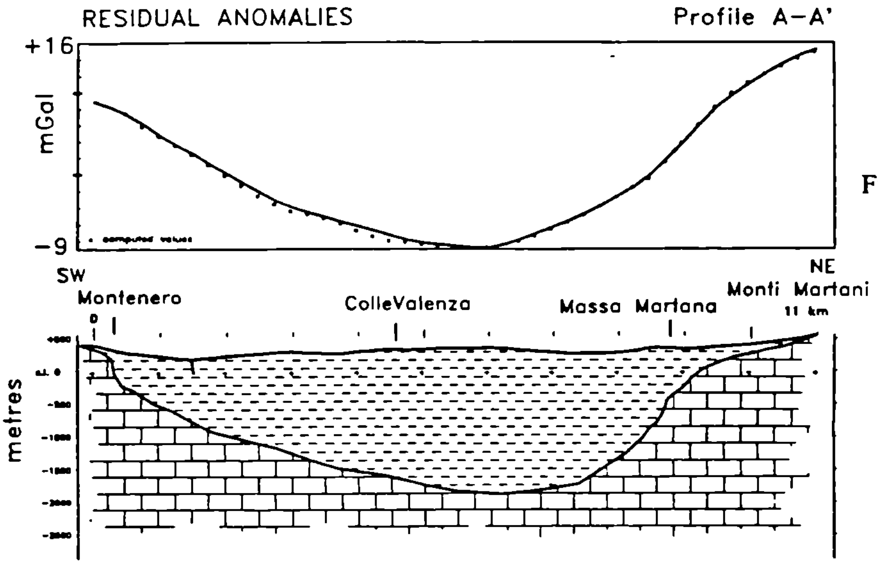


Fig. 3a - Geological profile based on gravimetric data (northern area).

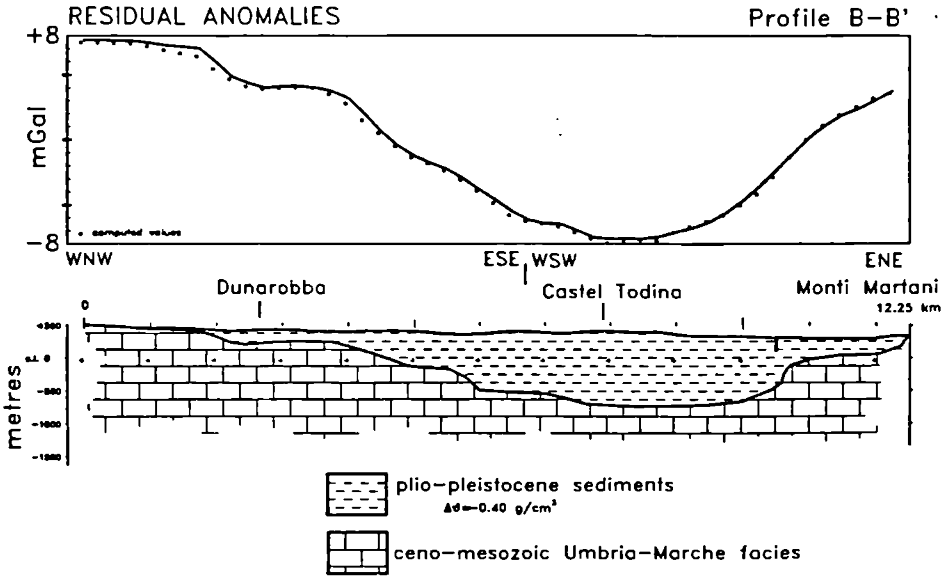


Fig. 3b - Geological profile based on gravimetric data (southern area).

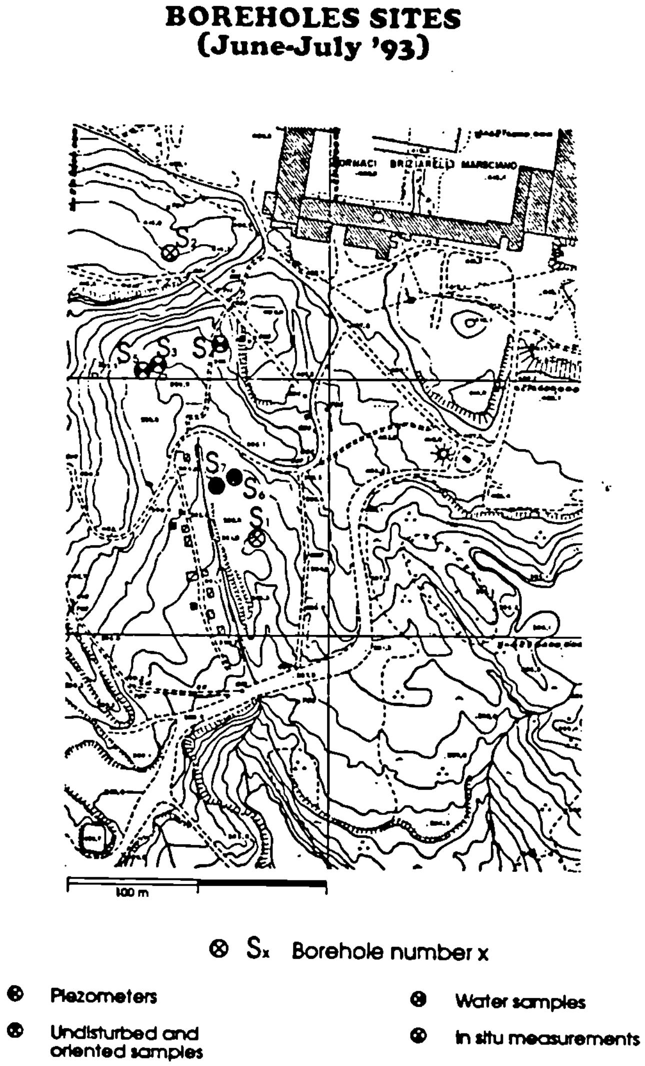


Fig. 4 -Borehole sites in the Dunarobba Forest area.

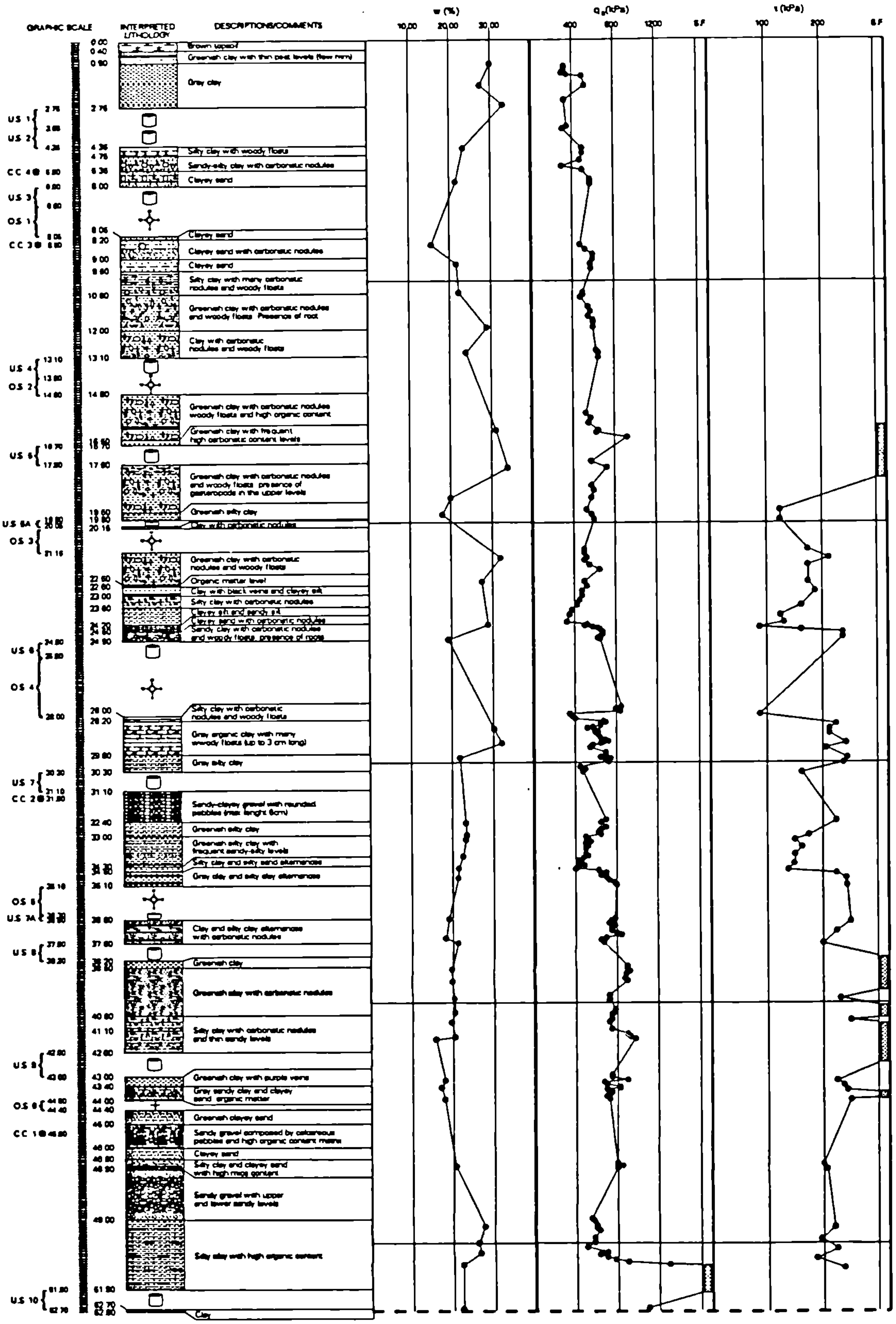


Fig. 5 - S6 Borehole lythostratigraphical reconstruction and physical parameters (moisture content, undrained strengths).

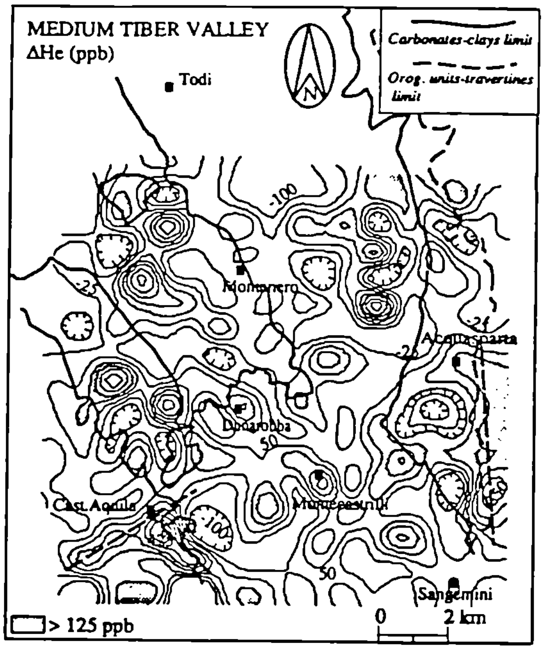


Fig. 6a

Fig. 6 - Soil gases maps (He, Rn, CO_2)

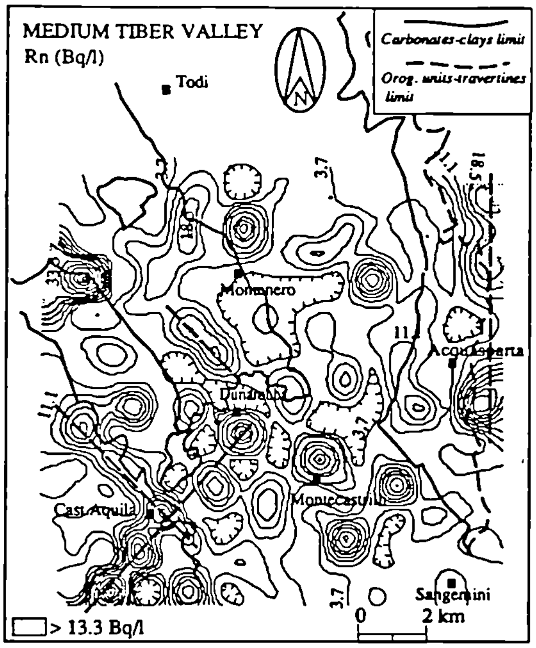


Fig. 6b

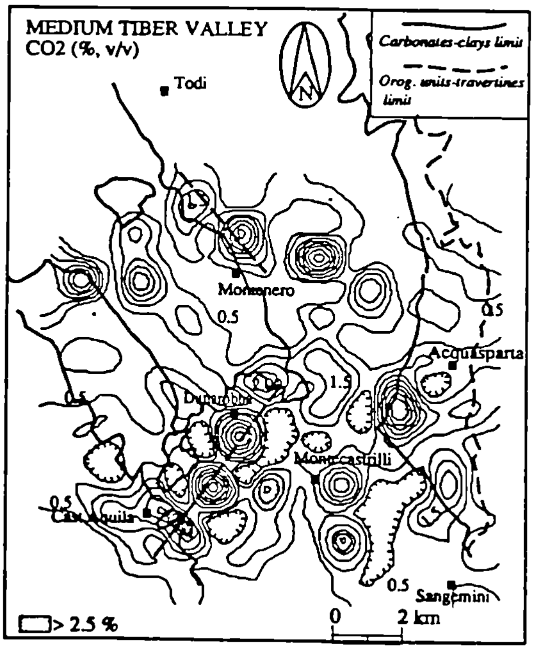


Fig. 6c

GAS	MEAN	ST. DEV.	Min.VAL.	Max.VAL.	SAMPLE N.
ΔHe (ppb)	35	134	-435	513	256
^{222}Rn (Bq/l)	8.84	9.13	0.74	61.05	256
CO_2 (%)	1.11	3.10	0.03	45.81	256

Table 1

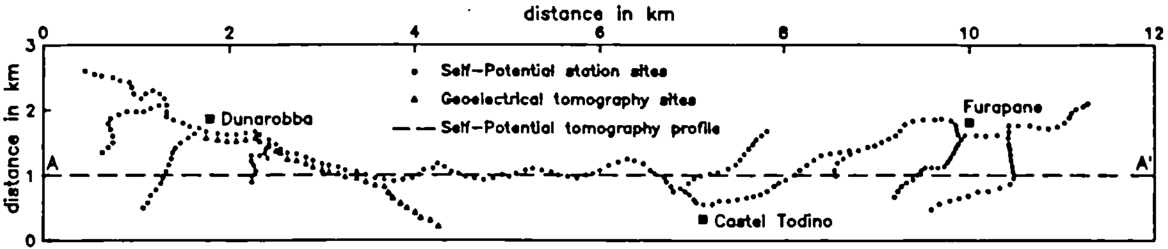


Fig. 7 – The geoelectrical survey area (southern sector)

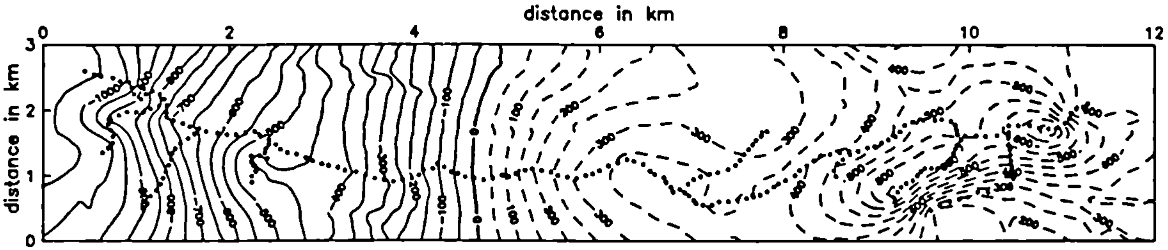


Fig. 8 – Self-Potential anomaly map (southern sector)

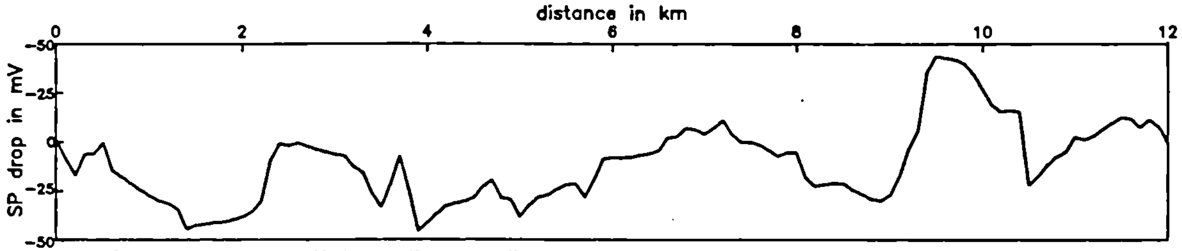


Fig. 9 – Self-Potential median profile AA'

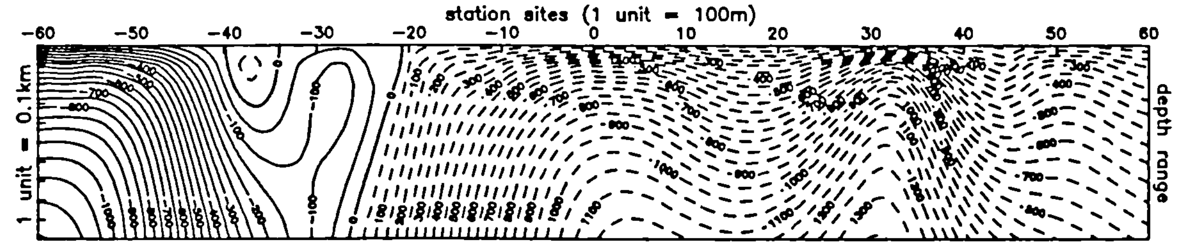


Fig. 10 – Self-Potential tomography – Profile AA' (southern sector)

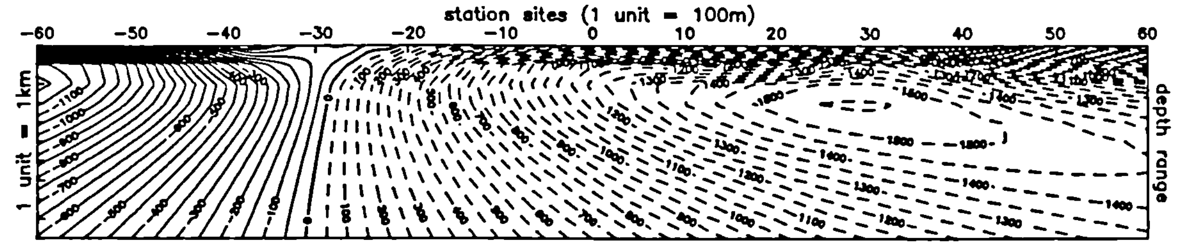


Fig. 11 – Self-Potential tomography – Profile AA' (southern sector)

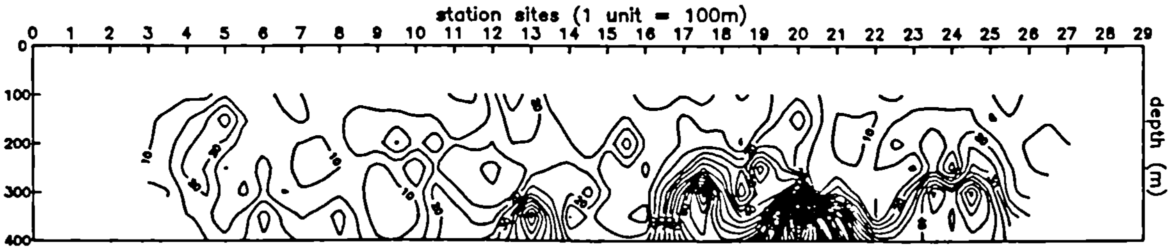
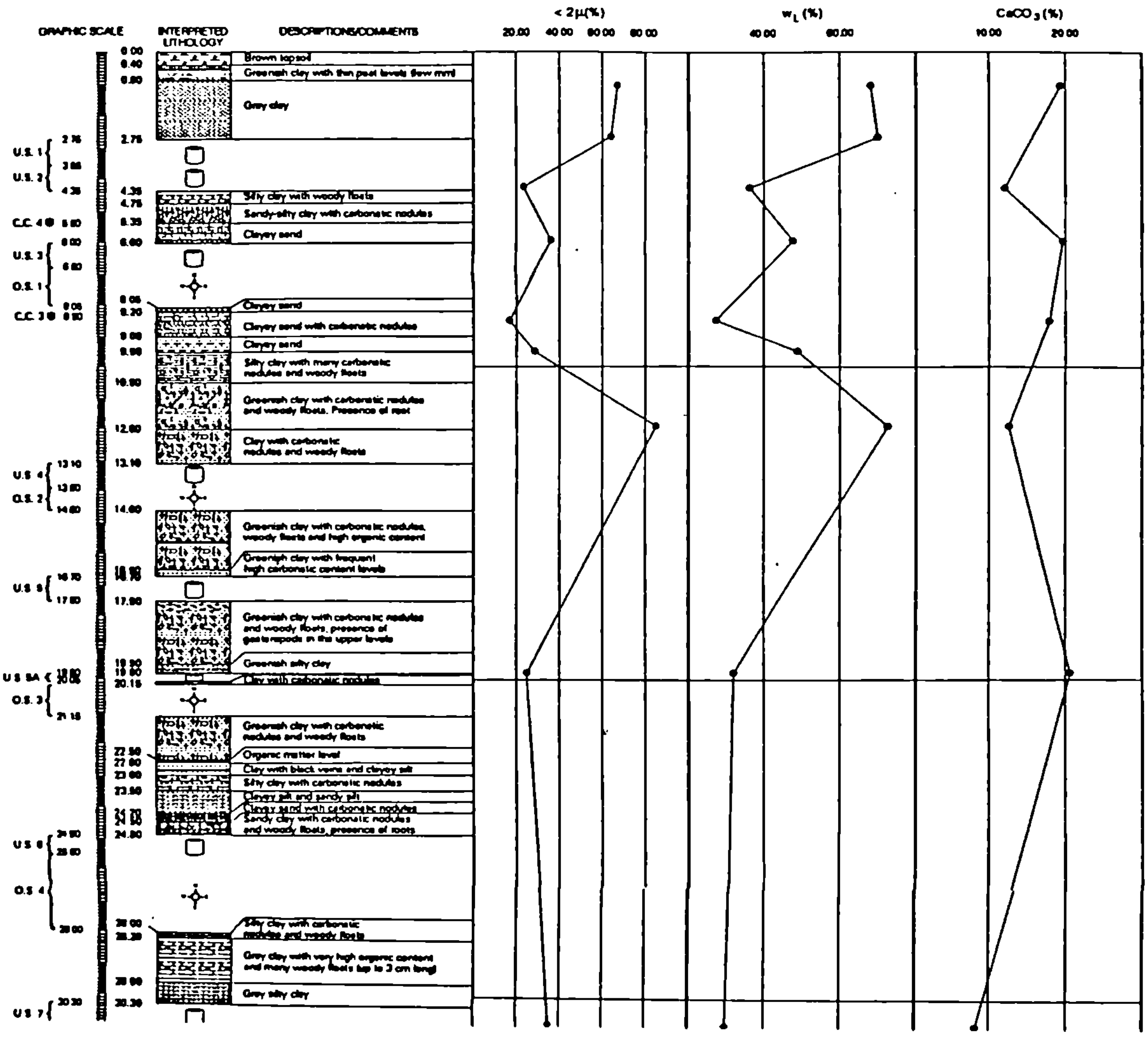


Fig. 12 – Dipole-Dipole geoelectrical tomography (contour lines in Ωm)

Fig. 13 - Clay fraction, liquid limit and carbonate contents along the vertical sequence (from borehole S6).



SAMPLE	DEPTH	SOIL UNIT WEIGHT VOLUME (γ_n)	VOID RATIO (e_0)	COMPRESSION INDEX (C_c)	SWELLING INDEX (C_s)	CONSOLIDATION COEFFICIENT (C_v)	HYDRAULIC CONDUCTIVITY (K)
-	(m)	(kN/m^3)	-	-	-	(m^2/s)	(m/s)
S6C.I.2	4.27	20.2	0.62	0.25	0.05	2.67E-07•	1.68E-10•
S6C.I.5A	19.8	20.7	0.55	0.24	0.09	1.03E-07••••	2.44E-13••••
S6C.I.7	30.8	20.5	0.60	0.21	0.09	2.08E-08•	1.28E-11•
S7C.I.3	58.5	20.5	0.60	0.31	0.09	6.33E-08•	2.42E-11•
S7C.I.5	93.0	20.4	0.51	0.36	0.09	1.60E-08•••	1.33E-12•••
S7C.S.I.4	114.6	20.4	0.60	0.29	0.10	4.80E-08••	9.32E-12••

Tab. 2

Oedometric pressure range

•	0.4-0.8 MPa
••	0.8-1.6 MPa
•••	1.6-3.2 MPa
••••	12.8-25.6 MPa

Title:	CHEMVAL2 THERMODYNAMIC DATABASE
Contractor:	WS Atkins Environment
Contract No.:	FI2W/0122
Duration of Contract:	11/92 to 12/94
Period covered:	01/93 to 12/93
Project Leader:	Dr. W.E. Falck

A. *OBJECTIVES AND SCOPE*

The principal objective of the CHEMVAL2 database project is the production of an extended, reviewed thermodynamic data compilation applicable to geochemical modelling studies in the EC member states. The database will be fully referenced to source and emphasises radio–elements and other chemical components of relevance to radioactive waste disposal.

The CHEMVAL thermodynamic database has been compiled as a result of collaborative work during the 1985–1989 CEC MIRAGE Project. Production of a standardised database has proved invaluable for comparison of simulations performed in different laboratories and has helped to increase the confidence in models now being used in national radiological safety assessments.

The continued need for a centralised database facility is clear and encompasses:

- data review for elements not currently included in the database
- coordination and compilation of data arising from the CHEMVAL2 activities and parallel research work coordinated within the CEC CoCo (Colloids and Complexes) activities.
- data management, primarily the collation and dissemination of frozen data sets.

B. *WORK PROGRAMME*

The work programme comprises three separate stages reflecting the various phases of the CHEMVAL2 project.

Stage 1 – agree scope of data reviews; establishment of format for database and its mode of distribution

Stage 2 – collation and review of thermodynamic data; annual issue of frozen data sets; coordination and management of less quantitative information arising from CHEMVAL2 and related projects

Stage 3 – final reporting

Database work will continue throughout the contractual period up to the completion of CHEMVAL2 in December 1994.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

Stage 1 of the project has largely been completed:

- the scope and priority of the data reviews has been agreed upon
- a Quality Control Plan has been set up as a basis for review work and subsequent data dissemination and to deal with comments/recommendations from users

Stage 2 of the project is well under way:

- Version 5.0 of the CHEMVAL tdb has been completed

Progress and Results

In Stage 1 of the project following list of elements not previously reviewed and sequence of data reviews had been agreed upon:

- errors/gaps already identified
- redox–equilibria of elements already contained in database
- Co, Ni, Se, As and V
- Cr, REE
- entropy data on all species as made available by the CHEMVAL2 topic group 'Temperature Correction'

Stage 2 saw the majority of errors and gaps in the reviews eliminated. Table 1 lists the aqueous species identified as being unreviewed and the current state of review. For all but a few species relevant references have been idenfied. A number of aqueous species for elements already in the database have been added (Table 3).

Most of the redox equilibria have been reviewed. The current state of work is given in Table 2.

The elements Ni and As have been added to the database. Aqueous species for Ni and As have been reviewed, along with a number of Ni-solids (Table 3).

Subsequently version 5.0 of the CHEMVAL tdb has been compiled, considering the above amendments and additions; it it now ready for distribution.

References on Co, Se, V and REE are being collated.

Entropy data on a large number of aqueous and solid species have been received from the CHEMVAL2 topic group 'Temperature Correction', now pending inclusion into the database.

Table 1: Aqueous species marked for review - progress

SPECIES	ID	in hand	compl.	SPECIES	ID	in hand	compl.
Am(OH)2(CO3)-	258	+		Ca(PO4)-	136		+
Cm(OH)+2	272		+	H(Cit)-2	1050		+
H2(Cit)-	1051		+	H3(Cit)	1052		+
H2SiO4-2	191		+	H3SiO4-	190		+
H(EDTA)-3	1140		+	H2(EDTA)-2	1141		+
H3(EDTA)-	1142		+	H4(EDTA)	1143		+
H5(EDTA)+	1144		+	HF	130		+
HF2-	131		+	H2BO3-	116	+	
I2Cl-	305		+	ICl-	306		+
ICl2-	307		+	I3-	295		+
HI	296		+	H2OI-	302		+
HIO	301		+	HIO3	304		+
I2O-2	300		+	IO-	297		+
IO3-	298		+	IO4-	299		+
I2OH-	303		+	Mg(EDTA)-2	1148		+
HNO3	115			NH4SO4-	114		
Pb(CO3)2-2	1355	+		PbCO3	1354	+	
Pb(SO4)2-2	1357	+		PbSO4	1356		+
H2PO4-	122		+	H3PO4	123		+
HPO4-2	121		+	Ra(SO4)	1301		+
HSO4-	101		+	Sr(Cit)-	1059		+
Sr(EDTA)-2	1213	+		H2TcO4	290	+	
HTcO4-	289	+					

Table 2: Redox-couples marked for review - progress

SPECIES	ID	in hand	compl.	SPECIES	ID	in hand	compl.
Am+4	265		+	AmO2+2	266		+
AmO2+	267		+	Fe+3	820		+
Mn+3	849		+	MnO4-	851		+
MnO4-2	850		+	NH4+	113		+
N2(g)	111		+	NH3(aq)	112		+
NO2-	110		+	Np+3	412		+
NpO2+	410		+	NpO2+2	411		+
Pu+3	462		+	PuO2+	461		+
PuO2+2	460		+	S-2	102		+
HS-	103		+	H2S	104		+
TcO4-2	287	+		TcO4-3	288	+	
Tc+3	294	+		TcO+2	291	+	
UO2+	212	NEA tdb to be considered					
UO2+2	213	NEA tdb to be considered					

Table 3: New species included in V 5.0 after review.

SPECIES	ID	in hand	compl.	SPECIES	ID	in hand	compl.
I2(aq)	308		+	H6(EDTA)-2	1148		+
RaCO3	1302		+	RaOH-	1303		+
RaCl-	1304		+	Ni+2	49		+
Ni(OH)+	2101		+	Ni(OH)2	2102		+
Ni(OH)3-1	2103		+	Ni(OH)4-2	2104		+
Ni4(OH)4+4	2105		+	NiCl+	2107		+
NiCl2	2108		+	NiF+	2109		+
NiBr+	2106		+	Ni(SO4)	2111		+
Ni(NO3)+	2110		+	AsO4-3	50		+
AsO2-	2049		+	HAsO4-2	2050		+
H2AsO4-	2051		+	H3AsO4	2052		+
AsO3-3	2053		+	HAsO3-2	2054		+
H2AsO3-	2055		+	H3AsO3	2056		+
HAs2O4-	2057		+	H2As3O6-	2059		+
AsS2-	2060		+	AsS4-3	2061		+
As2S4-2	2062		+	HAs2S4-	2063		+
H2As2S4	2064		+	As3S6-3	2065		+
HAs3S6-2	2066		+	H2As3S6-	2067		+
H3As3S6	2068		+				

List of Publications

An overview over the CHEMVAL Thermodynamic Database has been presented at a number of occasions:

FALCK, W.E., READ, D. and THOMAS, J., An Internally Consistent and Critically Reviewed Thermodynamic Database for Geochemical Modelling. In: Arendt, F., Annokkée, G.J., Bosman, R., van den Brink, W.J. [Eds.]: Contaminated Soil '93, pp. 491-92 (1993).

FALCK, W.E., READ, D. and THOMAS, J., Eine in sich konsistente und kritisch geprüfte Sammlung thermodynamischer Daten für geochemische Modellrechnungen, Poster given at Conference Geowissenschaftliche Umweltforschung, Heidelberg, 05/06 November 1993.

FALCK, W.E., RIDGE, D.M., CHEMVAL2: Thermodynamic Database, CEC Contract No. FI2W/CT92/0122, 1st and 2nd Periodic Progress Report (September 1992 - August 1993).

THE TREATMENT OF UNCERTAINTY IN GROUNDWATER FLOW AND TRANSPORT MODELLING

Contractor:	AEA Decommissioning & Radwaste, Windscale, UK.
Contract No:	FI2W / 0088
Duration of Contract:	1 April 1991 to 31 March 1995
Period Covered:	**January - December 1993**
Project Leader:	Dr J D Porter

A. OBJECTIVES AND SCOPE

Analysis and understanding of the groundwater flow in the neighbourhood of a radioactive waste repository play important roles in a performance assessment. Such analyses rely on numerical modelling in order to study the flow and transport over the very long times that must be considered. Two vital issues which must then be considered are the way in which the available data are used in constructing the mathematical model of the site and the uncertainty that is implied in the results of the model by uncertainties in the model parameters and in the model itself. The two tasks in this project address these issues. The first task is concerned with the investigation of novel approaches to the construction of mathematical models of a site. The second task is concerned with the investigation of methods for the estimation of uncertainty in groundwater flow and transport calculations.

B. WORK PROGRAMME

Task 1 Site Characterisation

1.1 Site Models: Mathematical models that can be used to represent a site will be reviewed. A computer package based on a selected method will then be written.

1.2 Inverse Problem Techniques: Methods for the inverse problem will be investigated and a selected approach will be applied in conjunction with the site models developed in Task 1.1.

1.3 Effective Properties: Methods for relating measured data to model parameters will be investigated using numerical calculations, based on the site models developed in Task 1.1.

Task 2 Treatment of Uncertainty

2.1 Methods for the Treatment of Uncertainty: Methods for the estimation of uncertainty in the results of groundwater flow and transport models will be investigated.

2.2 Parameter Sensitivity: Methods for the estimation of sensitivity coefficients will be investigated. The coefficients will be used to study the topic of data worth.

2.3 Model Uncertainty: The study of this topic will build on experience of "what-if" studies and will pay particular attention to long-timescale changes in hydrogeology.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The status of progress has not been forwarded to the Commission for 1993.

Title: Uncertainties in the modelling of migration.
Contractor: Risø National Laboratory, Denmark.
Contract N°:FI2W/0089.
Duration of contract: 1/9 1991 to 1/9 1994.
Period covered: 1/1 1993 to 31/12 1993
Project leader: B. Skytte Jensen

A. OBJECTIVES AND SCOPE

The objectives of the present investigation is to estimate the uncertainties to be described to the results of modelling of diffusion and convective flow in heterogeneous media.

Especially the uncertainties which are the consequences of the possible presence of unidentified heterogeneities in a given formation will be considered.

Only recently has attention been paid to the uncertainties to be ascribed to the modelling of migration, wherefore the relevant tools have not been firmly established yet.

Several approaches are possible mostly related to experimental field or the laboratory. In the present investigation, "computer-experiments" alone will will be used as the tool.

B. WORK PROGRAMME

To investigate the effects of inserting heterogeneities in two - and three dimensional "geological formations" on both diffusion and convective flow.

To develop the relevant mass-conserving algorithms which can handle diffusion in heterogeneous media.

To study the influence of "heterogeneities"on two dimensional convective flow by means of conformal mapping.

To investigate the possibilities of describing flow in fractures in the light of the previous studies.

PROGRESS OF WORK AND OBTAINED RESULTS

By 2D-modelling of convective flow under diverse geometrical conditions by means of conformal mapping techniques it has been shown, that pure convective flow may show pronounced longitudinal dispersion effects, although none such is assumed to occur within the individual flowtubes.

It was also shown, that the magnitudes of the calculated dispersions depends highly on the way "samples were extracted" from the set of calculated flowtubes, indicating that similar uncertainties have to be ascribed to field data.

The calculations have been performed by means of the programs HETEFLOW and SOURCEFLOW.
By semi-quantitative arguments have been demonstrated, that transversal dispersion effects will be expected to arise by convective flow in 3-D systems.
It is obvious, that due to the often pronounced concentration gradients arising in such calculations, unavoidable diffusion reactions will in actual systems tend to level these gradients out, wherefore modelled and experimental data will not be expected to coincide closely.

An important observation from these calculations is, that the modellings of different sampling techniques give an indication of the types of uncertainties if not their magnitudes, which have to be ascribed to experimental data optained by samling in the field. Due to these uncertainties it will hardly be possible by calculating backwards to identify or characterize the geological structures, which have been passed by the flow. If other evidence is not available, the model used might well be grossly in error due to mere ignorance.

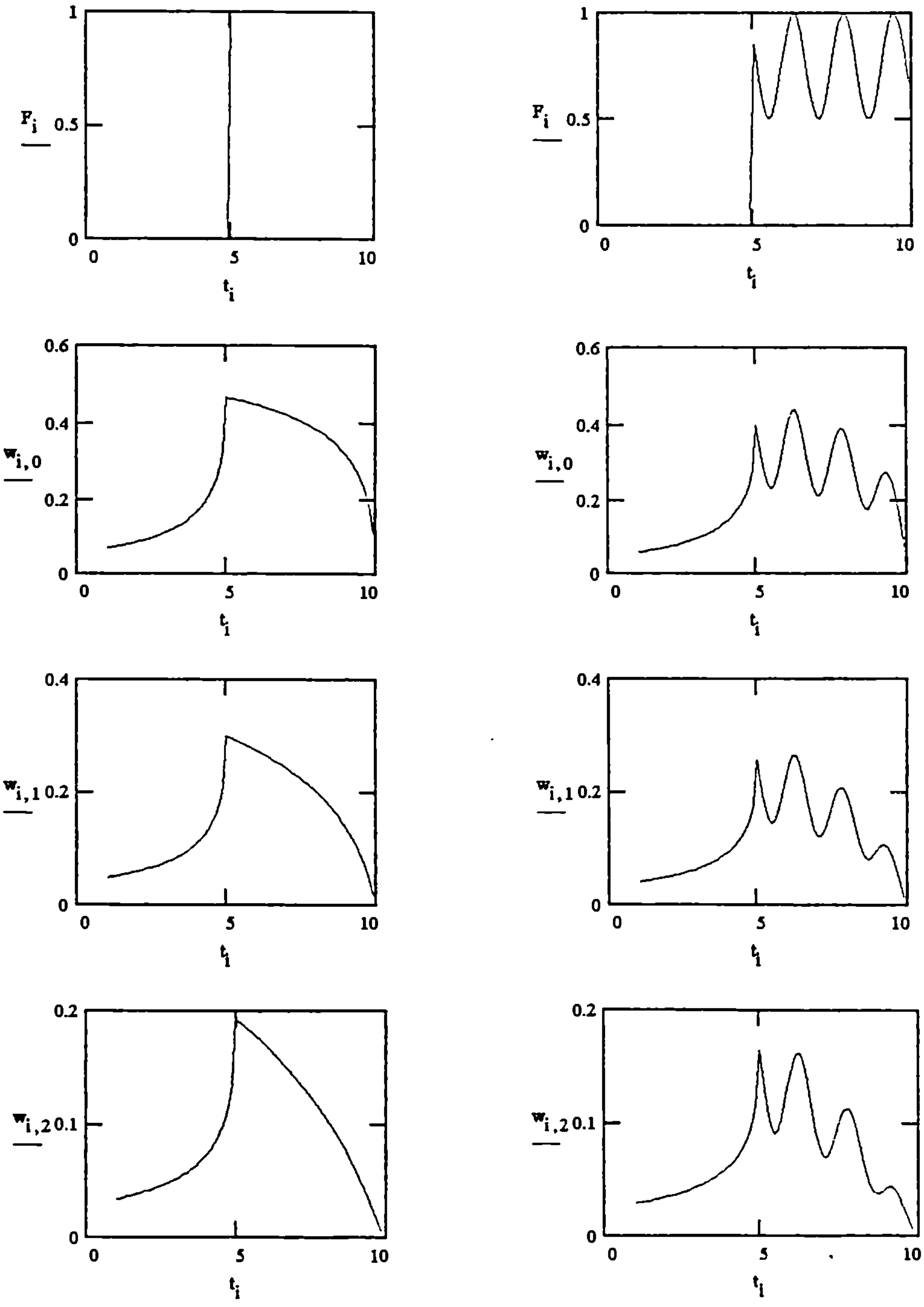
The flow of water through fractured rock is often modelled by analogy to the flow of electricity in a network of conductors by means of the Kirchoffs equations. This may work well for the flow of water, but to describe the flow of dissolved material the dispersion is alone "explained" by assuming different distributions of permeabilities and hold-up volumes in a large number of individual paths. This assumption is not supported by the present study which also ascribes dispersion effects to the individual paths, wherefore the passage through a small number of fractures might well be described. The former model may not give meaningful dispersions in this case.

In a recent investigation the dispersions expected by flow through a series of interconnected fractures have been investigated.
The flow in a single fracture was considered being adequately modelled as the flow from a source to a sink in an infinitely large two-dimensional layer. The distance between the source and sink is assumed to be finite, and may even be very small.
In a previous report has been shown, that a plug of dissolved matter in the inlet at the source will demonstrate a pronounced "dispersion" with time, when concentrations are measured at the outlet from the sink.

The mathematical expressions describing this ideal system have been derived - or approximated satisfactory - allowing for the calculation of concentration distributions obtained after the passage of any concentration distributions entering a source-sink system.

In figure 1. are given a couple of examples of different concentration distributions as input (F_i's) and how they are changed after the passage of one, two and three identical source-sink systems connected in series.($w_{i,0}$, $w_{i,1}$ and $w_{i,2}$)

Figure 1.



It has been shown, that in an ideal source-sink system as the one investigated investigated, appr. half of the added amount in a plug will pass the system quite rapidly and the rest more slowly giving rise to an infinite tailing.

In actual non-infinite systems the initial phase is believed to be quite similar to that for the infinite fracture, whereas the tailing is expected to approach zero at a steeper rate.

In the figure 1 presented above has been used a "normalized" time, t_N, as the abscissa. This time has been shown to be related to the real time, t_R, by the formula:

Eqn. 1

$$t_R = L^2 * t_N$$

where L is the distance between the source and sink.

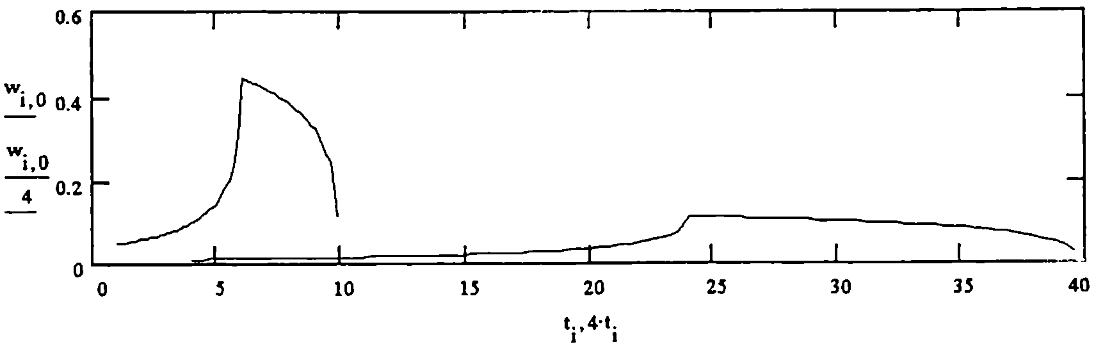
It will therefore be possible to model the effect of transport through a series of dissimilar source-sink systems in real time, even if the source-sink distances vary.

The graphs shown above demonstrate clearly, that a series of connected source-sink systems are quite effective in eliminating peak concentrations and in effectively diluting an added amount of a solute into the passing solvent. The pattern observed is similar to that expected for non-equilibrium flow through a system with large dead-end pores.

When branching transport between several source-sink systems are possible, this effect is even more pronounced, as will be shown in a coming report.

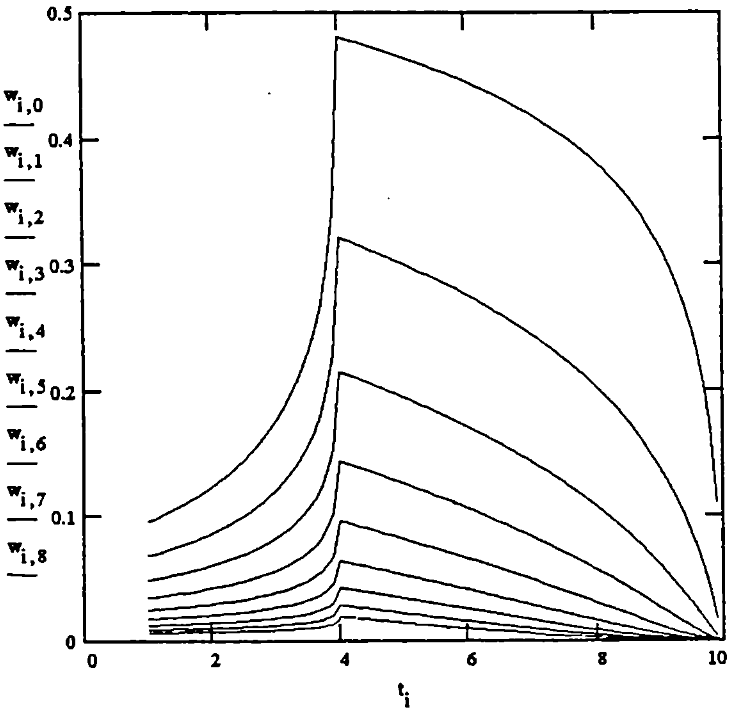
In the following figure 2. is shown the concentrations distributions expected by passage of a plug through source-sink systems differing in the distance between the source and sink by a factor of two, when plottet versus real time, t_R.

Figure 2.



In the following figure 3. is given an example of concentration distributions after 1-9 passes of an input through a series of "identical" source-sink systems.

Figure 3.



UNBIASED GUESS AS A CONCEPT TO COPE WITH FUZZY AND RANDOM PARAMETERS IN GEOCHEMICAL MODELLING

Title :	Unbiased Guess as a Concept to Cope with Fuzzy and Random Parameters in Geochemical Modelling
Contractor :	BRENK SYSTEMPLANUNG
Contract N° :	FI2W-CT91-0090
Duration of contract :	from 01.06.1991 to 30.09.1994
Period covered :	from 01.01.1993 to 31.12.1993
Project Leader :	Dr.-Ing. H.D. Brenk

A. *OBJECTIVES AND SCOPE*

Any risk analysis dealing with the transport of radionuclides from a radioactive waste repository on the basis of deterministic equations suffers from two severe problems. Firstly, all processes in reality are random in nature and, secondly, the data basis and the knowledge about the relevant processes will never be complete. The aim of the study is to investigate the applicability of fuzzy set theory in decision making and the potential of information theory in this context. Since ambiguity in the valuation of models and model parameters represents the main obstacle for a consent about the results, it seems very promising to apply a kind of maximum entropy method, the "method of unbiased guess", in order to deal with incomplete knowledge. While the incorporation of randomness into this approach is straightforward adequate methods have to be developed in order to deal with incomplete knowledge or subjective quantities (i.e. expert judgement). The main aim of the study is to propose a theoretically well-founded formalism serving this purpose. The capability of this formalism will be demonstrated on a non-trivial migration problem.

B. *WORK PROGRAM*

1. Compilation of the relevant aspects of information theory. Special emphasis is put onto the method of unbiased guess and its theoretical foundation.
2. Discussion of the problems of geochemical modelling in risk assessments with respect to uncertainty using probability density functions and the theory of fuzzy sets.
3. Development of a formalism for a consistent and unambiguous incorporation of incomplete knowledge employing the method of unbiased guess.
4. Demonstration of the applicability of the formalism using a simulated migration problem as a test case.
5. Documention
6. Project coordination

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In the last annual report the combined treatment of fuzzy and random variables was discussed. A useful tool for interpreting the results of the combined treatment has been developed by generalizing a transformation between probability and possibility. Moreover, the implementation of a numerical realization of the formalism on the computer has been started.

Progress and results

For the combined treatment of random variables, characterized by probability densities, and fuzzy variables, characterized by possibility distribution functions, we used the successive application of possibilistic conjection and probabilistic expectation to define the probability of a random fuzzy event. The interchange of the two procedures, that is first averaging with respect to the random variables and then calculating the possibility of the resulting membership function, which we might call "fuzzy random event", leads to another quantity which could be used as an alternative decision criterion. Unfortunately nobody has experience with the interpretation of these quantities. For a better understanding of the results it is useful to calculate bounds, which are purely probabilistic or possibilistic. For this purpose an invertible transformation /1/ was developed, which maps possibility distribution functions to reasonable probability densities and vice versa. With the help of this transformation one can either map all the possibility distribution functions of the fuzzy variables under consideration to corresponding probability densities to get a probabilistic lower bound or map all the probability densities of the random variables to corresponding possibility distribution functions to get a possibilistic upper bound.

We have recently begun to create computer programs, which allow for the calculation of arbitrary examples. With these examples, we will on the one hand, increase our experience concerning the interpretation of the results and on the other hand find a realistic model for geochemical transport, which can be treated by the developed algorithm.

List of publications

/1/ Wonneberger, S., Generalization of an invertible mapping between probability and possibility, submitted for publication in Fuzzy Sets and Systems

Review and development for modelling with uncertainty and variability

Contractor: Intera Information Technologies, Environmental Division;
University of Bristol, Advanced Computer Research Centre;
Université Libre de Bruxelles, IRIDIA.
Contract Number: FI2W/0091
Duration of contract: from 1 May 1991 to 31 October 1993
Period covered: 1 January 1993 to 31 October 1993
Project Leader: Dr. P. C. Robinson

A. Objectives and Scope

Any assessment of the safety of an underground repository for radioactive waste must consider various types of uncertainty. These uncertainties arise in each step of the assessment process: information gathering; experimentation; modelling; interpretation of results; and decision making.

These uncertainties are of many types, and are addressed with a variety of tools and techniques. For example, scenario analysis is widely used to tackle uncertainties in the future evolution of a site, and probabilistic calculations are often used for treating uncertain data.

The objective of this project is to review and investigate the types of uncertainties and techniques for handling them. In particular, an aim is to demonstrate techniques which are currently not widely used within the radioactive waste disposal community.

A particular area in which some potentially useful techniques are applied is that of Artificial Intelligence. The use of fuzzy logic is also a potentially useful area. Given this, a collaboration has been set up between those familiar with current practice (Intera), those with in-depth knowledge of artificial intelligence (IRIDIA) and a team with research experience in artificial intelligence, particularly in the application of fuzzy logic and related methods (ACRC).

B. Work Programme

B.1 Review

This phase consisted of an in-depth review of:

- types of uncertainty encountered in safety assessments internationally;
- tools and techniques for handling uncertainty, including those currently used in radioactive waste disposal and in other fields;
- available data sources and their uses, including experiment, expert judgement, detailed simulation;
- presentational methods for displaying uncertainty in inputs and outputs of assessments.

B.2 Definition and investigation of important test cases

In this phase, test cases were defined to cover the types of uncertainty and techniques identified as being most important in the first phase of the project. The aim was to demonstrate the practicalities of implementing various methodologies.

B.3 Investigation of further cases and lessons for general methodology

In this third phase, the focus was on recommendations for novel methodologies which could be used to address important issues. These were based on the experience gained in the trial applications of the previous phase.

C. Progress of Work

C.1 General

During 1993 the collaborative groups within the project have completed the development and application of various approaches identified from the review phase. These approaches have been tested on particular problems in the radioactive waste disposal field. A final project report has been produced detailing the development work undertaken and the conclusions are given below.

Conclusions

The following conclusions can be drawn from the work undertaken by the collaborators in the MUNVAR project.

Uncertainty Analysis in radioactive waste disposal assessments is well developed for parameter uncertainty, with the use of probabilistic safety assessment (PSA) techniques. Uncertainties in future conditions are generally handled by a scenario approach or by simulation. However, the assignment of probabilities to scenarios has proved difficult. Many of the uncertainties encountered can be resolved only by the use of expert judgement. In fact this is almost a definition of uncertainty - the real world has variability, human descriptions of it have uncertainty.

Other types of uncertainty, such as conceptual model uncertainty, are widely recognised but not systematically treated.

The handling of uncertainties in other diverse technical areas was considered. It was found that the approaches used are much less sophisticated than those used in radioactive waste assessments and thus there is no untapped pool of know-how in these other areas.

The key potential weakness in the PSA approach is the justification for manipulating subjective expert judgements according to the rules of probability. Another, more technical, weakness is risk dilution - where admitting more uncertainty reduces risks and therefore appears to make the system safer.

The management and manipulation of expert opinions of all types is an important area for study and has formed the basis for this project. Fuzzy approaches are possible for combining judgement and knowledge management systems can be used to maintain a knowledge base.

A top-down approach to knowledge management, as used by Bristol, has been demonstrated to allow expert judgements to be made accessible. The bottom-up approach, used by Brussels, has also been shown to be useful in making expert judgements more logically and systematiclly stated. Both approaches have encountered difficulties with the imprecise language commonly used by experts. Computer codes implimenting each approach have been developed.

A fuzzy approach to parameter uncertainty has been demonstrated to be practicable, using tools similar to those used in PSA. A code which can use a fuzzy or probabilistic paradigm has been developed.

The basic difference between the fuzzy and probabilistic approaches have been explored. The presentation of a fuzzy approach in terms of a nested interval analysis or nested set analysis has proved useful.

A probabilistic approach enables statements to be made concerning the chance of failure - given an imagined large set of identical situations. The fuzzy approach makes statements about the degree of belief which can be attached to the non-failure of a system. It is argued that this is more appropriate given the prevalence of expert judgements.

More sophisticated approaches to handling uncertainties, including mass assignments and transferable belief methods, are presented and discussed. Mass assignments allow fuzzy and probabilistic approaches to be unified, showing the fuzzy approach to be a generalisation of the probabilistic approach. The transferable belief methods enable ignorance about some possibilities to be handled coherently.

Evidential Support Logic has been described and applied to some example situations. It may be a useful tool for strategic studies if not for detailed assessments.

Cellular Automata were considered as a way of introducing uncertainty at a fundamental level. It is not clear whether this approach would be useful and its application was not pursued.

C.2 Progress at Intera (P.C.Robinson)

The work undertaken at Intera has focused on application of the QUEST computer application and consideration of the use of Nested Set Analysis to scenario analysis.

QUEST

Following on from the development of QUEST in 1992, in 1993 it was applied to some radwaste examples. Following on from this some minor errors in QUEST were located whcih were corrected. The results from the most recent version of QUEST are presented in the Final report.

Nested Set Analysis applied to Scenario Analysis

An important component of any safety assessment of the disposal of radioactive waste is the consideration of the long-term evolution of the total system (including the geosphere and the biosphere). This is normally undertaken by identifying possible future scenarios. However, there are significant, and unavoidable, uncertainties in the estimation of scenario probabilities. Hence the approach to scenarios used at present may be better interpreted by a fuzzy methodology rather than a probabilistic one.

When scenario likelihoods are represented by fuzzy distributions rather than probability distribution functions then Nested Set Analysis can be used to analysis the Scenarios in any assessment. Nested Set Analysis is a formulation of the simple concept that members of a set containing more supportable options are within any set of less supportable options for the same system. Thus in Nested Set Analysis it is only the relative values, rather than the absolute values, of parameters which matter.

For any system process model, containing all the possible scenarios, an influence diagram can be developed showing all links between processes. By giving each link a possibility (fuzzy membership) value, the system can be analysed using Nested Set Analysis. By additionally taking account of the importance of input and output processes, consistent influence diagrams can be produced for any belief level.

Thus the use of Nested Set Analysis to scenario development is a straight forward and easily applicable process. However, for it to be usable the scenario formulation must be developed within a fuzzy (degree of belief) rather than a probabilistic paradigm. Where there is a requirement to combine degrees of belief then existing techniques or, more consistently, those developed at IRIDIA during the MUNVAR Project could be used.

C.3 Progress at ACRC, Bristol (J.F.Baldwin, T.P.Martin and A.Tocatlidou)

The work undertaken at Bristol has focused on application of the SAFETIME package to the Project-90 report and consideration of the use of Evidential Support Logic, again with application to the results of Project-90.

SAFETIME

The SAFETIME expert system was developed by ACRC, Bristol based on the FRIL logic program. The exercise of applying SAFETIME to the Project-90 report was intended to show that complex technical documentation can be encapsulated in a computerised knowledge base and thus made accessible to a wider audience. Initial objectives for the intelligent manual were that the system should be able to: trace back from a conclusion to the information justifying that conclusion; find the modelling approach used for a given subproblem; and handle the uncertainty inherent in different modelling approaches.

The intelligent manual developed was shown to be considerably more than just a hypertext-based system, as it uses a much richer knowledge-based approach. This allows the implicit engineering knowledge to be modified, and inference to be performed. The intelligent manual can function in a similar manner to a hypertext system, allowing the user to navigate through related topics in any order and, when requested, display the original source text of the document. Additionally, the system was successfully interfaced to other software, specifically a numerical modelling code used to investigate different parts of the overall problem. SAFETIME can also act as an advisor on the use and limitations of such software.

Evidential Support Logic

Evidential Support Logic has been developed within the MUNVAR Project by ACRC, Bristol. It was introduced by Baldwin as an alternative to deductive logic for applications which require inductive or abductive reasoning.

Evidential Support Logic allows generalisations from known examples to new situations, and enables a rule based to be automatically generated from known examples. Each example is characterised in terms of features, which have degrees of importance attached to them. Fuzzy matching is used to assess the degree of similarity between features in different cases, and the inference process allows different combinations of features to contribute to the overall conclusion. The partial matching between fuzzy sets is based on the theories of semantic unification and mass assignments developed by Baldwin.

The new knowledge-based approach has been applied to the problem of site selection for a nuclear waste repository. The information used in this project is based on the scenario development exercise carried out in SKI Project-90. This uses the analysis of possible scenarios, represented here as a combination of external events that characterise its appearance. These consist mainly of geological events and chemical and climate changes, which may have important effects on the repository stability and performance.

Each possible site is described in terms of its topographic, geological and technical characteristics. These form the parameters that may be affected by the external events caused by each scenario. Evidential Support Logic is used to indicate which site the selected scenarios will have the minimum impact on.

The prototype system has been developed using the support logic language FRIL. Initial studies show that the techniques developed are robust and provide sensible results.

Further enhancements could be included into the model developed here to increase the capabilities of Evidential Support Logic: The use of fuzzy values at higher knowledge levels (for instance, to describe the various degrees of impact a scenario can have on a selected site); and a systematic study of the uncertainty propagation through the reasoning mechanism, and the knowledge characteristics.

C.4 Progress at IRIDIA, Bruxelles (V.Poznanski, P.Smets and S.Amarger)

Following on from the development of the prototype SALUT knowledge-based system in 1991/2, in 1993 IRIDIA applied it to the SKI Project-90 summary report. However in the implementation of SALUT to analyse the report, it was found that the caution used by the report authors made it difficult to extract knowledge. The process used, of translating the Project-90 report first into simplified English (in which all extraneous words had been removed), then translating into an appropriate logical form followed by a review undertaken by the report authors, proved to be highly time consuming. However, the knowledge elicitation process is also a means of communicating as the specialist and the non-specialist need to communicate using a common, non-ambiguous language.

Studies were also made into the computation of fuzzy probabilities, in particular the encoding of non-conditional probabilities and the evaluation of inference networks. The former was shown to be trivial whilst for the latter two techniques are proposed, one based on mathematical programming and one on graph theory. The former, Simplex-based method has been shown to be unable to cope with the complexities involved in fuzzy calculations. Whilst the algorithm based on the graph theoretic approach (called LocNum Quant) is sub-optimal in terms of the precision of the calculated bounds, the results are accurate enough and the techniques can cope with the complexities resulting from the fuzzy paradigm.

Task 5

"Method of Evaluating the Safety of Disposal Systems"

- List of contracts
- Introduction to Task 5

Topic 1 Complements to the previous evaluations

FI2W-CT90-0008	Global dispersion models for I-129 and C-14
FI2W-CT90-0016	Performance assessment of the geological disposal of spent fuel in a clay layer

Topic 2 Sensitivity studies

FI2W-CT90-0017	EVEREST : EValuation of Elements Responsible for the Equivalent doses associated with the final STorage of radioactive waste
FI2W-CT92-0123	Consideration of environmental changes in long-term radioactive waste disposal system evaluations

INTRODUCTION TO TASK 5 - METHOD OF EVALUATING THE SAFETY OF DISPOSAL SYSTEMS

A. Objectives

The methods developed hitherto shall be up-dated and the relative importance of the various radionuclide release and transport mechanisms assessed. Moreover the analysis should be extended to new types of waste so that a comprehensive safety assessment of disposal systems can be made.

B. Research performed under the 1985-1989 Programme

The projects PAGIS (Performance Assessment of Geological Isolation System for vitrified HLW) and PACOMA (Performance Assessment of Confinement of Medium-level and Alpha waste) have been completed. In addition support studies have been carried out on:

- the assessment of human intrusion into underground repository considered in PAGIS and PACOMA
- modelling the long-term evolution of geological disposal systems
- software quality assurance procedures for risk assessment codes

C. Present programme (1990-1994)

The research work to be developed covers two fields:

- Topic 1 "Complements to the previous evaluations"
  - Improved global dispersion models for Iodine-129 and Carbon-14 by NRPB-Chilton. The new models should appropriately represent possible future climatic states, which may influence the long term radiological impact from the two radionuclides.
  - Evaluation of radiological consequences from geological disposal systems in clay of UO_2 and MOx spent fuels (by CEN/SCK Mol). This study will allow to extend PAGIS evaluations to the disposal of unreprocessed spent fuel (UO_2) and recycled fuel at the end of its irradiation cycles.

- Topic 2 "Sensitivity studies"
  - EVEREST (Evaluation of the Elements Responsible of dose Equivalent associated to the final STorage of radioactive waste). This is a multi-partner project (CEA)IPSN; ANDRA; CEN/SCK; GRS and ECN) for studying the sensitivity of evaluated radiological consequences towards the elements of performance assessments (scenarios, phenomena, parameters) for deep waste repositories in granite, salt and clay at different sites.

  - State of the art analysis on environmental changes in the long-term radwaste disposal system evaluations. It should provide a complement to the evaluation of the sensitivity of the parameters related to environmental variations.

Title:	Global Dispersion Models for I-129 and C-14
Contractor:	National Radiological Protection Board, Chilton, UK
Contract N°:	FI2W/CT90/0008
Duration of Contract:	from 1 January 1991 to 31 December 1993
Period covered:	1 January 1993 to 31 December 1993
Project Leader:	Dr J R Cooper

A. OBJECTIVES AND SCOPE

The objective of this project is to provide up-to-date models for assessing the radiological impact arising from the global circulation of carbon-14 and iodine-129. These radionuclides are long-lived and mobile in the environment. This gives them the potential to delivery significant collective doses to the world's population over long timescales, if released either directly to the environment or from a geologic repository for solid radioactive waste.

In this project the National Radiological Protection Board (NRPB) is collecting information on existing models and parameter values for the global circulation of carbon-14 and iodine-129, in order to develop up-to-date models. The influence of environmental changes over long timescales, for example, climatic changes, is also being considered. The final report will contain a description of the proposed models, their parameter values and example results.

B. WORK PROGRAMME

B.1 Consultation and literature search to identify available models, their implementation on the NRPB computer and comparison of their results.

B.2 Consultation and literature search for information on important processes in the global circulation of carbon and iodine and for parameter values for use in models identified in task B.1.

B.3 Review of models obtained in task B.1 in the light of information on important processes and parameters obtained in task B.2 and construction of 'state of the art' models.

B.4 Calculation of collective doses using 'state of the art' models (task B.3) considering possible future climatic scenarios and quantification of possible ranges of results.

B.5 Preparation of final report.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The project is now complete and the draft final report has been prepared and sent for comment.

Progress and results

B.1 Identification and implementation of available models

Existing models for the global circulation of carbon-14 and iodine-129 were identified from literature searches and consultation with individuals and organisations. Eleven models for predicting the global circulation of stable carbon or carbon-14 were discovered and four of these were implemented on the NRPB computer system and their results compared.

In the case of iodine-129, three models were identified and they are all based on the model developed by Kocher at Oak Ridge National Laboratory /1/. These were implemented on the NRPB computer and their results compared.

This task is now completed.

B.2 Review of data on important processes and parameter values

The data on important processes and parameter values were obtained principally at the same time as information on the available global models. In the case of carbon, the ocean was identified as an important sink for carbon and the exchange between the atmosphere and ocean was identified as an important process. In the case of iodine, the inventories and fluxes between the various biosphere compartments were reviewed.

This task is now completed.

B.3 Construction of 'state of the art' models

A new compartmental model for the global circulation of carbon-14 has been constructed and is shown in Figure 1. The ocean compartments of this model were obtained by simplifying the MINIBOX model /2/. The terrestrial compartments were taken from the model of Emanuel et al /3/ with the addition of extra transfers from land to sea to take account of transport of carbon in rivers /4/. A fossil fuel compartment has also been introduced /5/ to allow for the assessment of the influence of fossil fuel burning on collective doses from carbon-14 releases. The model has been validated by comparison of carbon-14 to carbon-12 ratios in the oceans with model results using natural carbon-14 production rates and nuclear bomb test fallout data.

A revised compartmental model for the global circulation of iodine-129 has been constructed and is shown in Figure 2. This is based upon the model developed by Kocher /1/ with the revisions recommended by Smith and White /6/. In addition, the transfer of iodine-129 from sedimentary rock to the subsurface regions has been included, based on the work of Fabryka-Martin /7/. The transfers between some of the compartments and the stable iodine inventories within them have been updated following the review undertaken in task B.2.

This task is now completed.

B.4 Calculation of collective doses

The new models for the global circulation of carbon-14 and iodine-129 have been run with unit source term (1 TBq). A number of runs were performed for each model with the source in different compartments. In each case, the collective doses to the EC and world populations were calculated, integrated to a number of different times. World collective dose commitments for carbon-14 ranged from 92 manSv to 109 manSv depending upon the source compartment, and from 468 manSv to 727 manSv for iodine-129, again depending upon the source compartment. The corresponding results for the old global circulation models were 104 manSv to 110 manSv for carbon-14, and 547 manSv to 1170 manSv for iodine-129.

Additional runs were also performed for carbon-14 with fossil fuel burning included and this resulted in a reduction of about 15% in the predicted collective doses.

The effects of future climate change on the transport of carbon and iodine were not well understood at present. Therefore, in order to assess the possible influence of climate change on collective doses, the sensitivity of the results to changes in the exchange across the ocean - atmosphere interface was investigated. It was found that the collective dose commitments predicted by either the carbon model or the iodine model were not particularly sensitive to changes in these parameters.

This task is now completed.

B.5 Preparation of final report

A draft final report has been prepared and sent for comment.

List of publications

Work performed under this contract was presented at the following two meetings:

1) NERC: COGER 93, University of Newcastle-upon-Tyne, 20-22 September 1993. Paper entitled, "A new global dispersion model for ^{14}C" by J Titley.

2) Information Days on Waste Disposal Safety, Brussels, 22-23 November 1993, Management and Storage of Radioactive Waste, Task 5. Paper entitled, "Development of improved global dispersion models for ^{129}I and ^{14}C" by J Titley, S Mobbs, T Cabianca and G Lawson.

REFERENCES

/1/ KOCHER, D.C., Oak Ridge National Laboratory Report, ORNL/NUREG-59 (1979).
/2/ MOBBS, S.F. et al., CEC Report, EUR 11779 (1988).
/3/ BOLIN, B. (Editor), Carbon cycle modelling. Wiley, Chichester, p 335 (1981).
/4/ HOUGHTON, J.T. et al., Climate change, the IPCC scientific assessment. Cambridge University Press, Cambridge (1990).
/5/ CANNELL, M.G.R. and HOOPER, M.D., Institute of Terrestrial Ecology Research Publication No. 4 (1990).
/6/ SMITH, G.M and WHITE, I.F., NRPB Chilton Report, NRPB-M81 (1983).
/7/ FABRYKA-MARTIN, J. et al., Geochimica and Cosmochimica Acta 49 pp 337-347 (1985).

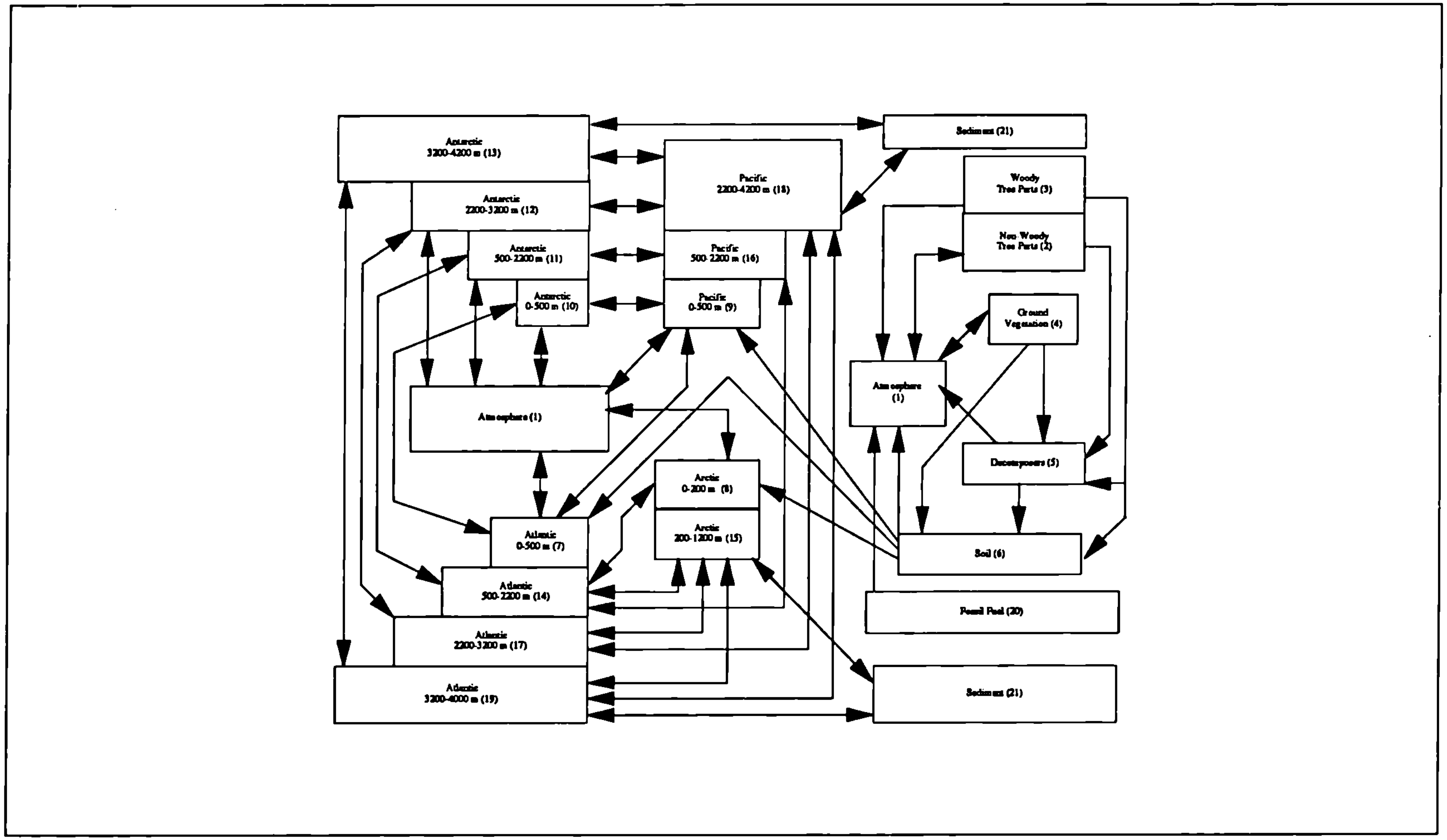


Figure 1 New model for global circulation of C-14

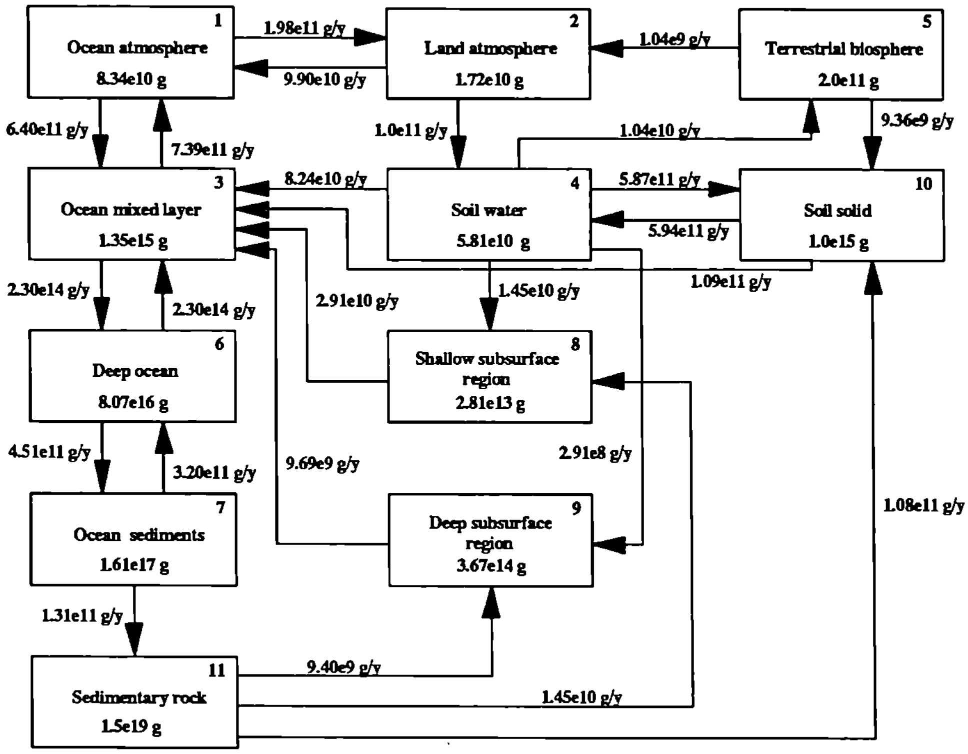


Figure 2 New model for global circulation of I-129

PERFORMANCE ASSESSMENT OF THE GEOLOGICAL DISPOSAL OF SPENT FUEL IN A CLAY LAYER

Title:	Performance assessment of the geological disposal of spent fuel in a clay layer
Contractor:	Centre d'Etude de l'Energie Nucléaire - Studiecentrum voor Kernenergie CEN/SCK
Contract N°:	FI2W/CT90/0016
Duration of contract:	from 1 March 1991 to 31 December 1994
Period covered:	from 1 January 1993 to 31 December 1993
Project leader:	J. Marivoet

A. OBJECTIVES AND SCOPE

Hitherto the performance assessments, which have been carried out within the C.E.C.'s R&D programme on radioactive waste management like PAGIS /1/ and PACOMA /2/, considered mainly waste types which result from the reprocessing of spent fuel. However for technical reasons the recycling cannot be repeated more than three cycles and the economical justification of the reprocessing becomes debatable because of the relatively low cost of fresh uranium. It is therefore reasonable to consider the direct disposal of uranium oxide and/or mixed oxide spent fuels as a realistic option.

The main objective of the study is the evaluation of the radiological consequences of the geological disposal of spent fuel in a hypothetical repository located in the Boom clay layer at the Mol site.

B. WORK PROGRAMME

1. Data collection
   - 1.1 Spent fuel inventories: the radionuclide inventories of UO_2 and MOX spent fuels resulting from an irradiation in a PWR reactor up to a burn ups of 33 and 45 MWd/kg are calculated.
   - 1.2 Repository concept: the existing repository concepts are adapted to allow for the disposal of spent fuel assemblies.
   - 1.3 Near field processes and characteristics: the near field model should take into account the typical processes describing the release of radionuclides from the spent fuel.
   - 1.4 Far field and biosphere data: the data collected for PAGIS and PACOMA will be updated.
2. Adaptation of the methodology
   The methodology developed within the EVEREST project has to be adapted to the case of spent fuel disposal.
3. Models and computer codes
   A new near field model is needed.
4. Deterministic calculations
   Individual dose rates and collective doses will be calculated.
5. Stochastic calculations
   The stochastic calculation will include sensitivity and uncertainty analyses.
6. Conclusions

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The data collection for the spent fuel assessment has been completed. The literature on the near field behaviour of spent fuel in disposal conditions has been reviewed and the most relevant processes have been identified.

The methodology that has been developed for the Mol site within the EVEREST project has been reexamined and adapted where necessary to make it applicable to the case of spent fuel disposal.

A near field model which considers the radionuclide releases from the various components of the spent fuel has been developed.

Progress and results

1. Data collection

In the literature various reports and papers on the behaviour of conditioned spent fuel in repository conditions have been found. It has to be noticed that most of the publications on spent fuel consider the case of disposal in hard rocks; publications on the behaviour of spent fuel in near field conditions corresponding to a repository in a clay formation were not available.

Natural and enriched uranium fuels have been studied in the literature. However no results of experimental studies are available for MOX fuels.

The literature review has shown that different release mechanisms take place. The gases present in the gap between the fuel pellets and the hulls are released rapidly. The corrosion of the hulls is considerably retarded by passivation. The dissolution of spent fuel is a very complex mechanism : on the one hand the uranium oxide is thermodynamically stable in reducing conditions but on the other hand local oxidizing conditions may arise as a result of the radiological decomposition of water. A detailed modelling of these complex mechanisms cannot be realized because of the lack of specific information and it is not required because of the preliminary character of the spent fuel assessment.

2. Adaptation of the methodology

The methodology /3/ that has been developed within the EVEREST project is also applied as far as possible for the spent fuel study. Each feature, event or process mentioned in the FEP catalogue /4/ has been systematically reexamined in order to check if that FEP can become more important in the case of spent fuel disposal than it is in the case of disposal of reprocessing waste. The reexamination of the FEP catalogue has not led to the selection of additional scenarios. However the description of the near field has to be thouroughly modified. The possible influence of the thermal field on the migration of radionuclides should also be evaluated.

3. Models and computer codes

In the near field model different release mechanisms are taken into account for the five considered components of the spent fuel:

- release of gases present in the gap between the fuel pellets and the hulls;
- leaching of radionuclides from the zircalloy hulls;
- leaching of radionuclides from the structural parts of the fuel assemblies;
- leaching of radionuclides from the grain boundaries of the fuel pellets;
- leaching of radionuclides from the uranium oxide matrix.

Rather simple mathematical models, mainly based on estimated corrosion times, are used to calculate the maximum release rates from each of the five components of the spent fuel. Because for many radionuclides the effective releases from the near field are strongly restricted by the solubility limits, the near field model takes the solubility limits into account.

The total radionuclide inventories of the spent fuel have been estimated in an earlier phase of the study. The inventories have now been partitioned over the five considered components of the spent fuel.

REFERENCES

/1/ Marivoet, J. and Bonne A., "PAGIS : Disposal in Clay Formations", C.E.C. Report EUR-11776 (1988)

/2/ Marivoet J. and Zeevaert T., "PACOMA : Performance Assessment of the Geological Disposal of Medium-level and Alpha Waste in a Clay Formation in Belgium", C.E.C. Report EUR-13042 (1991)

/3/ Raimbault, P., Escalier des Orres, P., Marivoet, J., Martens, K. and Prij, J., "Scenario selection procedures in the framework of the CEC project EVEREST", International Symposium on Geologic Disposal of Spent Fuel, High-level and Alpha-bearing Wastes, Antwerp, 19-23 October 1992. Proceedings pp 285-296.

/4/ Bronders, J., Patyn, J., Wemaere I. and Marivoet J., "Catalogue of events features and processes potentially relevant to radioactive waste disposal in the Boom clay layer at the Mol site, SCK/CEN, Mol, Report R-2987 Annex (1994)

Title: "EVEREST: **EV**aluation of **E**lements **R**esponsible for the dose **E**quivalent associated with the final **ST**orage of radioactive waste".
Contractors: CEA/IPSN* - ANDRA ** - CEN / SCK ° - ECN°° - GRS°°°
Contract n°: FI2W CT 90-0017
Duration:01/04/91 - 30/09/94
Period covered: from 01/01/93 to 31/12/93
Project leader: M. GOMIT (CEA/IPSN coordinator) - M. RAIMBAULT (ANDRA) - M. MARIVOET (CEN/SCK) - M. PRIJ (ECN) - M. MARTENS (GRS) -

A- OBJECTIVES AND SCOPE

The general objective is the evaluation of the sensitivity of the radiological consequences associated with deep nuclear waste disposal to the different elements in the performance assessment. The following geological formations are taken into consideration: clay, granite and salt, for HLW and MLW.
This work will be realized in four phases: 1-elaboration of the methodology, 2- model description and data collection, 3- calculations, 4- interpretation of results.

B- WORK PROGRAMM

B.I - Methodology: this phase will be divided into four steps: identification of main features controlling the radionuclide transfer to human beings, scenarios, definition of calculations to be performed and reflexion on different approaches and techniques of sensitivity analyses.
B.II - Model description and data collection: documentation and presentation of the models and codes to be used, compilation of the site data and of the other data (waste inventory, package, repository design...)
B.III - Calculations: deterministic and stochastic calculations for normal and altered selected scenarios for each site. The results obtained will be used for sensitivity analyses.
B.IV - Interpretation of the results: the final phase will lead to a hierarchized list of the most influential elements (scenarios, phenomena, RN..) for each site; this list can contribute to the definition of future orientation of the R&D programmes.

---

* Commissariat à l'Energie Atomique - ** Agence Nationale pour la gestion des Déchets Radioactifs - ° Centre d'Etudes pour l'énergie Nucléaire / Studiecentrum voor Kernenergie - °° Stiching Energieonderzoek Centrum Nederland - °°° Gesselschaft für Reaktorsicherheit mbH -

C- PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

After the methodology and the scenarios specifications (1992), data collection (inventory, waste package, design, site and geochemical data) has been finalized for clay and salt formations, and partially for granite formation.
The withdrawal of ANDRA from the project (April 1993) led to a new distribution of tasks and budget to ensure coverage of the initial objectives.
The Working Group 3 has fixed the strategy and approaches (deterministic/Stochastic) for evaluating sensitivity. Reference calculations and stochastic ones have been performed.
Main elements for biosphere strategy are available: four reference biospheres will be considered (moderate climate, hot-dry climate, cold and very cold climates, Würm and Riss types respectively). Mean and long term calculations will be performed and physical evolution of the biosphere will be taken into account.

Progress and results

B.II - Model description and data collection

CEN/SCK

CEN/SCK has updated the topical report on the input data that are used in the EVEREST calculations.

A number of alternative aquifer codes have been tested. The clay and aquifer codes that will be used in the final assessment have been selected on the basis of the results of the sensitivity studies which are described in paragraph B.III.

ECN

ECN used the data defined in the Dutch safety study performed in the OPLA phase 1A project. Most element and nuclide specific parameters are based on PAGIS and PACOMA. The deterministic analysis of the groundwater intrusion scenario have been performed with the code EMOS_ECN. This code is based on the code EMOS developed at GSF.

The probabilistic analysis of the subrosion scenarios have been performed with the code PANTER. This code is also based on EMOS.

GRS

Nearfield

1) Simulation of the Convergence-Diffusion Scenario (Brine Intrusion and Brine Pockets)

The uncertain parameters in this scenario and the associated distribution functions have been compiled and 100 random sample sets have been generated using the GRS-developed software system SUSA. From these sample sets, 100 input files for the near- and farfield will be generated.

In 1993, 40 input files have been generated and test calculations have been carried out. Essential features have been implemented in MARNIE to improve the capability of the code to simulate this scenario.

2) Simulation of the Cavern-Convection Scenario (Human Intrusion: Solution Mined Cavern)

The data to be used in this scenario including the uncertain parameters and the associated distribution functions have been compiled. 200 random sample sets have been generated, from which 200 input files will be produced. To simulate all the important features, arising in this scenario, new models have been implemented and tested.

3) Sensitivity Studies on Convergence Models

The results of the analysis of the 19 cases, agreed between ECN, GSF and GRS, have been obtained. Each of these cases represents a relevant situation in a repository located in a salt dome.

Farfield

The hypothetical repository is located in a salt dome under the Gorleben erosion channel. The channel consists of two aquifers (the upper "Saale" and the lower "Elster" aquifers) and some silt (aquiclude) and clay (aquifuge) layers. It crosses the Elbe River and two watershed boundaries in the South and in the North. A 2-D model of the channel was established with no flow boundary conditions at the bottom, in the south and in the north. The flow from the south to the north is governed by a given piezometric head at the top of the modelled area.

It was planned to perform the groundwater calculations with the USGS FD code MODFLOW. A MODFLOW discretisation of the 2D model was made. The results of the calculation depend on the degree of the mesh refinement. A sequence of calculations with more refined grids up to the limits of the code was made. However, the results did not converge. Therefore, it was decided to calculate the groundwater flow with the FE-code NAMMU developed by AEA/UK. A FE discretisation of the model area was made and reference groundwater calculations were performed. The resuls do not depend on the mesh refinement.
For the probabilistic calculations, 100 parameter sets were generated.

IPSN

Data collection which has not been achieved by ANDRA, has been completed by IPSN/DES and IPSN/DPEI, such as some of the geological and hydrogeological data, in particular regional data, fracturation characteristics and physical properties of the granite and clay host rocks, transport parameters (solubility limits, diffusion and distribution coefficients) and biosphere parameters.

For the granite site, 3D flow calculations will be performed with the computer code TRISEC for quasi-3D results comparison and to help to determine potential representative 2D cross sections.

For the clay site, models have been done using the NEWSAM model. NEWSAM is a multilayered finite difference flow model, based on a nested meshing grid type, in which the layers have to be alternatively aquifers (horizontal flow) and aquitards (vertical flow). Horizontally, a flux balance equation is established for each layer and vertical flow is commonly represented through a leakage factor, though for aquitards, an internal representation may be used with several layers in which leakage fluxes are calculated as for horizontal flow.

The dose equivalent calculations in the biosphere will be performed with the ABRICOT computer code.

A model for the salt consumption scenario has been used to determine the radiological consequences associated with salt extraction.

B.III - Calculations

ANDRA

The granite site has been modelled as an equivalent porous medium, with a permeability supposed to decrease with depth and a uniform porosity, explicit fractures are not taken into account. The topography at the surface gives the upper boundary conditions for the model. Both 3D regional and local flow calculations have been carried out with the computer code TRIO (general finite element fluid mechanical code). As a result, the velocities map shows the extreme complexity of the site (figure 1). Nevertheless, a pathway calculation performed on the local area surrounding the potential repository location has allowed the possibility to define four 2D vertical cross-sections in the main direction of the groundwater flow. The 3D-2D comparisons based on hydraulic heads, velocities and particle tracking calculations have given unsatisfying results for three cross-sections. One of these cross-sections seems better in terms of velocity but does not well reproduce the transfer times distribution's law. In fact, the "complexity" of the EVEREST granite site makes difficult the choice of a preferential 2D cross-section for the transport calculations. In order to perform multi-parameter sensitivity calculations, it would be advisable to build a unidimensional model based on the 3D modelling with respect to transfer time distribution and flow rates.

CEN/SCK

CEN/SCK has elaborated a number of deterministic sensitivity studies with respect to assumptions made for the clay and aquifer models.

For the clay model, the potential influence of the following phenomena or approximations on the calculated radionuclide fluxes at the clay-aquifer interface has been evaluated:
- boundary condition at the clay-aquifer interface (finite or infinite medium);
- considered source geometry (horizontal plane or discrete galleries);
- one or three-dimensional modelling approach;
- anisotropy of the diffusion;
- solubility limits;
- canister lifetime;
- complexation of trivalent actinides by fulvic acids.

The maxima of the fluxes released by the clay into the aquifer are about two times higher in the case of a finite medium (concentration zero at the clay-aquifer interface) than they are in the case of an infinite medium (concentration zero at infinity). The source geometry, the considered number of dimensions and the anisotropy of the diffusion strongly determine the shape of the concentration distributions in the clay layer. However, the total flux which reaches the aquifer is scarcely influenced.

An example of the results of the deterministic sensitivity studies is given in figure 2. This figure shows that the introduction of the solubility limit of Tc-99 drastically changes the calculated flux into the aquifer.

It has been examined if the canister lifetime can contribute to a reduction of the maximum dose due to I-129. A spreading of the corrosion times over a time span of 50,000 years results only in a decrease of 11 % of the maximum dose.
The potential influence of the complexation of trivalent radionuclides by small organic molecules, i.e. fulvic acids, has also been evaluated. The organic complexation can increase drastically the fluxes calculated at the clay-aquifer interface. The reversibility of the complexation mechanism requires further examination.

For the aquifer modelling the analytical one-, two- or three- dimensional AT123D code, the two-dimensional finite element AQUA code and the three-dimensional finite element WATERFLO code have been applied to simulate the water flow and the transport of radionuclides in the overlying (Neogene) and the underlying (sands of Ruisbroek and Berg) aquifers. A considerable advantage of the finite element codes is that they allow to take into account the geometry of the sand layers and the variability of their characteristics, and the dilution of the concentrations which results from the infiltration of rain water in the upper aquifer. An example of a calculated concentration distribution is given in figure 3. Relatively high concentrations occur in the direct vicinity of the repository area, but they decrease fast with the distance. For the stochastic calculations of the doses via a water well, the analytical AT123D code can be applied.

ECN

The doses for the water intrusion scenarios have been calculated deterministically with the computer code EMOS_ECN. The resulting maximum dose rates for the shallow diapir are less than 10^{-8} Sv/y and less than 10^{-11} Sv/y for the deep diapir. The risk related to the best estimate of the dose rate is estimated to be 10^{-10}/y for the shallow and 10^{-13}/y for the deep salt formation.

The dose calculations for the subrosion scenarios are made with the computer code PANTER. This code is able to account for uncertainties in the data. The maximum dose rate varies between 2.10^{-6} Sv/y and 4.10^{-6} Sv/y. The difference between the deep and shallow diapirs are very small. The risk related to the exposure was calculated assuming that the probability of the subrosion scenario is equal to one and the probability of the dose rate is given by the uncertainty distribution. For all calculated cases, the risk appears to be 10^{-9}/y. In the extreme case that the barrier function of the overburden is completely neglected, the resulting maximum exposure is 10^{-5} Sv/y.

IPSN

1) Normal Evolution Scenario (Granite site)

In the framework of the calculations relative to the granitic site, IPSN has used the MELODIE computer code for reference flow and transport calculations of the normal evolution scenario. In the first step of the methodology, two different scale models have been prepared in a quasi-3D representation: "regional scale model" (40x43 km) for flow calculations and "local scale model" (11x15 km) for flow and transport calculations.

The site is described as a fractured granite in a surrounding schist, the topography being treated with a 75x75 meters resolution. The limits of the "regional scale model" and the nodes of the meshed net are ajusted on the natural outlets (rivers) and on the various watersheds. The permeability of the three considered domains (granite, schist and fractures) is depth dependent. The influence of the permeability ratio granite/schist on the groundwater flow has been investigated. A tracer study from the repository location has showed that the flow lines converge to the south and the east of the area and have led to define the "local scale model", limited at the granitic area. The groundwater flow calculation has been used to define the outlets (figure 4). The potential influence of the dispersivity coefficient has been studied for various radionuclides transport.

2) Normal Evolution Scenario (Clay site)

The clay site is located on the south border of a large sedimentary basin (about 150,000 km^2). In order to comprehend the general hydraulic behavior of the basin, the model encompasses as much as possible natural boundary conditions. Local geological and hydrogeological data has been given by ANDRA: the stratigraphy comes from a deep geological borehole located at the repository location.

A regional area about 100x120 km^2, has been determined around the site in order to encompass natural boundaries (outcrops) in the southern part. This is of importance because flow in individualized units is closely linked to their outcrops piezometry on the basin border. Northern captive boundary conditions are obtained through the large basin modelling. A water table map, which will correspond to the surface boundary conditions, has been constructed by hand from topographical information and rivers average levels (figure 5) and is based on a regular grid with 2.5x2.5 km^2 meshes (figure 6). On this grid the repository location is figured by the black mesh and the main outcrops are shown. The corresponding basic units are numbered following the eight basic units which have been individualized as shown on the log interpretation of the borehole log given on figure 7.

With NEWSAM, first approach flow calculations have been done for the sedimentary basin using an 11 layered model from Trias to chalk units along with a 5 layers internal representation for the host formation. A simplified regional model has the been done with 13 layers (of which 4 for the host-clay), based on the grid presented on figure 6. Transient advective transport calculations have been conducted with an arbitrary concentration located in the black mesh of the middle host clay layer. An example of the results obtained is given on figure 8, where the dilution in aquifers can be seen as very important.

3) Salt Consumption Scenario(Salt site)

A sensitivity analysis for the salt consumption scenario has been performed with the PREP and SPOP computer codes to estimate the relationship between the dose equivalent and the input parameters of the model.

D- REFERENCES

BAUDOIN, P., and al., International Conference Safewaste'93, Avignon, 13 - 18 June 1993. Proceedings Volume 3 pp 267-278.

ESCALIER des ORRES, P., GRENECHE, D., International Conference Safewaste'93, Avignon, 13 - 18 June 1993. Proceedings Volume 2 pp 467-478.

MARIVOET, J., BONNE, A., VOLKAERT, G. and ZEEVAERT, T., ASME International Conference on Nuclear Waste Management and Environmental Remediation, Prague, 5-11 Sept. 1993. Proceedings pp. 733-736.

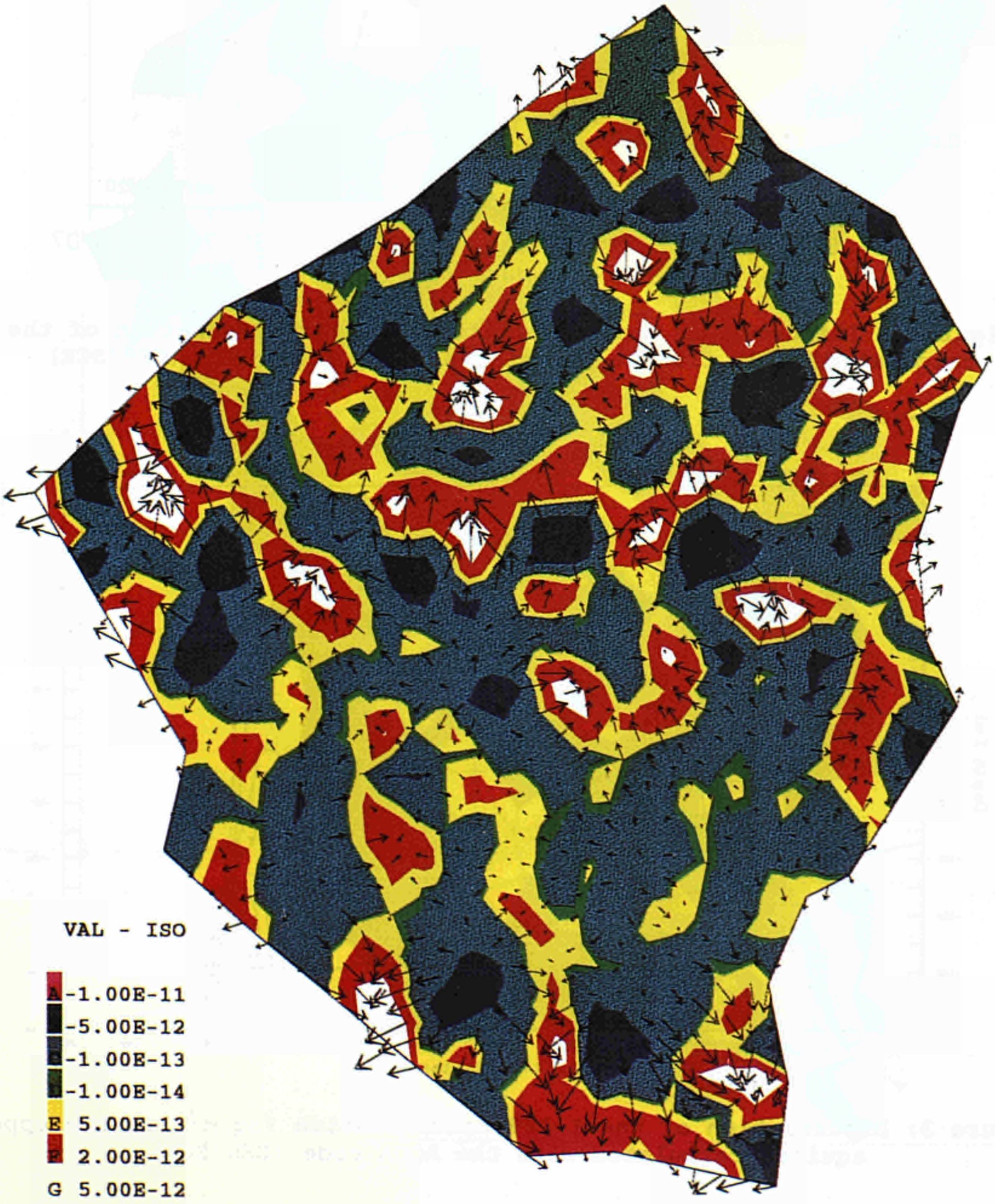


Figure 1: Regional flow calculation for the granite site - Velocities map (ANDRA)

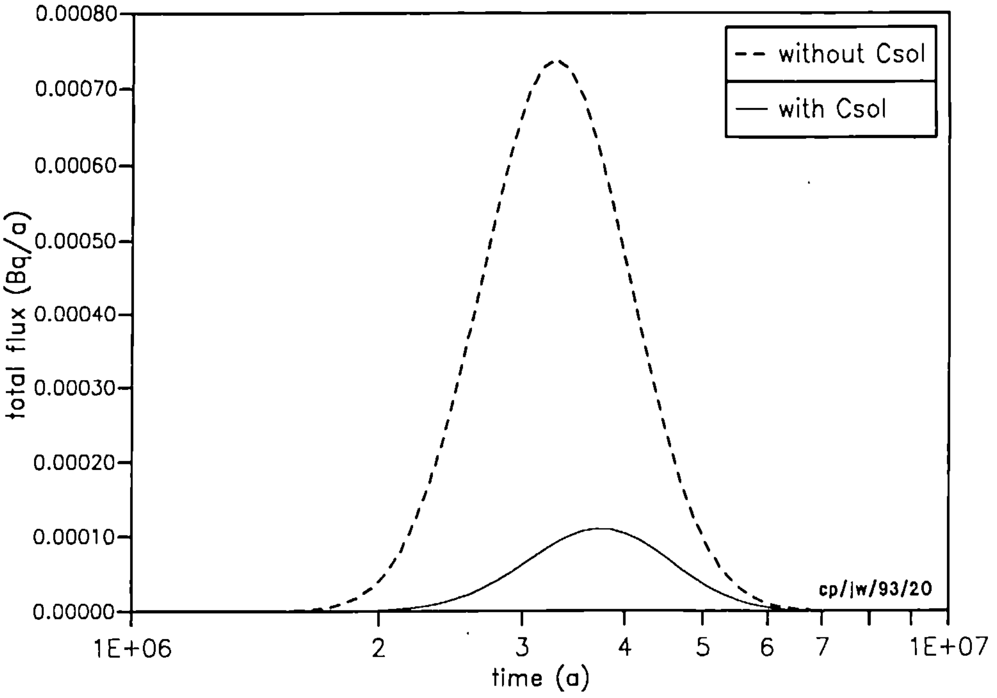


Figure 2: Influence of the solubility limit (Cs). Evolution of the calculated Tc-99 flux at the clay-aquifer interface (CEN/SCK)

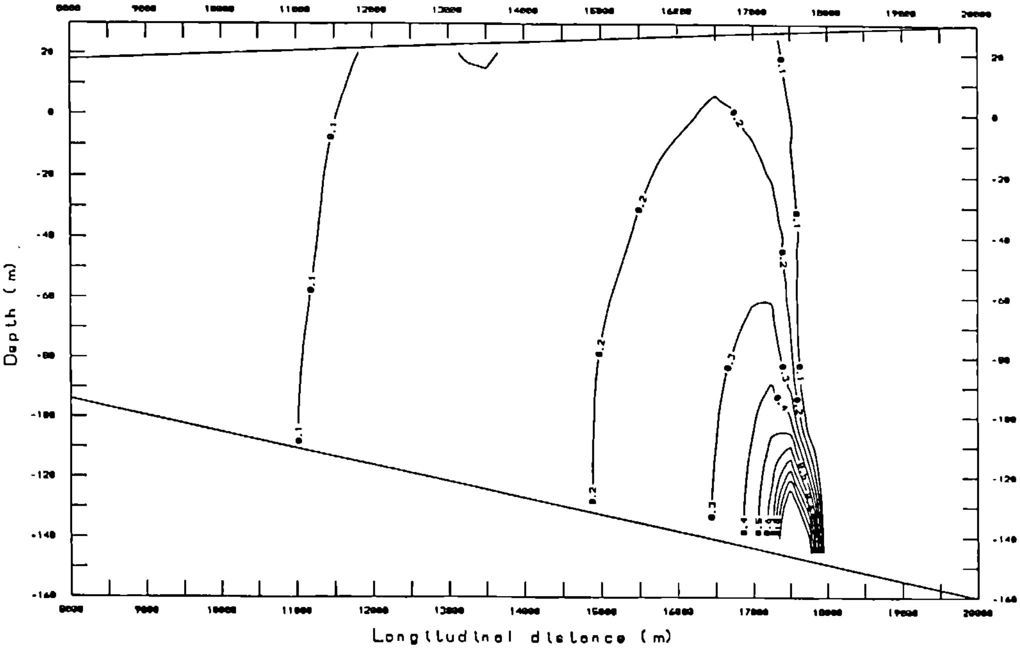


Figure 3: Distribution of the I-129 concentration (Bq/m^3) in the uppe aquifer calculated with the AQUA code (CEN/SCK)

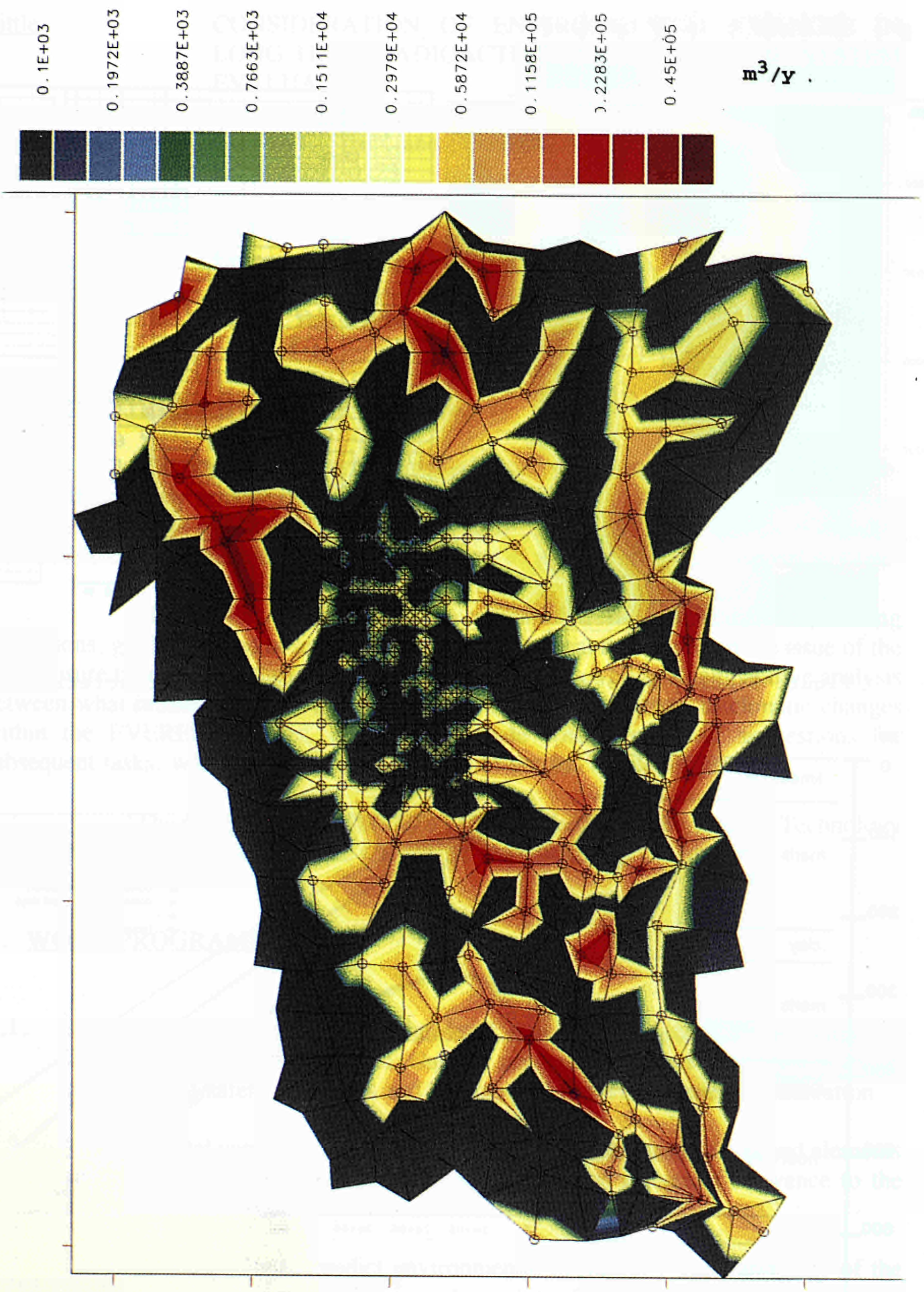


Figure 4: Flow reference calculation (Granite site) - Outlet identification (IPSN)

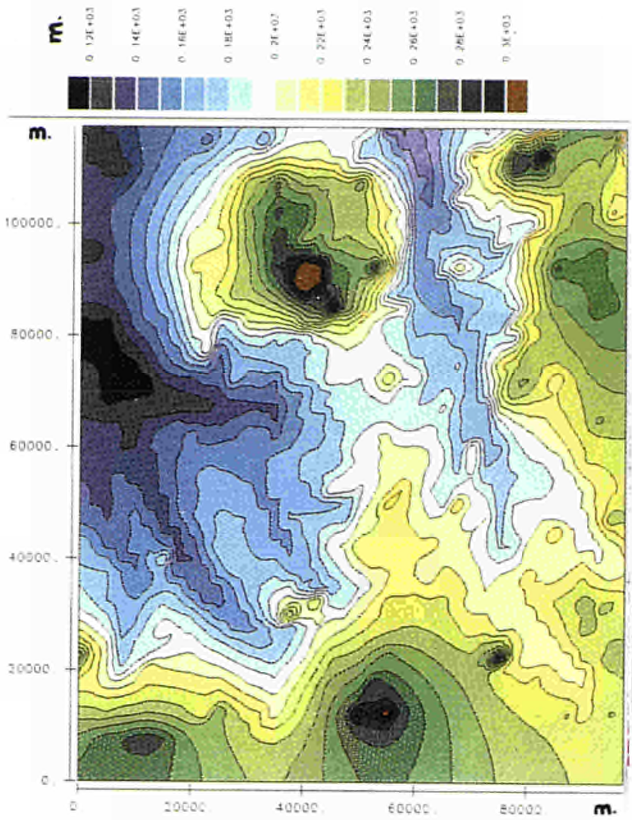


Figure 5: Clay site water table (IPSN)

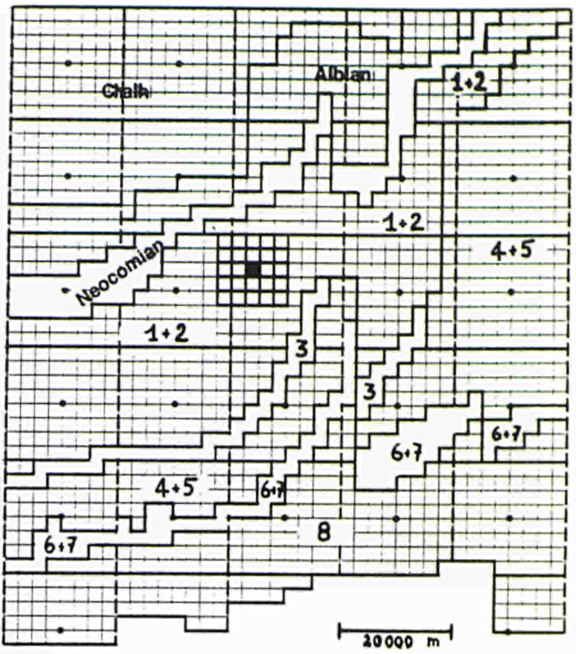


Figure 6: Geology discretization (IPSN)

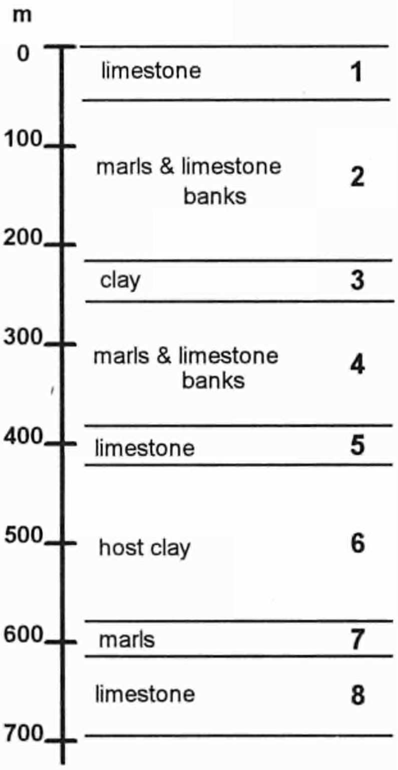


Figure 7: Individualized units at repository location (IPSN)

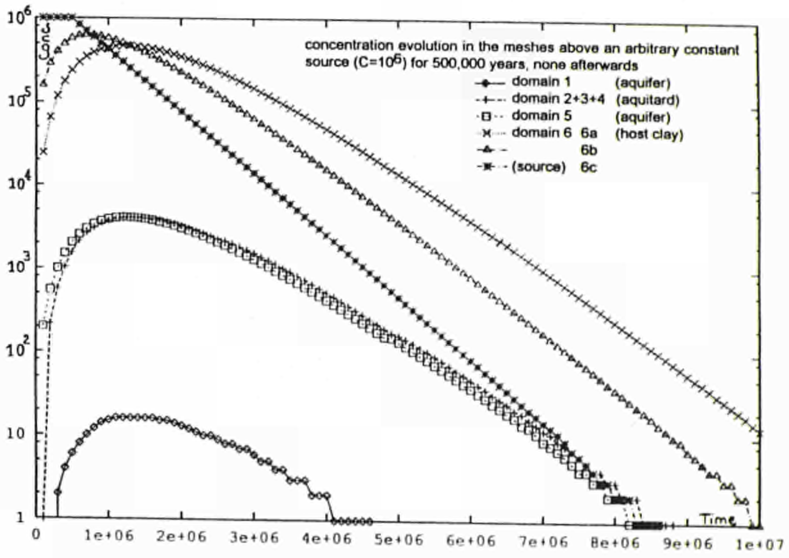


Figure 8: Example of concentration evolution (IPSN)

Tittle	CONSIDERATION OF ENVIRONMENTAL CHANGES IN LONG-TERM RADIOACTIVE WASTE DISPOSAL SYSTEM EVALUATIONS
Contractors	CIEMAT, Spain, and ENRESA, Spain
Contract N°	FI2W-CT92-0123
Duration of contract	19 months from December the 1st, 1992 to June 30th, 1994
Period covered	December 1992 to December 1993
Project Leader	Mr. F. Recreo (CIEMAT; coordinator) Ms. C. Bajos (ENRESA)

A. OBJECTIVES AND SCOPE

The objective of the work is a state-of-the-art analysis consisting basically in a well-founded, critical discussion of the phenomena of long-term environmental changes, their basis and the existing or foreseeable scientific and technological capacity for suitable consideration in the safety evaluation of radioactive waste disposal systems.

The analysis will include also a comparative study of the different existing regulations, guidelines and observable current international tendencies on the issue of the post-closure timescales in the context of safety analysis, as well as a comparative analysis between what is indicated above and the actual consideration given to climatic changes within the EVEREST project, and will conclude with a series of suggestions for subsequent tasks, which may be recommended to the EC for development.

The project is carried out by a collaborate effort of the Nuclear Technology and the Environmental Institutes of CIEMAT, and ENRESA.

B. WORK PROGRAMME

B.1. Basis for safety evaluation of high-level radioactive waste disposal systems : Safety objectives and principles. Current situation and observable tendencies on expression of safety principles and objectives and on timescales consideration.

B.2. Environmental variation and its effect on the disposal system : Basis and elements of environmental variation. Environmental variation effects of relevance to the safety of the repository.

B.3. The human capacity to predict environmental evolution : The variability of the climate systems over different timescales and its effect on geo-biospheric systems. Current capacity for evaluation and prediction; available methods and techniques : limits and levels of confidence.

B.4. Consideration of environmental change in disposal system safety evaluation : Existing methods and techniques. Approaches of different countries to consideration of environmental change.

B.5. Comparative analysis with the EVEREST project : Summary of the methods used in EVEREST for consideration of environmental changes. Qualitative comparison with the state-of-the-art.

B.6. Conclusions and recomendations for subsequent development : General conclusions and recommendations regarding environmental change and repository safety. Specific conclusions and recommendations regarding EC R & D activities related to the EVEREST project.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

During the period covered by this report a preliminary bibliographic study has been made, ending with the submittal of the preliminary draft report to EVEREST by July 1993.

The descriptive sections of the work carried out during this period centre on scientific and methodological aspects of significance in the field from B.1 to B.4 (see below) : information on physical processes currently considered to be important for the Earth's both short- and long-term environmental evolution; existing techniques for reconstructing the recent (Plio-Quaternary) geological past, and a comparative analysis of regulations and guidelines for high-level radioactive waste disposal systems evaluations. The review of research performed during this period also comprises a summary of work on the incorporation of environmental change evaluation into performance assessment of radioactive waste disposal in various countries around the world.

Progress and results

B.1. Basis for safety evaluation of high-level radioactive waste disposal systems

The main safety objective to meet is : "The disposal of high-level waste shall aim at protecting human health and the environment and limiting any burden placed on future generations, taking into account social and economic factors". In each case the applicability and rigoroudness of the different principles should have to depend on the time-frame under consideration. A revision of the safety principles and objectives as well as of the safety criteria and indicators is included : individual and collective dose; individual and collective risk; radiotoxicity indicators and the comparison with natural radiation, among other safety criteria and indicators.

B.2. Environmental variation and its effect on the disposal system

The timescales for the migration of radionuclides from radioactive waste repositories to the accesible environment are such that the exposure pathways which will be important at the time of release to the biosphere may not be those which would be important under present conditions [1]. This makes it essential for consideration to be given to the environmental change expected in the long term.

The environmental system is made up of 5 subsystems : the atmosphere, the oceans, the cryosphere, the lithosphere and the biosphere. These subsystems are interrelated by way of physical, chemical and biological processes, the response time and sensitivity of each subsystem being variable. The environmental system is thermodynamically controlled, solar radiation being the main external driving force.

The climate is a major component of environmental variability over tens of thousands of years. In a modern consideration [2], [3], the climate needs no astronomical variation to suffer a change of regime since its dynamics possess intrinsically stochastic components (autovariations). [4].

The theory that variations in seasonal solar radiation intensity as a result of astronomical factors might give rise to periodic glaciations was originally put forward by the French mathematician Joseph Adhémar at the end of the 19th century. The Yugoslavian astronomer M. Milankovitch refined and formalized Adhémar's hypothesis between 1920 and 1930. Milankovitch's theory associated glacial cycles with changes in the distribution of solar irradiance as a result of variations in the geometry of the Earth's orbit, depending on three elements : obliquity, equinoctial precession, and eccentricity. Precession is a cycle with a period of 23,000 to 26,000 years; the cycle of obliquity has a duration of 41,000 years, and the cycle of the orbit (which is a double one : oscillation of the eccentricity of the ellipse and rotation of the ellipse around the Sun), has a duration of 96,000 years.

Although climate variations are the result of variations in the amount of solar radiation received and retained by the system, an important part of the environmental variation is random and caused by processes internal to the system, amplified by feedback mechanisms.

The most significant evidence backing the theory of Milankovitch came from the isotopic variation of ^{18}O / ^{16}O in foraminifers from deep submarine samples. The Milankovitch theory explains clearly the Quaternary glacial/interglacial cycles by means of three orbital cycles of 100, 40 and 20 thousand years, possibly amplified by feedback mechanisms such as ice-albedo and CO_2.

The position and extent of the continents and oceans resulting from plate tectonics and polar drift is another of the variables controlling climate change. Plate tectonics have also conditioned relief (which in turn controls atmosphere circulation) and volcanic emissions of CO_2.

Apart from the natural causes of climate change, the appearance of man and of its capacity to modify the surroundings led to the possibility for anthropogenetic causes of climate pattern change, these being difficult to quantify and predict.

Variations in the atmospheric concentration of greenhouse gases is another of the variables controlling climate change. Water vapour, carbon dioxide and ozone are the three factors mainly responsible for the greenhouse effect. If duplication of CO_2 as a result of human activity were to saturate all the bands of absortion currently having some degree of transparency, the atmosphere would tend to become a 100 % black body. The best estimates of equilibrium global temperature rise associated with a doubling of CO_2 concentrations lie in the range 1.5 - 4.5 °C [5], [6].

Of all the forcing mechanisms that have been analyzed, climate and tectonic changes would appear to be those having the greatest influence on radioactive waste storage systems. This influence operates via modifications to the safety parameters of the geological barrier, and also by introducing changes and adaptations to the biospheric system surrounding the geological medium. The effects of climatic change are especially evident in relation to geomorphic and hydrological processes, sea level change and permafrost development. Glacial effects are of particular importance. Tectonic change is of interest primarily for its influence on permeability conditions around the repository. [7].

Although climate seems to play a fundamental role in determining groundwater flow, it may have a significantly delayed response and its effects are not simply determined. On the other hand, its time-dependent nature is difficult to quantify. The response time is dependent on several factors. Land elevation and sea level act as major boundary conditions of a groundwater system. Changes in these boundary conditions may lead to delayed response groundwater effects. [7].

There is a general consensus that the most probable climate changes over the next few thousand years will be those represented by the various climate episodes that have occurred during post-glacial time (the Holocene). [8]. Nevertheless, for the next 100,000 years the world's climate could be dominated by glaciations, as it has been over similar periods for the past million years. [9]. A realistic description of those conditions that might influence the performance of a repository during a glaciation cycle should consider an overview over the various mechanisms and processes involved in a typical glaciation cycle and an assessment of their influence on repository performance. The "glaciation scenario" covers from the present to the next interglacial, when the climatic conditions will once again return to the present conditions [9] 125,000 years AP.

Enhanced greenhouse warming is expected to cause changes that, in turn, will have implications for the climatic response to orbital forcing, such as changes in the cryosphere. Three possible patterns describing this relationship can be identified [10]:

The simplest assumption is that a relatively short (1 Kyr) period of greenhouse gas-induced warming will be followed by a switch back into the "natural" pattern of glacial/interglacial cycles. The second possibility is that, following a period of warming, the next glaciation will be delayed and will be less severe. The third possibility is that enhanced greenhouse warming will so weaken the positive feedback mechanisms which transform the relatively weak orbital forcing into global glacial/interglacial cycles, that the initiation of future glaciations will be prevented (the "irreversible greenhouse effect). According to the limited evidence available, Goodess et al. consider that the second possibility will delay the onset the next glaciation by about 5 Kyr, from 55 to 60 Kyr AP, and to reduce its severity. The transition to cooling is expected to be delayed for more than 1 Kyr. Goodess, Palutikof and Davies assume that the climate system will recover from the effects of enhanced greenhouse warming and that orbital forcing will operate much as it has over the Quaternary. Based on these assumptions, it is reasonable to use the geological record of the Quaternary period as a guide to the future, beyond the point of transition. [10].

B.3. The human capacity to predict environmental evolution

We might define the climate system as an open, complex, dissipative, non-linear system which organizes itself in a (meta)stable fashion. Some of this complex properties, particularly variability and memory, affect predictability. There would appear to be two sources of climatic variation : a) Variations to the forcing mechanisms external to the climate system, and b) internal, regional fluctuations, which subsequently wander, are amplified and dampened by the global system, and three classes of climatic variation : 1) "forced" by variations in the external forcing mechanisms, 2) "free", or self-generated fluctuations within the climate system, and 3) "resonant", any combination of the previous classes.

The Milankovitch forcing mechanism accounts only for 60 % of the variance recorded on the 780 Kyr registers in the frequency window between 19 Kyr and 100 Kyr, or 85 % of the variance if the windows are four narrow bands around the orbital cycles. [11]. The rest of the variance must be result of solar variability, volcanic activity, stochastic mechanisms, etc. [10]. Variability might be separated into a deterministic part and a random part associated with fluctuations in the weather.

The study describes the calculation tools currently used for the description, modelling and quantitative prediction of future climate, its regional features and its geological and environmental effects, making a distinction between descriptive or phenomenological (ARMA, ARIMA, Markovian) models and mechanismic (EBM, RCM, GCM) models, and reviewing some specific models already available.

B.4. Consideration of environmental change in disposal system evaluation.

There are two main approaches for the description and modelling of the geo-biospheric systems, able to estimate also the uncertainty of the prediction : a) the

Scenario Analysis Approach, and b) the Environmental Simulation Approach.

Probably the Scenario Approach has a simplicity and a degree of axiomatization that makes it very attractive as a tool for decision making by regulatory bodies. The Environmental Simulation Approach can be a good heuristic tool in the research of natural system behaviour as well as in more sophisticated ways of modelling these systems without losing the applied perspective.

A different kind of problems emerges when the scientific knowledge is unable to predict, even probabilistically, what variables will be important in the distant future and the state of a variable that may be important in the far future, as it is the case with many processes of the future biospheric system controlled by humans, e.g. agronomic practices, socioeconomic factors, etc. The human intrusion in the repository introduces a similar problem of unpredictability.

The Environmental Simulation Approach gives no method to take into account this kind of processes. The Scenario Analysis Approach makes it possible to illustrate the possible effect of this kind of processes, but the completeness and representativeness of the set of scenarios is in any case undefined.

The study contains a short description of the approaches of different countries to consideration of environmental change, with a specific analysis of time dependant codes of the English Methodology (TIME-2 and TIME-4), [12], [13] the French deterministic Program CASTOR, [14] and the AEGIS (USA) geological simulation codes GSM and FFSM.[15], [16].

References to the published literature.

[1] BARRACLOUGH, I.M., International Workshop on Future Climate Change and Radioactive Waste Disposal, Norwich, 1-3 November 1989. Proceedings pp 245-251.

[2] BENZI, R., Tellus 34, 10-16 (1982).

[3] NICOLIS, C., Tellus 34, 1, 1-9 (1982).

[4] LEITH, C.E., Nature 276, 352-355 (1978).

[5] MacCRAKEN, M.C., LUTHER, F.M., Carbon Dioxide Research Division, Office of Energy Research, US Department of Energy Report DOE/ER-0237 (1985).

[6] BOLIN, B., DÖÖS, B.R.; JÄGER, J., The Greenhouse Effect, Climatic Change and Ecosystems, SCOPE 29, Wiley, New York (1986).

[7] DAMES & MOORE INTERNATIONAL, Technical Report TR-D & M-12 (1989).

[8] SCHUMM, S.A. and CHORLEY, R.J., NUREG/CR-3276 RW (1983).

[9] AHLBOM, K., ÄIKÄS, T., ERICSSON, L.O., SKB Technical Report SKB TR-91-32 (1991).

[10] GOODESS, C.M.; PALUTIKOF, J.P. and DAVIES, t.d., The Nature and Causes of Climatic Change. Assessing the Long Term Future. Belhaven Press, London (1992).

[11] IMBRIE, J. et al., Milankovitch and Climate, D. Reidel, Dordrecht, pp 269-306 (1984).

[12] DAMES & MOORE, User Document UD-D&M-1, UK Department of the Environment Report No. DOE/RW/88.088 (1988).

[13] DAMES & MOORE, Technical Report TR-D & M-18, UK Department of the Environment Report No. DOE/HMIP/RR/91.050 (1991).

[14] CANCEILL, M. et al., Bureau de Recherches Géologiques et Minières Report 84 SGN 229 STO (1984).

[15] INTERA Environmental Consultants, Inc. Technical Report, ONWI-447 (1983).

[16] INTERA Environmental Consultants, Inc. Technical Report, ONWI-436 (1983).

PART B

Construction and/or operation of underground facilities

* List of contracts

* Introduction to Part B

PART B - LIST OF CONTRACTS

CONSTRUCTION AND/OR OPERATION OF UNDERGROUND FACILITIES OPEN TO COMMUNITY JOINT ACTIVITIES

Project B1 "The underground facility in the Asse Salt Mine (FRG)"

FI2W-CT90-0002	The HAW project : test disposal of highly radioactive canisters in the Asse salt mine
FI2W-CT90-0068	In-situ investigation of the long-term sealing system as a component of a dam construction
FI2W-CT90-0069	Active handling experiment with neutron sources
FI2W-CT92-0120	Thermo-mechanical study of the area in the vicinity of a storage borehole in salt formations (CPPS)

Project B2 "The underground facility HADES in the argillaceous layer under the Mol Site (B)"

FI2W-CT90-0003	Preliminary demonstration test for disposal of high-level radioactive waste in clay: a)CERBERUS, b)Mine-by-Test
FI2W-CT90-0001	Characterization of the clay under thermal loading for underground storage -CACTUS project
FI2W-CT91-0098	Demonstration of the in-situ application of an industrial clay-based backfill material (BACCHUS)
FI2W-CT91-0033	Modelling and testing of the hydration of backfill and sealing materials
FI2W-CT91-0102	Modelling and validation of the thermal, hydraulical, mechanical and geochemical behaviour of the clay barrier
FI2W-CT92-0117	Acquisition and regulation of water chemistry in an argillaceous medium (ARCHIMEDE)
FI2W-CT91-0116	Evaluation of hydraulic transfers between the argillaceous rock and the excavations (PHEBUS)

Project B4 "Underground validation facility at Sellafield (UK)"

FI2W-CT91-0114	Hydrological characterisation of fractured rock (Sellafield)

INTRODUCTION TO PART B : CONSTRUCTION AND/OR OPERATION OF UNDERGROUND FACILITIES OPEN TO COMMUNITY JOINT ACTIVITIES

A. Objectives

The main objective of this part of the programme is the construction and the operation of underground facilities to develop and demonstrate emplacement techniques and to validate site and design criteria of deep geological repositories. All these facilities have been declared, by the responsible bodies in the Member States on which territories the facilities are build, open to scientists of the Community for joint R&D activities.

B. Research performed under the programme 1985-1989

In the programme 1985-1989 joint research activities were already started at the Asse salt mine (FRG) and in the HADES underground facility at Mol (B). The research in the Asse salt mine concerned mainly the preparation of the test at Mol a Test Drift was excavated and various lining systems tested. Moreover, a combined heating/radiation experiment (CERBERUS) was started.

C. The present programme 1990-1994

Research activities at the facilities in the Asse salt mine and in the HADES facility in clay at Mol (Project B1 and B2 respectively) started during the previous programme were continued. Additional research projects have been initiated as described below. However, in December 1992 the Federal Government in Germany decided not to continue with the HAW project and to postpone the MAW/REV project dealing with test storage of Medium Level waste.

The construction of underground facilities in France (Project B3) has been delayed and the planned budget has been allocated to research activities on clay and salt, complementary to the investigations in Mol and Asse.

Site characterization work at Sellafield (UK) (Project B4) has started.

Project B1 : The underground facility at the Asse salt mine (FRG)

After the decision taken by the Federal Government in Germany in December 1992 not to continue with the HAW project and to postpone indefinitevely the MAW project, research was concentrated on the accompanying laboratory programme, consisting mainly of irradiation experiments in salt samples in the irradiation facilities at Saclay(F) and Petten(NL). The electrical heaters installed in two boreholes in the Asse mine and running since November 1988, were shut down under controlled conditions and retrieved.

Within the DAM project a multicomponent dam is being developed, constructed and tested in the Asse mine for use as an engineered barrier in galleries. The CEC is participating in a subproject concerning an in-situ experiment on the tightness of a long-term sealing component consisting of salt bricks. The seal will be tested on tightness first against gas and then against brine. However due to a review of the project, no in-situ work took place during 1993.

The AHE experiment (Active Handling Experiment) with neutron sources aims at studying the effect of neutron back-scattering on the overall neutron, and neutron induced gamma-dose rates during handling of highly active material in a repository in a salt formation.

The CPPS project, performed in the Amélie potash mine (F), concerns investigation of the thermo-mechanical behaviour of the near-field of waste emplacement boreholes in salt.

Project B2 : Experiments at the HADES underground facility at Mol (Belgium)

In the HADES underground facility in the Boom clay beneath the site of Mol, the following large projects are being carried out.
The PRACLAY project is a preliminary demonstration test for disposal of HLW canisters in horizontal mini-tunnels in clay. It is intended to feature a full scale simulation, over a length of 20 m of the cross sectional configuration of the waste environment, complete with heat generation (electrical heaters). The project was however suspended for various reasons in 1993 and no progress is reported.

The combined heating-radiation test(CERBERUS) aims at investigating the near-field effects in an argillaceous environment of a HLW canister. It uses a Co-60 radiation source of 397 TBq and two electrical heating elements each dissipating 365W.
In a mine-by test the response of the clay on the excavated Test Drift is monitored.

In the CACTUS project, the near-field thermo-hydro-mechanical behaviour of clay around boreholes with high-level waste is being investigated using electrical heaters.

The BACCHUS-2 project aims at optimizing and demonstrating an installation procedure for a clay based backfill material. The instrumentation of this experiment will be optimized in such a way that it can be used as a validation experiment for a hydromechanical model being developed.

The ARCHIMEDE project aims at the investigations of the water chemistry in clay and the PHEBUS project concerns the study of the hydrous behaviour of clay around ventilated excavations.

Project B3 : Underground facilities

The construction of underground facilities in France has been delayed. The planned budget has been allocated to research activities on clay (ARCHIMEDE and PHEBUS) and salt (CPPS) (see above B1 and B2). Furthermore the CEC is participating in the underground laboratory at Tournemire (see Task 4).

Project B4 : Underground facilities in the United Kingdom

The Commission is participating in some parts of the site characterisation programme carried out by UK Nirex Ltd. at Sellafield (UK).

THE HAW-PROJECT: TEST DISPOSAL OF HIGHLY RADIOACTIVE RADIATION SOURCES IN THE ASSE SALT MINE

Contractors: GSF-IfT/ Braunschweig-Germany, ECN/Petten-The Netherlands,
ANDRA/Fontenay-aux-Roses-France, ENRESA/Madrid-Spain
Contract No.: FI2W-0002
Duration of Contract: from May 1990 to December 1994
Period covered: January - December 1993
Project Leaders: T. Rothfuchs, L. Vons, M. Raynal, J. C. Major

A. OBJECTIVES AND SCOPE

In order to improve the final concept for the disposal of high-level radioactive waste (HAW) in boreholes drilled into salt formation plans were developed a couple of years ago for a full scale testing of the complete technical system of an underground repository. To satisfy the test objectives, thirty highly radioactive radiation sources were planned to be emplaced in six boreholes located in two test galleries at the 800-m-level in the Asse salt mine. A duration of testing of approximately five years was envisaged.

Because of licensing uncertainties the German Federal Government decided on December 3rd, 1992 to stop all activities for the preparation of the test disposal immediately.

In the course of the preparation of the test disposal, however, a system necessary for handling of the radiation sources was developed and installed in the Asse salt mine and two non-radioactive reference tests with electrical heaters were started in November 1988. These heater tests served for the investigation of thermal effects in comparison to the planned radioactive tests. An accompanying scientific investigation programme was performed in situ and in the laboratory. The programme comprised the estimation and observation of the thermal, mechanical and radiation-induced interaction between the rock salt and the electrical heaters and the radiation sources, respectively. The laboratory investigations were carried out at Braunschweig (FRG), Petten (NL), Saclay (F) and Barcelona (E).

As a consequence of the early termination of the project the working programme 1992 - 1994 was revised. The new programme for 1993 and 1994 agreed to by the project partners includes a controlled shut-down of the heater tests in 1993 and a continuation of the laboratory activities until the end of 1994.

B. WORK PROGRAMME

B.1 In-situ activities
B.1.1 Controlled shut-down of the heater experiments and continuation of in-situ measurements
B.1.2 Thermomechanical analysis
B.1.3 Post test sampling
B.2 Laboratory activities
B.2.1 Irradiations at Saclay
B.2.2 Irradiations at the HFR in Petten and modelling of radiation damage
B.2.3 Development of a measuring system for high doses
B.2.4 Gamma field and gamma spectra calculations
B.2.5 Post test analyses of salt and fluid phase samples
B.2.6 Post test analysis of corrosion specimens
B.3 Desk studies
B.3.1 Description of the mineralogical and geochemical properties of the underground test field
B.3.2 Evaluation of the experiences gained from the cold training with the handling system

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In May 1991 the handling system for the radiation sources was approved by the mining authorities and by the Technischer Überwachungsverein (TÜV). From November 1988 until August 1993 the two electrical reference tests were operated at the test sites A1 and B1 in the test galleries at the 800-meter-level of the Asse salt mine. Corresponding thermomechanical and geochemical in-situ investigations as well as laboratory investigations on radiolysis effects in salt are underway since beginning of the project. The results obtained until the end of 1992 were reported in (CEC, 1991), (CEC, 1992), (GSF-IfT, 1993).

Progress and results

1. In-situ-activities

1.1 Controlled shut-down of the heater experiments and continuation of the in-situ measurements

According to the results of a preceding thermomechanical analysis (compare section 1.2) the two electrical heaters in the HAW test field were shut-down linearly over a period of six months. The heater power was at zero on August 26, 1993. The shut-down procedure was accompanied by the measurement of salt temperatures, rock stresses and deformations and the release of fluids from the heated rock mass. Figure 1 shows the measured temperature drop at the wall of the heater borehole B1 and in the surrounding salt up to 4.24 m. Figure 2 shows as an example the concentration of hydrogen (H_2) in the atmosphere of borehole B1. The increase in concentration observed at the end of the heating period indicates an increase of the permeability of the rock mass which is the result of a limited cracking of the salt because of its cool-down.

Twelve tiltmeters have been installed by the Institut du Physique de Globe (Paris) in three locations around the HAW test field to survey the movements of salt. The measurements carried out in 1993 are satisfactory and confirm the previous results. Four tiltmeters are located at the bottom close to heater A1 and reveal an uprise of the floor from the middle of 20 mrad after 5 years (2 cm per meter). The inclination rate increased twice when the heat started and decreased when it what progressively turned off (Fig. 3). Heating of A1 does not seem to affect the two stations located outside the experimental galleries, since the values obtained there are of the order of magnitude of those recorded near A1 before heating.

1.2 Thermomechanical analysis

The thermomechanical analyses performed by ECN and GSF concern the isothermal as well as the heated phase of the experiment. The analyses concern the prediction of the temperature rise, the deformation of the galleries, and the distribution of the stresses in the HAW test field (Prij et al., 1991, Prij and Graefe, 1992).

The analyses performed in the reporting period concern the shut-down of the heaters. These analyses have been performed in close cooperation between ECN and GSF. Here the analyses performed at ECN will be summarized.

Another activity in 1993 was the comparison of the predictions and the measured values for the temperatures, deformations and stresses.

Shut-down of the heaters

To evaluate whether the shut-down period of six months will lead to a limited crack formation, finite element analyses have been performed of the thermomechanical behaviour of the HAW test field.

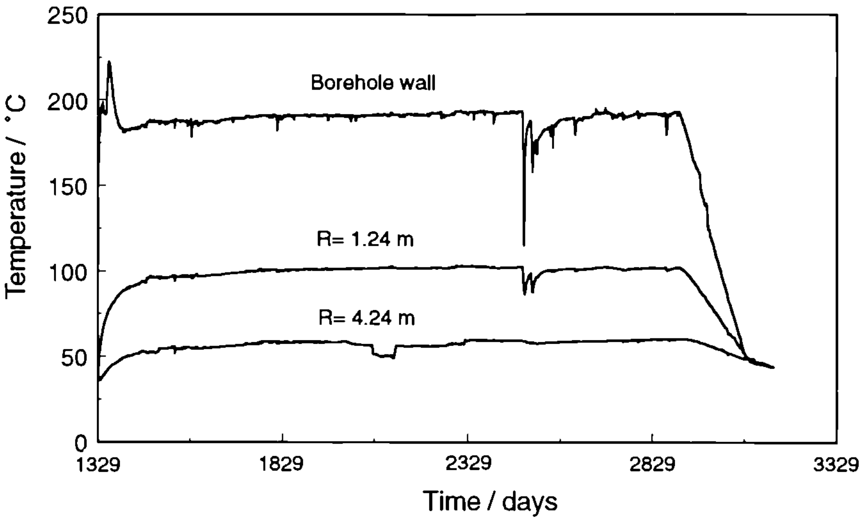


Fig. 1: Temperature versus time at the test site B1

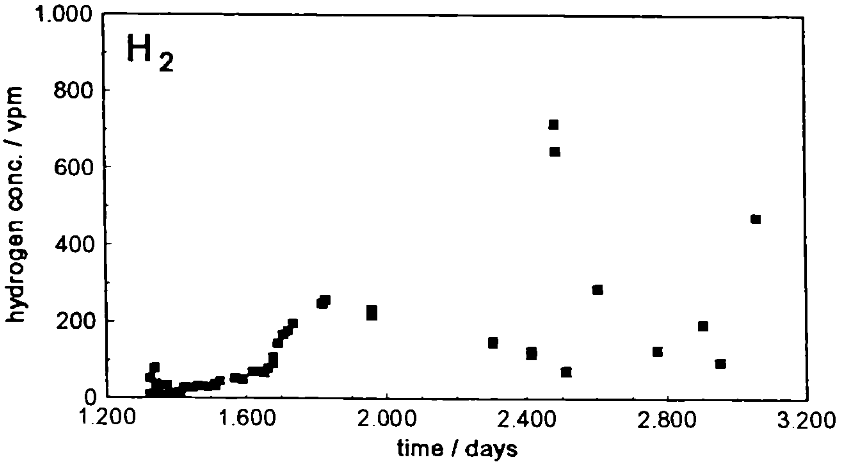


Fig. 2: H_2-concentration in the ring annulus of test site B1

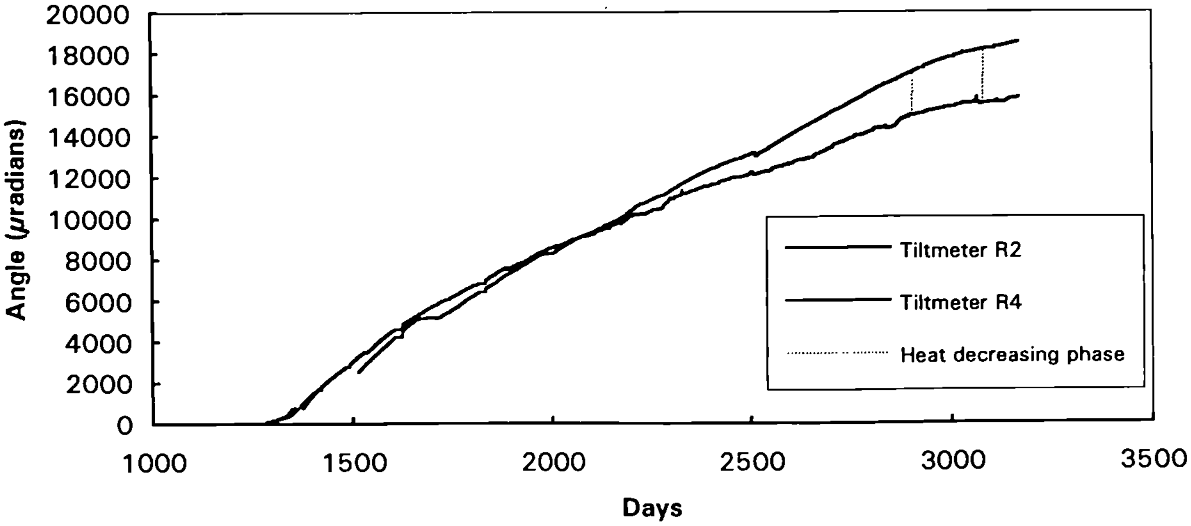


Fig. 3: Inclination versus time close to test site A1

The analyses have been performed with three different geometrical models, two different sets of constitutive models, and three different models of the liner. The maximum temperature calculated after the half year shut down period was 60 °C. To assess the calulated stresses, a fracture potential τ has been defined giving the ratio of the invariant octahedral shear stress to the shear fracture stress which in its term depends on the invariant octahedral normal stress:

$$\chi = \frac{\tau_o}{\tau_{o,fr}} = \frac{\tau_o}{a_0 + a_1\sigma_o + a_2\sigma_o^2}$$

The octahedral shear stress is related to the equivalent stress:

$$\tau_o = \frac{\sqrt{2}}{3}\sigma_{eq} = \frac{1}{3}\left((\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2\right)^{1/2}$$

The octahedral normal stress is equal to the mean normal stress:

$$\sigma_o = \frac{1}{3}\left(\sigma_1 + \sigma_2 + \sigma_3\right)$$

The shear fracture stress is taken from experiments of GSF (GSF-IfT, 1993, page 74).

Contours of the fracture potential τ are presented in Fig. 4. This figure shows the fracture potential at the end of heater-shut-down period. In the heater area a zone of potential crack risk begins to develop analog to the zone of high tensile stress. This means that the zone of τ values larger than one is limited to a cylindrical zone around the heater with a radius of roughly 3 to 4 meters.

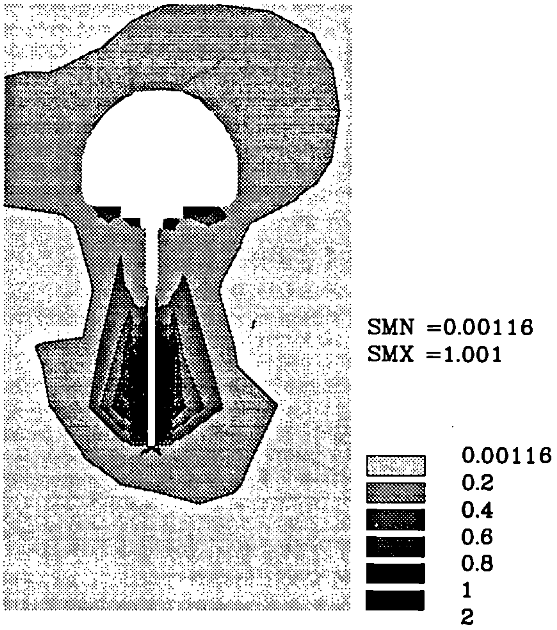


Fig. 4: Contours of the fracture potential at the end of the heater shut-down period

The results of the analyses have confirmed that in a small zone around the heaters cracks are to be expected. If these cracks are initiated the stresses will redistribute and consequently other cracks may initiate. This redistribution, however, has not been calculated. Based on the available stress distribution and the cause of the stresses, viz. a shrinkage of the heated area, it is concluded that the radial extent of the cracked zone will be limited to several meters. It further is considered to be very unlikely that the cracks will reach the floor of the galleries.

Comparison of measured and calculated values

In the analyses to be validated several assumptions had to be made. These assumptions being necessary to model the complex geometry and material behaviour must be kept in mind when the predicted values are compared with the measured ones. In the ideal case all differences between the measured values and predicted ones can be explained qualitatively and quantitatively.

The comparison of measured and calculated temperatures reveals that the differences between the predicted temperatures and the measured ones at the borehole wall can be explained by the geometrical modelling assumptions. The predicted temperature rises, however, at larger distances from the heaters correspond very good with the measured ones, and the temperatures close to the gallery floor are influenced by a summer and winter cycle which is not taken into account in the analyses.

Figure 5 gives the horizontal displacement of the two galleries in the test field. It can be observed that small differences exist between the measured displacements of the individual galleries but that these values differ significantly from the predicted values. Also in case of the vertical convergence of the two galleries the measured values are significantly larger than predicted. The measured deformation of the salt around the A and B gallery are difficult to explain with the thermomechanic models which are based on symmetry and homogenous rock salt. The most reasonable explanation for the observed differences and correspondences is a too low initial rock pressure. If the initial rock pressure would have been 12 MPa instead of the assumed 11 MPa the predictions of both the vertical and horizontal displacements should correspond much better with the measured values.

1.3 Post test sampling

After termination of heating an access drift similar to that of the Brine Migration Test Field in the Asse salt mine was mined in late 1993 for uncovering of the test site B1. The main reason is to retrieve 72 corrosion specimens representing possible waste canister materials (e. g. fine grain steel TStE 355, Hastelloy C4, Ti99.8-Pd, stainless steel X7 CrNi 2314). The specimens are attached to the surfaces of the liner in the borehole B1. The sampling will be performed in 1994 and the specimens will be analyzed by the Institut für Nukleare Entsorgungstechnik of the Nuclear Research Centre at Karlsruhe.

During excavation of the access drift salt sampling by coring as well as sampling of measuring sensors (thermocouples, stress gauges) was performed to investigate the in-place behaviour of the sensors in regard of an improvement of the measuring techniques.

The detailed investigation of the salt samples on their fluid content and the investigation of the retrieved measuring sensors is to be performed in 1994.

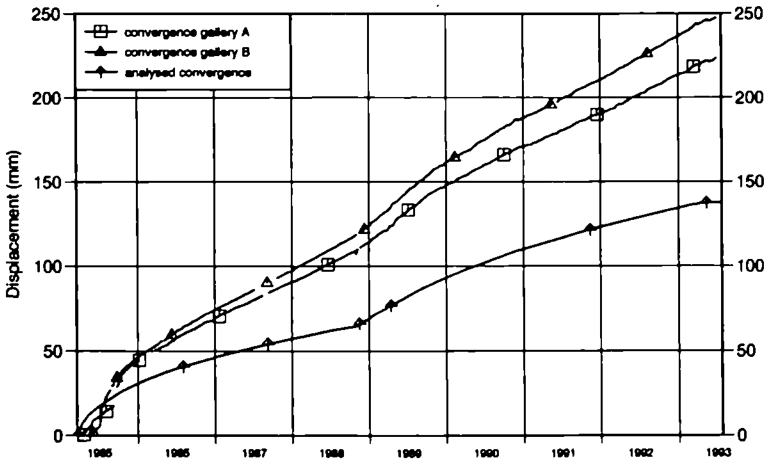


Fig. 5: Horizontal gallery convergence at the test sites A1 and B1

2. Laboratory activities

2.1 Irradiations at Saclay

The laboratory investigations on radiolytic gas formation and liberation from Asse salt have been terminated during the year 1993. Two experimental irradiations have been carried out during this period, aiming to study the effects of high integrated doses (resp. 60 and 130 MGy). The activity of the year was mainly dedicated to write a complete report on this work carried out between 1988 and 1993, i. e. data report, description of operating procedures, discussion of the results, possible extension of the work. The draft of this report will be submitted to the CEC for publication in January 1994.

2.2 Irradiations at the HFR in Petten and modelling of radiation damage

2.2.1 Irradiation experiments performed on behalf of ECN and ENRESA

Radiolysis effects in salt are studied by means of irradiation experiments performed at the Gamma Irradiation Facility (GIF) of the High Flux Reactor (HFR) in Petten (the Netherlands).

Calculations on the radiation damage which ought to be found in the samples following the modified Jain-Lidiard model (van Opbroek and den Hartog, 1985) are performed in Petten (ECN) for each of the experiments.

The experimental results are meant to produce a validation of theoretical models of radiation damage in rock salt which can be used for extrapolation to repository conditions.

Irradiation experiments at the HFR, GIF A

The objective of these experiments is to find the value of the integrated dose at which as many colloids are developed as annihilated.

Irradiations in GIF A of non-pressurized samples of Asse Speisesalz from the 800 m depth level, took place at 100 °C, at a variable dose rate (240 to 40 kGy/h), and up to different (cumulative) total doses.

In the experiments the modified Jain-Lidiard model gives a reasonable agreement with the experimental results of the stored energy measurements up to a total dose of about 450 MGy, above this total dose the predictions of this model are higher than the measured results, as can be seen in Fig. 6. In this figure the experimental data are also compared with the model developed by Soppe (Soppe, 1993). The predictions of this model are

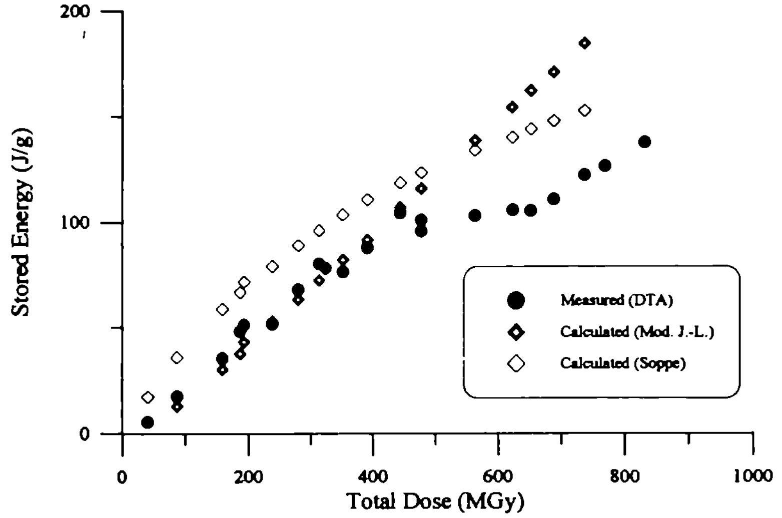


Fig. 6: Comparison of measured and calculated stored energy for irradiated Asse Speisesalz

systematicaly higher than the measured results but the model more or less reproduces the trend followed by them. For the experimental results there seems to be a temporarily stabilization betweeen 400 and 700 MGy but this cannot be concluded with great confidence. Above 700 MGy the stored energy increases again and a permanent stabilization of stored energy has not yet been found.

Irradiation experiments at the HFR, GIF B

The objective of these experiments is to elucidate the relationships between dose rate and radiation damage for different natural and artificial samples. The samples are irradiated at two different pressure conditions and up to different integrated doses. By varying the brine content of the samples and due to the different length of the experiments some information on anneal processes is also gathered through microstructural analyses.

A set of irradiations, in GIF B, of samples both pressurized and non-pressurized and of the same pure NaCl and natural rock salt samples planned to be used in the HAW test field (Mönig et al., 1990) proceeded during previous periods at 100 °C and constant dose rate of 15 kGy/h.

Stored energy measurements carried out on these samples by ECN at Utrecht University showed that before extensive colloid development the agreement with the Jain-Lidiard predictions was very poor (García Celma and Donker, 1992). Therefore, the Jain-Lidiard model was extended in order to include the nucleation process (Soppe, 1993). Comparison of the stored energy yields of pure single crystals with that of the most damaged (non-recrystallized) parts of natural rock samples simultaneously irradiated showed that at least in the experiments, natural rock samples (even in absence of recrystallization and of the endothermal effect of polyhalite dehydration) do not develop more stored energy than pure NaCl (García Celma and Donker, 1992).

Microstructural analysis, performed by ECN at Utrecht University showed that fluid assisted recrystallization mainly takes place by grain boundary migration. The extent of the recrystallized portion is proportional to the amount of brine contained in the samples as determined by TG at the Barcelona University.

Intracrystalline microstructural analysis was mainly performed and it has been shown that dislocations do not only originate by irradiation and are preferred sites of colloid nucleation, but also migrate dragging the colloids with them. However, the actual atomic level process involved in the colloid displacement is not well understood.

By irradiation the same succesive development of creep substructures as observed by deformation of rocksalt samples has been found (Garcia Celma and Donker, 1993).

After completion of the irradiation plan at 15 kGy/h in GIF B, a new set of irradiation experiments started, which differs from the previous in the dose rate value, now of 4 kGy/h.

From this set of experiments eight have been completed up to a total dose of 44.0 MGy.

Both models, the modified Jain-Lidiard model and the model developed by Soppe, show a reasonable agreement with the experimental results up to a total dose of 10 MGy. At a total dose of 44 MGy the model predictions are about a factor 1.5 to 3 higher than the measured results. This can be explained by the increase in importance of the recovery processes named above for longer experiments.

2.2.2 Investigations Performed for ENRESA at the University of Barcelona

Radiation damage

The determination of the radiation induced defects has been carried out by Light absorption and using hydrogen measurements of dissolved rock salt as countercheck for the determination of the fraction of metallic sodium. Samples came from the two sets of experiments performed at the HFR at Petten.

Samples irradiated in GIF A, showed very complex Light Absorption spectra, due to their high absorbed dose. Nevertheless, F- related centers and three sizes of colloidal sodium particles were detected. The total amount of colloidal sodium particles ranges between 2 * 10^{-4} mol and 4.3 * 10^{-3} mol and the amount of F-related center ranges between 1.14 * 10^{-4} and 3.74 * 10^{-4} mol.

In samples irradiated in GIF B the total amount of colloidal sodium particles ranges between 3 * 10^{-7} and 8.23 * 10^{-4} mol, the amount of F-related center ranges between 6 * 10^{-7} and 9.65 * 10^{-5} mol and the amount of M-center (when detected) ranges between 10^{-7} and 5.26 * 10^{-4} mol.

Moreover, there is an increase of the amount of defects with increasing dose. Comparing these samples, with their equivalents irradiated at 15 KGy/h a slightly higher efficiency at 4 KGy/h in generating defects can be observed, althought the concentrations of defects are of the same order of magnitude.

Radiolytic gas production

The study of radiolytical gas formation from Potasas de Llobregat rock salt has been launched to complement the experiments of the generation of radiation induced defects. The irradiations were performed with Co 60 sources at the industrial irradiator CESAR located at Granollers (Spain). Two irradiations to total doses of 500 KGy and 1 MGy with dose rate of 30 KGy/h and temperature from 20° up to 50 °C have been performed. The production of H_2 and the release of CO_2, O_2 and hydrocarbons has been determined by gas chromatography. Moreover, in some samples, an aliquot of 10 ml of gas was dissolved in a basic aqueous solution and total chlorides, NOx and SOx gases were quantified by ion chromatography.

CO_2 yields similar values than natural degassing of rock salt (Huertas et al., 1992), and increases with irradiation time, but it is not clear whether it is related to thermal desorption (since samples were irradiated to temperatures up to 50 °C) or to radiolysis. CH_4 was not detected, in contrast to natural degassification experiments.

The production of H_2 is dependent on dose and on the amount of water present in the rock salt, whereas NOx is an irradiation product of air which increases with increasing dose. Chloric gases increase with dose and are of the same order of magnitude of the expected amount of colloidal sodium. Finally, the origin of SOx (which also increases with the dose) and the behaviour of O_2 are still unclear and will need further investigations.

Geochemical and petrophysical characterization of salt samples

Microstructural observations on PLL samples irradiated in GIF B at doses between 0.4 and 44 MGy, have shown the absence of microstructures of grain boundary migration assisted by fluids, except for samples irradiated under pressure to a dose of 44 MGy, where large amounts of white halite could be quantified. In those crystals, high contents of H_2 (equivalent to 10^{-4} molar fraction of colloidal sodium) have been measured. Since H_2 is considered as one of the products of the reaction between colloidal sodium and water, it can be inferred that white halite crystals have grown by consuming old blue crystals which had at least a molar fraction of colloidal sodium of 10^{-4}.

The rest of the samples, are apparently homogeneous blue coloured, being the amount of white halite related basically to subgrain boundary microstructures, and to the presence of fluid inclusions in the rests of hopper crystals. In all the cases the amount of white halite is below 1.5 %. The amount of white halite in the studied samples is similar to their equivalents irradiated a dose rate of 15 KGy/h.

2.2.3 Irradiations experiments performed by GSF-IfT

An additional irradiation programme is performed by GSF-IfT in order to investigate the qualitative development of HCl, Cl_2 and collodial sodium. A special facility (GIRAF) was built at the high flux reactor in Petten.

For the irradiation 250 glass ampoules with 300 grams of ground salt in each and helium or synthetic air in the residual volume have been prepared.

Irradiation started in July 1993. The total dose to the salt in the ampoules will be 10^6, 10^7 and 10^8 Gy corresponding to an irradiation time of 20 hours, 8 days and 82 days. The temperature level during irradiation will be 100, 150, 200 and 250 °C with an accuracy of ± 5 °C. For each parameter set (total dose and temperature) 5 ampoules will be irradiated.

Till the end of 1993 60 ampoules have been irradiated and have been analyzed.

The very first qualitative results are: 1. Hydrogen is generated by radiolysis of the water in the rock salt. The amount increases with increasing dose, decreases with increasing temperature and is higher by the factor up to 10 in the ampoules with helium instead of air in the residual volume. 2. Additional carbon dioxide is generated in the ampoules with air instead of helium in the residual volume and its amount increases with increasing temperature as a result of oxidation of hydrocarbones in the rock salt. 3. Nitrogene oxides are generated in the ampoules with air (compare section 2.2.2) in the residual volume but not in these with helium. 4. Collodial sodium and chlorine is generated in both ampoules with air and helium in the residual volume. The amount increases with increasing dose. The maximum of the generation is in the temperature range of 150 °C. The amount is much less at 100 and 200 °C.

2.4 Gamma field and gamma spectra calculations

Dose calculations have been carried out on behalf of ANDRA to give a predictive map of gamma dose distribution in the salt surrounding the testfield. Preliminary analysis have determined the radiative phenomena which have to be considered. Calculations with Mercure-5 attenuation code were carried out for canisters loaded with 1 Ci of each isotope and for a limited number of points (125). And additional (custom-usable) software permits to obtain the result at any point in salt and for any kind of loading or arrangement of the canisters. Calculations with SN1D model gave the evolution of gamma spectrum versus distance in salt. These calculations show that most of the effects are due to Cesium. They also confirm the lowest is the energy of the gammas, the highest is their attenuation with distance from the sources.

The calculations performed by GSF-ISS were completed in 1993 and the final report will be published soon. These calculations based on a Monte-Carlo-method simulating photon transport resulted height profiles of the dose rate at the outside wall at the canister, at the outside wall of the borehole liners and the dose and doserate distributions in the salt around the radiation sources up to a radial distance of 80 cm.

3. Desk studies

Two project reports, one describing the mineralogical and geochemical properties of the underground test field, the other one containing an evaluation of the experience gained from the cold training with the transport- and emplacement system have been compiled and are available in a draft form. Both reports will be published in 1994.

REFERENCES

CEC, 1991: The HAW-Project: Demonstration Facility for the Disposal of High-Level Waste in Salt, Synthesis Report 1985 - 1989, Commission of the European Communities, Nuclear Science and Technology, EUR-Report 13263 EN

CEC, 1992: The HAW-Project: Test Disposal of Highly Radioactive Radiation Sources in the Asse Salt Mine, Summary Report May 90 - Dec. 91, Commission of the European Communities, Nuclear Science and Technology, EUR-Report 14531 EN

GSF-IfT, 1993: The HAW-Project: Test Disposal of Highly Radioactive Radiation Sources in the Asse Salt Mine, Progress Report January - June 1993, Abteilungsbericht IfT 5/93

Garcia Celma, A. and Donker, H., 1992: Stored Energy in Irradiated Salt Samples, Progress report June 1990-December 1991, Contract CEC FI-1W-0235-E (TT), ECN-C-92-055

Garcia Celma, A., Donker, H., Soppe, W. J., Miralles, L., 1993: Development and anneal of radiation damage in salt, End report August 1988 - August 1993, ECN-C--93-086, Petten, The Netherlands

Huertas, F., Mayor, J. C., del Olmo, C., 1992: Textural and Fluid Phase Analysis of Rock Salt subjected to the combined effects of Pressure, Heat and Gamma Radiation, Nuclear Science and Technology, EUR 14169 EN, 218 p

Mönig, J., Garcia Celma, A., Helmholdt, R. B., Hinsch, H., Huertas, F., Palut, J. M., 1990: The HAW-Project - Test Disposal of High-Level Waste in the Asse Salt Mine - International Test-Plan for Irradiation Experiments, Commission of the European Communities, EUR-Report 12946 EN

Prij, J. et al., 1991: Thermomechanical pre-test analyses for the HAW test field, Netherlands Energy Research Foundation ECN, ECN-R--91-001, Petten, January 1991

Prij, J. and Graefe, V., 1992: Thermomechanical analyses, In: Pilot tests on radioactive waste disposal in underground facilities, EUR 13985 EN 1992

Soppe, W. J., 1993: Computer Simulation of Radiation Damage in NaCl Using a Kinetic Rate Reaction Model, Journal of Physics, Condensed Matter 5, pp. 3519-354

Van Opbroek, G. and Den Hartog, H. W.: Radiation Damage of NaCl: Dose Rate Effects, Journal of Physics C, Solid State Physics 18, pp. 257-268

Title:	**IN SITU INVESTIGATION OF THE LONG-TERM SEALING SYSTEM AS A COMPONENT OF A DAM CONSTRUCTION**
Contractors:	Deutsche Gesellschaft zum Bau und Betrieb von Endlagern für Abfallstoffe mbH (DBE) GSF - Forschungszentrum für Umwelt und Gesundheit GmbH Agence Nationale pour la Gestion des Déchets Radioactifs (ANDRA) Empresa Nacional de Residuos Radiactivos, S.A. (ENRESA)
Contract No:	FI2W - CT 90 - 0068
Duration of contract:	April 1, 1991 - March 31, 1995
Period covered:	January 1, 1993 - December 31, 1993
Project Coordinator:	W. Bollingerfehr, DBE
Project Leaders:	W. Bollingerfehr, DBE N. Stockmann, GSF J. F. Laurens, ANDRA F. Huertas, ENRESA

A. OBJECTIVES AND SCOPE

Dam constructions represent an essential component of the multibarrier safety concept for a repository for radioactive waste in salt formations. Within the scope of the dam project the long-term seal, which is responsible for the long-term safety of a dam construction is subjected to an in situ test. The main objectives of the scientific investigation programme are:

- to provide proof of the tightness of the long-term seal as a dam construction component by means of experimental investigations to obtain essential data concerning the effectiveness and
- to prognosticate its function (tightness) over long time periods (up to approximately 500 years) via model calculations.

The long-term evolution of permeability and porosity will be considered, as well as investigating the chemical stability and the petrophysical behaviour.

The state of the art on calculations and codes for multiple-phase flow will be analyzed, and adequate mathematical models and computer codes are developed and verificated.

B. WORK PROGRAMME

According to the Technical Annex of the contract, the work programme consists of the following tasks:

for DBE and GSF

I/1. Conception, numerical preliminary investigations and detailed planning of the long-term seal test in the Asse Mine
I/2. Preliminary and parallel laboratory and in situ (borehole) tests
I/3. Instrumentation of the long-term seal construction
I/4. Performance of the large scale test long-term seal with gas and brine
I/5. Evaluation of the test results
I/6. Hydraulic modelling

for ANDRA

II/1. Physicochemical and petrophysical characterization
II/2. Evaluation of the solubility of materials
II/3. Dissolution kinetics
II/4. Laboratory batch experiments
II/5. Laboratory open system experiment
II/6. Pilot study in mine gallery (Amelie Mine)
II/7. Geochemical modelling
II/8. Petrophysical modelling
II/9. Interpretation and final modelling of the coupled system

for ENRESA:

III/1. Analysation of the state of the art on calculations and codes for multiple-phase flow

III/2. Conceiving laboratory experiments for measuring the permeability of the long-term seal against brine

III/3. Development of adequate mathematical models and computer codes for the numerical simulation of multiple-phase flow

III/4. Code verification

III/5. Interpretation of the in situ test measurements using the developed codes

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Since the beginning of 1993 the Bundesamt für Strahlenschutz (BfS) is responsible for the Dam project which is considered as final waste disposal facility related.

The negotiation with BfS concerning the possible co-funding of the dam project by BfS (on behalf of BMU) is still going on. However BfS decided in December 1993 to continue the project but requested a restart of the conceptual planning on the basis of an experts report. This experts report, evaluating the R&D-programme, recommended a. o. a restart of the conceptual planning as well as the further performance of laboratory and in-situ tests in order to investigate, in more detail, the behaviour of the long-term seal materials. With the beginning of 1994, the DBE and GSF are asked to start with the working programme, which contents the redesign of the dam concept and the cheque of the research programme.

In the year 1993, the DBE's and GSF's main activities were focussed on the negotiation with BfS; meanwhile the performance of the original DBE/GSF-programme was interrupted.

ANDRA who is in charge of the investigation of the geochemical behaviour of salt briquettes and its interactions with saturated brine, performed additional migration experiments in order to cheque the reasons of non feasibility of a pilot tests.

ENRESA continued the development of the multiple-phase-flow code CODE-BRIGHT as well as it's verification. In addition, permeability experiments have been carried out.

Progress and results

1. Activities of the DBE and the GSF

Since the responsibility change in the Federal Republic of Germany concerning the R+D project dam construction in salt formations at the beginning of 1993, the original working program of the DBE and the GSF has been interrupted. The negotiation with the BfS, explaining the background, the fundamentals, the design of the dam, the investigation program, needed 10 meetings in 1993. The activities of the DBE and the GSF were mainly focussed on this negotiational procedure with BfS, preparing and explaining papers and interim reports.

2. Activities of the ANDRA

2.1 New migration experiments

The first migration experiments carried on by BRGM in 1992 aimed to answer to the questions of the feasibility of the pilot test in Amelie mine.

It has been possible thanks to BRGM and to the interpretation made by CNRS to conclude on the non feasibility of this pilot test.

These experiments also raised some new questions:

- Can we model liquid migrations in salt compacted bricks taking only into account the capillary forces?

- Will the chemical exchanges between liquid and salt, that we have already described in the frame of the DAM Project, influence the fluid migrations; for example, by changing the geometry of the pores of the briquettes?

It has been decided to carry on four complementary experiments, using two different liquids: NaCl saturated brine and 2-butanol, a liquid having no chemical interaction with the salt, and two different types of compacted salt briquettes: DAM briquettes and bricks used for feeding animals (cattle) that we will call "animal bricks".

2.1.1 Characterization

A characterization program has been carried with the goal of measuring the surface tensions of the couples between the liquid-compacted salt. The results are shown in table I.

Table I: Surface tensions in dam briquettes and animal bricks

Superficial tensions in E-3N/m		
	Brine	2-butanol
Dam briquettes	55.88	24.90
Animal bricks	72.22	24.75

The main physical and chemical characteristics of the animal bricks have been measured. The results are shown in table II.

Table II: The main physical and chemical characteristics of dam briquettes and animal bricks

Comparison between two kinds of salt bricks		
	Dam briquettes	Animal bricks
Density	2.00	1.96
% Porosity	8.0	9.3
% NaCl	97.7	99.8
% Non Soluble	0.33	0.005
% H_2O	0.34	0.07

2.1.2 Migration experiments

The aim of these experiments is to measure the progression of the liquid into the compacted salt, the same experimental device that was used in 1992. The progression of the liquid is measured by γ dosimetry.

There are two kinds of experiments, one with free outlet, the other with closed outlet where the gas has no possibility to get out of the compacted salt.

Two "open outlet" experiments were conducted; one on DAM briquettes using a 2-butanol solution and another on "animal bricks" using a saturated brine solution. Two "closed outlet" experiments were also conducted; one on DAM briquettes using a brine solution and another on DAM briquettes using a 2-butanol solution.

The results of the experiments are shown in figure 1, 2, 3 and 4.

2.1.3 Interpretation of the results

The scientific analysis already initiated in 1992 is based upon the use of a simplified model called "pistonlike", shown in figure 5.

The driving force is the capillary pressure while the opposite forces are the viscosity (Darcy's law) and the pressure of trapped air.

From the "open outlet" experiments, it is discovered that the capillarity is the driving force of the migration and that, within the time scale of our experiments (one week), the influence of chemical exchanges between liquids and salts is negligeable.

The "closed outlet" experiments are more difficult to interpret. This is probably due to the fact that our model is too simple (we should use a two phases flow model) and to the fact that there is a high sensitivity in some parameters.

It has been possible, however, using a statistical analysis of the results, to show that these experiments are consistent with the hypothesis of capillary migration without chemical exchanges.

3. Activities of the ENRESA

3.1 Background

The project "In situ investigation of the long term sealing system as a component of a Dam Construction" started on April 1991. The main objective of the research to be developed by DIT-UPC group is to model and validate the effects of multiphase flow through the components of the long-term seal and at the interface between the seal and the host rock. These includes the following main tasks:

Task 1: State of the art-review
Task 2: Laboratory work
Task 3: Modelling
Task 4: Code verification
Task 5: Validation

From these tasks, the main research directions are the following:

- Constitutive modelling of the mechanical behaviour of porous salt aggregates.
- Development of a theoretical framework for the study and characterization of the coupled hydro-thermo-mechanical behaviour of a porous/non-porous saline system. This includes both, establishing the governing equations and the adoption of constitutive laws.
- Laboratory work. This includes deformation tests on granular aggregates under wet conditions (including unsaturated tests) and dry conditions. Permeability measurements under brine and gas flow are carried out during the tests.

3.1 Work performed during 1993

The constitutive model for the mechanical behaviour of porous salt aggregates is in a very advanced version. The model and examples of its capabilities were presented at the conference on "The Mechanical Behaviour of Salt" held in Paris /2/. On the other hand, the governing equations that serve as a basis for the numerical tool, have been revised in order to cast them in a final form. A paper for an International Journal /6/ has been written.

The computer code CODE-BRIGHT (COupled DEformation, BRIne, Gas and Heat Transport) has already been used to carry out several computations ranging from verification of simple exercises to more complex and realistic schemes.

The work at the laboratory includes two main parts: deformation and permeability tests performed at the DIT-UPC laboratory and, deformation tests performed at the University of Waterloo.

3.1.1 Mechanical constitutive model

The mechanical constitutive model includes creep behaviour caused by two different mechanisms of deformation: fluid assisted diffusional transfer creep and dislocation creep. The model, initially developed for isotropic stress states, has been generalized into three dimensions. The equations obtained from the geometry and physical basic mechanisms /1/, /2/ have been transformed into a generalized version /5/ which can be implemented in the computer code. The comparison of the model and experimental results of preliminary laboratory tests performed at DIT-UPC has also been performed.

3.1.2 Governing equations

As a further step for improvement of the quality of the theoretical development of the governing equations, a paper intended to be published in the international journal "Transport in Porous Media" /6/ has been written including all the aspects of the new formulation. The paper has been submitted for review by the journal.

3.1.3 CODE-BRIGHT computer code

The computer code CODE-BRIGHT has been verified by comparison with analytical solutions available in the literature and other known (e. g. numerical) solutions. Following the verification, an application for the study of the borehole seal behaviour has been carried out. This computation was performed under axisymmetric and plane strain conditions using one dimensional elements. The results /4/, /5/ have shown relevant aspects of the behaviour of such sealing system, specially related to the coupling between thermal, mechanical and hydraulic problems.

As a natural continuation of the work already developed, a simulation of a realistic scheme in two dimensions has been started. It consists of a gallery surrounded by the host rock. The gallery is filled with a low porosity material, say 10 to 20 % (bricks are designed to have 10 % of porosity). Convergence is induced by the lithostatic stress state gradually compressing the backfill. Coupling with hydraulic problem is also envisaged.

The computer code CODE-BRIGHT is also participating in the European Validation Exercise of Gas migration models (EVEGAS^{mm}).

3.1.4 Experimental work. Tests in progress

Using the equipment specifically developed for the study of the behaviour of porous salt aggregates, several tests have been carried out. These are:

- one preliminary long term test under stress steps: 0.8, 4.0, 6.0 and 30.0 MPa, grain size 520 µm. Some permeability measurements.
- two preliminary short term tests under 100 MPa and grain size 325 µm.
- three oedometric tests with low applied stress (steps: 0.2, 0.4, 0.8, 1.6 MPa) with the following grain sizes: 110, 325 and 950 µm. Brine permeability tests are performed during deformation. Tests in progress.
- three oedometric tests with high applied stress (steps: 2, 4, 8, 20 MPa) with the following grain sizes: 110, 325 and 950 µm. Brine permeability tests are performed during deformation. Tests in progress.

The results of the first long term test have been compared with the model predictions and several conclusions, about the model and about the test have been gained. Results from the test now in progress are being processed and analyzed.

Mr. D. Chumbe has spent 6 months at the Salt Mechanics Laboratory of the University of Waterloo performing oedometric as well as triaxial tests and gaining experience with their specialized equipment under the supervision of Professor M. Dusseault.

3.2 References

/1/ S. OLIVELLA, A. GENS, E. E. ALONSO, J. CARRERA, 1993. Modelo constitutivo para agregados porosos de sal. Memorias del 2° Congreso de Métodos Numéricos en Ingeniería, Eds. F. Navarrina y M. Casteleiro, La Gorunya, Spain, June 7 - 11, 1993, Vol 1 pp. 471:480

/2/ S. OLIVELLA, A. GENS, E. E. ALONSO, J. CARRERA, 1993. Behaviour of Porous Salt Aggregates. Constitutive and Field Equations for a Coupled Deformation, Brine, Gas and Heat Transport Model. Proceedings of the "3rd Conference on The Mechanical Behaviour of Salt". Organized by the Ecole Polytechnique, Paris, September 14 - 16, in press.

/3/ S. OLIVELLA, A. GENS, J. CARRERA, E. E. ALONSO, 1993. A General Model for Coupled Deformation, Brine Gas and Heat Transport Models. Pegasus Project Meeting, ECC, Köln, June 3 - 4, 1993.

/4/ S. OLIVELLA, A. GENS, J. CARRERA, E. E. ALONSO, 1994. A Model for Coupled Deformation and Non-isothermal Multiphase flow through Saline Media. Application to borehole seal behaviour. Submitted for review to the First International Congress on Environmental Geotechnics, Edmonton, Canada, July 10 - 15, 1994.

/5/ S. OLIVELLA, A. GENS, J. CARRERA, E. E. ALONSO, 1994. A Model for Coupled Deformation and Non-isothermal Multiphase Flow in Saline Media. Submitted to the 8th International Conference of the International Association for Computer Methods and Advances in Geomechanics, Morgantown, May 22 - 28, 1994.

/6/ S. OLIVELLA, J. CARRERA, A. GENS, E. E. ALONSO, 1994. Non-isothermal Multiphase Flow of Brine and Gas through Saline media. Submitted for review to the international journal "Transport in Porous Media"

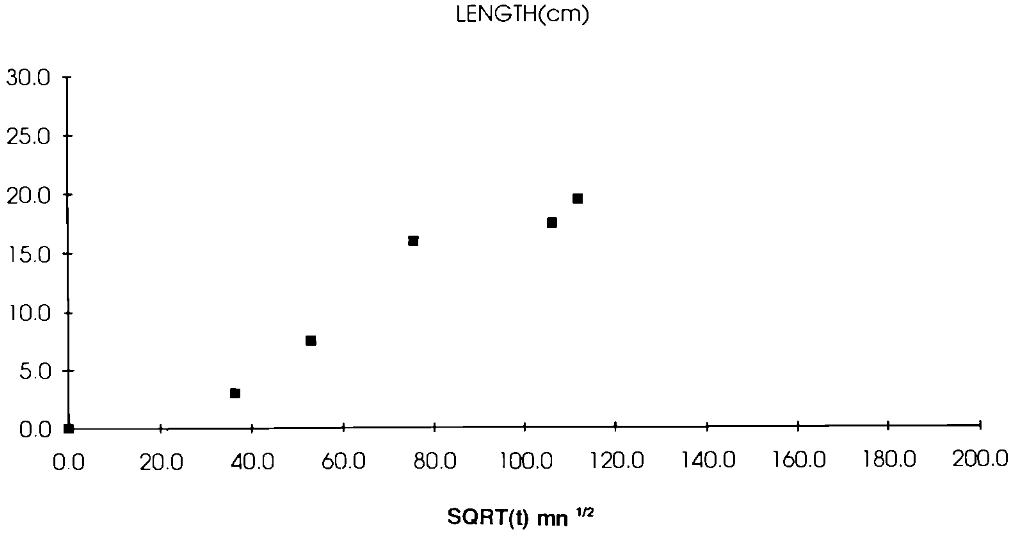


Figure 1: Open outlet - DAM bricks + 2-butanol

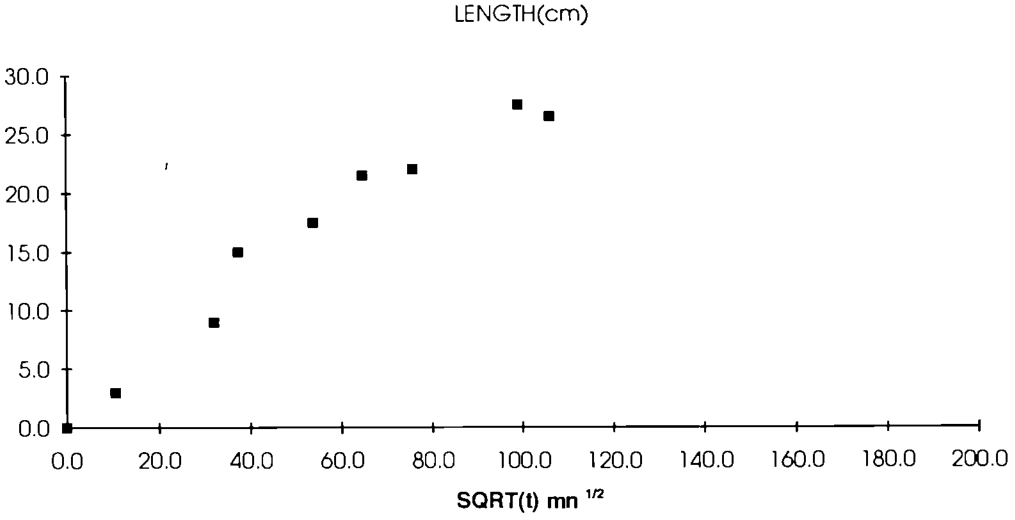


Figure 2: Open outlet - Animal bricks + brine

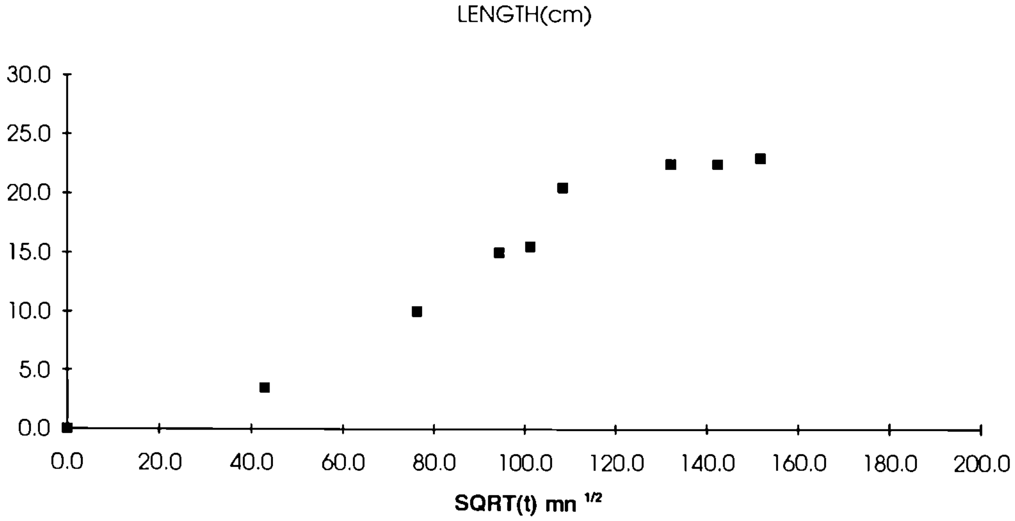


Figure 3: Closed outlet - DAM bricks + 2-butanol

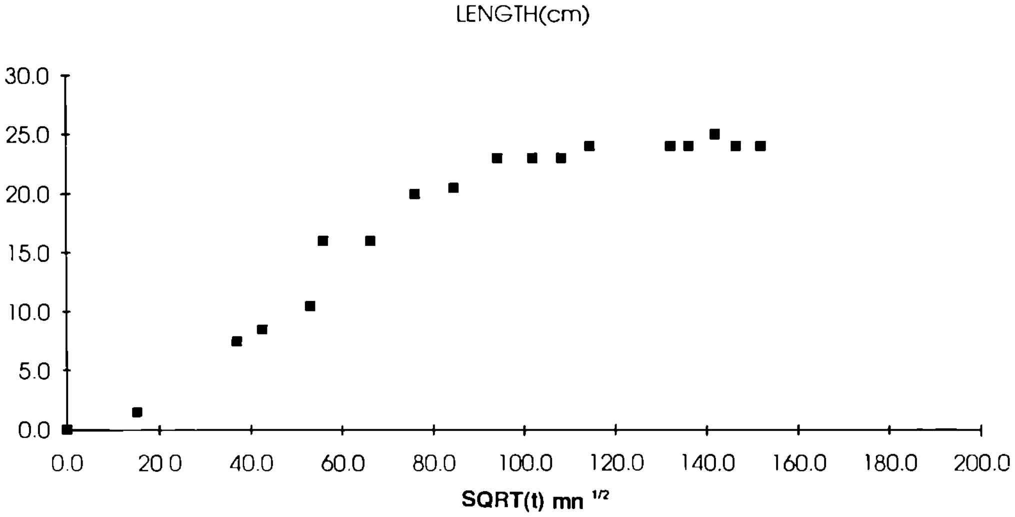


Figure 4: Closed outlet - DAM bricks + brine

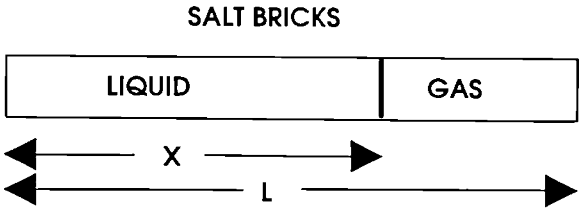


Figure 5: Simplified model "pistonlike"

Title: **ACTIVE HANDLING EXPERIMENT WITH NEUTRON SOURCES**
Contractors: Deutsche Gesellschaft zum Bau und Betrieb von Endlagern für Abfallstoffe mbH (DBE)
Agence Nationale pour la Gestion des Déchets Radioactifs (ANDRA)
Kernforschungszentrum Karlsruhe GmbH (KFK)
Contract No: FI2W - CT 90 - 0069
Duration of contract: 01.04.91 - 30.09.94
Period covered: 01.01.93 - 31.12.93
Project Coordinator: K. D. Closs (KfK)
Project Leaders: H. J. Engelmann (DBE), J. M. Potier (ANDRA)

A. OBJECTIVES AND SCOPE

The Active Handling Experiment with Neutron Sources (AHE) is a demonstration test which will be performed by DBE and ANDRA/CEA in the Asse mine with KfK acting as coordinator. Besides the CEC, the DBE contribution is supported by the Bundesministerium für Forschung und Technologie (BMFT) under contract 02 E 8472 7.

The objective of the AHE experiment is to investigate radiological aspects of handling high level waste (either spent fuel or vitrified high level waste) in an underground repository. Neutron dose rates are measured resulting from direct radiation and from neutrons scattered by the surrounding host rock (rock salt). Computer codes and model calculations are to be verified by these experiments. Thus, an experimentally validated tool will be available for future detailed repository planning with emphasis on minimizing the radiation exposure of the operating personnel.

B. WORK PROGRAMME

According to the Technical Annex of the contract, the overall programme consists of the following formal items

Design planning	1991/1992
Implementation planning	1992
Construction and acquisition	1992/1993
Execution and disposal	1993/1994
Evaluation and description	1994.

From a more practical point of view, the programme can be broken down into the following activities:

1. Shielding and backscattering calculations for a POLLUX cask with spent fuel and a transfer cask with vitrified high level waste
2. Design and construction of shielding casks which simulate a POLLUX cask and a transfer cask
3. Planning of test programme with shielding casks
4. Planning and design of instrumentation for experiment
5. Execution of the measurements
5.1 Above-ground measurements
5.2 Underground measurements in the ASSE mine
6. Evaluation and documentation of the results.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

It has been shown that a specially designed shielding cask with a Cf-252 neutron line source simulates the radiation field around a POLLUX cask loaded with spent fuel very very well and a transfer cask loaded with either spent fuel or vitrified waste quite well. The decision was therefore made to use only one shielding cask with a Cf-252 line source for the active test.

The measurement programme for the active test has been prepared. The above and underground measurement programme will be performed by Physikalisch Technische Bundesanstalt (PTB) under subcontract to DBE. A contract has been negotiated.

The application for handling neutron sources in the Asse mine was submitted to the Mining Authority (Bergamt Goslar) on March 29, 1993, and the license was granted on November 16, 1993.

Construction of the shielding cask is under way, and the neutron sources have been ordered. The cask will be delivered by the end of March 1994, and the cask will be loaded with the neutron sources in April 1994. Thus, the active test can start in May 1994. Underground measurements in the Asse mine will last until Dezember 1994. Evaluation and documentation of the results will be performed from January to June 1995.

Progress and results

1. Shielding and backscattering calculations for a transfer cask

POLLUX casks will be used for drift emplacement, and transfer casks will be used for handling canisters with chopped spent fuel pins or with vitrified reprocessing waste in a repository with the aim of emplacing the waste canisters into boreholes. The AHE project ist planned to compare the calculated dose-rates of a POLLUX cask and a transfer cask with and without salt environment with the measured dose-rates of a smaller experimental shielding cask with Cf-252 neutron sources.

In the annual progress reports 1991 and 1992, only neutron dose-rate and neutron spectra calculations for the POLLUX cask and the shielding cask have been presented. The following contribution deals with calculations for the transfer cask in order to study the influence of backscattering of neutrons in a borehole drift. It has to be checked, whether the same shielding cask which has been designed for the simulation of a POLLUX cask can also be used for the simulation of a transfer cask.

1.1 Description of the transfer cask

The transfer cask will be designed for the onside transport of a canister with fuel pins or vitrified waste from the reloading station above-ground to the borehole drift underground. The design of the model transfer cask is given in Figure 1 and the material composition in Table I.

The cask is made of nodular cast iron with embedded neutron moderator (PE). The top and bottom can be moved as a slider to fill the cask at the docking station above-ground or to empty it at the borehole slide underground.

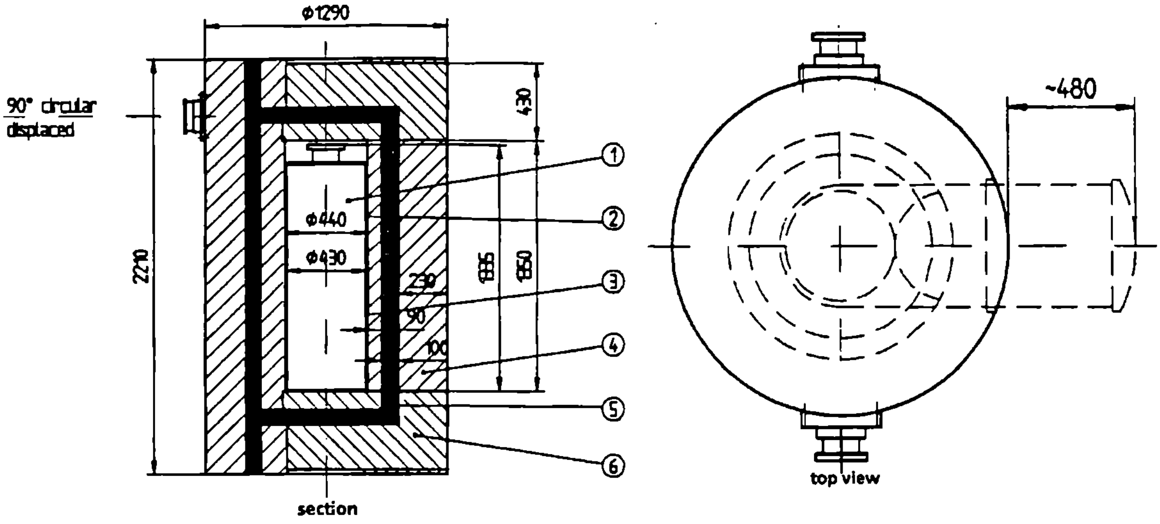


Figure 1: Geometry of the generic model transfer cask

Table I: Material composition of the transfer cask

Material No.	Composition	Nuclide Density [1/b cm] 1)
1 (Fuel rods)	O Zrly U-238	1,627 E-2 5,676 E-3 8,137 E-3
2 (Steel)	C Si Mn Fe Ni	7,06 E-4 5,85 E-4 1,41 E-3 8,16 E-2 6,80 E-4
3 (Vacuum)		
4 (Nodular cast iron)	C Si Mn Fe Ni	1,354 E-2 3,654 E-3 4,670 E-4 7,036 E-2 9,471 E-4
5 (PE)	H C	7,776 E-2 3,914 E-2
6 (Nodular cast iron)	C Si Mn Fe Ni	1,354 E-2 3,654 E-3 4,670 E-4 7,036 E-2 9,471 E-4

1) 1 b = 10^{-24} cm^2
Note: Neutron strength of fuel rods: 1,67 E8 n/s

Calculations were made for the transfer cask in the transport drift and in the borehole drift the dimensions of which are 7.0 m width by 4.0 m height and 5.5 m width by 7.0 m height, respectively. As an example, the results of the dose-rate calculations for the transfer cask in the borehole drift standing on the floor are shown in Figure 2.

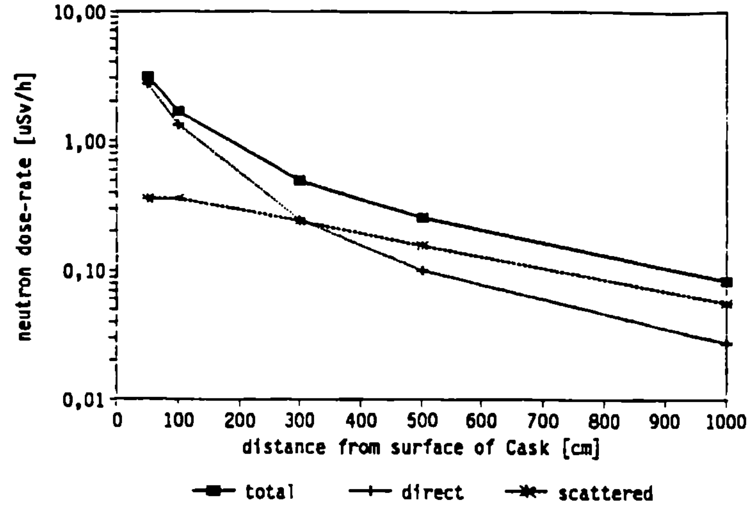


Figure 2: **Transfer cask with fuel canister in the borehole drift, standing on the floor**

Almost identical results were obtained for other positions and other drift dimensions. In order to analyse the difference between the neutron fields of the shielding cask and the transfer cask, the same set of calculations was carried out for the shielding cask under identical conditions.

The results of the calculated total neutron dose-rates for the shielding cask and the transfer cask are shown in Figure 3. Higher values are obtained for the shielding cask, but the shapes of the two curves are the same. The same holds true for the neutron spectra of the two casks in 1 m distance from the outer surface, as can be seen from Figure 4.

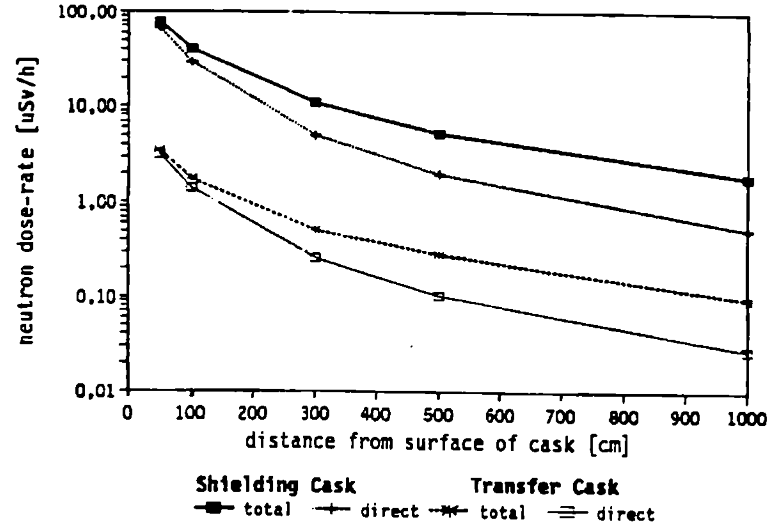


Figure 3: **Comparison of the neutron dose-rates for the transfer cask and the shielding cask in the borehole drift, standing on the floor**

The reason that the dose-rates for the transfer cask are lower than those for the shielding cask is mainly due to the different source strength of the spent fuel contained in a POLLUX cask and those contained in a canister within a transfer cask. The shielding cask is designed such that it simulates a POLLUX cask, which contains 8 PWR fuel elements. On

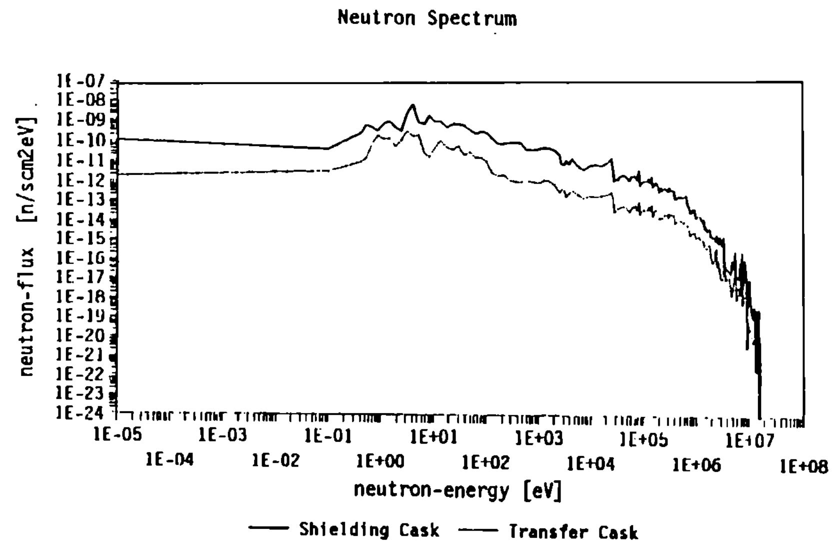


Figure 4: **Neutron spectra for the shielding cask and the transfer cask in the borehole drift, standing on the floor (values in 1 m distance from the surface of the cask)**

the other hand, a canister with chopped fuel pins contains only the equivalent of half a PWR fuel element.

From the calculation so far it can be concluded that the shielding cask also simulates the transfer cask quite well with respect to the shape of the neutron dose-rates and the neutron spectra. A second shielding cask to simulate the transfer cask is therefore not neccessary.

2. Experimental programme

Neutron dose-rates and neutron spectra will be measured above-ground (without neutron backscattering) and underground in the Asse mine (backscattering included), in order to see how much the dose-rate is increased during underground waste handling due to neutron backscattering.

2.1 Test components

The main test components are the neutron source,the shielding cask which is used also as transport cask, the bearing support for vertical and horizontal positioning, and the neutron detectors.

Californium-252 neutron capsule

The neutron source is a line source which consists of 40 Cf-252 neutron capsules. The radioactive material is doubly-encapsulated in welded stainless steel capsules, manufactured and examined by Amersham according to ISO-standard (ISO = International Organization for Standardization) as "Special Form Radioactive Material", see Figure 5.

Technical data of a neutron capsule:

Type of capsule:		X.1
Californium content:	approx.	2 µg
source strength:	approx.	$5 \cdot 10^6$ n/s
activity:	approx.	50 MBq
length:		10 mm
diameter:		7.8 mm
half-life time:		2.65 years
ISO-standard:		C 66544

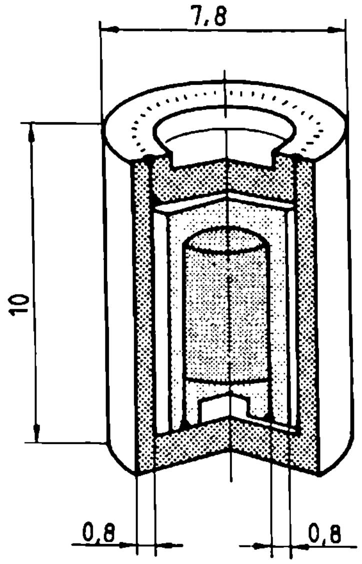


Figure 5: **Cf-252 neutron capsule, dimensions in mm**

Cf-252 is embedded in pellets or wires made from platinum/ iridium alloys or palladium and enclosed in a gas tight, inactive double-walled stainless steel container for safty and against the release of radioactive material during normal transport conditions, as well as their protection against mechanical and thermal impacts and corrosion.

Californium-252 line source

The Cf-252 line source consists of a bolted or welded high-grade stainless steel cladding tube which encloses 40 single neutron capsules with 20 intermediate spacers.

Technical specification of a line source:

number of neutron capsules:		40
total Cf-252 content:	approx.	80 µg
total source strength:	approx.	$2 \cdot 10^8$ n/s
total activity:	approx.	2 GBq
total length:		600 mm
outer diamter:		9.5 mm

Shielding cask

The AHE shielding cask is designed as type-A container according to the GGVS transport regulations (GGVS: Regulations on Road Transport of Dangerous Cargo). The structure of the shielding cask is comparable to a POLLUX cask. Technical data of the shielding cask were presented in the annual progress report 1992. The cask has a length of 1350 mm, a diameter of 912 and weighs something like 8 Mg.

Bearing support

The bearing support is a steel construction and is used to position the shielding cask in intended heights above the floor. A POLLUX radiation field is simulated by horizontal positioning of the shielding cask in the bearing support so that the axis center is 1500 mm above the floor, see Figure 6 (a). The radiation field of a transfer cask is simulated by vertical positioning of the shielding cask with its lower edge 500 mm above the floor, see Figure 6 (b). Two lifting lugs on the outer cylindric casing are used to position the shielding cask within the bearing support; they are arranged in a manner that the required distances to the floor can be reached in horizontal as well as vertical shielding cask position. Hoisting devices on cylindrical casing and on the lid are provided for handling the shielding cask during transport and test processes.

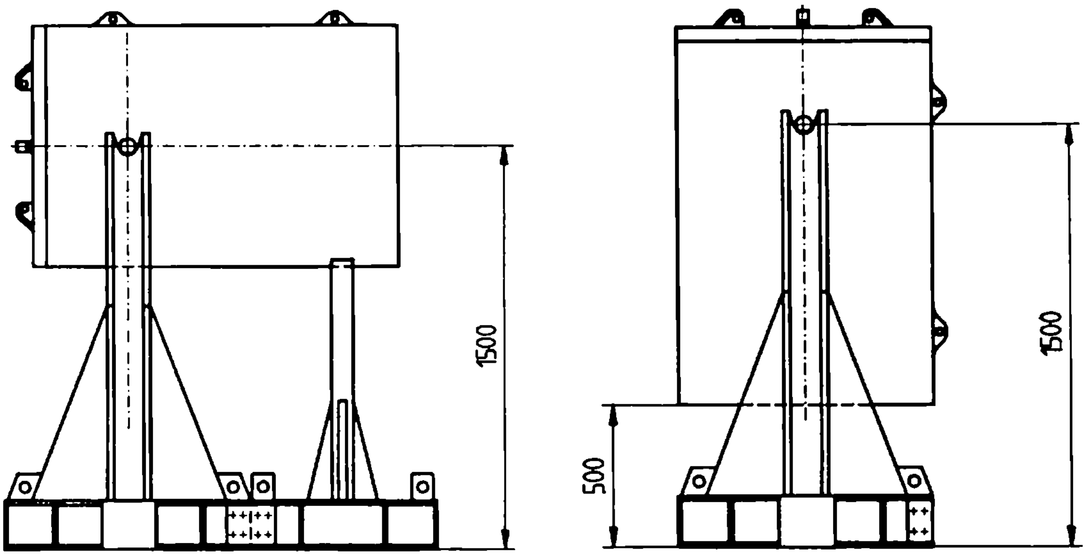


Figure 6: Test arrangement for the simulation of a POLLUX (a) and a transfer cask (b), all dimensions in mm

Neutron detectors

Neutron spectrometers to be used in radiation protection practice must cover a wide dynamic energy range (thermal to some tens of MeV) and should have an isotropic response and neutron detection efficiency large enough for the investigation of neutron fields causing a dose equivalent below 100 µSv/h. Two different types of spectrometer will be used in the experiment:

- a set of Bonner spheres (BS) with small ^{3}He proportional counters as the central detector for the entire energy range but with a limited energy resolution
- NE 213 liquid scintillation detectors for proton recoil spectrometry in the energy range above 0.5 MeV.

A set of 12 BS with diameters from 5.08 cm (2") to 45.72 cm (18") was manufactured using polyethylene with a density of 0.946 g/cm^3. Four ^{3}HE filled proportional counters will be used as central detectors, so four positions can be measured at the same time.

The NE 213 scintillation detector has an equivalent response function as the BS, but with a lower energy limit of 0,5 MeV. It is suited for the detection of fast neutrons.

The neutron dose-rates will be measured with a dose-meter.

2.2 Underground handling of the shielding cask and experimental area

The shielding cask loaded with a Cf-252 line source will be delivered by truck to the Asse mine. After unloading an incoming inspection is carried out in the shaft hall either with the help of the bridge crane (payload: 10 Mg) or with the help of a fork lift truck (payload: 15 Mg). It includes visual examination, dose rate measurements and contamination test. Afterwards, the shielding cask is transported to the hoisting shaft and brought into the mine.

The shielding cask is transported from the shaft station to the experimental area on the 800-m-level by the HAW-truck (see Figure 7) or by a fork lift truck. The location of the experimental area and the profiles of the drifts can be seen from Figures 8 and 9, respectively.

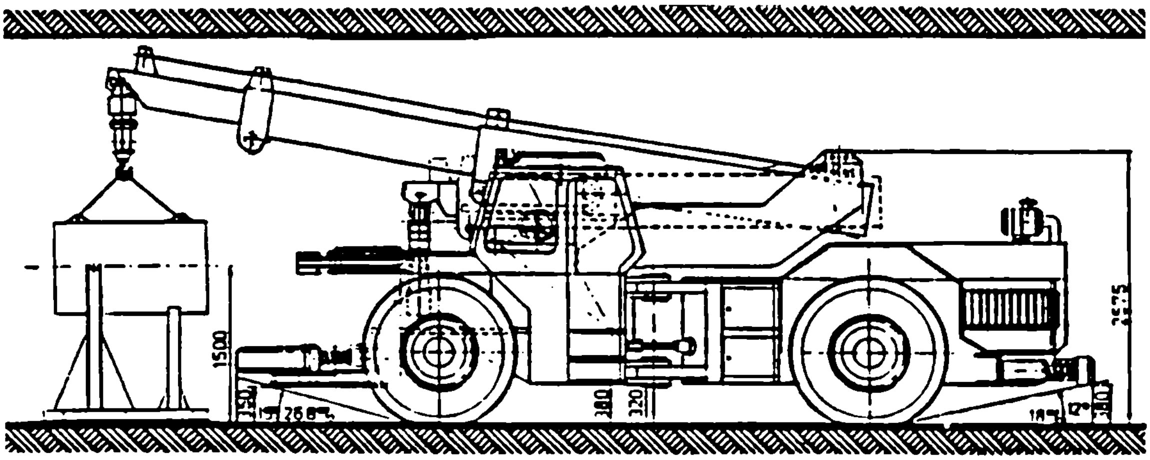


Figure 7: **HAW-truck**

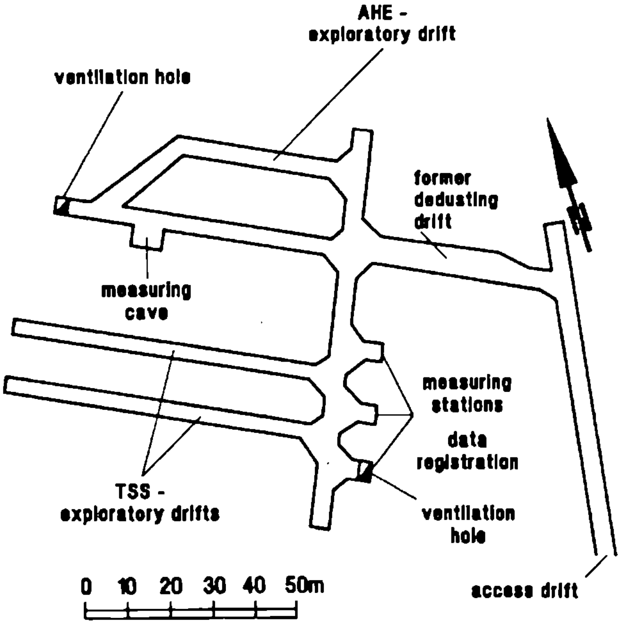


Figure 8: **Location of AHE-drift and former dedusting drift on the 800-m-level of the Asse mine**

The handling of the shielding cask is intended in the AHE-drift on the 800-m-level of the Asse mine which has a cross section of 15.5 m² and which simulates an emplacement drift for a POLLUX cask. Moreover, tests will be performed in the neighbouring drift - the former dedusting drift - with an extended cross section of approx. 27 m² which is representative for a transport drift. Furtheron, measurements are planned on the 800-m-level in the BGR-field (cross section approx. 40 m², representing a bore-

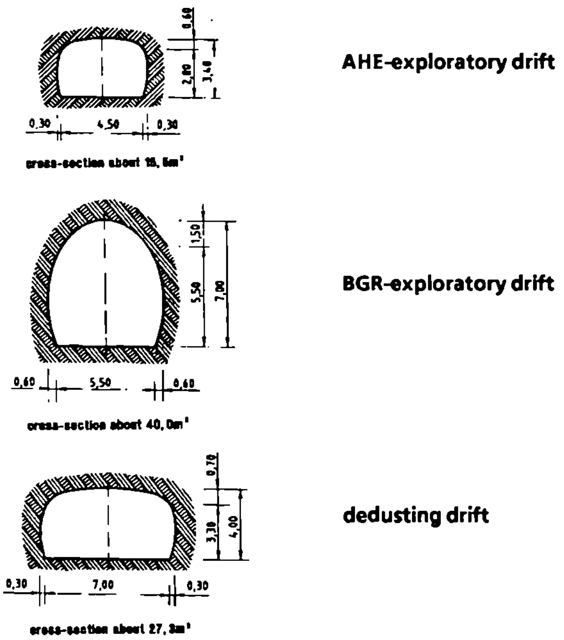


Figure 9: Drift profiles for the AHE experiment, all dimensions in mm

hole drift), in the shaft station on the 850-m-level and in a dead-end drift.

2.3 Measurement programme

The above- and underground measurement programme will be performed by Physikalisch Technische Bundesanstalt (PTB) under subcontract to DBE. The programme includes reference measurements of direct neutron radiation without the influence of backscattering by salt at the PTB area. Furtheron the programme includes underground measurements, in which the effects of neutron backscattering on rock salt and the drift geometry are to be investigated.

1. **Measurements of neutron energy distributions and neutron dose rates**

   Neutron energy distributions and neutron dose rates are measured in 4 positions with detectors in a distance of 1 m from the shielding cask in the AHE-drift. Measuring detectors are positioned along both, the POLLUX axis and the jacket, as well as above the shielding cask, see Figure 10. Measurements are carried out with the container lying on the floor and resting in the bearing support 1500 mm above the floor.

   Neutron dose rates and neutron energy distributions of the shielding cask will also be measured in horizontal and in vertical container positions in the BGR-drift and in the dedusting drift.

   Measurements in the vertical position require container positioning in the bearing support in a way that the lower edge of the test container has a distance of 500 mm to the floor. A second measuring position requires the shielding cask standing on the floor in a vertical position. For reasons of symmetry, measurements are carried out with three detectors.

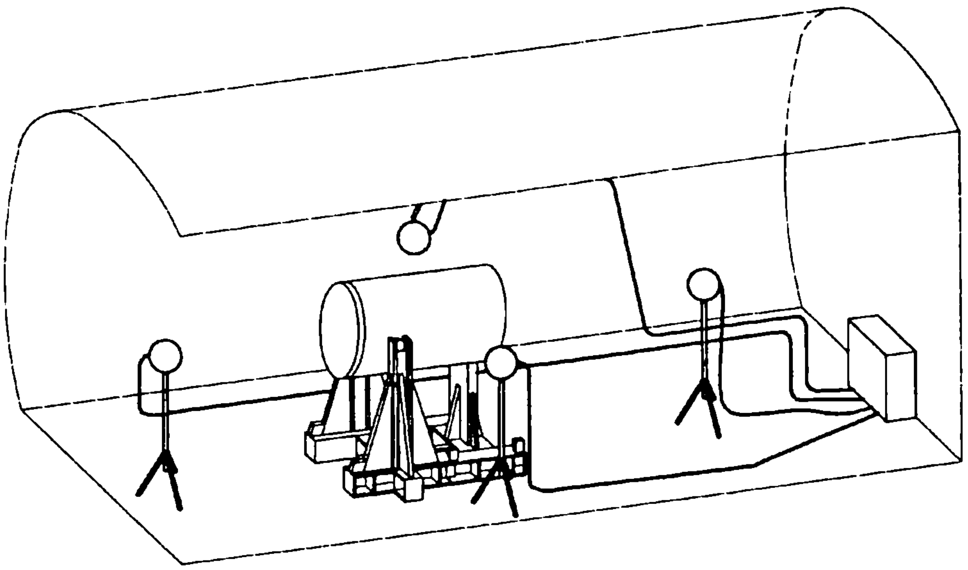


Figure 10: Measuring arrangement for neutron energy distributions

2. **Measurements of secondary Gamma-radiation**
   Parallel to the above mentioned measurements of all shielding cask options and positions, secondary gamma-radiation will be measured in all three drifts.

3. **Measurements of local dose rate**
   Additional measurements to determine neutron dose rates will be carried out using a rem-counter in different radial and axial positions at the shaft landing and near the dead-end of an emplacement drift.

Operational handling sequences with the shielding cask during the measurement programme as well as durations of stay in the vicinity of the shielding cask for those persons carrying out the measurements are compiled in Table II.

3. Status of the licensing procedure and the delivery of the components

Handling of radioactive material in the Asse mine requires a license according to Article 3 of the StrlSchV (Radiation Protection Regulations). The application for handling neutron sources in the Asse mine was submitted from GSF, the owner of the Asse mine, to the Mining Authority (Bergamt Goslar) on March 29, 1993.

The experiment was explained to the Mining Authority on April 7 and the requested additional documents were delivered on April 16, 1993. On Juli 23, a discussion took place with experts of the TÜV Niedersachsen/Sachsen-Anhalt, the Mining Authority, GSF and DBE on the subjects of construction of the shielding cask and on radiation protection. The recommendations of the TÜV concerning the load suspension devices and material composition were followed, requirements concerning radiation production are fulfilled. The principal concept of the experiment and the handling of the shielding cask were accepted.

The license was granted November 16, 1993.

Table II: Above-ground and underground handling sequences with the shielding cask

Nº	OPERATION	number of persons involved	DURATION	FREQUENCY
	Aboveground:			
1	Reloading of shielding cask from vehicle of delivery to an in-plant fork lift truck	1	30 min	1
2	Transport of shielding cask with fork lift truck to hoisting cage	1	10 min	1
	Underground:			
3	Transport from shaft station to AHE test drift with truck	1	20 min	1
	Positioning of shielding cask in test place	1	10 min	5
4	Transport to other AHE-test places	1	10 min	4
5	Return transportation from test place to shaft station by vehicle	1	20 min	1
6	Assembling of detectors	2	2.5 min	25
7	Replacement of detector balls	2	2 min	75
8	Measurement of neutron energy distribution	3	60 min	60
	Aboveground:			
9	Return transportation from hoisting cage to reloading place with fork lift truck	1	10 min	1
	Reloading of shielding cask to the lorry by fork lift truck	1	30 min	1

The buying order for the neutron source was dispatched October 7, 1993. Amersham will deliver the neutron source in April 1994. After termination of the test, the source will be sent back to Amersham.

The shielding cask was ordered October 25, 1993. It will be delivered by the end of March 1994.

Above-ground and underground measurements will be performed from May to June 1994 and September to December 1994, respectively. Evaluation and documentation of the results will take place from January to April 1995.

It is quite clear now, that due to the delay in granting the license the experiment cannot be terminated within the time frame of the existing contract. Time extension of the contract will be negotiated with CEC as soon as the active test has started.

List of publications

KHAMIS, M. et al, Berechnung der Neutronendosisleistung vom AHE-Versuchsbehälter mit einer Cf-252-Linienquelle. Sammlung der Vorträge anläßlich des 4. Statusberichtes Direkte Endlagerung am 28. und 29. Januar 1993. AE Nr. 27. Kernforschungszentrum Karlsruhe, Februar 1993, pp 5-1 to 5-26.

Title : Thermomechanical simulation of the near field of an emplacement borehole in a salt formation (Amélie Mine, France). "C.P.P.S. Test"
Contractors : CEA/ANDRA - Fontenay aux Roses, France, G.3S
Contract N° : FI2W-CT92-0120
Duration of contract : April 92 - March 95
Period covered : January - December 1993
Project leader : J.-F. Laurens

A/ OBJECTIVES AND SCOPE

The aim of "CPPS" test is to study the near field thermomechanical behaviour in deep layered salt around a borehole waste emplacement under thermal loading. This is of major importance for predicting the behaviour of radioactive waste storage particularly as regards to the temperature and the pressure that the canisters will have to withstand. The influence of marno anhydritic layers will be studied too.

The experiment is planed to include three tests in separate boreholes at Mine Amelie underground facilities, with identical heating probes but different types of thermal loadings and backfilling materials. The scientific interpretation of the results will be made by the G.3S (see figure 1).

B/ WORK PROGRAM

1. CPPS ONE : Emplacing of a prototype heater with an annulus between the heater and the borehole as small as possible (< 5 mm) and heating after having observed the borehole convergency.
2. CPPS TWO : Emplacing of a heater with an empty annulus and heating after having observed the borehole convergency.
3. CPPS THREE : Emplacing of a heater with the annulus filled with crushed salt and immediate heating.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

CPPS 1 probe was installed in December 1991. After a period of observation of the borehole creeping, the heater has been turned on in May 20th 1992. The heating power was 2.4 KW. After two months the heating power has been raised up to 4 KW in order to speed up the borehole creeping. The heating has been shut down in February 17th 1993 after nearly 9 months.

The fact that no major power cut happened during this nine months, will facilitate the scientific interpretation.

The CPPS 2 and 3 probes have been built. They include new pressure sensors more accurate.

They have been emplaced in December 1993.

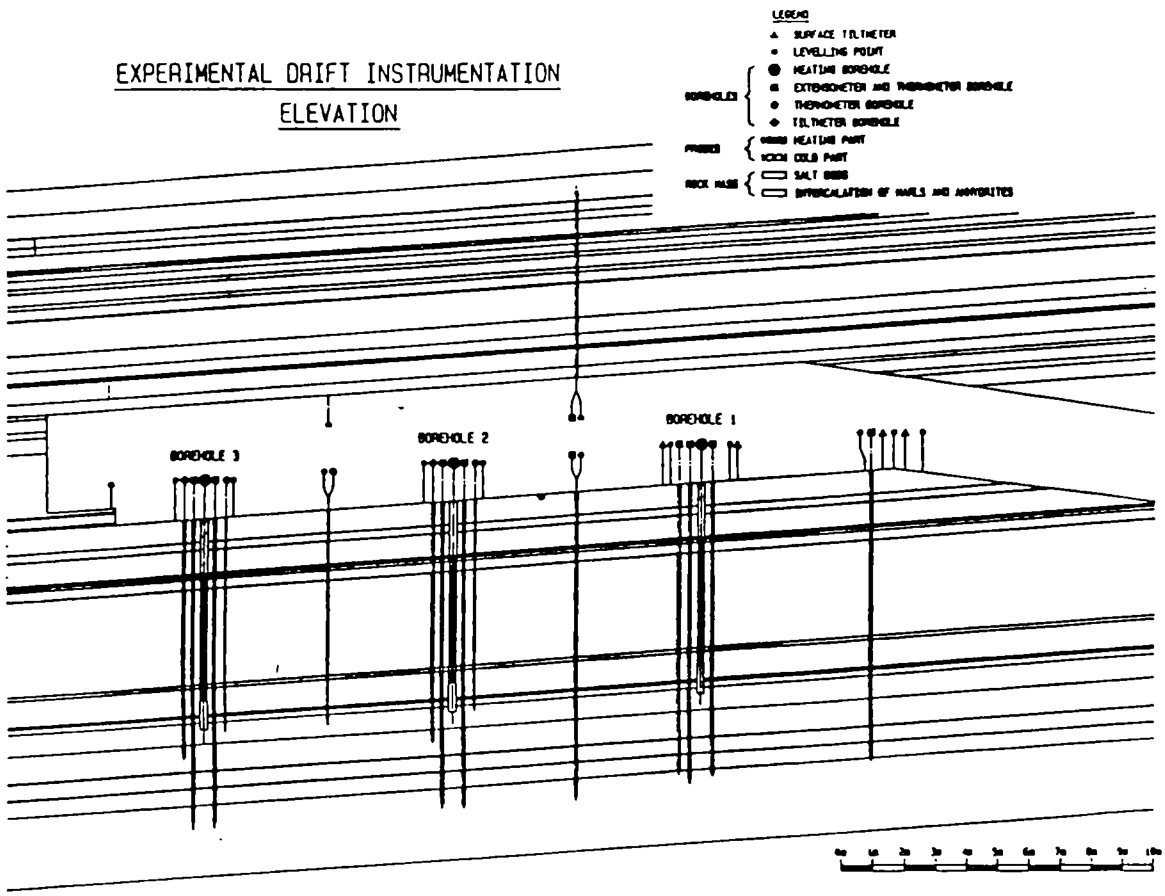


Figure 1

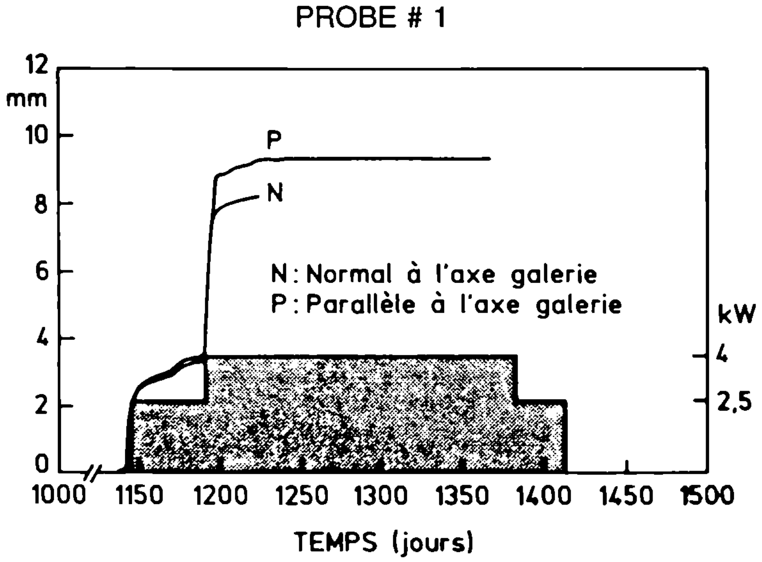
1) Results obtained during the heating

Heating power

After nearly two months at 2.4 KW the power has been raised up to 4 KW.
After eight months the power has been reduced to 2.4 KW and stopped after nearly nine months.

Borehole closure (see figure 2)

At the end of the first heating step the closure rate was very low.
Three days after the increase of power the borehole was in contact with the probe, the stiffness of the probe was such that after the contact no deformation was allowed.

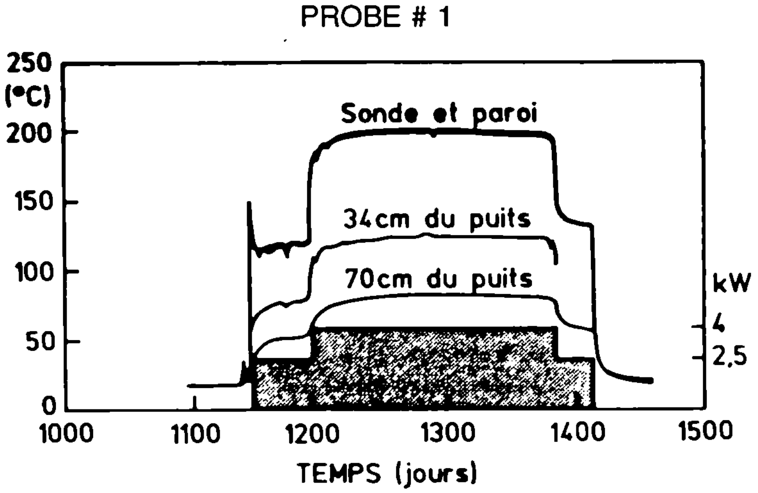


BOREHOLE CLOSURE
Figure 2

Temperature (see figure 3)

During the first step the maximum temperature was 120°C on the surface of the probe. During the second step the temperature has reached 200°C at this place and it's nearly stabilised.
At a distance of 70 cm from the axis of the probe the temperature reaches 70°C.

One month after the shut down of the heaters the rock temperature has returned to its normal value.

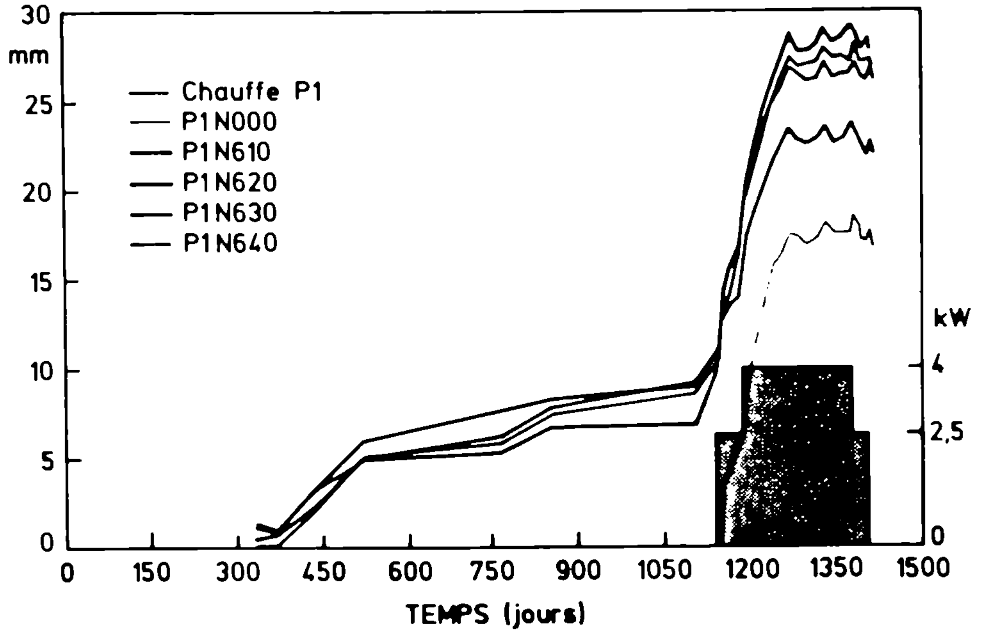


NEAR FIELD TEMPERATURE
Figure 3

Displacements in rock salt around the borehole (see figure 4)

The displacements of the rock salt reaches 9 mm in surface whereas 4 mm at a depth of 3.75 meters and 1 mm at a depth of 5.50 meters.

PROBE # 1

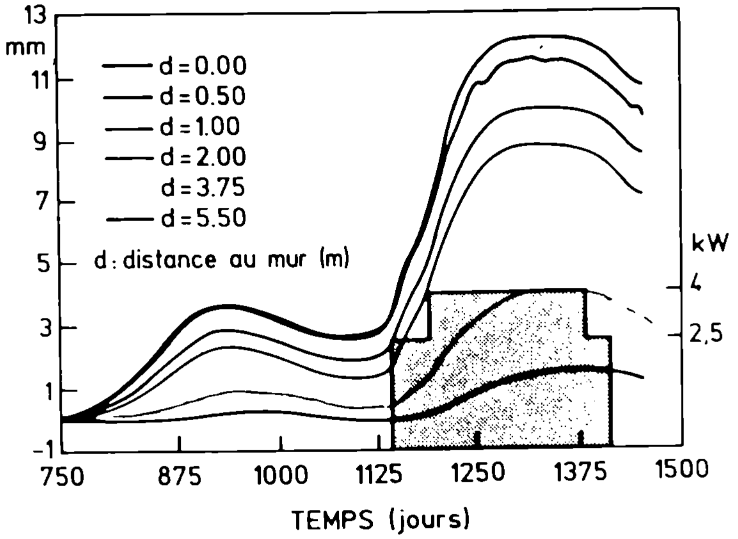


DISPLACEMENTS IN ROCK SALT AROUND BOREHOLE
Figure 4

Displacements at the floor of the gallery versus time (see figure 5)

The maximum displacement induced by the heating was approximately 20 mm.

PROBE # 1

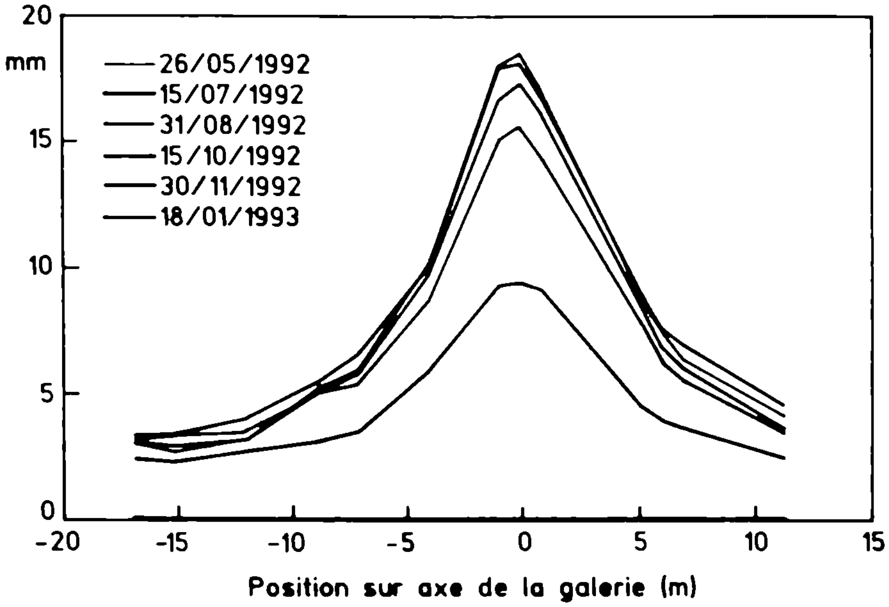


DISPLACEMENTS AT THE FLOOR OF THE GALLERY
Figure 5

Displacements at the floor of the gallery versus distance from the borehole and time (see figure 6)

The heating has influenced significatively the floor of the gallery 12 meters away from the borehole center.

PROBE # 1

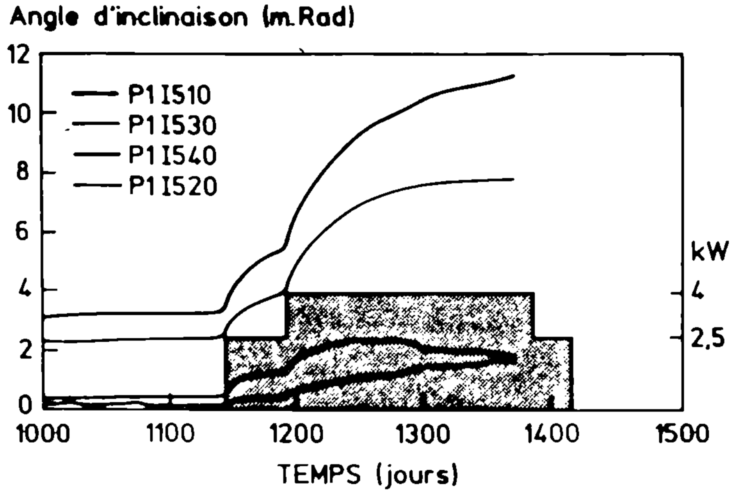


EVOLUTION OF THE DISPLACEMENTS AT THE FLOOR OF THE GALLERY
Figure 6

Dip angle of the floor around the borehole (see figure 7)

One can clearly see the two heating steps. The angle varies according to the directions. Dut to the effect of the walls of the gallery the angle measured perpendicularly to the gallery axis is much greater than the one measured parallely.

PROBE #.1

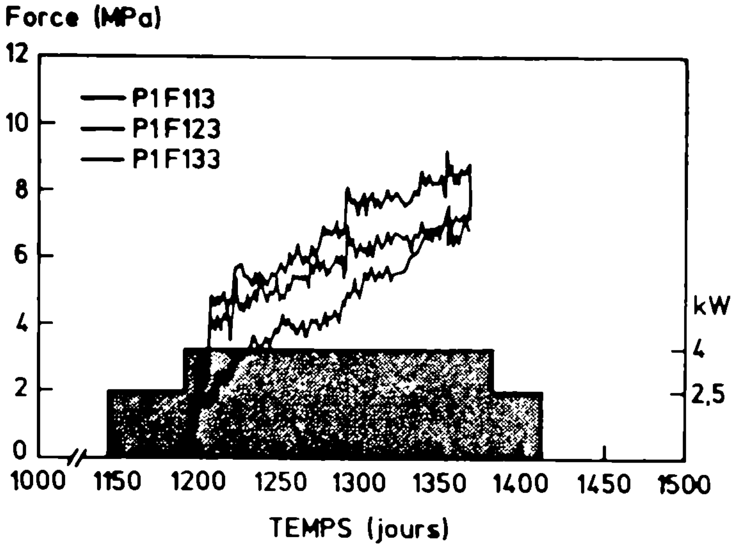


DIP ANGLE AROUND BOREHOLE
Figure 7

Pressure (see figure 8)

Though the measurements must be carefully interpreted, it seems that the pressure on the probe varies between 7 and 10 MPa.

PROBE # 1



PRESSURE ON THE PROBE
Figure 8

Publications

KAZAN Y., BAZARGAN B., GHOREYCHI M.
Premiers résultats thermomécaniques de l'essai CPPS sur le puits P1.
Rapport interne ANDRA n° 624 RP G3S 92-009.

KAZAN Y., GHOREYCHI M.
Mesures réalisées sur le site de l'essai CPPS jusqu'à l'été 1993.
Internal report n° 695 RP G3S 93-003.

The Cerberus test

Title:	CERBERUS Test
Contractor:	ONDRAF/NIRAS, Brussels, Belgium
Contract N°:	FI2W/0003
Duration of contract:	01-07-90 / 31-12-94
Period covered:	01-01-93 / 31-12-93
Project Leader:	ONDRAF : J. Van Miegroet CEN/SCK: B. Neerdael, L. Noynaert

A. OBJECTIVES AND SCOPE

The CERBERUS test (Control Experiment with Radiation of the BElgian Repository for Underground Storage) is aimed at simulating the near-field effects in an argillaceous environment of a Cogema HLW-canister after 50 years cooling time.

It mainly consists of a mock-up containing a ^{60}Co source of 397 TBq and 2 electrical heating elements each dissipating 365 W placed in the Boom clay from the Underground Research Facility located at Mol.

A monitoring of the thermo-hydro-mechanical fields and the chemical *in situ* conditions is foreseen.

It allows to launch various validation exercises of computer codes such as the program DOSEGEO (computation of dose-rate), the program SOURCE (computation of pore water pressure around drilling and digging works) and the program TEMPPRES (computation of the thermo-hydro-mechanical behaviour of the Boom clay).

B. WORK PROGRAMME

The work programme can be subdivided in 2 main items, the monitoring programme and the validation of existing codes.

The monitoring programme consists in the measurement of:

- dose-rate;
- temperature and heat transfer parameters;
- pore water pressure and hydraulic conductivity and diffusivity;
- total stress;
- pH/Eh;
- radiolysis effects;

The codes involved in the validation and interpretation trials are :

- the model DOSEGEO which allows to compute the dose-rate around a shielded γ source;
- the model SOURCE which allows to compute the pore water pressure evolution around a piezometer screen at a constant temperature;
- the thermo-hydro-mechanical model TEMPPRES.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The test is fully operational since the end of November 1989.

Progress and results

radiation field

The measurements of the dose-rate have been performed by means of an ionisation chamber. The measured values remain in good agreement with the results obtained with the model DOSEGEO. After compensation for the decrease of the ^{60}Co source and of the iron shielding thickness, the dose-rate can be assumed to remain constant.

thermal field

Due to the decrease of the ^{60}Co source, the temperature at all thermocouples and Pt100 probes are decreasing according to the values predicted by the model TEMPPRES.

hydrological field

The hydraulic conductivity values compensated to take into account the *in situ* temperature remain almost constant. At only one piezometer screen, the compensated hydraulic conductivity is still slowly decreasing. At this place, one has suspected that the heating phase had generated micro-cracks. The observed evolution of the hydraulic conductivity at this place can be a demonstration of the self healing capacity of the Boom clay.

thermo-hydro-mechanical field

A quasi steady state of pore water pressure is reached in the near field of the CERBERUS test indicating that the pore water pressure dissipation are now compensated by the pore water pressure regime imposed by the Test Drift.

chemical field

The main results are:

- the pH has reached a constant value of 6.9;
- the Eh still remains reducing (-202 mV versus SHE);

radiolysis effects

A concentration of 2.41 10^{-6} g H_2/kg H_2O has been detected after 4 years irradiation time, while a value of 0.52 10^{-6} g H_2/kg H_2O has been obtained after 3 years irradiation time.

list of publications

pm

Mine-by-Test

Title:	Mine-by-Test
Contractor:	NIRAS/ONDRAF
Contract N°:	FI2W/CT90/0003
Duration of contract:	from 1 July 1990 to 31 December 1994
Period covered:	from 1 January 1993 to 31 December 1993
Project leader Niras:	J. Van Miegroet
Project leader SCK:	M. Put and D. De Bruyn

A. OBJECTIVES AND SCOPE

The Mine-by-Test deals with the long-term behaviour of the so called *Test Drift* of the HADES Underground Research Facility. Follow-up and monitoring of the concrete lining and of the terminal shotcreted front ensure the Test Drift stability. Monitoring of the surrounding clay mass gives reliable data for assessing its rheological behaviour.

B. Work programme

Acquisition of field measurements and interpretation exercises are the two main items of the programme.

Measurements in the clay mass around the Test Drift are gathered from:

- one settlingmeter and one inclinometer devices installed above the Test Drift before the 1987 construction phase;
- six piezometer nests, one series of pore water pressure cells and one multiple-point extensometer installed from the Test Drift.

Monitoring of the concrete lining is ensured by:

- 34 load cells installed between the liners and 42 total pressure cells embedded in these liners;
- diametrical convergence measurements of seven instrumented sections.

Follow-up of the terminal shotcreted front occurs through:

- one multiple-point extensometer installed from the front up to 10 m depth in the clay mass;
- 15 reflectors installed on the surface of the shotcreted shell.

Interpretation of the collected data occurs with simple analytical elasto-plastic models or with finite-element analysis.

C. Progress of work and obtained results

State of advancement

The Mine-by-Test is in a phase of long term survey.

Progress and results

Measurements in and around the Test Drift do not show major differences since the last annual report:

- the total pressure on the lining still ranges from 1.7 to 2.4 MPa when calculated from load-cell measurements, pressure-cell measurements showing more scattering (from 0.5 to 3.3 MPa); several load cells, having reached their upper measuring limit, had to be disconnected to avoid mechanical disturbances in the data acquisition unit;
- the average convergence of the lining amounts 1.24% 2100 days after installation;
- fracturing in the shotcreted shell still increases in a significant way (convergence of the shell amounts locally up to 400 mm), and as a consequence the entrance in this part of the underground facility is still prohibited.

Besides the writing of the interim report for the period (01-07-1990 to 31-12-1992), the interpretation task has been limited this year to the update of the comparison, between the instrumented sections, of the pressure acting on the lining (by way of pressure-cell and load-cell measurements) and of the lining convergences.

Title : CHARACTERIZATION OF CLAY UNDER THERMAL LOADING FOR UNDERGROUND STORAGE - "CACTUS"

Contractors : CEA/ANDRA - Fontenay-aux-Roses - France

Contrat n° : FI2W-001

Duration of contract : from September 1990 to March 1993
Period covered : January 1993 - March 1993
Project leaders : M. RAYNAL, F. PLAS, B.VIGNAL

A/ OBJECTIVES AND SCOPE

The aim of CACTUS project is to study the near field thermo-hydro-mechanical couplings in deep clay around a waste emplacement borehole, under thermal loading by in situ experiments. This is a major importance for predicting the behaviour of radioactive waste storage, particulay as regards to the irreversible phenomena due to the effect of heating on stresses and pore pressure. The experiment includes two tests conducted in separate boreholes at Mol underground facilities, with identical heating probes and backfilling materials (clay mud) but different types of thermal loading and unloading cycles (Figure 1).

B/ WORK PROGRAM

"CACTUS" project is composed from two tests :

1. CACTUS ONE : Emplacing of a prototype heater with backfilling material (clay mud) and heating after hydro-mechanical equilibrium. It was planned as a preliminary test.

2. CACTUS TWO : Emplacing of a heater with backfillng material and earlier heating.

Both tests have the same peripheral instrumentation defined to follow the thermo-hydro-mechanical respons of clay at different distances from the heating cells (figures 2, 3):

- 24 thermal sensors are located on the heater and 30 are distributed in five peripheral boreholes.
- Water pressure is measured in the mud on the probe and inside the clay formation with CEN/SCK piezometrie nists.
- Water content and density in clay are obtained using a neutro-gamma probe inside another borehole.
- Mechanical measurements are total stresses (10 Glötzl cells placed in two boreholes) and vertical displacements.
- The variation of diameter and the strain of the heating cell body are also measured.

C/ PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

CACTUS 1 has been installed in May 1990 and power was switched on in September at a level of 1200 watts. This first heating cycle was interrupted in November after an electrical insulation fault has been detected.
Heating started again at the same power in March 1991 and stopped in January 1992, the cooling-down phase being observed since March 1994.

CACTUS 2 was re-designed and thoroughly tested after probe 1 problems, leading to significant increases in costs and delivery time. Therefore the second probe was installed at Mol in December 1991. Heating started in February 1992 and stopped at the begining of March 1994.

Progress and results

CACTUS 1

1/ Before heating, the peripheral instrumentation has made it possible to accurately observe the behaviour of the clay under isothermal conditions. When drilling the borehole, a drop in the pore pressures was particulary observed. (figure 4) i.e. hydromechanical expansion of the clay. Radial stresses dropped while tangential one rose (figures 5, 6). After emplacement of the probe, the pore pressures ans stresses reestablished a new state of equilibrium as the clay closed around the probe and the backfilling.

2/ When heating started, the pore pressures immediately increased and reached a peak in 20 days. These however began to dissipate while the temperatures continued to rise (figure 7), tending towards a state of initial equilibrium after 200 days (figure 4). This is because the Boom clay, of which permeability is very low, first reacts under undrained conditions. The final value is different from the value prior to heating. The total stresses (radial and orthoradial) increased in correlation. Stress level remained high during all the heating phase (figures 5, 6).

Measures of water contents and dry specific densities indicate an initial phase in which the clay expands followed by progressive collapse which appears to correspond to the dissipation of the pore pressures (figure 6). This behaviour may denote temperature consolidation, well-known in clay media.

3/ When cooling down, the pore pressure and the total stresses dropped. The evolution is similar to what occured during heating, with variation in other way.

4/ During Thermal Cycle 2, mechanical and hydraulical behaviour are identical as during cycle 1 (figure 4, 5). This seems not to be the case of density and water content : cycle 1 should evidence irreversible effects (thermal consolidation) whereas cycle 2 deformations were reversible (figure 6). These observations are consistent with the concept of thermal hardening.

CACTUS 2

Only one thermal loading and unloading cycle has been initiated. Compared to probe 1, the only difference is that the heating has begun after a shorter waiting time after emplacement (figure 2 à 4). The results indicate that the behaviour is similar to that of CACTUS 1, i.e. irreversible deformations.

List of publications

PICARD JM., BAZARGAN B., ROUSSET G. and VIGNAL B.
"Behaviour of Boom clay under thermal loading : first results from CACTUS 1 in situ test"
Braunschweig workshop on pilot tests on Radioactive Waste Disposal in Underground facilities - June 19-21 1991.

PICARD JM.
"Coupled Thermo-Hydro-Mechanical Modeling of in situ heating experiments in Boom clay"
Workshop on "Thermomechanics of clays and clay baniers" - October 20-22, 1993 - Bergamo - Italy

List of references

PICARD JM. : Essai thermo-hydro-mécanique dans une argile profonde (essai CACTUS) - Rapport d'avancement n°1 - Commission of the European Communities - Mars 1991

PLAS F. : Essai thermo-hydro-mécanique dans une argile profonde (essai CACTUS) - Rapport d'avancement n°2 - Commission of the European Communities - October 1991

PICARD JM. : Rapport d'avancement n°3 - Commission of the European Communities - Mars 1992

PICARD JM. : Rapport d'avancement n°4 - Commission of the European Communities - Octobre 1992

PICARD JM. : Rapport final - Commission of the European Communities - Septembre 1993 - Rapport ANDRA 697 RP G.3S 93.001

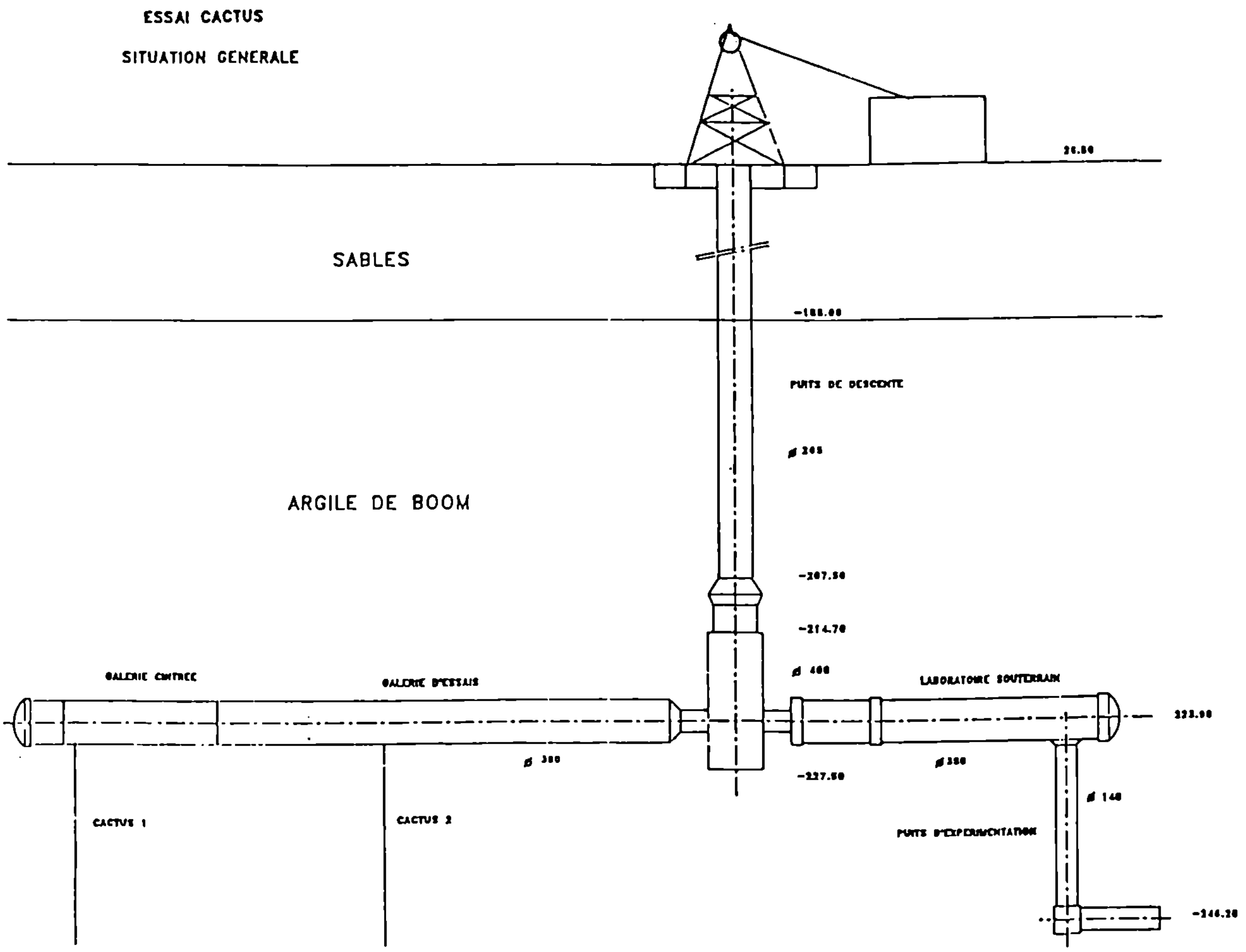


figure 1 - Mol Underground facilities : Emplacement of CACTUS tests

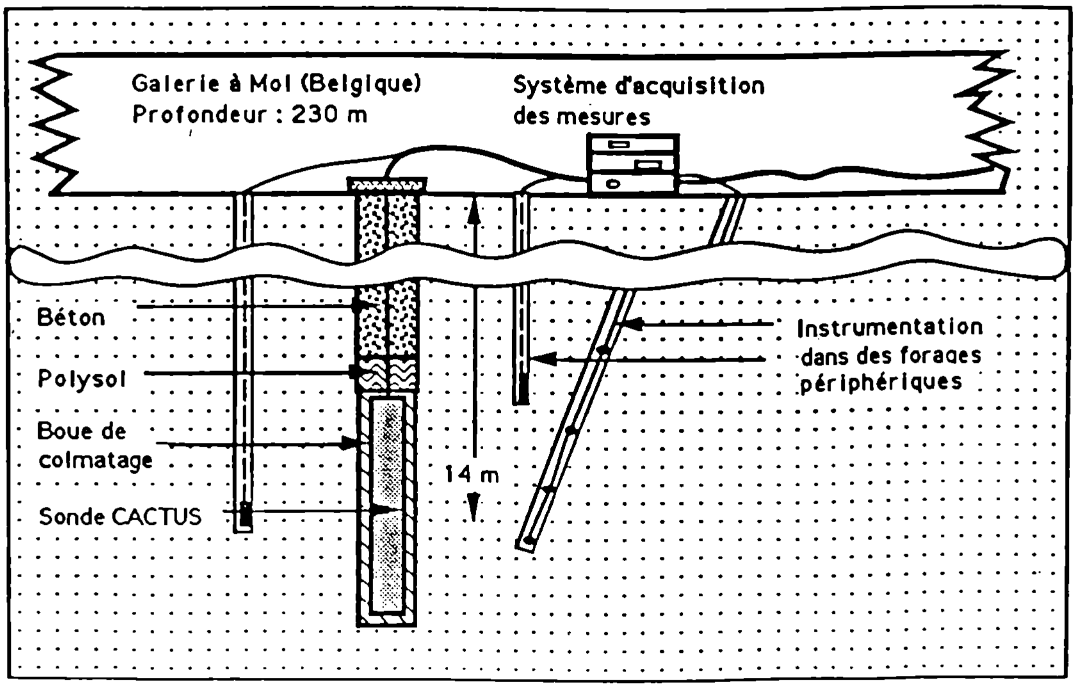
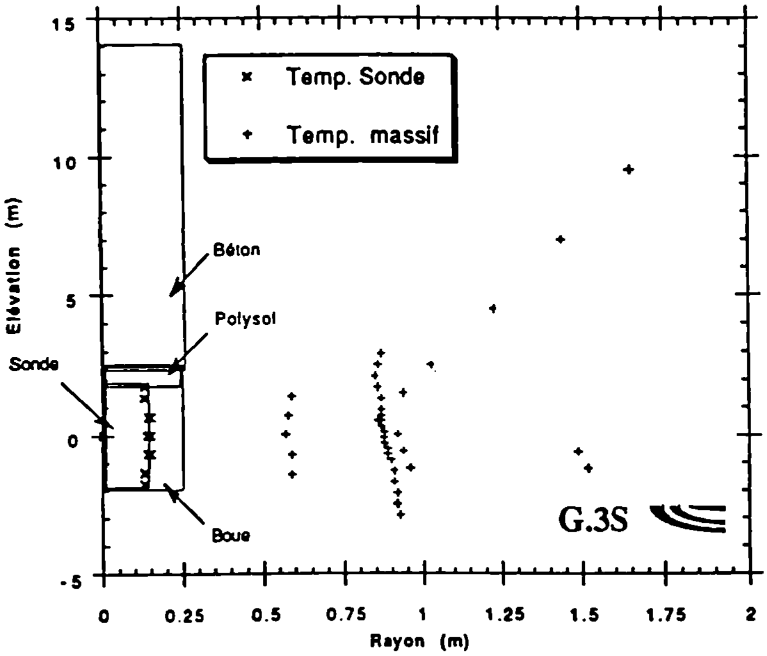
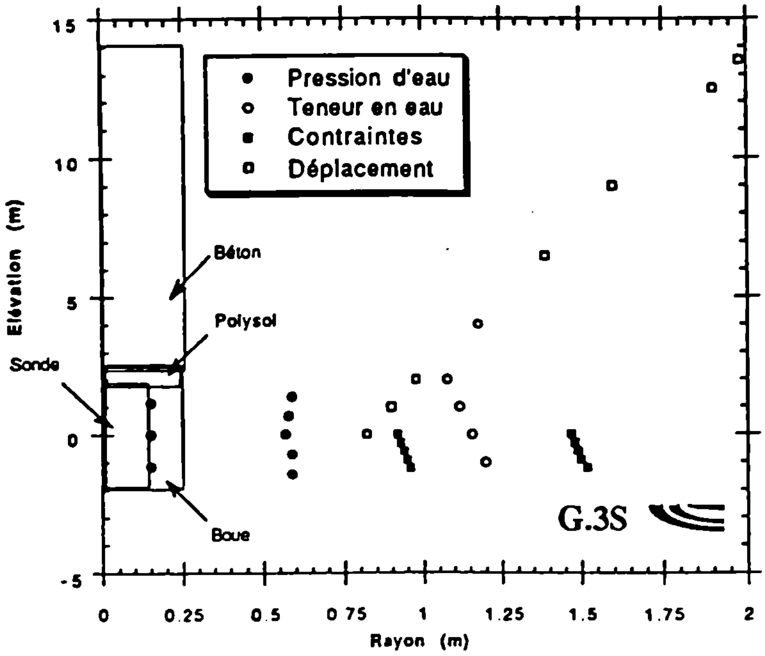


figure 2 - Scheme of a CACTUS test

figure 3 - CACTUS 1 : position of instrumentation



a- Thermal sensors



b- Stress, displacement, water pressure, water content and dry density

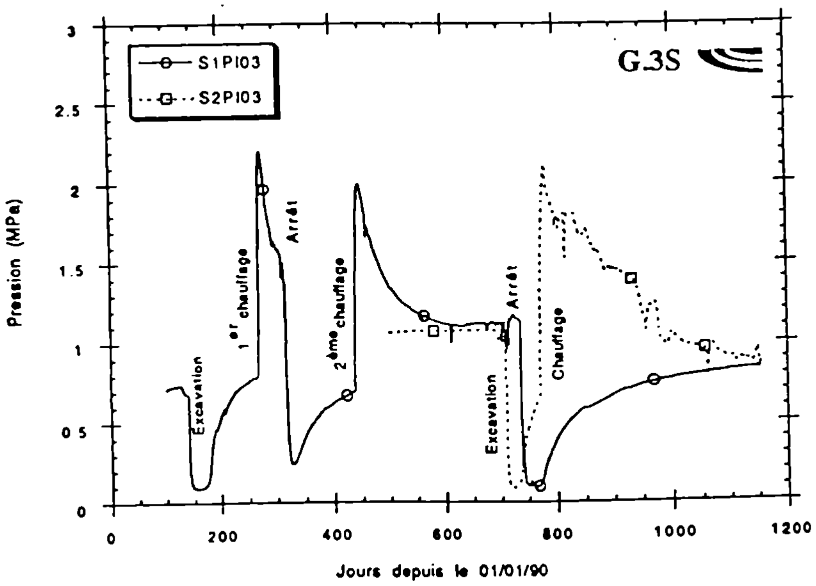


figure 4 - CACTUS 1 and 2 : Evolution of water pressure from january 1, 1990
(r= 60cm for CACTUS 1 and r= 70cm for CACTUS 2)

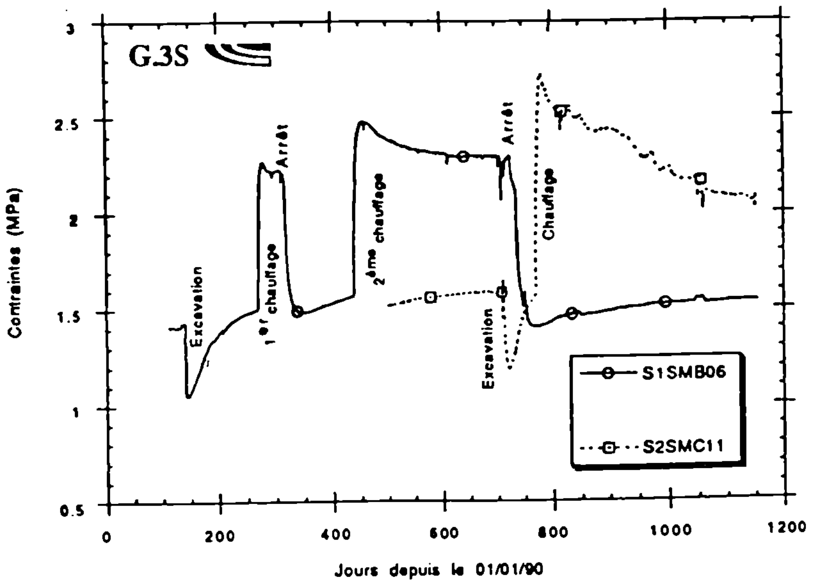


figure 5 - CACTUS 1 and 2 : Evolution of radial stress in the clay formation from january 1, 1990
(r= 95cm for CACTUS 1 and r= 70cm for CACTUS 2)

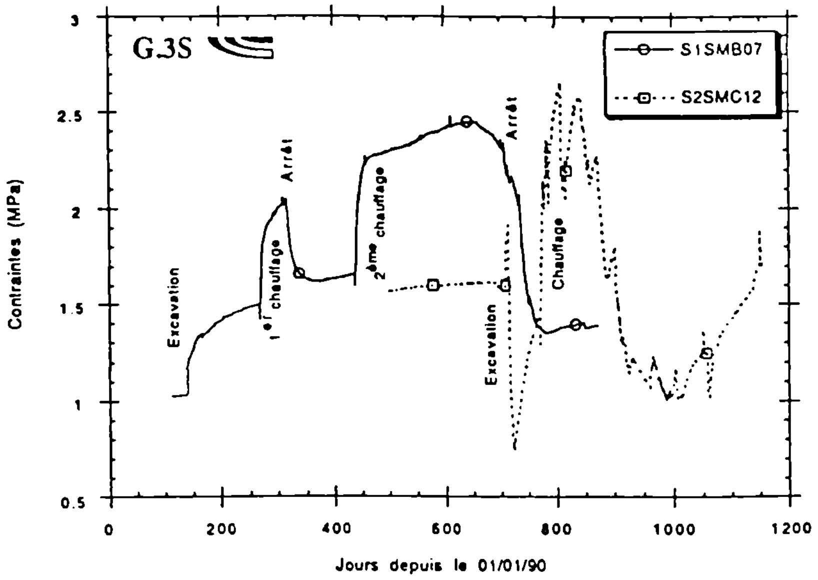


figure 6 - CACTUS 1 and 2 : Evolution of orthoradial stress in the clay formation from january 1, 1990 (r = 95cm for CACTUS 1 and r = 70cm for CACTUS 2)

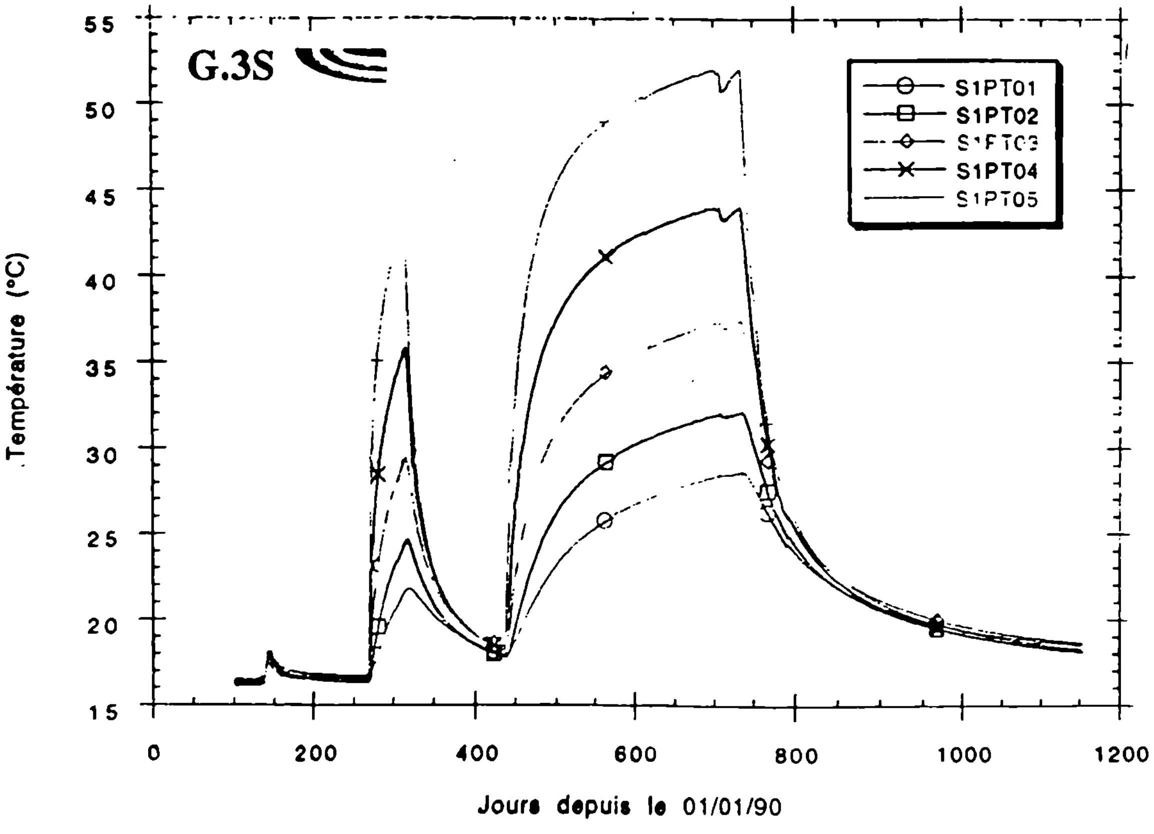
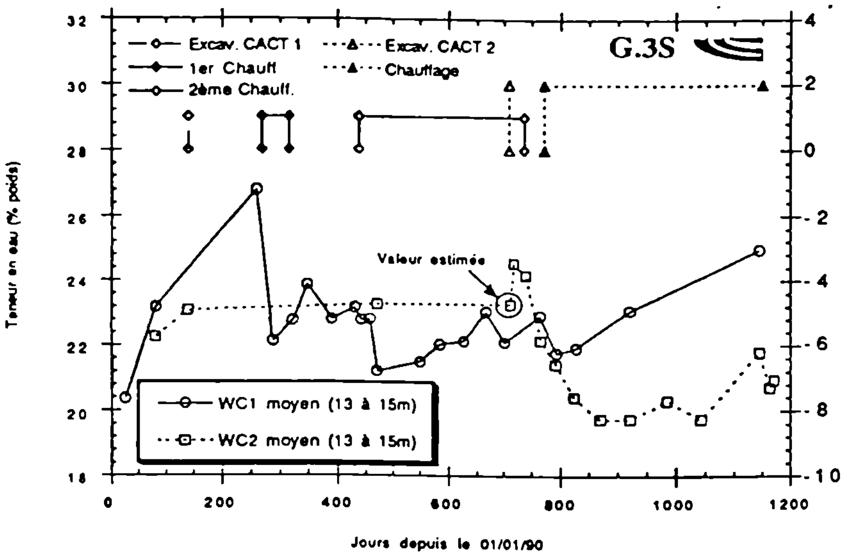
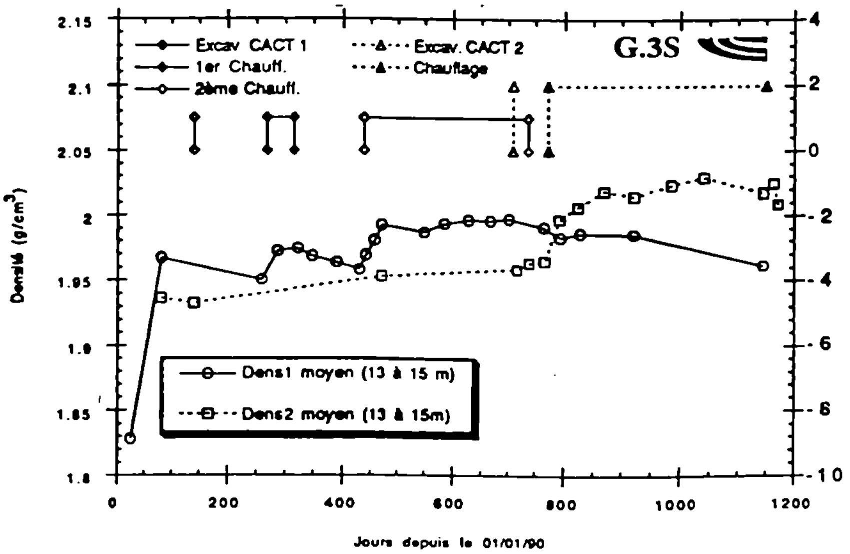


figure 7 - CACTUS 1 : Temperatures at different distance of thermal cell axis

figure 8 - CACTUS 1 and 2 : Evolution of water content and density in the clay formation from january 1, 1990



a - water content



b - density

DEMONSTRATION OF THE IN SITU APPLICATION OF AN INDUSTRIAL CLAY-BASED BACKFILL MATERIAL (BACCHUS 2)

Title :	Demonstration of the in situ application of an industrial clay-based backfill material (BACCHUS 2)
Contractors :	SCK/CEN, ANDRA, ENRESA
Contract N° :	FI2W-CT91-0098
Duration of contract :	from 01-10-1991 to 30-04-1995
Period covered :	from 01-01-1993 to 31-12-1993
Project leaders :	G. Volckaert (coordinator), C. Mayor, B. Vignal

A. *OBJECTIVES AND SCOPE*

The BACCHUS 2 experiment aims at the optimization and the demonstration of an installation procedure for a clay based backfill material. The installation procedure, materials and techniques have to be as close as possible to realistic industrial processes and capabilities.
The backfill material consist of a mixture of high density clay pellets and clay powder. The experiment is developed in cooperation with ENRESA and ANDRA/CEA.

The instrumentation of the experiment must be optimized in such a way that it can be used as a validation experiment for the hydro-mechanical model developed under CEC contract FI2W-CT90-0033.

The BACCHUS 2 project also includes the characterisation of the granular backfill, and the retrieval and the expertise of the BACCHUS 1 test mock up.

B. *WORK PROGRAMME*

The work programme consists in the three following points:

1. Study and optimization of the backfill material

The sealing material consist in a mixture of clay pellets and clay powder. The ratio powder/pellets and the density, size and water content of the pellets will be used as parameters in the optimization process.

Fundamental properties of this mixture such as the hydraulic conductivity and the swelling pressure will be measured.

2. Recuperation of the BACCHUS 1 experiment

The BACCHUS 1 mock-up installed in '88 will be retrieved by overcoring. The aspects and hydro-mechanical properties of the retrieved Boom clay seal and the FoCa-bentonite buffer will be studied.

3. In-situ demonstration of the application of the backfill material

The demonstration will consist in the sealing of the large borehole (50 cm diameter) left after the retrieval of the BACCHUS 1 mock-up. The backfill material described under point 1 will be installed around a central filter tube which will be used as support and access tube for the instrumentation.

Probes for water content measurement, based on the experience gained by CEA in the BACCHUS 1 project, will be embedded in the backfill material. Also the instrumentation installed previously in the host clay around the BACCHUS 1 mock-up, can be further used to monitor the host clay behaviour.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The characterisation of the granular backfill has been completed. The hydraulic conductivity and swelling pressure have been measured as a function of the dry density. X-ray tomography has been applied successfully to measure the evolution of the density distribution during hydration.

The BACCHUS 2 mock-up was constructed and the instrumentation was installed on it and tested. The thermal pulse system, which will be used to follow the hydration of the backfill, was completed. This system consists in three plates with in total 63 themocouples and a heater.

The drilling works for the retrieval of the BACCHUS 1 experiment were started in May 1993 and, on the 29th of June 1993, BACCHUS 1 was brought to surface in good condition. The remaining borehole was immediately cleaned and the BACCHUS 2 mock up installed in it without major problems.

The expertise of the retrieved BACCHUS 1 mock up has allowed to determine the cause of the early breakdown of the heater and to check the quality of the hydrated buffer material.

The evolution of the total stress and the pore water pressure in the host clay around the BACCHUS experiment and in the backfill of the BACCHUS 2 experiment was closely followed. All sensors still seem to work satisfactorily. The state of hydration of the BACCHUS 2 backfill was followed using the thermal shock system.

Progress and results

Characterisation of the granular backfill

In Table I the hydraulic conductivity and/or the swelling pressure of seven clay backfill samples with a dry density of 1.6 g/cm^3 (3 samples), 1.7 g/cm^3 (4 samples) and 1.8 g/cm^3 (3 samples) are given. The clay backfill samples are 50/50 mixtures of Boom clay powder and high density Boom clay pellets.

As expected the hydraulic conductivity decreases with density and swelling pressure increases. At a dry density of 1.8 g/cm^3, the hydraulic conductivity of the backfill is about two times the mean hydraulic conductivity of the in situ clay and the swelling pressure is about equal to that of the in situ clay. The evolution of the swelling pressure can be explained as follows:

- first the clay powder and pellets take up water rather fast. For the powder, this is due to its high hydraulic conductivity and for the pellets, this is due to the high suction potential (thus high driving force) and the high surface to volume ratio;
- as the clay pellets take up water, they develop an important swelling pressure and start to swell and to compact the powder surrounding them. As the pellets continue to swell their swelling pressure decreases.
- this process will continue until an equilibrium between the swelling of the pellets and the compression of the powder is reached.
- As the water uptake by the pellets is a faster process than the compression of the powder surrounding them, the "macro" swelling pressure goes through a maximum.

This explanation is confirmed by the X-ray tomography observations. X-ray tomography has been applied to monitor the progress of a hydration front through two backfill samples with a density of respectively 1.7 g/cm^3 and

1.8 g/cm^3. The changes in the mean density and the standard deviation are less pronounced for the denser sample (R1D1.8S1T). It is clear that the higher the mean density of the sample the lower the difference with the density of the pellets and the lower its standard deviation will be. If the density is higher, the porosity will be lower and thus the change in density during hydration is lower. This is also apparent from Table II which compares the mean radiological densities and their standard deviations for plugs R1D1.7S3T and R1D1.8S1T. In both cases the density of the samples becomes more homogeneous. In Table III the mean radiological density and its standard deviation of one pellet in sample R1D1.7S3T before and after hydration are given. The mean radiological density and the standard deviation drops during hydration. This proves the swelling of the pellet.

Retrieval of the BACCHUS 1 mock-up and installation of BACCHUS 2

It was foreseen to drill twelve 100 mm diameter boreholes around BACCHUS 1, then to perform a large diameter drilling around BACCHUS 1 over its full length (14.5 m), to retrieve BACCHUS 1, to clean the remaining borehole and finally to install BACCHUS 2. In practice some major difficulties were encountered and the original plan needed to be adapted.

First, two freezing tubes used during the construction of the gallery have complicate the drilling. Indead, to cut through the freezing tubes a special drilling head was made.

At the depth of the BACCHUS 1 experiment (13 to 14.5 m) very wet clay with a water content up to 30 weight % was encountered. In one borehole water inflow occurred. This water originated from the water accumulated in the central tube of the BACCHUS 1 experiment. This humidity made the drilling difficult and caused a quick convergence of the borehole. Therefore several boreholes needed to be redrilled or cleaned by applying a special drilling technique.

During the large diameter (540 mm) drilling, the freezing tubes caused trouble again. A special 540 mm drilling head was constructed to cut them through. At a depth of about 13 m, the friction had become so large that further drilling became very time consuming. Therefore it was decided to stop drilling and to install two hydraulic jacks, about 60 tons of force each, to push up BACCHUS 1. On the 29th of June 1993 BACCHUS 1 was brought to surface in good conditions.

The remaining borehole was cleaned and BACCHUS 2 was installed without major problems. Figure 1 shows the finalised BACCHUS 2 mock up just before installation and Figure 2 shows one of the three grids with 21 thermocouples used for the thermal pulse measurements.

Figure 3 shows how the BACCHUS 2 borehole was backfilled. In total 900 kg of the granular backfill material (50/50 pellets/powder mixture) was applied and a mean density between 1.5 and 1.6 g/cm^3 was obtained. The density can only be estimated because the exact form and diameter of the borehole are unknown. An important difference between the top level of the backfill and the level of the support plate of the thermocouples was measured at the first and third thermocouple level. This causes an extra uncertainty in the estimated densities.

BACCHUS 1 expertise

The FoCa clay blocks were no longer in contacts with their upper flange. Water and clay mud have infiltrated this flange through the openings for instrumentation cables and the Glötzl load cells. In this flange the three heating elements were connected in parallel to their alimentation cable. One branch of the connection was completely destroyed by the infiltrated water. This is certainly the reason of the breakdown of the heater in 1989. The heater was completely filled with water.

The carbon steel bolts used in this flange showed strong general corrosion (1 to 2 mm). All stainless steel (304) parts, which had been in direct contact with the borehole walls, showed severe pitting corrosion.

The joints between the FoCa and Boom clay blocks had well sealed. In the FoCa clay blocks the original position of the joints could only be traced back thanks to the instrumentation embedded in them.

First results on BACCHUS 2

The thermal conductivities derived from the thermal pulse measurements performed until now, show no systematic difference between the three thermocouple levels. This shows the homogenity of the backfill (constant density). Also the change in thermal conductivity with time seems to be very limited indicating that up to now the hydration of the backfill is very limited.

Figure 4 shows the total stress evolution on the central tube of the BACCHUS 2 mock up. Only on the south side of the central tube the pressure has clearly raised. Probably the pressure raises very slowly because the backfill is compressible. The drilling works lead to a strong decompression around the borehole so that at this interface the stress will only increase slowly after the sealing of the borehole.

Figures 5 shows the evolution of the pore water pressure in the clay host rock. All filters show a sharp pressure drop soon after the start of the drilling works. All pressures drop to about 3 to 4 bar except the lowermost filters. The lowermost filters seems to be less affected by the drilling works and their pressure starts to raise soon after the installation of BACCHUS 2. These filters are situated at the same depth as the BACCHUS 2 bottom flange. This explains why they are less affected.

Conclusion

The characterization of the granular backfill was finalised. The hydromechanical properties are of the same order of magnitude as those of the in situ Boom clay.

BACCHUS 1 was successfully retrieved and BACCHUS 2 successfully installed. The expertise of BACCHUS 1 has shown that water infiltration have caused the early failure of the BACCHUS 1 heater. The first results of BACCHUS 2 show a very slow pressure build up.

List of publications

/1/ G. Volckaert, B. Neerdael, M. Dardaine (CEA)
Demonstration of the in situ application of an industrial clay-based backfill material: Bacchus 2.
Prog. Report 1-10-1991/30-6-1992
CEC contract FI2W-CT91-0098

/2/ G. Volckaert, M. Dardaine (CEA)
Demonstration of the in situ application of an industrial clay-based backfill material : Bacchus 2
Annual Progress Report 1992
CEC contract FI2W-CT91-0098
Ed. : SCK, R-2953, 1993.

Table I Characterisation of the granular backfill material

sample number	dry density g/cm³	height cm	$P_{s,max}$ (b) MPa	$P_{s,eq}$ (c) MPa	K(d) m/s
R1D1.6S1	1.586	7.34	- (a)	-	$3.0\ 10^{-11}$
R1D1.7S1	1.690	6.89	0.6	0.56	$7.7\ 10^{-12}$
R1D1.7S2	1.700	6.85	-	-	$9.9\ 10^{-12}$
R1D1.6S2	1.600	7.28	0.35	0.28	$1.4\ 10^{-11}$
R1D1.7S3	1.700	4.34	-	-	$8.2\ 10^{-12}$
R1D1.6S3	1.600	7.28	0.22	0.09	$1.5\ 10^{-11}$
R1D1.7S4	1.700	6.84	0.54	0.38	$8.6\ 10^{-12}$
R1D1.8S1	1.800	4.09	-	-	$6.0\ 10^{-12}$
R1D1.8S2	1.800	6.47	0.95	0.79	$6.3\ 10^{-12}$
R1D1.8S3	1.800	6.47	0.82	0.76	$5.2\ 10^{-12}$

(a) = not determined
(b) = maximum swelling pressure
(c) = equilibrium swelling pressure
(d) = hydraulic conductivity

Table II : Mean radiological densities and their standard deviations for plugs R1D1.7S3T and R1D1.8S1T

code	time	mean rad. dens. HU	standard dev. HU
R1D1.7S3T	start	1133	374
	end	1375	110
R1D1.8S1T	start	1244	283
	end	1410	125

Table III : Mean radiological densities and their standard deviation of one pellet in sample R1D1.7S3T

time	mean rad. dens. HU	standard dev. HU
start	1696	67
end	1424	47

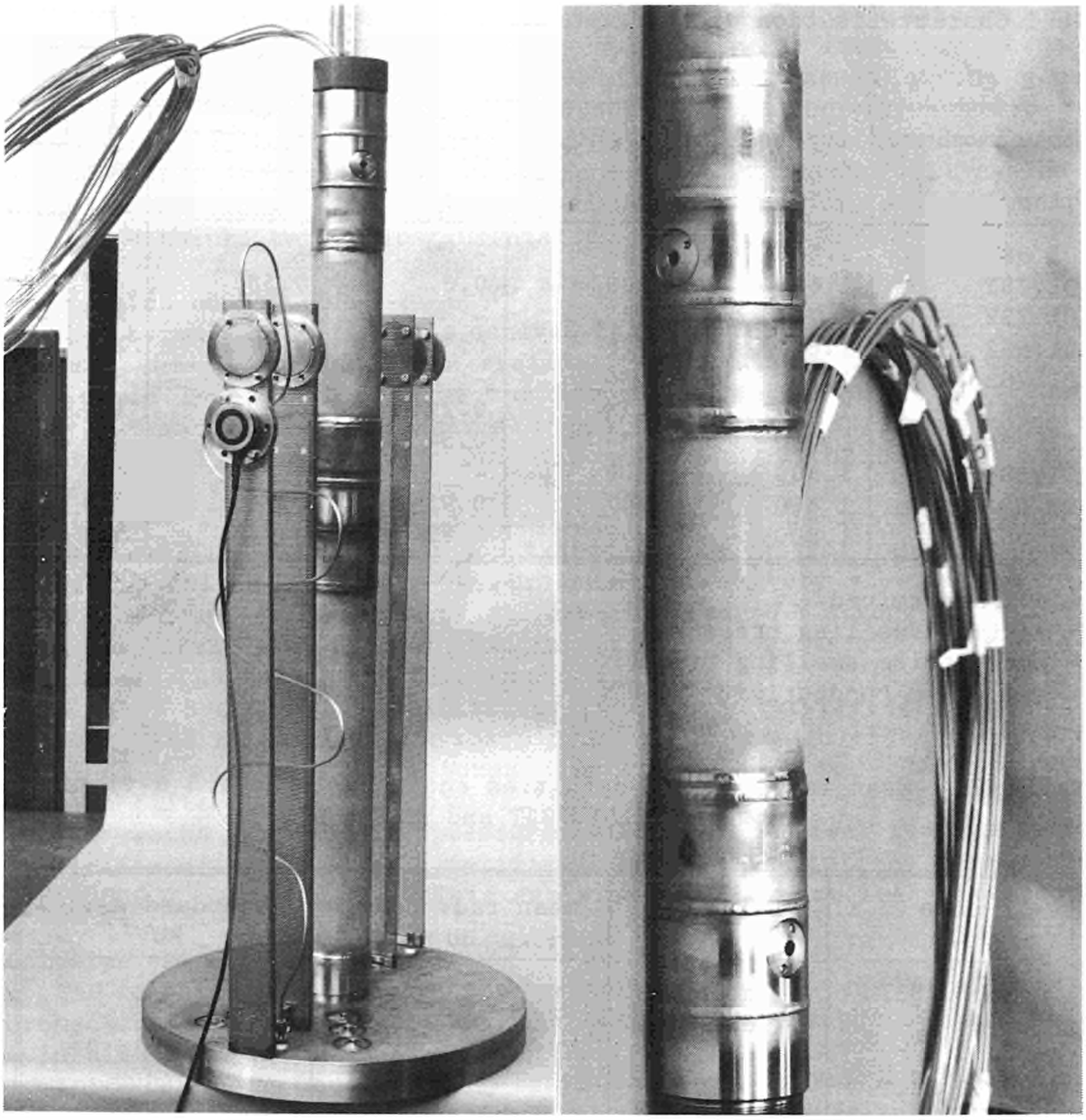


Figure 1: View of the BACCHUS2 mock-up

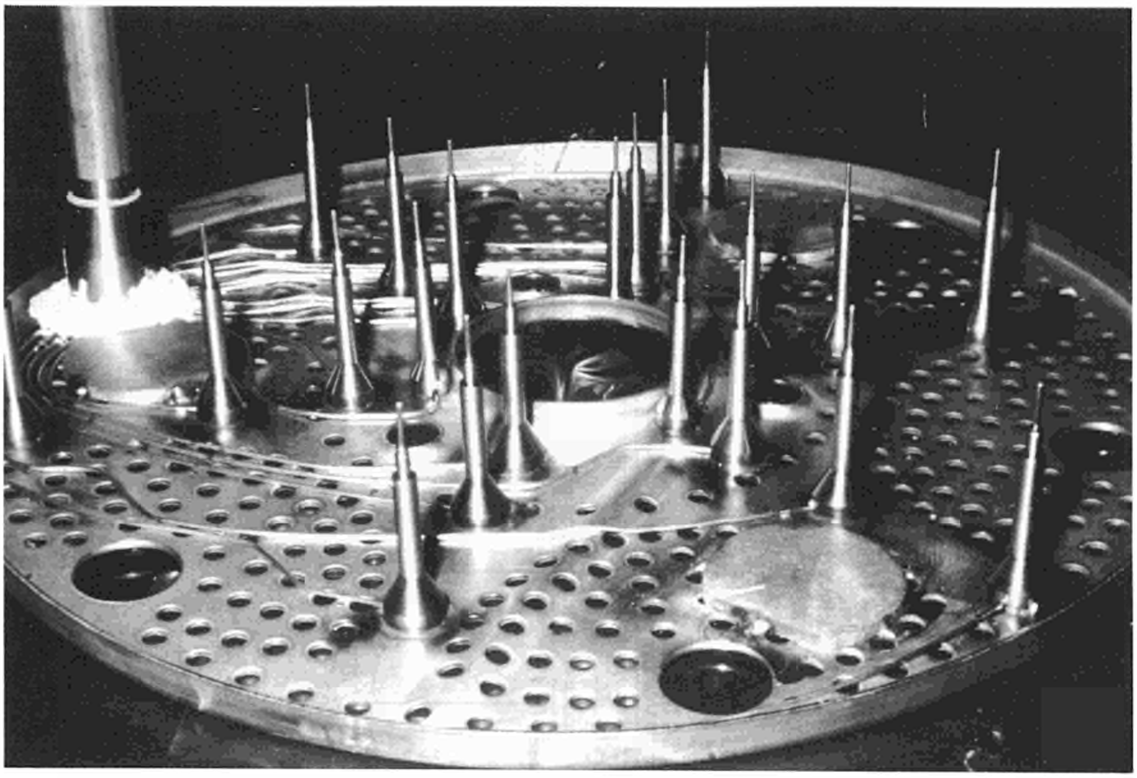


Figure 2: View of one of the three grids with 21 thermocouples for the thermal pulse measuring system.

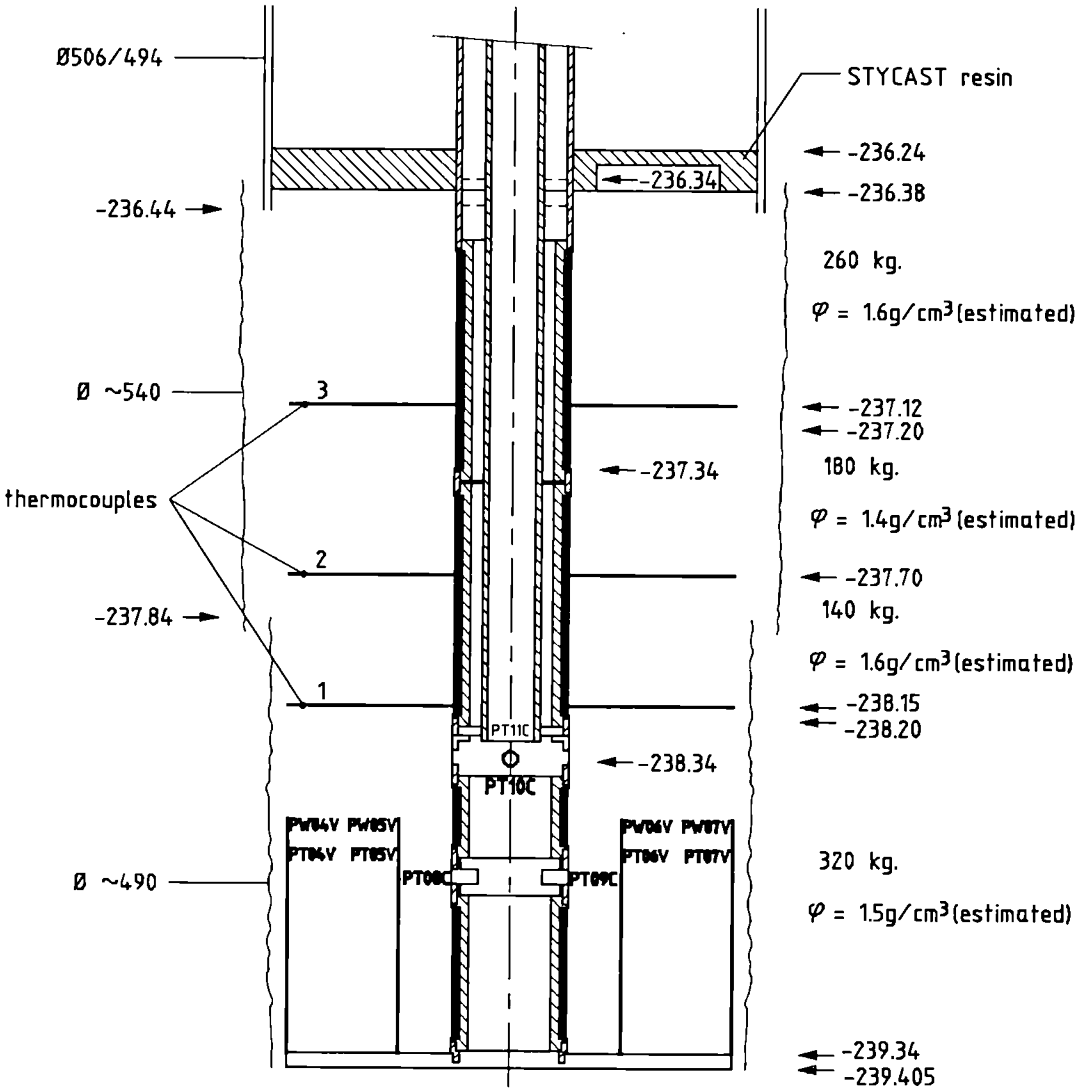


Figure 3: The BACCHUS 2 mock up after installation of the granular backfill and the plates with thermocouples. The estimated backfill density is also indicated.

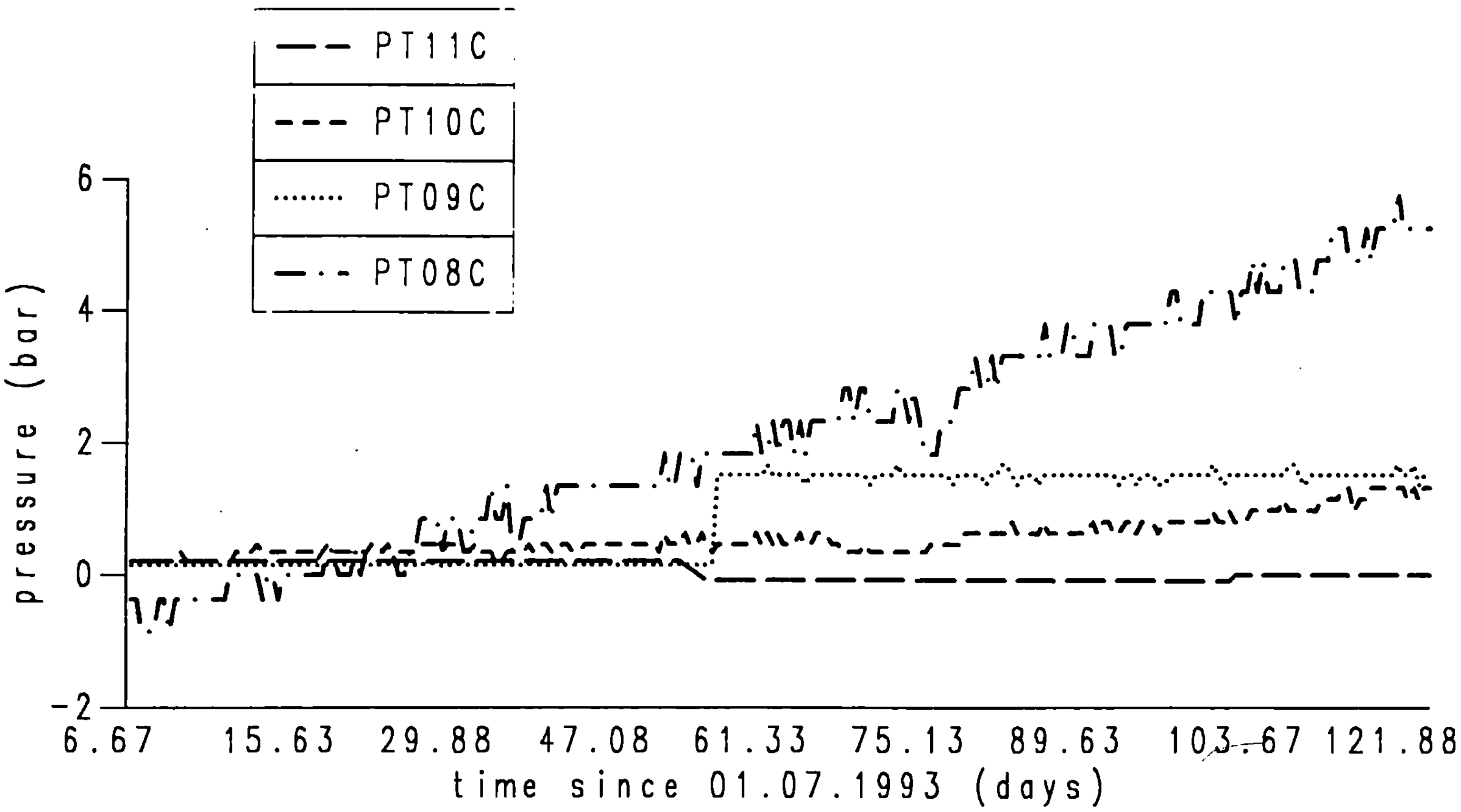


Figure 4: Total stress on the central tube of the BACCHUS 2 mock up

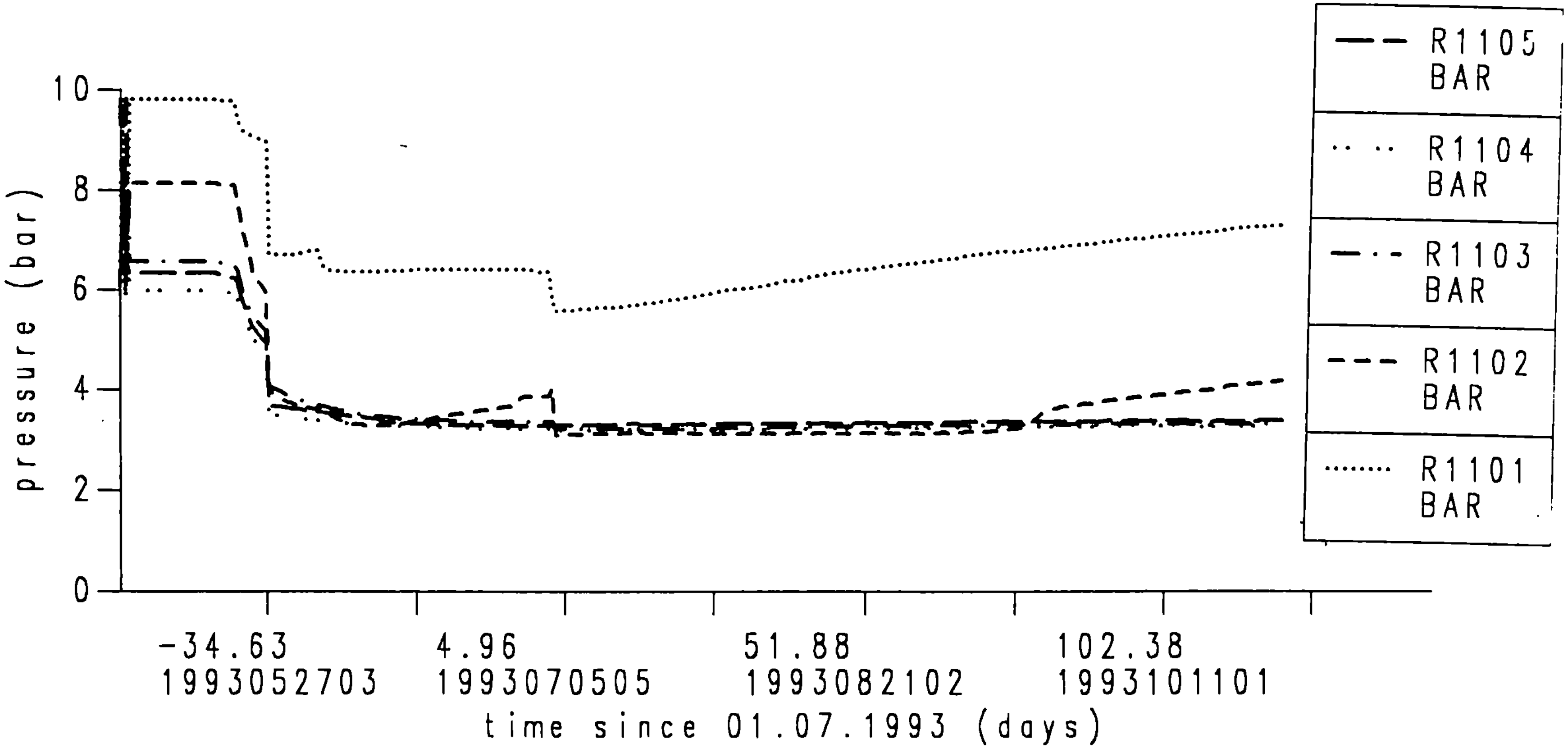


Figure 5: Pore water pressure evolution (in ring 11) around BACCHUS 2

MODELLING AND TESTING OF THE HYDRATION OF BACKFILL AND SEALING MATERIALS

Title :	Modelling and Testing of the Hydration of Backfill and Sealing Materials
Contractors :	SCK•CEN, CEA, UWCC, UPC
Contract N° :	FI2W-CT91-0033
Duration of contract :	from 01-07-91 to 30-06-94
Period covered :	from 01-01-93 to 31-12-93
Project leaders :	G. Volckaert (coordinator), C. Imbert, H. Thomas, E. Alonso

A. *OBJECTIVES AND SCOPE*

If compacted clay-based materials will be used for the backfill and sealing of radioactive waste repositories the hydro-mechanical behaviour of unsaturated materials have to be understood. When these materials are used as a backfilling around HLW packages, their behaviour during saturation is further complicated by the thermal transient due to the heat emission of the waste.

Elasto-plastic models of the Cam-Clay type are not able to describe the irreversible volumetric strain (swelling or collapse) or the evolution of the mechanical property limits due to changes in the water content. In the case of partly saturated clay materials the suction phenomena, which have a strong influence on the hydraulic, mechanical and thermal properties of the material, are to be considered.

The goal of the study is to analyze and model the behaviour of a clay based engineered barrier during its hydration phase under real repository conditions. The hydro-mechanical and thermo-hydraulical models will be coupled to describe stress/strain behaviour, moisture migration and heat transfer.

In this project the CEA and SCK•CEN are responsible for the main experimental work and the research groups at the universities of Cardiff and Catalunya are performing the modelling work.

B. *WORK PROGRAMME*

1. Hydration experiments

Uniaxial experiments determining the influence of the suction potential on the hydration rate, swelling or swelling pressure, will be performed. The progression of the hydration front will be followed by x-ray tomography.

2. Hydro-mechanical experiments

These experiments will determine the mechanical characteristics as a function of the water content and the suction potential of swelling clay at room temperature. Tests with imposed suction potential will be performed.

3. Modelling

The first step will be the adaptation of the existing models to dense, swelling clays. In the heat and moisture transfer model, strain and deformation effects will be included as independent variables, while in the moisture migration and stress/strain behaviour model, expansive soil effects will be included.

In the second step a coupling of the models will be done by the automation of the data transfer from one model to the other.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

SCK•CEN

A second hydration experiment on Boom clay was performed and the hydration profiles were measured non destructively by X-ray tomography.

The water content-suction relation was experimentally measured for Boom clay at different initial densities and at 25 °C and 40 °C.

A first suction controlled oedometer experiment was performed to study the swelling-collapse behaviour of Boom clay under constant vertical stress and decreasing suction.

CEA

The CEA has performed oedometer experiments on the French reference clay FoCa-7 and on Boom clay using samples with different initial suctions. The experimental results have been compared qualitatively with the predictions of the model of Alonso and Gens. In a second type of experiments, the free swelling of FoCa clay under different imposed suctions was measured.

UPC

The hydro-mechanical code NOSAT was further improved with regard to the correct representation of a "no tension" material. An improved modellisation of the BACCHUS 2 in situ backfill test was performed taking into account the installation phase. The new "no tension" version of the NOSAT code was applied.

Experiments on Boom clay were performed to determine the water retention curve and the swelling-collapse behaviour under hydration and controlled suction. The results will be used for the BACCHUS 2 modellisation.

Tests on a sand-expansive clay mixture were performed to test the theoretical predictions of a newly developed model for expansive soils.

A suction controlled triaxial cell was designed. The system includes a laser system for the measurement of radial deformations.

UWCC

Five numerical codes have become operational at UWCC. These codes can handle problems with different degrees of complexity ranging from relative simple heat and moisture transfer problems to complex problems with deformation calculations coupled with heat, water and gas transport. These models are currently being applied to experiments.

Progress and results

SCK•CEN

In a first hydration-X-ray tomography experiment a clay plug of 20 mm was used. The hydration took place quickly so that it was difficult to follow the progress of the hydration front. Therefore a second experiment using a 70 mm long clay plug was performed. The progress of the hydration front could be clearly measured as shown in Fig. 1.

The water content suction relationship for Boom clay was measured for an initial dry density of 1.1 g/cm^3, 1.6 g/cm^3, 1.7 g/cm^3 and 1.8 g/cm^3. The experiments were performed at 25 °C and 40 °C. The suction was controlled by saturated salt solutions and the temperature by the climatic cabinet in which the experiments were performed. The clay samples were unconfined and initially dry. The equilibrium water content of the samples was independent of the density. The equilibrium water content at 40°C is lower than at 25 °C for suctions below 50 MPa. At higher suction no difference is observed.

A suction controlled oedometer experiment was performed on Boom clay compacted to a dry density of 1.7 g/cm^3. A constant vertical stress of 2 MPa was applied on the sample. The deformation of the sample was measured while the suction was gradually decreased. The suction in the sample was controlled by circulating air with a constant relative humidity on both the bottom and top of the sample. The relative humidity of the circulating air was controlled by the use of saturated salt solutions.

CEA

Oedometer tests were performed on FoCa clay powder with different initial suctions. To control the initial suction the clay powder was first stabilized in an atmosphere with constant temperature and relative humidity. The suction-water content relationship has been determined for FoCa clay. To test the model developed by Alonso and Gens, five different stress-hydration paths were applied in the oedometric tests. An important consequence of this model is that for the same maximal stress applied during compaction, the swelling of an unsaturated clay sample under a constant vertical stress is larger than for a saturated sample when it is unloaded to the same stress. This feature was confirmed by the oedometric tests.

The free swelling of highly compacted FoCa clay was measured as a function of the suction. All samples has an initial water content of 10 % and were compacted to 60 or 100 MPa corresponding with an initial dry density of respectively 1.84 g/cm^3 or 1.89 g/cm^3. The moisture content and swelling of each sample was measured once it has reached equilibrium. The results are shown in Fig. 2. The samples swelled with decreasing suction. Only at very high suctions (> 150 MPa) a small shrinkage occurred.

UPC

Advances in the computer code NOSAT

In the preliminary analysis of the BACCHUS 2 experiment reported last year, strong tension stress states were calculated at some stages during the wetting process. It is unlikely that the expansive fill and the natural clay could develop such tension stress states. Therefore the NOSAT code was modified to include a "no tension" material option. Some parts of the code were reprogrammed to:

- identify the tension stress states and define the residual stresses. Two cases were considered: nodes whose principal stresses are all in tension and mixed compression-tension cases;
- include an iterative procedure in the mechanical part of the code which applies external nodal forces compatible with a no tension material.

Modelling of the BACCHUS 2 experiment

This modellisation still has a preliminary character as the soil parameters are still being determined. However, important improvements were introduced compared to the first modelling work. In particular special attention was given to:

- the definition of the initial conditions. The simulation of the installation of the experiment has required the following computational steps: drilling of the borehole and installation of the backfill inside the annular space between the test probe and the natural clay. The final stress state was taken as initial condition for the coupled flow-deformation analysis;
- the modelling of the boundary conditions at the probe-backfill contact;
- the "no tension" analysis and its comparison with the elastic case.

Figure 3 shows the computed radial displacements at steady state for the elastic as well as the "no-tension" analysis. Maximum displacements occured at the backfill-natural clay interface. The "no-tension" analysis leads, as expected, to larger overall displacements.

Laboratory experiments

Three series of conventional oedometric test were performed on Boom clay compacted to three different dry densities i.e. 1.2 g/cm^3, 1.7 g/cm^3 and 2.0 g/cm^3. These densities correspond respectively with the density of Boom clay powder, the mean density of the BACCHUS 2 backfill and the density of the Boom clay pellets in the backfill material. Also suction controlled tests were carried out. The results will be used in the BACCHUS 2 modelling exercise.

Progress was made in the design of a new suction-controlled triaxial apparatus. Compared to conventional triaxial equipment, the size of the test samples was reduced to facilitate the suction equilibration. The air pressure method will be applied to control suction. Volumetric deformations will be measured by laser transducers scanning the length of the sample. The design presently being built is shown in Fig. 4.

More comprehensive stress paths involving suction and loading cycles have been applied to dry-of-optimum compacted samples of sand-expansive clay mixtures. The main reason for testing this mixture is to have a relatively pervious material with reasonable equilibrium times. Tests results were compared with the theoretical predictions of the new elastoplastic model developed under contract FI2W-CT91-0102.

UWCC

Temperature/capillary potential/air pressure model

Attention has been focused on the interface between unsaturated and saturated behaviour under isothermal conditions. In particular, as the soil becomes saturated, the dissolution of air in the pore water was investigated. For isothermal cases the model was applied to experiments published in literature while for the non isothermal case the model was verified by comparing results with alternative numerical simulations. The application of the verified model to the experimental work of SCK•CEN has been started.

Soil suction/air pressure/deformation model

The model was applied to a full scale field problem about the seasonal ground movements of an unsaturated soil. In Fig. 5 the comparison between predicted and measured displacements is shown. The model was also further expanded to include the elastoplactic constitutive relationships of Alonso and Gens /1/.

Soil suction/temperature/air pressure/deformation model

As stated in last yearly report the development of the software framework within which the overall model can be accommodated, was completed. Several research models were developed within this framework. Three constitutive relationships were examined and three software models based on respectively a non-linear elastic approach, an elasto plastic relationship and a thermoplastic analysis were produced. In Table I an overview of the developed models is given. Application of these models to the laboratory experimental work performed under contract FI2W-CT91-0102 by CIEMAT is now under way. In first instance, the simplest model, the non-linear elastic constitutive approach, is applied before attempting the more complex elastoplastic models.

References

/1/ Alonso E., Gens A. and Josa A., A constitutive model for partially saturated soils. Geotechnique, 40, 3, 405-430, 1990.

List of publications

Volckaert G., Imbert C, Thomas H., Alonso E.
Modelling and testing of the hydration of clay backfilling and sealing materials.
Semestrial progress report 1st sem. 1992
CEC contract FI2W-CT90-0033
SCK•CEN, R 2955, 1993

Volckaert G., Imbert C, Thomas H., Alonso E.
Modelling and testing of the hydration of clay backfilling and sealing materials.
Annual progress report 1992
CEC contract FI2W-CT90-0033
SCK•CEN, R 2974, 1993

Table I : Overview of the codes developed by UWCC

Software	**Purpose**
HM	Coupled heat and moisture transfer in unsaturated soil
HMA	Coupled heat, moisture and air transfer in unsaturated soil
HMAE	Coupled heat, moisture, air and deformations in unsaturated soil, with deformations calculated by elasticity theory, combined with a state surface approach
HMAEP	Coupled heat, moisture, air and deformations in unsaturated soil, with deformations calculated by an elasto/plastic theory
HMATP	Coupled heat, moisture, air and deformations in unsaturated soil, with deformations calculated by a thermo/plasticity theory

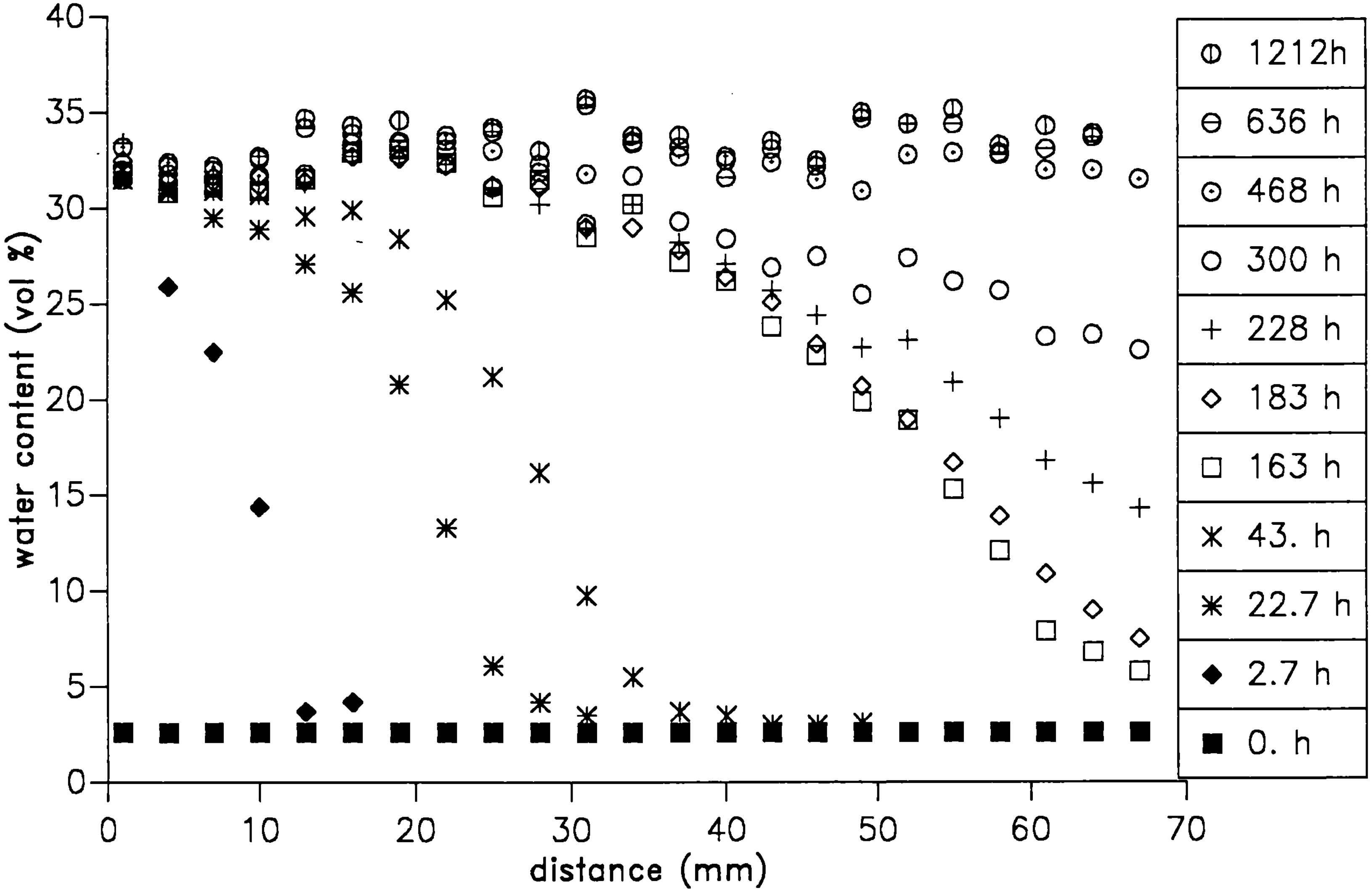


Figure 1 : Evolution of the hydration profile in a Boom clay plug with a dry density of 1.7 g/cm³ as measured by X-ray tomography

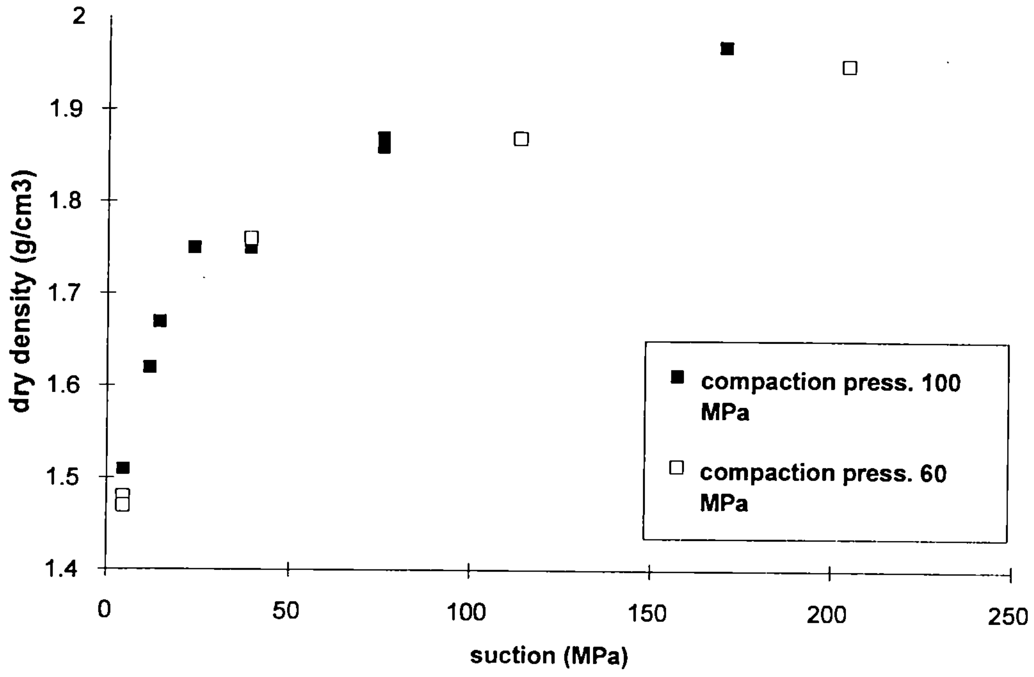


Figure 2 : Free swelling of compacted FoCa clay under different suctions

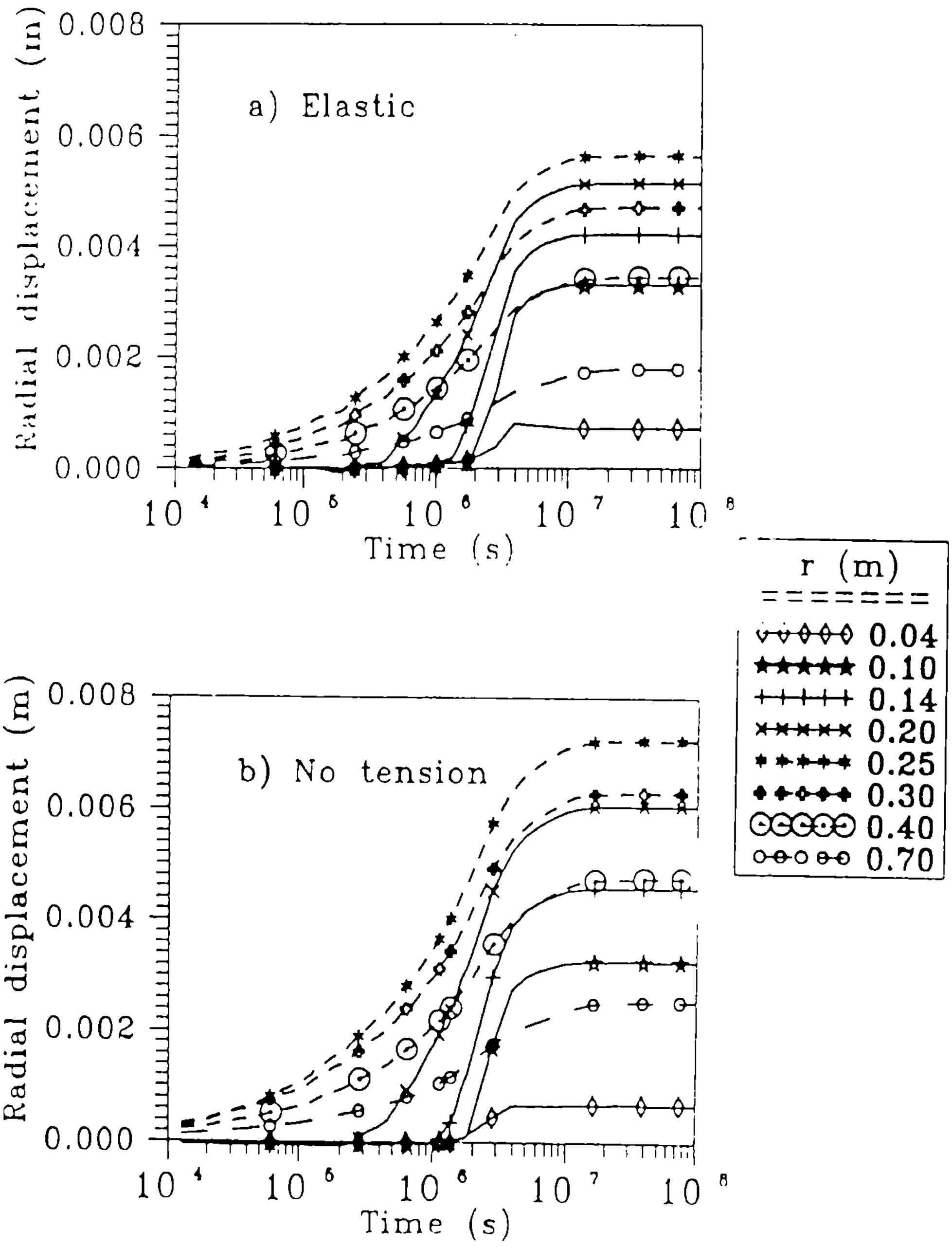


Figure 3 : Calculated radial displacements in the BACCHUS 2 experiment

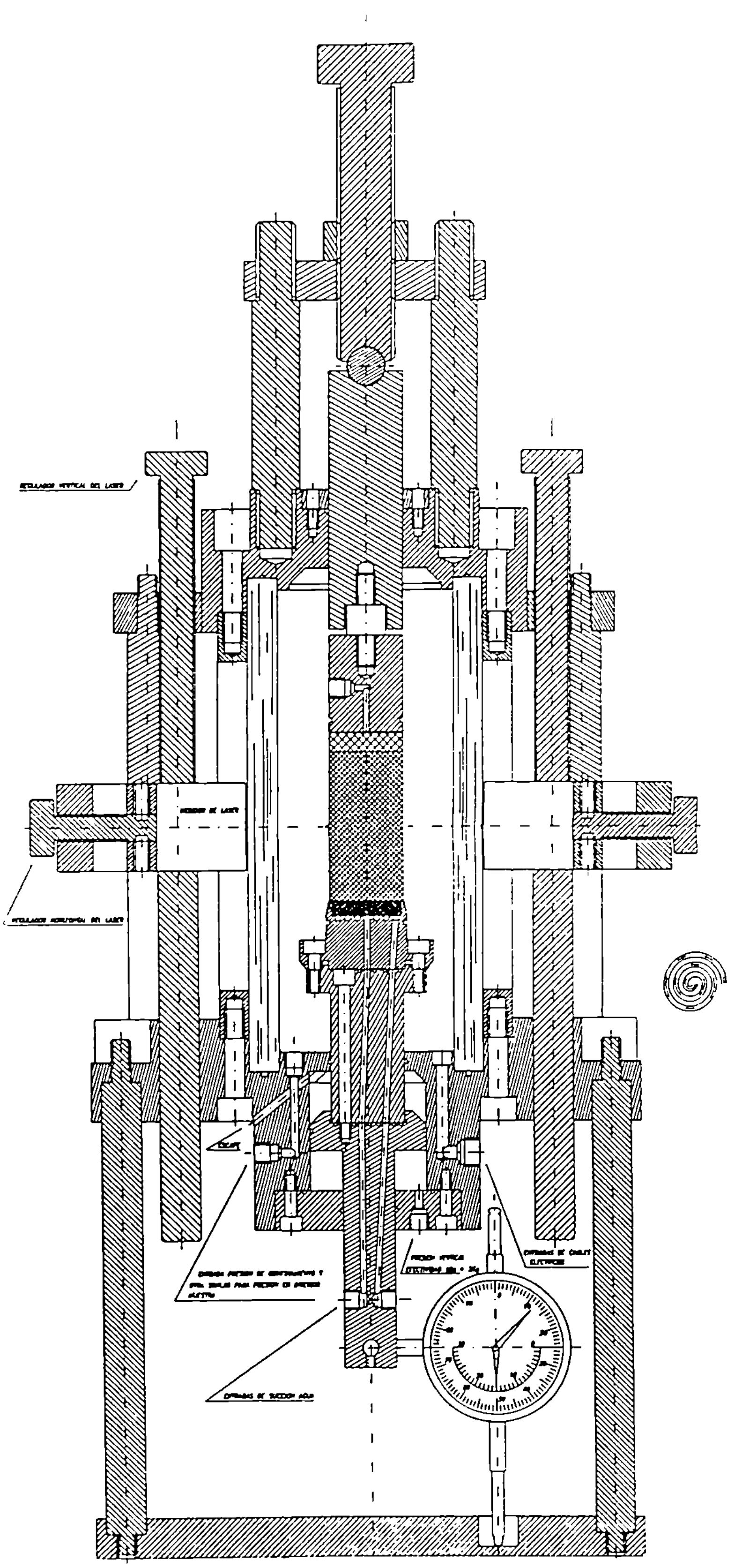


Figure 4 : Design of the new suction controlled triaxial apparatus

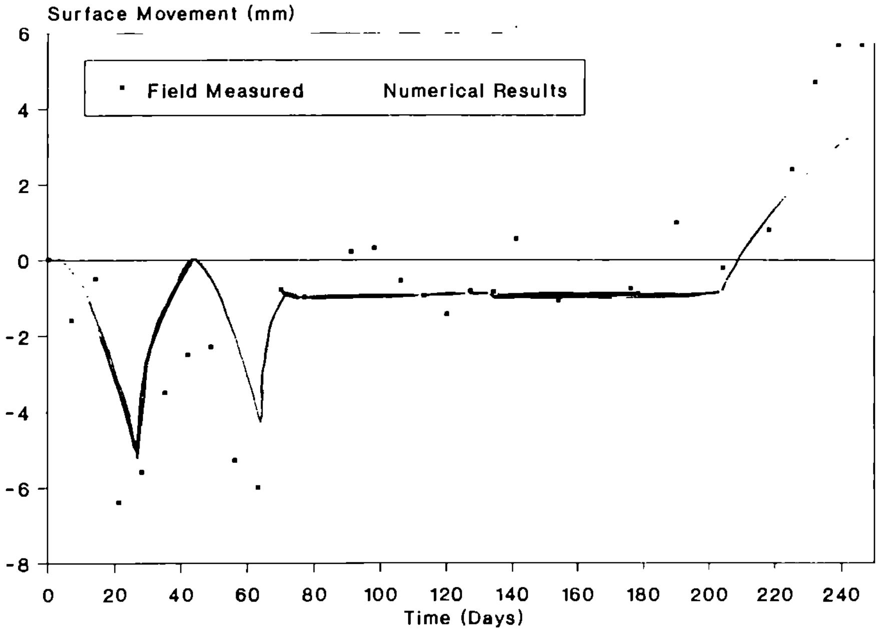


Figure 5 : Comparison between measured and predicted ground movements Swindon, UK, July 1988 - March 1989

MODELLING AND VALIDATION OF THE THERMAL-HYDRAULIC-MECHANICAL AND GEOCHEMICAL BEHAVIOUR OF THE CLAY BARRIER

Title :	Modelling and validation of the thermal-hydraulic-mechanical and geochemical behaviour of the clay barrier
Contractors :	SCK•CEN, ENRESA, CIEMAT
Contract N° :	FI2W-CT91-0102
Duration of contract :	from 01-10-91 to 30-09-94
Period covered :	from 01-01-93 to 31-12-93
Project leaders :	G. Volckaert (coordinator), C. Mayor, E. Alonso, J. Samper, M. Villar

A. OBJECTIVES AND SCOPE

When considering compacted clay-based materials as engineered barrier in the immediate environment of a HLW container, not only the hydromechanical performance needs to be studied but also thermal and hydrochemical evolution needs to be known.

The influence of temperature on the hydrological, mechanical and chemical field, was studied for each of these fields separately. However to be able to assess the overall performance of the clay barrier, it is the objective of this project to model the combined effect of temperature on the hydromechanical and hydrochemical field.

The development of codes for the simulation of multiphase flow under nonisothermal conditions and their application to the interpretation of the experimental work will be carried out by CIMNE (UPC-DIT) under subcontract with ENRESA.

The laboratory experiments will be designed by CIEMAT in cooperation with the modellers and the SCK•CEN.

B. WORK PROGRAMME

Code development

To simulate multiphase flow under nonisothermal conditions a code will be developed and, on the one hand coupled to a chemical transport code and on the other hand to an elasto-plastic model adapted to account for expansive material effects.

Experiments

Tests will be carried out on ad hoc designed cells that will allow to determine the evolution of temperature, pressure and fluid concentration fields, produced in the clay barrier by heating of the central zone and by flow of water.

Model application

The thermo-mechanical and thermo-chemical models will be used in the interpretation of the above experiments and experiments carried out in complementary CEC programs (contracts n° FI2W-CT90-0033, FI2W-CT91-0098).

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

Experiments

At CIEMAT one thermohydraulic cell, four membrane cells and ten suction controlled oedometers are now fully operational. For the cementation and mineralogical transformation studies an alteration cell was constructed and four experiment were already performed. An oedometric cell with suction and temperature control was designed and constructed. The development of an experimental set up for the extraction of interstitial clay water was delayed. A "squeezing" apparatus which allows for pressures up to 100 MPa is actually under construction.

UPC has developed an oedometer with suction and temperature control. It has now been put into operation and commissioning tests were carried out with success. First experiments on Boom clay were performed.

Due to the lack of data on dissolution rate constants for clay minerals, laboratory experiments were conducted using smectite samples similar to those being studied by ENRESA for the backfill clay barrier.

Model development

Thermo-hydro-mechanical

The constitutive model was further developed to include expansive soil and thermal effects. In particular, the effect of microstructural strain on irreversible macrostructural strain and the effect of cementation were included. The formulation of the thermo-plastic constitutive law for unsaturated soil was completed.

The development of the 3D finite element coupled code has well advanced. A coupled 1D programme is being developed to check the results of the main code and to use as testing ground for new algorithms before they are incorporated in the main code.

Thermo-hydro-chemical

To optimise the solution for complex coupled solute transport - chemical equilibrium problems, three one dimensional coupled codes were developed. These codes account for reactions taking place in the aqueous phase and mineral dissolution/precipitation reactions under isothermal conditions.

Progress and results

CIEMAT

In the thermo-hydraulic cell five experiences were performed on a Spanish montmorillonite compacted to a dry density of 1.65 g/cm^3. Three different initial water contents were applied i.e. 11%, 15% and 20%. A punctual and axial heater were used. The samples were hydrated by injecting water at 1.1 MPa while at the same time the sample was heated. During the experiment the temperature distribution, water uptake and pressure were measured. The final density, water content, electrical conductivity, free silica, specific surface and pore size distribution were determined destructively at the end of each test. The main conclusions drawn from these experiments are:

- the hydration is mainly affected by the initial water content and not

by the thermal gradient;
- the final water content distribution is related to the thermal gradient;
- at the water inlet, the density decreases due to swelling and by consequence increases in the surrounding areas;
- dissolved species migrate to the heater and create a local saline environment.

The "water content versus suction" curves were determined for montmorillonite with different initial water contents and dry densities, and for Boom clay. A logarithmic relationship was observed between the water content and suction. The relation seems to be independent of the initial dry density or water content.

The first set of suction controlled oedometer tests consist in a drying-hydration cycle at constant vertical load followed by a loading-unloading cycle at a given suction. The experiments were performed on montmorillonite. An example of the result of such a test is given in Fig. 1. The results will allow to test the UPC geomechanical model.

Triaxial tests were performed to study the influence of the water content on the friction angle and cohesion. In these tests the suction is not actually controlled. The results are summarized in table I.

UPC (main sub-contractor to ENRESA) - geomechanics

Constitutive model development

To incorporate the expansive soil effects mathematical expressions were selected for the description of:

- the microstructural behaviour;
- the relationship between microstructural volumetric strain and irreversible macrostructural strain.

These mathematical models were compared to experimental results on compacted clays reported in literature. This activity was iterative. Comparisons between model predictions and experimental results have suggested modifications of the particular equations selected initially and further refinements of the model.

The effects of cementation were incorporated in the general unsaturated constitutive model. Figure 2 shows the basic mechanisms of this model extension in the suction-stress space. The main effect of cementation is an increase in both cohesion and strength compared to the destructured soil. The effect of an increase in suction on a cemented soil, is more important than on a destructured soil.

To include temperature effects, the unsaturated elastoplastic model was coupled with the thermo-plastic model developed by Hueckel and co-workers. In this model the elastic behaviour is derived from a thermoplastic energy potential, which is a function of suction and temperature.

Code development

The microstructural level was introduced into the code by applying a "mixture theory" on the governing equations. Mass conservative numeric schemes and a range of time integration schemes were included in the code. The code was partially tested.

Laboratory testing

An oedometer apparatus with suction and temperature control has become operational. The test specimens are compacted directly into the oedometer (see Fig. 3). This improves the specimen repeatability and minimizes the risk of uncontrolled water content changes. Oedometer tests on Boom clay under suction control were carried out at 22 °C, 58 °C and 80 °C. The aim of these tests is to determine the dependence of the expansivity of unsaturated Boom clay on temperature.

UPC (main sub-contractor to ENRESA) - geochemistry

To obtain data on the dissolution rate constants for clay minerals, dissolution experiments on smectite at 80 °C under alkaline conditions pH 8.8 were performed. Two types of experiments were performed: flow-through kinetic experiments to measure the dissolution rate of the smectite and batch experiments to obtain equilibrium data. Figure 4 shows some preliminary results for the dissolution rate as a function of the saturation state expressed as the ion activity product (IAP). The dissolution rate increases with increasing undersaturation.

Three different numerical models were prepared for the solution of the coupled solute transport and chemical equations. The first is based on the direct substitution of the chemical equations into the transport differential equations. At the present stage, this approach can only consider kinetically controlled reactions. the second one is based on a sequential iteration scheme which solves separately the transport and chemical equations. So far this approach was implemented only for chemical equilibrium conditions. The third approach is the simplest and consists in coupling an existing chemical speciation code (in this case PHREEQE) to a transport code. Results obtained with the various approaches including equilibrium and kinetical calculations, are being compared. The advantages and limitations of each of them are being evaluated.

SCK/CEN

In order to coordinate this project with the related projects "BACCHUS 2" (contract n° FI2W-CT91-0098) and the project on modelling and testing of the hydration of clay backfilling and sealing materials (contract n° FI2W-CT90-0033) two meetings with the partners of the three contracts were organised.

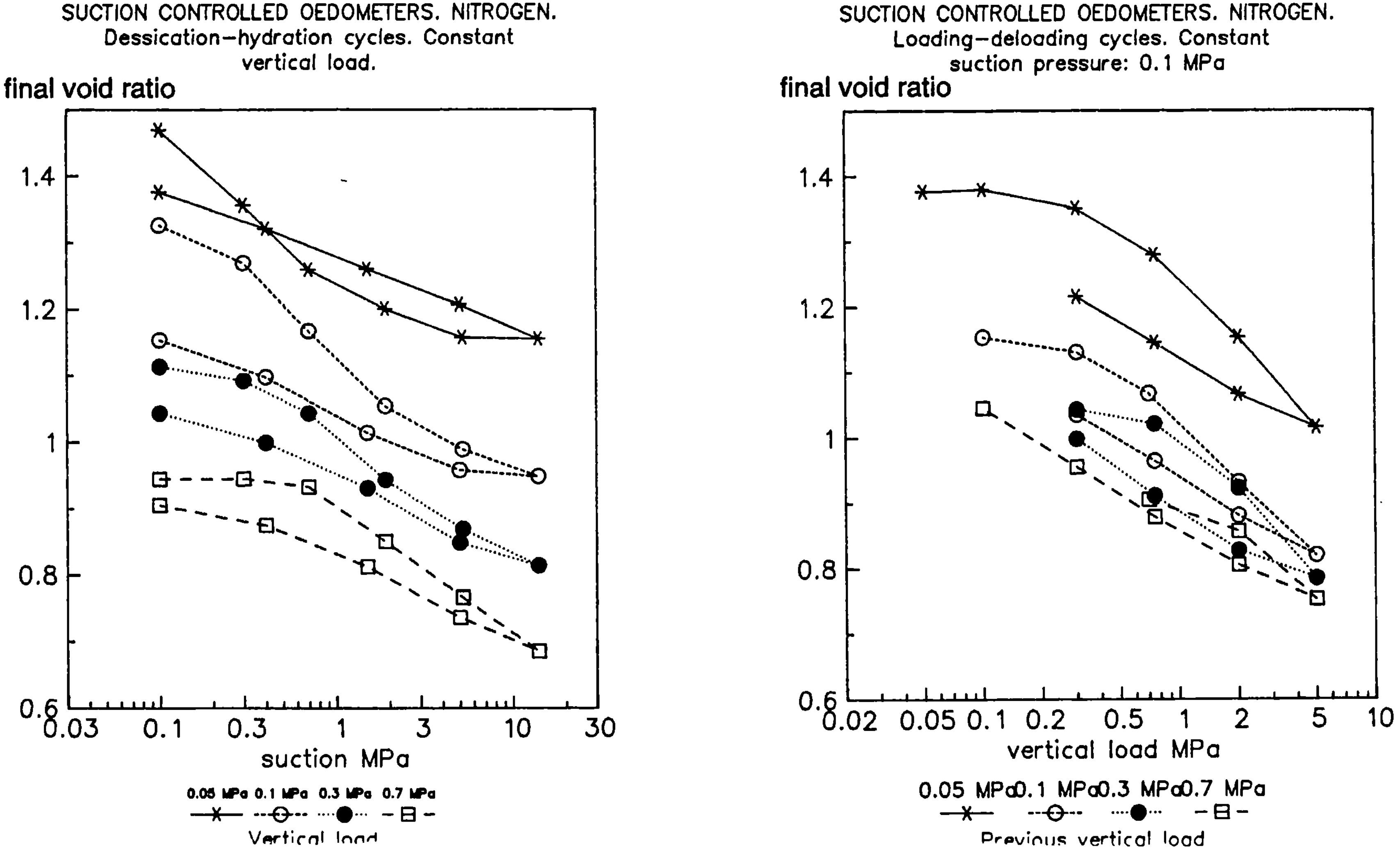
List of publications

E. Alonso, A. Gens, M. Villar, J. Samper, G. Volckaert
Model development and validation of the thermo-hydraulic-mechanical and geochemical behaviour of the clay barrier.
Semestrial progress report 1st sem 1992, CEC contract FI2W-CT91-0102
SCK/CEN R 2962

E. Alonso, A. Gens, M. Villar, J. Samper, G. Volckaert
Model development and validation of the thermo-hydraulic-mechanical and geochemical behaviour of the clay barrier.
Annual progress report 1992, CEC contract FI2W-CT91-0102
SCK/CEN R 2975

Table I Results of triaxial tests on montmorillonite showing the effect of water content on cohesion and friction angle

Water content	Range σ_3	Cohesion MPa	Friction angle °
10%	Low (0.5-3 MPa)	0.1	33
	High (10-30 MPa)	7	8
15%	Low	0.8	31
20%	Low	1.2	21
	High	3	2



SUCTION CONTROLLED OEDOMETERS. NITROGEN. Dessication–hydration cycles. Constant vertical load.

SUCTION CONTROLLED OEDOMETERS. NITROGEN. Loading–deloading cycles. Constant suction pressure: 0.1 MPa

Figure 1 Final void ratio at the end of each stress or suction step in a suction controlled oedometric test on a Spanish montmorillonite.

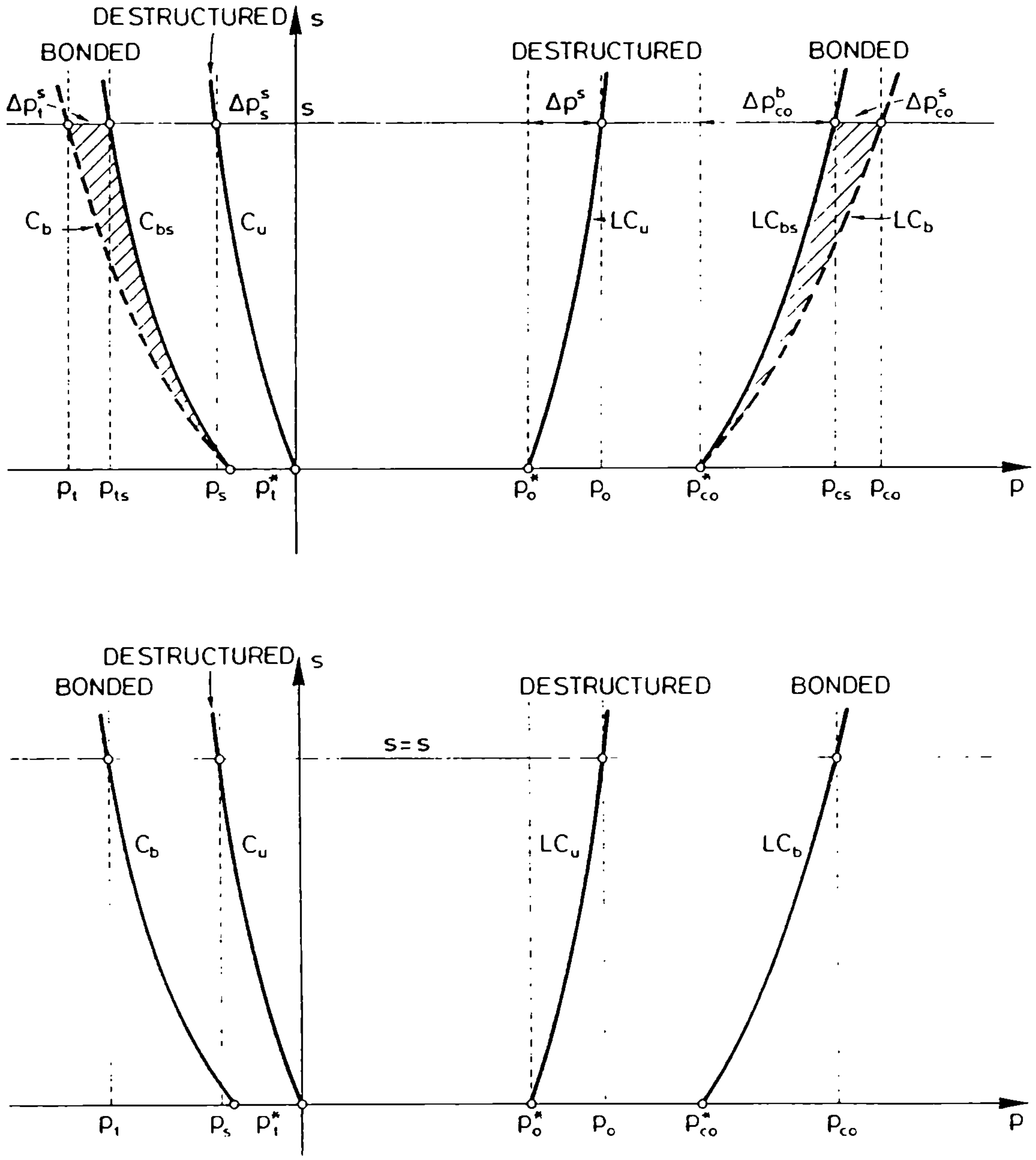


Figure 2 Basic mechanisms of the yield model, under isotropic stress conditions, for a unsaturated cemented soil.

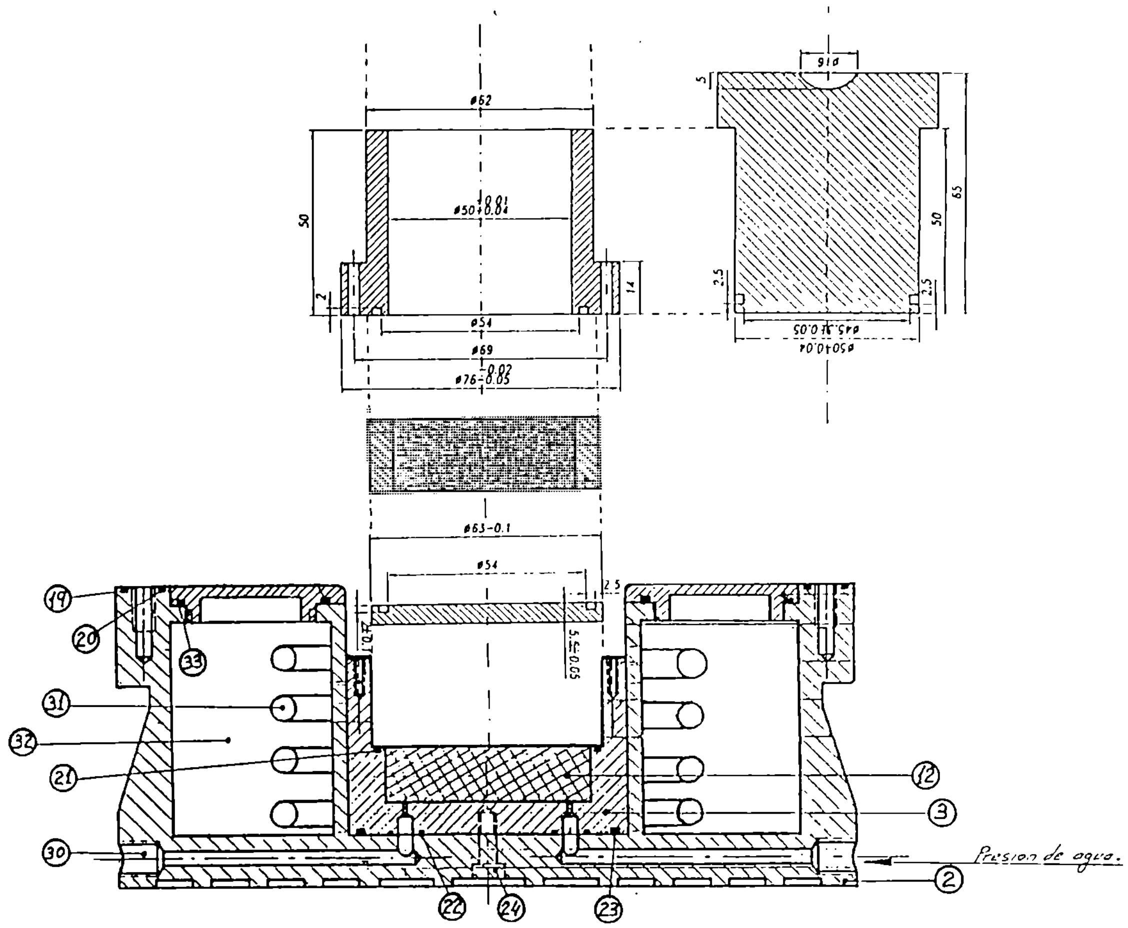


Figure 3 Oedometer apparatus with suction and temperature control.
The mould and piston for 'in apparatus' compaction are shown.

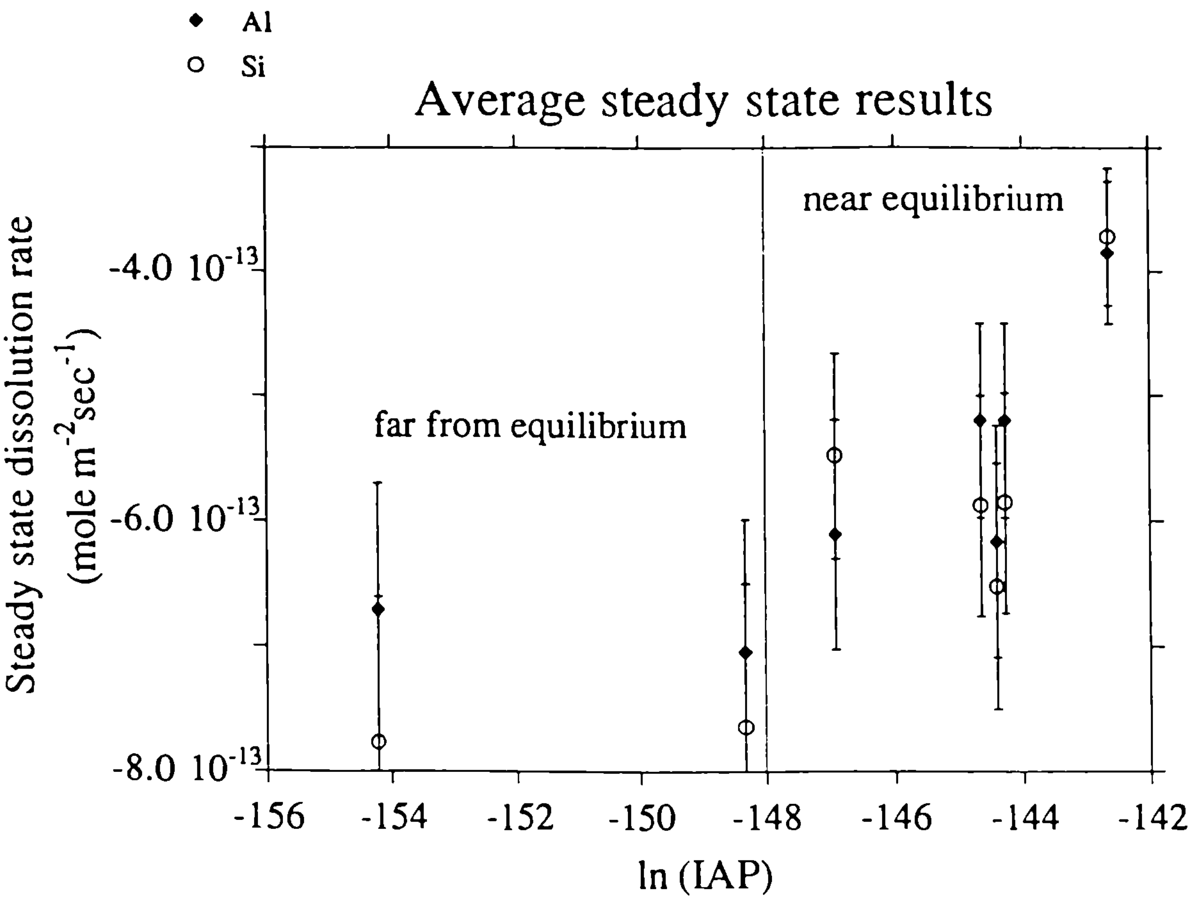


Figure 4 The dissolution rate dependence on saturation state expressed in terms of ln(IAP) (IAP = ion activity product) Experimental conditions: pH=8.8, T=80°C, duration 300-800 h, dioctohedral montmorillonite.

Title : Acquisition and regulation of water chemistry in an argillaceous medium (ARCHIMEDE)

Contractor : ANDRA, BRGM, CEN/SCK
Contract N° : FI2W-CT92-0117
Duration of contract : January 92 - December 94
Period covered : 1993
Project leaders : Dr. T. Merceron (ANDRA, Fontenay aux Roses, F - Coordinator), J.R. Mossmann (BRGM, Orléans, F)
B. Neerdael (CEN/SCK, Mol, B)

A) OBJECTIVES AND SCOPE

Clay is a candidate environment to host highly radioactive waste disposal. The radionucides can progressively arise from the waste into the host geological formation over a long period of time. The understanding of the behaviour of natural elements in clay formations is an unavoidable step towards the understanding of the fate of such radionuclides. Further laboratory studies are also needed to help forecast, by analogy, the behaviour of radioelements released from deep radioactive repositories.

The ARCHIMEDE project aims at three major goals :

i.- understanding the mechanisms of acquisition and regulation of formation water chemistry in clay environment, as a result of water-rock interactions ;

ii.- testing and validating physico-chemical parameters that describe the clay formation and its properties, and that feed geochemical models ;

iii.- applying these results at modelling a real clay environment : the Boom Clay Formation.

Rock sample characterization is generally realised in the laboratory after sampling. Sampling techniques usually applied can sometimes significantly disturb the original geochemical and microbial state of the sediment. In this study special attention has been paid to prevent such drawback : the Boom clay formation (solid, fluid and gaseous phases) was sampled from the Underground Research Facility in Mol (Belgium) under anaerobic and aseptic conditions, and experimental works were designed in order to measure non conservative (pH, Eh) or potentially versatile parameters (interstitial fluids, trapped gases, cation exchange capacity) directly in the formation. Microbiological techniques are developped for natural sample and willcomplement classical bacteriological studies using conventional microbial ecology techniques.

Four scientific teams are in charge of animation of the different phases of the project, under the coordination of ANDRA - DEEC (France) : SCK/CEN (Belgium), CEA-DSD (France), BRGM (France) and GRAM SA with the collaboration of CNRS (France). The ARCHIMEDE project will be achieved within three years (1992-1994).

B.) WORK PROGRAMME

The four main topics of the project are as follows :

1. fluid and solid sampling, in situ measurements : all teams are involved in this topic which is planned over 1992 for sampling and over 1993 for in situ measuring ;
2. fluid (CEA-DSD) and solid (BRGM) characterization. The main step of the project is planned over 1993 ;
3. microbial investigations (GRAM SA) will spread over three years (1992-1994) ;
4. fluid-rock interaction modelling (CEA-DSD and BRGM) will integrate the result obtained after the characterization step and will occur from late 1993 on.

C. PROGRESS WORK AND OBTAINED RESULTS

The second term of the ANDRA/CCE "ARCHIMEDE - Argile" project allowed a series of experiments to be performed in the laboratory as well as on the field aiming at precisely characterizing the Boom Clay Formation. The project is well on schedule :

- as far as microbiology is concerned, bacterial characterisation using conventional microbial ecology techniques is finished. Genetic sequencing of strains is on course. The first results obtained so far allow to distinguish essentially between bacterial strains brought into the formation by human activities or through materials used for building the underground gallery. Lack of detailed knowledge on autochthonous strains results partly from the fact that they are probably not abundant, and partly from lack of relevant data in the genetic data base for these strains. Further work will allow to task with this aspect of research ;
- as for geochemistry, two approaches aiming at modelling fluid chemistry acquisition and regulation have been investigated. The first approach, developped by CEA follows a global path based on the study of the behaviour of chemicals in interstitial fluid and in the surrounding aquifers. The second approach, developped by BRGM relies on the knowledge of clay/water interaction mechanisms and is based on small scale (local) equilibria. Both approaches lead to a model demonstrating that it is now possible to realistically forecast the behaviour of a rock/water system in clay based upon a few geochemical relationships.

2. Participant N° 2 (CEA/DCC, France)

2.1. Fluid phase characterisation

Interstitial fluids have been collected with the participation of the SCK/CEN staff in stainless steel cells, directly connected to the piezometers. Attention is focused on a good conservation of samples without oxidant contamination. So far, only the first piezometer has been sampled. Fluids are fractionated, filtered and conditionned in the laboratory for further analysis. Anions are determined on a 0.45μm filtered and non acidified subfraction, and cations on a 0.45μm filtered and acidified (pH: 1-2) aliquote. Trace elements and particularly metal ions are measured from an ultrafiltered and acidified fraction in order to prevent from any particular contribution. For fluids from aquifer, filtration and acidification are made directly on the field. In situ measurements are also required for some parameters such as pH, Eh, alkalinity and sulfide. Fluids are kept under N2 flow during the titration of sulfide by potentiometric measurement with HgCl2.

Analyses of fluids have been carried out using ion chromatography (major anions and cations), polarography (Cu, Co, Ni), atomic absorption spectrometry (Fe, Mn, Al), laser spectrofluorometry (U). Further analysis of trace elements (Rb,Sr, Cs, Ba) will be carried out by ICP-MS.

Specific devices have been tested during this project : a specific system to sample interstitial fluids for transition metals analysis.has been connected to a dialysis cell, especially designed to prevent metal contamination. The first fluids are about to be collected ; fiber optics has been successfully tested to measure in situ pH with a precision around 0.1 pH unit.

Groundwaters are sampled from different boreholes, reaching the rupelian aquifer at different depths from 50 to 530 m. The sampling system is set up at the required depth and a column of water is moved to the surface by a N_2 flow under pressure, after several flushes.

2.1.1. Results

2.1.1.1. Interstitial fluids

The chemical composition of interstitial fluids is generally homogeneous and independent of the distance from the main gallery. Bicarbonate is the major anion (1.25 .10^{-2} M) and Na the major cation (1.2. 10^{-3} M), pH is alkaline (8.5) and Eh is typical of reducing conditions (Eh = -310mV versus H^+/H_2, Cerberus data).

Generally, natural solutions exhibit mixed redox potentials, which are impossible to relate to a single dominating redox couple in solution. As it was shown during Cerberus test, Eh values remain remarkably stable during all the campaign, around the value of -310 mV. In this case, if this redox potential is significant, we must identify the involved redox couples. So, different species sensitive to oxidation are investigated to characterize redox conditions of pore-fluids.

The first results are as follows :

i.- evolution of NH_4 concentrations since the first sampling, to reach high concentrations of a few 10^{-4} M, after a great decrease

ii.- very low level of thiosulfate concentrations in the first samplings iii.- Fe and Mn concentrations controlled by siderite and rhodocrosite solubility.

It appears very important to follow these evolutions of NH_4 and thiosulfate with time.

The comparison of interstitial fluids with those obtained by squeezing (collaboration with BGS Keyworth) has shown that the chemical compositions are very similar in absence of oxidation (Table 1). In other cases, an oxidising perturbation seems to have occurred for solid samples taken between 3 and 12 meters from the gallery. Beyond this limit, samples do not exhibit any apparent oxidising perturbation. The preservation of solid samples from oxygen is very difficult. In many cases, the oxidation of pyrite, which is a common mineral in Boom clay, occurs, releasing sulfate and protons in solution. This oxidation process combined with ion exchange and mineral dissolution (carbonate, clay minerals), leads to fluids with neutral pH and high concentrations of SO_4 and Na. In this case, it seems that reactions of ion exchange are largely predominant.

In the future, it can be interesting to identify the origin of the oxidising perturbation : does it occur after or before sampling ? For exemple, can this perturbation be due to the tunnelling ? Analysis of $d^{18}O$ and $d^{34}S$ isotopes performed on interstitial fluids have shown that a main source of oxygen in dissolved sulphates ($d^{18}O$ -5 to -10 %o SMOW) from oxidised samples is interstitial water oxygen ($d^{18}O$ ~ -7 %o) and not directly atmospheric oxygen ($d^{18}O$ ~ 23 %o).

2.1.1.2.Fluids from Rupelian aquifer

The regional hydrogeological conditions are fondamental to quantify and to predict the possibility of migration of radioelements from waste disposal. Moreover the similarity between the chemical composition of the rupelian aquifer (in Mol) and the interstitial fluid implies to know the relationship between aquifers (particularly Rupelian) and interstitial fluids.

These waters evolve from sodium-bicarbonate to sodium-chloride fluids, with Cl concentrations around 100 mM. Generally alkaline pH decreases from 8.5 to 7.0 in Cl rich fluids (located in the northern part of the aquifer), whilst sulfate concentrations increase steadily, from 1.10^{-6} M to a few 10^{-3} M. Bicarbonate concentrations are globally constant. Therefore, the Cl increase is the major trend of evolution of the Rupelian aquifer.

O and H isotopes measurements have been performed and showed a marine origin for these waters. According to mixing model with sea-water, the marine contribution is expected to be up to 16% to the north of the area. So, the chemical composition of these fluids is the combined result of mixing with a marine component and water-rock interaction leading to Na, Ca, K, Mg/Cl ratios lower than those obtained by mixing only. This model should be further precised by the study of halogen elements and isotopic measurements (O, S, H)

The first step concerning global equilibria of the system is based on speciation calculations and saturation indexes of the main minerals. The PHREEQE software /1/ has been used.

All the studied samples (interstitial and aquifer) are saturated with respect to chalcedony.

In interstitial fluids, Ca and Mg are controlled by carbonate solubility, but a slight oversaturation is observed in most locations of the Rupelian, except for chlorinated fluids which are near saturation. This oversaturation could be explained by an extra production of CO_2, resulting from the degradation of organic matter.

In natural solutions, Fe is generally assumed to be at the valence II, despite positive measured redox potential, Fe (III) is rapidly removed from solution, as oxide or oxi-hydroxide mineral phases. In interstitial fluids and in the aquifer, Fe $^{++}$, $FeCO_3$ and $FeHCO_3{}^{+}$ are predominant species and Fe concentrations are also controlled by carbonate solubility. Chlorinated fluids are however undersaturated with respect to siderite and rhodocrosite. The relatively low concentrations of Fe could result of oxidation of pyrite, with beginning of oxides and oxi-hydroxide precipitations. If oxidation of pyrite (microbially catalysed) is incomplete, such as in marine sediments /2/, this oxidation produces sulfur species which cannot be measured by classical analytical methods : polysulphides, or colloidal sulphur. In this case, the acidification is lower and the SO_4 release is expected at a lower extent, and occurs later in the presence of O_2. Further $d^{18}O$ and $d^{34}S$ isotopes measurements should precise the origin of the sulphates in the aquifer and SEM observations of suspended particles could allow to validate the existence of colloidal sulphur or any trace of sulfide mineral in suspension.

2.2. Future work

In a first step, we will focus our attention on redox characterisation and identify which are the main redox couples in equilibrium.

In a second step, we should understand the mechanisms governing how interstitial water has acquired its chemical composition. Is this composition determined by equilibria with aluminosilicates or by reactions of ion exchange ?.

The examination of ion correlations in aquifers and Boom Clay Formation interstitial fluid allows to evaluate equilibrium constants for the Na-K -Al-SiO_2 system. These constants are very close to those usually retained for albite and microcline equilibria. It is hence proposed that regulation of fluid geochemistry in Boom clay derive from equilibria with aluminosilicates.

Finally, these concepts will be applied to trace elements (alkali and alkaline earth elements, and transition metals) in order to define the main processes (complexation, sorption, precipitation, ...) controlling their mobility in solution.

3. Participant N° 3 (BRGM, France)

3.1. Solid phase characterisation

Solid phase of the clay sediment is made up of the constitutive minerals and organic matter (Table II). When it turns out to modelling, fluid geochemistry can be considered as the consequence of the interaction between interstitial water and minerals, whereas the role of organic matter is not always taken into account. Thus solid phase characterisation has been undertaken in the scope of determining how and which mineral or organic phases take part to the geochemical processes of fluid chemistry acquisition.

The mechanisms potentially involved are dissolution-precipitation, ion exchange and organic matter transformation. Thus, solid phase characterisation involves not only mineralogical determination, but also testing for rock properties or the determination of mineral and organic phase evolution state.

To achieve this, a set of experiments has been conducted on fresh (i.e. undisturbed) or oxidized (i.e. disturbed) clay, some of them on site just after sampling in order to work on as fresh material as possible, some other in the lab when specific conditions or methods were requiered. Some tests are also carried out on the field, aiming at evaluating the Boom Clay Formation properties on a real scale.

The confrontation of the results obtained should help us disentangle the complex geochemical system formed by the mixture of clay, organics and water.

3.1.1 Results

The main results obtained so far concern the rock forming mineral composition and the main mechanisms involved in the water-clay interaction.

The bulk mineralogy of the clay can be summarised as quartz (20 to 25 %), pyrite, carbonates and some feldspar (plagioclase and microcline) all present in a few percent, in addition to a clayey phase that makes up about 60 % of the sediment. The clay mineralogy is dominated (about 50 % of the clay fraction) by illite smectite mixed layers (randomly interstratified, containing about 55 % illite), micas (mainly biotite and detrital illite and glauconite, making up altogether about 28 % of the clay fraction), kaolinite (around 20 % of clay) and up to 4 % of chloritic minerals. Pyrite appears as aggregates of euhedral crystals and framboids. In oxidized samples, this pyrite is partly replaced by anhydrite, and ferric sulfate and jarosite form if intense oxidation is maintained.

Total cation exchange capacity (as measured using Cobaltohexamine chloride) amounts to about 25 meq/100g dry sediment, 20 of them due to effective exchange with clay minerals, the rest being due to interference with other phases. After oxidation, the amount of exchanged calcium and magnesium significantly increases, indicating that clay can still incorporate these elements when rendered available by slight oxidation.

Carbonates are disseminated in the clay and appear mainly as calcite and dolomite from micro fauna tests. Mass balance calculation shows that at least during moderate oxidation, only part of the available carbonate is enough to account for measured alcalinity.

After pyrolysis, organic matter shows low maturation (Tmax = 430°C) with anomalously low Hydrogen Index (HI = 60) suggesting oxidation. Palynofacies studies along with carbon dioxid as main naturally released gase demonstrate that this organic matter is on the contrary well preserved, and probably not oxidised. It is essentially marine in origin (type III to type II), with some detrital organic inputs. It is suggested that clay matrix effect is responsible for hydrocarbon trapping during pyrolysis leading to an underestimation of the real Hydrogen Index.

Rock Eval pyrolysis performed after removal of the inorganic phase yielded IH values of 330, well in agreement with this type of organics. Several other indices point towards an intimate mixture of organic matter with clay. SEM examination of stained preparations, along with heavy metal mapping will allow to visualize organic matter partition within the sediment.

At present, these results have allowed to propose a model to explain the present porewater chemistry in the undisturbed clay.

In this model, the redox potential is maintained reducing by organic matter, whereas pH is buffered by carbonate dissolution and cation exchange with clays is responsible for the chemical pattern of Boom clay interstitial fluid. Clay minerals (mainly illite-smectite mixed layers) exchange principally sodium and a few potassium against protons, and sodium against calcium and magnesium produced by carbonate dissolution. Aluminum is apparently governed by kaolinite.

3.2.Future work

Further investigations are currently carried out in order to refine the model, principally in the view of a better account for exchange mechanisms. The final model will be later complemented in order to take into account also trace element geochemistry.

In the oxidative disturbed state, the system becomes more complex.

Pyrite oxidation yields high acidity that is eventually no longer buffered by carbonates. Porewater becomes enriched in sulphate.The geochemical system seems to stabilize to pH around 2 to 3 and probably passes under control of aluminosilicates.

The pattern suggested for the undisturbed state is no longer valid in this case : more phases are involved and dissolution - precipitation or transformation mechanisms might well become dominant. More specific investigations should be conducted in order to better evaluate the geochemical system induced by oxidation of this clay.

4. Participant N° 4 (GRAM SA, with CNRS, France)

4.1. Microbiological study

Bacteria can survive and even proliferate within deep-subsurface conditions /3,4,5/. The opening of a gallery induces drastic modifications to these environments, stimulating or inhibiting microbial activities. The new interface between subsurface sediments and human activity can be a propitious medium for bacteria brought by human activity. A study has thus been undertaken to investigate the nature and numbers of autochthonous bacteria present in the Boom clay deposit before any human processing, and the behaviour of allochthonous bacteria liable to be introduced in the deposit during the human activity in the gallery.

4.1.1.Sampling conditions

Three 40cm long core samples were sterile collected at 1, 10 and 20 meter depth from the gallery respectively, with the help of the SCK/CEN staff. Interstitial fluid microfauna was also recovered from sterile piezometers. Air and tool bacteria were sampled in order to check for allochthonous contamination.

We have analyzed the number of bacteria as a function of depth in clay deposit from the gallery as well as their activities as estimated in situ. Preliminary data of numerical taxonomy coupled with molecular phylogeny have been used in order to assess whether the bacteria isolated from clay samples are indigenous to the geological deposit, or if they are allochthonous organisms recently introduced from the surface.

If bacteria do survive in subsurface environments, they can often be present in quite low numbers. In these conditions, and even when the most stringent precautions are taken to work under aseptic conditions (wear of sterile gloves and protective masks by operators, accurate cleaning and sterilisation of all equipment), the bacteria that always contaminate any human or mechanic operation are extremely difficult to distinguish from the true but rare autochthonous bacteria.

5.1.2 Bacteria distribution

Large number of living bacteria (10^6-10^5 CFU g^{-1}) and molds (10^5-10^4 CFU g^{-1}) were characterized within a few centimeters from the gallery wall. Less bacteria were observed as depth increased. Beyond 80 cm very few bacteria (10^1-10^2 CFU g^{-1}) were counted. Highest counts were recorded in aerobic conditions; microaerophilic and anaerobic bacteria were lacking or poorly represented. Two samples of clay collected at 760 cm and 1960 cm from the gallery wall appeared sterile under all culture conditions.
In pore water samples collected at 3, 7 and 15 m depth, total counts ranged from 2,4 10^3 to 1,2 10^6 cells ml^{-1}. Viable counts ranged from none to $3x10^2$ colonies ml^{-1}. Bacterial densities in water do not correlate with sampling depth.

In clay, bacterial respiration appeared significant only within the outerlayer (less than 80 cm of depth from the gallery wall), decreasing from 92 to 0.2 nanomole CO_2 l^{-1} h^{-1} from the surface to 80 cm depth (Figure 4). Less than 2 picomole CO_2 l^{-1} h^{-1} were produced in deeper samples (15m, 19m). In collected water, bacterial respiration ranged from 3 to 80 picomole CO_2 l^{-1} h^{-1}, assimilation ranged from 0,5 to 230 picoat C l^{-1} h^{-1}.

5.1.3 Assessment of bacterial origin

A total of 163 bacterial strains were isolated. One hundred and six strains were isolated from clay and water samples: 80 from clay samples (gallery surface: 20; 5 cm: 15; 15 cm: 10; 30 cm: 8; 80 cm: 7; 100 cm: 2; 550 cm: 1; 735 cm: 7; 760 cm: 1; 900 cm: 5; 1100 cm: 1; 1780 cm: 2; 1960 cm: 1), and 26 from pore water samples (300 cm: 1; 700 cm: 12; 1500 cm: 13). Forty seven strains were also isolated from different samples of the gallery atmosphere and 10 were collected on the tools. A combined study by numerical taxonomy and molecular phylogeny was used to try to assess the indigenous or allochthonous origin of these bacteria. For phenotypic identification each strain was described by 107 morphological, physiological and biochemical features /6/. Strains were compared and clustered using KHI2 coefficient and variance analysis. For molecular phylogeny, species identification was obtained by comparing the 16S ribosomal RNA (rRNA) sequence of each species to sequences obtained in an already existing rRNA databank /7,8,9/. Most of the strains isolated from samples collected beyond 80 cm from the gallery wall cluster (phenotypically and genetically) with strains isolated from the gallery atmosphere or from the coring tools. They were considered as contaminants resulting from the processing of the samples. On the other hand, 57 strains (all but three) isolated from the surface of the gallery down to a depth of 80 cm appeared well separated from other strains, and were considered as autotochthonous. The phenotypical description allowed to identify each bacterial strain according to the reference manuals /10,11,12/. This identification was in good agreement with both the above mentionned phenotypical and genetical clusterings. The bacterial strains isolated from the surface of the gallery to a depth of 80 cm were identified as soil bacteria (mostly Nocardioïdes, Alcaligenes, Azotobacter, Acinetobacter, Paracoccus and Pseudomonas). Most bacterial species considered as contaminants belong to taxonomic groups recognized in previous studies as contaminants ordinarily present in a human environment (Staphylococcus, Streptococcus) or as airborne bacteria (Bacillus).

5.2 Future work

Our analyses clearly demonstrate that there is a gradient of bacteria in the studied sediments. Bacteria proliferate at the interface between the clay sediments and the gallery due to human activity. This fauna might originate primarily from the grouting material used, mainly made up of a mixture of quartz, sand and concrete.

Bacteria are very rare if not nonexisting in the undisturbed deeper depth of the clay sediments. If methods such as numerical taxonomy or molecular phylogeny had not been used to assess for bacterial diversity and identity, the study would have led to a completely false representation of the numbers of bacteria present in the clay, of their nature and geochemical roles.

It appears that most bacterial activities identified in this study were located within a penetration gradient in the outer most layer of the clay, near the gallery wall filling material.Work is in progress in order to analyse by combined classical and molecular methods the species that have been isolated and to characterize by molecular methods bacteria potentially living in clay, but that might been difficult to detect because many bacteria are not amenable to cultures.

6. References

/1/ Mc KINLEY I.,NAGRA, NTB Technical Report 88-26 (1989).

/2/ PARKURST D.L, THORSTENSSON D.C., PLUMMER L.N., U.S. Geol. Surv. Water Research Invest., 80-96 (1980)

/3/ BIANCHI A., HINOJOSA M., GARCIN, J. DELEBASSEE M., NORMAND M., RALIJOANA C., SOHIER L., VIANNA-DORIA E., VILLATA M., Le sondage Misedor, PELET R., (Ed.) Technip, Paris (1987).

/4/ KUZNETSOV S.I., IVANOV M.V., LYALIKOVA N.N., Introduction to geomicrobial microbiology. Mc Graw-Hill, New York (1963).

/5/ PEDERSEN K., EKENDAHL S., Microbiol. Ecol., 20-37 (1990).

/6/ Van WAMBEKE F., BIANCHI M., CAHET G., East. coast. Shelf Sci., 19-291 (1984).

/7/ AMANN R., KRUMHOLTZ L., STAHL D.A. ,J. Bacteriol., 172-762 (1990).

/8/ WERNER L., STACKEBRANDT E., J. Bacteriol., 174, (1992).

/9/ STACKEBRANDT E., LIESACK W., GOEBEL B.M., FASEB J., 7, 232 (1993).

/10/ KRIEG N.R., HOLT J.G., Bergey's Manual of systematic bacteriology. Vol.1. Williams & Wilkins, Baltimore (1984).

/11/ STALEY J.T., BRYANT M.V., PFENNIG N., HOLT J.G., Bergey's Manual of systematic bacteriology. Vol.3. Williams & Wilkins, Baltimore (1989).

/12/ STARR M.P., STOLP H., TRÜPPER H., BALOWS A., SCHLEGEL H.G., The prokaryotes. Vol. 1 & 2., Springer Verlag, Berlin (1981).

7. Tables

Table I : Chemical composition of interstitial fluids and aquifer.

	(1)	(2)	(3)		(1)	(2)	(3)
pH	8.75	7.65	8.5	**Na**	17	110.2	12.7
Eh (mV)	38	130	-310	**K**	0.25	1.06	0.25
Alkalinity	17.9	13.2	12.5	**Ca**	0.16	0.81	0.06
SO_4	0.013	4.06	0.05	**Mg**	0.04	1.83	0.12
Cl	0.77	92.7	0.5	**NH_4**	N.D	N.D	0.13
SiO_2	0.14	0.21	0.14				

The concentrations are expressed in mM/l; (1) : Mol; (2) : Meer, (3): interstitial fluid. (1) and (2) represent the two end-members of the Rupelian aquifer.

Table II : Boom Clay mineralogy.

WHOLE ROCK	%
Quartz	20 - 25
Microcline	4-5
Plagioclase	4-5
Pyrite	4.5
Carbonates	< 5
Sulfates	< 5
Clay Fraction	60

CLAY FRACTION		%
IS mixed layers, random $(R=0)$		50
IS mixed layers, oredered $(R \geq 3)$		Trace
Illite + Mica	25	
Kaolinite	20	
Chlorite	4-5	
oxides (Ti, Fe)		

Title: Phenomenology of Hydrical Exchanges Between Underground atmosphere and Storage host-rock

Contractors : Agence Nationale pour la gestion des Déchets RAdioactifs (**ANDRA**)
- France -

Contract n°: FI2W-CT-91-0116

Duration of contract: January 1992 to December 1994

Project leader: JM. PALUT

A/ OBJECTIVE AND SCOPE

The aim of the PHEBUS project concerns the study of the hydrous behaviour of a clay formation around ventilated excavations. It consists of a modelling, a laboratory mock-up and an in situ test carried out at Mol facility in Belgium. Potential effects of clay desaturation around ventilated galleries should be changes in permeability, fissuration or mechanical hardening. These effects may particularly influence lining concepts as well as sealing concepts.

In a first phase, this consists in developping methodological tests not on core samples but on remoulded highly compacted clays. This procedure provides an appropriate control of the hydrical and mechanical history of the sample, making it possible to understand the real hydrous phenomena.

An in situ test will then be carried out to validate the mock-up results. Using an appropriate apparatus, this phase permits to reach some parameters and their time-dependence that can't be measured on a mock-up. This short scale will allow to evaluate the usefullness of a gallery ventilation test and to assess its technical feasibility : ventilation system, lining conception and planning.

B/ WORK PROGRAM

B1. MODELLING

This part consists in developing a simplified model of the hydrical transfer, in isothermal conditions and without mechanical coupling (constant volume and porosity). This allows to study the parameters sensibility and to propose a first evaluation of the hydrical behaviour of the clay medium under a ventilation effect (orders of magnitude of water fluxes, desaturation area and phenomenon duration) on the basis of the present data.

B2. MOCK-UP TESTS

The mock-up tests aim to well understand the phenomenology of hydrical exchanges between a controlled humidity air and the initially saturated clay, and to validate the model. It consists to design and manufacture an apparatus to test under high stress a clay with a cylindrical opening in the centre that simulates the ventilated gallery. At the end of each test, the mock-up is dismantled in order to measure the hydrical state around the opening.

B3. IN-SITU TEST

This phase will be carried out in the Mol underground laboratory. It will consist in drilling an horizontal borehole with a porous lining and an adequate peripheral instrumentation. The ventilation of this borehole will be controlled (dry temperature and relative humidity) and the amount of extracted water measured. Simultaneously the measurement of the clay hydrical state around the borehole will allow to evaluate the desaturation line. The experimental results will be compared to the model predictions.

C/ PROGRESS WORK AND RESULTS

State of advancement

The modelling phase have been completed. The main parameters are the relative humidity of the air and the saturated clay permeability. It shows that the desaturation effect will concern a few meters area around the openings, sufficiently to affect the clay mechanical parameters and so the mechanical interaction between the clay and the lining. Under repository conditions the desaturated area should be independent of the radius of the gallery.

The modelling was used to dimension the mock-up apparatus. It mainly consists in an oedometer and a controlled ventilation system. Both have been delivered and tested during the year 1993. The first experiment carried out with Boom clay started in October and is still in progress.

Concerning the in situ test, the design of the equipement of the main borehole have been settled with the help of additional experiments. Peripheral boreholes have been drilled sucessfully and installed with instrumentation.

Progress and Results

B.1 MODELLING

The model is based on the analysis of the different types of pore water in clay (free, capillary and adsorbed water). In deep clay most of the water is in adsorbed state. The model considers the specific transfer mechanisms of each type of water. It has been shown that, when the gas phase is under constant pressure, the total water transfer could be addressed with one parameter similar to a diffusion coefficient and function of porosity and water condition. At saturation, this parameter is equal to the permeability. Both mock-up and in situ test have been dimensioned on this basis.

With a permeability of 10^{-12} m/s and for various relative humidities, we calculate the water flux per surface unit, the total water volume and the desaturation front. The water flux decreases rapidly and reaches after two months a pseudo-permanent state independent of the relative humidity. For our experiments that means that it wouldn't be significant to continue after 2 months.

B.2 MOCK-UP TESTS

The mock-up apparatus is based on an oedometer for high stress (0-20 MPa) which includes an additional cylindrical hole in the centre (fig. 1a). Each experiment comprizes three steps.
The first one consists in consolidating a paste obtained from natural clay to get a highly-compacted remoulded clay. During the first experiment in progress with Boom clay, the consolidation up to 5 MPa lasted five weeks (fig.1 b).
In the next step, an air flux of controled humidity circulate through the central hole to desaturate

the compacted clay and to simulate the ventilation in an underground gallery (fig. 2a). A relative humidity of 33 % is applied to the air by the mean of saturated salt solutions which capture the water in excess. This step is still in progress and should last about 3 months. Preliminary results show a good agreement between the amount of water collected and the model prediction (fig. 2b). Therefore, compaction re-started when ventilation was put on ; this unexpected observation will probably lead to improve the apparatus by addition of mechanical measurements in the clay.
The third step of the moke-up tests is dismantling and sampling of the remoulded clay to measure parameters such as water content *vs* distance to the central ventilated hole.

B.3 IN SITU TEST

The principle of this in situ test is to blow a dry air flux into a borehole in order to desaturate the surrounding clay through a porous lining. The water is extracted from the air at the output of the test chamber and measured. Peripheral instrumentation provide data about clay at different distances from the chamber (dry density, water content).

Location and dimensions of the test chamber have been defined according to the model calculations (cf. fig. 3a, 3b). The test zone will be located between 11 and 14 meters depth, far enough to reduce the mechanical or hydrical effects of existent excavations. The lining of the test chamber consists of a perforated casing supporting a porous medium of 300 mm in diameter which also supports pressure sensors. In 1993, in order to settle the definitive design of the chamber, preliminary laboratory tests were carried out to determine if the geometry choosen for it was appropriate from an aerodynamic point of view .

The controlled ventilation and water extraction system is still under definition, based on saturated salt solutions.

In October 93, the CEN/SCK drilled three boreholes for peripheral instrumentation consisting of water pressure and total pressure. The requirements concerning orientation of these boreholes have been filled and the installation of their equipement was satisfactory. These boreholes are also usable for water content measurements, carried out with the gamma-neutron probe already used in Mol, but accomodate to focus the measurements in one direction.

References

[1] Rapport 621 RP GEO 91.002
"Modélisation des transferts de masse entre un massif argileux et l'atmosphère des ouvrages souterrains profonds - Première approche" - EUROGEOMAT

[2] Rapport 621 RP 92.003
"Evaluation sur modèle réduit des transferts hydriques entre un massif argileux et l'atmosphère d'une galerie - PHEBUS"- EUROGEOMAT

[3] Rapport 621 RP GEO 92.004
"Etude paramétrique des transferts hydriques entre un massif argileux et l'atmosphère d'un ouvrage profond - Application aux argiles de l'Aisne et de Boom"- EUROGEOMAT

[4] Rapport 621 RP BRG 92.030
"Essai PHEBUS - Définition et dimensionnement du tubage poreux" - BRGM 04/93

[5] Rapport provisoire SCK/CEN
"Le Test PHEBUS test - (04/93 - 12/93)"

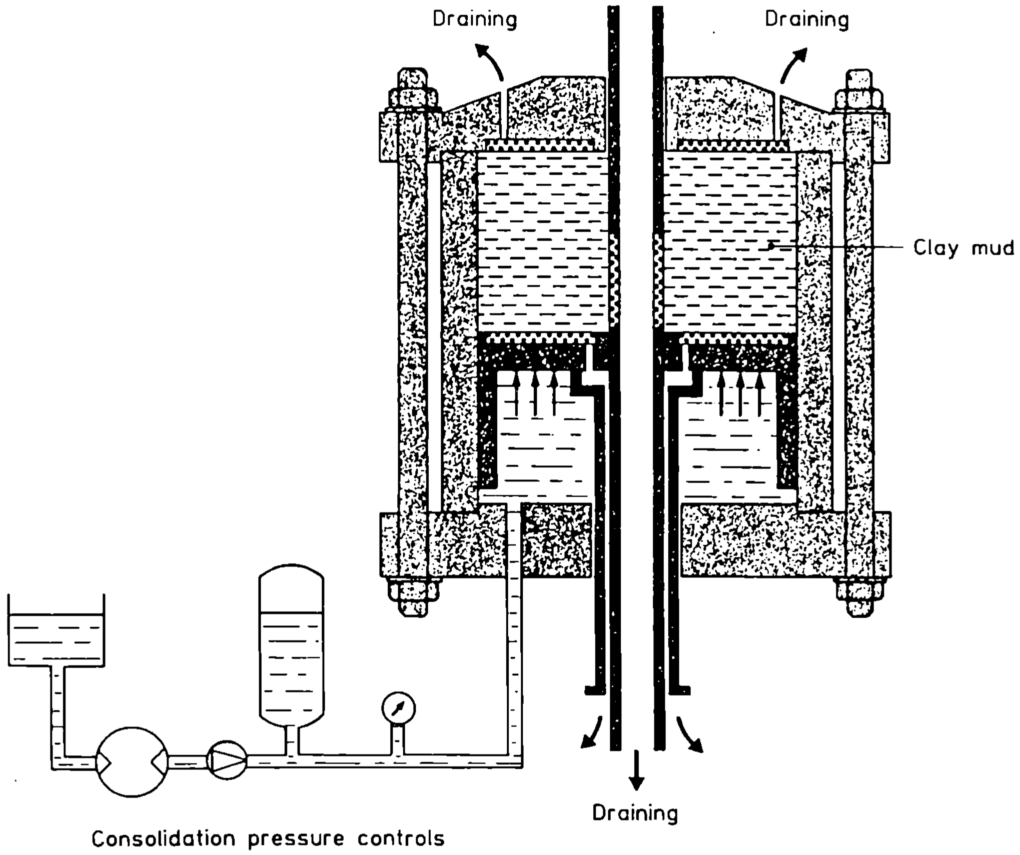


Fig. 1a Consolidation phase experimental setup

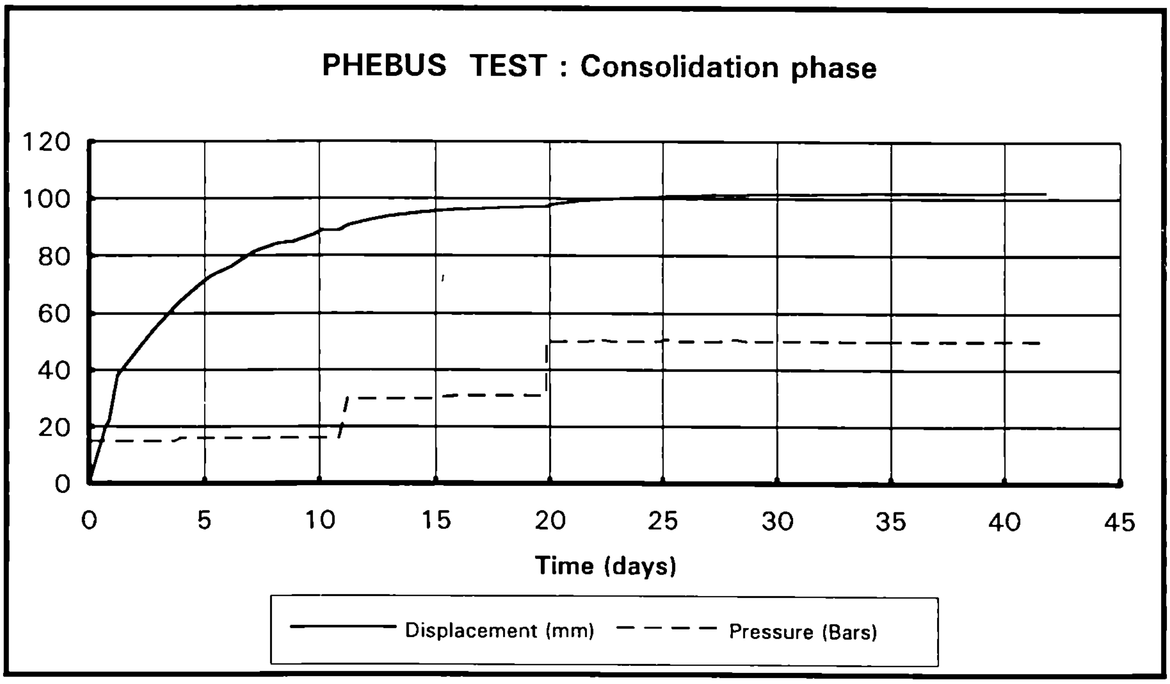


Fig. 1b Consolidation phase : results

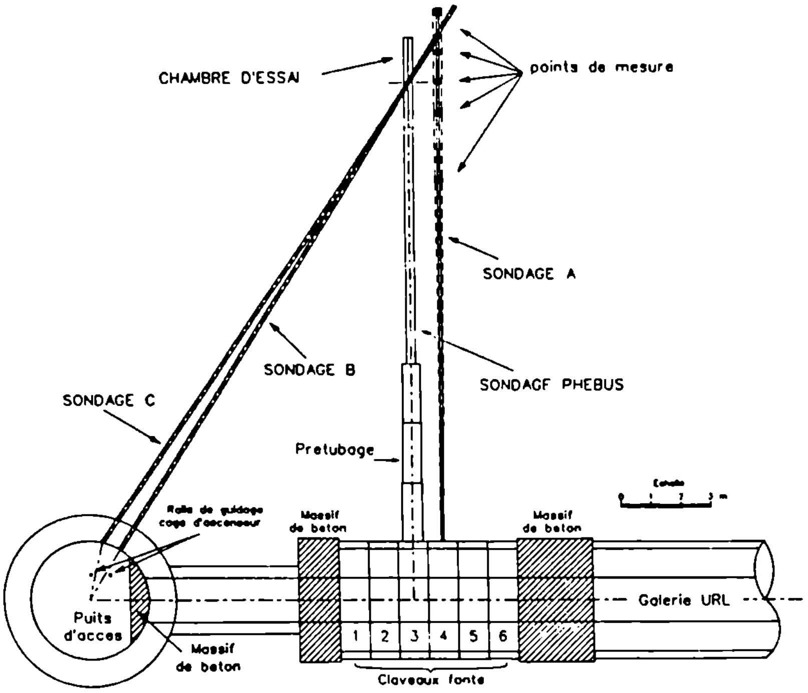


Fig. 3 a In-situ test site : horizontal cross section

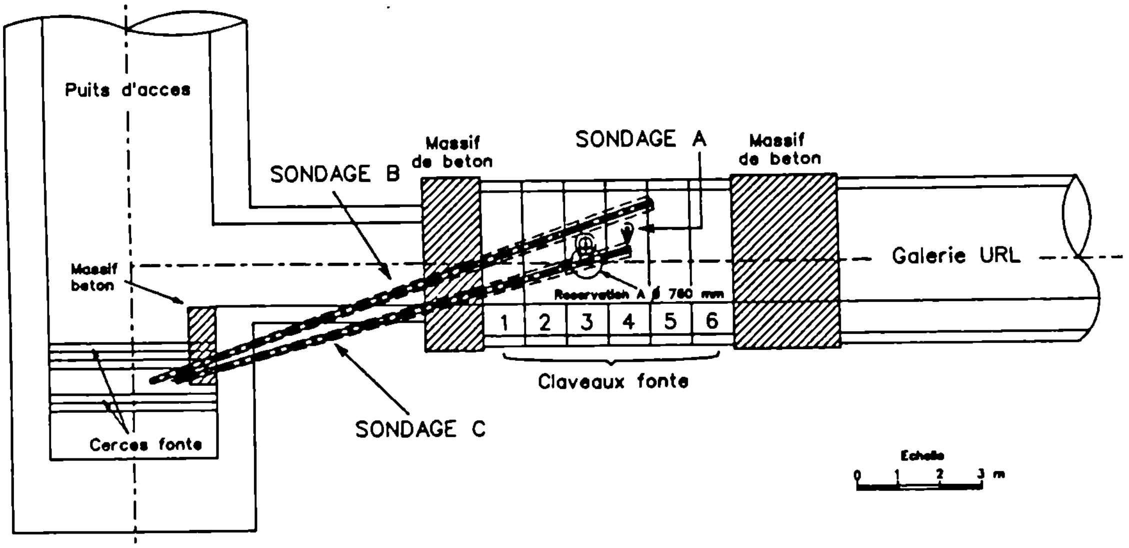


Fig. 3 b In-situ test site : vertical cross section

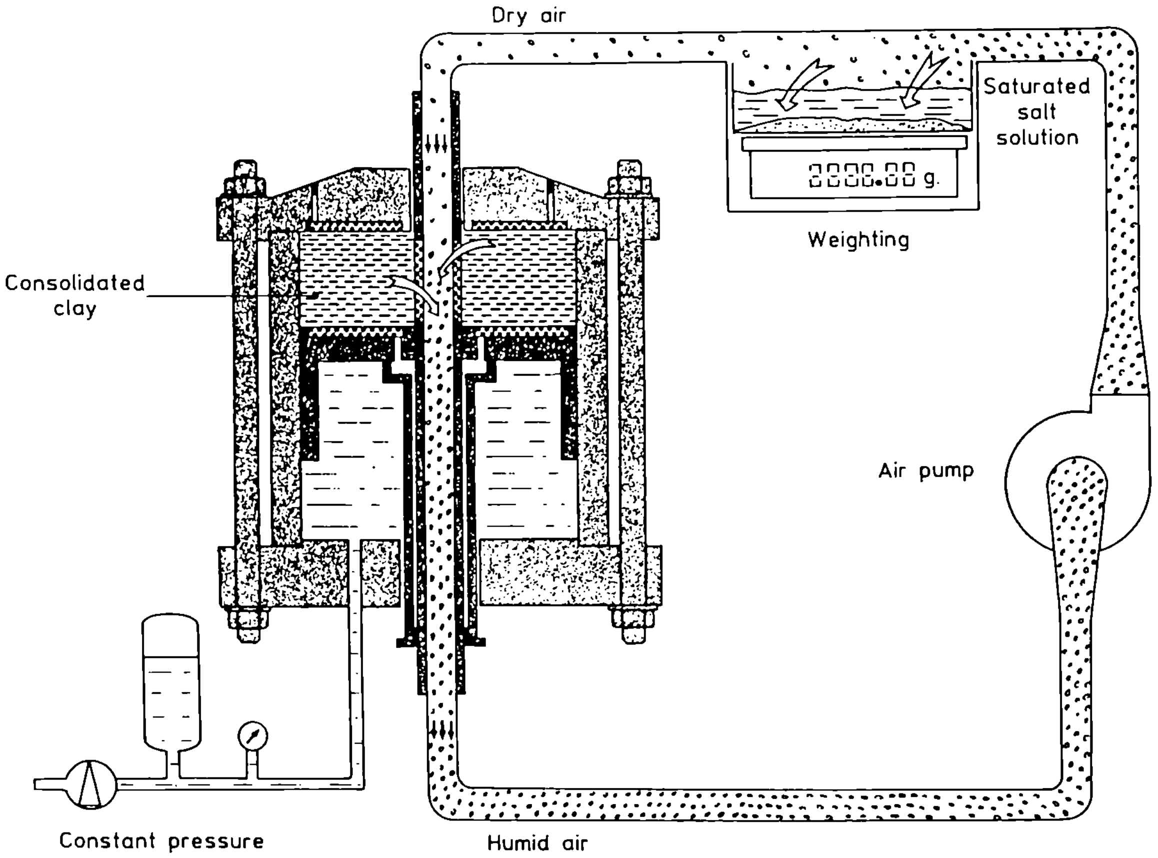


Fig. 2a Ventilation phase : experimental setup

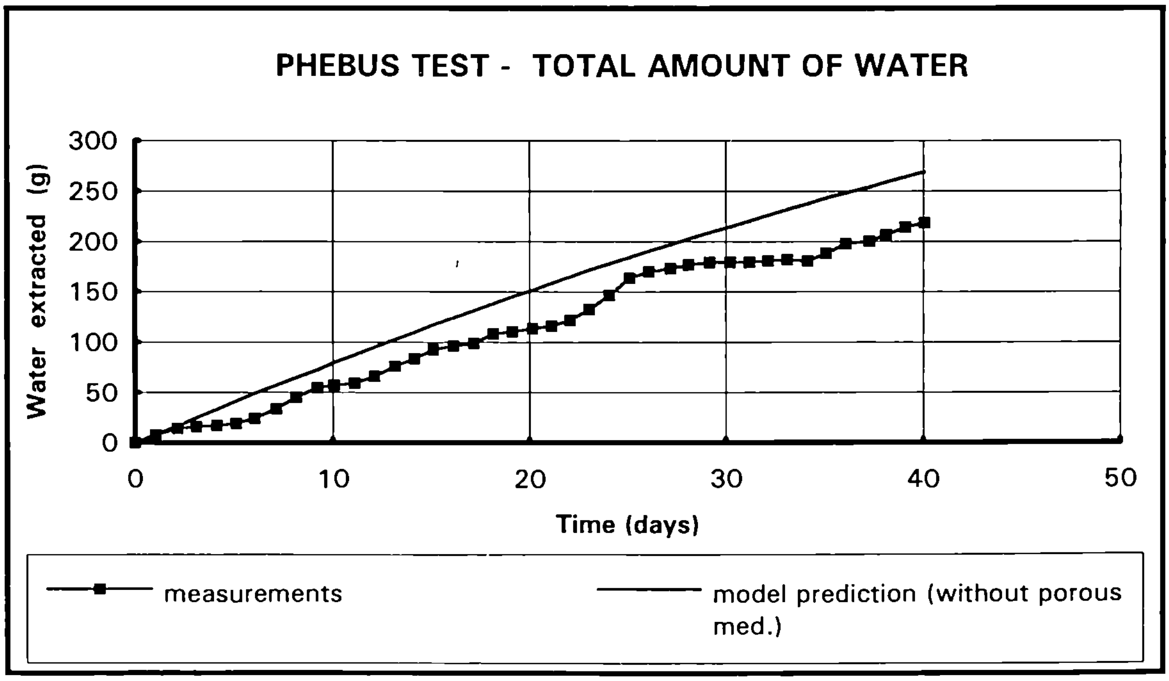


Fig. 2 b Ventilation phase : preliminary results

HYDROGEOLOGICAL CHARACTERISATION OF HARD FRACTURED ROCK AT SELLAFIELD

Contractor:	United Kingdom Nirex Limited
Contract No:	F12W/0114
Duration of Contract:	1 April 1992 to 31 December 1994
Period Covered:	1 January 1993 - 31 December 1993
Project Leader:	Dr A J Hooper

A. OBJECTIVES AND SCOPE

The overall objective of the project is to decrease uncertainties in the hydrogeological and structural characterisation of a volume of rock at Sellafield in Cumbria. This rock is currently being considered as a potential host for a low and intermediate level solid radioactive waste repository in the United Kingdom.

The specific aims of the work are to perform geophysical and hydrogeological tests in and between two boreholes in a fractured and layered volcanic rock sequence, the Borrowdale Volcanic Group. Geophysical data will be integrated into a model of the rock volume. The results of single and crosshole hydrogeological testing will be used to clarify the lithological and structural features or combinations which control groundwater flow in the Borrowdale Volcanic Group.
This model will be applied to develop and validate concepts of groundwater flow in the immediate vicinity of the proposed repository.

The work is being performed in conjunction with Sir Alexander Gibb and Partners, acting as Geological Consultant. In addition, the following contractors have been defined: Schlumberger, Golder Associates UK Ltd.

B. WORK PROGRAMME

1. Review methodologies and prepare Design Intent Memorandum.
2. Geophysical testing in Sellafield Borehole no 4.
3. Cross-borehole geophysical testing.
4. Single borehole hydraulic measurements in Borehole 4.
5. Design of cross-borehole interference testing.
6. Cross-borehole interference testing.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

During the year, cross borehole seismic tomography has been completed between Boreholes 2 and 4 and the results have been reported and interpreted. Tasks 1, 2, 3 and 4 are now complete. A programme design for the cross borehole interference testing between Boreholes 2 and 4 has been produced, based on pre-modelling using a fracture network model of the study area. Task 5 is thus complete. Progress towards the implementation of the crosshole testing has been made. Monitoring equipment has been installed in Borehole 4. Initial background results from this equipment have been obtained. Equipment for the source borehole is being procured. There have been technical problems with the monitoring equipment installed in Borehole 4; the equipment is under repair at the present time. The method of source signal generation has been evaluated, to ensure that it will provide data amenable to numerous forms of analysis. The collection of field data from this task is programmed to commence in February 1994, assuming full operation of the monitoring equipment.

Progress and results

Task 1 Review methodologies and prepare Design Intent Memorandum

This task is now complete. More detailed analyses regarding the design of the crosshole interference testing have been conducted under Task 5.

Task 2 Geophysical testing in Boreholes 4 and 2

Wireline logs and VSP have been run in Boreholes 2 and 4. The data have been plotted as composite plots with core logs and correlated between boreholes. A summary of the main structural features is shown in Figure 1. Faults intersected by the boreholes have been identified. Two main zones of fault deformation have been identified (Faults 1 and 200) which appear to be composite zones of deformation with several fault strands and associated synthetic and/or antithetic faults. They also appear to be associated with sets of sub-parallel fracture envelopes.

Task 3 Cross borehole geophysical testing

Crosshole seismic testing has been conducted between Boreholes 2 and 4 and excellent results have been obtained. Tomographic inversion of these data confirm the geological structure identified from the core and from the wireline logs, as presented in Figure 1. Some additional interborehole features have also been identified.

Borehole radar was not performed between Boreholes 2 and 4. A trial of omnidirectional cross borehole and directional single borehole radar conducted in Sellafield Borehole 7 indicated that the results would not significantly enhance data already obtained from the dual laterolog and the cross borehole seismics.

Task 4 Single borehole hydraulic testing in Borehole 4

This work was primarily carried out in Borehole 2 and the data indicate significant variability in both transmissivity and pressures. There is no clear correlation between zones of enhanced flow and major structure, although there is a possibility that the flow is associated with fracture envelopes around the major structures. Pressures increase with depth. The data are presented in Figure 2.

Task 5 Design of cross borehole interference testing

Pre-modelling of the crosshole interference testing has been performed using the FRACMAN discrete fracture network code. FracMan Pathways and Network Analysis have been used to investigate the best packer spacing, and the response to both constant head and constant rate pumping using generalised radial flow theory. In addition, the finite element code MAFIC is used to simulate flow in the network due to pumping. The results have shown that the maximum monitoring interval length for regions with a good chance of responding is 20m, and that first response should be due within 5 days of pumping. Based on this, six source zones have been identified in

Borehole 2, and Borehole 4 has been divided into 29 monitoring intervals. These are shown in Figures 3 and 4 respectively. All source zones in Borehole 2 will be monitored whilst any one zone is being pumped to provide greater definition of the intraborehole fracture network connections. Constant rate pumping will be performed at a rate of order $10^{-5}m^3s^{-1}$ initially for a period of up to 30 days. Recovery will also be allowed. The test programme will be divided into at least two phases, such that the results of the first two tests can be used to optimise the future test programme.

Task 6 Cross borehole interference testing

A 29 zone Westbay multipacker monitoring string was installed in Borehole 4 in October 1993. Background pressure data from the borehole are now being collected. However, a mechanical failure in the string was identified in December 1993 and is currently under repair. This may mean that data from one of the monitoring zones will be lost. A twelve packer string, with Baker packers run on a central tubing is being manufactured to be installed in the source borehole by April 1994. It is intended to conduct early crosshole works to evaluate the resolution of the source signal and to obtain early data. Using this information, the premodel will start to be constrained prior to completion of the twelve packer string manufacture.

List of publications

The following topical reports are due for completion in February 1994.

1. An Approach to Hydrogeological Characterisation of Hard Fractured Rock at Sellafield. A. K. Littleboy.
2. Borehole Radar Applications at Sellafield. S.J. Emsley.
3. Crosshole Seismic Studies at Sellafield. S.J. Emsley.
4. Post Completion Testing - Crosshole Seismic Tomography - Sellafield Boreholes 2 and 4. Nirex Report No. 385.

Documents regarding the design of the crosshole programme have been produced. An assessment of the characteristics of the flowing features in Boreholes 4 and 2 have been produced during the period.

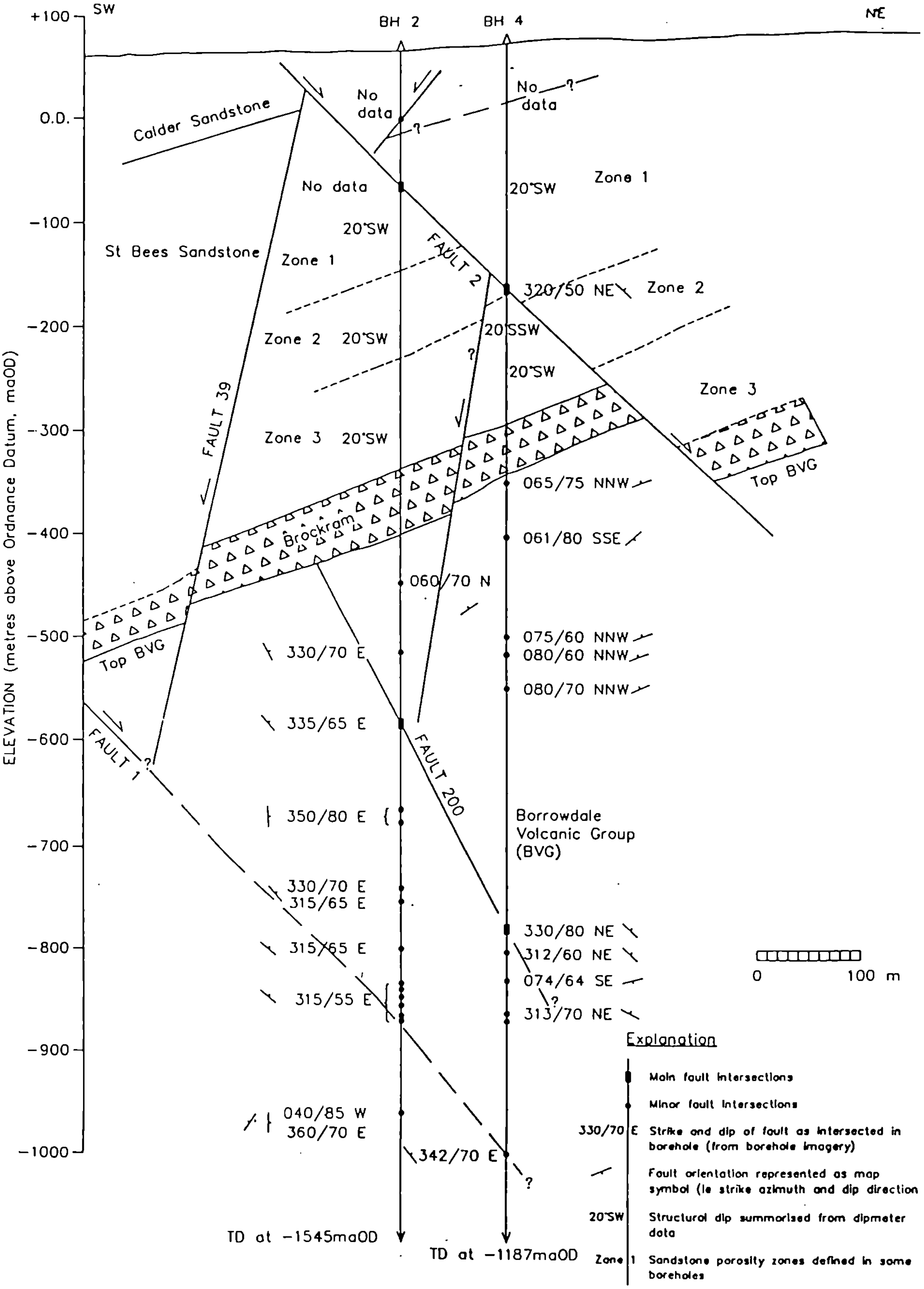


Figure 1 Borehole 4 Structure

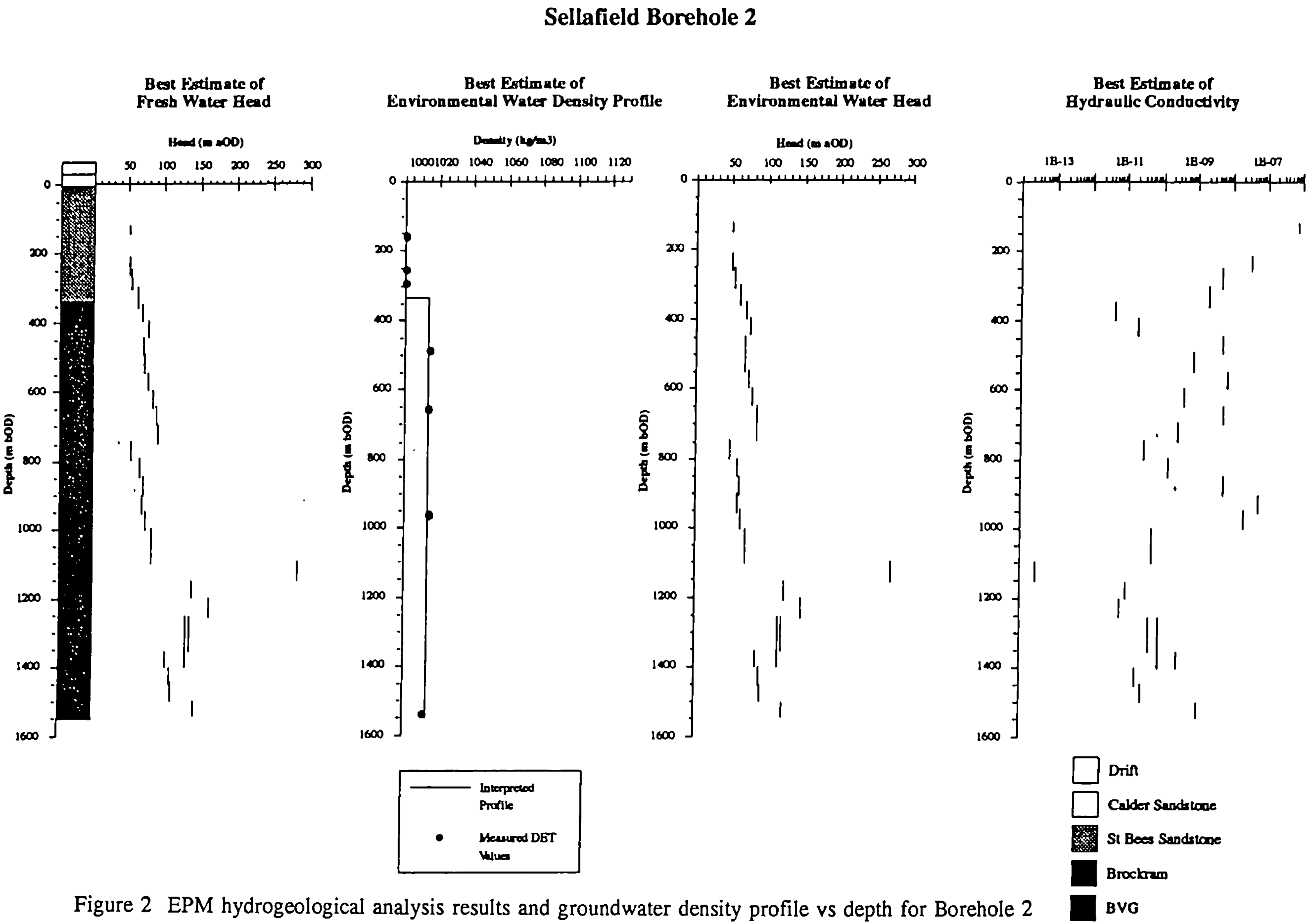


Figure 2 EPM hydrogeological analysis results and groundwater density profile vs depth for Borehole 2

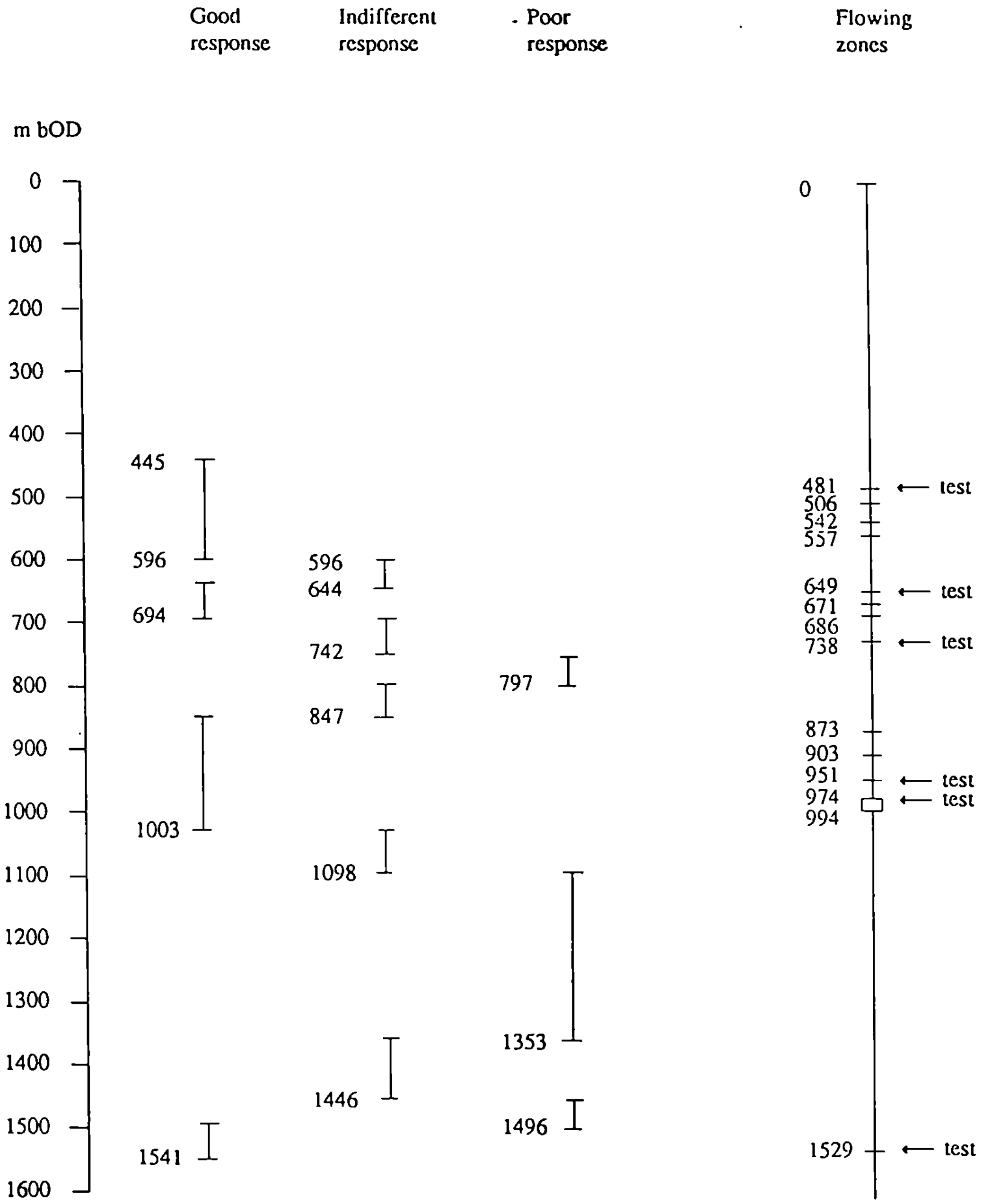


Figure 3 BH2 profile for producing responses in BH4, based on EPM conductivity measurements and full sector testing

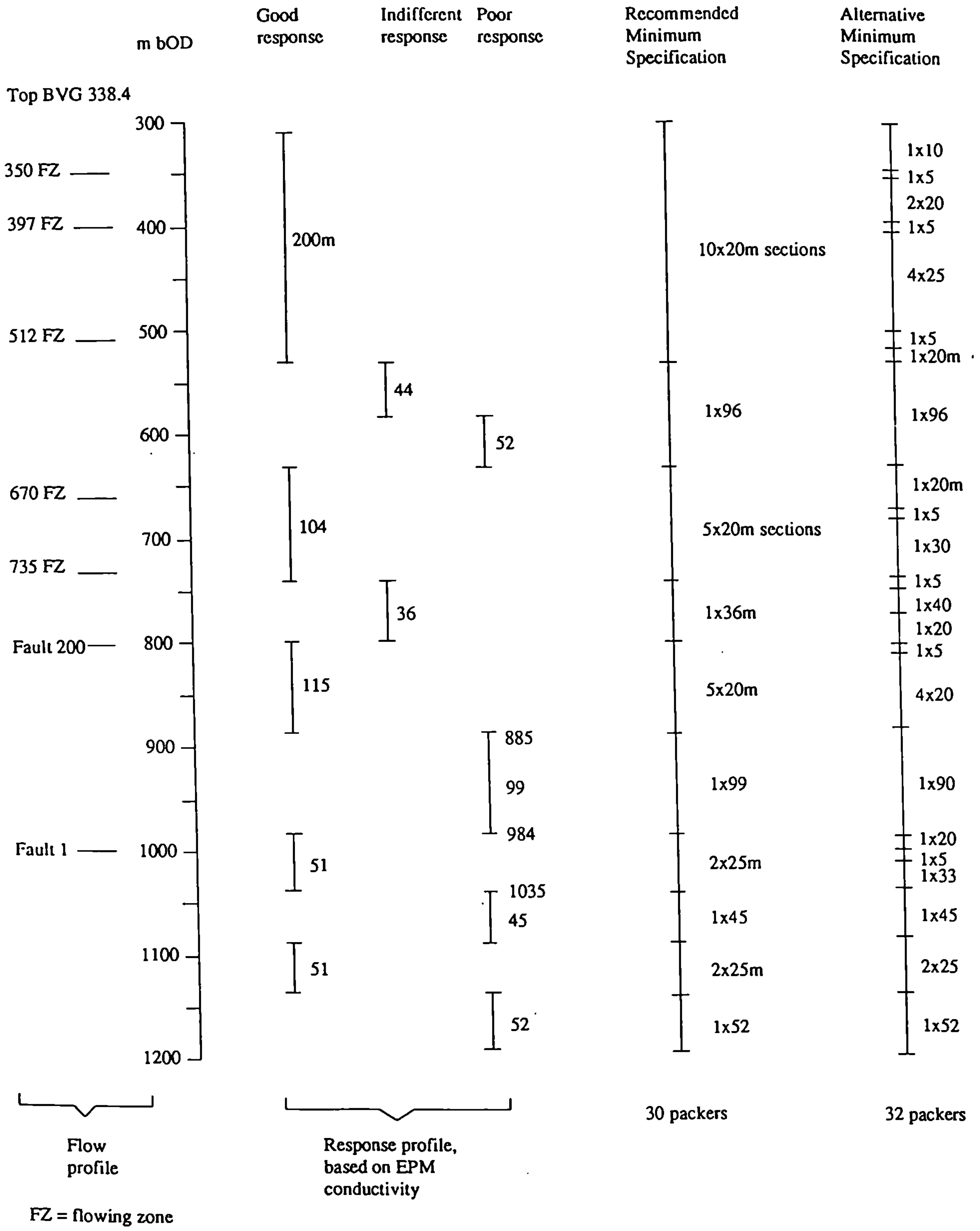


Figure 4 Cross-hole Test Design - Borehole 4 Monitoring Scheme based on EPM conductivity measurements and full sector testing

ANNEX : List of organisms and companies participating in the programme during 1993

AEA(UKAEA)-Dounreay	AEA (UKAEA) Dounreay Nuclear Power UK-THURSO, CAITHNESS KW14 7TZ
AEA(UKAEA) Harwell	AEA (UKAEA) Harwell Laboratory Didcot UK-OXFORDSHIRE OX11 ORA
AEA(UKEA)-Windscale	AEA(UKEA) UK-CUMBRIA CA20 1PF
AEA(UKAEA)-Winfrith	UKAEA-AEA Technology Winfrith Techn. Centre, B44 Dorchester UK-DORSET DT2 8DH
ANDRA	Agence Nationale pour la Gestion des Déchets Radioactifs Route du Panorama Robert Schuman B.P. 38 F-92266 FONTENAY-AUX-ROSES
ARMINES	Association pour la Recherche et le Développement de Méthodes et Processus Industriels Ecole Nationale Supérieure des Mines de Paris Rue Saint Honoré 35 F-77305 FONTAINEBLEAU
ATKINS	WS Atkins International Limited Woodcote Grove, Ashley Road UK-EPSOM, Surrey KT18 5BW
BAeSEMA	BAeSEMA Systems Division 20/26 Lambs Conduit Street UK-LONDON WC1N 3LF
BAM	Bundesanstalt für Materialforschung-u-Prüfung Unter den Eichen 87 D-W1000 BERLIN 45
BERTIN & CIE	Bertin & Cie Centre de Bayonne Z.I. F-40220 TARNOS
BGS (NERC)	British Geological Survey Natural Environment Research Council Kingsley Dunham Centre UK-KEYWORTH, NOTTINGHAM NG12 5GG

BNFL	British Nuclear Fuel Plc Risley UK-Warrington, Cheshire WA3 6AS
BRGM	Bureau de Recherches Géologiques et Minières Service Géologique National B.P. 6009 F-45060 ORLEANS Cédex 2
BS	Brenk Systemplanung Ingenieurbüro für Wissenschaftlich Tech. Umweltschutz Heinrichsallee 38 D-5100 AACHEN
CEA	Commissariat à l'Energie Atomique Rue de la Fédération 31-33 F-75752 PARIS Cédex 15
CEA-Cadarache	Commissariat à l'Energie Atomique Centre d'Etudes de Cadarache F-13108 ST. PAUL-LEZ-DURANCE Cédex
CEA-FAR	Commissariat à l'Energie Atomique Centre d'Etudes de Fontenay-aux-Roses B.P. 6 F-92265 FONTENAY-AUX-ROSES Cédex
CEA-IPSN	Commissariat à l'Energie Atomique Inst. de Protection et de Sûreté Nucléaire Ave. Général Leclerc 60-68 B.P. 6 F-92265 FONTENAY-AUX-ROSES
CEA-Saclay	Commissariat à l'Energie Atomique Centre d'Etudes de Saclay F-91191 GIF-SUR-YVETTE Cédex
CEA-VALRHO	Commissariat à l'Energie Atomique Centre d'Etudes de la Vallée du Rhône B.P. 171 F-30205 BAGNOLS-SUR-CEZE Cédex
CEN/SCK	Centre d'Etude de l'Energie Nucléaire Studiecentrum voor Kernenergie Boeretang 200 B-2400 MOL
CIEMAT	Centro de Investigaciones Energeticas Medio Ambientales y Tecnologicas Ministerio de Industria, Comercio y Turismo Avenida Complutense 22 E-28040 MADRID

CIMNE	Centro Intern. de Métodos Numéricos en Ingenieria Jordi Girona Sagaldo 31 E-08034 BARCELONA
CNRS	Centre Nat. de la Recherche Scientifique Géochimie de la Surface UPR6251 Rue Blessig 1 F-67084 STRASBOURG
CNRS-LSGC	Centre Nat. de la Recherche Scientifique Lab. Sciences du Génie Chimique Rue Granville 1 F-54042 NANCY Cédex
CNRS-ORSAY	Centre Nat. de la Recherche Scientifique Inst. Physique Nucléaire et des Particules F-91405 ORSAY CAMPUS
COMUF	Compagnie des Mines d'Uranium de Franceville Libreville GABON
CREGU	Centre de Recherche sur la Géologie des Matières Prim. Minérales et Energétiques Rue du Bois de la Champelle 3 F-54501 VANDOEUVRE-LEZ-NANCY
DBE	Deutsche Gesellschaft zum Bau und Betriebe von Endlagern für Abfallstoffe mbH Postfach 1169 D-3150 PEINE 1
EA	EMPRESARIOS AGRUPADOS-Unión Temporal- (EPTISA-GHESA-TRSA) Magallanes 3 E-28015 MADRID
ECN	Stichting Energieonderzoek Centrum Nederland Westerduinweg 3 NL-1755 ZG PETTEN
ENEA-Casaccia	Ente per le Nuove tecnologie, l'Energia e l'Ambiente CRE-Casaccia Via Anguillarese 301 I-00060 S. MARIA di GALERIA
ENEA-Saluggia	Ente per le Nuove tecnologie, l'Energia e l'Ambiente Impianto Eurex I-13040 SALUGGIA (Vc)

ENRESA	Empresa National de Residuos Radioactivos S.A. Calle Emilio Vargas 7 E-28043 MADRID
ENSMP	Ecole Nat. Supérieure des Mines de Paris Boulevard Saint Michel 62 F-76006 PARIS
FRAMATOME	FRAMATOME S.A. Direction Novatome Rue Juliette Récamier 10 F-69006 LYON 03
FREE UNIV.BERLIN	Freie Universität Berlin Takustraße 6 D-W-1000-BERLIN 33
GCI	GCI 36 Grosvenor Gardens UK-LONDON SW1W OEB
GEOSTOCK	Soc. Française de Stockages Géologiques Geostock Rue Eugène et Arnaud Peugeot 7 F-92563 RUEIL-MALMAISON Cédex
GERMETRAD	Université de Nantes Lab. Biochimie et Radiobiochimie Rue de la Houssinière 2 F-44072 NANTES 03
G.3S	Groupement pour l'Etude des Structures Souterraines de Stockage Route de Saclay F-91128 PALAISEAU
GOLDER ASS.	Goder Associates Ltd. Landmere Lane, Edwalton UK-NOTTINGHAM NG12 4DE
GRAM SA	Guiges Recherche Appliquée en Microbiologie Rue Pierre Duhem, 10 F-AIX-EN-PROVENCE
GRS	Gesellschaft für Reaktorsicherheit mbH Schwertnergasse 1 D-5000 KOELN 1
GSF-IfT	GSF-Forschungszentrum für Umwelt und Gesundheit GmbH Institut für Tieflagerung Theodor Heuss-Straße 4 D-3300 BRAUNSCHWEIG

GSF	GSF-Forschungszentrum für Umwelt und Gesundheit GmbH Institut für Hydrologie Ingolstädter Landstrasse, 1 D-8042 NEUHERBERG
INASMET	Asoc. de Investigación Metalurgica del Pais Vasco Camino de Portuetxe, 12 E-20009 SAN SEBASTIAN
INERIS	Inst. Nat. de l'Environnement industr. et des Risques Lab. Mécanique des Terrains Parc de Saurupt F-54042 NANCY
INFM	Università di Padova Dip. Fisica Via Marzolo 8 I-35131 PADOVA
INITEC	Empresa Nacional de Ingeneria y Technologica S.A. Padilla 17 E-28006 MADRID
INST. SYMLOG	Institut Symlog de France asbl Rue Camille Desmoulin, 9 F-94230 CACHAN
INTAKTA	Intakta France S.a.r.l. Rue des Jeuneurs 21 F-75002 PARIS
INTERA	Intera Information Technologies Ltd. Chiltern House, 45 Station Road UK-HENLEY-ON-THAMES, OXFORDSHIRE RG9 1AT
ISMES	Istituto Sperimentale Modelli e Strutture SpA Via Giulio Cesare 29 I-24100 BERGAMO
ITGE	Inst. Tecnologio Geominero de España Ingeniera Geoambiental Rios Rosas, 23 E-28003 MADRID
KEMA	Keuring van Elektrotechnische Materialen N.V. Utrechtseweg 310 NL-6812 AR ARNHEM

KFA	Forschungszentrum Jülich GmbH Postfach 1913 D-5170 JÜLICH
KfK	Kernforschungszentrum Karlsruhe Postfach 3640 D-7500 KARLSRUHE 1
KUL	Katholieke Universiteit Leuven Lab. v. Colloidchemie Kardinaal Mercierlaan, 92 B-3001 HEVERLEE
LABORELEC	Laboratoire Belge de l'Industrie Electrique Rue de Rhode 125 B-1630 LINKEBEEK
LNETI	Lab.Nacional de Engenharia e Tecnol. Industrial Estrade Nacional 10 P-2685 SACAVEM
LUT	Loughborough Univ. of Technology Dept of Chemistry UK-LOUGHBOROUGH LE11 3TU
MOTT-MACDONALD	MOTT MacDonald Civil Ltd Foundations & Geotechnics Div. Wellesley Road, 20-26 UK-CROYDON CR9 2UL
NCRS"DEMOKRITOS"	NRCS"DEMOKRITOS" Nuclear Techn. Radiation Protection Aghia Paraskevia, Attikis GR-15315 ATHENS
NERI	National Environment Research Institute DK-4000 ROSKILDE
NRI	Nuclear Research Institute CZ-25068 REZ
NRPB	National Radiological Protection Board Chilton, Didcot UK-OXFORDSHIRE OX11 ORQ
NUCLECO	NUCLECO Nucleare-Ecologia SpA Via Anguillarese 301 I-00060 S. MARIA DI GALERIA (Roma)

ONDRAF/NIRAS	Organisme National des Déchets Radioactifs et des Matières Fissiles Enrichies Place Madou 1 (Btes 24/25) B-1030 BRUSSELS
RGD	Rijks Geologische Dienst-Nederland Richard Holkade 10 NL-2000 AD HAARLEM
RISØ NL	Risø National Laboratory P.O. Box 49 DK-4000 ROSKILDE
RIVM	Rijksinstituut voor Volksgezondheid en Milieuhygiëne Antonie van Leeuwenhoeklaan 9 NL-3720 BA BILTHOVEN
SIEMENS (KWU)	Siemens AG - KWU P.O. Box 1001 00 D-5060 BERGISCH GLADBACH 1
SIF-BACHY	Soc. Sondages Injections Forages de Bachy Rue Ste Claire Deville-lez-Colonnades 4 F-92563 RUEIL-MALMAISON
SNIA - STE	SNIA-SpA Sistemi e Tecnologie per l'Energia Via Angelo Bargoni, 8 I-00153 ROMA
TU MÜNCHEN	Technische Universität München Inst. für Radiochemie Walther-Meissnerstraße 3 D-8046 GARCHING
UCL	Université Catholique de Louvain Lab. Génie Civil Place du Levant 1 B-1348 LOUVAIN-LA-NEUVE
UK-NIREX	UK NIREX Ltd Harwell Curie Avenue UK-DIDCOT OX11 ORH
ULB-IRIDIA	Université Libre de Bruxelles IRIDIA Avenue F. Roosevelt 50 B-1050 BRUXELLES

UNIV. ABERDEEN	University of Aberdeen Chemistry Dept. Meston Walk UK-ABERDEEN AB9 2UE
UNIV. BARCELONA	Universidad de Barcelona Facultad de Quimica Marti I Franques 1-11 E-08028 BARCELONA
UNIV. BELFAST	Queen's University Belfast School of Chemistry UK-BELFAST BT9 5AG Northern Ireland
UNIV. BES	Université Franche-Comté de Besançon Fac. Sciences et Techniques Route de Gray 16 F-25030 BESANCON
UNIV. BRISTOL	University of Bristol Inform.Techn.Research Centre University Walk UK-BRISTOL BS8 1TH
UNIV. EDINBURGH	University of Edinburgh Old College, South Bridge UK-EDINBURGH EH8 9YL
UNIV. EXETER	University of Exeter - Earth Resource Centre North Park Road UK-EXETER EX4 4QE
UNIV. LA SAPIENZA	Università degli Studi di Roma "La Sapienza" Dipt. Scienza della Terra Piazza Aldo Moro 5 I-00185 ROMA
UNIV. LIVERPOOL	University of Liverpool Inst. Prehist. Science & Archaeology Brownlow Street UK-LIVERPOOL L69 3BX
UNIV. MAINZ	J. Gutenberg Universität Mainz Abt. Lehramt Chemie J. Joachim Becher Weg, 345B1 D-6500 MAINZ
UNIV. NANTES	Université de Nantes Lab. Bio-Radiochimie Rue de la Houssinière 2 F-44072-NANTES

UNIV. OVIEDO	Universidad de Oviedo Depart. de Geologia C. Jesus Arias de Velasco E-33005 OVIEDO
UNIV. OXF	University of Oxford Dept of Materials Parks Road UK-OXFORD OX1 3PH
UNIV. PARMA	Università degli Studi di Parma Istituto chimica organica Viale delle Scienze I-43100 PARMA
UNIV. PERUGIA	Universita di Perugia Piazza Università I-61100-PERUGIA
UNIV. READING	University of Reading Dept. of chemistry Whiteknights UK-READING RG6 2AD
UNIV. SURREY	University of Surrey Robens Institute UK-GUILDFORD GU2 5XH
UNIV. TWENTE	University of Twente Dep. of Chemistry P.O. Box 217 NL-7500 AE ENSCHEDE
UPC	Universidad Politécnica de Cataluña Dep. Ingenieria del Terreno Jordi Girona Salgado 31 E-08034 BARCELONA
UPM	Universidad Politécnica de Madrid ETS de Ingenieros de Minas Rios Rosas 21 E-28003 MADRID
UWCC	University of Wales College of Cardiff Engineering School UK-CARDIFF CF2 1XH

For up-to-date information on European Community research

consult

CORDIS
The Community Research and Development Information Service

CORDIS is an on-line service set up under the VALUE programme to give quick and easy access to information on European Community research programmes.

The CORDIS service is at present offered free-of-charge by the European Commission Host Organisation (ECHO). A menu-based interface makes CORDIS simple to use even if you are not familiar with on-line information services. For experienced users, the standard Common Command Language (CCL) method of extracting data is also available.

CORDIS comprises eight databases:

- RTD-News: short announcements of Calls for Proposals, publications and events in the R&D field
- RTD-Programmes: details of all EC programmes in R&D and related areas
- RTD-Projects: containing 14,000 entries on individual activities within the programmes
- RTD-Publications: bibliographic details and summaries of more than 50,000 scientific and technical publications arising from EC activities
- RTD-Results: provides valuable leads and hot tips on prototypes ready for industrial exploitation and areas of research ripe for collaboration
- RTD-Comdocuments: details of Commission communications to the Council of Ministers and the European Parliament on research topics
- RTD-Acronyms: explains the thousands of acronyms and abbreviations current in the Community research area
- RTD-Partners: helps bring organisations and research centres together for collaboration on project proposals, exploitation of results, or marketing agreements.

For more information and CORDIS registration forms, contact
ECHO Customer Service
CORDIS Operations
BP 2373
L-1023 Luxembourg
Tel.: (+352) 34 98 11 Fax: (+352) 34 98 12 34

If you are already an ECHO user, please indicate your customer number.

European Commission

EUR 15853 — Community's research and development programme on radioactive waste management and storage - Shared cost action (1990-94). Annual progress report, 1993

Luxembourg: Office for Official Publications of the European Communities

1994 – VII, 772 pp., num. tab., fig. – 21.0 x 29.7 cm

Nuclear science and technology series

ISBN 92-826-8397-4

Price (excluding VAT) in Luxembourg: ECU 76

In December 1989, the Council of Ministers of the European Union adopted the fourth R&D programme on 'Management and storage of radioactive waste' for the period 1990 to 1994.

Contract negotiations for selected research proposals lead to the signature of contracts with some 115 bodies in charge of carrying out the working programme. This annual report, covering 100 contracts running in 1993, presents for each contract the objectives, the whole research programme and a synopsis of progress and results achieved as prepared by the contractor under the responsibility of the project leader.

Part A deals with the study of management systems, treatment and characterization of waste, general aspects of the waste disposal and the safety of geological disposal systems. The ongoing activities on construction and operation of underground facilities in candidated geological media for disposal are presented in Part B.

Venta y suscripciones • Salg og abonnement • Verkauf und Abonnement • Πωλήσεις και συνδρομές • Sales and subscriptions • Vente et abonnements • Vendita e abbonamenti • Verkoop en abonnementen • Venda e assinaturas

BELGIQUE / BELGIË

Moniteur belge /
Belgisch staatsblad

Rue de Louvain 42 / Leuvenseweg 42
1000 Bruxelles / 1000 Brussel
Tél. (02) 512 00 26
Fax (02) 511 01 84

Jean De Lannoy

Avenue du Roi 202 / Koningslaan 202
1060 Bruxelles / 1060 Brussel
Tél. (02) 538 51 69
Télex 63220 UNBOOK B
Fax (02) 538 08 41

Autres distributeurs/
Overige verkooppunten:

Librairie européenne/
Europese boekhandel

Rue de la Loi 244/Wetstraat 244
1040 Bruxelles / 1040 Brussel
Tél. (02) 231 04 35
Fax (02) 735 08 60

Document delivery:

Credoc

Rue de la Montagne 34 / Bergstraat 34
Bte 11 / Bus 11
1000 Bruxelles / 1000 Brussel
Tél. (02) 511 69 41
Fax (02) 513 31 95

DANMARK

J. H. Schultz Information A/S

Herstedvang 10-12
2620 Albertslund
Tlf. 43 63 23 00
Fax (Sales) 43 63 19 69
Fax (Management) 43 63 19 49

DEUTSCHLAND

Bundesanzeiger Verlag

Breite Straße 78-80
Postfach 10 05 34
50445 Köln
Tel. (02 21) 20 29-0
Telex ANZEIGER BONN 8 882 595
Fax 202 92 78

GREECE/ΕΛΛΑΔΑ

G.C. Eleftheroudakis SA

International Bookstore
Nikis Street 4
10563 Athens
Tel. (01) 322 63 23
Telex 219410 ELEF
Fax 323 98 21

ESPAÑA

Boletín Oficial del Estado

Trafalgar, 27-29
28071 Madrid
Tel. (91) 538 22 95
Fax (91) 538 23 49

Mundi-Prensa Libros, SA

Castelló, 37
28001 Madrid
Tel. (91) 431 33 99 (Libros)
431 32 22 (Suscripciones)
435 36 37 (Dirección)
Télex 49370-MPLI-E
Fax (91) 575 39 98

Sucursal:

Librería Internacional AEDOS

Consejo de Ciento, 391
08009 Barcelona
Tel. (93) 488 34 92
Fax (93) 487 76 59

Llibreria de la Generalitat
de Catalunya

Rambla dels Estudis, 118 (Palau Moja)
08002 Barcelona
Tel. (93) 302 68 35
Tel. (93) 302 64 62
Fax (93) 302 12 99

FRANCE

Journal officiel
Service des publications
des Communautés européennes

26, rue Desaix
75727 Paris Cedex 15
Tél. (1) 40 58 77 01/31
Fax (1) 40 58 77 00

IRELAND

Government Supplies Agency

4-5 Harcourt Road
Dublin 2
Tel. (1) 66 13 111
Fax (1) 47 80 645

ITALIA

Licosa SpA

Via Duca di Calabria 1/1
Casella postale 552
50125 Firenze
Tel. (055) 64 54 15
Fax 64 12 57
Telex 570466 LICOSA I

GRAND-DUCHÉ DE LUXEMBOURG

Messageries du livre

5, rue Raiffeisen
2411 Luxembourg
Tél. 40 10 20
Fax 49 06 61

NEDERLAND

SDU Overheidsinformatie

Externe Fondsen
Postbus 20014
2500 EA 's-Gravenhage
Tel. (070) 37 89 880
Fax (070) 37 89 783

PORTUGAL

Imprensa Nacional

Casa da Moeda, EP
Rua D. Francisco Manuel de Melo, 5
1092 Lisboa Codex
Tel. (01) 69 34 14
Fax (01) 69 31 66

Distribuidora de Livros
Bertrand, Ld.ª

Grupo Bertrand, SA

Rua das Terras dos Vales, 4-A
Apartado 37
2700 Amadora Codex
Tel. (01) 49 59 050
Telex 15798 BERDIS
Fax 49 60 255

UNITED KINGDOM

HMSO Books (Agency section)

HMSO Publications Centre
51 Nine Elms Lane
London SW8 5DR
Tel. (071) 873 9090
Fax 873 8463
Telex 29 71 138

ÖSTERREICH

Manz'sche Verlags-
und Universitätsbuchhandlung

Kohlmarkt 16
1014 Wien
Tel. (1) 531 610
Telex 112 500 BOX A
Fax (1) 531 61-181

SUOMI/FINLAND

Akateeminen Kirjakauppa

Keskuskatu 1
PO Box 218
00381 Helsinki
Tel. (0) 121 41
Fax (0) 121 44 41

NORGE

Narvesen Info Center

Bertrand Narvesens vei 2
PO Box 6125 Etterstad
0602 Oslo 6
Tel. (22) 57 33 00
Telex 79668 NIC N
Fax (22) 68 19 01

SVERIGE

BTJ AB

Traktorvgen 13
22100 Lund
Tel. (046) 18 00 00
Fax (046) 18 01 25
30 79 47

ICELAND

BOKABUD
LARUSAR BLÖNDAL

Skólavördustíg, 2
101 Reykjavik
Tel. 11 56 50
Fax 12 55 60

SCHWEIZ / SUISSE / SVIZZERA

OSEC

Stampfenbachstraße 85
8035 Zürich
Tel. (01) 365 54 49
Fax (01) 365 54 11

BĂLGARIJA

Europress Klassica BK
Ltd

66, bd Vitosha
1463 Sofia
Tel./Fax 2 52 74 75

ČESKÁ REPUBLIKA

NIS ČR

Havelkova 22
130 00 Praha 3
Tel. (2) 24 22 94 33
Fax (2) 24 22 14 84

MAGYARORSZÁG

Euro-Info-Service

Honvéd Europá Ház
Margitsziget
1138 Budapest
Tel./Fax 1 111 60 61
1 111 62 16

POLSKA

Business Foundation

ul. Krucza 38/42
00-512 Warszawa
Tel. (2) 621 99 93, 628-28-82
International Fax&Phone
(0-39) 12-00-77

ROMÂNIA

Euromedia

65, Strada Dionisie Lupu
70184 Bucuresti
Tel./Fax 0 12 96 46

RUSSIA

CCEC

9,60-letiya Oktyabrya Avenue
117312 Moscow
Tel./Fax (095) 135 52 27

SLOVAKIA

Slovak Technical
Library

Nm. slobody 19
812 23 Bratislava 1
Tel. (7) 220 452
Fax : (7) 295 785

CYPRUS

Cyprus Chamber of Commerce and Industry

Chamber Building
38 Grivas Dhigenis Ave
3 Deligiorgis Street
PO Box 1455
Nicosia
Tel. (2) 449500/462312
Fax (2) 458630

MALTA

Miller distributors Ltd

PO Box 25
Malta International Airport
LQA 05 Malta
Tel. 66 44 88
Fax 67 67 99

TÜRKIYE

Pres Gazete Kitap Dergi
Pazarlama Dagitim Ticaret ve sanayi
AŞ

Narlibaçhe Sokak N. 15
Istanbul-Cagaloğlu
Tel. (1) 520 92 96 - 528 55 66
Fax 520 64 57
Telex 23822 DSVO-TR

ISRAEL

ROY International

PO Box 13056
41 Mishmar Hayarden Street
Tel Aviv 61130
Tel. 3 496 108
Fax 3 648 60 39

EGYPT/ MIDDLE EAST

Middle East Observer

41 Sherif St.
Cairo
Tel/Fax 39 39 732

UNITED STATES OF AMERICA / CANADA

UNIPUB

4611-F Assembly Drive
Lanham, MD 20706-4391
Tel. Toll Free (800) 274 4888
Fax (301) 459 0056

CANADA

Subscriptions only
Uniquement abonnements

Renouf Publishing Co. Ltd

1294 Algoma Road
Ottawa, Ontario K1B 3W8
Tel. (613) 741 43 33
Fax (613) 741 54 39
Telex 0534783

AUSTRALIA

Hunter Publications

58A Gipps Street
Collingwood
Victoria 3066
Tel. (3) 417 5361
Fax (3) 419 7154

JAPAN

Kinokuniya Company Ltd

17-7 Shinjuku 3-Chome
Shinjuku-ku
Tokyo 160-91
Tel. (03) 3439-0121

Journal Department

PO Box 55 Chitose
Tokyo 156
Tel. (03) 3439-0124

SOUTH-EAST ASIA

Legal Library Services Ltd

Orchard
PO Box 0523
Singapore 9123
Tel. 73 04 24 1
Fax 24 32 47 9

SOUTH AFRICA

Safto

5th Floor, Export House
Cnr Maude & West Streets
Sandton 2146
Tel. (011) 883-3737
Fax (011) 883-6569

AUTRES PAYS OTHER COUNTRIES ANDERE LÄNDER

Office des publications officielles
des Communautés européennes

2, rue Mercier
2985 Luxembourg
Tél. 499 28-1
Télex PUBOF LU 1324 b
Fax 48 85 73/48 68 17

NOTICE TO THE READER

All scientific and technical reports published by the European Commission are announced in the monthly periodical '**euro abstracts**'. For subscription (1 year: ECU 60) please write to the address below.

15

CD-NA-15853-EN-C

Price (excluding VAT) in Luxembourg: ECU 76

OFFICE FOR OFFICIAL PUBLICATIONS
OF THE EUROPEAN COMMUNITIES

L-2985 Luxembourg

ISBN 92-826-8397-4

9 789282 683972