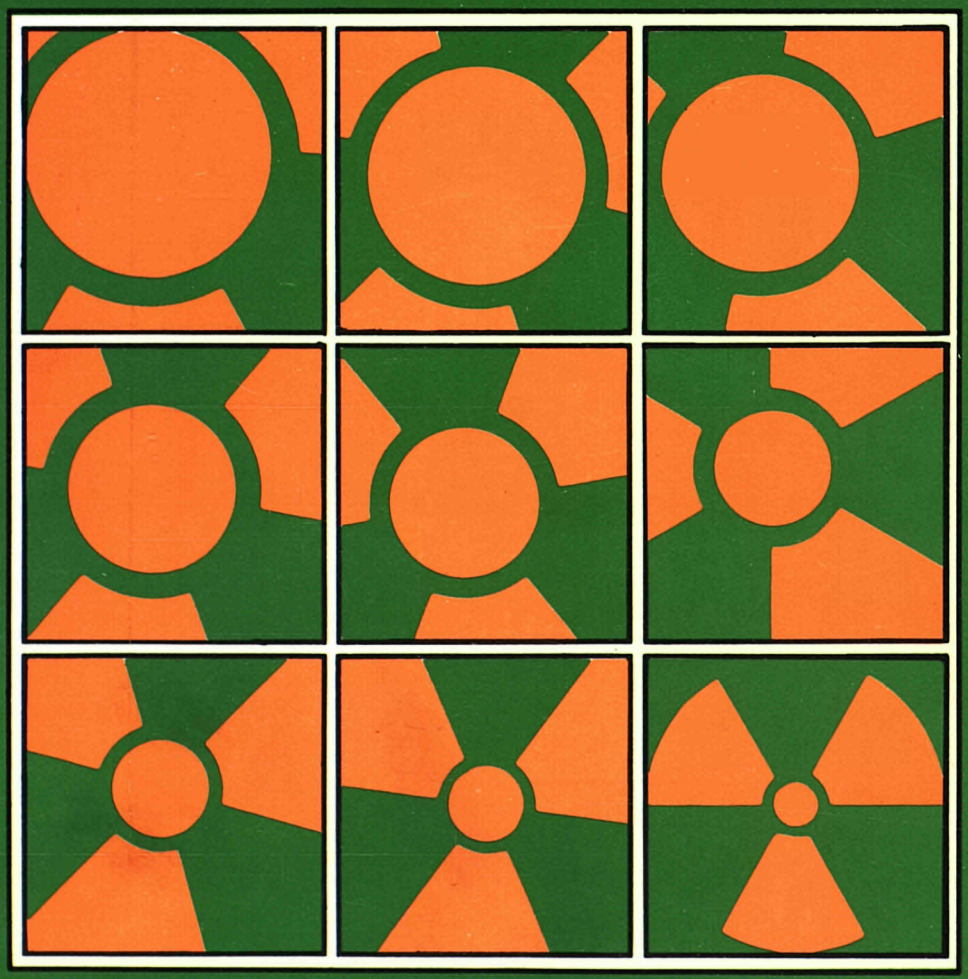
Commission of the European Communities

nuclear science and technology

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

Annual progress report 1991



Report

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Directorate-General
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Abstract

In December 1989 the Council of Ministers of the European Communities adopted the fourth R&D programme on "Management and Storage of radioactive waste" for the period 1990-1994.
Contract negotiations for selected research proposals lead to the signature of contracts with some 93 bodies in charge of carrying out the working programme. This annual report, covering the year 1991 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 running activities on construction and operation of underground facilities in candidated geological media for disposal is presented in part B.

CONTENTS

FOREWORD

This report covers the progress of research work and activities started and developed during 1991 in the framework of the five-year programme (1990-1994) of the European 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 Community 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 programme is subdivided in :

- Part A : Waste management and associated R&D projects.
- Part B : Construction and/or operation of underground facilities open to Community joint activities.

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 in 1991 of 93 contracts including 7 contracts for the Part B of the Programme.

The total amount of funding for the Community's contribution to the research cost is 79,6 million ECU over the five-year period.

The 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 Commmunity.

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 are presented as prepared by the contractors, under the responsability of the project leader(s).

The 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) and EUR-12761/Vol. 1 and 2 (for 1989). 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).

S. ORLOWSKI
Head, Radioactive Waste and
Fuel Cycle Division

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(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 No 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"

Topic 1	:	System studies
Topic 2	:	Harmonisation of radioactive waste management practices and policies
Topic 3	:	Comparative assessment of disposal practices in various management schemes for toxic and radioactive waste
Topic 4	:	Information of the public
Topic 5	:	Transmutation studies

Task 1

Topic 1 : System studies

Contract

FI2W/0037 Study on depleted uranium (tails) and on uranium residues from reprocessing with respect to quantities, characteristics, storage, possible disposal routes, and radiation exposure.

FI2W/0038 Systems analysis for a dual-purpose repository.

FI2W/0041 Waste management studies for large volumes of very low-level waste.

FI2W/0044 Treatment, disposal, re-use of building demolition and site cleaning wastes from nuclear facilities.

FI2W/0058 Study treatment of contaminated sodium with a view to decommissioning of FBR.

FI2W/0067 Studies of minimising transport of spent fuel.

Topic 2 : Harmonisation of radioactive waste management practices and policies

FI2W/0060 Assessment and proposal for activity limits for release of very low-level radioactive waste to landfills.

FI2W/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/0042 Comparison of safety assessment methods for toxic and radioactive wastes.

FI2W/0045 Study concerning the evaluation of toxic elements present in nuclear wastes.

FI2W/0061 Disposal of radioactive waste and toxic waste in underground repositories.

FI2W/0110 Use of methods and programmes developed in nuclear field for treatment and disposal of toxic and hazardous wastes.

Topic 4 : Information of the public

FI2W/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/0043 Information of the public in the field of decommissioning waste. Study of strategies and means for specific information.

FI2W/0074 The evolution and implementation of a public information strategy on radioactive waste management.

Topic 5 : Transmutation studies

FI2W/0103 Transmutation of long-lived radionuclides by advanced converters.

FI2W/0104 Participation in a CEC strategy study on nuclear waste transmutation.

FI2W/0106 Potentialities and costs of partition and transmutation of long-lived radionuclides.

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 practices 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 routes 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 practices 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 breeder reactors, with long-lived radionuclides added in a homogeneous or heterogeneous way. Advanced possibilities considered are spallation devices and reactors with special fuel types.

Title: Study on depleted uranium (tails) and on uranium residues from reprocessing with respect to quantities, characteristics, storage, possible disposal routes, and radiation exposure.

Contractors: NUKEM GmbH/Alzenau/FRG; WASTECHEM Ldt./Manchester/UK

Contract N°: FI2W-CT90-0037

Duration of contract: from 1.3.91 to 31.10.92

Period covered: 1.3.91 - 31.12.91

Project Leader: Dr. H J Wingender (NUKEM); J Doran (WasteChem)

A. OBJECTIVES AND SCOPE

The objectives of the study are to:

- determine the quantities and rates of accumulation of **depleted uranium tails** arisings from enrichment of natural uranium in the past and the foreseeable future (until about 2010 A.D.),
- allocate these data to the storages currently in existence,
- characterise the substances with respect to their chemical, physical, and radiological properties,
- identify and quantify possible ways to use and/or to dispose of these quantities.

Estimates of radiation and dose rate levels will be made for the different treatment steps. Similar investigations will be performed for **reprocessed uranium** as it is and for the **tails** generated by re-enrichment of the reprocessed uranium. Based on a predefined 20 GWe nuclear capacity scenario, the results for the three types of residues, ie. uranium tails, reprocessed uranium, and tails from the re-enrichment of this will be compared and conclusions derived.

B. WORK PROGRAMME

1. Basic data evaluation
2. Investigation of use or disposal of the materials
3. Relating the data to a predefined scenario
4. Safety considerations
5. Comparison and conclusions

C. PROGRESS OF WORK AND RESULTS OBTAINED STATE OF ADVANCEMENT

The study has proceeded generally in line with the expected timescale, although delay was experienced in obtaining the major portion of the data from the main operational sources of such materials. Although estimates could have been done, it was agreed that source data were vital for the study to be realistic and acceptable. With the exception of french facilities these data were finally obtained, and are now in the process of being collated and evaluated prior to investigation of the possible re-use or disposal of the materials.

Thus, task B1 - basic data collection and evaluation, is nearing completion, B2 - investigation of use or disposal of the materials, is now under consideration, B3 - relating the data to the predefined scenario, will follow thereafter, as soon as possible.

Wether the delays mentioned above can be recovered within the contract timescales, remains doubtful.

C.1 PROGRESS AND RESULTS BASIC DATA EVALUATION

The objectives of the study concern nuclear fuel cycle facilities in the UK, Holland, Belgium, and F.R.G.

C.1.1 Reprocessed Uranium (U_{re})

The reference facility in the UK for U_{re} is the BNFL reprocessing plant at Sellafield, UK which, inter alia, comprises a magnox reprocessing unit with a capacity of 1500 tonne/annum for magnox fuel, and the new Thermal

Oxide Reprocessing Plant (THORP), due to come on stream in late 1992 with a planned output of 700 tonne/annum within the first ten years.

The magnox plant handles fuel with a burn-up of 5-6 GWd/te U and a fuel cooling time of one year. THORP will reprocess AGR and LWR fuels with burn-ups of respectively, 20 GWd/te U, and 33-45 GWd/te U, both with cooling times of 5 years.

In Belgium the EUROCHEMIC plant was operated for 8 years (1966 - 1974) by an international board of thirteen menber countries. During this period the plant reprocessed 181 U tons of natural and low enriched uranium and about 31 tons of spent fuel elements from MTR, containing highly enriched uranium.

The unique plant operating in Germany (WAK) with a nominal capacity of 35 t_{HM}/year has ceased operation in 1990. Since 1971 200 tons nuclear fuel also from power reactors has been reprocessed . Small amounts of the reprocessed uranium are now stored there.

Other basic data collected for the product U_{re} comprise: product specification, homogeneity, current inventories and accumulated arisings to 2010 A.D., storage capacities, storage times, product characteristics, transport requirements.

Major composition differences exist between U_{re} and natural uranium (U_{nat}). U_{re} can be contaminated with transuranics (neptunium and plutonium), fission products (ruthenium and technecium) and minor uranium isotopes. The latter include U_{232}, which produces the high energy gamma emitter Tl_{208}, and U_{236}, a strong neutron absorber, nee-

ding increased U_{235} enrichment to compensate, and finally U_{234}, a very alpha active isotope, necessitating lower ingestion limits and stricter containment. Thus, decisions on prolonged storage and early re-cycle will be influenced by the above data. Tables I, II and III give detailed data on the uranium isotopes in fuel with varying enrichment, burn-ups and cooling times.

The effect of expected increased fuel burn-ups on the content of U_{232} on reprocessed uranium is shown in Figure 2.

All the data collected will be used in the consideration of use and/or disposal of U_{re}, on which subject much of the available information has been assembled.

C.1.2 **Uranium Tails**

Uranium tails from both enrichment of natural U and enrichment of U_{re} are generated in the reference enrichment plants in Holland, the former F.R.G. and the UK - all of which are operating under the international consortium Urenco Ldt.

The position of the tails in the nuclear fuel cycle is shown in Figure 1. Also the effect of the degree of enrichment, and storage times on the isotopic composition of uranium in the spent fuel as shown in Table I, II, and III; note particularly the concentrations of the two isotopes of concern, U_{232}, and U_{234}, in relation to the future use or disposal of U_{re} tails. Little of the transuranics, or fission products remain in the tails.

Although a diffusion plant operated in the UK at Capenhurst from 1953 to 1982, this was replaced by a centrifuge plant operated by Urenco since 1976 in co-operation with

two other plants, at Almelo in Holland and Gronau in Germany, all giving a combined output of 2,570,000 SWU/year.

Other relevant operating data for the plants have been collected, together with data on both types of tails, including, material specifications, inventories, annual arisings, accumulated stocks, storage capacities and transport requirements.

Additionally hazards are noted in dealing with both types of tails, which are fluorides, carrying the attendant risks of chemical exposure, and, in the case of U_{re}, the added content of transuranics and fission products, albeit minimal.

Having collated the above data, consideration is now being given to the possible use and/or dispoasal of the materials. This will be followed by re-arrangement of the data within the predefined 20 GWe scenario, so providing a standard for reference purposes.

Isotopic composition of Uranium as function of initial enrichment, nuclear burnup, after unloading (Unl.), and a five years cooling (Cool.) time after unloading

Table I: Burnup 33 GWd/tHM

Nuclide [%]	Enr. 3,2% Unl.	Enr. 3,2% Cool. 5 yrs	Enr. 3,5% Unl.	Enr. 3,5% Cool. 5 yrs	Enr. 3,8% Unl.	Enr. 3,8% Cool. 5 yrs
U-232	4,38E-8	1,33E-7	4,38E-8	1,28E-7	4,36E-8	1,24E-7
U-233	1,41E-7	2,20E-7	1,54E-7	2,34E-7	1,66E-7	2,46E-7
U-234	1,71E-2	1,77E-2	1,93E-2	1,99E-2	2,17E-2	2,22E-2
U-235	0,927	0,927	1,087	1,087	1,260	1,260
U-236	0,410	0,410	0,439	0,440	0,467	0,467
U-237	1,10E-3	3,83E-9	1,08E-3	3,63E-9	1,09E-3	3,43E-9
U-238	98,646	98,645	98,453	98,454	98,251	98,252

Isotopic composition of Uranium as function of initial enrichment, nuclear burnup, after unloading (Unl.), and a five years cooling (Cool.) time after unloading

Table II: Burnup 45 GWd/tHM

Nuclide [%]	Enr. 3,5% Unl.	Enr. 3,5% Cool. 5 yrs	Enr. 3,8% Unl.	Enr. 3,8% Cool. 5 yrs	Enr. 4,1% Unl.	Enr. 4,1% Cool. 5 yrs
U-232	9,34E-8	2,60E-7	9,41E-8	2,56E-7	9,42E-8	2,51E-7
U-233	1,59E-7	2,82E-7	1,77E-7	3,00E-7	1,89E-7	3,17E-7
U-234	1,59E-2	1,70E-2	1,80E-2	1,91E-2	2,01E-2	2,12E-2
U-235	0,656	0,656	0,775	0,775	0,905	0,905
U-236	0,491	0,491	0,528	0,529	0,564	0,564
U-237	1,41E-3	5,63E-9	1,45E-3	5,48E-9	1,49E-3	5,31E-9
U-238	98,835	98,835	98,678	98,678	98,510	98,510

Isotopic composition of Uranium as function of initial enrichment, nuclear burnup, after unloading (Unl.), and a five years cooling (Cool.) time after unloading

Table III: Burnup 50 GWd/tHM

Nuclide	Enr. 3,8%		Enr. 4,1%		Enr. 4,4%	
[%]	Unl.	Cool. 5 yrs	Unl.	Cool. 5 yrs	Unl.	Cool. 5 yrs
U-232	1,22E-7	3,27E-7	1,23E-7	3,23E-7	1,23E-7	3,18E-7
U-233	1,75E-7	3,19E-7	1,90E-7	3,37E-7	2,06E-7	3,55E-7
U-234	1,65E-2	1,80E-2	1,85E-2	2,00E-2	2,07E-2	2,20E-2
U-235	0,624	0,624	0,734	0,734	0,855	0,855
U-236	0,542	0,542	0,581	0,581	0,618	0,618
U-237	1,51E-3	5,52E-9	1,55E-3	5,42E-9	1,59E-3	5,29E-9
U-238	98,816	98,816	98,665	98,665	98,504	98,504

Figure 1: Source of Arisings of Uranium Tails in the Nuclear Fuel Cycle

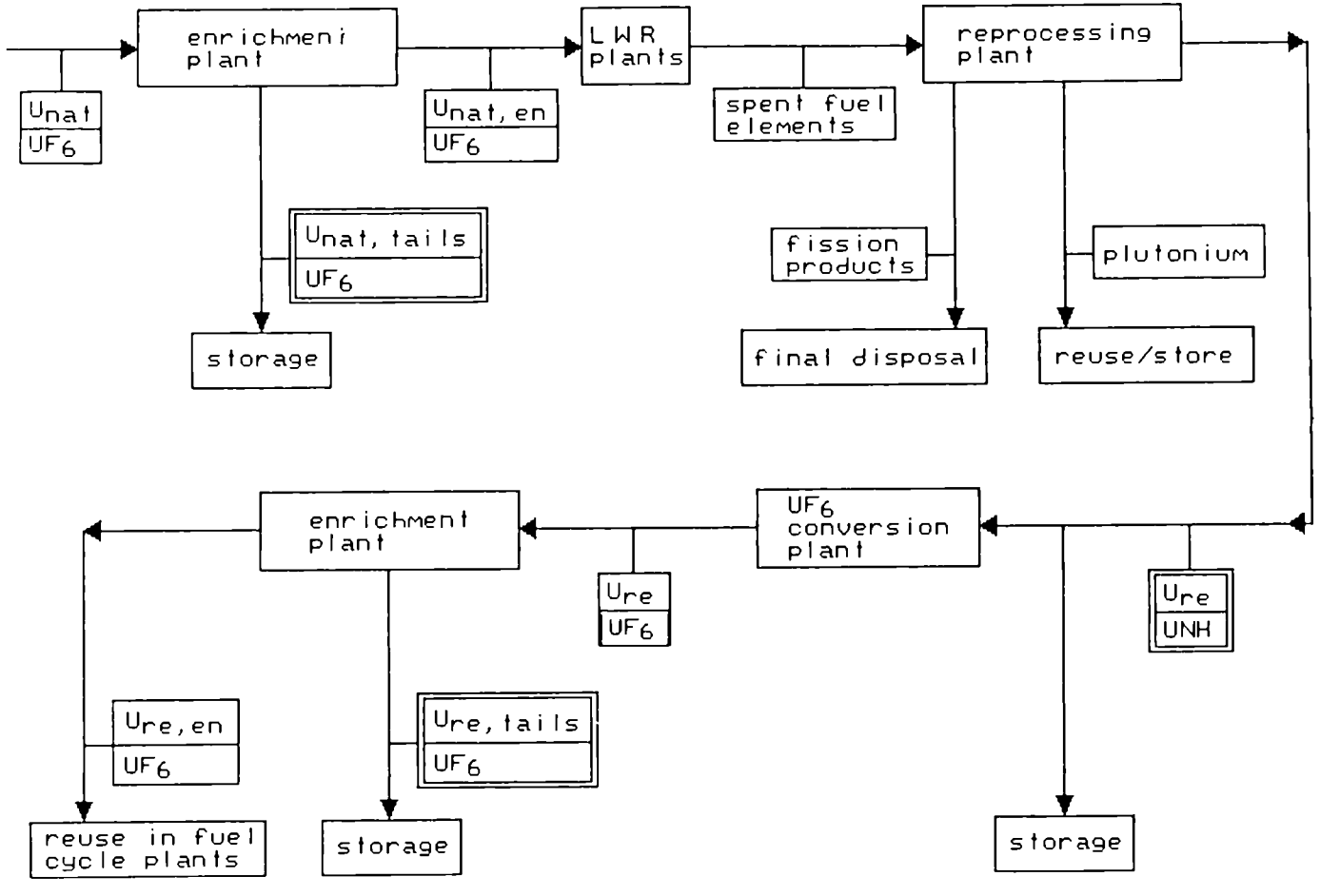
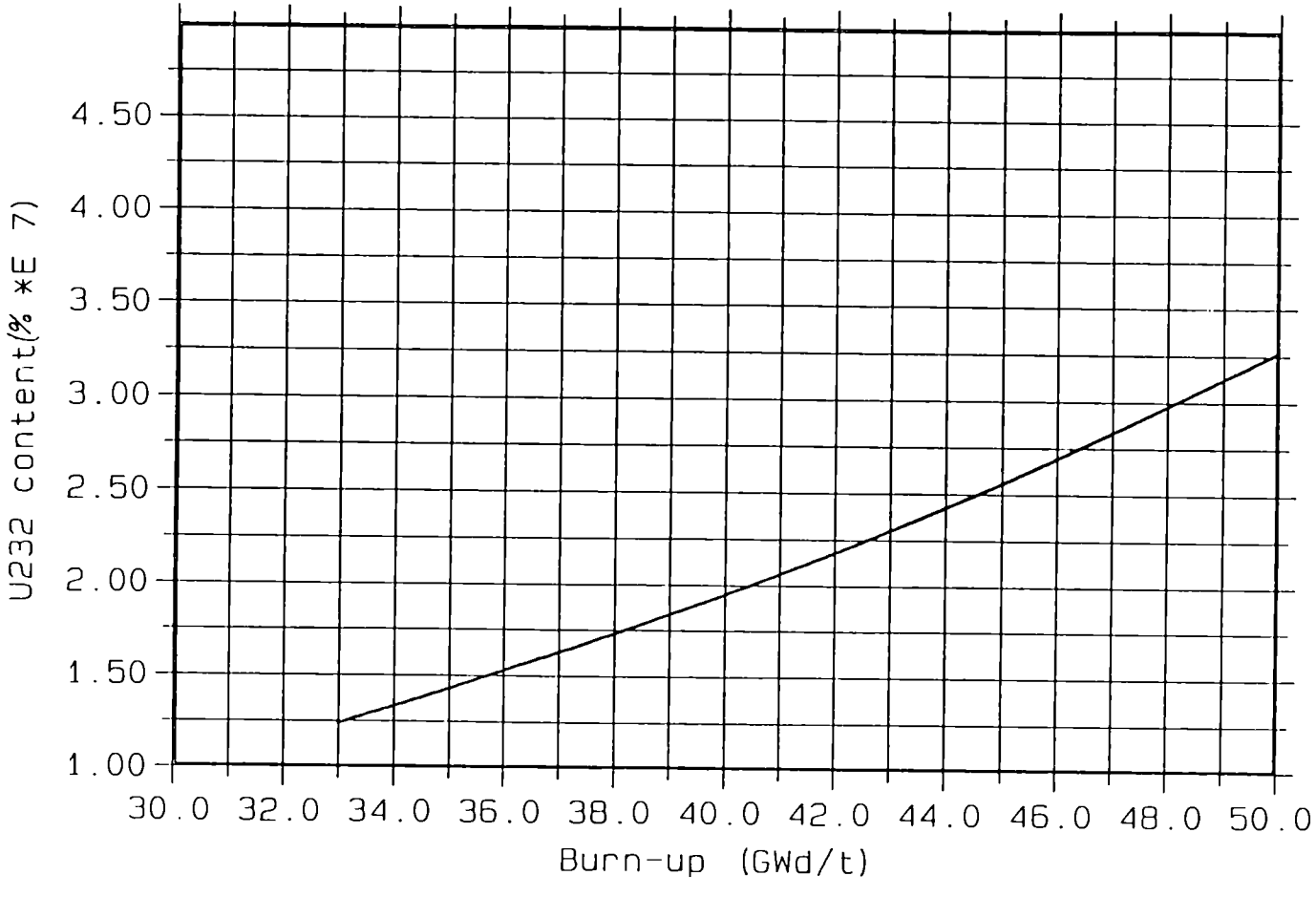


Figure 2: Increasing U_{232}-Content as Function of Burn-up;
Initial Enrichment 3,8% U_{235}; Cooling Time 5 years



Title: Systems Analysis for a Dual-Purpose Repository
Contractor: Kernforschungszentrum Karlsruhe GmbH
Contract No: FI2W - CT 90 - 0038
Duration of contract: February 1, 1991 - January 31, 1992
Period covered: 1991
Project Leader: R. Papp

A. Objective and Scope

For a repository in rock salt accommodating both heat generating waste from reprocessing and spent fuel, the most favorable combination of waste/spent fuel conditioning technologies and disposal alternatives is sought. The annual arisings of spent fuel are subject to fuel reprocessing and direct disposal, respectively, whereby the extent of both paths is determined by the Entsorgung* ratio.This type of analysis gained of importance after the German government ruled in 1985 that the spent fuel disposal technology be developed so that it could be included in the German approach to spent fuel management.

This analysis focuses on the underground part of the entire system, i.e., the repository. Beside the effects of heat in the near- and the far-field, the consequences of release scenarios are analysed in order to assess the long-term performance of the underground system.

In addition, economical and radiological aspects are considered, allowing to eventually compare the alternatives on a broad basis. The results will be included by the competent German authority submitting the licensing documents for the Gorleben exploratory mine.

B. Work Programme

1. Background: Fuel reprocessing is the German reference approach to spent fuel management but some sorts of spent fuel lend themselves to direct disposal.
2. Technical Concepts: Conditioning technologies for spent fuel and reprocessing waste are main requisites for making best use of the room available in model repositories.
3. Individual Analyses: The thermal loading associated with various disposal concepts is key to thermal and thermomechanical effects in both the near- and the far-field.
4. Evaluation: Concepts are sought which score highest with respect to a series of evaluation criteria.

* Entsorgung ist the versatile German term describing all steps at the back-end of the fuel cycle

C. Progress of Work and Obtained Results

State of Advancement

The situation in Germany resulting from the Atomic Energy Act is such that spent fuel reprocessing is mandatory as long as the underlying technology is economically sound. On the other hand the German government ruled in 1985 that direct disposal of spent fuel be developed as a back-up solution. This led, among other things, to the development of an adequate conditioning technology for spent LWR fuel. Based on this technical boundary condition, the effects on the host rock - salt - were evaluated for both reprocessing waste and spent fuel thereby anticipating a situation which is, most likely, going to be encountered in the prospective German repository.

One main concern of repository design is to make best use of the space available in the repository. This is accomplished by varying the emplacement pattern of the waste/spent fuel packages considered, taking fully into account a near-field design temperature of 200°C. Far-field analysis is focused on the interface between the salt dome and the overlying strata with special emphasis on possible tensile stress in this interface, thereby opening pathways to intrusion of brine. The possible consequences of such a scenario have been analysed.

Progress and Results

1 Background

The objective of the systems analysis is to establish a planning instrument for the repository accommodating both heat-generating waste from reprocessing and spent fuel. The analysis is based on 700 tons of spent fuel discharged annually from LWRs and, with less emphasis, spent fuel from the German HTR program. An Entsorgung ratio - the ratio of the amount of spent fuel being reprocessed or disposed of directly - was varied within a wide range with emphasis on the ratio 500/200.

2 Technical Concepts

The reference cask for spent LWR fuel disposal is dubbed POLLUX. It relies on a double-shell principle with the inner shell withstanding the lithostatic pressure at great depth (~ 1000 m) and the outer shell providing radiation protection so that the cask can be handled hands-on. In this study the cask accommodates the rods of eight PWR assemblies and the accompanying structural material. Its length and diameter are 5.5 and 1.5 m, respectively, its weight is 65 tons. It is emplaced horizontally in drifts and backfilled with crushed salt.

As an alternative a POLLUX-canister has been developed which holds the fuel rods of half a PWR assembly, the rods being cut into 1-m-pieces. This canister is of the same size as the one for vitrified high-level waste (HLW) from reprocessing (length 1.34 m, diam 0.43 m) thereby enabling it to be disposed of in deep vertical boreholes (300 m).

Heat-generating intermediate-level waste, ILW(Q), mainly stems from LWR fuel reprocessing and includes structural parts of the disassembling process, fuel cladding, and feed clarification sludge. The reference conditioning method consists in cementation and packaging in 400-l-drums, its disposal occurs in vertical borehole. Cemented waste must not be heated up higher than 100°C. Advanced treatment of ILW focuses on techniques such as compaction etc. without employing water. This allows higher thermal loads for the ILW and its coemplacement with HLW or spent fuel.

Concerning disposal, various geometric arrangements have been considered which all belong to one of the following three types: Borehole concepts,

drift concepts, a combination of borehole and drift emplacement. The main design basis for repository planning was the near-field temperature in the package/salt interface (200°C) while the temperature of conventionally treated ILW(Q) was limited to 100°C.

3 Individual Analysis

3.1 Near-Field Analysis

One main assumption affecting the temperature in the repository near-field is dealing with the compaction of backfill material (crushed salt) surrounding the packages disposed of in drifts. The initial porosity of the backfill was assumed to be 30 percent; its decrease is governed by an exponential law with a 5-year half-life which, in turn, makes the thermal conductivity of the backfill eventually reach the one of the ambient rock salt. The results of the area calculations for various disposal concepts and Entsorgung ratios can be summarized as follows: The space required in the repository can be made equal for spent fuel and reprocessing waste; spacings between packages are dominated by short-term effects (< 100 yr) which result from the main fission products in both spent fuel and HLW. Secondly, the space required for HLW in vertical boreholes and spent LWR fuel in horizontal drifts, respectively, is about equal; it is assumed that boreholes are 300 m deep while drift emplacement occurs on three horizons.

Thermomechanical calculations for the three emplacement horizons (870, 1020, and 1170 m) exhibited a strong dependence of room closure rates on both depth and pillar width between adjacent drifts. Room closure rates are of paramount importance for scenario analyses and associated releases (compare Sec. 3.3).

3.2 Far-Field Analysis

The heat generated by the emplaced waste/spent fuel causes the lithostatic pressure to rise in the emplacement zone while it leads to a pressure relief the closer one gets to the interface between salt dome and overlying strata ("salt mirror"). This effect for different geometric layouts, i.e., repository concepts, was studied by relying on a simplified model of the Gorleben salt dome with only four homogeneous zones. The resultant stress in the salt mirror does not differ significantly between the different concepts but can turn into tensile stress (~ 2 MPa) if unfavorable assumptions are made for salt creep. Maximal stress in the salt mirror is attained after about 35-45 years, which is significantly earlier than the occurrence of the maximum temperature in the emplacement zone itself.

3.3 Long-Term Safety Analysis

The release scenario underlying the long-term safety analysis is a combination of two scenarios, the first being the unlimited intrusion of brine via the main anhydrite, the second the drainage of an undetected brine pocket.

As pointed out in Sec. 3.2, stress-incluced fissures may develop in the salt mirror above the repository, especially at its intersection with the main anhydrite, thereby opening a pathway down into the infrastructure region of the closed-down repository located between the shafts and the main access drifts. Tensile stress in the salt mirror reaches its maximum 35-45 years after repository closure. As a life time of 40 years is assumed for the "dams"* sealing off the shafts from the infrastructure

* term used in Germany for large sealing structures

region, a best-estimate value of about 85 years for the onset of brine intrusion via the main anhydrite was used in deterministic calculations. In probabilistic calculations, the earliest time for brine intrusion is assumed to be right after repository closure, the latest after about 1000 years just before all void space has disappeared and the backfill material has reached the permeability of the ambient rock salt through consolidation.

The second scenario involves brine pockets with volumes ranging between a few and about 1000 m^3 that remained undetected during excavation work. A stress-induced drainage of brine into the emplacement zone may cause a mobilization of radionuclides at an early point in time. In addition, the brine could inhibit the consolidation of crushed salt, thereby keeping pathways open to the emplacement sites for an extended period of time. It is in line with the conservative approach chosen in this study to assume the most adverse location for the occurrence of this brine pocket which is close to an emplacement site in the vicinity of the main access drift.

The computer code EMOS /1/ has been developed to calculate the long-term radiological consequences for individuals due to the occurrence of the aforementioned scenarios. All EMOS runs performed relied on both accident scenarios combining the unlimited intrusion of brine into the infrastructure via the main anhydrite with the drainage of undetected brine pockets. Provided the amount of brine from the pockets is sufficiently large, it may leach out radionuclides and move on into the access drifts where it can delay the consolidation process of the backfill material, thereby enabling a contact with external brine. In case the volume of the brine pocket is not large enough the external brine can only flood the access drifts connecting the infrastructure zone with the first emplacement panel if this panel is relatively cold, thereby delaying backfill consolidation in the access drifts.

EMOS calculations with best-estimate parameters yield radionuclide releases only for 3-level drift emplacement with ILW(Q) conditioned conventionally, i. e. , with cement and if the cold emplacement panel is next to the access drifts from the infrastructure zone.

Monte-Carlo sampling of the input parameters produced radionuclide releases for about 15% of the associated 5000 EMOS runs performed for two disposal concepts (pure borehole concept, borehole & drift concept). Dose rate maxima exceed the limit of the German radioation prodection ordinance ($3 \cdot 10^{-4}$ Sv/yr) in about one out of 1000 runs.

Global sensitivity analysis in conjunction with Monte-Carlo simulations revealed six parameters to be overly important for the variability of dose rates associated with the borehole concept:

- reference room closure rate, temperature dependence of room closure, reduced closure of ILW and HTR borehohles
- dam permeability, the exponent relating porosity with permeability
- time of brine intrusion via the main anhydrite.

In the Monte-Carlo simulation for this concept relying exclusively on borehole emplacement the radionuclides U-233, Ra-226, I-129, and U-234 provide the main contribution to the dose rates

Sensitivity analysis for the concept combining borehole and drift emplacement provided a clear result only for one parameter - volume of the brine pocket -, while the ranking of the other parameters is not as straightforward. But still the parameters dealing with room closure and permeability are among the eight highest ranking parameters. In addition, two parameters characterizing the overlying strata come into the picture. The radionuclides which mainly cause the dose burden are Np-237, I-129,

Ra-226, and Cs-135; in some cases Ni-59, Se-79, and Tc-99 are of importance. The differences stemming from the nuclide spectrum are due to their various origins, either HLW, ILW, or spent fuel. The presence of U-233 is an evidence for HTR-fuel to be the source.

/1/ STORCK, R. et al., EMOS, Programmpaket zur Langzeitsicherheitsanalyse eines Endlagers für radioaktive Abfälle, Version 4, GSF-Bericht 32/90, Braunschweig (1990).

Title:	Waste Management Studies for Large Volumes of Very Low-Level Waste
Contractor:	Intera Information Technologies, United Kingdom
Contract N°:	FI2W-CT90-0041
Duration of Contract:	March 1991 - September 1992
Period Covered:	March 1991 - December 1991
Project Leader:	G M Smith

A. Objectives and Scope

A significant proportion of the radioactive material which arises on decommissioning of nuclear facilities contains only small amounts and low concentrations of radionuclides, either as surface contamination, or as activation products within the body of the material. The objective of this study is to investigate the implications for waste management systems of various levels and forms of exemption criteria and the corresponding implications for routing low-level waste materials arising from decommissioning. Following a review of the existing information on the volumes and radionuclide contents of the most significant low level materials which arise during decommissioning, and the current legislative background relevant to the disposal, recycling or reuse of such materials, the study will investigate the full range of radiological implications of adopting alternative clearance levels now under consideration. A number of related factors, such as volumes of materials which would require disposal as "radioactive" waste, the timing and the degree of dismantling, and the requirements for waste packaging are also addressed.

B. Work Programme

B.1. Characterisation of the waste arisings, the options for the management of the arisings, and the exemption principles and criteria within which the options have to be applied.

B.2. Ranging of parameters which characterise the system identified in B.1, particularly those associated with the formulation of exemption.

B.3. Evaluation of the radiological impacts following adoption of the relevant sets of parameter values characterising the system.

B.4. Evaluation of the implications for routing of wastes following adoption of alternative formulations and levels for exemption by means of a comprehensive assessment and sensitivity analysis.

C. Progress of Work and Obtained Results

State of Advancement

The work carried out during the year 1991 has focussed mainly on the items B1 and B2 of the programme, and are now essentially complete. The various large volume, low level wastes from decommissioning of nuclear facilities have been identified, quantified and characterised. This has been accomplished by conducting a wide-ranging review of recent open literature, including that resulting from Community Programmes. A short review of the options for management of these arisings has been completed. These include unrestricted release, and various forms of controlled release via particular routes, such as the disposal of solid material to near surface and deep geologic facilities. The various forms of exemption principles and criteria under discussion internationally have been summarised and formulations relevant to the kinds of waste and release options described. A detailed progress report on the above has been produced /1/.

Following on from the above, work has commenced on the quantification of the radiological and other implications of adopting different formulations and levels for exemption, taking into account the management options identified. This has involved the setting up of computer models and data for the quantification of the impact of the various routing options and exemption levels, and the use of previously published studies relevant to this work.

Progress and Results

1. Characterisation of the System (B.1. and B.2.)

Decommissioning of nuclear power reactors and other plant associated with the nuclear fuel cycle will give rise to large volumes of low level waste material (concrete, steel and other metals) and used components (such as motors and valves). Available information on low and very low level arisings contained in studies conducted by government agencies, international bodies and operators was reviewed. Of particular interest was the possibility that subsequent to a practical (ie. modest) monitoring programme or even the specification of the particular waste stream itself (such as contaminated concrete away from the main sources of activity in particular facility types) the characterisation of radionuclide content can be sufficiently known or adequately inferred as to justify appropriate routing of significant amounts of the waste. Such knowledge would be particularly useful in allowing efficient management of such wastes in the light of their large volumes and low radionuclide contents. In addition, very low level streams which appear to be the strongest candidates for exemption were identified.

It was discovered that the greatest research effort to date on the characterisation of decommissioning waste has been concentrated on research and power reactors. The total inventories and the specific concentrations of radionuclides are substantially dependent on both facility type (PWR, gas cooled reactors) and operating history. In particular, the specific activities of radionuclides in materials removed in stage 2 decommissioning for a particular facility are difficult to predict prior to dismantling, and due to the shortage of characterising measurements, are subject to the greatest uncertainty. Much of the information in detail was found to relate to single installations and therefore difficult to apply more generally owing to the variability

referred to above.

For a wide range of waste streams (eg. contaminated and activated concrete, contaminated metals, including mild and stainless steel) a significant fraction of the total radionuclide inventory, even at the very low levels, occupies only a small fraction of the total volume. In addition, much of the total waste volume was found to contain only natural concentrations of radionuclides. Many ways of presenting inventory data in the literature tend to obscure this. Semi-empirical estimates of radionuclide dispositions for generalised waste streams, together with theoretical considerations, suggest that underlying concentration distributions are relatively similar and can be justifiably applied to many waste streams not subject to detailed radionuclide monitoring.

Notwithstanding the inventory variations referred to above considerable agreement was found among the studied research findings on the relative importance of radionuclides in various waste streams and the fractions of the total mass of materials which may be candidates for some form of recycling or unrestricted disposal. Between about 30% and 80% of reactor steels which become contaminated away from the reactor core region can be recycled, whereas much higher fractions of low level activated and contaminated concrete can be classified as "inactive" under existing legislative frameworks.

Depending on such factors as radionuclide content, physical and chemical form, volume, ease of dismantling and definitions of what comprises radioactive material, large volume waste streams may be considered for one or more of the following management options:

i) storage, temporary or indefinite
ii) unrestricted recycle/reuse/disposal
iii) restricted/controlled recycle/reuse
iv) processing and disposal as radioactive waste.

The features and relevance of these options for large volumes of low level materials arising during decommissioning were discussed in the context of the wastes arising (above), and the exemption principles and criteria reviewed below. It was noted that in general treatment of material as radioactive as distinct from "inactive" involves a greater financial overhead and that the potential for practical recycling certain very low active materials (such as steels) is considerable.

The final aspect of the characterisation of the decommissioning waste management system addressed comprised a review of exemption legislation within and outside the European Community. National and international provisions for the exemption of low level materials from the requirements of licensing and control were reviewed in the context of the types of waste materials arising during decommissioning and the options for disposal and recycling. Issues addressed included the various "clearance" levels in force or under consideration by various countries (these usually specify activity or radionuclide activity per unit area or mass), together with the broader considerations of the various definitions of the "practice" subject to any exemption, potential monitoring problems at low levels and the mass or area over which any numerical limit would apply. Notwithstanding the lack of firm international consensus in this area, considerable agreement in principle was found both in terms of the general approach to exemption and the numerical clearance limits proposed.

The above work is described in detail in reference /1/.

2. Radiological Evaluation and the Implications for Waste Management Systems (B.2, B.3. and B.4.)

Work is in progress to quantify the radiological implications of adoption of relevant sets of parameter values which can characterise the waste management system as a whole. The radiological impacts which arise at each stage of the management of decommissioning wastes (maximum and individual doses and collective dose commitments) will be estimated in the main using appropriately constructed assessment models and relevant available data. In this context pertinent previous research findings have been used. However, the need to ensure internal consistency in the present study, together with the necessary conciseness of the presentation of much of the previous numerical work precluded significant savings in effort in this regard.

In order to be as comprehensive as possible regarding the management options considered, doses to operational personnel and to the general public were estimated for the widest possible range of identifiable practices associated with these options. These included the dismantling and decontamination processes, the transport of low level material to final disposal or processing (recycling) facilities, operational and long term impacts of disposal, and operational and long term impacts of the recycling. In most cases the exposures which arise from normal practices are of primary concern, although where possible, accidental occurrences, such as intrusion into completed waste disposal facilities, are addressed. Following the standardised characterisation carried out in tasks B.1. and B.2. of low level materials the calculational methodology will allow the radiological and other implications of the application of various exemption criteria applied to the numerous waste streams to be investigated.

References

/1/ Charles, D and Smith G M, Waste Management Study for Large Volumes of Very Low Level Waste from Decommissioning of Nuclear Installations, Intera Information Technologies Report IE2713-1 Version 1, CEC Progress Report on Task 1 under Contract FI2W-CT90-0041 for the CEC, October 1991.

Title: Treatment, Disposal, Re-Use of Building Demolition and Site Cleaning Wastes from Nuclear Facilities

Contractors: NUKEM GmbH, FRG; WasteChem Limited, UK; SGN, F
Contract No: FI2W-CT90-0044
Duration of contract: February 91 - October 92
Period covered: February 91 - December 91
Project Leaders: H.J. Wingender (NUKEM), J. Doran (WasteChem), H. Cadiou (SGN)

A. OBJECTIVES AND SCOPE

The study concerns waste materials arising from building demolition and from site cleaning activities associated with decommissioning of nuclear facilities. The study does not consider wastes such as dismantled and/or disassembled process equipment, radioactive process inventories, etc., as these wastes are assumed to have been removed from the facilities prior to building demolition and site cleaning.

The objectives are:
- Establish an overview of building demolition and site cleaning wastes arising from various types of fuel cycle facilities (enrichment, fuel manufacturing, power reactors, reprocessing, waste treatment, spent fuel encapsulation).
- Consider sampling, monitoring and analysis tools enabling the characterization and classification of these wastes.
- Classify these wastes according to a 3 class scheme (release for unrestricted use, release for restricted use only, radioactive waste) and describe possible ways of re-use or disposal.

Information from FRG, UK and France is to be used. Three partners contribute to the study (NUKEM GmbH-FRG: enrichment, fuel fabrication, reactors, fuel encapsulation; SGN-F: reprocessing, waste treatment; WasteChem-UK enrichment, fuel fabrication, reactors, reprocessing, waste treatment).

B. WORK PROGRAMME

The programme of the study is structured according to following tasks (see time schedule, Figure 1):

B.1 Collection and compilation of waste data and characterization (3 partners)

B.2 Investigation of sampling, monitoring and analysis tools (NUKEM)

B.3 Material classification and investigation of re-use and disposal possibilities (3 partners)

For standardization purposes, the information obtained is to be re-arranged in such a way that it reflects the waste arisings, etc., as to be expected from a 20 GWe fuel cycle scenario (equivalent to 600 metric tons of heavy metal per annum).

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The study is currently in line with the initial time schedule, i.e., task B.1 is approaching completion, tasks B.2 and B.3 are under investigation.

It has to be mentioned that considerable difficulties occurred during the data collection and compilation phase; difficulties such as: data accessibility, completeness, interpretation, consistency and comparability. As result: the man power needed exceeds the initial ideas, the data handling and the re-arrangement procedures have become difficult and have required the use of a computerized data bank and related evaluation codes. This tool has become even more important when the classification task according to different national regulations was started.

Although the study has not suffered from any delay yet, it cannot be concluded that this situation will continue.

Progress and results

C.1 Determination of the waste arisings

The objectives of the study concern various facilities in the nuclear fuel cycle.

C.1.1 Facilities in Federal Republic of Germany

For each reference nuclear facility in Germany - enrichment, fuel fabrication, nuclear power, and encapsulation plant - the following information is filed nearly completely on the data bank:

- general description of the operational characteristics
- radionuclide content, distributions, concentrations in the structure material and surface dose rate levels
- compilation of waste arisings (see Table I)

According to the scope of the programme, the results from different countries and different facilities must be compiled in a unified scheme and parameters concerning the possible variations of radionuclide concentration limits and dose levels with corresponding uncertainties evaluated. The scheme produced forms a basis for comparisons. In this regard, a data bank was created and a computer programme development begun. For the data evaluation, at first, general premises and assumptions were necessary to establish which can be derived from the experiences of different decommissioning studies and on plant operational data.

The following decontamination procedure can be assumed: In the first stage, a dose level distribution of the surface is evaluated by monitoring. When the total surface is contaminated a thin layer is removed. This procedure was repeated un-

til only hot spots are detected. Then this part of the wall is removed up to few centimeters depth. When no significant dose rate is detected the demolition is carried out. Based on this data, different methodologies of demolition procedures and waste treatments can be discussed. Different areas are fitted with stainless steel liners. In this instance, total removal of the liners has proven as more effective.

The data bank system created contains the following information for each area with different dose rate levels, radionuclide compositions and operational parameters:

- area description
- surface dimensions
- dimension of the surface liner (thickness and material)
- thickness of removal layer (concrete)
- part of the surface where hot spots are positioned
- thickness of removal wall in the hot spot area
- expected release of radioactive material and/or activation products (content, distributions, concentrations, dose levels)
- reduction factors of radioactive material by decontamination procedures before demolition phase

With this information, the waste arising and its characterization can be evaluated. The parameters may be varied including the time period between shutdown and the start of demolition.

For determination of the radioactive content before demolition a classification of different areas is accomplished with regard to different dose rate levels and to different operating procedures during the operational phase. The contamination is caused by release of radioactive material, by activation and by transferring radioactive material out of the contaminated area to other areas. From the operating data the release rates of radioactive material, the activation rate of shielding materials, the possibilities for transfer of radioactive material out of hot areas, and the remaining contamination was determined.

In reality no nuclear facility according to the scenario fuel cycle currently exists in decommissioning phase. Thus, a model was developed re-arranging the data in relation to existing facilities either in operation or under construction. For each area the released radioactive material generating contamination and the activation products were adjusted to the throughput of fissile material and to the plant factor, for instance the throughput of the reference encapsulation facility is 35 tons heavy material, the reference plant factor of the nuclear power plant is 250 MWe. Only the areas which can be contaminated are concerned. Other buildings are not taken into account.

C.1.2 Facilities in the UK

This section reports on progress to date on this study for all the fuel cycle facilities in The UK, i.e., enrichment, fuel fabrication, reactors, reprocessing and waste treatment.

Waste arisings are calculated from construction volumes with the split of intermediate wastes/low level wastes (ILW/LLW) derived from in-cell/out-cell proportions for earlier plants, and from material types for later plants. Packing factors are then applied to these raw volumes.

Work has proceeded from the early 1980's in assessing the global decommissioning waste quantities, based on materials of construction and an ILW/LLW split, where, essentially, it is assumed all plant and equipment (P & E) in process cells are contaminated and therefore ILW; other materials are assumed to be non IWL. No trace or non-active waste categories are assumed.

For later plants, waste arisings were similarly derived from construction volumes but the IWL/LLW split was based on estimates of IWL/LLW proportions for different types of material, i.e., concrete, reinforcement, pipework, steelwork, P & E, and for different categories of plant. Packing factors for the various materials were applied to the raw ILW volumes, assuming packaging into 12 m^3 boxes for disposal.

A more detailed approach, as indicated above, was used for assessing the total volumes arising in the demolition of later plants.

a) First the respective volumes produced by the demolition of all fuel cycle plants - including and excluding foundations removal - were sought. Secondly, the closer categorization of IWL and LLW was investigated, in order to facilitate ILW segregation for ultimate deep disposal under todays regulatory requirements. The method used was to obtain all major construction materials quantities from records or estimates, for all later plants. Using these data, waste arisings from demolition were converted to volumes (m^3) and then subjected to a conversion factor (CF) eg. the CF for concrete is 1 (packed volume as installed volume), and CF for ducting is 0.036 (using a typical cross section and reduction factor of 10).

b) Then for each waste type (concrete, ducts, etc.) and for each plant category, factors were produced using the projected level of IWL contamination and the degree of difficulty in decontamination and dismantling of each plant.

   Thus, to the total values derived for waste volumes, a) above, these factors were applied to give the volume of IWL for each plant. For disposal into 12 m^3 boxes a packaging factor for each type of waste had to be applied eg. concrete 2.1, ducting 6.8, etc.

c) Foundation volumes were calculated, assuming a 2 meter foundation for all plants, and using the available or calculated total plant surface areas.

The principal items of the above methodology are also applied to reactor decommissioning, much of the original data produced was for gas cooled graphite moderated reactors. This methodology is now being applied to the UK's first PWR Sizewell "B", and volumes of waste arisings from demolition estimated.

The philosophy for reactor decommissioning in the UK has been changed recently to one known as the Deferred Safestore Strategy.

The revised strategy for reactor decommissioning using a delaying a safestore period until about 135 -150 years after shutdown has shown that the cost can be reduced by about 25 %. This is achieved by using the radioactive decay of reactor activated radionuclides, making safe dismantling a much safer task, and reducing the quantity of radwaste for disposal either to deep repository (IWL) or near surface repository (LLW).

For all the nuclear fuel cycle facilities in UK, a vast amount of data has to be produced; although the work is well under way, it is not yet complete. When enough data have been produced, these will be evaluated, and then related to the 20 GWe scenario. Thereafter task B3, classification, re-use and disposal, considerations will be completed.

C.1.3 Reprocessing plants in France

To estimate the structure demolition wastes the data from decommissioning assessment studies of COGEMA reprocessing plants has been used. Cells of reprocessing plant have been classified in eight categories, in relation to the radiation level left after equipments have dismantled, and considering an alternate option of final cleaning of walls and floors. From the radiation level, surface contamination has been evaluated in each category considering that 20% of the wall contamination have migrated into the wall thickness. Furthermore, there was considered that:

- the non-contaminated cells have been demolished separately as dismantling activity,
- steel frame has been dismounted,
- caped penetrations have been left into floors and walls, after decontamination,
- then, the building has been crashed down, concrete block crushed into parts of 15 to 20 cm, and wastes laid out.

Afterwards, there has been assumed that:

- methods of measuring activity of bulk materials would have been engineered (to try to classify the produced wastes),
- residual contamination values will be part of regulations procedures.

- surface contamination sharing out keeps regularly during dismantling of equipment,
- sharing out of the radionuclides is homogeneous which is not true as activity spectrum is not the same for any facility.

The waste arisings compilation is shown in Table II.

C.2 Sampling, Monitoring and Analysis Tools

The research programme has been concerned with a category of measuring techniques to detect localized areas of gamma emitting radionuclides, the radionuclide content in the removal structure material, probe sampling techniques and classification of waste packages.

Using the sampling technique, the activity is determined at grid points up to a depth where the material is free of radioactivity. The advantage of this method is the precise determination of the radionuclide content and its distribution. Furthermore, the radionuclides emitted beta, alpha and low energy gamma ray can be detected. The principal difficulty is that the activity is estimated at grid points. To estimate the activity at locations between the points it is necessary to make assumptions of the activity distributions. The experiences in this area show that a linear interpolation is in good agreement with the measurement data. More sophisticated models and using statistical analysis procedures should be useful for measurements with more efficiency.

To determine surface contaminations the adaptive moving detector system /1/ seems to fulfill the criteria applicable in this area. The detection limit of 10^5 Bq is attainable for the 662 keV gamma ray of Cs-137 near surface using likelihood ratio techniques. This system uses a special analysis code for error determination. Thus, a complete data evaluation is obtained. More precise estimation of data is available accumulating a spectrum over a longer time period. However, a short measuring time is demanded. Thus, a special measuring programme has to be created to attain a reduction of waste quantities in an acceptable measuring time.

Measuring systems for the dose rate determination on the surface of waste packages are established and sufficiently precise for waste classification. In the case of detecting fissile material and/or alpha emitters the passive and/or active neutron measurements are available. The detection limit is 100 mg $Pu_{effective}$ in a 200 l drum. This limit is not sufficient for waste disposal in land burial. Developments in this area could be successful to attain a detection limit of 1 mg $Pu_{effective}$ for waste before conditioning /2/.

In the case of non-destructive examination techniques for large radioactive waste packages, the experiments and the routine measurements demonstrate the applicability of a monitoring system /3/. The accuracy of these measurements depends

on: design of detectors and collimators, material distribution and probe location, shieldings. The detection limit for containers (cross section < 1.2 m x 1.2 m) is 10^3 Bq Co-60 even with steel shielding of 2 cm thickness.

Measurement systems are developed in the area of radioautography. In this case a fairly high radionuclide content is necessary. These methods are not important for waste classification and will be not considered in the study.

C.3 Material Classification

The classification of waste material governs the categorization of the material as
- radioactive waste
- ready for restricted use
- ready for unrestricted use.

The limits are given by the respective national regulations which differ from country to country.

C.3.1 Federal Republic of Germany

For classification of the wastes, the criteria are set down in the Radiation Protection Ordinance. The values of allowance (A) are specified for each radiotoxic nuclide. The material arising in the protected area can be classified as unrestricted re-use if the mass related activity concentration is lower than a factor 10^{-4} of the value (A). The limits on surface contamination are 0.05 Bq/cm^2 for most alpha emitters ($A<5*10^3$ Bq), 5 Bq/cm^2 for beta/gamma (electron capture) emitters ($A<5*10^6$) and 0.5 Bq/cm^2 for remaining radionuclides. No mass or surface area restrictions apply to any of these values. Even if these limits will not be exceeded, a further demonstration of tolerability is to be performed by assessing the expected radiation exposure for realistic re-use scenarios. Unrestricted use or recycling is permissible if the specific activity of the material does not exceed 0.1 Bq/g.

C.3.2 France

Two targets are generally involved that lead to fix up rules and especially values of residual contamination:
- one concerns the classification of industrial plants
- the other concerns the reuse, indeed the exemption of radiological control, of materials which have been used in nuclear facilities.

In France classification of industrial plants in Nuclear Plants (INB) and in Installations Classified for Protection of Environments (ICPE) involve the following rules:
- one INB can only contain $3.7*10^{14}$ Bq of total activity. Note that a facility can be an INB, so the whole site can be.
- an authorized ICPE can contain $3.7*10^{10}$ Bq.
- if activity is less than $3.7*10^8$ Bq, access to the facilities is free.

Rules for reuse of materials are:
- Rubbish drums must not receive any contaminated material.
- Present regulations apply to any waste the activity of which is higher than 100 Bq/g.
- Up to now no deminimus value has been fixed up; would this value reach a few Bq/g, monitoring and measuring low activity would have to be developed for controlling bulk materials.
- At present, all projects of reusing decontaminated materials outside nuclear sites, must have the agreement of the National Authorities.
- Values proposed by the French Safety Authorities:
  a) 10 Bq/g and 50 Bq/cm^2 whatever the radionuclide is.
  b) 10 Bq/g and 0.5 Bq/cm^2 for α-emitter (U & Pu).
  c) 10 Bq/g and 10 Bq/cm^2 for U and Pb-210.

In fact, a considerable amount of man power is required and the extensive time necessary to make severe controls, few parts or materials leave the nuclear sites.

The calculation of average value of mass contamination in Bq/g was carried out from the following data:
- the total surface activity is the activity measured after dismantling
- the volume of concrete is the volume of the structure

Assuming that a homogeneity of the radioactive material can be made by crushing the wastes, the mass activity is less than 1 Bq/cm^2; the hot parts, before demolition, have been eliminated by sawing the pieces in small parts.

Uncertainties must be considered as to classification and as to eventual reuse of materials, although the mass activity of wastes, calculated as here above indicated, is much less than 1 Bq/g.

At present, in France, wastes with an average mass activity less than 1 Bq/cm^2 would be stored in near surface disposal.

REFERENCES

/1/ McMAHON, T.D., GRAY, P.W., D`Er, A.M., NABOULSI, A.H., KOUTSOYANNOPOULOS, C., EUR 13071 EN, 1990

/2/ SIMON, G.G, EYRICH, W.,Proceedings Spectrum '90, 1990

/3/ AULER, I., HELK, F., NEUKÄTER, E., Zimmermann, U., NIS-report, Hanau (FRG), 1990

Table I: Radioactive and Non-radioactive Material (reference facilities, FRG)

Facility	Concrete Mg	Steel Mg
Enrichment[1]	190 000	19 000
Fuel Fabrication[1]	58 000	4 300
PWR[2]	150 000	5 900
Encapsulation[1]	85 000	7 700

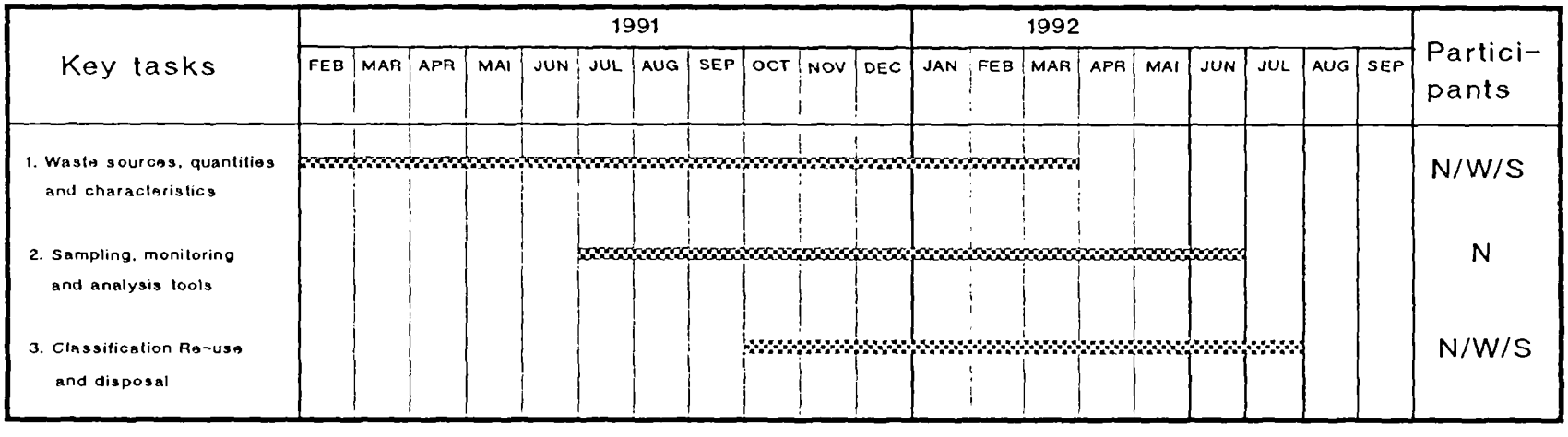
[1]) control and surveillance area
[2]) control area

Tabel II: Reinforced Concrete Quantities 600 t/year Plant, France

Facility Area	Surface m^2	Concrete m^3
Shearing Dissolution	25 100	12 550
Separation U-Pu	32 740	16 370
U-Purification	16 700	5 000
Pu-Purification	16 300	4 075
Vitrification	18 300	10 050
Liquid Waste Treatment	40 600	10 150
Pools	51 000	13 000
Reagents	8 160	2 015
Solid Wastes	18 200	4 550
Outside Trenches	534	190

Figure 1: Time schedule for work programe.

Title: "Treatment, Disposal, Re-use of Building Demolition and Site Cleaning Waste from Nuclear Facilities"



Legend:

N: NUKEM GmbH - FRG

W: WasteChem - UK

S: SGN - F

Title : Study Treatment of Contaminated Sodium with a View to Decommissioning of FBR
Contractor : CEA - IA - FRAMATOME
Contract No: FI2W-CT90-0058
Duration of contract : from April 1991 to April 1993
Period covered : March 1991 - December 1991
Project leader : CEA : Mr LATGE
IA : Mr HANEBECK
FRAMATOME : Mr de SEROUX

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" and FRAMATOME, and the German INTERATOM GmbH. CEA is the coordinator of the project.

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 propose an optimized scenario for sodium destruction or recycling, employing a technical and an economic point of view. Moreover a Research & Development (R&D) orientation will be provided to improve the selected scenario and to allow a better understanding of fundamental processes.

B. WORK PROGRAMME

To perform the above scope of work, five main stages must be achieved :

1. 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 to set the scenarios to be proposed later on are set.

2. Assessment of sodium behaviour and characteristics :

From an estimated contamination, provided by mathematical models which have been validated using experimental data, it is possible to predict the behavior and characteristics of the sodium to be treated.

3. 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 axes are defined, according to the required level of knowledge in the waste treatment domain.

4. Main scenarios :

Using the previous steps as a reference, main scenarios are reviewed, with both a technical and an economic vision. This twofold approach allows the working group to select

the scenarios to be analysed.

5. Best available scenarios :

These processes, having been defined as suitable scenarios for sodium treatment, will be described. Further needs for R&D programs will be 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.

A first semestrial report was published on November 27th, 1991, /1/. It described the sodium balance and the sodium pollution. The main findings of this report were presented during the "Radioactive Waste Management Task 1 - Progress Meeting", held in Brussels on October 22nd, 1991.

This annual report summarizes the main points of the ongoing studies and presents the planned actions for 1992.

The milestones with regard to the sodium treatment in a decommissioning framework presented on figure F1.

C.II. INVENTORY OF THE SODIUM NEEDS

The inventory of the sodium needs has been established using available data on existing FBRs, on a worldwide approach. The chart T1 summarizes the sodium quantities potentially contaminated, which will be considered as a waste to be reprocessed.

Some reactors are already shut down, either due to obsolescence or because the assigned objectives have been achieved.

In the ECC, two units are in this status : RAPSODIE (1983) and KNK (1991). The sodium of both plants is mainly used for laboratory tests and waste processing experimentation. These units are not integrated into the global waste account.

In the Commonwealth of Independent States (CIS), BOR 60 was shut down in 1988.

For the near future, the scheduled decommission of the FBRs would be the following:

* ECC		* OTHERS	
PFR :	1994	EBR-2 :	1993
PHENIX :	2003	BN 350 :	2002
SUPERPHENIX :	2015	FFTF :	2010
		JOYO :	2010
		BN 600 :	2010
		FBTR :	2015
		MONJU :	2023

To illustrate the sodium inventories, in a European context, the estimated balance has been identified /2/.

It is important to pinpoint the impact of the EFR programme, or future European FBRs, on the graph F2.

Using the assumption that the contaminated sodium can be recycled for use in the two first EFR units, the balance shows that it will be necessary to supply sodium for EFR 3, in 2018.

In 2022, 8000 tons more have to be added, as 8000 tons of contaminated sodium are also recycled.

Concerning the international approach to sodium management, programs are not yet settled. We guess that two FBRs will be in operation in the CIS, in 2005. This accounts for 3360 tons which have to be supplied.

For other countries such as China, Japan or India, future involvements are not yet clearly identified. We do not integrate these opportunities in the global balance /3/. This global balance is illustred on the figure F3.

Assuming the FBR programs are clearly identified and the first units are in operation in the 2010's, the sodium recycling can be considered as an attractive way to manage the waste problem.

Otherwise, if the operating experience on existing reactors shows some projects need to be delayed, the final treatment of sodium has to be re-evaluated.

C.III. ASSESSMENT OF SODIUM BEHAVIOUR

3.1. Sodium characterization /4/

Sodium is an alkaline metal, with a single stable nuclide : ^{23}Na.

Under a neutron flux, five radio nucleides are generated :

^{20}Na, with a half life of	.23	seconds,
^{21}Na, with a half life of	22.8	seconds,
^{22}Na, with a half life of	2.6	years,
^{24}Na, with a half life of	14.9	hours,
^{25}Na, with a half life of	60	seconds.

Under the scope of this study, only ^{22}Na has to be considered as a radioactive significant isotope.

Like the other alkaline metals (M), sodium reacts with water and oxygen :

$$M + H_2O \rightarrow M(OH) + \tfrac{1}{2}H_2$$

This is an exothermic reaction with potential for self inflammation and hydrogen release.

3.1.1. Physical characteristics :

* The melting point is 97.9°C and the boiling point is 882°C.

* The volumic mass is given by :

$\varrho = A + B\theta + C\theta^2 + D\theta^3$

ϱ : Volumic mass, in Kg/m^3

θ : Temperature, in °C

$A = 950,0483$

$B = - 0,2297537$

$C = - 14,60 \times 10^{-6}$

$D = 5,637 \times 10^{-9}$

3.1.2. Chemical characteristics :

* With regard to oxydo-reduction potential, sodium has a potential value of 2.7 V. So in an acid media, the reaction is:

$Na + H^+ \rightarrow Na^+ + ½ H_2$

* In various gaseous environments, the behaviour is :
  - Oxygen : Spontaneous burning begins at 150°C in air, and at 100°C if the sodium is in drop form,
  - Hydrogen : Formation of hydride begins spontaneously at 100°C,
  - Water : Formation of caustic soda and hydrogen release, in a strongly exothermic reaction,
  - Alcohol : Formation of alcoholates. As the reaction is less vigorous than with water, alcohol is a good reagent for sodium cleaning,
  - Carbon dioxide : Sodium combustion is activated by the carbon dioxide decomposition at hight temperatures,
  - Na_2CO_3 : Inert with sodium,
  - N_2 : Inert with sodium.

3.2. Sodium as a heat transfer medium

Sodium is mainly used in FBRs because it possesses a good thermal conductivity (71.6 W/m°C). This figure is rather high so sodium can efficiently transfer significant thermal flux from the core to Steam Generators.

However the impurities have to be held as low as possible, in order to limit the radioactive background of the primary coolant.

The specification of Nuclear grade Sodium is summarized on table TII.

3.3. Sodium pollution and contamination

The sodium is first polluted, as soon as it fills the circuits for the first time.

Nevertheless, in operation, the pollution is mainly attributed to oxygen, hydrogen and water ingress, from new assemblies surfaces, from adjustments on the pools gaseous protection and heavy component maintenance.

Another important pollution source is attributed to hydrogen diffusion, through steam generator to primary systems, from Steam System to primary sodium.

About contamination, cesium, activated sodium and tritium are the three main factors which will require further purification process developments and waste reprocessing scenarios.

If, on the primary side, the sodium activation seems to be an unavoidable contamination to deal with, cesium purification (from fuel releases) and tritium eliminations (mainly due to nuclear reactions) are potential elements to be looked at, in the search for an optimized sodium management.

On the secondary side, the sodium is circulated through heat exchangers, to ensure the heat transfer to the steam system. It is not affected by activation phenomena and the contamination is due to tritium which migrates from the primary side to the steam system.

The already begun point 2 "sodium behavior" and point 3 "purification processes" of this particular study must present significant results in the near future.

References :

/1/ de SEROUX, JEAN - Etude du traitement du sodium contaminé en vue du démantèlement des RNR - FRAMATOME - NOVA-NOV 20172 INV.

/2/ Nuclear Europe Magazine - November1985

/3/ Directory of Nuclear Reactor IAEA

/4/ Nouveau traité de Chimie Minérale - Tome II - Paul PASCAL - 1966

Table TI : Sodium quantities by country and by class of reactor
Thermal power : MW - Sodium inventory : metric tons.

	Unit	Country	Design	Thermal Power	Sodium (Primary Side) (1)	Sodium (Global Inventory) (2)
Experimental Reactors	RAPSODIE	France	Loop	40	37	57
	KNK	Germany	Loop	58	19	77
	EBR 2	USA	Pool	62	286	327
	FERMI 1	USA	Loop	200	-	-
	FFTF	USA	Pool	400	406	605
	FBTR	India	Loop	42	27	71
	BOR 60	CIS	Loop	60	16	41
	JOYO	Japan	Loop	100	126	199
Prototypes	PHENIX	France	Pool	563	800	1281
	PFR	U.K.	Pool	670	850	1150
	BR 350	CIS	Loop	1000	470	920
	MONJU	Japan	Loop	730	912	1675
Commercial units	SUPERPHENIX	France	Pool	3000	3300	5540
	BN 600	CIS	Pool	1470	770	1600

(1) The sodium used on the "Primary Side" is directly in contact with fuel elements. It is activated and mainly contamined by corrosion products, cesium and tritium. The spent fuel storage capacities are included in these figures.

(2) The global inventory is the amount of sodium used in the FBRs. It is composed by the sodium on the primary side and by the sodium used in the intermediate loops, between the reactor and the steam generators.

Table TII : Specification of Nuclear Grade Sodium (French Requirements)

Element	Typical content (ppm)
Calcium	< 10
Baryum	5
Carbon	30
Sulphur	30
Chlorine + Bromine	20
Boron	5
Lithium	10
Silver	3
Uranium	0,01
Potassium	300

Other very low impurities (< 5 ppm) : oxygen, aluminium, bismuth, copper, tin, magnesium, molybdenum, nickel, lead, titanium, ...

Figure 1 : Main milestones

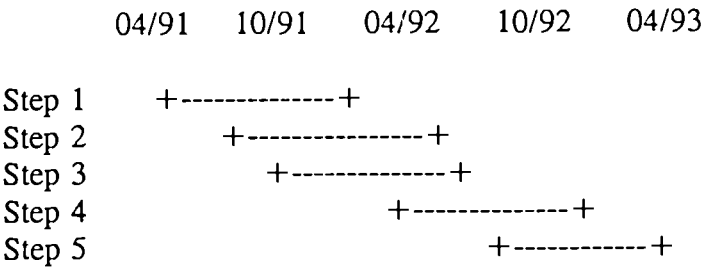


Figure F2 : Balances of Sodium needs and contaminated quantities (Europe)

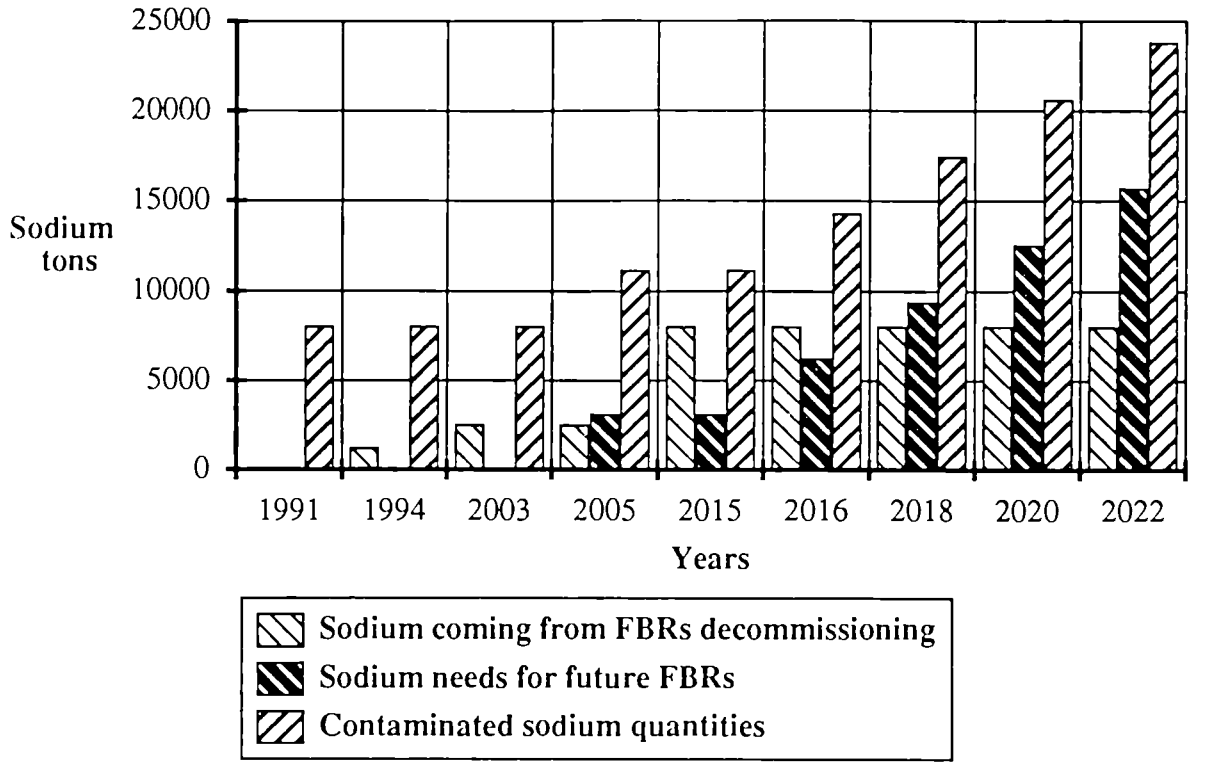
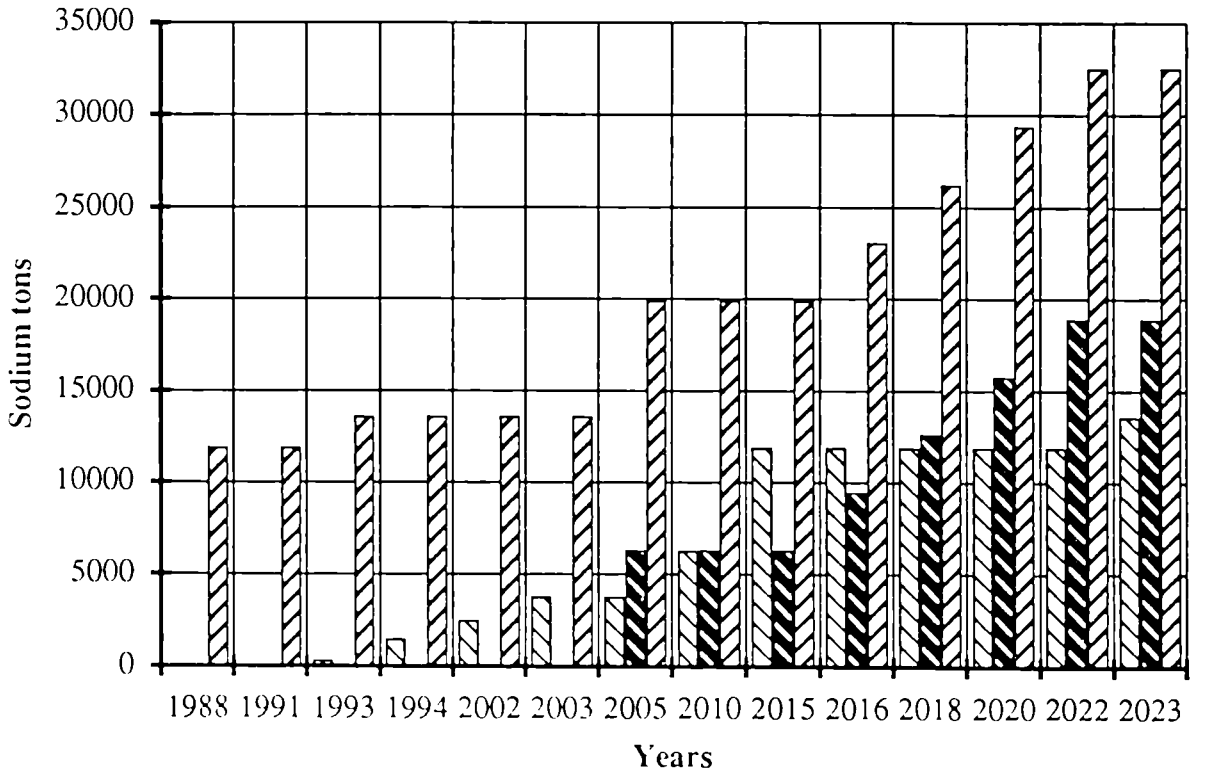


Figure F3 : Balances of Sodium needs and contaminated quantities (World)



Title : Studies of Minimising Transport of Spent Fuel
Contractor : BAeSEMA
Contract No: FI2W-CT90-0067
Duration of contract : September 1991 to February 1993
Period covered : September to December 1991
Project leader : Jonathan B. Taylor

A. OBJECTIVES AND SCOPE

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 fuel using multi-attribute utility analysis and linear programming techniques.

The objectives are therefore:

- to define two realistic, illustrative 'base case' scenarios for the management of spent fuel and a framework for analysing their cost, transport requirements and environmental impact using an enhanced version of the DISPOSALS model
- to define the data needed for analyses, and collect data for illustrative cases
- to enhance, test and document the DISPOSALS model
- to carry out illustrative analyses and report on the results.

B. WORK PROGRAMME

1. Task 1: Formulation of the Problem

The costs and environmental impacts which need to be taken into account will be identified and a high level design document setting out the structure of the analytic model will be prepared.

2. Task 2: Data Requirements

A report describing the model's data requirements will be produced.

3. Task 3: Data Collection

The best available data meeting the requirements identified in Task 2 will be collected and a summary report produced.

4. Task 4: Model Development

Building upon the previous DISPOSALS work, a revised model will be developed to enable the illustrative analysis to be carried out.

5. Task 5: Illustrative Analysis

Using the revised model an illustrative study will be carried out based on the scenarios developed under Task 1.

PROGRESS OF WORK AND OBTAINED RESULTS

Statement of Advancement

Work on the contract started in September 1991 and is currently concerned with Task 1 of the main programme: "Formulation of the Problem". This task is subdivided into the following main activities:

a) preparation of an overview of the general situation in the EC and specific states
b) developing a management system for data control and analysis
c) selection of scenarios to form the basis of model
d) identification of Model Enhancements
e) strategy for the study.

Activity is currently centred on the preparation of an overview, with some aspects of setting up a data management system being concurrently addressed. In order to prepare the overview, a literature survey has been conducted, including a database search by the British Library Environmental Information Service. This indicates that data relating to the forecast expansion of nuclear power programs (and hence transported waste/spent fuel volumes) beyond the year 2000 is scarce or not widely published, which will hinder our development of an authenticated model for the coming decades. Similarly, published data, understandably, concentrates on transport of waste/spent fuel in terms of the reprocessing cycle.

A discussion paper "Outline Requirements for Radioactive Waste Transport Minimisation Model" was prepared in October and made available at the Progress Meeting. This paper will form a baseline from which to initiate the remaining activities in the first Task and provide a starting point for the report on the Task.

Progress and Results

1. Task 1: Formulation of Problem

The discussion paper on the outline requirements for a radioactive waste transport minimisation model considers the basic framework that will be required for the study in terms of the multi-attribute analysis/linear programming approach to be adopted. It provides an outline of the main features of the model which will be developed, including the overall setup of the model, options for the basic scenarios (centring on the main Waste Management Strategies available, namely reprocessing and conditioning of spent fuel for direct disposal) to be compared, and which decision variables (such as choice of route, reactor burnup, etc) may be amendable to adjustment within the model to minimise impacts. Consideration is also given to data types and requirements. As such, the paper provides initial input and a starting point for most of the sub-tasks addressed in Task 1, as listed above.

It has become clear that the detailed situation, current and forecast, for the whole of Europe cannot be modelled within the scope of this contract, and the overall setup for the model should be based on the actual and forecastable situations in a limited, representative, selection of states. A suitable selection may be Germany, the UK and Sweden on the basis that: Germany has a similar sized nuclear programme to the 20 GWe scenario used in the earlier Task 3 studies, has made most advances on the direct disposal option and contains several potential final disposal sites on which data is available; Sweden relies entirely on transport of wastes and spent fuel by sea; and the UK is a major reprocessor of both German and Swedish spent fuel.

Before embarking on a more detailed definition of the model setup and basic scenarios, it was decided that a better understanding and an overview of the current and, as far as possible, future situation in Europe and its component states was required. Currently, literature has been gathered on:

- historic, current and extrapolated nuclear power capacity in the EC
- historic, current and extrapolated nuclear power capacity in member states
- historic, current and, where available, future predictions of spent fuel processing and/or storage strategies in the EC and member states
- historic, current and, to a limited extent, future models of transport, quantities, turnaround times, etc.

These data are being used to build up the overview from which to extract and develop a realistic, though clearly simplified, subset as the basic model setup. It is also giving a clearer indication of what data will be required as a prelude to the main Data Requirement Definition Task (Task 2) and where it will be necessary to extrapolate or make assumptions.

Title: Assessment and proposal for activity limits for release of very low-level radioactive waste to landfills

Contractor: CEA/IPSN, France and ONDRAF/NIRAS, Belgium
Contract No.: FI2W/CT-90/0060
Duration of contract: April 91 - March 93
Period covered: April 91 - December 91
Project leader: Ph.Guetat (CEA/IPSN, coordinator), A. de Goeyse (ONDRAF/NIRAS)

A. OBJECTIVES AND SCOPE

In the frame of studies dealing with exemption of particular streams from regulatory control, the project aims to establish acceptance criteria for municipal and industrial landfill for unconditionnal and conditionnal exemption.

Correspondances between level of exposure and levels of radioactivity will be established.

From this work, it will be possible to derive specific and surface activity levels corresponding to acceptance criteria for landfill for the two types of exemption.

B WORK PROGRAMME

Three steps have been defined:

F and B : Analysis of landfill disposal technics of industrial and municipal waste.

A particular attention is paid to the regulatory context and on working conditions encountered in the different installations.

Evaluation of the waste streams, at the level of some to hundred $Bq.g^{-1}$ for the most radiotoxic nuclides.

F : Development of a radioprotection code CERISE, to establish the relations between exposure and radioactivity of waste, including a data bank for dose conversion factors.

Evaluation of the exposures resulting of the water pathway using the code GEOLE (geosphere) and ABRICOT (biosphere).

Separate calculations will be persued for workers and public.

F and B : Establishement of the correspondance between exposure and specific and surface activities of the wastes.

Proposal of levels of radioactivities for the waste acceptance in the different type of landfill and for different dose criteria.

Final report

C PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

CEA

Phase 1 and 2 are well in advance. No measurement has been done presently in the landfills.

First data concerning waste streams have been received. They only concern operating "non radioactive waste" production in reactors.

Phase 3 has already started on generic basis.

ONDRAF

Phase 1 is achieved concerning regulation aspects. Dust measurements are in progress on a industrial landfill (class 1) site . From preliminary contacts with some producers, it appeared difficult to estimate quantities of exemptable waste. Therefore additional direct measurements or indirect estimation will be requested.

Progress and results

CEA

Information concerning regulation has been collected and the synthesis is practically achieved.

Visits have been done and scenarios of exposure have been determined. Three types of landfills will be studied: large and small landfills for municipal waste and one for industrial waste.

The code CERISE includes 18 reference scenarios based on the four pathways of exposure : external irradiation, contamination, inhalation and ingestion.

Calculations establish the relation between surfacic, specific and/or total activities, and doses. Results can be expressed as doses for an average activity unit, or as average activities for a set of reference doses (defined for the different scenarios analysed).

In this last case, it selects automatically the lowest value obtained and the corresponding scenario.

When several plants are concerned by a practice, results are given for each plant and the minimal activity for the whole practice is extracted with the associated limiting plant and summarized in a single table.

The data bank include presently 120 radionuclides and 10 dose conversion factors for each radionuclide.

The code has been transfered on PC.

Particular calculations for tritium and C14 have still to be included.

Most of the report on CERISE has been written.

Data requirements have been adressed to ONDRAF to run the code GEOLE and ABRICOT for the Belgium sites.

ONDRAF

1 LEGAL AND TECHNICAL CONTEXT OF LANDFILLING IN BELGIUM

Notwithstanding the regionalisation of this matter, we can assume in a first approach, bearing in mind the specific aspects of this study, that classification and operation conditions of landfills are quite similar in Flanders and Wallonia (Brussels region has no landfill).

Industrial non toxic waste is assigned to class 1 landfill, whereas inert waste is intended to class 3 landfill.

We paid no further attention to class 2 landfills (household waste or waste assilimated to it) for the following reasons :

- most of the exemptable streams belong obviously to waste dedicated to class 1 or 3 landfills ;
- some marginal streams could theoretically be assimilated to household waste, but their origin (nuclear sector) will be a major obstacle to the assimilation procedure

In the context of burial of exempted waste, we note for the class 1, a legal limitation of impact on the environment by :

- watertight bottom and sides by means of clay or plastic layer,
- treatment of percolates before release.

These pratices are not in force for class 3 landfills.

Regarding the potential exposure of workers to waste, we observed during visits on sites the folllowing :

- Manipulation of waste on a class 3 landfill is limited to a strict minimum (about 1 hour per day).

- Some recycling activities are often associated to class 3 sites, as granulation units for bricks and concrete, to produce balast for roads or industrial zonings. In such situations, the production of dust could have a significant influence on the exposure of workers to residual radioactivity (inhalation pathway).
- The stabilisation of industrial waste on a class 1 site occurs on a more rational basis, using full time staff and specific machines.

Dust measures are in progress on a class 1 site, and will be performed at several seasons and under different meteorological conditions.

Premilary results seem to confirm that potential inhalation of dust on such site is quite limited.

Measurements on a class 3 site with recycling facilities are also foreseen.

2. ESTIMATION OF QUANTITIES OF EXEMPTABLE WASTE

This aspect will be part of general inquiry on national scale, aiming to a better knowledge of radioactive waste, which will cover the following aspects :

- general description, origin, quantities ;
- physico-chemical properties ;
- radiological properties.

Indeed, in lack of any actual legal exemption procedure, a lot of producers have not a precise knowledge of the activity of their (very) low level waste.

A first problem encountered during these first contacts, is the need to take account of a potential "dilution at the source" of exemptable waste by conventional waste on the site of production. In fact, once waste is exempted from further regulatory control, it is directed to the non radioactive industrial waste stream and mixed with other such waste.

Given the legal context of conventional waste or wastewater where any kind of dilution is strictly forbidden, we opted for a conservative position, excluding this first dilution possibility.

In any case, we mean that the physical allocation of exempted waste on a landfill site will be more efficient, more constant and more measurable than any hypothetical "dilution at the source".

Two meetings of coordination have been organized between CEA/IPSN and ONDRAF.

REFERENCE

/1/ Presentation of the objectives, methodology and the project progress status in Brussels (October 1991)

Title : Definition of reference level for exemption of wastes, suitable for incineration
Contractor : CEA/IPSN, France and Empresarios Agrupados (EPTISA, GHESA, TRSA), Spain
Contract No: FI2W-CT90-0066
Duration of contract : January 1991 to June 1993
Period covered : 1 January 1991 - 31 December 1991
Project leader : O. Cahuzac (CEA/IPSN, coordinator), F. Andaluz (E.A.)

A. OBJECTIVES AND SCOPE

In the frame of studies intended for groups of experts to develop common criteria for exemption of particular waste streams from regulatory control, the project aims to give correlations between waste activity levels and the individual doses due to their incineration.

The approach for establishing radiological protection criteria for the incineration of very low level radioactive waste involves :

- The identification of possible waste management scenarios including : sources terms, incinerator data, composition of wastes streams, mode of disposal or reuse of the residues.
- The establishemt of dose levels corresponding to incineration of very low level radioactive burnable material in a classical installation.
- The establisment, for each scenario defined, of environment pathways and dose assessments.

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

CEA/IPSN (France) and EA (Spain) take part on this study, EA investigating specially biological and organic wastes produced in Spain.

B. WORK PROGRAMME

Four steps are envisionned :

1. Data acquisition and analysis :
- Data collection and analysis of base information on incinerator types, processes and working conditions.
- Definition of the characteristics of burnable very low level radioactive wastes and expected quantities.

2. Analysis
- Sampling and dust in situ measurement.

3. Evaluation of the radiological impact :
- Definition of scenarios corresponding to significant pathways for workers and members of public.
- Adaptation of computer code CERISE to specific case of incineration.
- Assessment of individual doses for the workers and radiological impact to the public as a fonction of quantities, waste activities and incinerator and site characteristics.

4. Correlation betwen activity levels and individual doses
- Individual doses due to unitary activity concentration of the waste in the considered scenarios.
- Determination of the average activity of the wastes corresponding to the individual dose exemption limit.
- Determination of pratical limits by groups of the nuclides.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

CEA

Information concerning the burnable very low level radioactive wastes and characteristics of municipal wastes is being collected.

Scenarios related to release of fumes and disposal of bottom ashes are initiated for the case of municipal incinerators.

EA

All the first item activities have been already performed, so the first step "Acquisition and analysis of the data" has been fulfilled. The data scheduled to performed this step is june 1992.

Several activities (3.1 and 3.2) of the thirth item or step "Evaluation of the radiological impact" have been initiated as shown later in the next paragraph.

Progress and results

1. Data acquisition and analysis

CEA

- Characterization of waste to be incinerated

Regarding the nuclear facilities, we collected some data from reactors operation and we estimate that, on an average, 23 t/y per reactor of very low level radioactive wastes are burnable.

- Data collection related to incineration facilities

The data collection on incinerators in France has not been carried out by inventory as foreseen. The new regulation will involve the modification in gas treatment or stoppage of some incinerators. So, we collect information about the most usual incinerators conformable to the regulation. The data concerning incineration mechanism, fumes treatment, disposal of dust, bottom ash, and dechlorination residues have been widely compiled. Valorisation of bottom ashes has also been considered.

Specific case of municipal incinerator has been studied.

When incineration is carried out, it is always accompagnied by the production of combustion gases that sweep along fly ashes. This fly ashes are generally hazardous and/or a carrier of radioactivity. We studied how fumes are treated, before the gases are released to the atmosphere.

With this information we expect to define the partition of the radioactivity between the different by-products.

EA

- Characterization and quantification of wastes to be incinerated.

The wastes to be burnt in incinerators in Spain are biological and organic wastes generated by the sector of small-scale Spanish producers. Their characteristics and quantities have been determined by surveys and visits covering 64 facilities considered to produce the two types of wastes continuously.

The centres producing these two kinds of wastes were categorized into the following two groups :

Group 1 Medical centres, including hospitals, laboratories for radioimmunoanalysis (RIA) and clinical analysis : 37 facilities from this group were canvassed.

Group 2 Laboratories and research centres, including phamaceutical, university and educational centre laboratories and, in general, any type of laboratory not included in Group 1 : 27 facilities from this group were canvassed.

The biological solids stream comprises animal carcasses, remains of tissues and organs and solid excrement from living beings treated with radioisotopes.

The organic liquids stream consists basically of scintillation liquids which contained dissolved biological samples treated with radioisotopes.

Tables I and II contain the characteristic parameters of these streams, obtained from the surveys. These parameters are : isotopic composition, contaminated mass, density and specific activity.

Table 1 : Shows the values of biological and organic wastes generated annually by small-scale Spanish producers, calculated on the basis of their production data.

Table II : Shows the annual production for each stream from a centre with the largest production in terms of total activity and concentration in terms of total activity and concentration of activity.

To obtain the above information, a questionnaire was formulated and sent to a selection of centres representative of the small-scale production sector, to be filled out with real production data ; at the same time, the managers of radioactive facilities of these centres were contacted on the phone for their comments and details regarding the peculiarities of the facilities. Additionally, 9 supervisors of 17 radioactive facilities were interviewed to complete or particularize the information supplied, or to request their collaboration.

- Inventory of incineration facilities and data collection

A list has been prepared of urban solid waste incinerators in the different municipalities and provinces of each autonomous region, indicating the processing capacity of each, expressed in metric tonnes per year. There is a total number of 20 facilities, with a processing capacity varying from 250 to 288 000 metric tons per year.

Additionally, three small incinerators used individually or privately to burn wastes in laboratories, hospitals and research centres have been selected. Their processing capacity is lower than 700 kg/day.

Contacts have been made with heads of certain facilities prior to obtaining pertinent data (process characteristics, operating conditions, working methods, number of workers, etc.).

A questionnaire was formulated and sent to the heads of facilities in july 1991, to obtain the information required to evaluate the radiological impact from incineration of biological and organic wastes in these facilities

In order to obtain additional information, visits were made to the following incinerating facilities in october and november.

. Valdemingomez (Madrid)	. for clinical and urban solid wastes
. F. Jimenez Diaz (Madrid)	. for hospital wastes
. Bellaterra (Barcelona)	. for hospital and laboratory wastes
. Ubrique (Cadiz)	. for urban solid wastes
. Bahia (Cadiz)	. for urban solid wastes
. Moncada (Barcelona)	. for urban solid wastes
. Vila de Cans (Barcelona)	. for urban solid wastes

Data collection and analysis have already been completed.

2. Analysis

No sampling or in situ measurement has been carried out.

3. Evaluation of the radiological impact

CEA

Scenarios for release of gas and disposal or valorization of bottom ash has been defined in the frame of incineration of municipal wastes. The generic calculation points out the importance of the partition coefficient (distribution of the radionuclides between dust, bottom ash and gas).

The computer code CERISE has been carried out with view of assessing, for different situations, the individual doses corresponding to the activity of concerned

materials. For incineration, the release of ^{3}H and ^{14}C needs special scenarios : the adaptation of the code is in progress.

EA

A preliminary version of the IPSN computer code for dose calculation was delivered to EA in october, and a meeting with IPSN was held in november for comments and explanations on the code. The computer code tests are under way.

Scenarios, pathways and parameters are also being defined.

REFERENCE

/1/ Presentation of the objectives, methodology and the project progress status in Brussels (october 1991)

TABLE I

WASTE STREAMS
CHARACTERISTIC PARAMETERS OF TOTAL PRODUCTION
(275 facilities)

STREAMS	DENSITY (kg/l)	CONTAMINATED MASS (kg/year)	RADIONUCLIDES	SPECIF. ACT. AT SOURCE (MBq/kg)
BIOLOGICAL SOLIDS	1	960	P 32 S 35 I 125 Fe 59 H 3 C 14	1.166 0.012 0.005 0.031 0.578 0.048
ORGANIC LIQUIDS	1	15,570	P 32 S 35 Ca 45 H 3 C 14	0.019 0.250 0.003 0.454 0.165

TABLE II

WASTE STREAMS
CHARACTERISTIC PARAMETERS OF PRODUCTION
OF THE CENTRE WITH HIGHEST PRODUCTION

STREAMS	DENSITY (kg/l)	CONTAMINATED MASS (kg/year)	RADIONUCLIDES	SPECIF. ACT. AT SOURCE (MBq/kg)
BIOLOGICAL SOLIDS	1	63	P 32 S 35 I 125 Fe 59 H 3 C 14	0.051 0.077 0.028 0.034 1.681 0.224
ORGANIC LIQUIDS	1	341	P 32 S 35 Ca 45 H 3 C 14	0.651 9.114 0.026 3.469 0.109

Title : Comparison of Safety Assessment Methods for Toxic and Radioactive Wastes
Contractor : INTERA Information Techn. Ltd., United Kingdom
CIEMAT, Spain
Contract No: FI2W-CT90-0042
Duration of contract : March 1991 to February 1993
Period covered : March 1991 - December 1991
Project leader : Graham Smith (INTERA) and Carlos Torres (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 of disposals 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 detrimental environmental effects, post-disposal. The associated work programme is being undertaken jointly by Intera Information Technologies, Environmental Division, United Kingdom (UK), and Instituto de Medio Ambiente (IMA) of Centro de Investigaciones Energéticas Medioambientales y Tecnológicas (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 the use of a scenario analysis, according to a well defined procedure, to determine how such impacts may arise.

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

B.6. To test the application of the proposed 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

The following programme items have been successfully completed without need for modification of the programme:

- the review of the different waste types and comparison of the concepts and methods adopted for their land-based disposal.
- the review of the criteria adopted for authorising disposals, in so far as they relate to post-disposal environmental impact.
- the review of the different assessment methods which have been used to assess post-disposal environmental impacts and initial evaluation of the advantages and disadvantages of the assessment methods.
- consideration of the use of scenario analysis to determine how post-disposal impacts might arise.

The items which remain to be completed by February 1993 are:

- the identification of the types of post-disposal impact which might arise and the use a scenario analysis to determine which factors need to be incorporated into assessment models.
- the collation of models and data into a practicable framework for assessment of post-disposal safety for waste disposals to land-based facilities.
- the application of the proposed framework on a representative set of examples.

Progress and results

1. Waste types and disposal methods (B.1.)

1.1. Toxic waste

The European Community (EC) produces about 2 x 10^9 tonnes of "toxic" waste per year /1/. Five main sources have been identified which can be used to categorise the wastes:

- municipal (household and commercial) waste,
- industrial waste,
- agricultural waste,
- mining and quarrying waste,
- sewage sludge and dredged spoil.

The relative contribution of these sources to each EC country's waste production is given in Table I. Variations between countries result from factors such as differences in waste categorisation schemes and levels of social and economic development.

The general trend within EC countries is towards waste minimisation. The net result of this trend will be to reduce the total volume of waste arisings and modify its average composition. Even so, the requirements for disposal appear likely to remain and in the majority of countries land-based disposal remains the most common disposal method (see for example Figure 1). Common methods of land-based disposal are:

- landfill/landraise,
- lagooning, trenching, spraying,
- land farming,
- deep underground disposal.

The relative importance of these methods varies between countries reflecting differences in availability of suitable sites, government policies, waste arisings, and economy.

1.2. Radioactive waste

Solid radioactive wastes arise from activities such as:

- the civil nuclear power industry,
- military applications,

- diagnostic and therapeutic medical procedures,
- medical and other (non-nuclear power) research,
- industrial uses of radioactive materials.

The proportions of wastes arising in different countries from the various applications vary according to industrial and other developments.

While the application is sometimes used to categorise wastes (for example to differentiate military and civil arisings), the hazard is indifferent to the provenance. Substantially, therefore, wastes are categorised according to the amount of radioactivity, the volume or mass radioactivity concentration, and/or half-life. Radioactive waste is usually categorised as being low level waste (LLW), intermediate level waste (ILW), or high level waste (HLW). The volume of wastes arising in these categories in the UK and Spain is given in Table II.

There are two main disposal options for the land-based disposal of solid radioactive waste; shallow disposal and deep disposal /2/. The shallow burial of radioactive waste has been limited to only LLW and/or some types of ILW, and nearly all such disposals have been to purpose built facilities such as Drigg and Centre de la Manche (Figure 2). Engineered deep burial is necessary because certain waste types, such as HLW, are unsuitable for shallow burial. It is also becoming increasingly necessary due to concerns over the long term safety of shallow facilities. Deep facilities for LLW and ILW have been built at Forsmark, Sweden (Figure 3), are under construction at Olkiluoto, Finland, and are planned in the UK and Switzerland.

2. Disposal criteria (B.2.)

2.1. Toxic waste

Until recently little legislation has been introduced either at an EC or the national level which has specifically addressed the post-disposal aspects of toxic waste in land-based disposal facilities. What legislation there has been mainly qualitative, for example requiring the need to ensure that waste is disposed of without endangering human health and without harming the environment rather than specifying maximum admissible doses or health impacts. However, recent legislation in Europe is following the trend established in the United States of America (USA) and is evolving rapidly and starting to address post-disposal aspects. For example the Draft EC Landfill Directive /3/ specifies: performance criteria for landfill barriers; leachate and gas collection, treatment, and monitoring requirements; and an after-care period of 30 years. Furthermore, legislation is being introduced in some member states, such as Germany, which requires that long-term safety of disposal is demonstrated prior to its authorisation.

2.2. Radioactive waste

Criteria for radioactive waste disposal have been the subject of much international effort through the activities of the International Commission on Radiological Protection (ICRP), the International Atomic Energy Agency (IAEA), the Nuclear Energy Agency (NEA) of the Organisation for Economic Co-operation and Development (OECD) and Commission of the European Communities (CEC). Although there is a considerable consensus at the international level on criteria, that consensus is less obvious from the viewpoint of the various national regulatory requirements. For example, some countries have risk based criteria whilst others have dose based criteria. The basic criteria /4/ are concerned with protection of the health of individuals through specification of quantitative limits on annual radiation doses and risks, and optimisation of protection so as to ensure the radiological impact is as low as reasonably achievable.

3. Assessment Methods (B.3.)

The assessment methods for both toxic and radioactive waste disposals have been used by regulators and operators to guide decisions on acceptable disposals, investigation and development of sites, use of engineered barriers and deployment of remediation measures. The assessments have also been used to guide and support research in all these areas. It is clear that the assessment objectives may be different in each of these areas, that criteria of interest are different and that therefore the calculational end points of the assessments are different. In particular, the differences in the assessment methods for toxic and radioactive waste tend to reflect the differences in disposal criteria for the two waste categories discussed above. They also partly reflect the greater funding which on a site by site basis has been available for radioactive waste disposal assessment.

3.1 Toxic waste

Toxic waste assessment methods are poorly developed within the EC. The methods which have been developed tend to be less quantitative and sophisticated than those for radioactive waste disposals, and are mainly used to rank hazards rather than quantify risks. However, the adoption of more quantitative toxic waste criteria will encourage the use of more quantitative methods. For example, in the USA, due to more quantitative criteria, some quantitative codes have been developed (for example the Systems Analysis of Waste Burial model /6/). Those quantitative codes which have been developed have a range of calculational end points, ranging from rate of erosion and/or infiltration for cover performance codes through to media concentrations for groundwater and biosphere codes. Furthermore, the timescales of interest are often limited to a few decades at most.

3.2 Radioactive waste

There has been considerable international cooperation in the development of quantitative assessment methods for radioactive waste disposals through international projects such as PAGIS for HLW performance assessment /5/. This has resulted in a certain degree of commonality in the assessment methods used by different countries (Figure 4). Whilst codes, which have a range of calculational end points, have been developed to assess certain detailed aspects of disposals, there are several integrated radioactive waste disposal assessment codes, such as VANDAL /7/, which have a common calculational end point - dose/risk. Furthermore, these codes are often sufficiently sophisticated to allow the integration into the assessment of uncertainty and long timescales.

4. Scenario analysis (B.4.)

Uncertainty pervades any realistic estimate of impacts from waste disposal. Uncertainty due to lack of knowledge of particular site or waste characteristics is most easily recognised, but can generally be dealt with by incorporation of numerical uncertainty into model parameter estimates. More fundamental is uncertainty at the conceptual level. All the features of the site and waste, and the processes that may affect the disposal facility performance must first be identified. Adequate understanding of these processes must be incorporated into the conceptual models on which the mathematical models are based. If this is not so, then any results from subsequent modelling are incomplete and may be seriously misleading. The role of scenario analysis is to identify all relevant features, processes and interactions, and to take these into account so as to provide a logical framework for quantitative modelling.

Few scenario development exercises have been carried out in respect of non-radioactive waste disposal facilities, one exception being /8/, although the hazard checklist ranking systems are a rudimentary form of scenario development. In contrast scenario development has been a subject of particular interest in radioactive waste disposal assessment /9/.

List of publications

TORRES, C., SIMON, I., LITTLE, R.H. and GROGAN, H.A., Comparison of Safety Assessment Methods for Toxic and Radioactive Wastes. Paper presented at the International Conference on the Implications of the new ICRP Recommendations on Radiation Protection Practices and Interventions. Salamanca, Spain, November 1991.

GROGAN, H.A, LITTLE, R.H., SMITH, G.M. and TORRES, C., Land Disposal Practices in Europe and North America. Paper to be presented at the Institution of Water and Environmental Management 1992 Conference. Birmingham, UK, April 1992.

References

/1/ EUROSTAT, Environmental Statistics, Statistical Office of the European Communities, Luxembourg (1990)

/2/ OLIVIER, J.-P., Joint International Symposium on Environmental Consequences of Hazardous Waste Disposal, Stockholm, 27-31 May 1991. Proceedings Vol. 1, pp 143-154.

/3/ CEC, Proposal for a Council Directive on the Landfill of Waste, COM (91) 102 Final, SYN335, Commission of the European Communities, Brussels (1991)

/4/ ICRP, Radiation Protection Principles for the Disposal of Solid Radioactive Waste, ICRP Publication 46, Ann. ICRP 15, No. 4, Pergamon Press, Oxford (1985)

/5/ CEC, PAGIS, Performance Assessment of Geological Isolation Systems for Radioactive Wastes: Summary. Commission of the European Communities, Luxembourg (1988)

/6/ ADAM, J.A., An Integral Risk Assessment Model for Hazardous Wastes, In Waste Isolation in the US and Elsewhere, Technical Programs and Public Communications. Vol. 1, General. Univ. Arizona, Tuscon, Arizona (1982)

/7/ LAURENS, J.M., THOMPSON, B.G.J. and SUMERLING, T.J., Symposium on Safety Assessment of Radioactive Waste Repositories, Paris, 9-13 October 1990. Proceedings pp 627-638.

/8/ GROGAN, H.A, CHARLES, D. and SMITH, G.M., UKDoE Report DOE/HMIP/RR/91/058 (1991)

/9/ SUMERLING, T.J. and HODGKINSON, D.P., International Conference on Probabilistic Safety Assessment and Management, Beverly Hills, 4-7 February 1991. Proceedings pp 641-648.

/10/ UKDoE, Digest of Environmental Protection and Water Statistics, No. 13, Her Majesty's Stationery Office, London (1991)

/11/ RWMAC, Ninth Annual Report, Her Majesty's Stationery Office, London (1988)

/12/ MOPU, Residuos Radioactivos. Unidades temáticas ambientales de la Dirección General de Medio Ambiente, Madrid (1989)

/13/ ERL, The Disposal of Radioactive Waste in Sweden, West Germany and France, Environmental Resources Limited, London, (1987)

/14/ CARLSSON, J., FORSSTROM, H and PAPP, T., Symposium on Safety Assessment of Radioactive Waste Repositories, Paris, 9-13 October 1990. Proceedings pp 157-166.

Table I: Waste generated by source in the mid 1980s (after /1/ and /10/)

	Municipal %	Industrial %	Agricultural %	Mining & Quarrying %	Sewage Sludge & Dredged Spoil %	Total (10^6 tonnes)
Belgium	4	12	74	10	-	71.2
Denmark	36	62	-	-	2	5.9
France	3	9	70	18	-	565.0
Germany	19	76	-	3	2	103.4
Greece	18	55	-	27	-	14.1
Ireland	4	7	80	7	2	27.6
Italy	10	26	22	42	-	136.8
Luxembourg	47	49	-	-	4	0.3
Netherlands	8	15	48	-	29	82.8
Portugal	13	65	-	22	-	17.6
Spain	4	2	18	72	4	250.7
UK	6	15	37	34	8	700.0

Table II: HLW, ILW and LLW arisings in the UK and Spain (after /11/ and /12/)

	UK conditioned waste volumes, m^3 to 2030	Volumes, m^3, to be managed in Spain, assuming 30 year life for existing plant.
HLW	1,300	9,700
ILW	182,000	243,500
LLW	1,250,000	

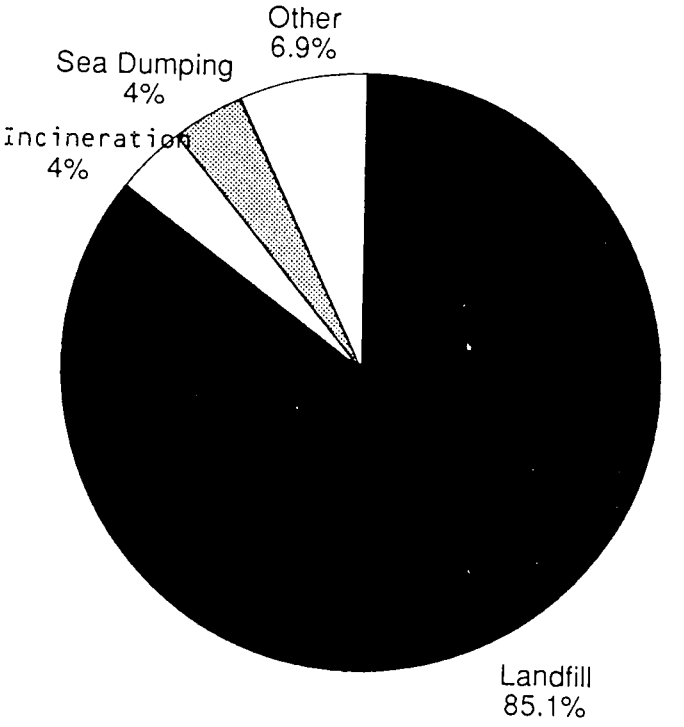


Figure 1: Annual waste disposal in the UK (after /10/)

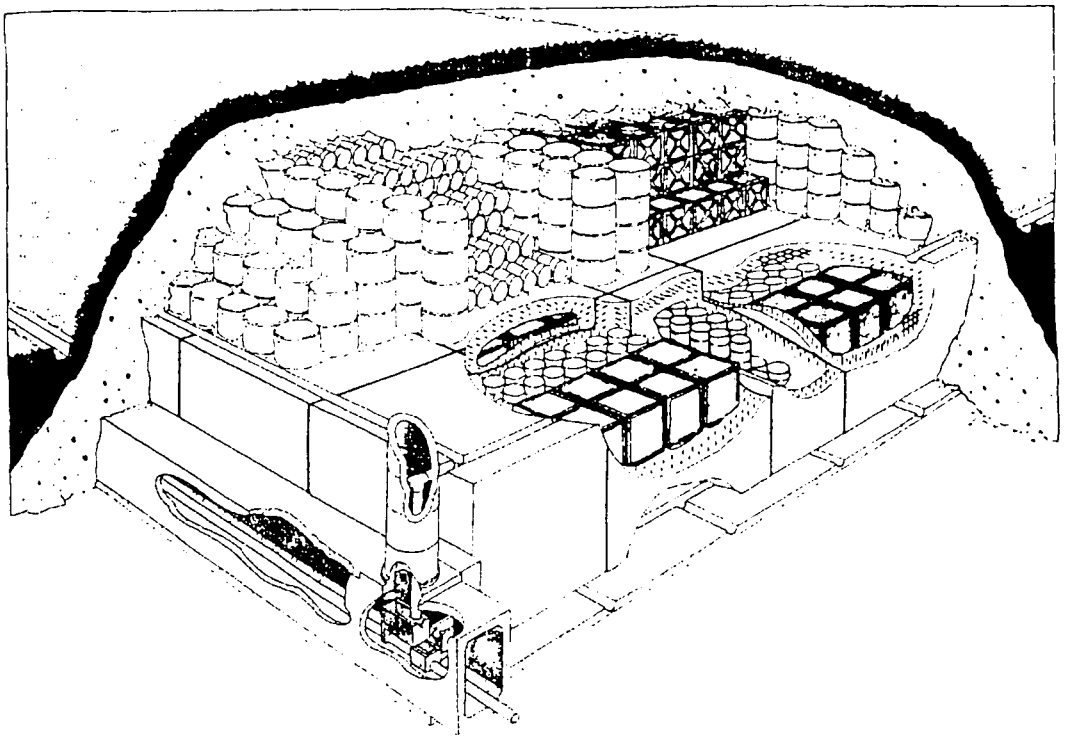


Figure 2: Section through Centre de la Manche (after /13/)

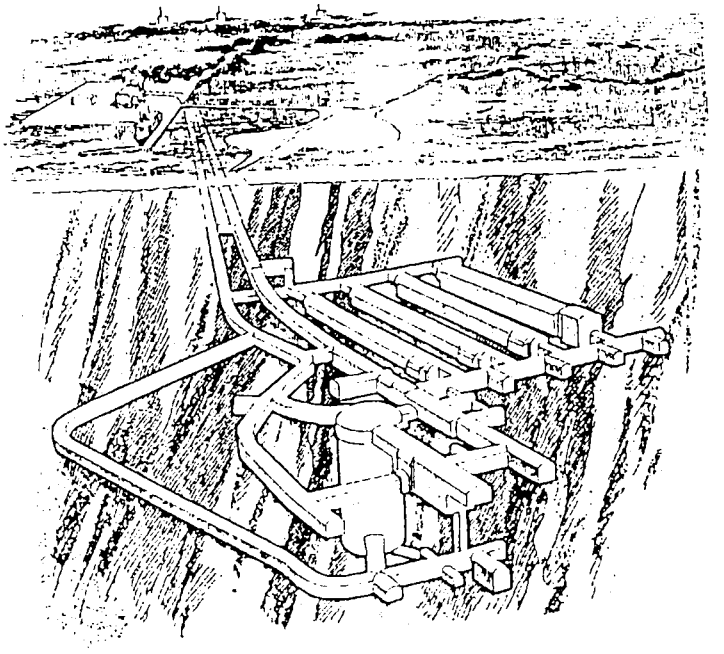


Figure 3: General layout of the deep repository at Forsmark (after /14/)

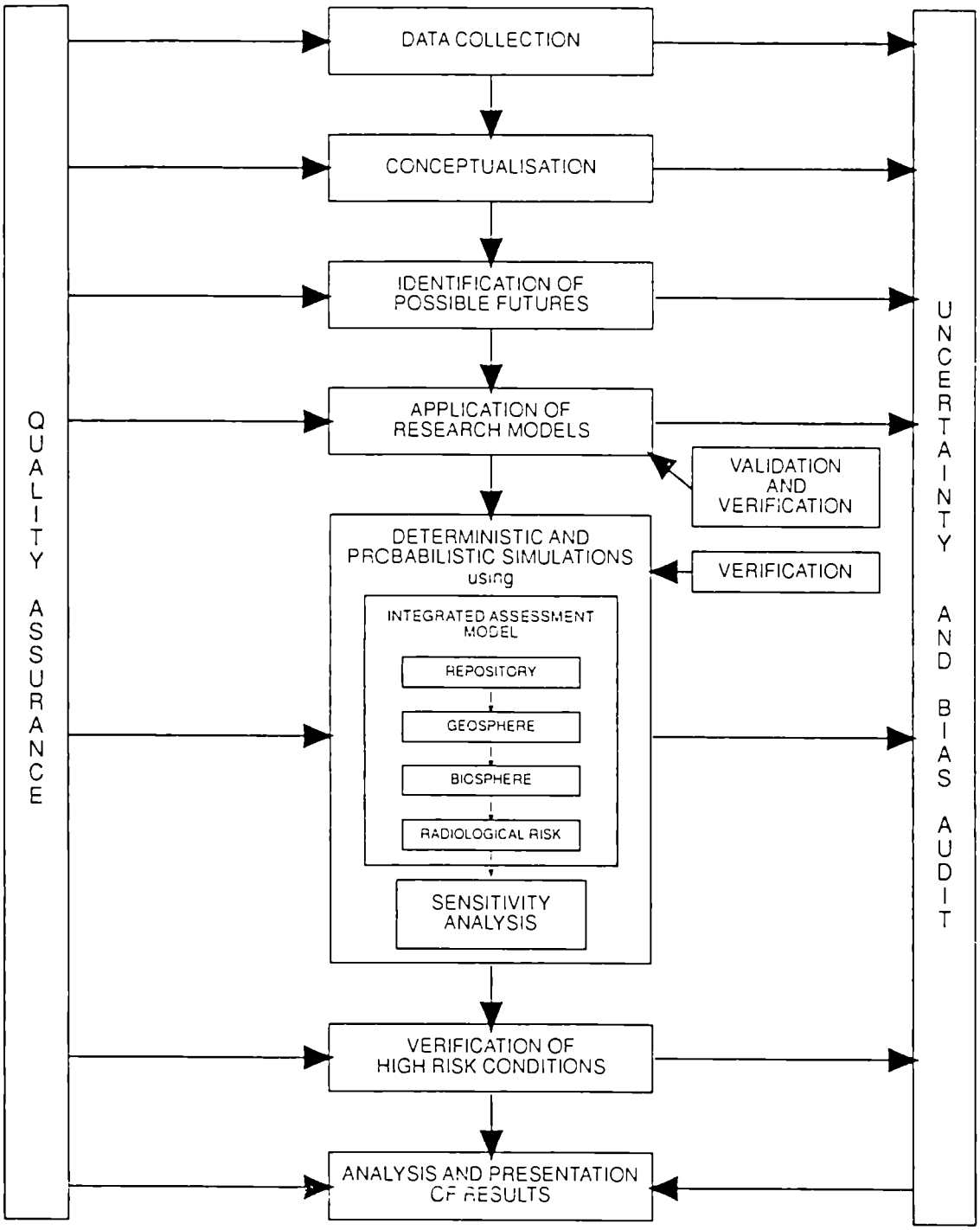


Figure 4: Generic radiological risk assessment procedure

Title : Study concerning the evaluation of toxic elements present in nuclear wastes
Contractor : ONDRAF/NIRAS, Belgium
Contract No: FI2W-CT90-0045
Duration of contract : from 01.04.1991 to 31.03.1993
Period covered : 01.04.1991 to 31.12.1991
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 components 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, conditionning,...).

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 actual local, national and european legal context.
2. Evaluation of the presence of these toxic elements in the nuclear wastes, and structuration of the collected information based on the following criteria : - type of producer
   - type of process
3. Definition of toxic elements/limits (orders of magnitude) acceptable for the admission of waste on a shallow land burial, referring to the operation criteria for conventional landfilling of industrial waste.
4. Definition of measurements or evaluation methods to identify and quantify the toxic elements in nuclear wastes.
5. Preventive actions to avoid the use of toxic elements in the nuclear installations.

C. Progress of work and obtained results

State of advancement

A compilation of the Belgian legislation on toxic waste was performed. There are recent evolutions in it, taking account of the published EEC-directives. But the radioactivity remains out of the field of application, as the chemical toxicity remains out of the field of application of the law on nuclear waste.

As a result, the actual nuclear waste management in Belgium does not formally accept any toxic materials in radioactive waste and consequently, there is less information available on the chemical content of nuclear waste.

Therefore, in place of a specific investigation, limited on the toxic heavy metals through the whole chain of the nuclear waste (production, packaging, intermediate storage, conditionning, treatment and final evacuation), we propose to treat the chemical aspects as a global problem, and to perform the investigation, step by step, through the nuclear chain, beginning with the initial one, the operational production at the level of the producers of nuclear waste.

This wide approach gives us arguments to motivate the producers to participate to this systematic inquiry.

Progress and results

1. Definition of the toxic elements in function of the legal context.

By the regionalisation of Belgium (1981), the protection of the environment has been transferred to the regional authorities.

In spite of the continuous evolution of this matter, we can assume that, until now, the original national law on toxic waste and the decree of 1976 taken in application of it remain the common basis of the regional legislation for Flanders and Wallonia.

For this reason, we will investigate in a first step the toxic elements of the nuclear waste referring to this national legislation.

The toxic wastes are classified in 3 categories based on 3 criteria :

First criterion : the presence, without threshold value, of defined pesticides or defined phytopharmaceuticals.

Second criterion : the concentration of toxic elements :
- solvents, cyanides, nitriles, soluble fluorides, organo-halogenated compounds,..
- heavy metals and their soluble compounds : As, Cd, Hg
- soluble compounds of heavy metals : Be, Tl

Third criterion : the origin :
chemical process by the pharmaceutical and phytopharmaceutical industries, and from research laboratories.

Taking into account the quite restricted character of this definition as well as the expected evolution of the regional laws, largely imbued with the european directives, we opted in a second step for the investigation of the "toxic and dangerous" waste as defined in the european directive 78/319/EEC of 20 march 1978.
This text contains a list of substances giving a dangerous character to waste, without reference to specific threshold values. Furthermore, a lot of substances not mentioned in the belgian law are considered as toxic or dangerous. This is specially the case of some metals.
In the context of the management of nuclear waste, particulary in the option of shallow land burial, the long term chemical evolution of heavy metals may cause some contamination of ground- and surface water. Therefore, we decided to include in our list of metals for investigation, those mentioned in the EEC-directives 80/68/EEC and 76/464/EEC defining the noxious elements respectively for ground- and surface water.

The combination of the 3 above mentioned legal references gives a total of 22 metals, as summarized in table I. It is to be noted that in this table I, the metals of a given group are automatically included in the group(s) mentioned on the right.
As uranium is automatically inventoried for its radioactivity, it is not necessary to include this isotope in the actual study.
We decided also to exclude titanium of the study : the toxic problemacy of this metal is mostly linked to the waste produced during the extraction/purification of the metal, or by the titane dioxide industry.
According to these remarks, we obtained a list of 20 metals to inquire.

2. Evaluation of toxic elements in the nuclear waste.
Preliminary contacts with producers of nuclear waste have proved that the only possibility to reach some valuable information on the chemical composition of the waste, was to organize a systematic investigation by means of a detailed form, explained in a separate note.
To take a maximum advantage of such an inquiry, we opted for the combination of several information requests, in one form :

- general information (identification, origin, total activity,...)
- physico-chemical information
- radionuclide content

Such a polyvalent form is now tested in house before distribution to the producers of nuclear waste.

The belgian producers of nuclear waste can be classified into 5 categories :
- Power plants
- Research centers/producers of sealed sources/cyclotrons
- Producers of nuclear fuel
- Waste treatment facilities
- Small producers (universities, hospitals, industries,...)

The investigation occurs per producer and per flux. The waste flux is the basic entity of primordial importance, defined by homogeneous radiological and chemical properties, priority being given to the radiological aspect.
Depending on the situation, a flux can be sent as such to the treatment plant for conditioning and treatment, or first undergo a pre-treatment (including mixing with other fluxes) before conditionning. It is important to know that conditionned wastes are automatically defined as a flux different from the corresponding unconditionned one.
In the codification of waste fluxes, a further distinction is made between :

- the operational waste (standardized or special)
- the technological waste : produced during the life of a defined installation but not resulting from the direct production process (e.g. waste resulting from important modifications or partial renovation of the installation)
- the dismantling waste.

The inquiry foresees the following items regarding the chemical properties :

- general chemical constituents
- content of toxic and dangerous metals (20)
- content of inorganic anions
- content of complexing agents
- content of toxic substances according to the royal decree of 09.02.1976
- content of toxic and dangerous substances according to the EEC directive 78/319/EEC.

Additionally, an other section of the inquiry refers to physico-chemical properties of the waste, as water and ash content, calorific value, flash point, pH and redox potential, viscosity and danger category (R-S code, ADR, UN, ...).

The objectives of this chemical characterization are :

- to comply with the regulations on transport, packaging, storage
- to warrant safety for workers coming in contact with the waste
- to warrant effectiveness of selected treatment process
- to avoid unexpected reaction during treatment
- to assess long term chemical impact on the environment, in the option of shallow land or deep geological burial.

3. Chemical acceptance criteria for the shallow land burial of nuclear waste.

The proposal of acceptance criteria will refer to the existing criteria in the conventional management of landfills .
In this sector, it is absolutely forbidden to accept waste, legally defined as toxic, on a landfill. In other terms, waste identified as toxic according to the regional legislation (for exemple containing heavy metals in concentration above the legal limit) can not be directly landfilled.
Liquids, flammable and reactive waste are also excluded for direct landfilling.
All those wastes have to undergo a pre-treatment (incineration, neutralisation, precipitation,...) before landfilling.
In addition to these exclusions, wastes are accepted or refused not in regard of their chemical composition, but in regard of their solubility (or the solubility of their constituents) in water, determined by means of a standardized leaching test.

A landfill is in fact considered as a manufacture having waste as input and waste water (percolate) as output. This output has to respect pre-established standards. The definition of new standards for landfills are presently in discussion on regional as well as on european level, so that we hope to have a more clear situation at the moment of the final report.
Actually, we can confirm that the phylosophy guiding the legislator is to promote a fundamental change of mentalities : landfilling has no more to be considered as a universal (and the most economically acceptable) solution for treatment of waste, but only as the ultimate solution, in absence of any better alternative.

TABLE I : SELECTION OF THE HEAVY METALS FOR INVENTORY

Group I National waste act	Group II Regional waste acts EEC waste-directive	Group III EEC water-directive
As	Cr	Ag
Be	Cu	B
Cd	Pb	Ba
Hg	Sb	Co
TI	Se	Mo
	Te	Ni
		Sn
		Ti
		U
		V
		Zn

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:	March 1st - December 31st, 1991
Project Leader:	Th. Brasser (GSF - Coordinator) L.H. Vons (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.

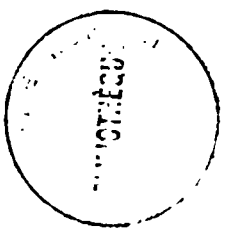
B. WORK PROGRAMM

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

2.1 Legal Stipulations

2.1.1 Legislation in the Federal Republic of Germany

2.1.1.1 Radioactive Wastes

The memorandum of association of the European Atomic Community (EURATOM/EAG) of March 25, 1957 between Belgium, France, Italy, Luxembourg, The Netherlands, and the Federal Republic of Germany was to promote the development of an extensive nuclear energy industry with the objective of attaining such a high degree of safety that all conceivable hazards to life and health of the population could be excluded.

Apart from this constitutional contract, a number of guidelines resp. statutory ordinances were issued during the last thirty years by various executive bodies of the European Community. Within this context special mention should be made of the basic-standards-Euratom-guideline in its current version of September 3, 1984. This guideline bases on the Euratom contract and is valid for the handling, usage, possession, storage, transport and removal of natural and artifical radioactive substances (Article 2); basic rules for dose limits under controlled radiation exposure conditions and boundary values are stipulated.

Statutory ordinance (Euratom) No. 3227/76, issued by the Commission on October 19, 1976 on the application of Euratom safety measures, as well as the guidelines of the Advisory Committee of June 27, 1986 on the environmental compatibility of certain public and private projects must be mentioned in this connection. Direct guidelines for the final disposal of radioactive wastes are not included in the statutes of the European Community, the competence for issuing specifications is determined in accordance with the legislation of the member states.

With passing of the Act on the Peaceful Use of Nuclear Energy and Protection against its Hazards (Atomic Energy Act, AtG) of Dec. 23, 1959, the Federal Republic of Germany has complied with its international obligations which originated, e. g., from the Euratom contract and the Atomic Weapons Prohibition Act.

The Atomic Energy Act of July 15, 1985 (with subsequent individual amendments) incorporates the rules on the following three topics: Governmental supervision, liability for damage, and corresponding measures by the Government in the event of violation of the regulations.

The utilization of radioactive residues and removal of radioactive wastes is subject to § 9a AtG. Applicable here is the basic principle that the residues must first find unhazardous reutilization, and they can only be removed systematically as radioactive wastes provided that this is impossible. Competent for the provision of repositories is, according to § 3 of this section, the Federal Government.

Construction and operation of such governmental facilities are subject to a plan approval (§ 9 AtG). The basic radioactive substances in the sense of the Atomic Energy Act are listed in § 2 AtG.

Additional important ordinances are based upon the Atomic Energy Act, such as, e.g., the Radiation Protection Ordinance (StrSchV). It regulates licensing and obligation to notify, import, export, and transportation and gives instructions regarding the organization and physico-technical measures for the prevention of damage to man and material from ionizing radiation from radioactive material.

Of significance to planning and operating of a repository for radioactive wastes is, besides adherence to the dose limits for persons occupationally exposed to radiation (§ 49 to § 52 StrSchV) and protection of the

population against ionizing radiation (§ 46 StrSchV), the protection of air, water, and soil (§ 46 StrSchV).

The dose limits of 0,3 Millisievert, specified in § 45 StrSchV under point 1, are also taken into consideration by the "30 Millirem-concept" constituting the main groundwork for a quantitative assessment of the long-term safety analysis to be performed according to the safety criteria for the disposal of radioactive wastes in a mine.

Moreover, a large number of additional ordinances are to be derived from the aforementioned Acts.

The jurisdiction of the Federal and State Authorities is governed by the Atomic Energy Act (§§ 22 - 24 AtG) as well as by the Radiation Protection Ordinance. A large number of the executive actions of the Federal Government are carried out by the Federal Office for Radiation Protection (BfS) (§ 23 AtG).

Besides the Federal Office for Radiation Protection (BfS) and the Bundesamt für gewerbliche Wirtschaft - responsible for import and export - the appropriate authorities of the Federal States will take on the administrative functions by order of the Federal Government.

Conversion of the concept for the disposal of radioactive wastes does not result from the Atomic Energy Act nor one of the ordinances. Basis for the "Entsorgungs-" (waste management and disposal) policy is the Atomic Energy Act in combination with the so-called "integrated waste management and disposal concept" which puts the statutory provisions into concrete terms. This concept was already drawn up by the Federal Government in 1974. It was confirmed by the resolution of the heads of government of Federal and State Authorities on the "Entsorgung" of nuclear power stations of Sept. 28, 1979 and is embodied in a law on basic principles concerning the provision for "Entsorgung" of nuclear power stations which was issued by the Minister of the Interior (BMI) according to an agreement of the states dated March 19, 1980.

The integrated Entsorgungskonzept of the Federal Government comprises four essential steps:

1. Interim storage of the irradiated (spent) fuel elements in the nuclear power stations and external interim storage;
2. Reprocessing of the spent fuel elements and utilization of the reobtained nuclear fuel by means of renewed usage in nuclear power stations (recycling).
3. Removal of the radioactive wastes by means of conditioning; interim storage in the nuclear facilities, in external storage or state-owned collecting centres; interim storage of the high-level, heat developing wastes (glass blocks) in interim storage; final disposal.
4. Development of direct disposal methods for such spent fuel elements for which, according to § 9a AtG, reprocessing is technically impossible or uneconomical; further development of the technique for the direct disposal of spent fuel elements from ligh water reactors.

Moreover, this concept envisages removal of radioactive wastes exclusively by means of emplacement in deep geological subsurface formations.

The Ministry of the Interior has, in its circular letter of April 20, 1983 - basing on recommendations of the Reactor Safety Commission of Dec. 17, 1982 - conferred upon the licensing and supervisory authorities of the States administrative authority regarding the "safety criteria for the disposal of radioactive wastes in a mine".

These safety criteria lastly regulate the actual final disposal and incorporate protective aims and measures, site requirements, prerequisites for construction and operation of a repository, site exploration, construction and operation, wastes, decommissioning and the post-operational phase.

One essential element of the safety criteria is the demand for safety analyses during which partial systems and events taking place in the entire system of a repository are simulated by means of suitable models.

Issues pertinent to mining activities concerning construction and operation of a final repository are principally regulated by the Federal Mining Law of Aug. 13, 1980. Special reference to the disposal of radioactive wastes in the sense of the Atomic Energy Act is comprised by § 126, Section 3 of the Federal Mining Law, with reference to further paragraphs of this Law.

Moreover, some aspects of final disposal are additionally treated by the Water Resources Conservation Act, WHG) with the formulation of the so-called "Besorgnisgrundsatz".

The penal code (StGB) is applicable for offences concerning radioactive materials.

2.1.1.2 Emplacement of hazardous waste

The European Community has - basing on the memorandum of association of the European Economic Community of March 25, 1957 - issued a large number of guidelines on the waste law. They are, however, not immediately applicable and, in order to attain validity, in need of adaptation according to the regulations of the national states.

Special mention must be made of the guidelines on wastes by the advisory committee of July 15, 1975 and the guidelines of March 20, 1978 in the register of legal regulations of the European Community on toxic and hazardous wastes.

The guideline for wastes of 1975 fully incorporates the current principles of modern waste management. The precepts for the avoidance of waste, waste utilization, and lawful removal are accordingly stipulated.

The "polluter pays" principle is explicitly embodied in article 11 of this guideline by the European Community.

Further intensified measures are listed in the guideline of 1978 on toxic and hazardous wastes under the provision of being adapted to suit the requirements of the member states.

The member states are to exercise a vigorous surveillance and monitoring function over these wastes. The storage, treatment and/or emplacement of toxic and hazardous wastes is subject to licensing.

Qualification for licensing is to be seen in the obtention of positive results from an environmental compatibility test, as is stipulated in the guideline of June 27, 1986 for the environmental compatibility examination for defined public and private projects.

The waste-specific legal stipulations of the European Community delineated in the aforementioned guidelines were fully adapted in the Federal Republic of Germany and have exerted their influence on the law pertaining to the avoidance of wastes (Abfallgesetz, AbfG - Waste Act).

A number of statutory ordinances and administrative regulations as well as Waste Acts of the individual Federal States are ready for implementation and supplementation.

For the first time basic principles for a modern waste management policy were incorporated in the new Waste Act (AbfG) of Aug. 27, 1986: Whenever possible waste production should already be avoided within the industrial and commercial sphere. Unavoidable wastes or such wastes which cannot

be reutilized are to be preferably subjected to the normal processes of waste removal resp. be disposed of in an unhazardous manner. In order to enforce measures for the avoidance of waste, especially in the field of hazardous wastes, the Federal Government is authorized to issue corresponding regulations by means of respective ordinances.

The responsible authorities of the Federal states exercise the function of providing plans for waste removal in accordance with the basic ruling of Art. 83 GG.

§ 4 of the Waste Act regulates the waste management and disposal ordinance. In accordance with § 4, Section 5, the Federal Government is authorized to issue general administrative regulations concerning the requirements of waste management and disposal - especially for hazardous wastes - according to the current state of techniques. This includes stipulations for collection processes, treatment, storage and disposal, which usually provide for environmental compatibility in view of waste management and disposal.

Subsequent to issuing a General Administrative Regulation on Jan. 31, 1990 on groundwater protection in the event of storage and emplacement of wastes, the 2. General Administrative Regulation on the Waste Act, known as "Technical Manual for Waste Management" (TA Abfall), has been in force since April 1, 1991. The Federal Government pursues the following objectives under these aspects:

- Obtention of uniformity regarding the standard of waste management and disposal in the Federal Republic of Germany on a very high technical level. This also includes measures towards the avoidance of wastes and waste reutilization.
- Improvement of the surveillance methods by the authorities, the corresponding measures are to be standardized.
- Planning, licensing, construction, and operation of facilities are to be made more predictable and calculable.
- The acceptance of the required facilities is to be improved.

Special requirements on underground repositories in rock salt in connection with the disposal of wastes are formulated in chapter 4, resp. 10, of the TA Abfall. They are particularly concerned with exclusion criteria for underground repositories, properties of the host rock, geotechnical safety analysis, transport methods, waste conditioning and sealing measures.

Also several types of wastes are designated not to be stored in underground repositories (chapter 4.4.3.2 TA Abfall), e.g. spontaneously inflammable wastes and wastes which could - under storage conditions - lead to hazardous reactions which could prove hazardous for the operational safety and the integrity of the barriers.

Another essential element of the TA Abfall is the long-term safety assessment. This is to validate that the construction, operation and post-operational phase of an underground repository does not exert a negative influence on the biosphere.

In view of this objective, the barriers of the underground repository (e.g. waste form, backfill and seals of shafts and boreholes, the behaviour of the salt rock, the surrounding rock and the overlying rock) as well as possible events taking place within the entire system are to be modelled and evaluated on the basis of concrete site data or sufficiently conservative estimates. The geochemical-hydrogeological situation, such as groundwater movements and solution potential (barrier effectiveness), are to be considered.

According to the legislation of the Federal States, the corporations under public law (cities, counties) are responsible for administrative execution in the sense of § 3, section 2 Waste Act. The competent State Authorities are nominated in the Waste Acts of the States according to § 19 Waste Act in combination with § 11, section 1, of the Waste Act.

Responsibility for the removal of wastes in the old Federal States is regulated according to the Waste Acts of the States and is largely in the hands of the Water Board, Mining Authorities and Environmental Protection Agencies.

The Mining Authorities are responsible for the removal of wastes into underground repositories (Bergamt, Oberbergamt).

The responsible authorities regulate execution by means of monitoring, surveillance, and licensing while observing the rights of each respective Federal State resp. the law and ordinances of the Federal Government. They must, therefore, take related fields of legislation into consideration, such as the Water Resources Conservation Act (WHG), especially § 34. According to the existing comments, this section (§ 34 WHG) is also valid for the storage of wastes on disposal sites.

To assess the entire underground repository system, the drinking water ordinance (TrinkwV) (esp. §§ 2 and 3) with its specified limiting values (addendum III) can be referred to (cf. § 45 par. 1 StrlSchV for radioactive wastes).

The regulations of the Federal Mining Law (BBergG) are applicable to the construction and operation of an underground repository. In contrast to the storage of radioactive wastes (§ 126, section 3 BBergG) no direct reference to an emplacement of wastes is comprised by this Law. According to the opinion of the Mining Authorities it is therefore necessary to adapt the TA Abfall into the Federal Mining Law.

2.1.1.3 Summary

The legal regulations for the management and disposal of radioactive wastes and those for nonradioactive wastes are based upon completely separate legal concepts. The disposal of radioactive wastes is governed by the Atomic Energy Law, while the disposal of nonradioactive wastes is subject of the Waste Law.

On the European level, the Euratom Contract of 1957 and the basic-standards-Euratom-guideline represent the foundation for the peaceful use of nuclear energy and, consequently, also for the disposal of wastes. By and large the contract of the European Economic Community of 1957, followed by corresponding guidelines (first guideline issued in 1975), is of significance to the disposal of nonradioactive wastes.

By means of the Atomic Energy Act (1959) and the Radiation Protection Ordinance of 1960 the Federal Government complied with its obligation for adaptation to German Federal Law. In 1974 the Federal Government submitted a technical concept on the management and disposal of radioactive wastes.

The compilation of a waste law, on the other hand, was started in the Federal Republic of Germany in the seventies only; an up-to-date Waste Act was issued in 1986 with the subsequent technical regulations and ordinances, which largely appeared during the last five years.

Despite these discrepancies in the development of the Atomic law and the Waste law, up to the differences in the selected terminology of laws and ordinances, essential conformities are to be found in the concepts.

Plan approval and an environmental compatibility examination are foreseen by both legal domains. Residues, which according to the present state of science and technology as well as for reasons of economy cannot be

reutilized, are to be disposed of according to a specified system. Limiting values for an assessment of environmental compatibility are stipulated by the Atomic law. With regard to the Waste law, however, reference has to be taken to additional legal domains concerned with environmental protection (esp. Water Resources Regulations).

As a component of the waste management and disposal concept, radioactive wastes are to be finally disposed of exclusively in a mine. The underground storage of nonradioactive wastes is also a constituent of the Waste law, represents, however, only one of the possible means of storage.

The concepts are comparable. Basic principle or objective is in both cases to protect man and his environment. Investigations of the wastes, the site, and of the long-term safety are to provide evidence of the protective and beneficial character of these means of waste management and disposal.

2.1.2 Final Waste Disposal and the Dutch Law

2.1.2.1 Introduction

Since man started sedentary life he stockpiled his refuse and discarded tools and equipment nearby in pits, mostly in his backyard. Much later, after discovering the connection with plagues and the more concentrated production following the industrial revolution, a centralized waste collection and disposal as landfills was organized. Only very recently it became apparent that the massive amounts of wastes produced and their composition endanger normal biological life cycles. In order to prevent further degradation of the environment rules and laws are formulated regarding the production, composition and handling of wastes. Shocked by the consequences of waste disposal practices in the past, society has at this moment no clear view on waste disposal of persistant toxic materials. Legislation regarding the final disposal of untreatable toxic wastes is accordingly not formulated in The Netherlands.

2.1.2.2 Existing legislation in relation to underground waste disposal

The Mine Law (1810 - 1903)

The basis of exploring and exploiting valuable materials in the earth is still the Napoleontic law of 1810. At that time The Netherlands formed a part of the French Empire. In principle this law regulates the questions about the propriety rights. Exploration is only possible with the consent of the land owners. Once valuable minerals have been traced one has to apply for a concession at the authorities. If the person or company show to be able to carry out the work and is solvant, the authorities have to grant the concession.

The law indicates the safety rules for the underground activities concerning the workers and regulates claims about damages to surface properties. A state instituion is provided for to control the works underground, according to the concession and the law.

A revision of this mine law has been published nearby hundred years later (mine-law of 1903) to provide for the changes of the competent authorities mentioned in the Napoleonic law and a new indication of working conditions in the mine. The specifications have been published later by ministerial decree as mine rules. Nothing is mentioned about the use of underground cavities resulting from mining activities for disposal of wastes.

The Nuclear Energy Act (1963)

Concerning radioactive waste, lower limits are defined of radioactive constituents for classification. All radioactive material above the lower

limit that the owner does not want to possess any longer has to be handed over to an organization designated by the goverment.

This organization (COVRA) has to store the radioactive waste until a decision is taken by the government for final disposal. The interim storage at COVRA is intended for a period up to 50 or 100 years. Before 1982 the ocean dumping practice was permitted according to the rules of the London Dumping Convention.

The Chemical Waste Act (1976)

In the Chemical Waste Act and the following decrees definitions are given of matter considered Chemical Waste based on concentrations of toxic components. The law and the decrees indicate the prference for reuse, recycling or detoxifying the wastes. Disposal is in general not permitted; exemption may be made by competent authorities only if the disposal forms no burden on the environment.

The Protection Act

Soil according to this law is considered all solid material of the earth including water, gases and living organisms present. The law means to protect the environment (agriculture, drinking water supply, protected areas, endangered species of flora and fauna). Also according to this law disposal of wastes is only possible if no harm to the environment results.

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At the moment the devisability of disposal of toxic chemical wastes in the underground is under study by the Department of the Environment. This action may result in a law or decree permitting under certain conditions to dispose waste in the underground.

This action implies also that the Mine Law has to be amended or revised by the department (Ministry) of economic affairs to permit concessing for mining with the aim to dispose wastes.

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

Contractor : NUCLECO SpA - Roma (I)
STE - Roma (I)
Contract No: FI2W-CT91-00110
Duration of contract : 1 January 1992 - 31 June 1993
Period covered : -
Project leader : F. Lo Giudice (NUCLECO SpA)
V. Pellecchia (STE)

A. OBJECTIVES AND SCOPE

The research goal is to demonstrate that radwastes treatment and disposal techniques, already widely tested and applied, can be extended to toxic and hazardous wastes (THW) too.
The research is mainly focused on the technical and economic feasibility of such a kind of technological transfer, as far as :

- THW volume reduction,
- transformation of THW in an inert form, in order to declassify them, decreasing in this way the costs for disposal,
- environmental impact reduction,

are concerned.

B. WORK PROGRAMME

B1 : To select and evaluate THW groups, featured by an environmental impact involving particularly restrictive management rules similar to low activity radwastes.

B2 : To select the radwastes treatment and disposal techniques already tested and used.

B3 : To analyze the feasibility of converting specific kinds of THW into an inert form, with reduced volume and hazard, allowing a landfill disposal.

B4 : To develop the basic design of a pilot plant performing a selected process for THW treatment.

B5 : To study for the process : costs/benefits analysis, environmental impact, future experimental campaign with the pilot plant, interventions in-situ.

Title : 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
Contractor : ONDRAF/NIRAS, Belgium
Contract No: FI2W-CT90-0036
Duration of contract : from April 1991 to March 1993
Period covered : April - December 1991
Project leader : J. Van Der Haegen

A. OBJECTIVES AND SCOPE

Starting from the hypothesis that the information of the public on radioactive waste management is confronted with a lack of knowledge, 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 give the public the basic knowledge to understand the approach of ONDRAF/NIRAS.

The study consists of two phases :

1. Identify the target : determine the origin and state of the knowledge of the target group on the subject concerned; work out documentation and arguments by following the general argumentation of ONDRAF/NIRAS and by adapting it to the target group;

2. Apply this argumentation to the target group and register the resulting modifications of public opinion.

The survey is based on an opinion poll taking stock of the expectations and attitudes of the target group in matters of nuclear waste.

ONDRAF/NIRAS called upon the expertise and experience of the communication consultancy 'Infopublic' (Brussels) to conduct the survey; the attitude survey was assigned to the specialized 'Marketing Unit' office (Brussels) and a team of socio-psychologists who supervised the opinion poll.

B. WORK PROGRAMME

B1 : To define a sample of the population, to enter into dialogue with the educational committee and to elaborate the first test.
B2 : If necessary, application of the first test on the population sample, to analyze the results; to prepare the discourse, to select and elaborate the educational tools.
B3 : To spread the information to the population sample. To realize the tests and inquiry aiming at assessing the modifications of knowledge and opinions.
B4 : To compare the results of the tests. To assess the efficiency of the method. To examine the possibility of applying the knowledge coming out of this experience in view of undertaking an information action on the target and/or others targets. To draw-up and present the final report.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The following facts are worth mentioning for the period March- December 1991 :

1. Choice of the consultancy, methodology and target group

1.1. The first phase consisted in selecting the communication consultancy that would supervise the study. 'Infopublic' (Brussels) was chosen among several candidates for its original working plan proposal based on its experience in analogous studies, which remained moreover within the budgeted bracket.

1.2. The methodology proposed by 'Infopublic' to obtain the desired information is of a qualitative nature. This way, the consultancy expects to achieve a very thorough knowledge of the attitude of the persons involved. The qualitative approach emphasizes less the statistic representativity of the rather limited random sample survey than the value of the results from the thorough analysis of the target group's attitude and motives.

This technique is best used with relatively homogeneous targets, i.e. where differences of views are going to stimulate discussion and not inhibit it. This technique is also advisable when the views of the persons questioned might focus on various aspects of the problem, which also seems probable when the point of view of teachers of exact and social sciences is envisaged.

The social dimension of this approach promotes the enhancement of the information gathered on account of the confrontation of the participants' points of view.

The methodology applied consists of two phases :

1. attitude survey
2. attitude survey for the pedagogical pretest package

1.3. Reference target group

The reference target group selected for this study is composed of 15-to-18 year old youngsters.

This choice has been inspired by :

- the conviction that this public has the required maturity and can be moved to listen to the message conveyed by ONDRAF/ NIRAS;

- the qualitative importance of this public, which comprises most of our future opinion leaders;

- the moral and political weight of the youngsters' opinions.

An important aspect of the methodology is to get in touch with the youngsters (students), in order to be able to make a more detailed analysis of their attitude and motives.

The youngsters' teachers are also actively involved in the project. Experience shows that the teachers are often not or hardly informed, which hampers the transfer of information.

2. First attitude survey

2.1. General

The pretest was aimed at analyzing the attitude of the youngsters and their teachers as well as their receptivity with regard to the problem of radioactive waste management. The most appropriate channels to form the public's opinion were also evaluated.

Prior to the actual attitude survey, a number of criteria were established for the selection of the target group and a questionnaire was drawn up to be used as a guide for the attitude survey.

During the period considered (March to December 1991) the actual attitude survey was conducted (October) and the first conclusions were made available.

The survey was conducted by Marketing Unit and a team of sociopsychologists who supervised the opinion poll.

2.2. Objectives of the first opinion poll

The three parties involved, i.e. ONDRAF/NIRAS, Infopublic and Marketing Unit, compiled a questionnaire to be used as a guide for the actual opinion poll.

This survey, which should eventually lead to an explanatory model of the target group's attitude towards radioactive waste management, implies the following actions :

1. highlight the possible psychological barriers in matters of nuclear waste;
2. define how young people see such a problem;
3. determine the content of the most relevant and efficient information for schools.

2.3. Information collection technique

On account of the diversity of persons to question, both pupils and teachers, it proved necessary to use two different information collection techniques :

2.3.1. Discussion group

The approach used with students consists in convening 8 to 10 participants to an open discussion of about one hour and a half to two hours.

The group is moderated by a psychologist and relies on a animation guide.

2.3.2. Thorough individual interviews

This approach is used with teachers and consists in inviting a single person to talk openly on the subject, which makes it possible to thoroughly examine his attitudes, opinions and motivations.

The interview generally lasts one hour and is best used with persons who can only be convened with difficulty for reasons of availability, which is often the case of teachers.

2.4. Interviews

In all, five discussion groups and twelve thorough individual interviews were conducted with the following distribution :

5 discussion groups

- 2 in Brussels (1 at the European School)
- 1 in Liège
- 1 in Ghent
- 1 in Antwerp

12 thorough individual interviews

- 3 geography teachers
- 3 physics teachers
- 3 chemistry teachers
- 3 religion or moral philosophy teachers

- 7 in French
- 5 in Dutch

2.5. Conclusions

Conclusions were drawn at the end of the following steps :

- debriefings with group moderators and interviewers;

- full transcription of group discussions and interviews from audio and video cassettes;

- analysis of the content using an analysis grid derived from Carl Gustav Jung's personality theory.

In the conclusions, the points of view of teachers and pupils were treated separately only when there were significant differences. In all other cases the analysis was general, i.e. valid for the various people questioned and for the various selection criteria considered by the study.

The conclusions of the study consider :

1. Nuclear energy

   The public is not explicitly asking for information on nuclear energy as involving oneself in this issue raises a conflictual debate in one's own personality between the "pros and cons" of nuclear energy.

   Currently, there are gaps in the information of the public. The public is only informed in case of an accident and thus only in distressing circumstances.

   Information outside of accident situations, focusing on the economic and moral aspects of nuclear power, seems to help overcome psychological barriers, i.e. provide the individual person with objective information enabling him to participate in the debate and try to solve it.

2. Nuclear waste

- The level of information on nuclear waste and on its management is very low. There is no materialization of nuclear waste.

- The public does not know who deals with the management of nuclear waste and supposes that it is the power stations themselves. This reinforces the basic fear as there seems to be no guarantee for the quality of management.

- Even if nuclear waste is part and parcel of nuclear energy and thus touches all levels of this issue, it is more particularly linked to the technical and moral aspects. Information on technical aspects is essential.

The guidelines for an information programme consider some elements which have a direct incidence on the development of the information programme :

1. nuclear energy constitutes a vast issue touching various fields. Information on nuclear waste seems difficult to isolate from the whole issue.
   Consequently, the approach must be comprehensive.

2. The level of implication of the public is low, which means that there is no spontaneous demand for this type of information. In other words, as the approach is not supported by expectation, it will be of a voluntarist nature. The approach will have to minimize the degree of freedom of the listener, i.e. it will have to be highly structured and placed in a structuring environment (school, courses, ...).

3. The absence of explicit demand for information on nuclear waste implies the need for a structured approach within a structured environment.

Of course, the pupils' attention will have to be as high as possible, which seems to imply :

- the intervention of a person from outside the school, a member of an competent body, to increase the credibility of the information;

- the intervention in schools, which implies that school governors will have to be convinced first. It appears to be difficult to raise interest outside schools or an equally structured environment.

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
Contract No: FI2W-CT90-0043
Duration of contract : June 91 - May 94
Period covered : June 91 - December 91
Project leader : J.M. Courouble

A. OBJECTIVES AND SCOPE

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

The first step of the work aims at : searching and defining a good media dissertation and realizing a pilot operation of communication.
The results expected will form a practical contribution to solve sociological problems issued by waste management, whether they be 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, two 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.

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. : EL4, 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 proposed discourse.
B4 : Methodology of pilot operation : study of original communication charter; meetings with support producers; contacts with the media.
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.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement :

During the latter months of 1991, meetings and visits were organised between experts of CEA (Unit of the Commissioning of nuclear installations), having several years of experience, and the partners in order to give them the first explanations on the technical field of the work.

Title:	The Evolution and Implementation of a Public Information Strategy on Radioactive Waste Management
Contractor:	McAvoy Bayley/GCI London
Contract No:	F12W-CT90-0074
Duration of Contract:	From 1st July 1991 to 30th June 1993
Period covered:	1st July 1991-31st December 1991
Project Leader:	Michael McAvoy

A. OBJECTIVES AND SCOPE

To provide a firm basis for the evolution of Community policy on the public information aspects of radioactive waste disposal, to enable the communications lessons learned by individual Member Country authorities to be shared across the Community, and to provide a resource base of independent and authoritative communications materials to be used in the communications programmes of Member Countries.

B. WORK PROGRAMME

In this period the work consisted of establishing what knowledge exists on radioactive waste on the part of the general public; establishing what public information programmes are doing to improve that knowledge; and developing an information strategy for the CEC to help close the gaps in knowledge revealed by this research. In addition, following discussion with DG X11, a basic information leaflet on the management of radioactive waste, for the use of and distribution by the CEC, was written and designed.

PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The limitations of conventional opinion research, as a basis for the evolution of an information strategy, have been identified. More sophisticated psychological approaches to the analysis of public attitudes are necessary. The defects in the nuclear industry's present public information strategy have also been identified. This involved a structure of consultation with communications professionals in the industry, and the sharing of best practice across the EC. A review of young people's knowledge of our attitudes to radioactive waste has been conducted, plus a survey of relevant information materials available for schools' and teachers' use. The materials currently available fail to tackle attitudinal blockage to learning. An approach is suggested for developing a flexible teaching package which could be incorporated in various EC syllabuses for the 14-16 age range.

Progress and Results

Published opinion research findings, by the CEC, OECD and the British Nuclear Forum were reviewed and analysed and compared with more sophisticated approaches, eg, of Lee and Allen of the University of Surrey and of Atomic Energy of Canada. The latter seems likely to provide a more solid basis for evolving a public information strategy, since the public have an emotive attitude to simple questions about radioactive waste. The public information practices of the nuclear and of the radioactive waste agencies were reviewed and materials collected. It is concluded that because insufficient attention has been paid to audience needs and attitudes, the industry has an unrealistically broad range of target audiences, has a technological bias in the content of its messages, fails to convey the benefits associated with radioactive waste, has perhaps relied too much on the waste agencies to communicate with the public; and the agencies themselves can seem anonymous and impersonal.

Nevertheless, it is the industry which must shoulder the burden of communications; the CEC cannot perform this role but should help and encourage the industry. Ways of disseminating best communications practice throughout the industry are suggested through questionnaires and seminars. The CEC should produce and publish a certain amount of information itself - a basic leaflet has been written and designed - but should consult with the industry about future video or exhibition material. The CEC should discuss co-operation with ANDRA on public information, with special reference to the information value of the new Centre de L'Aube facility at Soulaines.

In the eduction sector, our extensive literature search was undertaken for research on young people's knowledge and attitudes to radioactive waste and other topics. The specific topic of radioactive waste management has received little systematic study. In general, young people's knowledge and attitude to radioactivity is heavily influenced by the media, which are often emotive and inaccurate in their reporting. Young people bring the attitudes they formed to their studies. A critical review of the educational materials from the industry shows that they often fail to recognise these implanted attitudes. In the light of this, and of the variation in syllabuses and teaching approaches in different EC Member States, a rationale was devised for developing a flexible teaching package consisting of linked but free-standing units of work, which could be incorporated in a range of different syllabuses for the 14-16 range. It is recommended that a panel of EC teachers be established to advise on the design of this material.

Title:	Transmutation of long-lived radionuclides by advanced converters
Contractor:	Siemens AG Power Generation Group (KWU)
Contract No:	FI2W-CT91-0103 Task 1
Duration of contract:	October 1st 1991 to September 30th 1993
Period covered:	01.10.1991 to 31.12.1991
Project Leader:	Dr U. Wehmann

A. Objectives and Scope

The study will analyse the possibilities, limits and technological development steps needed for transmutation 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 a coupled system of fast and superfast zones or a small unit, which mainly will be constructed for transmutation. The other advanced transmutation devices are special accelerators, spallation machines and fusion reactors.

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

B. Work Programme

1. Large fast reactors with MOX- and metal fuel, fast zones and high axial leakage.
2. Fast reactors, small units
3. Spallation machines
4. Fusion reactors

C. Progress of Work and Obtained Results

State of advancement

Referring to programme items 1 and 2 some reference cores with MOX-fuel and sodium coolant have been defined and calculations have been started to determine the most important nuclear parameters.
For items 3 and 4 only available publications have been collected.

Progress and results

The period upon which it is reported is the start up phase of the planned work. To harmonize the work to be done by the different organisations the first coordination meeting took place in Cadarache on October 4, 1991.

The work began with the definition and basic design of the 3 following reference cores within the core size variation:

total thermal power / MW /	3600	2500	450
core height / cm /	100	70	70
no. of fuel subassemblies	387	387	84
no. of pins per S/A	331	331	271

The fuel pin diameter of 8.2 mm was kept constant within this study together with the maximum linear ratings of 520 W/cm and 410 W/cm at BOL and EOL and the maximum burnup of 20 at%.

Up to 15 % of the heavy metal content was replaced by Minor Actinides with a composition which is typical for the discharged fuel of Light Water Reactors. The fuel was burnt over 6 years. The most important nuclear parameters to be studied are the burnup reactivity loss, the sodium void effect, the Doppler constant and the absorber worth values.

Title : Participation in a CEC strategy study on nuclear waste transmutation
Contractor : Stichting Energieonderzoek Centrum Nederland-ECN
Contract No: FI2W-CT91-0104
Duration of contract : from November 1991 to October 1993
Period covered : from 1 November to 31 December 1991
Project leader : K. Abrahams

A. OBJECTIVES AND SCOPE

This project has as objective the improvement of the nuclear data base needed for strategy study on nuclear waste transmutation, including inventory calculations. Further a contribution to the CEC strategy study will be made in the form of a paper on transmutation of long-lived fission products.

Although the Netherlands Energy Research Foundation ECN, acts as the sole contractor for this contract, there is a close collaboration in related strategy studies, such as the ones of CEA and Siemens.

This project fits into a much broader ECN Integral Research Program 1991-1994 for the study of Recycling Actinides and Fission Products [1]. This research programme on transmutation of nuclear waste has the intention to give a contribution to an international effort to evaluate the recycling option of the nuclear waste problem. Besides strategy and scenario studies, reactor physics research, and an effort towards small scale demonstrations of transmutation possibilities, the above mentioned program contains the present project, which is focused on the nuclear parameters, relevant for transmutation.

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 asses 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.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

In coordination with CEA and Siemens a harmonization has been discussed of three Community contracts, which regard to studies on possibilities to reduce the long-term radio-toxicity of nuclear waste. The ECN proposal is of vital interest, as far as it aims towards common data sets and standardized libraries for relevant cross sections. Also the proposed ECN work on long-lived fission products is considered to be an important contribution to the joint studies.

As a first step the Petten group now has started to adapt codes and libraries (ORIGEN and FISPACT, and especially working libraries of cross sections, nuclear decay constants, and risk data) for reactor physics and burnup calculations. With respect to the work on codes and libraries the ECN data set will be used. Especially for nuclear data on actinides and long-lived fission products this data set should be improved. Now the most recent European JEF-2 library is being inspected on quality and completeness. As the JEF-1 library is readily available in processed data, it can be used as a back up. Last but not least there was a substantial progress in the study of fission product transmutation (work programme 2.4 is emphasized in this report).

Progress and results:

Chapter 1. Work programme 2.1 and 2.2: Common data sets

During the period covered (two months), limitations and formats were defined in agreement with other CEC strategy studies:

- All partners will use as much as possible the JEF-2 data. Meanwhile preparations have been made at Petten to process this very new library by means of the NJOY code.

- CEA will make available the new French risk data as a basis for this study.

- ECN will check the JEF-2 files for completeness and will deliver improved I-129 and Tc-99 compilations. The I-129 evaluation has already been finished and forwarded to CEA-Cadarache. An update of the Tc-99 evaluation is under way.

- The laboratories engaged in the present study will average the data over some standard spectra (PWR en FBR), which will be exchanged. Resulting one group data for important

actinides will be compared in early 1992.

- Standardized libraries will be used, for example CEA uses JEF-2 libraries, which are associated with the new European cell code ECCO. On request CEA may deliver this library to its partners.

- Work of the partners will be coordinated on quarterly meetings.

- Neutron spectra, which are typical for Phenix moderated blankets, were received by ECN from CEA-Cadarache. These data will be used to calculate the effectiveness of such blankets for fission product transmutation.

Chapter 2. Work programme 2.3 : Sample burn-up calculations

As the updated nuclear data library will not be available until the work mentioned above under item 2.2 has been rounded off, the sample burn-up calculations could not yet start. There is however some material available on LWR's and LMFBR's, which resulted from calculations with the old data set. Although final conclusions can only be made when these calculations have been repeated with the new library, a summary of preliminary conclusions showed to be a good preparation for the work to be done.

Chapter 3. Work programme 2.4: Study of possibilities of transmutation of fission products by means of thermal neutrons

Some first considerations on this study are given below. Under coordination with the partners a full discussion paper on this subject will be given, which may serve as a basis for the final report on fission product transmutation.

3a. Consideration of risks

Considerations on the risk of waste disposal will depend on scenarios for leaching out waste from imposed barriers. If these scenarios would also involve leaching out by water, after human intrusion of the disposal site, the high mobility amplifies the risk of Tc-99, I-129 and Np-237. Although toxicity of freshly spent fuel is hardly determined by Tc-99 or by I-129, the long half life and the high yield in the fission process is such that the risk for these two radionuclides will be amplified to a value, which already may be dominant after expiration of a few hundred years period.

In order to reduce the long-term risk, one may decide on

transmuting Tc-99 and I-129 to stable Ru-100 and Xe-130 by means of low-energy neutron capture. An intense flux of thermal neutrons may be created with a spallation source, an accelerator-driven reactor, a fast reactor with a flux trap, such as the Tauber reactor, a thermal high flux reactor or any other high flux device, based on fission, fusion, spallation or a combination of these processes. Unfavourable for any incineration scheme, which uses neutrons generated in the fission process is that the very fission process yielding these neutrons, also yields fission product waste. Simple calculations show that for fission products such as Tc-99 (yield about 6 %) and I-129 (yield about 1 %), the amount of newly formed fission products competes significantly with the amount of transmuted fission products unless the concentration of the fission products in the reactor is high. Environmental economy therefore may favour transmutation in an intense thermal neutron field in a special burner High Flux Reactor or in a flux produced by a spallation neutron source.

Besides the above mentioned long-term risks, one should also consider short time risks. Especially transmutation of I-129 imposes some risk factors during and shortly after the irradiation itself. During a long irradiation time one has to deal with the iodine, compounds of which are very corrosive, volatile and unstable at high temperatures. Further, the transmutation product, which is xenon gas, could cause swelling and fuel rod pressurization problems. For these reasons the transmutation of iodine has been considered to be only marginally feasible for quite some time [2]. Some new ideas, involving vented pins and ceramic iodides as fuel may show a way out [3], as is currently studied also at ECN.

Other obvious points in risk analysis relate to formation of new radio-isotopes by activation in and around the device, which is used to generate the neutrons. Low activation construction materials for the neutron generator and the sample encapsulation are searched for, and it still should be demonstrated that, for example the spallation products from an accelerator-based neutron source are less bothersome than fission products from a reactor based neutron source.

3b. Economy of fission product transmutation and practical demonstrations

In contrast to the burn-up of actinides no useful energy will be released during the transmutation of fission-products. So first the question should be answered whether the energy cost of transmuting the fission product is not outweighing the energy generated during the creation of these products. This question may be answered by judging the cost of this transmutation process, as compared to the cost of nuclear

fuel. Probably there are two major cost factors, the neutron cost and the chemical handling and shielding costs. An estimate of the costs can be based on earlier studies of breeding Pu-239 by thermal neutron irradiation of U-238. In this case neutron cost and handling cost are not supposed to exceed practical limits [4], and it seems likely that the cost per atom should be lower for I-129 as well as for Tc-99. With this in mind, and supposing a competitive price for breeding fuel in the future, the cost of transmutation of long-lived fission products would be about 7% of the cost of the fuel from which this waste originated. Obviously, as breeding fuel is not yet competitive, the cost of transmutation, as a fraction of the fuel price is much higher. Clearly the economics should be verified e.g. by more quantitative study and finally by practical demonstrations in a pilot plant. Especially the assumption that handling costs can remain on a relatively low level ought to be tested.

As mentioned under 3a, ECN will make an effort towards small-scale demonstrations of transmutation possibilities by using the Petten High Flux Reactor (HFR), which is an ideal test reactor for thermal transmutation. This effort in itself is not subject to the present contract, but it is strongly related and all relevant information will be used to be included in the report for this contract. For example: In order to support these demonstrations, some nuclear data are required: capture and (n,2n) cross sections of Tc-98, 99, of Ru-100, I-128, 129, Xe-130 and also for elements in carrier materials and elements in cladding. These data are extracted from the same libraries as the ones needed for this contract.

References

[1] H. Gruppelaar and K. Abrahams, Recycling Actinides and Fission Products , proposal for an ECN Research programme 1991-1994

[2] ORNL-5566 ACTINIDE PARTITIONING-TRANSMUTATION PROGRAM 1980 FINAL REPORT by A.G. Croff, J.O. Blomeke, and B.C. Finney

[3] Irradiation Targets to transmute I-129, H.R.Brager, L.D. Blackburn and D.W. Wootan (Westinghouse Hanford), ANS Winter Meeting, November 11-15, 62 (1990) 103.

[4] Proc.Information Meeting on Accelerator-Breeding, Brookhaven, ERDA report CONF-770107 (1977).

Title : Potentialities and costs of partition and transmutation of long-lived radionuclides
Contractor : CEA, France
Contract No: FI2W-CT91/0106
Duration of contract : October 1991 to September 1993
Period covered : October 91 - December 1991
Project leader : Fuel Cycle Direction CEA (G. Baudin)

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 ; technical ways and costs will be evaluated.

In a first step reference scenario will be defined i.e 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 different items of this program are the following :

1.- References scenarios :
- . definition of involved reactors (number, type, ...)
- . evaluation of produced radionuclides (Am, Np ...)
- . potential radiotoxicities.

2.- Step one : available technologies :
- . Separations :
  - . definition of processes
  - . evaluaton 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 OBTAINED RESULTS

In the three months period from 01.10.1991 to 31.12.1991 the following actions have been launched :

Detailed specifications of scenarii to be studied, with three distinct phases, have been identified :

a.1 - without any recycling of actinides i.e direct disposal of PWR fuels.

a.2 - recycling of actinides taking into account present efficiencies of partition and transmutation.

. i.e PWR UOX with recycling of all Pu coming from reprocessing in MOX reactors till 2020 and introduction of FBR after 2020,

. incineration of minors actinides (Am, Np) in PWR or FBR.

Examples of scenario is given in fig.1, scenario R2, for fuel cycle (PWR UOX and MOX) and in fig.2 for incineration in reactor, scenario RP1.

Schema for computing data for the considered scenarii will be build up especially, core neutronic computation giving physics parameters correlated to different types of recycling necessary for :

. computation of in-reactor evolution that gives considered elements balances. Those values being necessary to compute strategy where all technological data concerning fuel cycle are take into account and finally gives the variation of radiotoxicity balances of wastes with time.

a.3 - recycling of all minors actinides including Cm and some long lived fission products with high partition yield and transmutation in reactors (special for incineration) or accelerators.

FIGURE 1 - SCENARIO R2 - FUEL CYCLE
WITHOUT INCINERATION

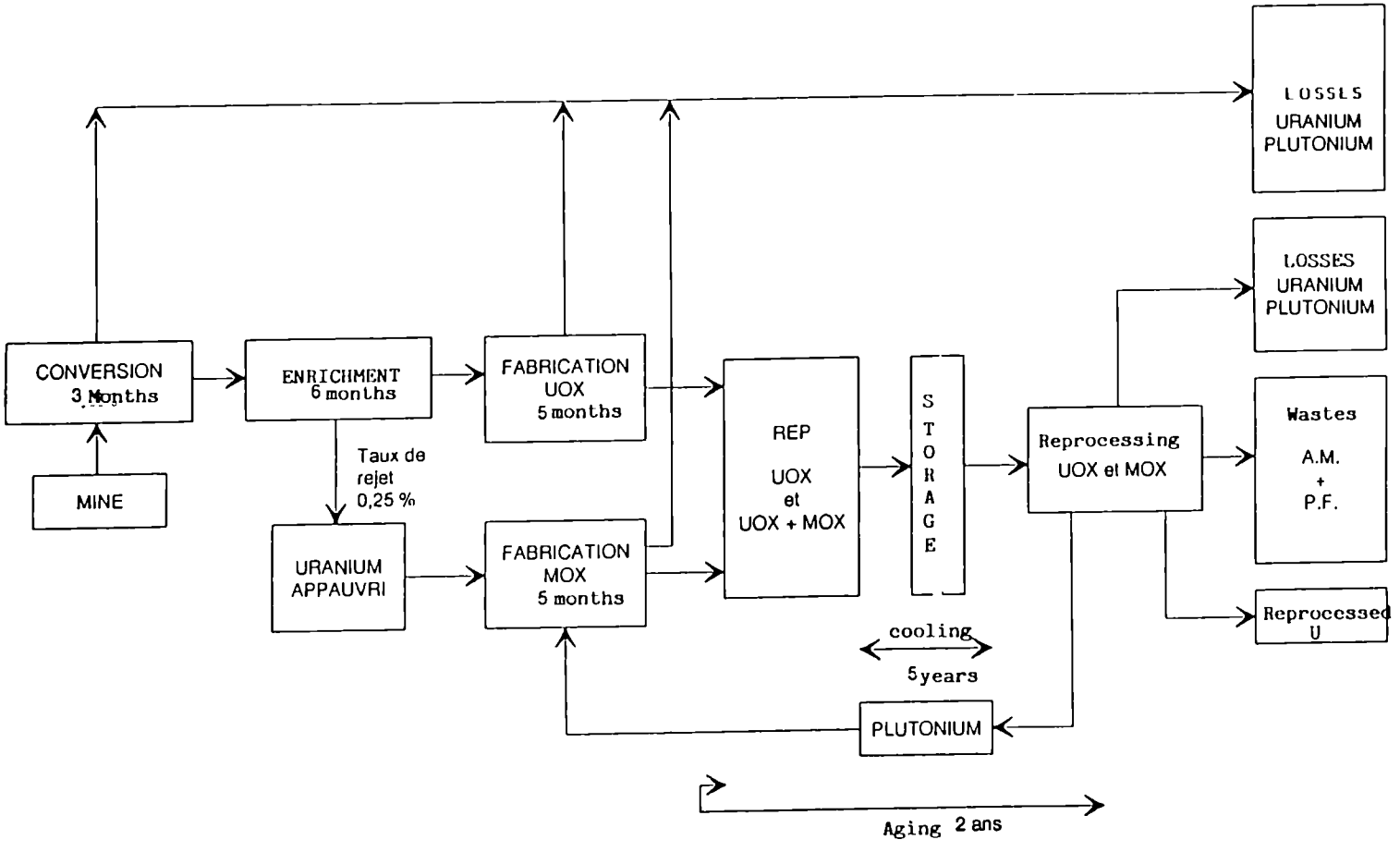
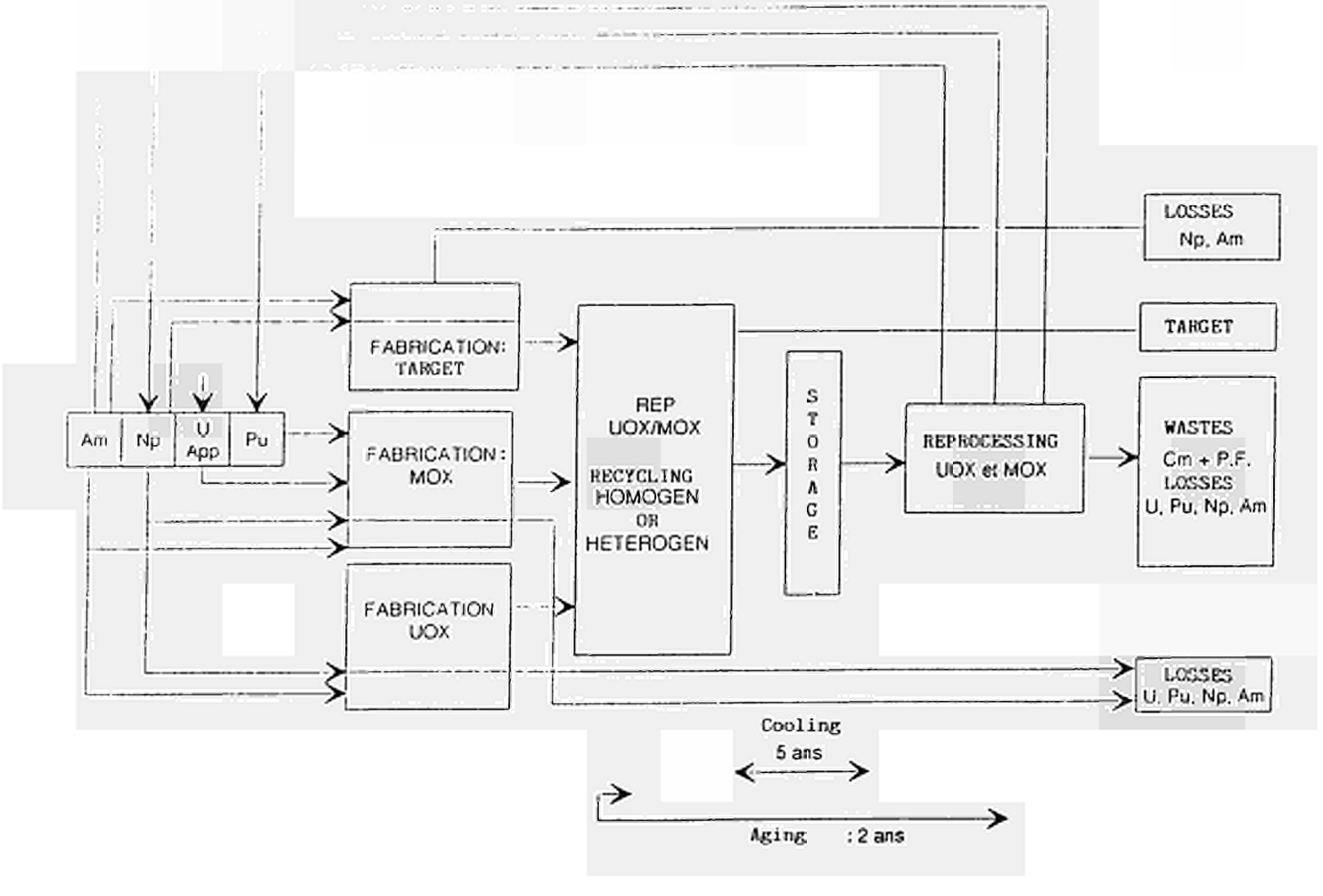


FIGURE 2 - SCENARIO RP1 - FUEL CYCLE INCINERATION



A2: WASTE TREATMENT

Task 2

"Treatment of Radioactive Waste"

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

Topic 1 : Minimization of radioactive discharges

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

FI2W/0057 (Part of work programme carried out by LNETI = see topic 2)

Topic 2 : Reduction of waste volumes to be disposed of

FI2W/0052 Compaction of radioactive hulls by high-temperature melting in a cold crucible.

FI2W/0053 Wet oxidation of organic containing wastes.

FI2W/0057 Advanced processes for the treatment of low level liquid wastes at a pilot plant scale.

FI2W/0095 Process design and feasibility study for incineration under pressure, condensation and effluent treatment of radioactive waste.

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

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

FI2W/0070 Decontamination of solid alpha, beta, gamma waste for de-categorisation purposes in terms of disposal route.

Topic 5 : Potentialities of transmutation of long-lived radionuclides

FI2W/0047 Partition of radioactive wastes.

FI2W/0056 Advanced management of radioactive wastes : comparative evaluation of processes for enhanced separation of very long-life radioactive species.

FI2W/0112 High-level liquid waste partioning by means of completely incinerable extractants.

TASK Nr. 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 wolumes 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 partioning 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

Presently Task 2 comprises 13 research contracts, four of them being multinational. They cover the following topics :

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, 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 oxigen under pressure (Bertin, CEA-Cadarache and INITEC).

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, ENEA-Casaccia and KfK.

Title :	Improvement in the performance of the conventional Treatment of Liquid Effluents by Co-Precipitation
Contractor :	CEA-DCC
Contrat N° :	FI2W/CT90/0054 Task 2
Duration of Contract :	From May 1st 1991 to April 30 Th 1995
Period Covered :	May-December 1991
Projet Leader :	FROMONT Michel

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 :

- 45 000 Ci ($1\,665.10^3$GBq) for all radioelements (except tritium) including 6 000 Ci (222.10^3 GBq) for Sr^{90} and Cs^{137} ;
- 45 Ci (1 700 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 :

10/90 to 10/92

- the characterization 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.

10/92 to 10/94

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

10/93 to 10/94

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

C. *PROGRESS OF WORK AND RESULTS OBTAINED*

- State of Advancement

During 1991, an assessment was made of the radioactivity releases from the STE plant of The Hague, from its beginning until 1990. The period covered by the present contract will see a shift to "top gear" at the UP3 plant then at the UP 2800 plant, which makes it difficult to estimate the evolution of releases and therefore to select the complementary process to implement in order to reduce the radioactivity released by a factor, that we have arbitrarily fixed, of 10.

It is to be noted in particular that, following a change in effluent management in the various reprocessing workshops, the share of the Ru/Rh 106 pair was reduced during the first half of 1991 from 85 % to 60 % as regards the activity of the effluents to be reprocessed, thus showing that higher decontamination must be sought for above all in the Sb 125 and in the Sr-Y90 pair.

Low and medium activity radioactive effluents from the STE reprocessing plant were received at Cadarache and characterized. In particular, the ionic forms of ruthenium and antimony were determined by electrophoresis, in relation to the medium acidity.

Insolubilization and filtration tests were performed on the available V effluents, while, using synthetic effluents labeled with Sr 90, the interest of carboxylic and complexing resins was confirmed.

PROGRESS AND RESULTS

1. THE FACTS OF THE ISSUE

Up until 1989, radioactive liquid waste from the UP2 400 reprocessing plant (400 tonnes of fuel per year) was received and treated at the STE2 liquid effluent reprocessing plant except for solutions of fission products. As the years went by, treatment by chemical co-precipitation applied respectively to low and medium activity effluents evolved with the augmentation of the specific radioactivity of the effluents, an expression of both the power increase of the plant and the rise of the burn-up rate, as well as with the nature of the fuel.

Figure 1 shows the evolution of the beta activity of the effluents received and treated in the STE2 plant, a comparable evolution being observed for alpha activity, both having always met release regulation standards.

More adapted to present reprocessing, the STE3 plant (Figure 2) has progressively replaced the STE2 plant.

As it has already been pointed out, the implementation of new workshops, together with an improvement in the performance of the ST3 plant, has recently altered the spectrum of radionuclides present in the treated effluents. Research on complementary decontamination processes will be directed according to the distribution observed in 1991, that is to say :

- 125 Sb : 40 to 50 %,
- 106 Ru-Rh : 20 to 25 %,
- 90 Sr : 10 to 15 %,
- 137 Cs : 4 to 5 %.

Finally, it must be recalled that, in order to reduce the alpha content of discharges, V effluents should be investigated as they account for 50 % of the discharged alpha activity, although they represent only 3.5 % of β activity.

2. CHARACTERIZATION OF THE EFFLUENTS TO BE TREATED

At the conclusion of the chemical treatment shown in Figure 2, the effluents had the following characteristics :

- sodium nitrate 0.5 to 1 mol l^{-1},
- sodium sulfate 0.05 to 0.08 mol l^{-1},
- 8.5 < pH < 10.5,

Ru106 : 0.05 to 0.2 Ci/m^3 Cs137 : 0.001 to 0.005 Ci/m^3
Sr90 : 0.005 to 0.01 Ci/m^3 Sb125 : 0.01 to 0.1 Ci/m^3
Total alpha : 1 to 2.10^{-4} Ci/m^3

In 1990, 92 886 m^3 of V effluents were discharged representing a total β activity of 286 Ci and α activity of 3.5 Ci.

3. IONIC FORMS OF RUTHENIUM AND ANTIMONY

The first ionic form identification tests carried out by means of electrophoresis show that in an actual treated effluent :

- antimony is in cationic form in an acid environment and anionic form in an alkaline environment,
- ruthenium is in the form of anionic, neutral and cationic complexes all at the same time, the distribution depending on the pH ; with high acidity, the cationic forms are in majority.

The only slightly ionic character of these species rules out fixation by ionic exchange. As regards ruthenium and antimony, fixation by sorption or by complexing seems to be the most suitable.

4. TREATMENT BY MEANS OF FILTRATION, INSOLUBILIZATION AND SORPTION

On V effluents, retention of the radioelements by filtration or even ultrafiltration is not very satisfactory except for manganese 54 (DF > 40, 25 μm filtration), and to a lesser degree for cobalt 60 (DF $\simeq$ 8, 5 μm filtration). Insolubilization of radioelements with the mineral exchangers tested to date, followed by filtration, is of no advantage in relation to filtration alone ; the same is true of treatment with small doses of ferric iron or titanium.

In the absence of actual low and medium activity effluents at the beginning of this study, tests were carried out on synthetic effluents with added Sr85 and these confirmed the fixation of this radioelement on carboxylic and/or complexing resins. The effect of the pH on the decontamination factor was examined using the carboxylic resin CNP 80 and the iminodiacetic resins TP 207.

Figures 3 and 4 show, as was expected, that the best results are obtained with a distinctly alkaline pH (pH = 10-11), a range that is compatible with the pH of the effluents.

Tests will be pursued using real effluents.

LIST OF PUBLICATIONS

No publications dealing with the work under this contract.

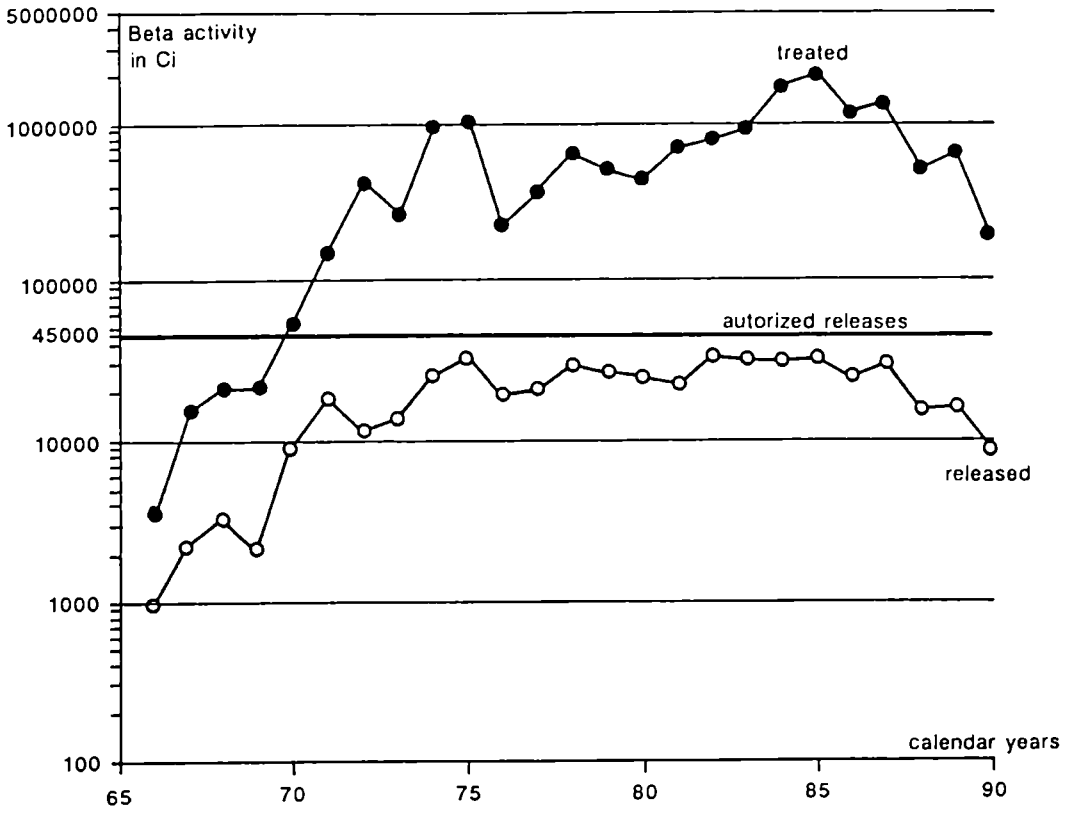


Figure 1 : STE reprocessing plant - Beta activity received and released from 1966 to 1990

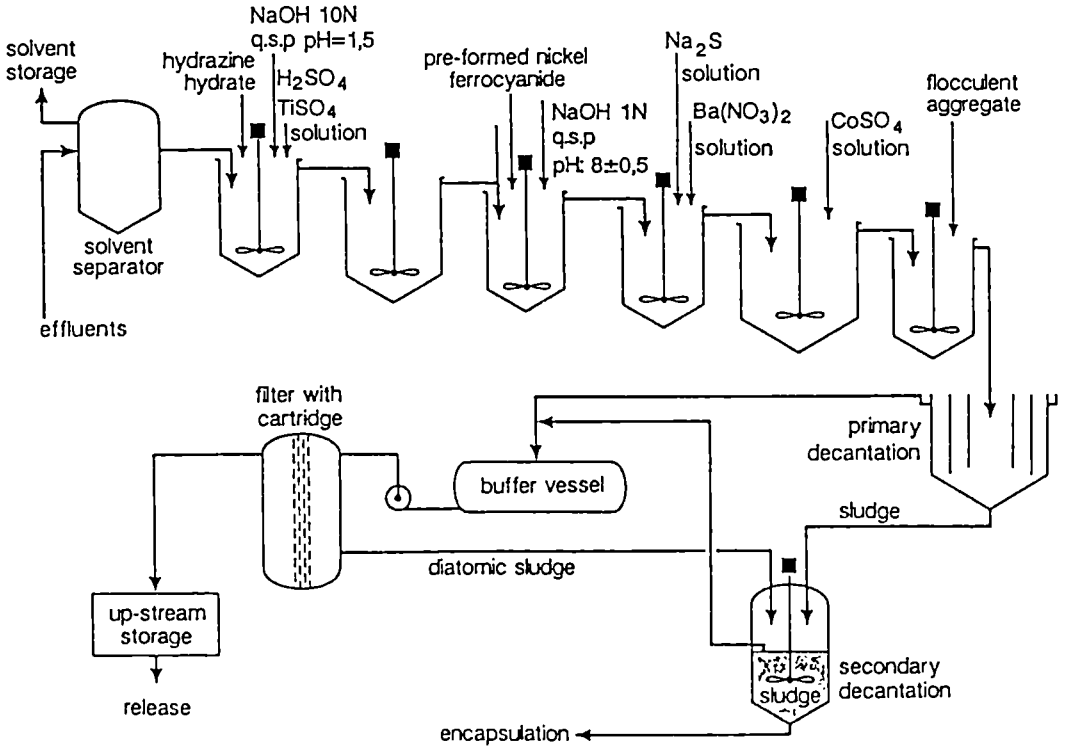


Figure 2 : Diagram of the effluent reprocessing principle

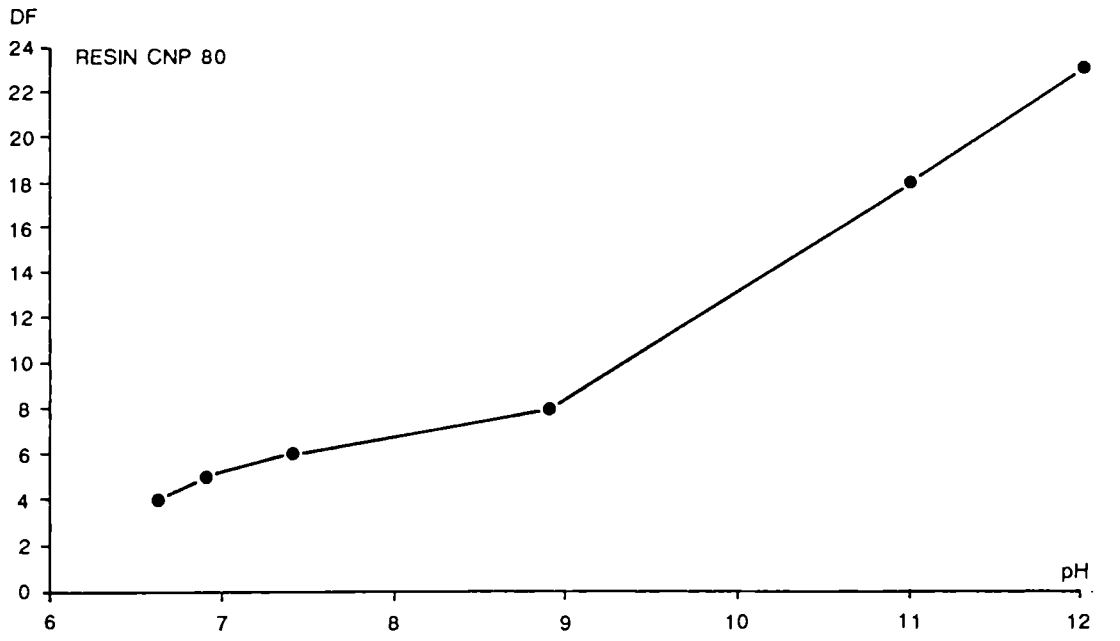


Figure 3 : DF for Sr function of pH Synthetic effluent after STE3 treatment

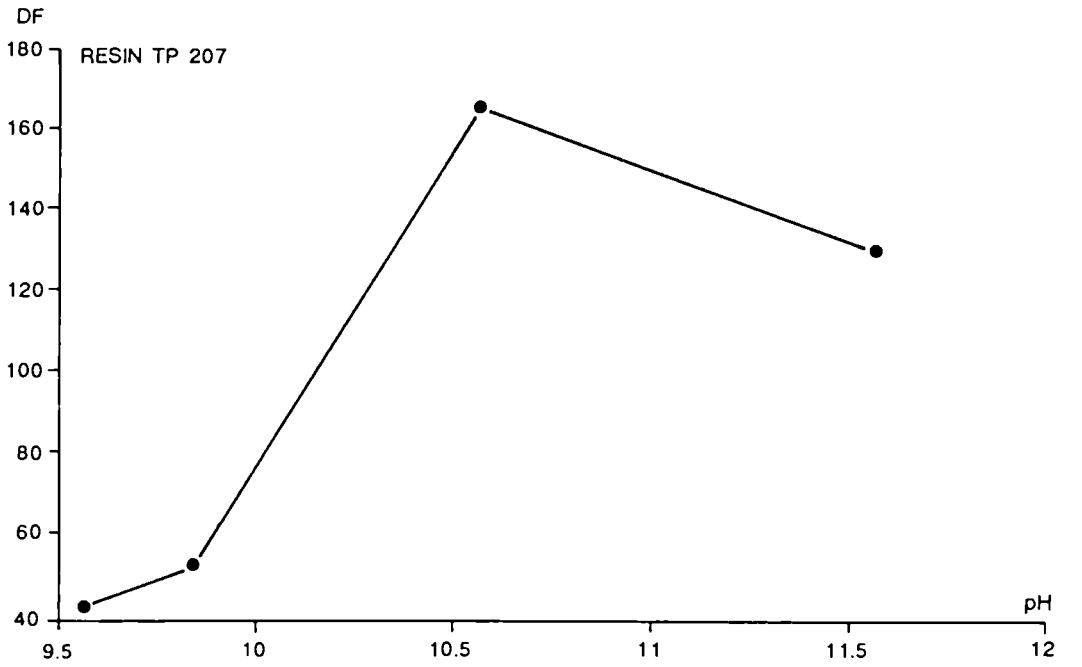


Figure 4 : Same test with RESIN TP207

COMPACTION OF RADIOACTIVE HULLS
BY HIGH-TEMPERATURE MELTING IN A COLD CRUCIBLE

Contractor: CEA - CEN Valrhô - DCC
Contract No: FI 2W/CT90/0052
Contract duration: January 1991 to December 1992
Period covered: January 1991 to December 1991
Project leader: R. Piccinato

A. OBJECTIVE AND SCOPE

The cold-crucible high-temperature melting process for compaction of cladding hulls has been developed in France by the CEA at Marcoule since 1982 under inactive conditions in a full-scale industrial prototype, and since 1988 under active conditions in a laboratory facility (Cell 73). This method reduces the waste volume and exchange surface area, and eliminates any occluded radioactive gases. Its feasibility has been demonstrated for conditioning radioactive stainless steel hulls.

This research project involves compacting radioactive zircaloy cladding hulls in Cell 73. The programme objectives are:

- to produce zircaloy ingots from radioactive hulls;
- to characterize the ingots;
- to determine the volatility balances;
- to assess the decontamination factor obtained.

B. WORK PROGRAMME

B.1 Production of four radioactive ingots in Cell 73 with zircaloy hulls from the Obrigheim reactor.

B.2 Investigation of the activity partition between the flux and ingot.

B.3 Characterization of two ingots:
- Structural homogeneity
- Internal activity distribution
- Leaching resistance.

B.4 Determination of the process volatilization balance.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

Three zircaloy ingots were produced with a melting flux containing equal weight percentages of CaF_2 and BaF_2. Variable parameters included the flux percentage, the generator power, the ingot drawing rate and the chemical purity of the flux.

Alpha decontamination was low (3 to 6%), while beta decontamination was higher (about 50%). Most of the ^{137}Cs was volatilized and trapped on the cold crucible head and in the particle separator; much of the ^{90}Sr was retained in the flux. Problems were encountered with tritium trapping.

The current state of advancement is as follows:

B.1 Three active ingots have been produced: Zi-03, Zi-04 & Zi-06.

B.2 The activity partition between the flux and ingots has been determined for ingots Zi-03 and Zi-04, and is still in progress for ingot Zi-06.

B.3 Characterization will be performed in 1992.

B.4 The process volatilization balance has been determined for ingots Zi-03 and Zi-04.

Progress and Results

1. Ingot Production (B.1)

The ingots were produced from a mixture of 90% active zircaloy hulls and 10% inactive stainless steel hulls; the mixture was required on the basis of safety studies, and allowed melting at a lower temperature. Melting was initiated on a zircaloy seal weld topped by a stainless steel washer. The flux fraction varied from 7 to 14% of the active hull weight. No major problems occurred during melting. Some incompletely melted hulls are visible at the top of ingots Zi-04 and Zi-06.

The material mass balance shows a deficit of about 1% for the metals, and between 4 and 14% for the flux. The reasons for this situation are now being investigated.

The ingot melting process parameters and characteristics are summarized in Table I.

2. Radionuclide Volatilization (B.4)

The volatilized activity is the sum of the activities recovered in the off-gas treatment system components (particle separator, scrubbing column, filter) and the activity measured on the cold-crucible head.

The most volatile element was ^{137}Cs (84-89%), followed by ^{134}Cs; the volatility of ^{90}Sr was low, and the remaining elements (notably the alpha-emitters) showed very low volatility. Tritium was satisfactorily trapped only for ingot Zi-03: 47.5% of the theoretical activity in the hulls was recovered. Technical problems arose for the other ingots.

3. Flux Activity (B.2)

The flux was easily prepared for analysis: the ingots were descaled, then the flux was crushed and subjected to alkaline melting.

The flux contained approximately 25% of the beta-gamma activity but very little (1.5-4.5%) of the alpha activity. The trapped radionuclide concentrations were similar in the flux for the melts analyzed to date:

- transuranic nuclides: 65% of the $^{238}Pu+^{241}Am$, 15% of the $^{239-242}Pu$ and 20% of the ^{244}Cm;
- beta-emitters: 90% of the ^{90}Sr.

4. Ingot Activity and Chemical Analysis (B.2)

The ingot was cut up with a reciprocating saw to remove test coupons; the cutting operation was relatively time-consuming.

Elemental analysis showed a uniform metal chemical composition. The α and $\beta\gamma$ activity was also uniformly distributed, notably for ^{60}Co and ^{125}Sb; the uncertainty margin was inevitably greater for the nuclides present in small amounts.

The ingots contained most (94-97%) of the alpha-emitters and virtually all the beta-emitters (^{60}Co, ^{125}Sb, ^{144}Ce, ^{54}Mn).

The activity distribution in the off-gas stream, the flux and the ingots is indicated together with the corresponding decontamination efficiency in Tables II and III.

Table I. Process Parameters and Characteristics of Ingots Zi-03, Zi-04 and Zi-06

Parameter	**Zi-03**	**Zi-04**	**Zi-06**
Composition of hulls	Zr 90% SS 10%	Zr 90% SS 10%	Zr 90% SS 10%
Active Zr hull mass (g)	1690	1520	2110
Mass of Zr seal weld + stainless steel washer (g)	690.4	698.2	695.3
Ingot mass (g)	2512	2323.6	2980.6
Height of seal weld + washer (mm)	40	40	40
Height of ingot (mm)	142	138	170
Flux composition (wt%)	CaF_2 50% BaF_2 50%	CaF_2 50% BaF_2 50%	CaF_2 50% BaF_2 50%
Chemical purity of flux components	CaF_2 90 % BaF_2 99 %	CaF_2 90 % BaF_2 99 %	CaF_2 97% BaF_2 99%
Flux percentage relative to Zr hull mass	7.45	14.4	9.8
Flux percentage relative to ingot mass	5.8	8.8	6.9
Initial flux mass on seal weld (g)	55	61.6	66.3
Generator power (kW)	65	65	75
Ingot drawing rate ($g \cdot min^{-1}$)	38.7	31.2	29.8

Table II. Activity Distribution for Ingot Zi-03
Activity Percentages as of April 30, 1991

Nuclides	A Volatility %	B Slag %	C Ingot %	A+B Decontamination Efficiency (%)
90Sr+Y	6.63	85.92	7.45	92.55
137 Cs	87.97	7.41	4.62	95.38
134 Cs	63.78	4.84	31.38	68.62
106 Rh-Ru	2.85	0.01	97.14	2.86
144 Ce-Pr	3.27	2.22	94.51	5.49
125 Sb	0.69	0.28	99.03	0.97
60 Co	0.02	0.12	99.86	0.14
54 Mn	1.78		98.22	1.80
154 Eu		15.99	84.01	15.99
Total beta	25.21	27.33	47.46	52.54
239-242 Pu	0.54	0.54	98.92	1.08
238 Pu+241 Am	1.78	1.47	96.75	3.25
244 Cm	2.48	4.97	92.55	7.45
242 Cm			100.00	0.00
Total alpha	1.29	1.25	97.46	2.54

Table III. Activity Distribution for Ingot Zi-04
Activity Percentages as of April 30, 1991

Nuclides	A Volatility %	B Slag %	C Ingot %	A+B Decontamination Efficiency (%)
90Sr+Y	4.52	92.89	2.59	97.41
137 Cs	84.45	13.67	1.88	98.12
134 Cs	36.14	5.89	57.97	42.03
106 Rh+Ru	1.65	1.44	96.91	3.09
144 Ce-Pr	0.59	0.78	98.63	1.37
125 Sb	0.79	0.88	98.33	1.67
60 Co	0.08	0.00	99.92	0.08
154 Eu		21.16	78.84	21.16
54 Mn	0.48	2.44	97.08	2.92
Total beta	18.49	23.88	57.63	42.37
239-242 Pu	2.89	2.00	95.11	4.89
238 Pu+241 Am	0.99	4.95	94.06	5.94
244 Cm	1.02	8.12	90.86	9.14
242 Cm			100.00	0.00
Total alpha	1.55	4.49	93.96	6.04

Wet Oxidation of Organic Containing Wastes

Contractor:	AEA Decommissioning and Radwaste
Contract No:	FI2W/CT90/0053 Task 2
Duration of contract:	from March 1991 to February 1995
Period covered:	March - December 1991
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 Radwaste) 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 (IX) 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 inactive resin batch using pilot scale plant for the above applications.

The main objective of this programme is to demonstrate the feasibility of the wet oxidation technology 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 investigation include:-

- IX 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 waste in UK and EC context.
Task 2.3	Evaluation of previous experimental results outside this CEC contract.
Task 2.4	Completion of Wet Oxidation experiments at small scale for both inactive and active conditions.
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 flow sheets
Task 2.9	Analysis of safety and economic aspects

C. Progress of Work and Obtained Results

State of Advancement

Good progress has been made in Tasks 2.2 to 2.5, all of which are in-line with respect to completion of the programme. Progress for the first six months of the contract is detailed in the first semestrial report /1/.

The world-wide literature survey and the assessment of candidate wastes in the UK has been completed. Comprehensive information on candidate EC wastes has been obtained, and is currently being evaluated to establish the potential role of wet oxidation in its management.

Experimental studies have concentrated on IX resins, which have been identified as the major candidate waste type for treatment in the UK. Emphasis has been placed on determining the optimum catalyst requirements and pH control regime, which is necessary for process optimisation and safety considerations.

The appraisal of plant concepts has been completed, and the conclusions support the adoption of a semi-continuous process. This will incorporate many of the features of the batch process, and allow a partially continuous waste feed combined with batch discharge of the product.

Assessment of experimental results obtained from previous inactive treatment tests on organic containing wastes is being carried out.

Progress and Results

Task 2.2 - Analysis of Literature Data

Several waste streams in the UK have been specifically identified as suitable from a chemical and process stand-point for organics removal by hydrogen peroxide based wet oxidation /2/. The strongest case is for Intermediate Level Waste (ILW) containing significant quantities of ion exchange(IX) resin, on the basis of providing volume reduction and a product which is more acceptable for disposal. Direct cementation is currently the primary choice for final waste treatment in the UK. The treatment of cellulosic waste found in transuranic (TRU) contaminated and beta/gamma waste has also been selected for further investigation. Where existing disposal routes prove unsuitable for liquid wastes, such as decontamination liquors and scintillation cocktails, organics removal by wet oxidation may provide both volume reduction and a product more compatible with downstream processing.

In addition, a paper has been produced /3/, which reviews the information available in the open literature. The review is concerned with the development of the wet oxidation technique for application to radioactive waste streams. Wet oxidation has been taken to refer to oxidation of organics by catalysed hydrogen peroxide solutions. The process has been investigated by a number of groups world-wide for potential application to a range of wastes. A brief summary of the methods developed and the results obtained is provided in the review. ASEA Atom and Vattenfall of Sweden are concluded to have progressed the

method furthest for application to a single waste stream, while AEA Technology are shown to have progressed the method over a range of experimental scales and waste types, including work with radioactive material. The protection of rights to the process, or key aspects of the process, is also discussed.

Task 2.3 - Evaluation of Previous Experimental Results

An evaluation of previous experimental studies in the UK is well advanced. This will include a summary of work carried out by AEA Technology for the UK Department of the Environment.

Task 2.4 - Completion of Wet Oxidation Experiments

Small scale inactive studies have initially concentrated on ion exchange resins due to their position as the major candidate UK waste type. The susceptibility of three types of ion exchange resin to treatment by Wet Oxidation was examined. The general reaction scheme used was similar to that established at demonstration plant scale for the treatment of Winfrith SGHWR sludge tank waste /4/.

The aim of these experiments was to establish the effect of variation in reaction conditions for the Wet Oxidation of three types of ion exchange resin. From this information, optimum reaction conditions suitable for treatment at plant scale may be identified. Several requirements need to be met for a process applicable at plant scale to radioactive resin :

a) Kinetic Control

The consequences of high concentrations of hydrogen peroxide in the reaction mixture are potentially serious. Control of peroxide addition rate, reaction pH, temperature and catalyst concentration are necessary to prevent this occurring. For cationic resin treatment without pH control, highly acidic conditions (pH<1) are generated which lead to peroxide stabilisation. The establishment of safe operating conditions was considered a priority of the experimental programme.

b) Volume Reduction

The principal aim of the process is to effect a maximal reduction in conditioned waste volume, by removing the bulk of organic carbon from the resin and enhancing its compatibility with the conditioning process.

c) Peroxide usage and reaction time

Reaction conditions which minimise unproductive reactions of hydrogen peroxide are desirable to reduce operating costs for the process. A reaction time of under six hours is required for optimal use of plant, allowing one batch to be processed per day. A short reaction time requires increased peroxide addition rates, and hence can present process control problems. A balance between these extremes is required.

Distillation conditions were chosen as this simplifies temperature control, and minimises reaction vessel size. The peroxide addition rate was approximately constant for all experiments, and was based on previous experience with Winfrith SGHWR sludge. For each resin type, the catalyst to resin ratio, and pH were varied to establish their effect on the parameters described above. Most experiments used only iron(II)

catalyst. A few experiments were conducted using a mixed copper/iron catalyst to investigate possible synergic effects. Work began with Lewatit resin, and based on the experience gained for this type, fewer experiments were required for subsequent resins.

It appears from the results that two distinct sets of reaction conditions are capable of producing maximised volume reduction with good TOC removal. These conditions may be applied to all three resin types, although the peroxide requirement for IRN 150L and POWDEX may be increased. Organic carbon removal of over 95% has been demonstrated for each resin type, Volume reduction factors (relative to direct cementation) are estimated at 0.3-0.5, depending on resin type.

At high resin loadings (>10% dry weight) in the initial reaction mixture, and using distillation conditions, control of reaction pH by addition of calcium hydroxide slurry provides an effective means of reaction control.

Studies have now progressed to the evaluation of semi-continuous reactions with IX resin, and to the treatment of other forms of simulated waste streams such as cellulosics and decontamination liquors.

Task 2.5 Appraisal of Alternative Plant Concepts

Previous development work carried out in the UK by AEA Technology and Nuclear Electric (NE) has focused on batch operation only. The alternative options of semi-continuous (continuous feed/batch discharge) and fully continuous operation offer a number of potential advantages including reduced reaction vessel size, higher throughput, reduced radioactive and organic inventories (continuous only) and increased hydrogen peroxide utilisation. Under task 2.5 of the programme these alternative plant concepts have been reviewed in relation to an outline specification for a mobile plant based on a throughput of 1 m^3/day of flooded damp ion exchange resin. The activity was specified as 5 TBq/m^3 in the feed material and 25 TBq/m^3 in the residue which would be up to 50% by weight solids containing <2000 ppm dissolved carbon and in the pH range 10-12 suitable for cementation. Although ion exchange bead resins were specified as the primary waste, consideration has been given to the ability of the plant to deal with the other candidate wastes including mixed organic and inorganic exchangers, reactor sludges (WSGHWR), decontamination liquors and soft shredded waste, e.g., cellulosics.

The study has considered a number of alternative equipment options for transferring, mixing and dewatering of resins and sludges. Various fluidisation and waste transfer options have been considered in relation to the interface of the mobile plant with the waste storage facility which will vary depending on the site and may be a large holding tank, silo or drum store. Reaction vessel mixing options have included mechanical agitation, jet pumping, air sparging, pulsed mixing and vortex mixing. Alternative product dewatering options have also been assessed including evaporation (in vessel and external wiped film evaporator), freeze concentration, natural evaporator (sparging) and ultrafiltration.

The semi-continuous option requires a reaction vessel approximately half the size of the batch reactor, i.e., 0.75 m^3 compared

with 1.5 m^3 for the 1 m^3/day (8 hour day) throughput. In this mode of operation the IX resin would be transferred from the store to a separate feed vessel/hopper from which an initial batch loading would be transferred to the reaction vessel. Once the reaction had progressed to a certain stage, further resin would be added on a continuous basis.

Several fully continuous options have been considered including a single continuously stirred tank reactor (CSTR) with continuous solids recovery via a recycle loop which includes a hydrocyclone, solids washing and ultrafiltration. The filtrate and washings containing unreacted soluble organics would be recycled back to the reactor. Flowsheets have also been considered for a multiple CSTR cascade and a series of stirred tank reactors (STR) with periodic transfer of material from one stage to another. Typically 3-4 stages would be necessary to ensure a satisfactory organics destruction efficiency. In general, although the reaction vessel volumes are significantly smaller (around 0.2 m^3 for the specified 1 m^3/d throughput) this is offset by either the need for a complex product removal system as in the single CSTR option, or the need for multiple reactors which increases operational complexity and maintenance/decontamination requirements.

A simple pipe reactor based on the plug flow concept has also been considered but this is entirely inappropriate due to the incompatibility of the long residence time and solids suspension requirements.

The study has concluded that the semi-continuous process offers sufficient advantages over the batch system to be considered as the lead option - in particular with regard to throughput which could be doubled and hydrogen peroxide efficiency of usage which could be increased by 20-30%. Advantages are also gained in having a larger product volume in relation to the reaction vessel size regarding the control of the final solids concentration. The use of a small reaction vessel is particularly important in the context of mobile plant when employing a size constraint such as that of a standard ISO container as suitable for road transport.

The safety considerations of a semi-continuous system have been assessed by undertaking a hazard and operability analysis (HAZOP 1) on a preliminary flowsheet. This has indicated a number of key features which are being incorporated in the design of the mobile active pilot plant.

List of Publications

/1/ TWISSELL, M.A., WILKS, J.P., HOLT, N.S.,"First Semestrial Report to CEC Task 2",AEA D&R Report CPDD(91)P673 (1991)

/2/ TWISSELL, M.A., WILKS, J.P., "An Examination of Candidate UK Radioactive Waste Streams for Treatment by Wet Oxidation", AEA D&R Report CPDD(91)P671 (1991)

/3/ WILKS, J.P., TWISSELL, M.A., HOLT, N.S., "Application of Wet Oxidation to Radioactive Waste Streams", AEA D&R Report AEA-D&R-0218

/4/ HOLMAN, D.J., WILKS, J.P., HOLT N.S., "Pilot Scale Demonstration of Spent Ion Exchange Resin Treatment by Wet Oxidation", Joint International Waste Management Conference, October 1991. Proceedings Vol 1. pp 559 - 565.

Title	Advanced processes for the treatment of low level liquid wastes at a pilot plant scale.
Contractors	LABORELEC (B) - CEN/SCK (B) - AEA-Harwell (UK) - LNETI (P)
Contract N°	FI2W-CT90-0057
Duration of contract	April 1/1991 - December 31/1994
Period covered	1991
Project leader	Coordinator R. ROOFTHOOFT CEN/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^3) 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

State of advancement

Waste streams have been identified and corresponding simulant solutions have been defined.

For PWR-simulant tests have been done both with electrodialysis and distillation. Encouraging results have been obtained. The presence of complexing agents such as EDTA has no deleterious effect on the results with electrodialysis.

The feasibility of the boron trimethylester distillation process has also been demonstrated. Drawbacks have been overcome by adjusting the experimental parameters. Some questions remain under investigation in order to complete the knowledge before starting scale-up experiments. Experiments with ion exchange are less encouraging because of a lack of either resin capacity or low kinetics of the exchange process.

Electrochemical ion exchange has been tested on Harwell LLW in a preprogramme benchtop study. Decontamination factors in excess of 10 have been obtained. A plant with a throughput of 3,4 m^3/h has been projected. (cost 50.000 - 100.000 GBP). Borate recovery has been examined in a small cell. Up to 98,5 % of borate has been found in the effluent with chloride lower than 0,2 ppm and sodium lower than 0,1 ppm; cobalt is not detected. The volume reduction factor is currently maximum 80 (ratio of flow rates) but will be improved.

Uranium mining wastes have been experimented in Portugal by LNETI. Precipitation studies have been performed. Lime was adopted as the most suitable neutralizing agent. A concentration of 20 mg l^{-1} of $BaCl_2$ has shown to be suitable to obtain an adequate decontamination level.

Progress and results

1. Electrodialysis on PWR-waste

The simulant solution is shown in Table I.

All tests on this simulant have been carried out on a modified Aquamite unit from Ionics. The membrane-stack is formed of two stages each containing 60 cation membranes and 60 anion membranes. Product and concentrate circuits are independant and the solutions are collected in two storage tanks of 200 l. The flowrate in each circuit is 200 l/h.

The main conclusions of the tests are :

- B has a low mobility as long as pH is not too high (pH < 9).
- Cl^- is removed with good efficiency. All chloride is transported to the concentrate.
- PO_4^{3-} is removed efficiently.
- Co disappears from the product water but is not found in the concentrate. Absorption phenomena can occur on the membranes.
- Cs disappears in the beginning of the test period but gets nearly into balance later when the membranes get in equilibrium with the solution to be treated.

The boron losses to the concentrate as a function of pH are shown in figure 1.

2. Reverse osmosis on PWR-waste

A small lab-test apparatus has been chosen and bought. The testing itself is planned for the beginning of 1992.

3. Distillation on PWR-waste

The distillation of boron trimethylester involves the formation of a volatile compound in a strongly acidic medium.

$$H_3BO_3 + 3\ CH_3OH \quad B(OCH_3)_3 + 3\ H_2O$$

The boiling point of the B-trimethylester is 68,5°C, which means that it easily can be distilled off but an excess of water can impair the ester formation by hydrolysing the desired product.

Laboratory scale experiments include a preliminary step during which the simulant is completely evaporated to dryness.

The preliminary tests have given following results :

- complete leaktightness of the equipment is absolutely required to obtain consistent results
- the overall efficiency of the process increases with the ratio of methanol to boron (see figure 2)
- the overall efficiency is also a function of the ratio of sulphuric acid to boron
- more than 95 % of the boron can be extracted

However Cs and Co can pass along the distillation column together with boron in amounts which are not acceptable in the case of active isotopes. Further experiments are running to confirm this and to find solutions to this problem.

Distillation on real waste from Belgian nuclear power stations showed apparent efficiency to be much lower than with the simulant. This is due to the slightly acidic pH during the evaporation phase. Neutralizing the solution before evaporating overcomes this problem.

4. Ion-exchange on PWR-waste

Three different anion exchangers have been tested (Dowex 2-X4, Bio-rex 9 and Amberlyst A26). Preliminary tests discarded Bio-rex 9 and Amberlyst A26 because of their low capacity to fix borate ions. On Dowex 2-X4 which shows a low but acceptable capacity, breakthrough curves have been obtained. These results indicate that the resin reacts very slowly.

5. Electrical ion exchange on research center-waste

The first tasks in the programme relate to cell design, which is runnning in collaboration with Loughborough University, and development of continous EIX. Figure 3 shows the concept of a half-cell for continuous EIX. For the application on PWR-waste the EIX can first be used as a pretreatment in order to purify the solution (see figure 4) and afterwards in a second cell to recover boric acid (figure 5).

On a simulant stream the first part has been tested and showed following results in the effluent :

- chloride in effluent < 0,2 ppm
- sodium in effluent < 0,1 ppm
- cobalt not detectable
- borate recovery 98,5 %

and in the concentrate :

- chloride > 1000 ppm
- sodium > 770 ppm
- volume reduction factor 80

The cell for boron reconcentration is under test.

6. Treatment of uranium mine tailings

The composition of the simulant is given in table II.

Precipitation studies have been performed by LNETI concerning neutralization agents and barium chloride doses for radium decontamination. From the results achieved, lime was adopted as the most suitble neutralizing agent. Radioactivity is at acceptable levels with pH-values above 7. A concentration of 20 mg l^{-1} of $BaCl_2$ is suitable to obtain an adequate decontamination level.

Table I : Simulant solution for PWR-waste

		Added as
pH	4-10	
B	500 ppm	H_3BO_3
PO_4^{3-}	2 ppm	Na_3PO_4
Cl^-	50 ppm	NaCl
Cs	1 ppm	CsCl
Co	1 ppm	$CoCl_2$

In a second step the sodium salt of EDTA will be added in a concentration of 20 ppm.

Table II : Simulant solution for U-mine tailings

$SO^{=}_4$	26 g/l
Cl^-	1,5 g/l
PO_4^{3-}	0,7 g/l
Fe	1 g/l
Mg^{++}	0,5 g/l
Mn^{++}	0,5 g/l
Ca^{++}	0,7 g/l
Na^+	0,3 g/l

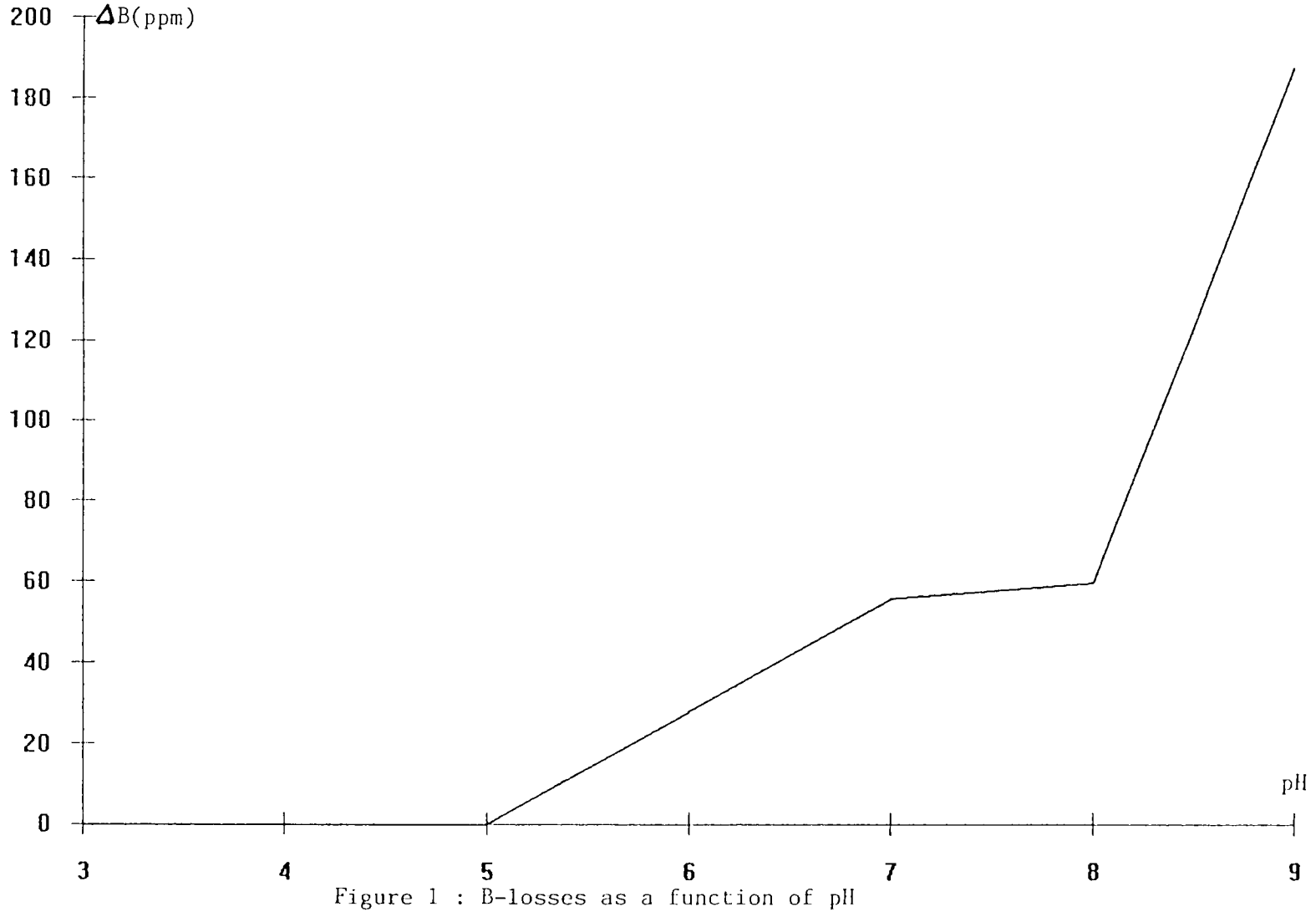


Figure 1 : B-losses as a function of pH

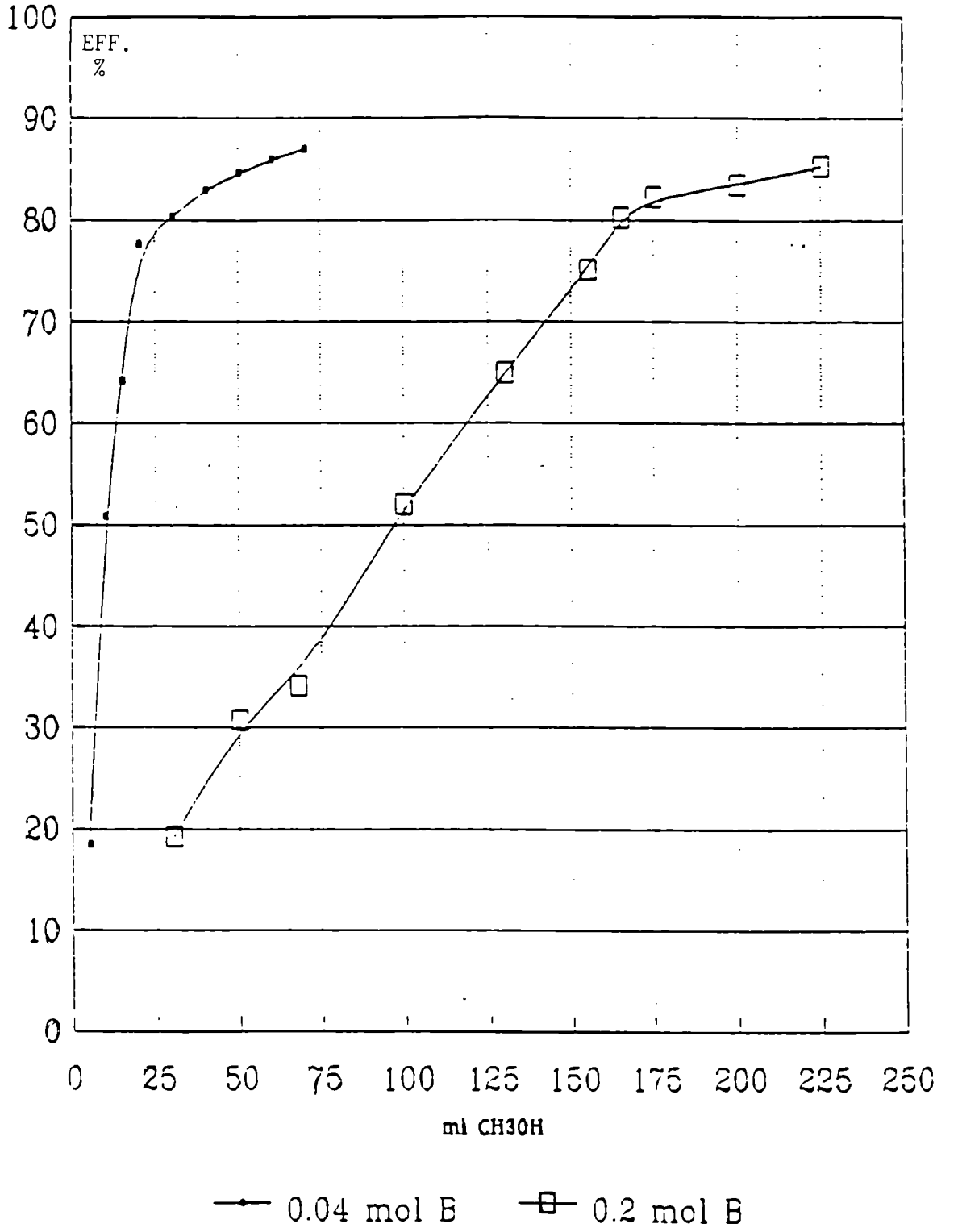


Figure 2 : Influence of CH_3OH volume

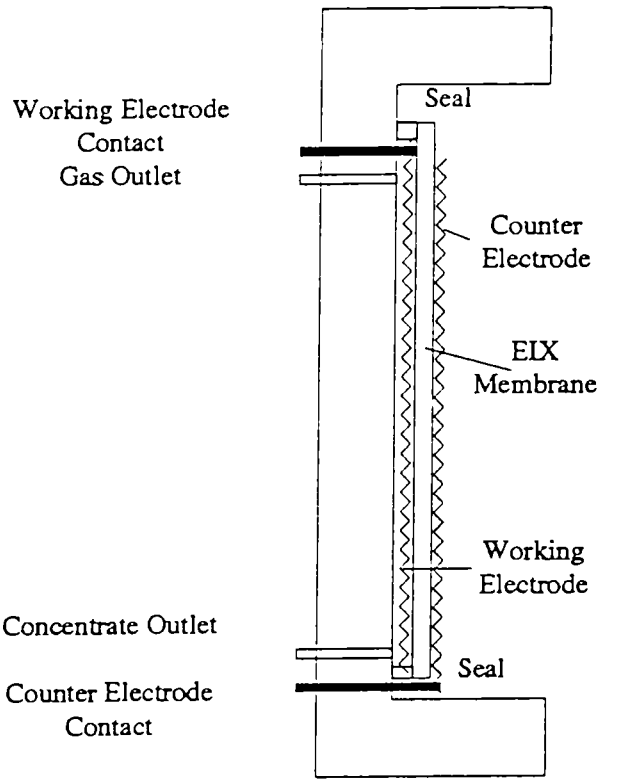


Figure 3 : Half-Cell for an continuous EIX

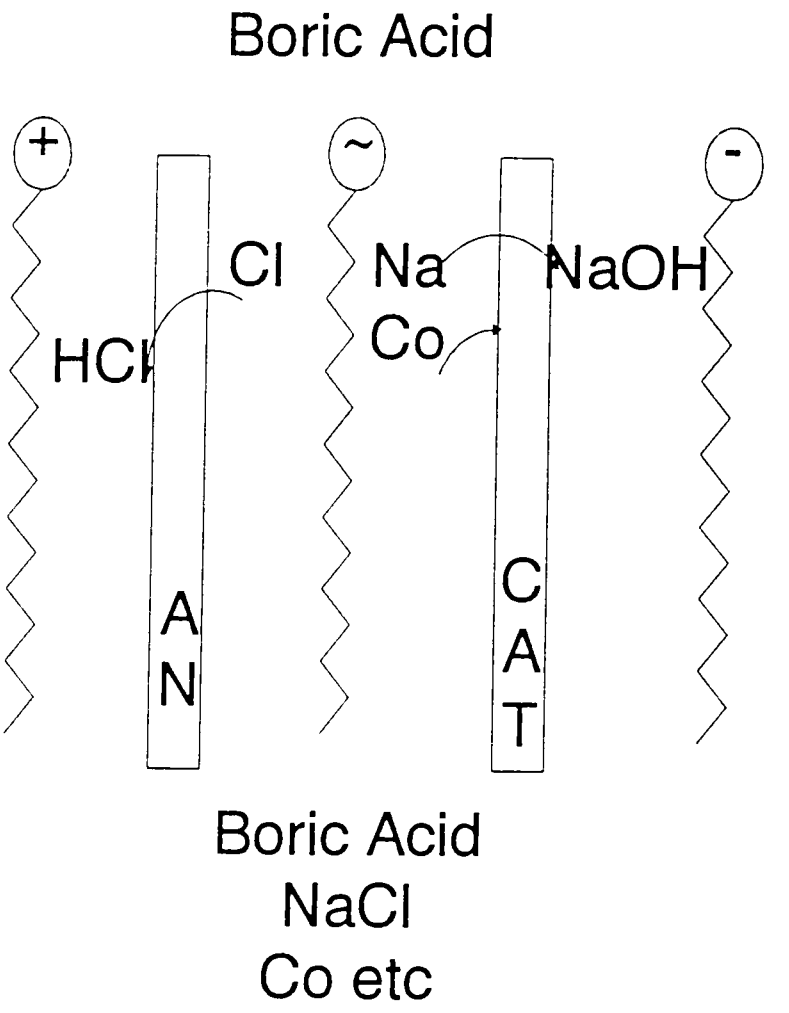


Figure 4 : EIX as pretreatment

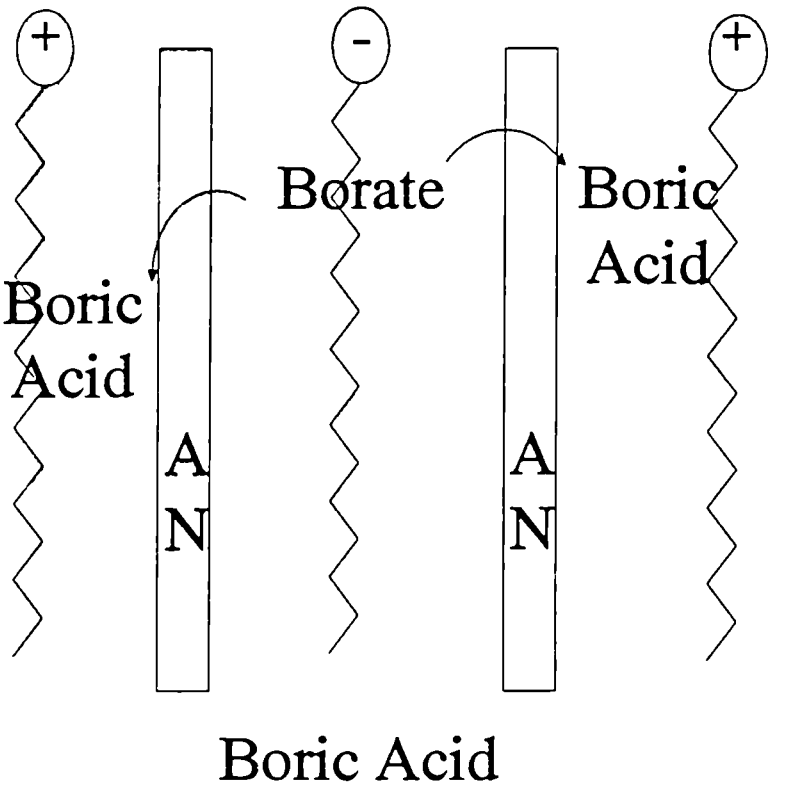


Figure 5 : Boric acid recovery

Title	Process design and feasibility study for incineration under pressure, condensation and effluent treatment of radioactive waste	
Contractors	BERTIN & Cie, CEA-Cadarache and INITEC	
Contract N°	FI2W-CT91-0095	
Duration of contract	July 1991 - December 1993	
Period covered	July - December 1991	
Project leader	D. VIVIEN	Coordinator
	G. NAUD	CEA
	M. SANCHEZ DELGADO	INITEC

A. OBJECTIVES AND SCOPE

The main objective of this research activity is the evaluation of the technical feasability as well as the economical and the safety implications of the combustion of a range of organic containing radioactive wastes by means of oxygen under pressure using a new type of incinerator relying on the recent technical developments achieved within the MESMA (Autonomous Underwater 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 giving rise to release of only inactive gases (in terms of radioactivity and chemical toxicity).
The work to be performed will mainly be focused on the study of the adaptation of a closed loop for combustion under pressure operating at 60 bar (see figure 1) - including the setting-up of a suitable off-gas treatment - to the incineration of at least four types of typical organic containing radioactive wastes (spent ion-exchange resins/sludges according to French and UK formulations, spent solvent used in the Eurex plant, decontamination liquors).
BERTIN has to adapt the process, developed for the MESMA project, to the case of waste incineration. The CEA will make a review of the possible waste to be processed, and will perform some laboratory trials in order to check the behaviour of waste samples under conditions of incineration. INITEC will design the main components of a plant, based on a 10 kg/hour throughput, and will make an evaluation of the process safety.

B. WORK PROGRAMME

The work programme comprises eight distinct steps :

1. Identification of radioactive waste ; different organic wastes will be analysed. The choice will take into account the incineration characteristics as well as the interest

to remove organics from the waste (amount produced, existing solution for removal, ...).
2. Drawing-up of process flow-sheet ; for several selected wastes, the best process and its main operating parameters will be defined.
3. Design of the main plant components ; relying to the hereabove flow-sheets, all the components of a 10 kg/hour throughput pilot plant will be designed.
4. Treatment and conditioning of secondary wastes ; ashes, dust, liquids and gases (uncondensable gases and the release of storage tanks under pressure).
5. Process safety ; the analysis of the risks will define the control and safety procedures of the plant.
6. Bench-scale tests ; some tests will confirm the hypothesis made upon the waste gasification and flue gases amount.
7. Technico-economical evaluation ; they will be done for a full scale incineration plant, around 50 to 100 kg/hour throughput.
8. Radiological impact ; assessment will be made by following the belgatom's methodology for instance or another tried method.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. State of advancement

A collect of data about possible wastes that can be incinerated has been done.
The C.E.A. (FRANCE) has reviewed all types of waste that could be burnt in order to reduce their volume. For the study, four wastes have been selected ; they are :
- spent solvent which is mainly composed of tributylphosphate
- a cationic resin, type DUOLITE C20
- an anionic resin, type DUOLITE A101D
- decontamination liquors.

Data from the WINFRITH's sludge are available ; the aim about this waste is to compare the new process with the wet oxidation process in progress at the WINFRITH's Centre.
The spent solvent from the EUREX's plant is also selected.
Some flow-sheets are available, under several assumptions on incineration, for the spent tributylphosphate.

2. Progress and results

2.1. Selection of several wastes

Table I summurizes the main characteristics available for incineration, on six types of waste.
Because of the pressure in the process, solid wastes are not selected.
Liquid and sludge are good candidates, and the selection comprises the following :
- the french TBP is apparently easy to be burnt because of its high calorific value. Moreover it is already incinerated in 3 facilities in FRANCE, and it will be possible to compare the costs with the assessment made in this present study.
- two types of Ion Exchange Resin, commonly used in FRANCE are a cationic one, type DUOLITE C20, and an anionic one, type DUOLITE A101D.
  The destruction of spent IER has no industrial solution, and the current practice consists in direct solidification.
  It is difficult to know anything about incineration without making tests, because of the large content of water.

The ash rate is unknown ; it probably depends on the origin of the IER and the use that has been done. Table I doesn't take into account the ashes, but it will be considered further at a rate around 2 %.

- The decontamination liquor is another type of waste containing 85 % of water. It's clear that it cannot burn alone, and the goal is to investigate the possibilities of a combustion process under pressure and with oxygen, because the french production is important (2000 m^3/year). Combustion will require an additionnal fuel.
- The sludge produced in the WINFRITH Center is of great interest because its composition is different from the french spent IER, especially about water content, and because wet oxidation is under progress in U.K.. So comparisons could be done.
- The solvent coming from the EUREX plant is rather different from the french TBP effluent.
  The solution involved for these two wastes will probably be similar, that is the reason why the incineration of this solvent is being studied further.

2.2. Some comments about incineration characteristics

In table I, several characteristics have been reported, concerning some incineration features :

- the net calorific value
- the viscosity ; this feature is necessary to size the atomization nozzle (liquid injection)
- the stoichiometric oxygen volume (VO_2) is the exact demand of oxygen to achieve complete combustion of the product
- the adiabatic temperature (of flue gases) corresponds to the complete combustion under stoichiometric conditions
- several informations about the radioactivity level and the yearly production are available.

2.3. Analysis of the process for spent TBP (task 2)

This analysis is based on a waste throughput of 10 kg/h.

2.3.1. Stoichiometric combustion with oxygen

The flow-sheet in figure 2 provides the main characteristics of the flow involved in such a configuration. Several possibilities exist for the couple of parameters, namely the operating pressure and the temperature at the exit of the condenser. Variations of these two parameters will be investigated in order to find the best arrangement for condensed and uncondensed gases.

2.3.2. Open loop process with phosphoric neutralization

In order to remove the phosphoric acid as soon as possible, an injection of calcium formate is added ahead of the combustion chamber. The formate has to be diluted at 150 g per liter of water, and the neutralization requires 490 g of formate per kg TBP. The relevant flow sheet appears in figure 3, supposed to be at atmospheric pressure.

2.3.3. Combustion with a large oxygen rate

As it can be seen on figure 2, the adiabatic temperature can reach very high level, and that needs injection of cooling water in the flue gases. In order to reduce the adiabatic

flame temperature, a large oxygen excess is investigated for the combustion chamber. In order to recover the excess of oxygen, a recirculation loop is added.
The relevant flow-sheet is in figure 4. Here again, the two parameters, pressure and exit temperature, will be adjusted at an advantageous level.

2.3.4. Evaporation of TBP

This simple process can possibly be applied to the case of spent TBP. However, care should be taken on the radionucleide species such as uranyl nitrate [UO_2 $(NO_3)_2$] or plutonium nitrate [P_u $(NO_3)_4$] which are the main radioactive species of the spent TBP. The chemistry of derivated compounds is complicated, so the main investigations will be done on laboratory tests. Temperature level (close to the pure TBP boiling point) as well as pressure up to 100 bar, could be tested. These tests are part of the task 6 of the program.

2.4. Considerations about some choices to be done on the process

2.4.1. The recirculation loop

To recover the energy from combustion is not the purpose. So, recirculating flue gases could be done in order to save the oxygen excess and to cool the flame in the combustion chamber. Off-gases could be reduced to uncondensed gases only.

2.4.2. Cleaning flue gases

In order to remove radioactive fly ashes, high efficiency filters are required. A first stage comprising a cyclonic filter can also be included. Their location in the process is a parameter of the study.

2.4.3. Cooling flue gases

Several means are available :

- to quench the flue gases with water, advantages come from its high efficiency, but the higher rate of vapor in the gases is not compatible with bag-house filters
- to exchange calorific power through an adapted exchanger
- to dilute the flue gases with air is not compatible with the process which uses oxygen as comburant in order ot minimize the amount of flue gases.

TABLE I - SELECTED WASTES
MAIN CHARACTERISTICS FOR INCINERATION

	CEA TBP	CEA Res.A	CEA Res.C	CEA Liquors	WINFRITH	EUREX solvent
H_2O	0	50	47	85,2	70	0
C	54.14	40,9	27,8	4,4	13	86,3
H	10.15	5,1	2,3	0,9	-	10,8
O	24.06	-	13,7	6,2	-	2,0
N	-	4,0	-	1,4	3,9	0,2
S	-	-	9,2	-	2,2	-
P	11,65	-	-	-	-	0,7
Ashes	-	-	-	1,9	10,9	-
Net calorific value MJ/kg	30	$\leq$ 19,6	$\leq$ 12,7	0,13	4,28	$\simeq$ 30 estim.
Viscosity mP Pa.S	33 0,0033	N.A.	N.A.	N.A.	700 to 2700 0,07 to 0,27	N.A.
ϕ part (mm) or liquid	liq.	ϕ 0,3-1,2	ϕ 0,3-1,2	liquid	sludge bead ϕ 1 mm	liq.
VO_2 kg O_2/kg	2,17	1,55	1,04	0,14	0,41	2,18
Tad (est) °C	> > 2500	N.S.	N.S.	N.S.	N.S.	> > 2500
Density (26°C) kg/l	0,98	estimated 1,2	estimated 1,2	1,15	1,2	0,86
Radioactivity MBq/l	630	$\leq$ 11000	$\leq$ 11000	0,008	160	0,5
m^3/year	25	180		2000	N.A.	N.A.
Stored (m^3)	at present destroyed	-	-	embedded	280	25

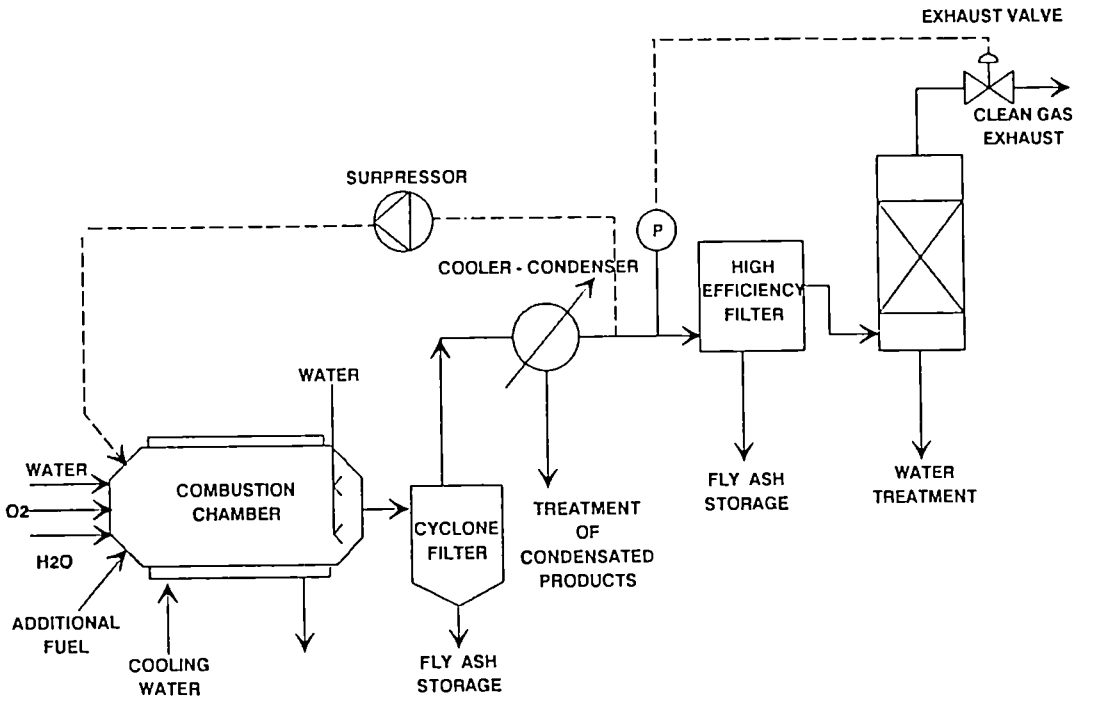


Figure 1 : Basic scheme of the process

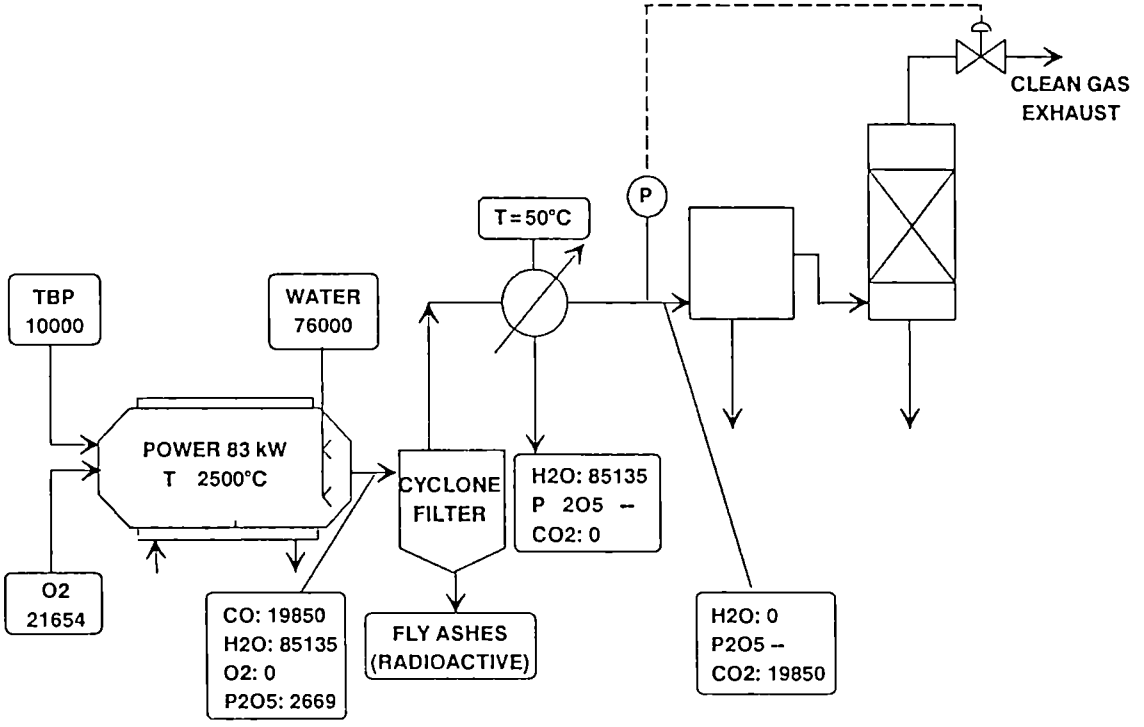


Figure 2 : Stoechiometric combustion (Open Loop)

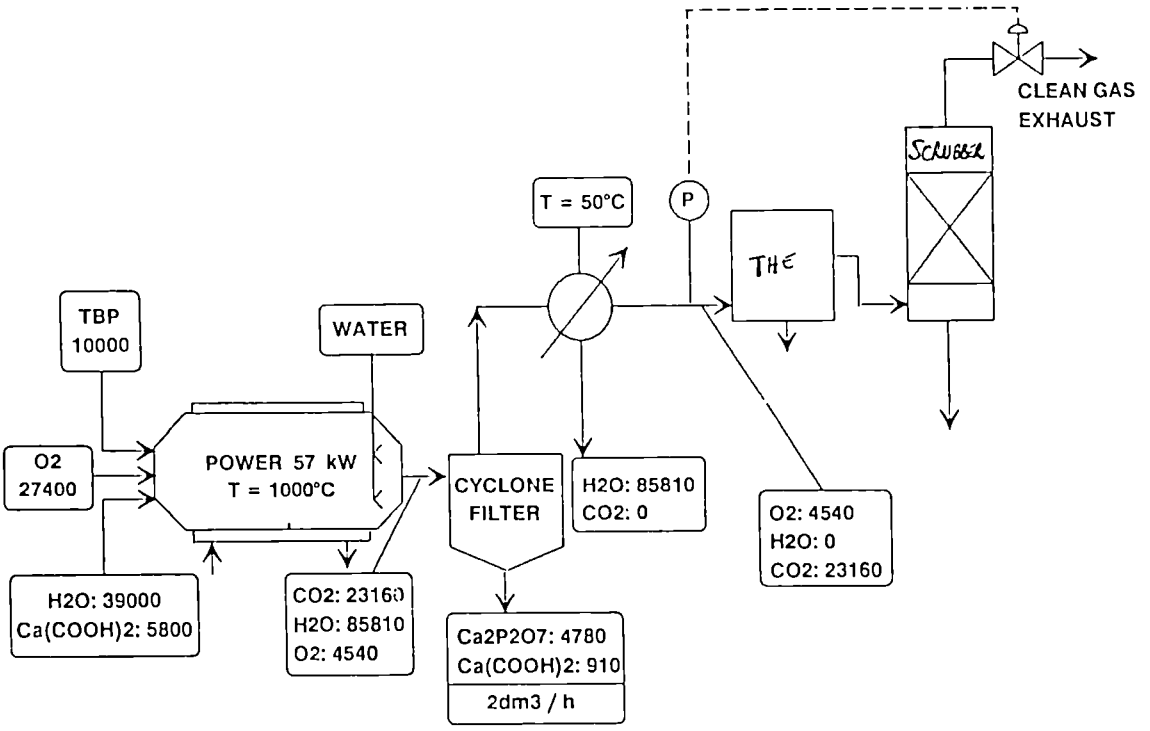


Figure 3 : TBP - Open loop incinerators process with 20 % oxygen excess and phosphoric neutralization

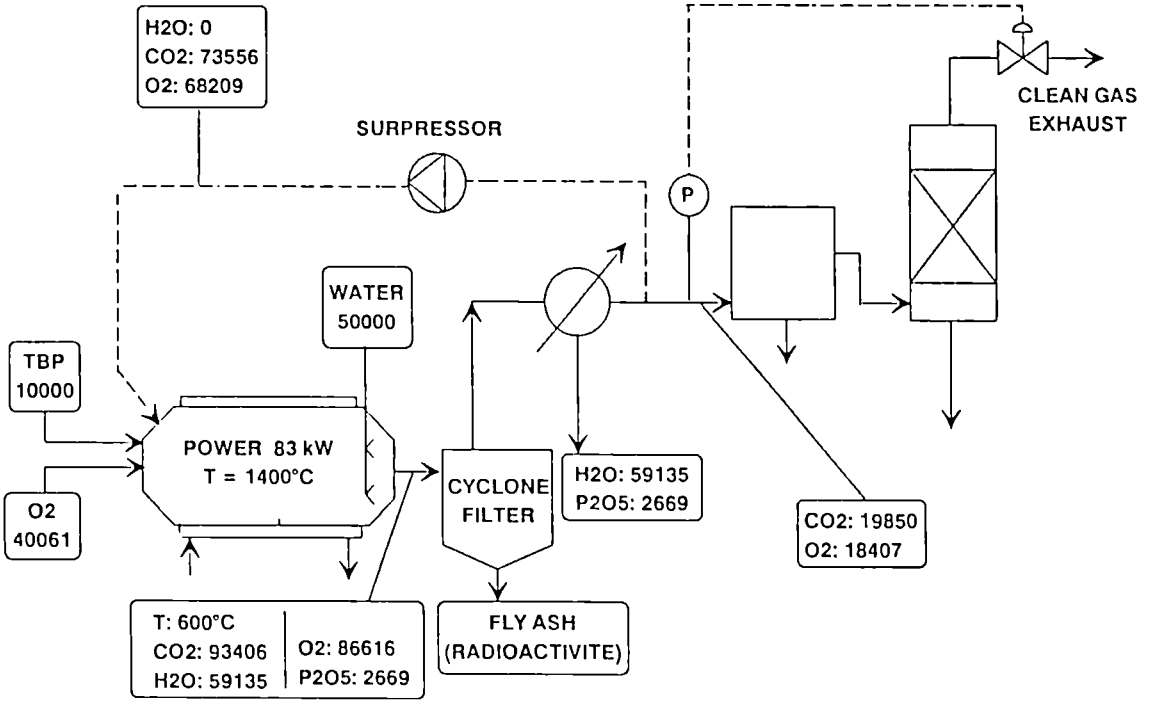


Figure 4 : TBP - Combustion with a large oxygen excess and gas recirculation

Title : New macrocyclic extractants for radioactive waste treatment : Ionizable crown ethers and functionalized calixarenes.

Contractors : CEA - U. of Barcelona - U. of Belfast - U. of Mainz - U. of Parma - U. of Strasbourg - U. of Twente.
Contract n° F12W/CT90/0062 - Task 2

Duration of contract : January 1991 - August 1995

Project leader : Coordinator : J.F. Dozol - Task leaders : Pr F. Lopez Calahorra - Pr A.Mc Kervey - Pr V.Boehmer - Pr R. Ungaro - Pr M.J.Schwing - Pr D.Reinhoudt.

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, caesium 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 macrocycle compounds from the various p-alkyl-calixarenes (Fig. 1) will be carried out in order to obtain very strong and selective extractants for long-lived radioactive cations such as strontium, caesium and actinides. The Barcelona laboratory synthesizes crown ethers which possess pendant ionizable groups. Compared with the classical crown ethers, the presence of these groups facilitates the extraction or transport of metal ions.
The CEA (DSD/SEP/SETED) which has been working in the field of liquid wastes for many years, will inform the different laboratories of the nature of the various liquid wastes to be treated in the nuclear industry and will test the effectiveness of these extractants on simulated and genuine liquid wastes.
The four laboratories working on calixarenes and already collaborating in more basic research, and the laboratory in Barcelona which synthesizes crown ethers, will provide functionalized calixarenes and ionizable crown ethers for the CEA which in turn will test these different products.
The laboratory of EHIC Strasbourg has considerable expertise in the study of cation binding ability and the selectivity of macrocycle receptors with very small amounts of receptor.
The decontamination process of concentrates, and more generally, of liquid wastes arising from reprocessing plants will use functionalized calixarenes and ionizable crown ethers. These macrocycles must enable the selective removal of actinides, strontium and caesium from high salinity liquid wastes.
The functionalized calixarenes and the ionizable crown ethers being expensive extractants, the selected techniques will involve a low extractant inventory : supported liquid membranes, polymer based membranes....

The extractants will be "tailored" in order to make it possible to directly remove radionuclides from high sodium content acidic concentrate.
The decontamination tests will be carried out on simulated wastes followed by genuine liquid wastes from reprocessing plants.
The CEA is the coordinator of the project, begun on September the first 1991, with four contractors, the Universities of : Barcelona (Pr F.Lopez Calahorra), Belfast (Pr A.Mc Kervey), Mainz (Pr V.Boehmer), Parma (Pr R. Ungaro), the laboratories of Twente and Strasbourg being the subcontractors respectively of the Universities of Parma and Belfast. In 1992, these two laboratories will be contractors, their tasks being increased owing to an extra fee from the C.E.C.
In the previous C.E.C. contract (FI1W-0016), the interest of classic crown ethers and CMPO was shown for the respective removal of strontium and actinides from a high salinity solution (Fig. 2 - 3).
Due to the strong competition of sodium present in high concentrations in the wastes and to the poor extractability of nitrates, crown ethers failed to remove caesium. Adding ionizable pendant groups to the crown ethers offers an advantage in that cation extraction does not simultaneously require nitrate extraction and thus must improve the removal of caesium from a high nitrate content medium (Fig. 4).
The new process defined with functionalized calixarenes or ionizable crown ethers will be compared with the process using CMPO and neutral crown ethers, particularly in terms of decontamination factors and concentration factors.

B. WORK PROGRAMME

1. The coordinating laboratory of Cadarache will test the extractants prepared by the various universities involved in the project.

1.1. The conditions of utilisation of each extractant will be sought in order to use these compounds in liquid-liquid extraction (and in SLMs in particular).

1.2. The range of acidity, the range of salt concentrations in which the macrocycles are effective for the removal of long-lived radionuclides will be determined.

1.3. The techniques rendering the use of these compounds possible will be developed (supported or contained liquid membranes) and the most promising processes tested in hot cells.

2. The four universities (Belfast, Mainz, Parma, Twente) working on the synthesis and basic research of calixarenes will devote their efforts to prepare selective extractants and will work in close collaboration, but each of them will work more specifically in the following areas:

2.1. Parma University will synthesize calixarene podands, calix crowns and calix spherands with acidic chains in order to remove caesium and strontium and functionalized calixarenes for the elimination of actinides.

2.2. Belfast University will prepare new calixarenes with various functions (ester, ketone, amide...) and then switchable calixarenes.

2.3. Mainz University will synthesize tetraester derivatives of bridged calixarenes and also tetraamide derivatives and compounds with various functions on the "lower rim" of bridged calixarenes.

2.4. The University of Twente will test the potential of synthesized macrocycles for the separation/transport of cations via S.L.M. and if necessary will modify the structure of the macrocycles in order to improve the stability of the membrane and the transport of cations through this membrane.

3. The University of Barcelona will synthesize crown ethers with pendant ionizable groups such as phosphoric and sulfonic in order to allow for the removal of caesium and strontium from a highly acidic solution.

4. The EHIC Strasbourg will determine the complexation powers of the macrocycles towards cations by the determination of the stability constants of the cation-receptor complexes. The medium in which the measurements will be carried out will have to be the closest possible to the nitric nitrate medium used in the nuclear industry.

5. During the first two years, synthesis, basic studies, measurements of characteristics and of distribution coefficients of nuclides between organic and aqueous phases will be carried out.

6. Different kinds of membranes will be built with macrocycles for the transport or the separation of cations.

7. The new process defined with functionalized calixarenes or ionizable crown ethers will be compared with the process using CMPO and neutral crown ethers.

C. PROGRESS OF WORK AND OBTAINED RESULTS

1. State of advancement

During the four months of 1991 (September - December), the various Universities synthesized the first functionalized calixarenes or ionizable crown ethers.
Cadarache prepared the tests necessary for determining the effectiveness of macrocycles to remove cations from high sodium content acidic solutions.

2. Progress and results obtained in the various laboratories

2.1. Cadarache

The four months of 1991 were devoted to perfecting the measurements necessary for determining the effectiveness of macrocycles by using very small amounts of macrocycles :
- Determination of distribution coefficients of numerous cations between the organic phase containing the extractant and the aqueous phase simulating the radioactive liquid waste. Gamma spectrometry was used to determine the activities of several nuclides : or the

inductive coupled plasma mass spectrometry (I.C.P.M.S) which enables us to measure simultaneously a great number of cations was also used.
- Transport of cations with the measurement set-up developed at Twente for the transport of cations through SLMs. The measurements of the distribution coefficients were carried out on the first calixarenes synthesized at Parma and Belfast.
The calixarenes synthesized at Parma are :
- Podand calixarene
- Amide calixarene
- Hydroxamate calixarene
- Calix crown arene ;
The calixarene synthesized at Belfast :
- Ester calixarene

2.2. University of Belfast

The principal objectives are to design new calixarenes with good selectivity for caesium and lanthanides, to assess through physicochemical measurements in the EHICS, Strasbourg, their ability to extract and transport these ions, and to develop polymeric and immobilised calixarenes for possible applications in membranes and chromatographic processes.
In the preliminary stages of the contract (October-December 1991) we have concentrated on the synthesis of new receptors. Our approach has been to introduce onto the lower rim of calix[4],[5] and [6]arenes functional groups capable of participating in ion binding. These functional groups include esters, ketones, carboxylic acids, amides, ethers and thioamides. Whereas in the tetramer ester series the selectivity strongly favours sodium ion over the other alkali cations, in the hexamer ester series there is a clear preference for caesium ion. Preliminary work with the pentamer ester series shows promise for caesium extraction though the Cs^+/Na^+ selectivity is lower than that obtained in the hexamer series. Compounds which have now been synthesized are :
(i) pentamer esters
(ii) large quantities of hexamer derivatives
(iii) several tetramers with amide bridges
(iv) several amides with different alkyl residues on the nitrogen atom
(v) tetramers with large alkyl residues ($>$ 20 carbons) at the para positions.
The preparation of (iv) and (v) was undertaken to enable us to exploit differences in lipophilicity and thereby modulate cation complexing properties. Preliminary work with a group of tetramer amides with different N-alkyl groups shows that it is possible to influence cation extraction preferences in this way. In the next phase of the work a series of hexamer amides will be prepared and examined for caesium selectivity.

2.3. University of Mainz

A series of calix[4]arenes in which two opposite p-positions are connected by an aliphatic chain (n=5-10) were prepared and converted to tetraester derivatives. The stability constants of their complexes with Na^+, K^+ and Ag^+ were determined in MeOH (work done in Strasbourg), in order to obtain a more detailed knowledge of the conformational requirements for metal ion complexation. There is in general for all three cations a drastic decrease of log β (more than 5 for Na^+) for the shorter chains (n 7), where also changes in selectivity were observed.

Several calixarene derivatives (ester, amide) have been synthesized (together with Belfast) in which the residue attached to the phenolic oxygen contains further ligating functions. The underlying idea is, that Na^+ ions, present in large excess in the highly acidic solutions of nuclear wastes, could be used with these compounds in two ways :

a) to stabilize the ester groups against hydrolysis. (A detailed study has shown that tetraester derivatives are hydrolysed in the presence of a strong acid in apolar solvents, while the Na^+ complex is completely stable).

b) to preorganise the pendant chains, so that an additional metal ion can be held between the additional ligating functions.

Further studies have to show if this concept is valid for the extraction of e.g. Sr^{2+} actinides or heavy metal.

Attempts to obtain double calixarenes by the reactions of a 1,3-diacid dichloride with various diamines (including bis-aza-crown ethers) led in all cases to "lower rim" bridged single calixarenes. (Work has to be coordinated with Enschede therefore). Due to the remaining two phenolic hydroxyl groups, these compounds can form neutral complexes with divalent cations. Again complexation studies have to be made in the future.

2.4. University of Parma

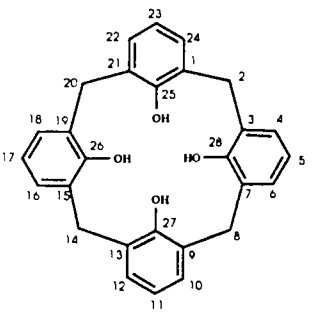
Part of the research activity has been devoted to re-synthesize some calixarene ionophores developed previously at Parma University in order to check their extraction behaviour in the conditions of the waste concentrate of the Cogema Marcoule process. Gram quantities of podand calixarenes, amide calixarenes, hydroxamate calixarenes were prepared at Parma and tested at Cadarache.

Since the podand calixarenes showed very poor extraction ability towards most of the tested cations at $pH < 5$, a calix crown arene has been designed for the selective complexation of the caesium cation. The extraction properties of this compound are presently being studied at Cadarache.

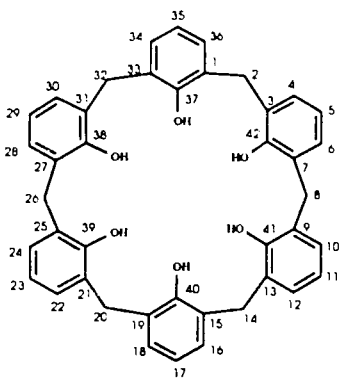
2.5. University of Barcelona

The University of Barcelona has undertaken the synthesis of crown ethers with pendant ionizable groups. In their ionized forms, these crown ether acids offer the following advantage : the cation extraction (or transport) does not require a simultaneous extraction (or transport) of an anion. This property is particularly interesting when operating in a high nitrate content medium due to the difficulty in dehydrating the nitrate and transferring it into the organic phase.

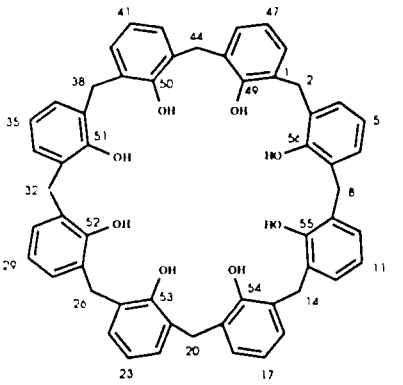
At first, Barcelona U. prepared in considerable amounts "building blocks", first stages in the synthesis of crown ethers, and then, several 18C6 or 21C7 crown ethers with sulfonic pendant groups.



25,26,27,28-tetrahydroxycalix[4]arene

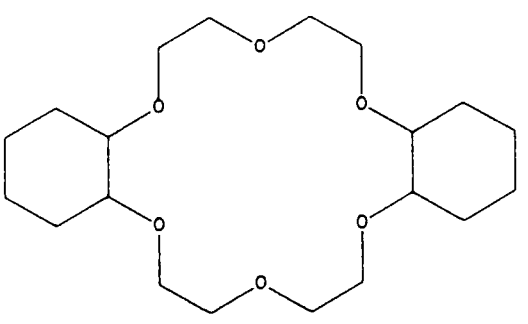


36,37,38,39,40,41,42-hexahydroxycalix[6]arene

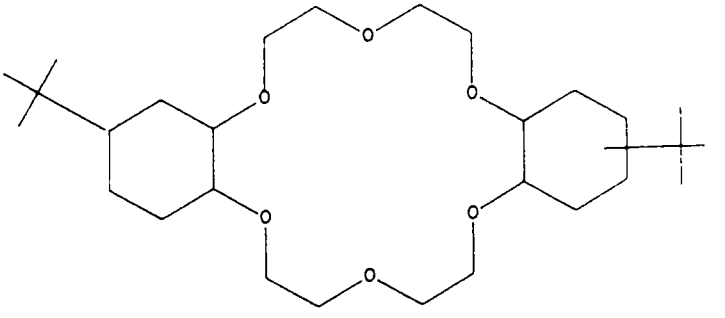


49,50,51,52,53,54,55,56-octahydroxycalix[8]arene

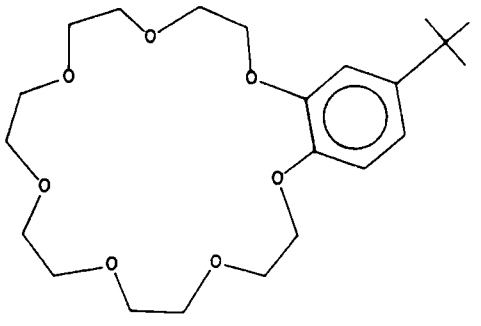
Fig. 1 - Calixarenes



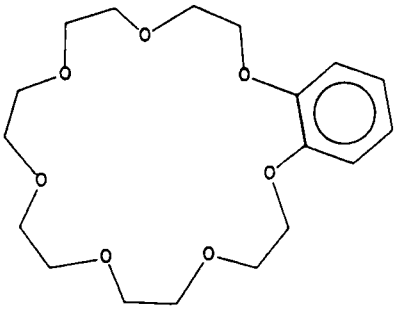
DC18C6



DtBuC18C6



tBuB21C7



B21C7

Fig. 2 - Neutral crown ethers

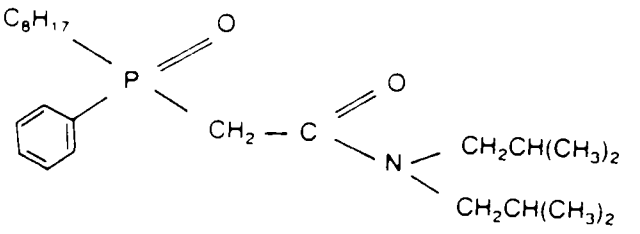


Fig. 3 - CMPO

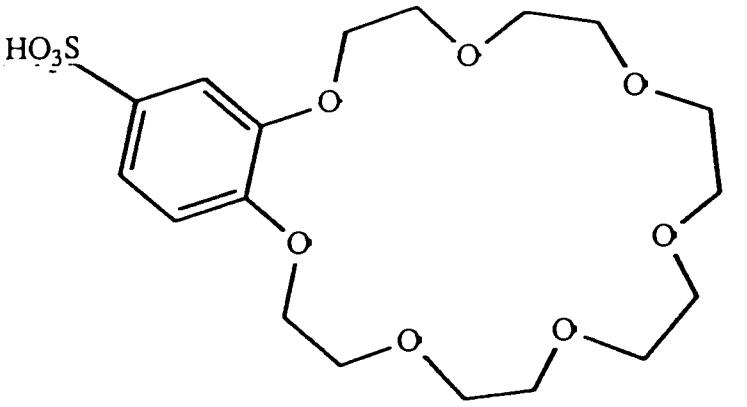


Fig. 4 - Ionizable crown ethers

Title	: "Decontamination of Solid Alpha, Beta, Gamma Waste for De-Categorisation Purposes in Terms of Disposal Route"
Contractor	: Commissariat à l'Energie Atomique (CEA) - Centre d'Etudes Nucléaires de Fontenay-aux-Roses (CEN/FAR) - Departement des Procédés de Retraitement (DPR)
Contract N°	: FI2W/CT90/0070
Duration of contract	: from April 1991 to March 1993
Period covered	: April 1991 - December 1991
Project leader	: J. BOURGES

A. OBJECTIVES AND SCOPE

Nuclear activities in the radiochemistry building of Nuclear Research Center in Fontenay-aux-Roses, concern principally the study of fuel reprocessing and the production of transuranium isotopes. During these activities solid wastes are produced that are contaminated with α, β, γ emitters for hot-cells studies and with α emitters only for glove-box experiments. In order to improve the management of these wastes, two facilities are engaged :

- ELISE , a group of glove-boxes for the treatment of α active solid wastes ;
- PROLIXE, a hot-cell for the treatment of α, β, γ active solid wastes.

In these facilities, leaching processes were developped in order to :

- decontaminate these wastes, especially in α emitters, to obtain a level of residual alpha contamination < 0.1 Ci/t of the conditioned wastes which will be suitable for surface site disposal ;
- recover actinide elements and recycle redox agents.

The leaching process is based on the use of electrogenerated oxidizing agents (Ag(II)) in nitric acid or reducing agents (Cr(II), Ti(III), V(II)) in sulphuric acid, which are particularly suitable to provoke the dissolution of plutonium dioxide.

B. WORK PROGRAMME

II. Laboratory scale studies

II.1. Oxidizing process : the following studies were scheduled : oxidizing dissolution of different compounds of plutonium such as fluoride, phosphate, carbide, nitride... ; exhaustive alpha decontamination of zircaloy hulls of irradiated mixed oxide fuel by Ag(II) leaching method ; electrochemical destruction of organic species.

II.2. Reducing process : characterization of redox couples, comparison of their performances and choice of reaction media will be realized.

II.3. Recycling of electrochemical mediators : the study of processes for recycling of silver will be performed.

III. Pilot scale experiments

III.1. Silver(II), leaching process : in PROLIXE and ELISE facilities, runs on about 20 kg of different kind (mineral, metallic, organic) of α, β, γ wastes will be achieved. More than 1 500 kg of wastes will be treated in 2 years.

III.2. Recovery of actinides and redox mediators : the recovery of actinides will be systematically realized. The recycling of silver will be performed at pilot scale.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

During the period : April 91 - December 91, efforts have been made on the following topics :

Electrochemical destruction of organic species :

Spent ion exchange resins and organic extractants contaminated with plutonium constitute a major active waste to be managed. The use of Ag(II) in nitric medium to destroy organic species has been considered ; experimentations on 1 kg of DOWEX 21 K and 0.1 kg of TBP have been achieved.

Recycling of silver used in the silver II leaching process :

An electrolytic process for the recovery and the recycling of silver from concentrated leaching solutions has been studied ; after laboratory scale experiments, an electrolyser with a 30 l capacity has been implemented.

Study of electrogenerated reducing agents :

The reducing leaching process was studied at laboratory scale, based on the use of electrogenerated powerful reducing agents like : Cr(II), V(II), U(III), Ti(III) in dilute H_2SO_4 medium. The results were very encouraging : high plutonium dissolution yields were achieved and it was found that the process was insensitive to the presence of cellulosic materials.

ELISE and PROLIXE exploitation :

300 kg of alpha solid wastes have been treated in ELISE ; these wastes were subjected to the sorting and crushing operations.

In PROLIXE : 280 kg of α, β, γ solid wastes have been treated. About 150 kg of metallic wastes contaminated with α, β, γ emitters, produced during the dismantling of RM II hot-cell, have been processed.

The goal of the exhaustive decontamination of these wastes have been achieved.

Progress and results

Oxidizing process (II.1.) :

The electrochemical oxidation of organic species have been investigated to recover α, β, γ emitters (particularly the plutonium) from contaminated organic materials and to destroy completely some organic compounds.

The principe of the process is based on the action of Ag(II) which attacks organic species that are converted to carbon dioxide, water and inorganic acids.

The detailed mechanism of this destruction is not yet clearly understood, but the limiting step in the kinetics is the electrogeneration of Ag(II) ions.

A special reactor was designed and used to destroy tributyl phosphate or ion exchange resins at 1 kg scale with electrogenerated Ag(II). Successful experiments were done using these two organic compounds ; pure TBP and DOWEX 21 K resin. The destructions were quantative and with electrical yields close to 30 %.

Recycling of electrochemical mediators (II.3.) :

Processes for the recovery and recycling of silver have been studied. The most attractive process is the selective electrodeposition of silver ; Ag(I) is reduced to Ag°

by the passage of an imposed cathodic current and Ag° is deposited on the cathode. The major problem is due to the competitive reaction of reduction of HNO_3 to HNO_2 because nitrous acid autocatalyses HNO_3 oxidation of Ag° and limits the deposition of silver metal ; an answer is the use of nitrite suppressor such as urea (CH_4N_2O), hydrazine (N_2H_4) or sulfamic acid (NH_2SO_3H).

The parametric studies have been achieved conducting to process optimization and design of a 100 Amperes prototype electrolyser. For example, more than 1.5 kg silver have been recovered in 4 hours from 30 l of a 0.44 M $AgNO_3$ synthetic solution with a 99.27 % yield recovery and 90% current efficiency.

Silver(II) leaching process (III.1.) :

150 kg of α, β, γ metallic wastes from hot-cell dismantling have been treated by silver(II) leaching process in PROLIXE. Six lixiviation campaigns on 8 to 35 kg batches of metallic (stainless steel essentially) were performed ; each campaign comprising 2 or 3 oxidizing treatments plus a washing with water.

From initial alpha activities of 1 to 5 Ci/t, alpha residual contaminations of 0.86 to 31 mCi/t of the non-conditionned wastes were achieved. The goal of the de-categorisation was obtained.

Title:	**Partition of Radioactive Wastes**
Contractor:	Kernforschungszentrum Karlsruhe (KfK)
Contract N°:	FI2W-CT90-0047
Duration of contract:	from 1st March, 1991, to 28 February, 1993
Period covered:	from 1st March, 1991, to 31st December, 1991
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 develop the flowsheet of a solvent extraction process for the separation of plutonium, neptunium, americium, curium and technetium from the Purex wastes.
- 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. Compilation and assessment work, including the elaboration of a survey report and the formulation of conclusions for the start of the experimental work.
2. Measurement of distribution and kinetic data for the elements to be separated and for lanthanides, and the working out of a proposal of a flowsheet.
3. Test of the flowsheet in a laboratory counter-current device, using a simulated waste solution.

C. PROGESS OF WORK AND OBTAINED RESULTS

State of advancement

The compilation and assessment work was finished. The experimental work was concentrated on the extraction of americium(III) and its separation from lanthanides(III). A solution of n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (henceforth OΦD(iB)CMPO) in dodecane was used as solvent. It was shown that lauronitrile can be used as a solvent modifier instead of commonly used tributyl phosphate (henceforth TBP). Lauronitrile solubilizes extracted OΦD(iB)CMPO complexes better than TBP and extracts much less nitric acid. Transplutonide(III) thiocyanates were shown to be extracted by OΦD(iB)CMPO over lanthanide(III) thiocyanates. A separation factor of 10 - 12 was reached in the extraction from 0.005 - 0.02 M NH_4SCN + 0.05 M HCl. Further work was devoted to the oxidation of Np(V) to the extractable Np(VI) valence state. Nitrite oxidizes Np(V) in 4 - 6 M nitric acid after a period of $\geq$10 min.

Progress and results

1. Compilation and assessment work

A report was published (KfK 4945) which gives a critical survey of informations about the separation of long-lived actinides and fission products from high-level radioactive wastes. Emphasis was laid on the basic separation chemistry of transplutonides, plutonium, neptunium, lanthanides, technetium, strontium and cesium. Attention was paid to single unit operations as components of potential separation processes, rather than to existing process flowsheets. Discussed are the scope, particular aspects and aims of the waste partitioning; the separation of transplutonides(III), also including the separation from lanthanides(III); the separation of plutonium and neptunium; the separation of cesium, strontium and technetium; and waste management, process engineering and economical considerations.

Following conclusions could be drawn from the compilation work: The composition of a simulated HAW solution, as given in an internal document of the project /1/, is fully acceptable. It reasonably agrees with comparable published data /2/-/4/. The extraction of complexes of Am(IV) and, especially, of Cm(IV) does not promise an adequate effectiveness for reaching the target decontamination factors 50000, and the selectivity would neither be appropriate. Common, readily available extractants are hardly able to extract transplutonides(III) with a sufficient selectivity over lanthanides(III); search for sofisticated, "soft-donor" extractants is labourious and lies outside of our possibilities. Also labourious would be search for new selective complexants for transplutonides(III) or lanthanides(III) in the aqueous phase. The application of diethylenetriaminepentaacetic acid (DTPA) for the separation of transplutonides(III) from lanthanides(III) is a possible option. Extraction of salts other than nitrates with solvating extractants is a possible way of separating transplutonides(III) from lanthanides(III). Bifunctional phosphoryl/carbonyl or diamide compounds are suitable solvating extractants. No detailed conclusions can at present be drawn about the redox behaviour of Pu and Np in the HAW solution, the distribution behaviour of Zr, Mo and Pt metals in the extraction of nitrates with TBP and in the back extraction, and about the chemical stability of extractants and complexing agents.

2. Experimental work

The experimental work was concentrated on the separation of transplutonides(III) from lanthanides(III) by the extraction with OΦD(iB)CMPO . Less extensive was the investigation of the oxidation of neptunium(VI) before or during the extraction with TBP.

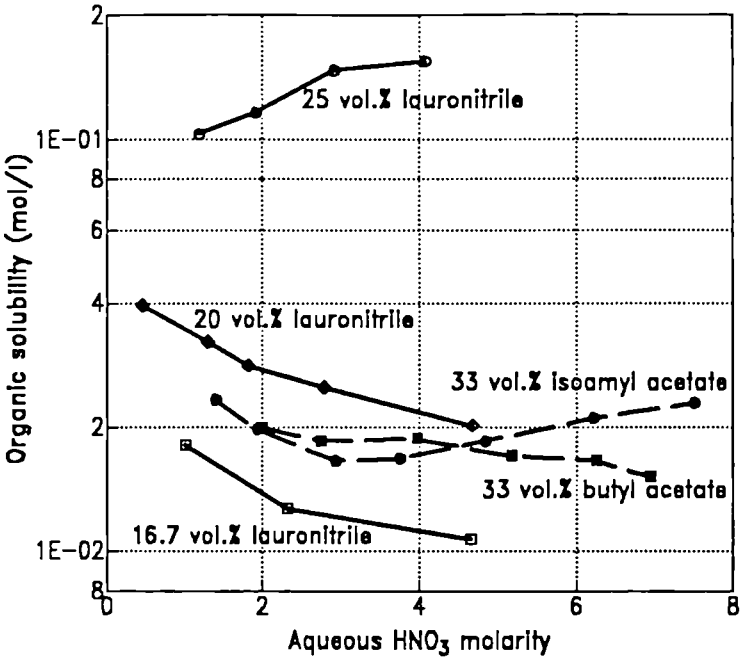


Figure 1. Solubilization effect of alkyl acetate and lauronitrile modifiers: Solubility of Nd(III) nitrate in modified 0.2 M OΦD(iB)CMPO in n-dodecane at 25.0°C (for the experimental procedure see /6/).

2.1. Solvent modifier

Metal nitrate solvates of OΦD(iB)CMPO are very slightly soluble in aliphatic diluents, and their solubility must be enhanced by adding a polar solvent modifier. TBP has exclusively been used for this purpose. Since the TBP concentration must be as high as 1.2 - 1.4 M (i.e. 33 - 38 vol.%) /5/, the solvent extracts considerable amounts of nitric acid. This can disturb in potential subsequent operations like selective back extraction of transplutonides(III) with a DTPA solution. We therefore sought a modifier which extracts less nitric acid, but enhances the solubility of extracted OΦD(iB)CMPO complexes at least as efficiently as TBP.

To assess the solubilizing efficiency of modifiers, we measured the solubility of neodymium(III) in modified 0.2 M solutions of OΦD(iB)CMPO in n-dodecane. We excluded alcohols as modifiers, because they strongly suppress the extraction ability of OΦD(iB)CMPO. Ketones and carboxylic acids are inefficient. Butyl and isoamyl acetates are more efficient (see Figure 1), but not so much as TBP at the same concentration. 2-Ethylhexyl acetate and ethyl isovalerate are ineffective modifiers, and low molecular weight esters like ethyl acetate are too soluble in water and were not tested.

Good results were obtained with lauronitrile (see Figure 1). We chose a lauronitrile concetration of 25 vol.% as an adequate level for later distribution studies with metals. At this concentration lauronitrile solubilizes the extracted Nd(III) solvate much more than TBP at a concentration of 33 vol.% /6/. No formation of a second organic phase was observed at 33 vol.% lauronitrile, even at >0.2 M Nd(III) in the aqueous phase.

Lauronitrile little contributes to the extraction of nitric acid by OΦD(iB)CMPO itself. With lauronitrile as modifier, the extraction of nitric acid by the modified solvent is lower than with isoamyl acetate and much lower than with TBP. An example can be given for 2.5 M HNO_3 in the equilibrium aqueous phase and 33 vol.% modifier in the organic phase: a 0.2 M OΦD(iB)CMPO solution extracts 0.78 M HNO_3 in the presence of TBP,

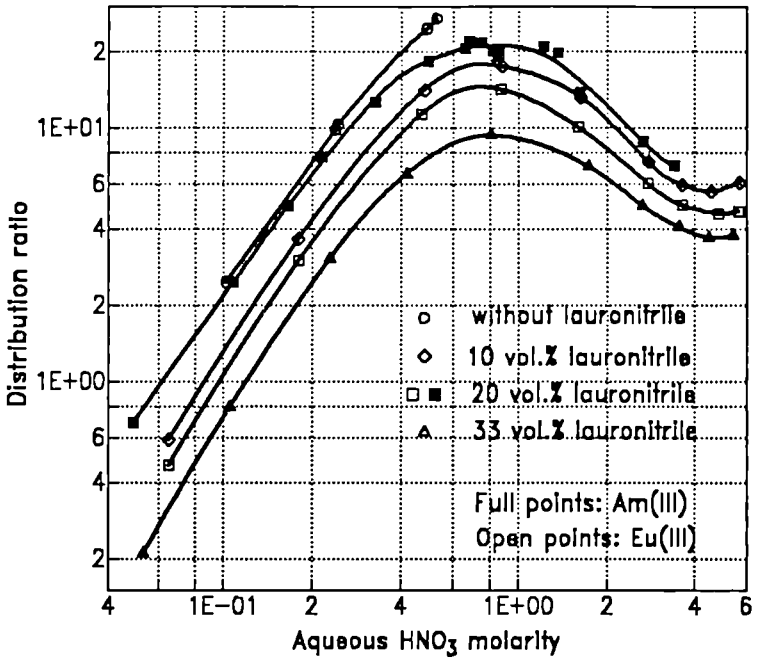


Figure 2. Extraction of trace Eu(III) and Am(III) in the presence of lauronitrile modifier: The solvent was modified 0.2 M OΦD(iB)CMPO in n-dodecane, and $< 10^{-5}$ M Eu(III) or Am(III) was present in the initial auqoues phase. Room temperature.

0.23 M HNO_3 in the presence of isoamyl acetate, and 0.19 M HNO_3 in the presence of lauronitrile.

Lauronitrile slightly suppresses the distribution ratio of Eu(III) (see Figure 2). The maximum D_{Eu} value is reached at ~0.9 M HNO_3, while with the TBP modifier it is attained at 2 - 3 M HNO_3 /5/. As seen in Figure 2, Am(III) is extracted somewhat more efficiently than Eu(III). The separation effect is not strong enough for selective extraction of transplutonides(III) over lanthanides, but may be useful if it is superimposed on additional separation effects.

The stability of lauronitrile towards hydrolysis was checked by infrared spectrometry. No absorption band of lauryl amide was found in the spectrum of the solvent after a 20 h contact with 3 M HNO_3

2.2. Extraction of transplutonide(III) and lanthanide(III) salts other than nitrates

Transplutonide(III) thiocyanates, iodides and bromides are extracted by a dodecane solution of OΦD(iB)CMPO with a beter selectivity over the corresponding lanthanide(III) salts than nitrates. Since the separation effect is weak with bromides, and iodides are oxidized in acidic solutions, we investigated the thiocyanate system. We did it in the presence of HCl, because HNO_3 oxidized the thiocyanate ion. The effect of the thiocyanate and HCl concentrations on the extraction and separation of Am(III) with OΦD(iB)CMPO is shown in Figure 3. Am/Eu separation factors of 10 - 12 can be reached in the system.

2.3. Oxidation of neptunium(V)

To render neptunium extractable with 30% TBP in an alkane diluent from high-level liquid wastes, it must be oxidized to its hexavalent state. We tested the oxidation with

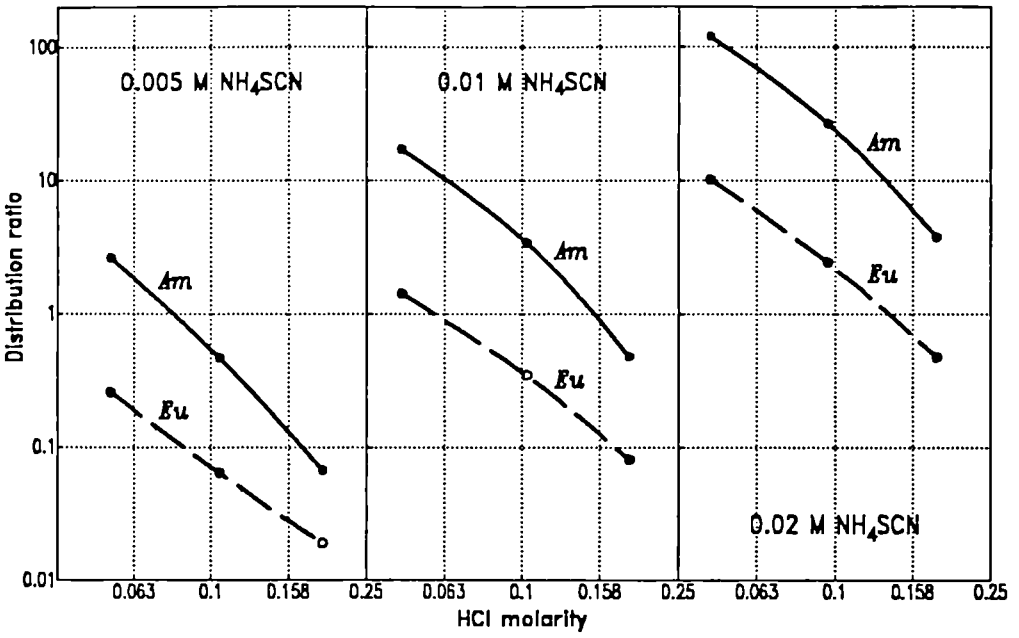


Figure 3. Extraction of trace Eu(III) and Am(III) in the presence NH_4SCN: The solvent was 0.2 M OΦD(iB)CMPO + 25 vol.% lauronitrile in n-dodecane, and $< 10^{-5}$ M Eu(III) or Am(III) and given concentrations of NH_4SCN were present in the initial auqoues phase. Room temperature.

nitrite, which does not cooxidize the well extractable Pu(IV) to the less extractable Pu(VI). At 4 - 6 M HNO_3 and $\geq$0.005 M nitrite the oxidation time was $>$10 min both in a homogenous aqueous solutions and in a liquid-liquid dispersion. The oxidation kinetics is further studied as a function of the nitrite and HNO_3 concentrations.

3. References

/1/ Proposition of a reference chemical composition for the preparation of simulated HLLW based on UP3 reprocessing plant operation (5th July, 1991).

/2/ CECILLE, L., LANDAT, D., LE STANG, M., and MANNONE, F., *Proc. 1st Technn. Meeting Nucl. Transmutation of Actinides* (Report EUR 5897), Ispra, Italy, Apr. 16-18, 1977, p. 145.

/3/ CECILLE, L., LANDAT, D., and MANNONE, F., *Radiochem. Radioanal. Let.* **31**, 19 (1977).

/4/ Report ORNL-4451 (1970).

/5/ HORWITZ, E. P., KALINA, D. G., DIAMOND, H., VANDEGRIFT, G. F., and SCHULZ, W. W., *Solvent Extr. Ion Exch.* **3**, 75 (1985).

/6/ KOLARIK, Z., and HORWITZ, E. P., *Solvent Extr. Ion Exch.* **6**, 61 (1988).

List of publications

KOLARIK, Z., Separation of Actinides and Long-Lived Fission Products from High-Level Radioactive Wastes (A Review), Report KfK 4945 (Nov. 1991), 74 pp.

Title	Advanced management of radioactive wastes : comparative evaluation of processes for enhanced separation of very long-life radioactive species.
Contractor	ENEA, Nuclear Area, IRD, CRE Casaccia
Contract N°	FI2W/CT90/0056
Duration of contract	March 1991 - February 1993
Period covered	March - December 1991
Project leader	G. GROSSI

A. OBJECTIVES AND SCOPE

For evaluation of advanced HLW management, it is convenient to categorize the nuclear waste constituents into two parts : short lived radioisotopes, mainly fission products, comprised of hundreds of various isotopes, and long lived radioisotopes, mainly actinides, comprised of uranium and transuranic elements (neptunium, plutonium, americium, curium).
Most of fission products decay in relatively much shorter periods than actinides. In the order of few centuries, the fission products decay to a sufficient low level so that their radiological risk factor drops below the risk level due to their original uranium ore.
Actinides, as well as some long lived fission products such as Tc-99, I-129, on the other hand, have longer half lifes and their radiological risk factor remains to be orders of magnitude higher than that due to fission products for million of years.
The main objective of this research programme is to test and demonstrate the feasibility of the enhanced separation of the long-lived radioisotopes (mainly actinides) from high activity liquid radioactive wastes, in order to obtain a residual HLW stream practically alpha-free (less than 10-100 nanocuries/g of long-lived alpha emitters).
The feasibility study will be based on the application of known technologies or on minor extrapolations from them.

B. WORK PROGRAMME

The research programme will be developed according to the following main phases :

Phase 1 : Criterial review of the present state of the art on separation processes for actinides and long-lived fission products.

Phase 2 : Comparative evaluation (lab scale) of the selected separation agents, computer modelling, and definition of an optimized flowsheet.

C. PROGRESS OF THE WORK AND OBTAINED RESULTS

During the covered period, after preliminary definition of the principal reference criteria, mainly concerning the chemical and radiochemical composition of the reference HLLW solution, as well as the reference final decontamination factors to be achieved, the major effort has been devoted to a careful literature survey.
A thorough examination of the current available literature has been performed with the purpose of collecting all the data useful to perform the selection of the most promising processes.
The long-lived radionuclides under consideration were mainly the transuranic element Np, Pu, Am, but attention was also given to some long-lived fission products such at Tc-99, Sr-90 and Cs-137.

Concerning the separation agents, the following classes of reagents were reviewed :
- organo-phosphorous compounds;
- organo-nitrogen compounds;
- organo phosphorus-nitrogen compounds;
- macrocyclic derivatives;
- soft donor ligands;
- others.

All the information collected have been organized in a report and classified in a magnetic support for PC.

More detailed information have been achieved by direct contacts with selected Research Institutes, such as Argonne National Laboratory (ANL, USA) Vernadski Institute of Geochemistry and Analytical Chemistry (VIGAC, Moscow, Russia), Westinghouse Hanford-Battelle Pacific Northwest Laboratory (WA-PNL, USA), Khlopin Radium Institute (KRI, St. Petersburg, Russia).

Apart from the extracting systems under study at CEA-Fontenay-aux-Roses, KfK Karlsruhe and University of Reading, which form the object of other specific CEC contracts, the most promising separation systems until now found are the following :

CMPO (octyl phenyl N,N diisobutyl carbamoyl methyl phosphine oxide).
This reagent, proposed by Argonne National Laboratory as extractant of the TRUEX process for the removal of all actinides (+3, +4, +6) in strong acidic media, is also potentially useful for removal of Tc-99. Since until now the TRUEX process has been studied for the removal of plutonium and transplutonium actinides (mailly Am), further studies are needed to verify the separation of neptunium and technetium.

Ph_2Bu_2 (diphenyl dibutyl carbamoyl methyl phosphine oxide).
This reagent has been developed by the Vernadski Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences (Moscow, Russia) and it is claimed to perform very high decontamination factors for actinides especially by adding traces of perchhoric acid to the nitric acid solution of HLLW. More thorough investigation is needed to confirm this behaviour.

Primene JM-T (commercial mixture of long-chain aliphatic primary amines).
This reagent is proposed by Westinghouse Hanford - Battelle PNL (USA) as a selective extracting agent of technetium in acidic media, especially with respect to uranium and other actinides.

Crown Ether 4,4' (5') di tert butyl cyclohexano 18 crown 6.
This reagent, developed at Argonne National Laboratory (USA) is claimed as a powerful and selective extracting agent of strontium in acidic media.

BSC-187 (a new selective resorcinol-formaldehyde ion exchange resin).
This new reagent has been developed by Savannah River Laboratory (USA) and according to preliminary studies carried out by Battelle PNL (USA) it performs better than any other known ion exchange resin for the selective removal of cesium.

Cobalt dicarbolide
A conceptual flowsheet developed in cooperation between the Institute of Nuclear Research (Czechoslovakia) and the Khlopin Radium Institute (St. Petersburg, Russia), based on this reagent diluted in a polar diluent, is claimed to separate cesium, strontium, rare earths and transplutonium actinides into individual fractions with efficiency over 99%..

D. ONGOING WORK

A laboratory scale evaluation of the performance of most of the selected separation systems, using a reference simulated HLLW solution, is under way.

C. PROGRESS OF THE WORK AND OBTAINED RESULTS.

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D. ONGOING WORK.

A laboratory scale evaluation of the performance of most of the selected separation systems, using a reference simulated HLLW solution, is under way.

Title	High-level liquid waste partioning 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 1993
Period covered	October - December 1991
Project leader	C. MUSIKAS (CEA, Coordinator); M. 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.
In terms of decontamination performances, these extractants have to demonstrate at least equivalent properties as bifunctional organophosphorous extractants (like CMPO) for actinide removal and as the combination of HDEHP with DTPA for the separation of lanthanides from trivalent actinides while being capable to be completely incinerable in order to avoid secondary wastes.
This research, which is closely co-ordinated with those currently under study at the ENEA-Casaccia and the KfK Karlsruhe should result in the drawing-up of flow-sheets for HLLW partioning as input data for a possible subsequent validation with genuine waste.

B. WORK PROGRAMME

This study will comprise the implementation of the following steps :

B1 - Synthethis of new organic extractants (di-amides and triazine-based).
B2 - Determination of their extraction performances on simulated HLLW (batch tests).
B3 - Quantification of the extractants stability in the long term towards chemical attack and irradiation.
B4 - Drawing-up of possible partioning flow-sheets on the basis of the results from B2.
B5 - Verification of two flow-sheets 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.
B6 - Scaling up of the preparation procedure for diamides, triazine-extractants.
B7 - Definition and verification of solvent regeneration treatments.
B8 - Cooperation with laboratories working on HLLW partioning in the framework of Task 2 of the EC programme.

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

Task 3 "Characterisation and Qualification of Waste Forms, Packages and their Environment"

Task 4 "Disposal of Radioactive Waste : Research to Back-up the Development of Underground Repositories"

Task 5 "Method of Evaluating the Safety of Disposal Systems"

Part A3

Task 3

"Characterisation and Qualification of Waste Forms, Packages and their Environment"

Topic 1 Waste form characterisation and performance

Topic 2 Containment and barrier properties of the near-field (including modelling)

Topic 3 Radionuclide assay

Topic 4 Quality control of waste conditioning

Task 3

Topic 1 Waste form characterisation and performance

FI2W/0012 The behaviour of Pu, Am, Np and Tc during the corrosion of the Cogema-HLLW glass R7T7 in a salt brine.

FI2W/0020 Consequences associated with gas production in geological repositories (PEGASE).

FI2W/0025 Characteristics of bitumenized radioactive wastes.

FI2W/0026 Natural analogues of bitumen matrices in a deep repository.

FI2W/0027 Aqueous corrosion of nuclear glasses: influence of disposal conditions.

FI2W/0028 Effect of insoluble active dissolution fines on fission product glasses.

FI2W/0031 The corrosion of nuclear waste glasses in a clay environment: mechanisms and modelling.

FI2W/0032 Basic leaching for pure Beta long-lived emitters in radioactive wastes.

FI2W/0055 Chemistry of the reaction of fabricated and high burnup spent UO_2 fuel with saline brines.

FI2W/0077 Container properties ensuring safety: gas emission, biodegradation, corrosion.

FI2W/0094 Gas generation in supercompacted waste products.

FI2W/0099 Impact of additives and waste streams constituents on the immobilisation potential of cementitious materials.

Topic 2: Containment and barrier properties of the near-field (including modelling).

FI2W/0022 The effect of microbial activity on the near and far fields of a deep repository.

FI2W/0030 Corrosion of selected packaging materials for disposal of heat-generating radioactive wastes in rock salt formations.

FI2W/0033 Modelling and testing of the hydration of backfill and sealing materials.

FI2W/0035 Theoretical and experimental study of degradation mechanisms of cement in the repository environment.

FI2W/0040 The performance of cementitious barriers in repositories.

FI2W/0102 Modelling and validation of the thermal-hydraulic-mechanical and geochemical behaviour of the clay barrier.

Topic 3 Radionuclide assay.

FI2W/0010 Determination of fissile material by neutron transport interrogation.

FI2W/0034 Inventory and characterisation of important radionuclides for safety storage and disposal. Correlation with key nuclides which are easy to measure in typical waste streams.

FI2W/0109 Inventory and characterisation of important radionuclides in reactor and reprocessing waste.

Topic 4 Quality control of waste conditioning.

FI2W/0009 Construction and testing of a computer tomography assembly for routine operation.

FI2W/0014 Behaviour of low-level radioactive waste under fire accident conditions.

FI2W/0018 Non-nuclear non-destruction testing methods to determine free water, gas pressure and matrix level in waste drums.

FI2W/0019 Test for process control during treatment of low and medium radioactive waste in practise.

FI2W/0021 Establishment of non-destructive or partially destructive test procedures for determining the characteristics of waste containers.

FI2W/0023 Non-destructive examination of nuclear radioactive waste packages by advanced radiometric methods.

FI2W/0107 High Energy Accelerator Tomography (HEAT).

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 under 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 of 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
- Theoretical and experimental study of degradation mechanisms 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

The above topics and areas of research are being tackled under 28 contracts, the majority of which are multi partner and trans-european. Further details are provided in the summary reports listed hereafter.

Title:	The behaviour of Pu, Am, Np and Tc during the corrosion of the Cogema-HLLW-glass R7T7 in a salt brine
Contractor:	Kernforschungszentrum Karlsruhe GmbH
Contract:	FI2W/CT90/0012
Duration of contract:	1.3.91 - 28.2.95
Period covered:	1.3.91 - 31.12.91
Project Leader:	Dr. Werner Lutze, (KfK-INE)

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 under construction and will 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 one of the 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 funtion of time and temperature. This work complements previous investigations on the durability of a very similar but non-radioactive glass by measuring the release behaviour of Pu, Am, Np and Tc.

B. Work programme

1. Installation of the hot cells: One hot cell has to be equipped with crushing, milling and sieving devices to prepare glass powder. The other cell has to be equipped with three ovens, devices to handle autoclaves, balances, a pH-Meter and sampling and filtering devices.

2. Modification of analytical techniques: Tc, Pu, Am and Np have to be separated from concentrated salt solutions for activity measurements (α,β,γ spectrometry).

3. Equipment for corrosion tests: Tests shall be performed in autoclaves. Previously used Teflon liners for inactive glass have to be replaced by tantalum to resist both radiation and chemical corrosion.

4. Corrosion test conditions: Powdered glass (4.5 g, average grain size 86 µm) shall be corroded in 25 mL (S/V = 10,000 m^{-1}) of salt solution at 110, 150 and 190°C for 45, 130, 180, 360, 720 and about 1000 days (individual experiments in duplicate for each time and temperature).

5. Solution analyses: Samples shall be taken after completion of each experiment. The leachates shall be filtered to separate colloids. Concentrations of B, Si (glass formers) and of Tc, Pu, Am and Np shall be determined. pH shall be measured in the unfiltered leachate.

6. Analysis of corrosion layers: Sample surfaces will be observed under the light microscope and in the SEM. Host phases for actinoids and Tc will be searched and analysed, if possible.

C. Progress of work and obtained results

State of advancement

The radioactive glass block was delivered from Marcoule to the Institute for Transuranium Elements (TUI) by the end of 1989. Originally, the glass block should be crushed and sieved in the cells at TUI, but technical difficulties were encountered and it was necessary to transport the glass block from TUI to the KfK hot cells. The transport was delayed for unexpected schedule problems (availabiltiy of transfer units and proper equipment for transport). The glass was transported in November of 1991.

Progress and results

1. Installation of the hot cells

Two KfK hot cells were equipped with the necessary instruments to perform the corrosion experiments. One cell was prepared to perform the crushing (left side in figure 1) and sieving (right side in figure 1) of the glass.The second cell will contain the equipment to perform the corrosion tests in autoclaves. The installation is in progress, but was delayed because of a shielding problem.

The remotely handled equipment (furnaces, autoclaves, balances, pH-meter, sampling devices, a device to filter the leachates) have been operated in "cold" tests and are ready to be used in the cell.

2. Preparation of glass samples and setup of the experiments

The radioactive glass block was destroyed in three steps. Chunks were produced by impact and subsequently crushed mechanically to produce grains which could then be milled to produce powder. Sieving of the powder to prepare the appropriate grain size fraction (86 µm average grain size) shall be finished before the end of February). The powder will then be transferred to the other hot cell in the same building to load the autoclaves. The startup of the corrosion experiments has now been scheduled for the end of March.

A remotely operated device was built to replace the air in the autoclaves by argon. This is shown in figures 2, 3 and 4. The autoclave (Fig. 2) will be filled with glass powder and leachant (salt solution) and placed under a hood (Fig. 3). Argon is bubbled through the solution (composition in table I) prior to filling the autoclaves. The air under the hood and in the autoclave is replaced by argon entering through the tube and leaving through a whole in the lid of the hood. The lid of the autoclave is already in place as shown. Finally, the tube is removed from the autoclave and the lid closes the autoclave. The lid is than quickly thightened by the screws (Fig. 4). In this way, most of the air should be replaced by argon and the remaining traces of nitrogen and oxygen are not expected to form enough NOx to lower the pH of the solution.
Table II gives the glass composition and the total activities of the radionuclides as provided by CEA Marcoule. Note that values for Tc and Np are not given. They are not available and have to be determined in the course of the project.

Table I: Composition of the salt solution

	(mol/1000 mol H_2O)
NaCl	1.5
$MgCl_2$	97.2
$MgSO_4$	5.7
$CaCl_2$	5.7
$CaSO_4$	0.01
KCl	0.4

Table II: Composition of the highly radioactive French borosilicate glass.

glass frit	weight %	radionuclides	Bq/L of glass (1991)	radionuclides	Bq/L of glass (1991)
SiO_2	58.8	Sr-90	1.3 E12	Pu-241	4.0 E11
B_2O_3	18.2	Cs-137	8.0 E11	Pu-238	4.9 E11
Al_2O_3	4.3	Cs-134	4.4 E9	Pu-239	3.0 E9
Na_2O	7.0	Ru-106	1.5 E8	Pu-240	4.1 E9
Li_2O	2.6	Ce-144	3.3 E8	Am-241	4.1 E10
ZnO	3.5	Sb-125	3.7 E9	Cm-244	4.1 E10
ZrO_2	0.7	Co-60	1.5 E8		
waste oxides	23.3				

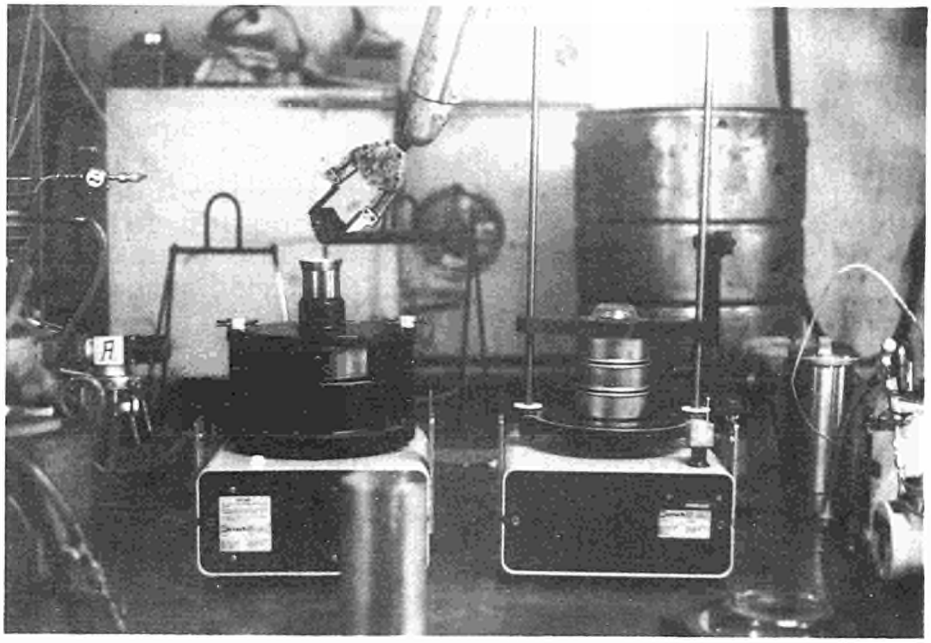


Figure 1: View into the hot cell containing the mill (left) and the sieving device (right)

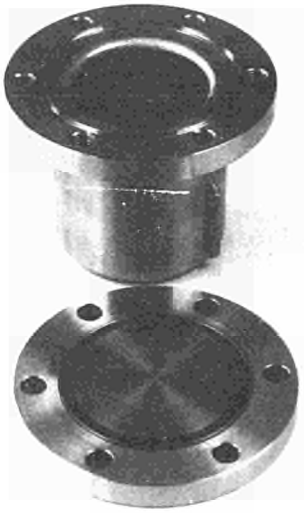


Figure 2: Autoclave (open) with tantalum liner

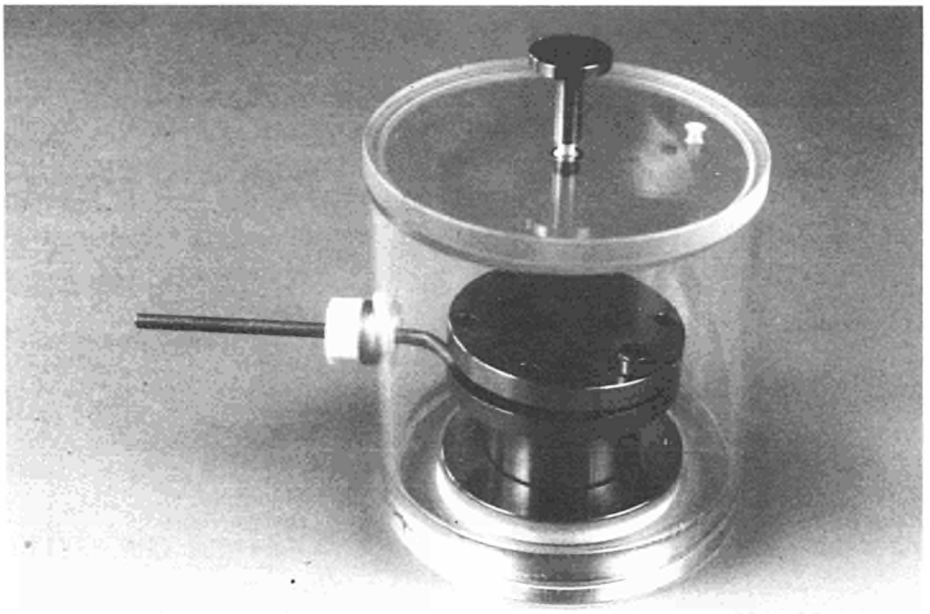


Figure 3: Autoclave under the argon hood (gas purge) to remove the air from the system

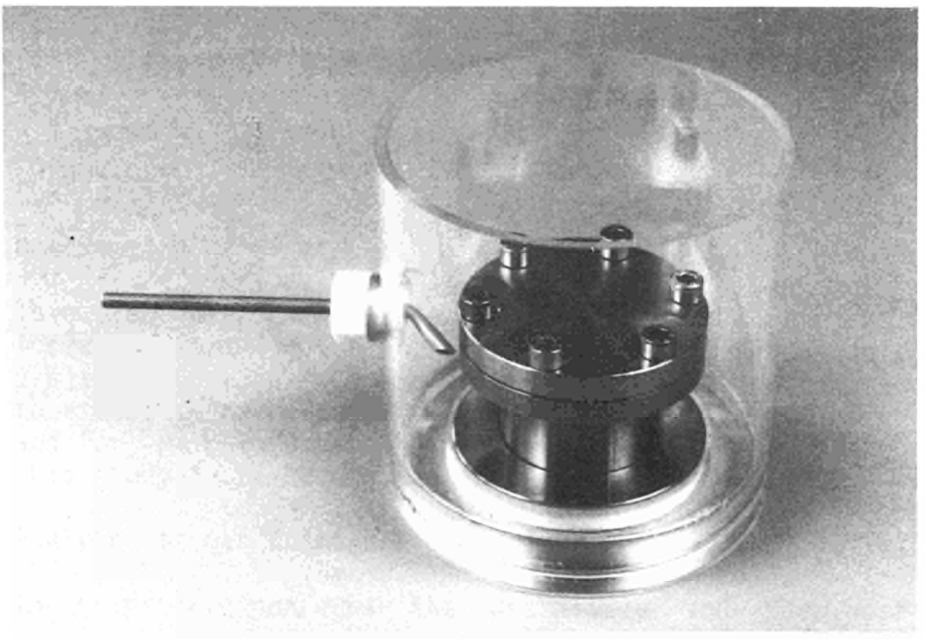


Figure 4: Sealed autoclave with argon atmosphere inside

Title: Consequences associated with gas production in geological repositories (PEGASE)

Contractor: ANDRA, France - ENRESA, Spain - GRS, Germany
Contract No.: FI2W/CT90/0020
Duration of contract: 1 August 1991 to 31 July 1994
Period covered: January 91 - December 91
Project leader: Mrs. Voinis (ANDRA, coordinator), Mr. Gago (ENRESA)
Mr. Müller (GRS)

A. OBJECTIVES AND SCOPES

This project intends to model the overall impact of gas production in the nearfield 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-Analyses of gas transport mechanisms ; 3-Modelling of the system ; 4-Calculations in specific disposal conditions.

Three partners are concerned : 1-ANDRA with BERTIN as subcontractor ; 2-ENRESA with INITEC as subcontractor ; 3-GRS.

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) Analyses of gas transport mechanisms

The transport concerns the near-fiels 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 condidered 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) State of advancement

On the basis of an exchange of informations ; working group 1 (ANDRA/ENRESA/GRS) created for task 1 is currently elaborating two project reports. The first corresponds to the data reference necessary for the development of the different models and particularly for the physical study of gas formation and transport. These data will evolve in function of the definition of the different scenarios and the repository concepts in the future months. The second corresponds to the listing of the different mechanisms governing gas formation. This analysis is only based on the bibliographic research and concerns the different types of waste and the different concepts considered by each partner.

C.2) Progress and results

C.2.1.) Data reference :

The first step consisted in listing the different parameters necessary 1-for the physical analysis of the different phenomena governing the gas transport, 2- for the modelling and 3- for the calculations. A first report is being elaborated. It includes three principal chapters :

1. Characteristics of wastes
2. Concepts
3. Scenarios

ANDRA is concerned with vitrified wastes and will deal with a crystalline rock disposal. ENRESA is concerned with spent fuel disposal in a crystalline rock formation. GRS is concerned with HLW and ILW in salt formation.

At this time and after several exchanges, the first two chapters are practicaly completed and permit to begin the physical analysis defined in the work program/ref1/. The radioactive composition is not yet completely defined and must be discussed in future meetings. In the same way, some values corresponding to characteristics of backfilling materials are sometimes only order of magnitudes and must be precised. We can already note that the most precise informations are about the borehole backfilling materials . The knowledge of the characteristics of the borehole plug and the tight blockhead must be improved. The definition of the scenarios is actually in progress. The post-operational period is studied. The cooling time for the vitrified wastes (ANDRA) is 30 years and for the spent fuel (ENRESA) 32 years. Some informations on the concept are missing and will be completed in the next months by each partner.

A draft on the reference data has been established. The progress report will be available in six months.

C.2.2.) Gas mechanisms :

The aim of this work consists in establishing the first state of the art as regard gas formation mechanisms. A full description of the phenomena leading to gas formation has been submitted. The different mechanisms to be considered are/ref 2 :

- . Anaerobic corrosion of containers
- . Radiolysis
  - - in backfill materials
  - - in the host rock
  - - in water/steam
  - - in residual air
- . Thermal gas release
  - - from the host rock
  - - by evaporation
- . Primary gas release
- . Helium production
- . Production of gaseous radioactive decay products
- . Microbial degradation

a.) **Corrosion :**

The bibliographic analysis shows that the influencing parameters are :

- . corroding material (steel, copper, titanum...)
- . corrosive media
- . temperature
- . pressure
- . radiation
- . chemical conditions (pH, Eh)
- . presence of oxygen
- . presence of salts, impurities

b.) **Radiolysis :**

The effect of radiation in a repository will result in atom ionisation and the subsequent production of fundamental chemical changes, with groups of atoms splitting from the parent molecule. The influencing factors are :

- dose rate, dose
- backfilling material
- host-rock
- temperature
- pressure
- water availability
- chemical conditions
- impurities

The mechanisms that should be studied are the interaction between corrosion and radiolysis ; the fact that the availibility of water is limited must be considered.

c.) **Thermal gas release**

This mechanism is most important for HLW. Three main consequences are observed, they are :

- vaporisation of water in backfill material and host rock
- release of gases stored in host rock
- brine migration

d.) **Microbial degradation**

Degradation of organic matter can occur by oxidation, often being catalysed by microbial action. These microbes use the energy released in these reactions in their metabolic processes. For these metabolic processes to operate, nutrient sources and water are required.

Other less important gas formation mechanisms could appears with a lower rate production. They are :

- Helium production issue from alpha radionuclide decay
- Formation of radioactive gases like Rn220, Rn222
- Primary gas release

A first bibliographic synthesis is compiled in a report. The second step of this task is either to determine the analytical law for each of the main phenomena or to evaluate the gas production rate. Before to integrate the gas formation mechanisms in the gas transport model ; a selection of the main phenomena will be performed, it will be based on gas generation estimated maximum expected. A progress report will be finalised in six months.

C.3) List of publications

1. S. Voinis, ANDRA ; J. Gago, ENRESA ; W. Müller, GRS ; Gas formation through crystalline rock . PEGASUS meeting. Brussels. 22th May 1991

2. S. Voinis, ANDRA ; J. Gago, ENRESA ; W. Müller, GRS ; The analytical modelling of gas generation. NEA workshop on gas generation and release from radioactive waste repositories : Aix en Provence. 23rd-26th September 1991.

Title: Characteristics of bituminised radioactive wastes

Contractor: CEA/DCC (Cadarache and Saclay, France) - SCK/CEN, Belgium - Risø Laboratory, Denmark
Contract No.: FI2W/CT90/0025
Duration of contract : from 01.12.91 to 30.11.94
Period covered : 01.12.91 to 31.12.91
Project leader : Coordinator : G.BRUNEL, - Tasks leaders : J.C.NOMINE, P.VAN ISEGHEM, R. SWENNNEN, K. 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 compareason of Eurobitumen 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 medium conditions constitued by water (CEA Cadarache), by a cement/clay mixture or by a clay/claywater 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 bituminized materials are disposed of under saturated as well as unsaturated conditions and quantification of swelling, swelling pressure and leaching phenomena are improved by Rïso Laboratory.
The small size bitumen samples will be prepared by CEA Cadarache.

B. WORK PROGRAMME

B.1. Sampling
Samples are taken from an inactive as well as an active drum or are fabricated in a suitably equipepped 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/claywater mixture, at 23°C and 40°C, for duration until 480 days. Emphasis will be on the leaching kinetics of the inactive wast constituents.

B.3. Active leaching tests

Tests are carried out in similar conditions as B.2 (media, temperature, durations) 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 by CEA Cadarache and on 200 l, 20 l and 2 l by CEA Saclay. Emphasis will be on leaching processes and kinetics of the active waste constituents.

B.4. Migration of water and 134 Cs ions through bitumen product membranes

Tests are performed to investigate the migration of (tritiated) water and 134 Cs ions through membrane of pure bitumen, bitumen containing sludge particules and cristals of soluble salts such as $NaNO_3$. The diffusion measurements will be supplemented with measurement electrical conductivity over a membrane.

B.5. Swelling studies

The development of swelling pressure due to the water uptake in confined sample of bituminized materials containing soluble salt will be studied using cement mortar and barrier materials and a previously developed method based on mercury as combined pressure and volume change measurement.

B.6. Model describing the water uptake

A research model describing the water uptake phenomenon on micro-scale is under development. The model can used diffusion coefficients and other results obtained in the above mentioned experiments.

C. PROGRESS OF WORK AND OBTAINED RESULTS

The signing of the contract is fairly recent. The number of samples of different type and size being high, the work schedules of everyone involved have been defined as regards sample fabrication.

C.1. CEA Cadarache

With this object in view, we are preparing, at Cadarache, a shielded cell from our facilities which we are suitably modifying and equipping for this fabrication.

General description :

The cell is a 30 m^3 parallelepiped with a tight 8 m^3 tank. It is equipped with four remote manipulators and two rectangular observation parts, fittings for cendrillon type flasks (liquids) and RD 15 type flasks (solids).

The last months of 1991 were devoted to the interior dismantling and to the decontamination of the cell as it was and to the setting-up of the two shipping flasks.

The interior equipment which will enable us to carry out the coating is the following:

- Synthesis and spiking of the waste :
The requisite equipment for this operation is a decanting mixer that will allow us to fabricate the sludge required for encapsulation using real or spiked effluents ; means for measuring the chemical oxygen potential, the pH and the dry extract will be provided.

- Sludge encapsulation
The cell is equipped with a 1 liter stainless steel mixer with heated double casing ; it also has a condenser for distillate hold-up during encapsulation and a sludge flow valve. All this equipment can be remote operated and both the driving and monitoring operations are outside the cell.

C.2. CEA Saclay

C.2a. Samples of bitumen sludges (80/100 matrix) are to day in preparation. They will be melted in shape of cylinders (ϕ 80, h 80 mm) and they will contain 239 Pu, 238 Pu, 137 Cs and 60 Co as the mains radionuclides samples of Eurobitum are too under preparation.

C.2b. For the scale effect study CE Saclay bitumen facility is preparing several samples of different sizes. The unitary volume of these samples will be : 1 x 200 l; 1 x 20 l; 4 x 2 l and 2 x 0.2 l. The 40/50 matrix will encapsulate reprocessing waste containing $\beta\gamma$ emitters with some α traces.

The two categories of samples will be avalaible for the leaching test in March 1992. The formens samples will be introduced in leaching loop (stainless steel) which are now operationnel.

C.3. NIRAS ONDRAF/SCK Mol
The drums to be used in the programme were identified. Sampling procedures were discussed, and are being elaborated.

The inactive drum to be sampled will be transferred from Belgoprocess to SCK/CEN. The drum was prepared in the Eurobitum plant, during the start-up runs, using simulated waste. During sampling, the same technique and geometry will be used as for the active drum.
The active drum has been selected, and will be transferred soon to the hot cell where sampling will be carried out.

C.4. Risö Laboratory
No new experimental results are available because of the delay in contract signature. The methods which will be employed in the planned experimental work are described in reports on previous CEC-supported research [1][2]
Considerable progress has been made concerning development of the model mentioned under B.4. However, the actual model development is considered as laying outside the contract.

LIST OF PUBLICATIONS

[1] K.Brodersen and K.Nilsson, "Mechanisms and Interaction Phenomena Influencing Releases in Low- and Medium Level Waste Disposal Systems", Final report 1985 1990. EUR-13662 EN, CEC (1991), also available as Risö-M-2908

[2] K.Brodersen, "Chemical and Thermal Stability of Waste Products" pp.242-256 in L.Cecille ed., Proc. Third European Conf. on "Radioactive Waste Management and Disposal", Luxembourg 1990. Elsevier, EUR 13389.

Title: **Natural analogues of bitumen matrices in a deep repository**
Contractors: **CEA, CE-FAR and CREGU**
Contract n°: **FI2W/CT90/0026**
Duration of contract: **from 1991 to 1994**
Period Covered: **second semester 1991**
Project leader: **J.-C. Petit (CEA) and P. Landais (CREGU)**

A. OBJECTIVE AND SCOPE

Bitumens are used for the solidification of low-activity alpha-containing wastes and their long-term behaviour in geological conditions remain questionable. It is thus proposed in this work to gain some understanding on this issue by studying natural analogues of technological bitumens which have been poorly investigated, from this viewpoint, until now. In particular, we intend to characterize the organic matter associated with the Oklo nuclear reactors (Gabon) and to estimate the specific consequences of radiation damages, notably radiolytic effects, by comparison with organic matter collected outside the reaction zones and having variable uranium concentrations. The work will concentrate on two distinct aspects: firstly, the structural and chemical modifications induced by the radiation damages in the organic matter; secondly, the changes in the leaching behaviour of various elements (e.g. U, REE, etc.) possibly deriving from these radiation-induced alterations.

The Oklo reactors are a priori favourable, as natural analogues, because of the long time scale involved, the association of bitumen and uraninite (UO_2), the presence of daughters of fission products and transuranium elements generated by the nuclear reactions which induced various radiation effects.

B. WORK PROGRAMME

Task 1: Geochemical characterization of the Oklo organic matter
Task 1.1: Global geochemistry
Task 1.2: microscopic characterization
Task 2: Experimental study of the mobility of uranium and fission products
Task 3: Experimental study of radiation effects
Task 3.1: Calibration experiments
Task 3.2: Modification of structure and leaching characteristics

C. PROGRESS OF WORK AN RESULTS OBTAINED

State of advancement

The main emphasis in the work during this period has been as follows:

* collection of samples throughout the Oklo uranium ore deposit.
* preliminary structural analysis by ^{13}C NMR
* ion implantation (^{207}Pb, 1 kev/amu, simulating alpha recoils)
* leaching experiments in autoclaves
* RBS analysis of unleached and leached samples

Progress and results

The sampling of this material in Oklo is not an easy task because the organic matter can not always be easily distinguished from other facies (e.g. uraninite-rich ones). Only subsequent petrographical observations and chemical analyses, when back at the laboratory, can confirm the appropriateness of the collected samples to this investigation. Some samples have been brought back to France for the purpose of starting the study, the majority of them being surface mailed from Gabon are not yet arrived.

Ten samples of organic matter (OM) have been analysed by ^{13}C NMR with the Cross-Polarization Magic Angle Spinning (CP/MAS) technique. This technique has the advantage of giving quantitative information on the structure of OM, their functionality and the distribution of aromatic carbons. Different polarization times have been used in order to obtain the best possible signal/background ratio as well as a good response homogeneity throughout the spectral domain considered.

The samples present high aromacity factors ($60\% < Fa < 87\%$) corresponding to highly evolved OM. Contrary to what can be observed in other precambrian uranium ore deposits (Witwatersrand, Saskatchewan), the Fa variations are not strictly correlated to the uranium concentration but rather to the geological environment of the sample. Indeed, one easily discriminates samples collected in the different surrounding layers (labelled FA, FB and FC at Oklo) as well as in function of the distance to the reactor. In addition, the substitution parameters of the aromatic nuclei and the mean length aliphatic chains do not exhibit any significant correlation with the uranium concentration.

In order to evaluate the effects of radiolysis, it is necessary to compare identical facies. In these conditions, some classical variations, such as the positive correlation between Fa and uranium content, are observed. The origin of these OM must therefore be taken into account in the evaluation of thermal and/or radiolytic alteration processes. In particular, the influence of the distance to reactors will not be determined but by comparing samples of identical initial chemical composition.

The experiments involving ion implantations and/or RBS analyses have been so far quite difficult to perform because such techniques necessitate high vacuum in the implantation/detection chamber. In fact, the Oklo OM are not very favourable because (as far as the samples already examined are concerned) they produce an intense degasing which tends to break the vacuum, thus hampering analysis. In addition, they also contaminate the chamber with organic molecules which should imperatively be avoided. The design and development of a special cold-stage fitted sample chamber is under consideration for future works in order to prevent this deleterious behaviour of materials. However, by taking a series of cautions (e.g. very small samples, etc.), we could nevertheless perform some ion implantations and RBS analyses. Another difficulty comes from the high mechanical instability of these OM which leads, in particular, to their falling into pieces in some leaching experiments. The firm embedding of samples into an epoxy resin partly solves such a problem. In spite of these difficulties, some preliminary results have been obtained.

Concerning ion implantations, one does not observe macroscopic degradation of OM, at least up to doses of lead ions of 10^{14} ions/cm^2. When followed by leaching, one notes under the optical microscope that the implanted areas seem to present a distinct dissolution behaviour, in being apparently more resistant to aqueous corrosion than the unimplanted areas. This feature could be correlated with the likely aromatization of the material upon bombardment (to be checked).

The RBS spectra of the samples analysed exhibit, both before and after leaching, a shape which is typical of heterogeneously distributed uranium. In fact, from these spectra, one can suspect that the majority of uranium in indeed concentrated in U-rich grains distributed throughout the material. Such spectra are conveniently simulated by a computer code based on the ion-matter interaction theory. No marked difference is noted in both the uranium concentration (may be a slight decrease) and uranium distribution after leaching up to 24 hours at

100°C in DI-water. The distribution of uranium is indeed confirmed by OM and SEM+EDX observations which show that this element is essentially found in uraninite grains. This feature is not favourable for the RBS programme that we intend to carry out within the framework of this project since much less information can potentially be derived from such spectra on the near-surface behaviour of this element upon ion implantation and/or leaching.

List of publications

The work is not sufficiently advanced yet to deserve the writing of a full paper but it is our intend to publish results, as soon as possible, in international journals.

Title: Acqueous corrosion of nuclear glasses: influence of disposal conditions

Contractor: CEA-CEN Valrhô, DPR/SCD, France
Contract No.: FI2W/CT90/0027
Duration of contract: April91 to March 95
Period covered: April 91 - December 91
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

State of Advancement

Part I: Basic research on aqueous corrosion of nuclear glass

The initial dissolution rates, equilibrium limits and equilibrium pH values were determined by ICP analysis of the alteration solutions for magnesium-enriched R7T7 glass and for M7 glass, which contains less silica than R7T7 glass. Two test temperatures and two experimental protocols were selected: 100°C in Soxhlet mode to measure the initial dissolution rates, and 90°C in static mode to observe the variations in the dissolution kinetics as the reaction progresses. Several SA/V ratios were tested at 90°C: 50, 2000, 8000 and 20000 m^{-1}; the high SA/V ratios simulate long-term glass corrosion behavior because of the very high reaction progress.

Crystallographic and chemical investigations of the alteration products that form on the surface of these two types of glass are now in progress (X-ray diffraction on glass powder, electron microdiffraction on ultramicrotome sections observed by transmission electron microscopy). The results, together with ongoing calculations on the distribution and activity of the aqueous species, should ascertain the possible role of these secondary phases in controlling the dissolved silica activity — and thus on the glass corrosion kinetics.

Tests with glass specimens enriched in aluminum oxide, in boron or in fission product oxides have not yet been initiated.

The effect of metallic cations on R7T7 glass corrosion kinetics will be studied after final selection of the salts to be dissolved. Some of the R7T7 glass dissolution experiments in the presence of the NS24 alloy canister have been completed and the alteration solutions have been analyzed, notably for the following conditions: 5, 50 or 500 mg of NS24 previously altered in nitrohydrochloric acid, then 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.

The experimental protocol is now being specified to investigate the effects of the ionic strength on the initial R7T7 glass corrosion kinetics.

Experimental protocols involving alternating fluid circulation on the glass test coupons had to be developed for the experimental investigation of the sorption and diffusion barrier properties of the interface gels. Preliminary measurements of the silica diffusion coefficients in the gels formed by alteration of R7T7 glass (planned at 70, 90 and 110°C) are now in progress at 90°C.

Part II: Influence of the disposal site

The experiments required to determine the R7T7 glass equilibrium limits in the presence of five site materials (granite, 2 clays, schist and salt) have all been initiated at 90°C with an SA/V ratio of 5800 m^{-1} for test periods ranging from 7 days to 1 year. The shortest experiments have already been terminated, and the solutions are now being analyzed.

The parameter experiments have been initiated:

- All the R7T7 glass corrosion tests with various schists are now in progress (90°C, 50 m^{-1} for durations of 28, 56, 91 and 182 days). Tests have been completed with schist crushed to different grain sizes, and the alteration solutions have been analyzed and interpreted.
- R7T7 glass alteration was investigated in contact with two deep underground natural clay samples for 1, 2, 3 and 6 months at 90°C. The clay materials were

ultracentrifuged after testing to recover the leachate for pH and element concentration measurements.

- One set of tests has been undertaken to assess the effects of the granite grain size on the R7T7 glass dissolution rate (90°C and 50 m^{-1} with 4 different grain sizes for durations of 1, 2, 3 and x months). Another set of tests with natural groundwater can only be initiated when granitic water samples from the Auriat site become available.
- R7T7 glass corrosion tests in contact are in progress with 2 types of salt (90°C, 70 m^{-1} for 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 been completed. The other alteration solutions have been analyzed and the crystalline phases identified by X-ray diffraction.

Three integral ("TAV") experiments are planned: in granite (an ongoing experiment that began 7 years ago), clay and schist, for periods of 1 to 24 months at 90°C with environmental materials and R7T7 glass at an SA/V ratio of 70 m^{-1}. The clay and schist experiments will begin shortly.

Part III: Development of a glass behavior model

The mechanistic model is based on a first-order kinetic law that takes account of ① the silica diffusion coefficient in the gel, ② the silica partition coefficient between the solution and the gel, ③ the solution flow rate, ④ the solution pH and ⑤ the temperature.

The geochemical model is developed from the "KINDIS" kinetic and thermodynamic code, which includes ① the reversible and irreversible chemical equilibria between the primary and secondary solids and the aqueous species between 0 and 300°C, ② the first-order kinetic laws for the initial reactants (glass and minerals from the host rock), ③ a flow rate term now being investigated.

The initial simulations of R7T7 glass dissolution in the presence of smectite 4a and bentonite are now being analyzed. Preliminary tests to determine the conditions for simulating glass alteration in contact with granite are now being defined. Simulations will subsequently be conducted with other repository materials, including corrosion products and schists.

Progress and Results

Part I: Basic research on aqueous corrosion of nuclear glass

The results indicate that increasing the MgO content of the R7T7 glass matrix causes a slight but significant increase in the initial dissolution rate, and persistently higher long-term dissolution rates than for standard R7T7 glass, which does not contain magnesium.

The experimental results also indicate that M7 glass, with a lower silica content and larger amounts of "fluxing" elements (Na, Li and B) than R7T7 glass, dissolves more quickly and has a higher silica solubility limit than R7T7 glass. All other parameters being equal, adding MgO to M7 glass (which normally contains no magnesium) also results in persistently higher long-term corrosion rates than for the standard composition.

Comparing the ratio between the initial dissolution rate (based on the 3-day normalized boron mass loss at 90°C and 50 m^{-1}) and the dissolution rate corresponding to the most advanced reaction progress (based on the 28-day normalized boron mass loss at 90°C and 20000 m^{-1}) shows that the rates diminished by the following factors:

R7T7:	2333
R7T7 + 2% MgO	16
R7T7 + 5% MgO	10
M7:	75
M7 + 2% MgO	11

Part II: Influence of the disposal site

The degree of alteration of R7T7 glass in water at 90°C in contact with schist depends on the grain size: a monolithic schist sample has no significant effect on the glass dissolution rate, which rises as the schist is ground increasingly fine.

R7T7 glass alteration between 1 and 6 months in the presence of two deep underground clays is greater than in pure water. A second set of tests was conducted with the same durations but after adding a silica gel to the glass/clay system, which considerably reduced the R7T7 glass corrosion rate.

In the presence of brine, the R7T7 glass dissolution is not much higher than in distilled water at 90 and 150°C. However, the nature of the brine determines the secondary crystalline phases that develop at the glass-brine interface: saponites in brine containing magnesium, and a mixture of analcime, hydrated calcium silicate and smectite containing iron and zinc in soda-chloride brine.

Part III: Development of a glass behavior model

The mechanistic model was tested at 90°C by varying the coefficient of silica diffusion in the gel. Small variations in this parameter value led to major variations in the calculated element concentrations in solution.

Simulated R7T7 glass dissolution at 90°C in contact with bentonite matched the experimental results: the glass dissolution rate did not increase much in the presence of bentonite. Conversely, the thermodynamic and kinetic calculations are unable to account for the experimentally observed increase in the R7T7 glass dissolution rate in the presence of smectite 4a. The assumption that a higher dissolution rate was imposed by a secondary clay precipitate with a higher silica content was invalidated.

List of Publications

ANDRIAMBOLOLONA Z., GODON N., VERNAZ E., "Effect of a Siliceous Additive in a Clay Engineered Barrier on Aqueous Corrosion of R7T7 Nuclear Waste Glass", E-MRS Symposium, Strasbourg (1991), to be published in *Scientific Basis for Nuclear Waste Management.*

CROVISIER J.L., Vernaz E., Dussossoy J.L., Caurel J., "Early Phyllosilicates Formed by Alteration of R7T7 Glass in Water at 250°C", E-MRS Symposium, Strasbourg (1991), to be published in *Scientific Basis for Nuclear Waste Management.*

GIN S., BEAUFORT D., GODON N., VERNAZ E., THOMASSIN J.H., "Experimental Alteration of R7T7 Glass in Salt Brines at 90°C and 150°C.", E-MRS Symposium, Strasbourg (1991), to be published in *Scientific Basis for Nuclear Waste Management.*

GODON N., VERNAZ E., "R7T7 Nuclear Waste Glass Alteration in Geological Repository Media", Joint Int. Waste Management Conference, Seoul (1991).

VERNAZ E., "Leaching of Actinides from Nuclear Waste Glass: French Experience", E-MRS Symposium, Strasbourg (1991), to be published in *Scientific Basis for Nuclear Waste Management.*

Table I. Experimental parameters for all glass compositions investigated at 90°C according to SA/V ratio: pH, steady-state silica concentrations in ultrafiltered solution, normalized boron mass loss, dissolution rate

Parameters	R7T7	R7T7+2%MgO	R7T7+5% MgO	M7	M7+2% MgO
2000 m^{-1} (14-28 days)					
pH 90°C	9.17 (± 0.03)	9.32 (± 0.03)	9.40 (± 0.02)	9.27 (± 0.02)	9.35 (± 0.03)
C(Si) ultraf ($mg \cdot l^{-1}$)	75.4 (± 4.9) steady-state	97.2 (± 4.5) steady-state	102 (± 2.9) steady-state	114.4 (± 8.3)	139.3 (± 2.2) steady-state
NL(B) (10^{-2} $g \cdot m^{-2}$)	95.2 (28d)	143.04 (28d)	979.54 (28d)	178.32 (14d)	461.64 (14d)
r (10^{-2} $g \cdot m^{-2} \cdot d^{-1}$)	0.16 (56-273d)	1.24 (Na)	23.9	-	-
8000 m^{-1} (14-140 days)					
pH 90°C	9.33 (± 0.03)	9.41 (± 0.05)	9.44 (± 0.06)	9.38 (± 0.04)	9.43 (± 0.07)
C(Si) ultraf ($mg \cdot l^{-1}$)	100.7 (± 7.0) steady-state	120.6 (± 4.9) steady-state	131.5 (91d)	161.3 (140d)	204.1 (119d)
NL(B) (10^{-2} $g \cdot m^{-2}$)	59.4 (364d)	143.85 (138d)	1289.79 (140d)	187.84 (140d)	1300.28 (140d)
r (10^{-2} $g \cdot m^{-2} \cdot d^{-1}$)	0.08 (56-364d)	0.30 (14-138d)	6.46 (56-140d)	0.80 (14-140d)	0.71 (91-140d)
20000 m^{-1} (14-28 days)					
pH 90°C	9.45 (± 0.07)	9.48 (± 0.02)	9.51 (± 0.04)	9.38 (± 0.04)	9.53 (± 0.04)
C(Si) ultraf ($mg \cdot l^{-1}$)	135.6 (± 12.1) (7-364d)	148.8 (± 4.3) (28d)	133.7 (± 5.1) (14-28d)	163.4 (± 5.7) (14-28d)	212.4 (± 11.0) (14-28d)
NL(B) (10^{-2} $g \cdot m^{-2}$)	39.1 (28d)	143.04 (28d)	476.78 (28d)	84.98 (28d)	536.36 (28d)
r (10^{-2} $g \cdot m^{-2} \cdot d^{-1}$)	0.03 (14-28d)	3.19 (14-28d)	6.64 (14-28d)	0.81 (14-28d)	9.66 (14-28d)

EFFECT OF INSOLUBLE ACTIVE DISSOLUTION FINES ON FISSION PRODUCT GLASSES

Contractor: CEA - CEN Valrhô, SCD, F

Contract No: FI 2W - CT90 - 0028
Duration of Contract: March 1991 to February 1995
Period Covered: March 1991 to December 1991

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

State of Advancement

B.1 The method is now under development.

B.2 A method for measuring the radionuclide homogeneity distribution is now operational. True activity measurements have not been initiated.

B.3 The glass rods have been fabricated. The method for quantifying and characterizing the fines is now being developed.

B.4 The glass test specimens have been cut from the rods, after measuring the radionuclide distribution along 4 generatrices and two diameters. Five distribution profiles were obtained along one diameter.

B.5 Work is in progress to assess the containment properties at room temperature and at 90°C.

B.6 The Soxhlet devices are now being prepared.

B.7 The X-ray diffraction spectra have been obtained and analyzed. Electron microprobe examinations are now in progress.

B.8 Heat-treated glass rods have been cut up, and the glass containment properties evaluated at room temperature. The X-ray diffraction examinations have been completed. Containment and alterability tests at 90°C are now in progress, as are electron microprobe examinations.

Progress and Results

A glass composition designated A130 was produced, containing actual fines from dissolution of fuel irradiated in the Advanced Prototype Boiler (CAP) at Cadarache. Two rods 40 mm in diameter and about 140 mm long, weighing about 400 g each, were produced together with a shorter casting heel. The total weight of the three samples is 1056 g. The platinoid concentration ranges from 0.16% to 0.46%. Several characterization tests are now in progress.

The homogeneity of the distribution of five radionuclides was assessed by γ scanning: ^{60}Co, ^{106}Ru, ^{125}Sb, ^{134}Cs and ^{137}Cs. Analysis of the scanning data indicates a relatively uniform distribution.

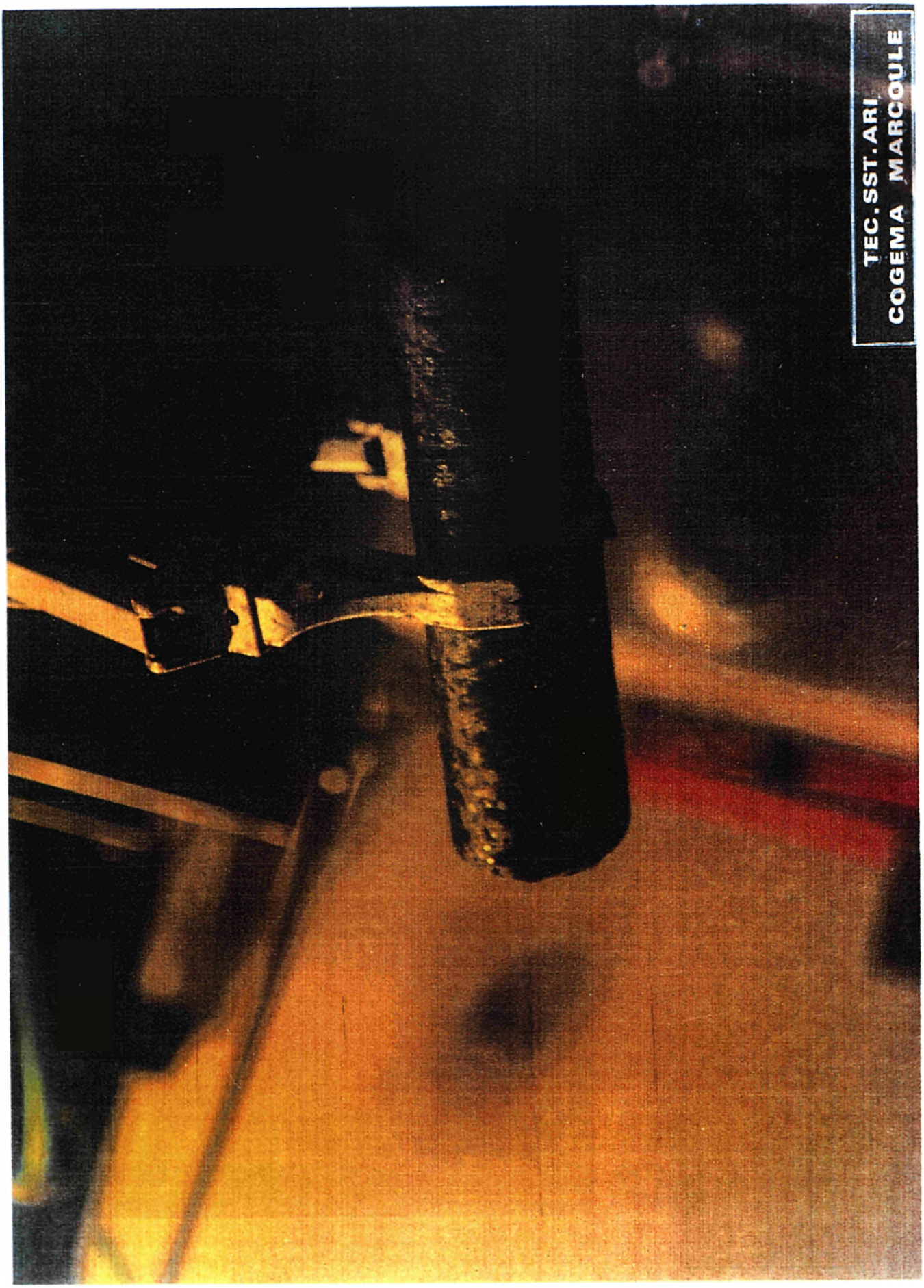
The chemical composition of the glass matrix and the elements or oxides contained was determined in two steps: complete dissolution of the glass, followed by ICP analysis and radiometry. The acid and alkaline processes investigated have not been qualified; the presence of platinoids raises some problems.

Concerning the glass microhomogeneity, the X-ray diffraction spectra before and after heat treatment show a dominant phase consisting of calcium molybdate, as well as ruthenium oxide (RuO_2) and zinc, nickel and magnesium chromites.

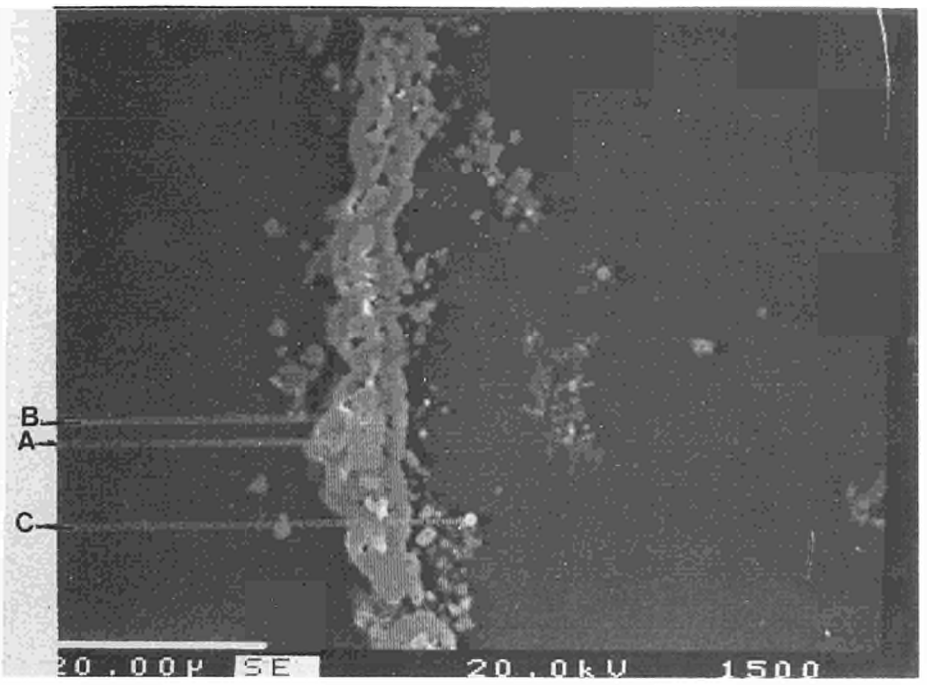
Electron microprobe analysis revealed clusters of inclusions: metallic ruthenium surrounded by ruthenium oxide (RuO_2); zinc chromite with very little ruthenium; palladium, often associated with tellurium; and calcium molybdate microcrystals uniformly distributed in the glass matrix.

Image analysis revealed a heterogeneity volume percentage of less than 1%.

The containment properties for the major radionuclides were determined at room temperature. The concentrations of ^{137}Cs, ^{125}Sb and ^{134}Cs were determined in solution, as well as the total alpha- and total beta-emitters. The leach rates ($g \cdot cm^{-2} d^{-1}$) were determined before and after heat treatment. The glass heat treatment increased the leach rates by a factor of 2 for cesium, and by a factor of 4 for antimony and for the total β activity. The pH remained stable at about 8.7.



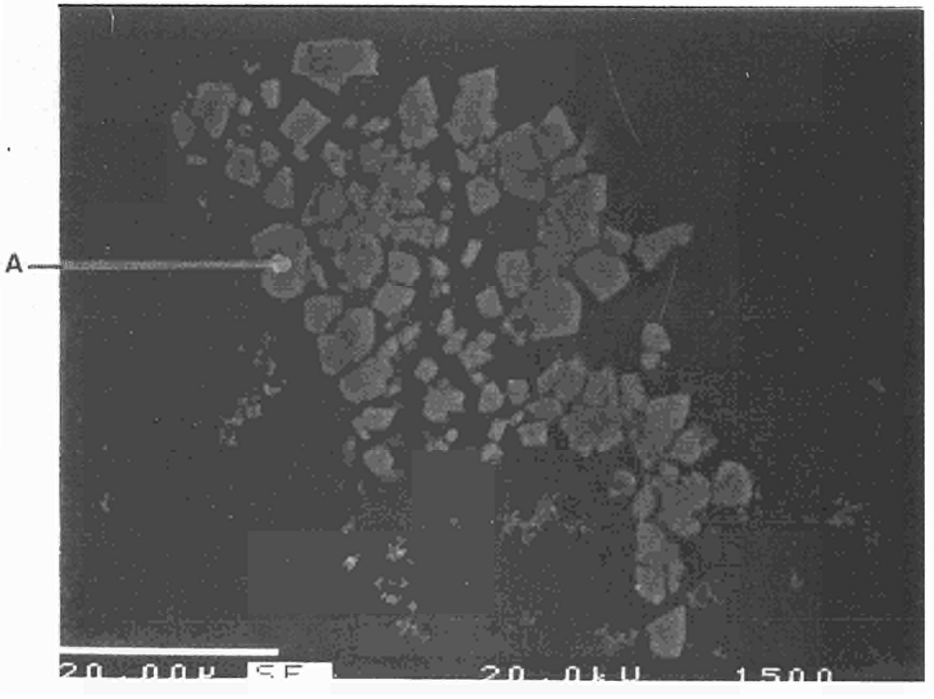
A130 glass rod containing CAP fines: Sample F2



%	a	b	c
Fe	0.2	0.1	0.7
Ni	0.1	0.1	0.3
Cr	1.2		2.3
Zn	0.8	0.5	2.7
Co			
Si	1.2		6.8
Na	0.3		0.7
Al	0.2		1.5
Mg			
Ru	70.0	96.7	0.9
Sn	0.3	0.4	0.5
Pd	2.2	3.5	29.5
Tc			6.9
Nd			1.0
Mo			0.9
Zr			0.5
P			0.2
Ca			1.4
O	24.5	2.1	27.3

Electron microprobe image:
Metallic ruthenium surrounded by ruthenium oxide RuO_2

%	a	b	c
Fe	1.8		
Ni	1.3		
Cr	46.2		
Zn	16.2		
Co			
Si	0.2		
Na	0.4		
Al	0.7		
Mg	0.1		
Ru			
Sn	0.2		
Pd			
Tc			
Nd			
Mo	0.2		
Zr			
P			
Ca	0.1		
O	30.6		



Electron microprobe image: Chromites

Title: The corrosion of nuclear waste glasses in a clay environment: mechanisms and modelling

Contractor: ONDRAF/NIRAS, Belgium
Contract No.: FI2W/CT90/0031
Duration of contract: 1 March 1991 to 28 February 1995
Period covered: 1 March 91 - 31 December 91
Project leader: R. Swennen (ONDRAF/NIRAS, coordinator)
P. van Iseghem (SCK/CEN)

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 Belgian 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 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 (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

1. Accelerated tests, inactive
2. Accelerated tests, active
3. Integrated tests, inactive
4. Integrated tests, active
5. Modelling

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

All attention has been focussed on the starting up of the experiments. By the end of 1991 the inactive accelerated tests were partly started. The remaining accelerated tests, the inactive integrated tests and the tracered meltings were in preparation. The modelling effort will commence at a later stage.

Progress and results

1. Accelerated tests, inactive : the inactive accelerated tests at 40 and 90°C were partly started. No results are available as yet. The inactive tests at 150°C will be started next.
2. Accelerated test, active : three series will be started, tracered with respectively Pu/Cs134/Sr90, Np237/Tc99/Fe55 and Am-241 ; some preliminary tests were started to define the most appropriate SA/V value.
3. Integrated tests, inactive : in preparation
4. Integrated tests, active : The glasses will be tracered with the same radio-isotopes as for the accelerated tests. The SA/V value will be defined, based on the results of the preliminary tests.

An overview of the experimental programme is shown in Table I.

TABLE 1 : OVERVIEW OF 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	CCSICM + CP + BF1, CCSICM + CP + BF2	CCSICM + CP + BF1
SA/V (m^{-1})	500, 2500, 10000	Not yet defined	500, 2500	Not yet defined
Test duration (days)	28, 90, 180, 360, 720	90, 180, 360	28, 90, 180, 360, 720	90, 180, 360

DW : distilled water
SIC : synthetic interstitial clay water
CCSICM : concentrated clay / synthetic interstitial clay water mixture
CP : corrosion product (Fe2O3)
BF1 : backfill bentonite
BF2 : backfill cement

Title: **Basic Leaching Tests for Pure Beta Long-lived Emitters in Radioactive Wastes**

Contractor: CEA Cadarache / CIEMAT Madrid
Contract No.: FI2W/CT-90/0032
Duration of contract: 1.5.91 to 30.4.94
Period covered: 1.5.91 to 31.12.91
Project leader: C. Riglet (CEA Cadarache)

A. OBJECTIVES AND SCOPE

The technical solution under study is the storage of long-lived radioactive wastes and consists of:
- embedding them in suitable confining matrices (glass, cement, bitumen)
- and burying the coats in stable geological sites where the radioactivity will decrease naturally.

The valuation of the confining capability of the matrices used - determined by implementing leaching tests - enables 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 beta and alpha long-lived emitters in real or simulated wastes, in order to collect basic results about those radionuclides which are critical for the safety analysis of disposal storage and for which no reliable data is available at the moment.

The main objectives of the study are:
- Collection of leaching data for beta and alpha emitters to achieve the best evaluation of the confining properties of various matrices (bitumen, thermo-setting resin).
- Definition and validation of an experimental leaching procedure suitable to the various types of conditioning and enabling comparisons.
- Speciation of the leached forms and definition of the leaching mechanisms, to modelize the long-term behaviour of the waste packages.

The two countries involved in the programme are Spain (CIEMAT) and France (CEA).

B. WORK PROGRAMME

B.1. (CEA - CIEMAT)
- Working organisation
- Setting-up of a working programme
- Harmonisation 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 formulations and of the elements to take into account
- Implementation of leaching experiments on simulated waste
- Optimisation of the analytical procedures
- Collection of the data and interpretation

B.4. (CIEMAT)
- Implementation of leaching experiments with actual 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 OBTAINED RESULTS

STATE OF ADVANCEMENT

At this stage of the programme, task B1 is completed while tasks B2 and B3 have started.

Concerning the CEA programme, various technical difficulties connected to the preparation of the sludges and the manufacturing of the samples have delayed the implementation of the leaching experiments for at least four months (as regard to the initial planning).

Concerning the CIEMAT progamme, work is progressing on schedule and the reference leaching tests (with demineralized water) have just been implemented.

Some work concerning the optimization of analytical procedures (to determine the leached species) has also been accomplished.

PROGRESS AND RESULTS

The lauching of this 4 year CEC programme, related to a leaching study for long-lived radionuclides, has consisted, during the first eight months of the contract, in establishing a commun working frame, agreeing on the leaching methodologies, updating the initial propositions, manufacturing the samples and performing some preliminary tests.

B.1. SETTING UP OF A WORKING PROGRAMME

The samples are made of ion-exchange resins (REI), evaporator-sodium borate-concentrates or chemical STE3 La Hague sludge, containing Cs, TC, Th, U, I, ^{90}Sr or ^{63}Ni and embedded in cement, bitumen or thermo-setting resins (table I). The leachant is either demineralized water either natural water from EVIAN or EL CABRIL. The influence of pH, complexing agents (EDTA, degradation products or REI), irradiation and temperature will be investigated (table II).

The cement or thermo-setting resin specimens are cylindrical samples, completely immerged in the water, while the bituminous samples are flat disks, kept into their original mould, and whose top surfaces are covered with the leachant (Figure 1).

Each leaching tests last 455 days. Eight sampling sequences are scheduled : the first five ones are planned within the first 90 days in order to study the "transitory regime". The last three ones, of 90 days each, are meant to follow the "permanent regime" (Figure 2).

After each removal, the leachant is filtered and the soluble and insoluble fractions (after acidification or mineralisation) are analysed, usind alpha spectrometry, liquid scintillation countings or inductivedly coupled plasma mass spectrometry (ICP/MS).

At each sequence and for each element, the measured concentrations are converted into sequentiel leaching velocity according to the formula :

$$\Phi v_i = \frac{a_i}{A_0} \times \frac{V}{S} \times \frac{1}{t_i} \text{ (cm/day)} \qquad [1]$$

where :

- t_i : duration of the sequence i (day)
- a_i : quantity of leached specie (soluble + insoluble) during the time i
- A_0 : initial quantity of specie in the sample
- V : volume of the sample (cm^3)
- S : leached surface of the sample (cm^2)

The results are then represented graphically as a function of time. A comparison of the confining properties of the various matrices, based on the collected data, will be performed.

B2. DEFINITION AND MANUFACTURING OF THE SAMPLES

The initial composition of the samples has been calculated in considering.

- The formula of the sequential leaching velocity of an element (equation (1)),
- the detection limits of the analytical techniques used,
- estimations of the leaching velocities of the elements to take into account.

Therefore, the calulations have lead to the selected composition given in table III.

At present, the manufacturing of the sludges which will be later embedded in the various matrices has just started. The STE3 LH sludges are made with a pilote STE3 machine similar to that used at La Hague (scale 1/50), according to the nominal process. After the primary and secondary decantations, the doping elements (U, Th, Tc, I, Cs) are added to the sludges.

B3. SELECTION OF THE WASTES AND CEMENT FORMULATIONS

Among different kinds of ion exchange resins generated in spanish nuclear power plants, the ones reported in table I were selected : EPIFLOC 21 H resin are 50 % saturated with NaCl solution while DUOLITE ARM-9381 are 100 % saturated with NaCl and H_3BO_3 solutions. Both resins are labeled with ^{90}Sr and ^{63}Ni.

The compositions of the selected formulations for the leaching tests are reported in table IV.

B3. REFERENCE LEACHING TESTS

Leaching tests have been carried out at three temperatures (25°C - 40°C - 50°C) with demineralized water. Three leachant renewal steps (after 3, 15 and 45 immersion days) have been already completed but the analytical results are not yet available.

TABLE I

NATURE OF THE WASTES AND OF THE MATRICES

TYPE OF WASTE	MATRICE
(1) Ion exchange resins	cement
(2) Evaporator concentrates	bitumen
(3) Sludge type "STE3 LH"	RTD

RTD : Thermo-setting resin.

(1) : Mixed anion-cation **resins DUOLITE ARM 9381** from PWR nuclear power plant loaded with ^{90}Sr and ^{63}Ni.

or

Mixed anion-cation **resins EPIFLOC** from BWR nuclear power plant loaded with 90Sr and ^{63}Ni.

(2) : **Evaporator - sodium borate - concentrates**, from PWR, loaded with Cs, Tc, Th, U and I.

(3) : **Chemical STE3 La Hague type sludge**, loaded with Cs, Tc, Th, U and I.

TABLE II :
SCHEDULED LEACHING TESTS

Type of sample	Leaching tests
Bituminous coats	- demineralized water - EVIAN water - water pH = 6 - water pH = 8 - EVIAN water under irradiation
RTD coats	- demineralized water - EVIAN water - demineralized water with EDTA - EVIAN water under irradiation
Cement coats/ Evaporator concentrates	- demineralized water - EVIAN water
Cement coats/ Ion exchange resins	- demineralized water at 25°C, 40°C, and 50°C - demineralized water with degradation products of REI - demineralized water with EDTA - natural water EL CABRIL

TABLE III :
COMPOSITION OF THE SAMPLES :
Quantity of doping elements introduced per sample

Element	Amount per sample A_o	Chemical form
U	5 g	UO
Th	5 g	ThO_2
Tc	5 mg	$NaTcO_4$
I	100 mg	AgI
Cs	3 mg	$CsNO_3$

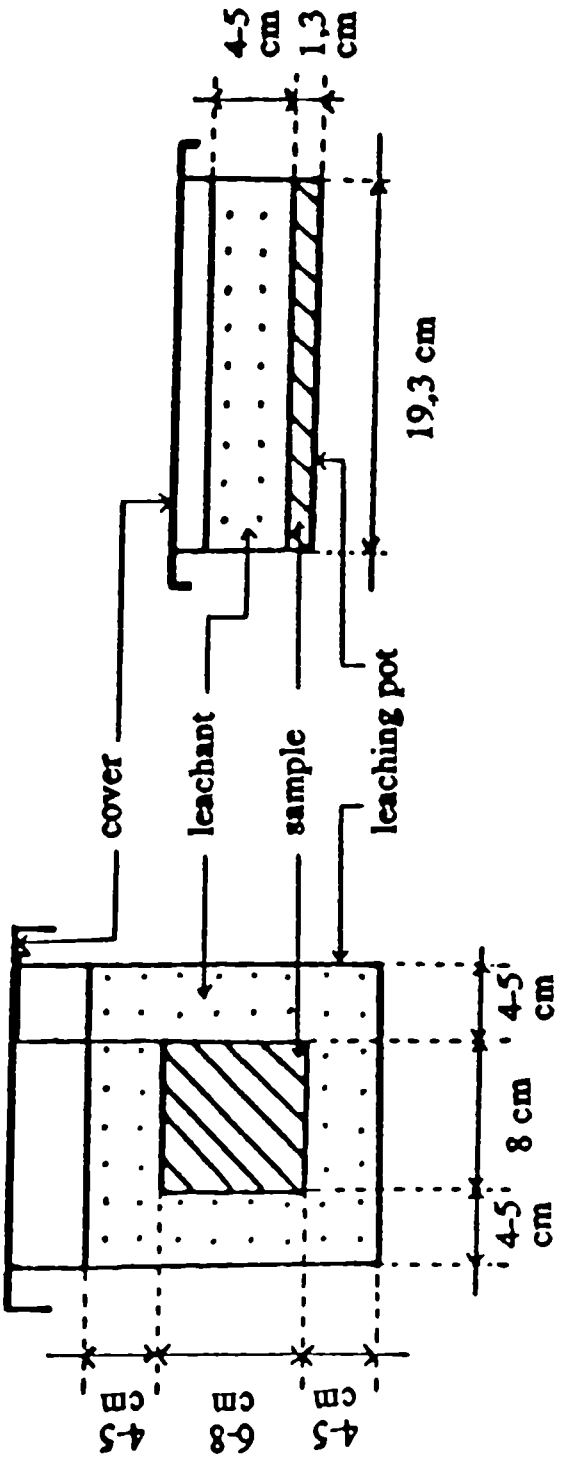
- U and Th are introduced as oxydes UO_2 and ThO_2 (PROLABO)
- I is introduced as the insoluble salt AgI, prepared by mixing $AgNO_3$ and KI solutions (PROLABO)
- Cs is introduced as $CsNO_3$ ((PROLABO)
- Tc is introduced as Na TcO_4 (DUPONT DE NEMOURS).

TABLE IV :
COMPOSTION OF THE IMMOBILIZED ION EXCHAGE RESINS USED FOR LEACHING TESTS

	Formulation 1	Formulation 2
Resin type	EPIFLOC 21H	DUOLITE ARM-9381
Cement type	BFS (III-1/35A)	Sulphate resistant (I-35A/SR-MR)
Dry resin weight	10.25 %	9 %
Cement weight	50.00 %	56 %
Water weight	38.45 %	31.00 %
Lime weight	1.30 %	4.00 %

FIGURE 1

OPERATING CONDITIONS : Dimensions of the samples



Bituminous samples

Cement and RTD samples

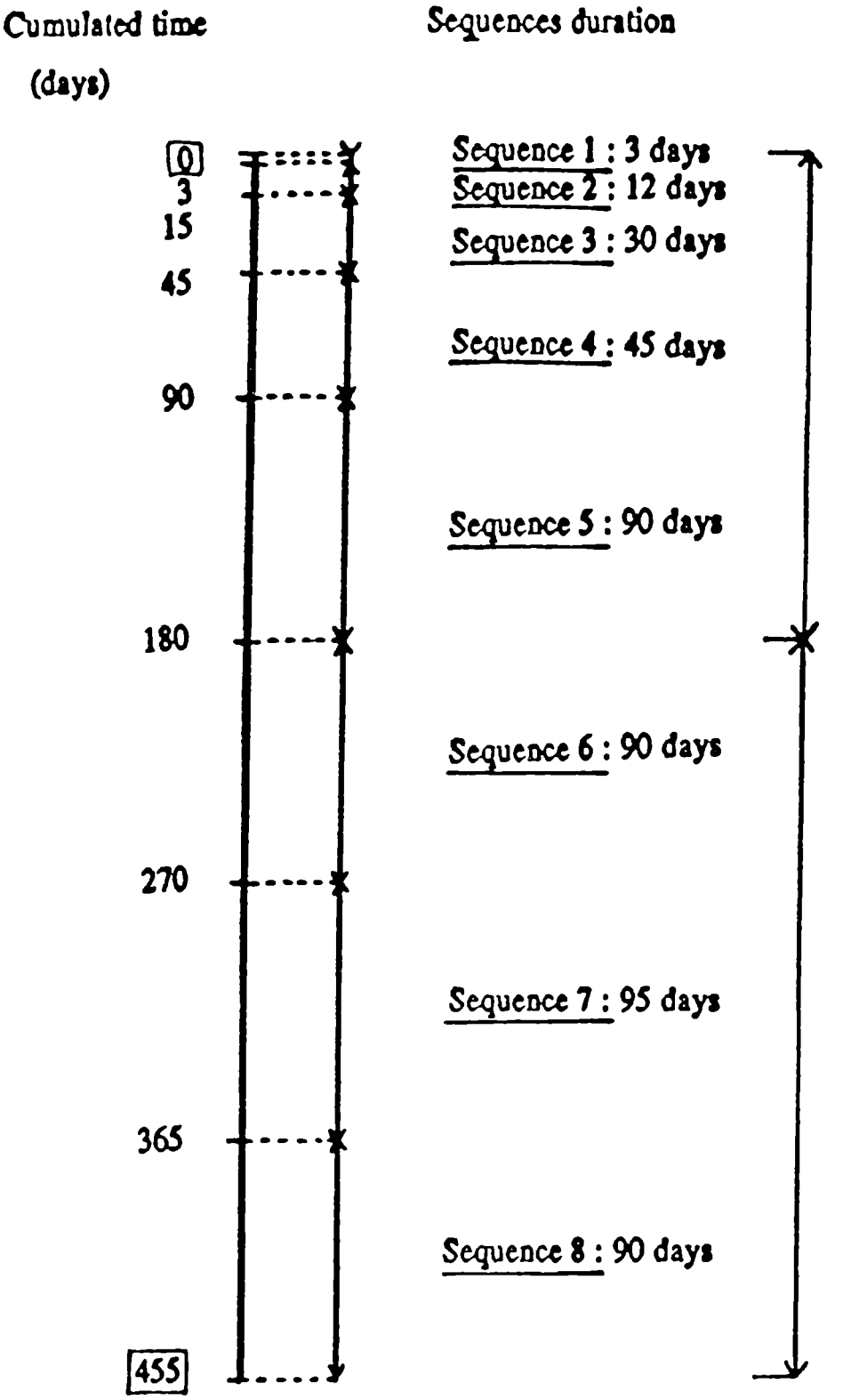
→ volumes of the samples identical : 400 cm^3

leached surfaces identical : 300 cm^2

volumes of the leachants identical : 1,5 l

FIGURE 2 :

OPERATING CONDITIONS : Sampling sequences



Title: **Chemistry of the Reaction of Fabricated and High Burnup Spent UO_2 Fuel with Saline Brines**

Coordinator: Kernforschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgungstechnik, Abt. Chemie (KfK), B. Grambow, A. Loida, G. Karsten, K. Müller, T. Fanghähnel

Participant: Empresa Nacional de Residuos Radiactivos S.A., Departamento de Ingenieria (ENRESA), J. Gago

I. Casas, J. de Pablo, J. Giménez, M.E. Torrero

Contract No. FI2W/CT-90-0055
Duration of contract: from 1.3.1991 to 28.2.1995
Period covered: 1.3.1991 - 31.12.1991
Project Leader: B.Grambow

A. Objectives and Scope

The research programme 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

- Acquisition, cutting and transport of high burnup UO_2-fuel
- Reservation, organization and installations in the hot cells (HZ-cell 5a and 'Boxenlinie' at INE) and glove boxes
- Construction of reaction vessels (autoclaves) for spent fuel dissolution studies
- Development of solid sample preparation techniques and of separation techniques for radiochemical and uranium solution analyses in salt brines
- Solution analyses for radionuclides in salt brines
- Solid state analyses of samples for example by X-ray, SEM

II. Characterization of the durability of spent UO_2-fuel in saturated NaCl brines

- The effect of time, redox potential, temperature and of the ratio of the spent fuel surface area to the brine solution volume (S/V) on durability will be studied under static conditions for 2 years in 6 experiments.

III. Solubility tests with unirradiated UO_2

- Influence of particle size (10 micron to 1mm)
- Influence of brine composition and ionic strength at constant pH and particle size
  NaCl solutions (0-5 M) $MgCl_2$ solutions (0-3 M)
- Influence of redox potential

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 was obtained, the hot cell and glove box equipments including heating cabinets and leaching vessels (autoclaves) were set up and are now ready for starting the experiments. There was a slight delay in the preparation of spent fuel samples for the corrosion tests, but samples will now be fabricated in february 1992. Experiments will start immediately (the same day) after sample preparation. A decision has been made to perform all radiochemical solution analyses at INE/KfK. This requires the acquisition of separation techniques for Pu, Np, U, Tc, Sr and Cs and the use of ion exchange resins to separate the major salt constituents from rare earth elements and actinides.
Dissolution tests with unirradiated UO_2 have begun successfully and first results were obtained concerning the effect of particle size on UO_2 solubility and on the dependence of UO_2 solubility on the redox state in a Mg-rich salt brine.

Progress and results

I. General preparations, analytical techniques, and sample preparations

A high burnup UO_2-fuel rod (KKGg-BS1108) for corrosion studies has been obtained (1.26 kg) from SIEMENS/KWU from the PWR-Reactor Gösgen in Switzerland. A segment with the following specifications will be used in the tests:

segment No.	N0203
total length	51.8 cm
enriched pellets	37
filling gas	He, 21.5 bar
burnup	50 MWd/kgU
time in reactor	1226 d
removal from reactor	27-5-1989
initial enrichment	3.8% U-235
average linear power	260 W/m
maximum linear power	315 W/m
initial fuel density	10.41 g/cm^3
activity (1-2-92)	2.0 Ci/g
Pu-tot	1.18 w/o

Work space in the hot cells (HZ-cell 5a and 'Boxenlinie' at INE) has been organized. Heating cabinets were converted to be handled remotely and were installed with the electronic control unit located outside of the hot cells. Six reaction vessels for spent fuel dissolution studies (autoclaves) with two gas valves

and tantalum liners were built as is shown schematically in Fig. 1. A device has been made which allows stable positioning of the autoclaves in the hot cells and heating cabinets. Calculations of fuel inventories of radionuclides were performed using KORIGEN in order to estimate expected concentrations of nuclides in solution to guide the design of the analytical procedures.

II. Characterization of the durability of spent UO_2-fuel in saturated NaCl brines

Corrosion studies have not yet been started.

III. Solubility tests with unirradiated UO_2

Methods have been developed to measure U concentrations as low as 1 ppb from the UO_2 dissolution test in salt brines. The method is based on the sorption and desorption of U on silica gel and solution analyses by laser induced fluorescence. The effect of Cl^- and Mg^{++} concentration on the fluorescence signal was determined.

UO_2 dissolution has been studied as a function of leaching time in sequential tests using three particle sizes (0.01-0.05 mm, 0.1-0.3 mm and 900-1100 mm) and unirradiated fuel pellets. Results are given in Fig. 2. The dissolution rates have been normalized using the surface area measured by the BET method. Results seem to indicate two different dissolution rates, a high initial rate which may be governed by the dissolution of an oxidized surface layer and a slower rate for longer dissolution periods.

The dissolution of 1mm sized UO_2-particles has been studied in sequential tests under reducing conditions (H_2/Pd) and in air, using Q-brine (a $MgCl_2$ rich brine) as leachant. The data from the test under reducing conditions are compared with results from a similar test in 1 M NaCl solution. Under reducing conditions there is an initial increase of the uranium concentration with contact time. After this relatively high initial dissolution the solution concentration gradually decreases to an apparently constant value of log U = -6.4. Under oxidizing conditions the uranium concentration in solution increases during the first 100 days of contact, until a value of about log [U] = -4.6 is reached.

Figure 1: Autoclave designed to be used for corrosion tests with spent UO_2 fuel

a) stainless steel autoclave
b) Ta or Ti/Pd liner
c) stainless steel lid with Ta or Ti/Pd innner side with ball valves

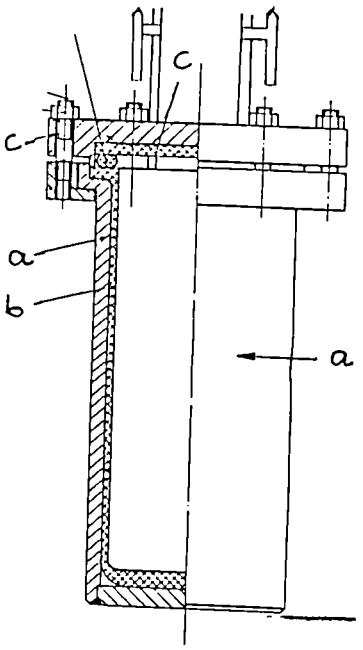
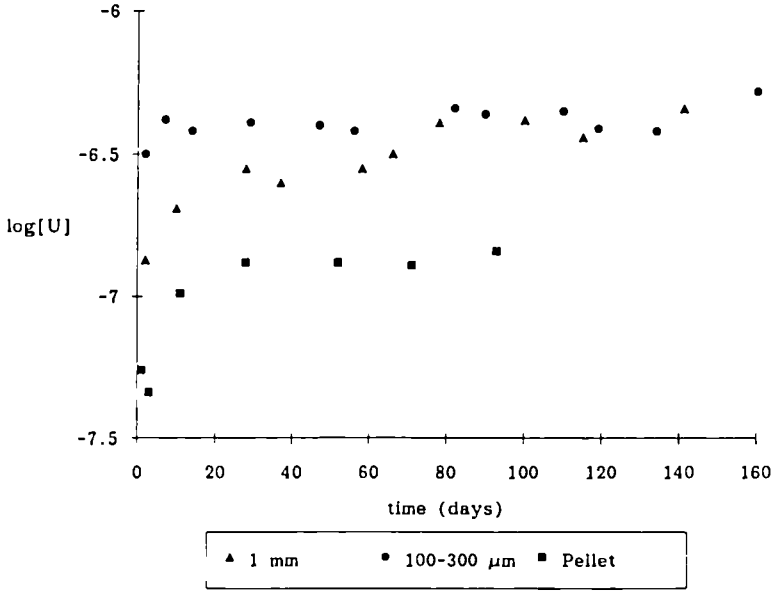


Fig. 2: Effect of particle size on the dissolution of unirradiated UO_2 samples at pH 7 in deionized water under oxidizing, CO_2-free conditions



Title: Container properties ensuring safety: gas emission, biodegradation, corrosion

Contractor: CEA, France
Co-Contractor: AEA Technology Harwell, UK
Contract No.: FI2W/CT-90/0077
Duration of contract: October 1991 - September 1994
Period covered: October 1991 - December 1991
Project leader: P. Lessart (CEA Cadarache, coordinator), A. Rosevear (AEA)

A. *OBJECTIVES AND SCOPE*

The knowledge of possible evolution of conditionned wastes 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 microbiological corrosion of coating matrix and structural material,
- the radiolysis of organic compounds included in the waste.

Living microorganisms can also produce complexing agents and organic or mineral acids able to promote corrosion and modifying the oxydo-reduction conditions and the pH of the repository.

The part of the project undertaken at AEA Harwell is concerned with assessing the effects of alkalitolerant microorganisms on a cementetious 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 coating matrix. Acid and gas production. Physico-chemical modifications of the material.

Programme 02 : gas production by an genuine concrete conditionned waste with high content of radon producers.

Programme 03 : effects of organic complexing agents in concrete and bitumen conditionned 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 providedata to assist in setting design criteria for cementitious materials used to conditionthe pore water chemistry in a radwaste repository.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

This contract has just begun on October 1991, so we don't have any result. This report will just summarize how we plan to do the studies (choice of the apparatus and of the samples).

The CEA Cadarache studies are linked to ANDRA and COGEMA projects and includes sub-contract work by LBR CEA Saclay for concrete samples preparation and analysis.

Some problem appeared to manufacture the mixtures of bitumen and TBP that will be submitted to external gamma irradiation. Experimental procedure has to be precised.

The AEA section is linked to a part of the Safety Assesment Research Programm (NSARP) funded by Nirex UK and includes sub-contract work by the University of Leicester (Dr Bill Grant) and Oxford Polytechnic (Dr Chris Hawes).

Our first plenary meeting took place on September 26th in Cadarache with Dr ROSEVEAR .

One of the main problem for microbial effects study is that no quantitative information exists on the pore water chemistry in a radwaste repository and even the qualitative information is not specific of the repository situation (i.e. calcium alkalinity, anaerobic, oligotrophic).

Progress and results

PROGRAMME 01 a : biodeterioration of bitumen and of bitumen conditionned waste.

Anaerobic hydrocarbon biodegradation is now confirmed.

These studies will be done under low oxygen content conditions because strict anaerobic conditions will not be present in a deep repository on account of gas production by radiolysis.

Previous studies done under aerobic conditions have shown that some fractions of bitumen are sligtly deteriorated producing mainly carbonic gas. Intermediate biodegradation compounds have not been detected. It seems that the biodegradation was only a surface attack (to be confirmed).

Microorganisms : the micro-organisms used in previous studies are very commonly founded in oil contaminated soils. They can grow in aero-anaerobic conditions. *Pseudomonas* species have been chosen. We can suppose that these microorganisms will be present in the deep repository and/or in the package. First an aerobic degradation will begin consumming oxygen, and then will continue to biodegradate bitumen by the optional anaerobic metabolism when the repository will be closed.

The microorganisms will be put as a suspension in a culture medium. In these experiments, the only carbon source will be bituminen.

Bitumen samples : in order to measure the effect of the ratio area/volume of bitumen, we plan to use various bitumen samples (bitumen 80/100, the same as used by COGEMA at STE3 La Hague) :

- disk samples of bitumen put into stainless steel melting-pot (see figure n°1). The thickness of bitumen will be 0.5, 1, 2, and 4 mm and the diameter 56.4 mm.

- suspension of bitumen powder.

Experimental conditions : bitumen samples will be completly immersed in culture media in which bitumen will be the only carbon source.

Instead of using a single culture chamber in which anaerobic conditions can be controled for all samples, we shall use individual vessels that will be filled under low oxygen content atmosphere and will allow gas production measurement for each sample.

We are discussing with IFP (French Institute for Petroleum) about a thesis financement.

PROGRAMME 01 b : cement biodeterioration

Experimental conditions have been determined according to previous works.

Microorganisms : two kinds of microorganisms have been chosen. Heterotrophic microorganisms that produce organic acids and autotrophic microorganisms producing mineral acids.

The heteroprophic culture contains a mixed culture of two fungal strains : *Aspergillus niger* and *Trichoderma viride*. The autotrophic culture contains a mixed culture of *Thiobacillus* corresponding to a large range of optimum pH growth conditions : *Thiobacillus thiooxydans* (pH 2-4), *Thiobacillus neapolitanus* (pH 6.6-7), *Thiobacillus novellus* (pH 7.5-8.5), *Thiobacillus thioparus* (pH 6.6).

Concrete samples : according to LBR (Concrete Research Laboratory) CEA Saclay, disk samples of cement of 70mm diameter and 10 mm thick have been chosen. The samples will be pure CPA 45, pure CLC 55 and non active incinerator ashes in CLC 55. They are being made by LBR. We must receive them before the end of february.

Experimental conditions : The samples will be completly immersed in culture media. It seems necessary to keep constant the ratio volume of leatching solution on surface of the samples, and to work in static conditions with the objective of keeping a diffusion layer near the cement.

We are making the vessels in which microbial deterioration of those samples will take place.

All thoses studies will be done under aerobic conditions : the culture medium will be change by half each two weeks.

The culture medium for *Thiobacillus* will content all mineral compounds necessary for bacterial growth and thiosulfate as sulfur source and carbonate as carbon source. The pH is adjusted at 7.

For heterotrophic microbial culture, the medium will content glucose as a carbon source, all mineral compounds necessary and initial pH will be near 9.

About 20 various organic acids will be produced. We plan to quantify their production by HPLC (method under development).

PROGRAMME 02 : concrete behaviour for high radon producing wastes

The qualitative and quantitative evaluation of gaseous produstion from waste package allows the determination of their storage conditions.

The experimental following of this gas production is planned to be made on a full scale package after adaptation of the already existing gas sampling device (ASPIC).

Two packages have been selected : a cementitious embedded alpha wastes one (sludges from liquid waste filtration, containing alpha emiters) and a radifere one. These twice packages, slightly radioactive, will be supplied by DRD Cadarache (Waste and Fuel Management Department).

They will be perfectly identified by :

- knowledge of the packaging process,
- determination of chemical and radiochemical composition, using the MARCO system (device for gamma-spectrometry measurements on industrial packages) developed in our laboratory.

Gas sampling from drum atmosphere wiil be performed using the ASPIC system shown on figure n°3 (Appareillage de Surveillance, Prélèvement et Instrumentation pour conteneurs) after adjustment of its container size to those of selected packages.

Gas collected will be analysed by gas chromatography, with special attention to H_2, O_2, Tritium and Radon.

PROGRAMME 03 a : effects of TBP on gas production from bitumen

TBP is one of the solvent that could be present in wastes because its solubility in water vary from 0.1 to 0.3 g/l (if partly hydrolysed), what may occur when reprocessing spent fuels. With the objective to increase the effects of gas production under gamma irradiation when included in bitumen, we chose to incorporate it at a concentration (0.4%) about ten times higher than the concentration that can be expected in wastes. This sample and a sample containing the mean expected concentration (0.04%) will be compared to the bitumen matrix containing 10% of $NaNO_3$ and Na_2SO_4. This mixture (90% bitumen, 10% salts resulting from the basis of the STE3 treatment) is considered as the reference composition for all the irradiation tests.

First experiments have been carried out in order to incorporate TBP alone into this basis mixture. Analytical problems still remain. At the present time, the validity of the experimental conditions has not been proved. Complementary analysis are expected.

If mixing problems subsist, we shall try to incorporate TPB/dodecane mixtures (on a 30/70 ratio) with diatomaceous silica as fixing agent, knowing this mineral material is not radiosensitive.

Bitumen 80/100, the same as used by Cogema at STE3 La Hague, will be used for all these experiments.

PROGRAMME 03 b: effects of EDTA on gas production from cement

EDTA is a complexing agent very much used for decontamination. Those wastes, after concentration and evaporation are planned to be concrete conditioned and then stocked in deep repository.

The concrete that we plan to use is based on cement CLC 45. Its composition is the following :

CLC 45	:	1000 g
Sand 0-5	:	723.5 g
Water	:	400 g

The samples are parallelepipedic rods 160 mm long, 40 mm wide and 40 mm high. We plan to put 2.5 and 5% of EDTA acid disodium salt.

Corresponding to the time delay for concrete aging, the irradiation of those samples may begin at the end of march.

PROGRAMME 04 : Biodeterioration of concrete

Done by AEA Technology Harwell, this study is taking place in conjunction with the Nirex funded research programme on the effects of microbial activity on the safe disposal of low and intermediate level radioactive wastes. Conditions have therefore been selected to be relevant to an underground repository in which organic solid waste is packaged in containers held in a cementitious matrix.

Suitable anaerobic, microbial isolates have been identified from columns that were enriched in the presence of crushed concrete and from a number of industrial sites that handle alkaline wastes. Materials and microorganisms identified in the main Nirex programme are being provided for this specific study. A preliminary design for exposing coupons of concrete in the flowing system is being assessed prior to construction of a suitable experimental rig. Supplies of suitable concrete are being arranged.

The AEA work package is aimed at growing a suitable biofilm on the cement matrices relevant to the British and the French repository designs and studying these by physical and microbiological methods. Attention will be given to the alkaliphilic, anaerobic organisms.

The principal objective of this study will only be met if a suitable biofilm can be realiably grown on cementitious materials. To this end, blocks of both structural concrete (1 cm cubes) and grout (1.5 cm cubes) have been placed in simple chemostats (1 liter glass bottles packed with blocks and fed by a peristaltic pump from a reservoir containing the feed solution). These blocks are being conditioned with a nutrient solution selected to simulate the pore water expected in an Low Level Waste repository. This simulant is formulated from black liquor (liquid waste from the sulfide process for pulping wood to make paper). The liquor is very alkaline and strongly reducing and is first treated by acid precipitation with phosphoric acid and heat coagulation to remove the greater part of the lignin fraction. The pH is adjusted to 10.5, yeast extract added to give a final concentration of 0.05% w/v and the volume adjusted to give an overall dilution of 1 in 40 for the black liquor.

This system is being equilibrated for 3 weeks under anaerobic conditions before introducing a known alkalitolerant microbial consortium isolated from wood taken out of a high pH soda lake in Kenya. Some adsorption of coloured material to the concrete surface is noticeable already. Once an active biofilm is established, it is planned to study individual blocks in an electron microscope.

The buffer capacity of the concrete blocks will be measured as the biofilm developed, sacrifying blocks at intervals for this purpose. Blancks will be included to measure the effects of natural carbonation and the adsorption of acidic polysaccharides. As noticeable changes occur, these samples will be send for examination by SEM (at Oxford Polytechnic) and confocal microscopy (at Leicester University). Slow growing populations using sugar acids as nutrients will be used in these studies and so the titration of these on the surfaces will also be followed.

The SEM studies will require the development of techniques to section the coated concrete and selectively stain the biofilm components. Estimating the amount of organic material tied up in living cells and in extracellular materials will be an important objective of these examinations. It is hoped that the spectral analysis may locate the distribution of dissolved calcium.

Modelling of movement of nutrients in the biofilm will involve development "diffusion with reaction" modelling equations. Data on the rate of metabolism and rate of loss of limiting nutrients from solution will be required to predict the appearance and disappearance of potentially corrosive acids in the biofilm and adjacent to the concrete.

List of publications

No publications dealing with the work under this contract.

On previous work :

PERFETINI J.V., REVERTEGAT E. and LANGOMAZINO N., Experientia 47 (6), 527-532 (1991)

AIT-LANGOMAZINO N., SELLIER R., JOUQUET G. and TRESCINSKI M., Experientia 47 (6), 533-538 (1991)

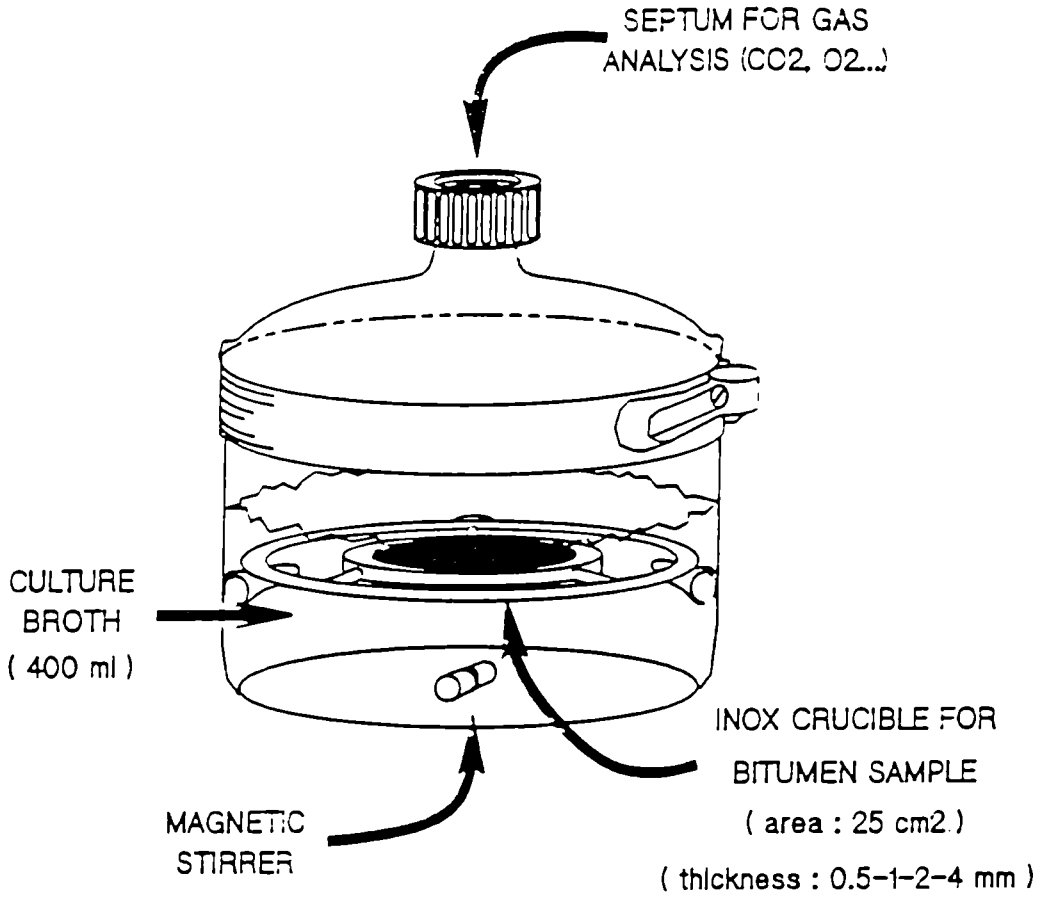


figure n° 1 : Bitumen disks samples. Effect of thickness

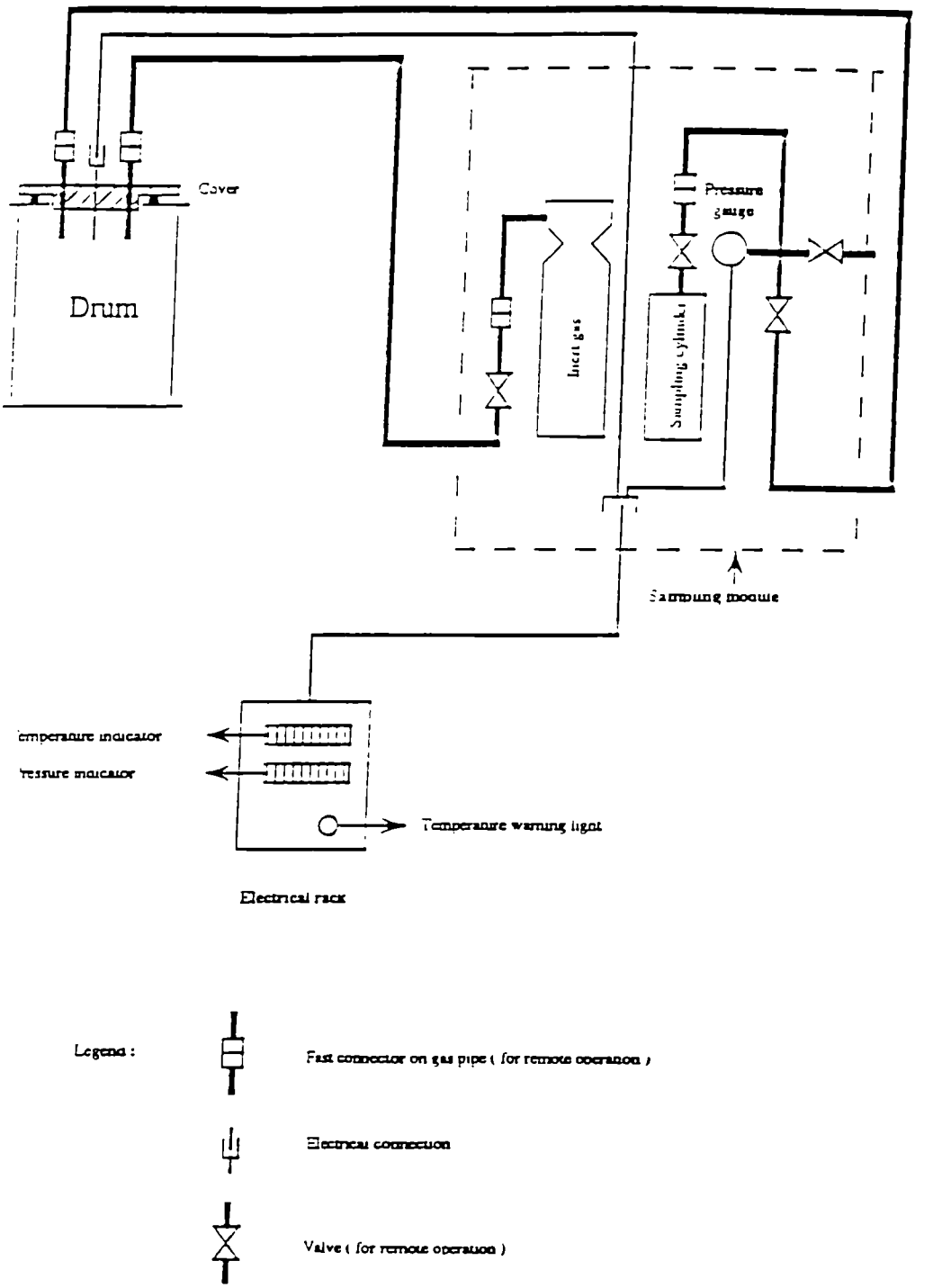


Figure 2: ASPIC device

Title : **Gas Generation in supercompacted Waste Products**
Contractor : KFA Jülich
Contract No: FI2W-CT91-0094
Duration of contract : 1.10.91 - 31.1.95
Period covered : -
Project leader : Dr R. Odoj

No contribution has been received for this project.

Title: **Impact of Additives and Waste Streams Constituents on the Immobilisation Potential of Cementitious Materials**

Contractor: University of Aberdeen / Free University of Berlin / AEA Windscale
Contract No.: FI2W/CT-90/0099
Duration of contract: 1.10.91 to 31.12.94
Period covered: 1.10.91 to 31.12.91
Project leader: F.P. Glasser (Univ. Aberdeen), G. Marx (T.U. Berlin), N.J. Angus (AEA)

A. OBJECTIVES 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 the 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 aqueous phase and solid phase compositions for cement and blended cement using inactive controls and 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 together with the role of certain organic complexing agents. The impact of selected inorganic ions on cement performance at longer ages will also be measured. The above experiment will be carried out at three isotherms, ambient, (~ 22°) 55° and 80°C.

The experimental data gathered will be used to jointly develop models for cement performance.

B. WORK PROGRAMME

1. Literature studies
2. Preparation of cement hydrates and measurement of their sorption properties for actinides under conditions relevant to nuclear waste repositories.
3. Examine the impact of selected organic and inorganic waste stream constituents on cement properties.
4. Determine the pore fluid chemistry of cemented intermediate-level waste forms.
5. Modelling and validation of cement performance.

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. A literature study on the sorption of radionuclides has been carried out. In addition, a large data base containing stability constants relevant to the present project was set up.
A literature study on interactions between cementitious materials and I, Cl, Cs and Ni is being carried out. Solutions containing Ni at various pH's and $Ca(OH)_2$ have been prepared and the solubility will be measured in the near future.

2.& 3. The following samples were synthesised in 80 g batches and are to be used in preliminary studies and to assess which hydrates will be used for more comprehensive sorption studies.
Cement nomenclature: C=CaO, A=A_2O_3, S=SiO_2, H=H_2O, M=MgO, S=SO_4
Ettringite, AF_6 (C_6 AS_3 H_{32})
Gehlenite Hydrate, GH, (C_2 ASH_8)
Hydrotalcite, HT, (M_{4-6} AH_{10-13})
Hydrogarnet, HG, (C_3 AH_6)
Calcium Silicate Hydrate Gel (C-S-H)

Problems have been encountered in manufacturing a pure crystallised sample of tobermorite.
Experimental determination of the sorption properties have recently commenced. The solid samples are being left to equilibrate so that their pH's can be measured. The samples will be adjusted to this pH after the addition of the radionuclide and the complexing agent. The first set of experiments are the solubility measurements of U(VI) and Np(V) in pure water and saturated NaCl at 25°C. The effects of EDTA, oxalate and DBP on this system will also be measured.

Three methods for the measurement of uranium have been evaluated, these consist of: (a) liquid scintillation counting for concentrations $>10^{-5}$M, (b)spectrophotometrically, using an improved arsenazo-III method for concentrations up to 10^{-8} and (c) a polarographic method which is currently undergoing assessment.
After discussions with partners it was decided that sludge type wastes be used rather than larger particles, e.g. fuel hulls, which may take longer to equilibrate. Of the available wastes, two are being considered: ferric flocs and stainless steel corrosion products. Consideration is being given to the artificial generation of steel corrosion products by electrochemical means.

4. This task is now under way with a series of development trials, designed to prove that the cement pore fluid expression technique is capable of expressing fluids at elevated temperatures. It is important in these experiments that the pore fluid expression is carried out at the same temperature as the curing temperatures of the sample. This eliminates the possibility of solution chemistry changes due to cooling. On completion of these trials the main part of this task will commence.

5. This task depends on work/results from the above tasks and is scheduled for later in the programme.

Title: The effect of microbial activity on the near and far fields of a deep repository

Contractor: CEA, France
Contract No.: FI2W/CT90/0022
Duration of contract: October 1991 to September 1993
Period covered: October 91 - December 91
Project leader: P. Lessart, CEA Cadarache

A. *OBJECTIVES AND SCOPE*

Microorganisms can produce organic or mineral acids able to promote corrosion and complexing agents that can modify the characteristics of the repository. So, radionuclides that have been immobilized by cement or bitumen based containments can be solubilized again (effect of biocorrosion of the containment), and their mobility (apparent diffusion coefficient in the near field) can increase if they react with complexing compounds.

On the other hand, opposite effect, micro-organisms have important sorption capacities corresponding to the properties of cell membranes, electrical charge and polymers production (especially polysaccharides), and also to bioaccumulation in the cell. So, the mobility of initially soluble radionuclides can decrease in the presence of micro-organisms.

The objective of the present work is to determine the global effect of microbial presence on the mobility of radionuclides supposed immobilized in the near field (clay or cement).

The experiments will be done on samples of pure cement (cylinder of 40 mm diameter and 250 mm high) and fine mote (about 2 mm) of clay in a column of 42 mm diameter. Both clay and cement content U (introduced as $UO_2(NO_3)_2$) or Cs (introduced as CsCl).

B. *WORK PROGRAMME*

Hydraulic tests of the laboratory pilot plant.

Metabolism study of cellulolytic microorganisms.

Lixiviation of U and Cs contained in cementitious or clay matrix by the culture medium containing microorganisms.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

This contract has just began on October 1991 so we don't have any important result.

The bibliographical report is quite finished.

The pilot plant has been factoried in october. It is now under hydraulic experiments. A short description is given thereafter.

Culture conditions of *Trichoderma viride* on cellulose have been determined. About 20 organic acids are produced as result of cellulose degradation. We are improving the method to detect and to quantify them by HPLC.

Progress and results

Justification of our choices

With the objective to know the effect of microorganisms on mobility of radionuclides, a laboratory scale pilot plant is investigated to measure the solubilisation of U and Cs from clay and cement. U is representative of alpha wastes (cement conditionned) and can have various oxydation state, and Cs is one of the main radionucleides that can be found in medium level radioactive wastes (for example : sludges from STE3 La Hague, conditionned in bitumen).

Bitumen excepted, one of the main organic carbon source we can find in a deep repository site is cellulose that can be found especially in technological wastes (especially from nuclear research centers). Two cellulolytic micro-organisms are planned to be used : *Trichoderma viride* and *Cellulomonas uda.*
The twice phenomena, lixiviation-complexation (actions of the acids, that will increase the nuclides mobility) and bio-accumulation in micro-organisms (that, in a real repository, will decrease the mobility), would be studied simultaneously. In this aim, there is no separation between the microbial culture vessel and the lixiviation column. The advantage is that the lixiviation solution will contain both micro-organisms and metabolism products from cellulose.

The problem of biofouling of the columns could be overcome by a decrease of the flow of the feed solution.

Description of the biolixiviation pilot plant

This pilot may permit to :

- control a continuous microbial culture using cellulose as carbon source, including oxygen supply (without concentration control) and temperature regulation,
- supply this culture by a regulated flow of sterile solution of mineral salts,
- control a continuous flow of the lixiviation solution around the samples, at a controled temperature,
- preserve the characteristics of the lixiviate (by a low temperature) before analysis.

With the objective of a continuous operation for a long time (more than 12 mounth we hope), we choose to control it by an automaton.

This pilot will allow to measure simultaneously the biolixiviation of two nuclides (Uranium and Cesium), included in two materials (cement and clay), by the acids produced by two micro-organisms (*Trichoderma viride* and *Cellulomonas uda*). These lixiviates will be compared with the lixiviate obtained by percolation of the sterile saline solutions on the same samples.

So, this pilot is composed by two identical frames, each of them composed by 4 identical basis units (see figure n°1).

On this basis units, the various apparatus are disposed on 4 levels :

- level 4 : this upper level corresponds to the sterile storage of the sterile saline solution.
- level 3 : pumps for the feeding of the microbial culture. The flow will be very low (between 10 and 20 ml/d), so we choose a sequential feeding using 5 electrovalves (the figure n°2 describes the feeding cycle).
- level 2 : this level is thermostated about 30°C and can be protected from light. The microbial culture vessels are in the upper part of this level. The saline solution is distributed on cellulose on which micro-organisms grow, producing organic acids. These vessels can be isolated from the others part for microbial inoculation or analysis. The solution then drops from those culture vessels on the samples of clay or cement contained in a plexiglass column (42 mm internal diameter, 500 mm high). For cement samples, the residence time of the lixiviating solution will be about 1.5 day. W
- level 1 : The lixiviates are collected in glass bottles and keeped in cold conditions (about 2°C) before analysis.

Hydraulic tests of the pilot are now conclusive.

Sample preparation :

Cement. we use cylinder of pure CPA of 40 mm diameter and 250 mm high,made by LBR (Concrete Research Laboratory) CEA Saclay that will do the main physical analysis after lixiviation.

Clay. They will be done in our laboratory. Cesium will be incorporated by 3 successive ionic exchanges using CsCl. Uranium will be incorporated by the same way using $UO_2(NO_3)_2$. The clay will be introduce in the column as granulates of about 2mm size prepared by successive humidification, drying, grinding and sifting. This technic will allow diffusion of aqueous solution through the clay.

List of publications

No publications.

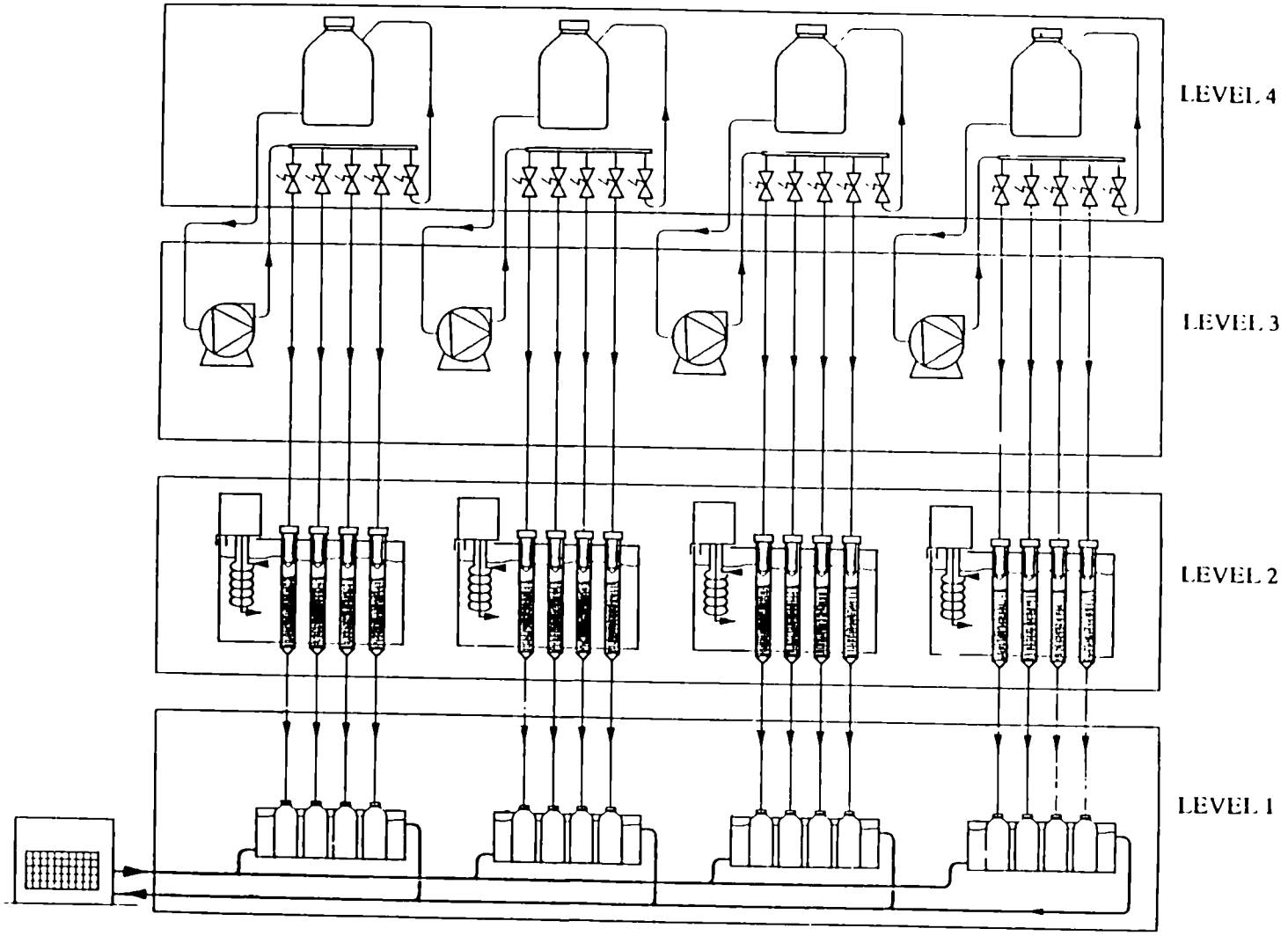


Figure n°1 : Diagram of the biolixiviation pilot plant

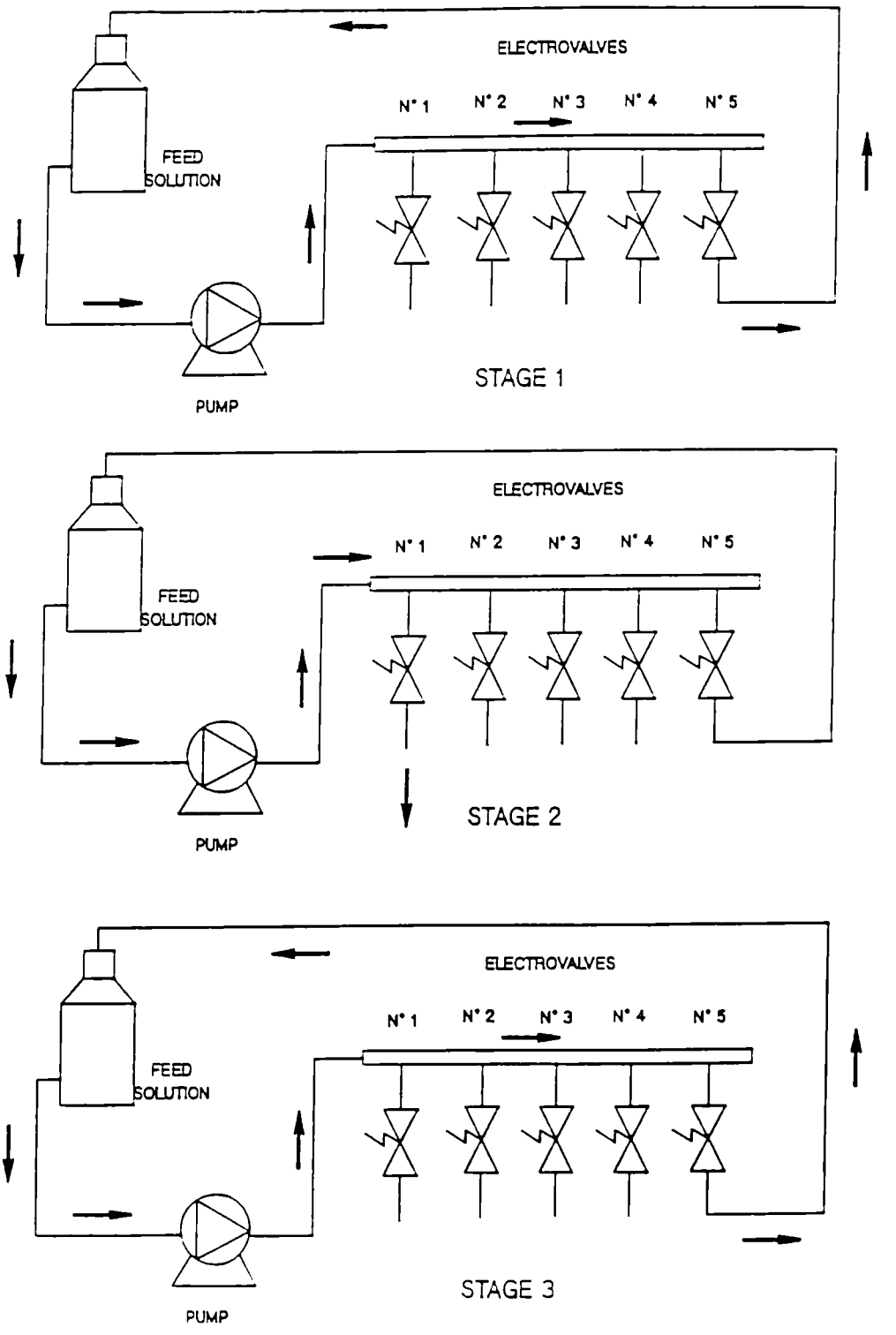


Figure n°2 : The feeding cycle

Title: Corrosion of Selected Packaging Materials for Disposal of Heat-Generating Radioactive Wastes in Rock Salt Formations

Contractors: KfK Karlsruhe, ENRESA Madrid
Contract No.: FI 2W-CT-90-0030
Duration of contract: January 1991 - December 1994
Period covered: January 1991 - December 1991
Poject Leader: E. Smailos, KfK (coordinator)

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 parameter 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, laboratory-scale and in-situ corrosion studies were performed on three preselected carbon steels (one unalloyed, two low-alloyed steels) as well as on cast-steel tubes plated with either Ti 99.8-Pd or Hastelloy C4 in salt brines.

In the laboratory-scale experiments, corrosion results were obtained for the low-alloyed steels TStE 460 and 15 MnNi 6.3 of up to one year in three disposal relevant brines at 150°C. Furthermore, stress corrosion cracking studies by means of the slow strain rate technique were performed on the steels TStE 460, 15 MnNi 6.3 and TStE 355 (unalloyed fine-grained steel) in an $MgCl_2$-rich brine at 170°C and strain rates of 10^{-4} - 10^{-6} s^{-1}.

In the in-situ corrosion experiments conducted in the Asse salt mine, the influence of selected container manufacturing characteristics on the corrosion behaviour of Ti 99.8-Pd or Hastelloy C4 in salt brines was examined. For this, four electron-beam welded cast-steel tubes plated with either Ti 99.8-Pd or Hastelloy C4 were tested for 18 months in salt brines at temperatures of 90°C - 200°C.

PROGRESS AND RESULTS

B.2.2 Corrosion studies on low-alloyed steels in salt brines (KfK).

Two low-alloyed steels, namely TStE 460 and 15 MnNi 6.3, were investigated, which are discussed in Germany as container materials for the disposal of spent fuel in the galleries of a rock-salt repository. The steels were tested of up to 1 year in three disposal relevant brines at 150°C. The TStE 460 steel was examined in the hot-rolled and annealed condition, the 15 MnNi 6.3 steel in the forged and annealed condition. The steels had the following compositions in wt.%:

TSt E 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.

Three salt brines differing qualitatively and quantitatively were used as corrosion media. Two of them (brines 1 and 2) are highly concentrated in $MgCl_2$, the third (brine 3) has a high concentration of NaCl. The compositions, pH-values and O_2-contents of the brines are given in Table I.

Besides specimens of the parent materials, also submerged-arc welded (SAW) specimens were investigated in order to examine the influence of this welding technique selected for the spent fuel disposal container (POLLUX) closure on the corrosion. The 15 MnNi 6.3 welded specimens were taken from an original welded lid of the POLLUX container. The TStE 460 welded specimens were prepared from a welded lid simulated by welding together two rings. Plane specimens having the dimensions of 40 mm x 20 mm x 4 mm were used.

The experiments were performed at 150°C and a brine volume to specimen surface ratio (V/S) of 5ml/cm^2. The testing times were 4, 8 and 12 months. All specimens were examined for general and local corrosion by gravimetry, microscopic evaluation, measurements of pit depths, surface profilometry and metallography.

The corrosion results obtained for unwelded and welded steel specimens after 1 year in the various brines at 150°C are compiled in the Tables II and III and can be summarized as follows:

- The parent materials (unwelded specimens) were resistant to pitting corrosion in all test brines. A non-uniform general corrosion was observed. The lowest

corrosion rates occurred in the NaCl-rich brine 3 with values of 29 µm/a for TSt E 460 and 72 µm/a for 15 MnNi 6.3, respectively. In the $MgCl_2$-rich brines 1 (Q-brine) and 2, clearly higher corrosion rates (90-175 µm/a for TSt E 460, 112-127 µm/a for 15 MnNi 6.3) were obtained compared to the values of the NaCl-rich brine. This is attributed to the lower pH-values of the $MgCl_2$-rich brines due to the formation of HCl from the hydrolysis of $MgCl_2$.

- Submerged - arc welding (SAW) did not influence noticeably the corrosion behaviour of the steels in the NaCl-rich brine. The welded specimens underwent a non-uniform corrosion in this brine as did the unwelded specimens, and the corrosion rates corresponded to the values obtained for the parent materials. In the $MgCl_2$-rich brines, however, considerable corrosion attaks were detected for both steels in the heat-affected zone of the welded specimens. The depth of these corrosion attacks increased with exposure time to the brines and reached after 1 year values between 1.5 mm and 3.9 mm, depending on the steel and the brine.

In general, it can be stated that the corrosion rates obtained so far for the parent materials imply corrosion allowances technically acceptable for the thick-walled packagings discussed here. However, submerged-arc welding strongly reduces the corrosion resistance of the steels in $MgCl_2$-rich brines. Further corrosion experiments of up to 18 months are in progress.

B.2.4 In-situ corrosion studies on cast-steel tubes plated with Ti 99.8-Pd / Hastelloy C4 (KfK).

On the basis of the corrosion results obtained so far and considering mechanical aspects, a thick-walled carbon steel container with or without a corrosion protection made of Ti 99.8-Pd was identified for the packaging of the HLW waste. As an alternative to Ti 99.8-Pd the use of Hastelloy C4 as a corrosion protection material is being examined.

An important aspect of the in-situ studies is the investigation of the influence of selected container manufacturing characteristics (e.g. sealing technique, application mode of the corrosion protecting layer on the steel) on the corrosion behaviour under simulated disposal conditions. In the period under review, four tubes, two of them with a corrosion protection layer of Ti 99.8-Pd and two of Hastelloy C4 applied by explosion plating and electron-beam welding (EB) were examined in salt brines.

The materials used had the following compositions in wt.%:

Cast steel:	0.16 C: 0.66 Si; 1.51 Mn; bal. Fe.
Hastelloy C4:	15.5 Cr; 15.3 Mo; 0.8 Fe; bal. Ni.
Ti 99.8-Pd:	0.2 Pd; 0.03 Fe; bal. Ni.

The tubes (500 mm length, 40 mm outside diameter, 10 mm thickness) were examined both in NaCl-brine (26.9 wt.% NaCl, 73.1 wt.% H_2O) and $MgCl_2$-rich brine (26.8 wt.% $MgCl_2$, 4.7 wt.% KCl, 1.4 wt.% $MgSO_4$, 1.4 wt.% NaCl, 65.7 wt.% H_2O). The tubes were stored for 18 months in 2 m deep heated boreholes in the Asse salt mine. The annular gap between the tubes and the borehole wall was filled with 100 ml brine. The vertical temperature profile in the boreholes ranged from 90°C to 200°C; the maximum temperature occurred in the center of the heated zone and the minimum temperature of the upper part of the tube. The maximum pressure measured was 0.28 MPa. This corresponds to a brine boiling point of 140°C. This means that the water contained in the brine evaporates at points of elevated temperature and recondences at the upper cooler end of the tubes (90°C).

The examination of the cast-steel tubes by means of stereo-microscopy and surface profilometry has shown that those tubes plated with Ti 99.8-Pd were resistant to corrosion in both brines. Neither on the overturning surface nor on the hot-rolled and EB-welded Ti 99.8-Pd has shown any signs of local corrosion. Even a crack produced by a steel needle to simulate severe conditions during the handling of the containers did not stimulate a corrosion attack. These results confirm the findings of previous long-term immersion tests [1] and electrochemical corrosion studies [2] which indicate that the passive oxide layer (mainly consisting of Ti O_2) formed on the surface of Ti 99.8-Pd is very stable in salt brines.

The cast-steel tube with a corrosion protection of Hastelloy C4 was resistant to local corrosion in the NaCl brine. In the $MgCl_2$-rich Q-brine, however, a large number of ruptures were detected on the Hastelloy surface layer. They preferably occurred at the overturning surface exposed to test temperatures between 150°C and 200°C. The ruptures are marked on the tube section shown in Fig.1a. The corrosion attacks on the surface of Hastelloy C4 (Fig.1b) covered a mean area of about 1 mm^2. Comparative metallographic examinations of non-etched specimens before and after 1.5 years exposure to Q-brine revealed small pits with a maximum depth of 5 µm (see Fig.1c).

Detailed investigations of the corrosion attack of Hastelloy C4 by means of scanning electron microscopy (Fig.1d) have shown
- the complete destruction of the surface layer by converging pits of 1-2 µm in size;
- the development of a new pattern of pits with approximately 10 µm in diameter and about 10-15 µm in depth.

The in-situ corrosion results obtained for Hastelloy C4 in the $MgCl_2$-rich Q-brine are in good agreement with those of previous electrochemical studies [3,4] which have shown that this material is susceptible to local corrosion in this brine at elevated temperatures. The investigations of cast-steel tubes will be continued.

B.2.6 Stress corrosion cracking studies on carbon steels (ENRESA / INASMET)

Stress corrosion cracking studies were performed on the low-alloyed steels TStE 460 and 15 MnNi 6.3 (compositon see Session B.2.2.) and the unalloyed fine-grained steel TStE 355 (wt.%: 0.16 C; 0.41 Si; 1.5 Mn, bal. Fe) by means of the slow strain rate technique. The steels TStE 355 and TStE 460 were examined in the hot-rolled and annealed condition, the steel 15 MnNi 6.3 in the forged and annealed condition.

The steels were examined in the $MgCl_2$-rich brine (composition see TableI). The experiments were conducted in Hastelloy C-276 autoclaves at strain rates of 10^{-4}, 10^{-5}, 10^{-6}, s^{-1}, a temperature of 170°C and an argon pressure of 13MPa. In order to be able to interpret the results obtained in the brine, additional comparative investigations were carried out in argon as an inert medium. For the tests round specimens of 6 mm diameter, finished with 1000 grade emery paper were used.

Load, position, time and temperature data were continuously logged by the microprocessor that controls the testing 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 measured. To examine whether secondary cracks were present, the fractured specimens were examined by metallography. Fractographic studies by means of scanning electron microscopy (SEM) are in progress. The

results of the slow strain rate tests obtained so far for the three steels in argon and Q-brine at 170°C and various strain rates are given in Figs.2 and 3. The values are average of at least two tests. Compared to the values in argon, a clear diminishing of the elongation, reduction of area, energy and true stress at fracture occurred for all steels in Q-brine, mainly at strain rates of 10^{-5} s^{-1} and 10^{-6} s^{-1}. The values for the yield strength and maximum load in Q-brine, however, are very closed to those obtained in argon.

In the optical and metallographic examinations of specimens made of the hot-rolled steels TStE 355 and TStE 460, a non-uniform general corrosion due to local and repetitive breaking of the corrosion surface layer near the fracture zone was observed. Secondary cracks typical for stress corrosion cracking were not observed. For this reason, the reduction in ductility of these steels in Q-brine cannot be attributed to stress corrosion cracking. For the loss of ductility in this brine other mechanisms such as strengthening or embrittlement could be responsible.

In case of the forged steel 15 MnNi 6.3, a clear susceptibility to stress corrosion cracking in Q-brine was observed. In the metallographic examinations, besides a non-uniform general corrosion, extensive lateral secondary cracks were identified after testing in this brine at a strain rate of 10^{-5} s^{-1} (Fig. 4).

To examine the fracture surface morphology of the steels, fractographic studies by means of a scanning electron microscope are in progress. Furthermore, stress corrosion cracking studies in argon and Q-brine at 25°C and 90°C are under way.

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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: Linear corrosion rates of the unwelded steels TST E 460 and 15 MnNi 6.3 in the test brines at 150°C

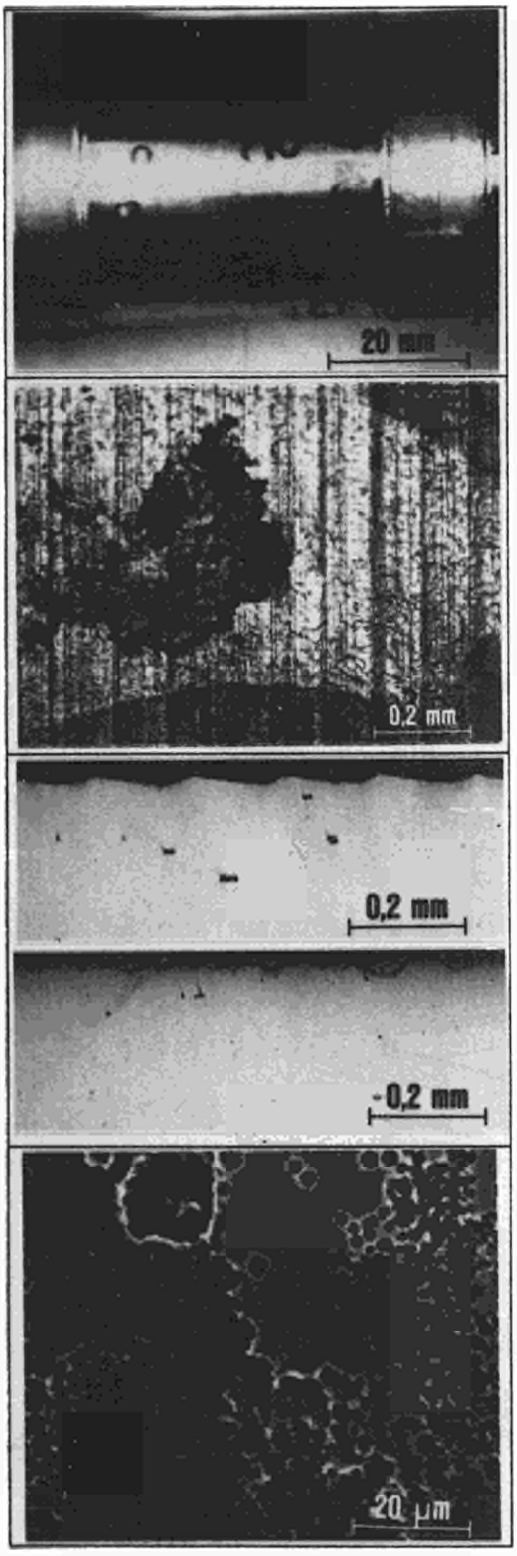
Material	Corrosion rate (µm/a)		
	Brine 1	Brine 2	Brine 3
TStE 460	175.2	90.0	29.0
15 MnNi 6.3	127.5	112.0	72.0

brines 1 and 2: $MgCl_2$ - rich; brine 3: NaCl - rich
test duration: 4 - 12 months

Table III: Maximum penetration depth of corrosion in the HAZ[+)] of the submerged arc welded steels TStE460 and 15 MnNi 6.3 after 12 months exposure to brines at 150°C

Material	Maximum penetration depth (mm)		
	Brine 1	Brine 2	Brine 3
TStE 460	1.5	2.2	0.05
15 MnNi 6.3	1.8	3.9	0.08

[+)] heat - affected zone



a) Optical macrograph of the surface of the tube section

b) Optical micrograph of the surface layer

c) Optical micrographs before exposure (above) and after exposure (below)

d) SEM photograph, detail of the surface layer

Fig.1: Corrosion of a cast-steel tube plated with Hastelloy C4 after in-situ storage (1.5 a in rock-salt + 100 ml added $MgCl_2$-rich Q-brine at 90°C-200°C)

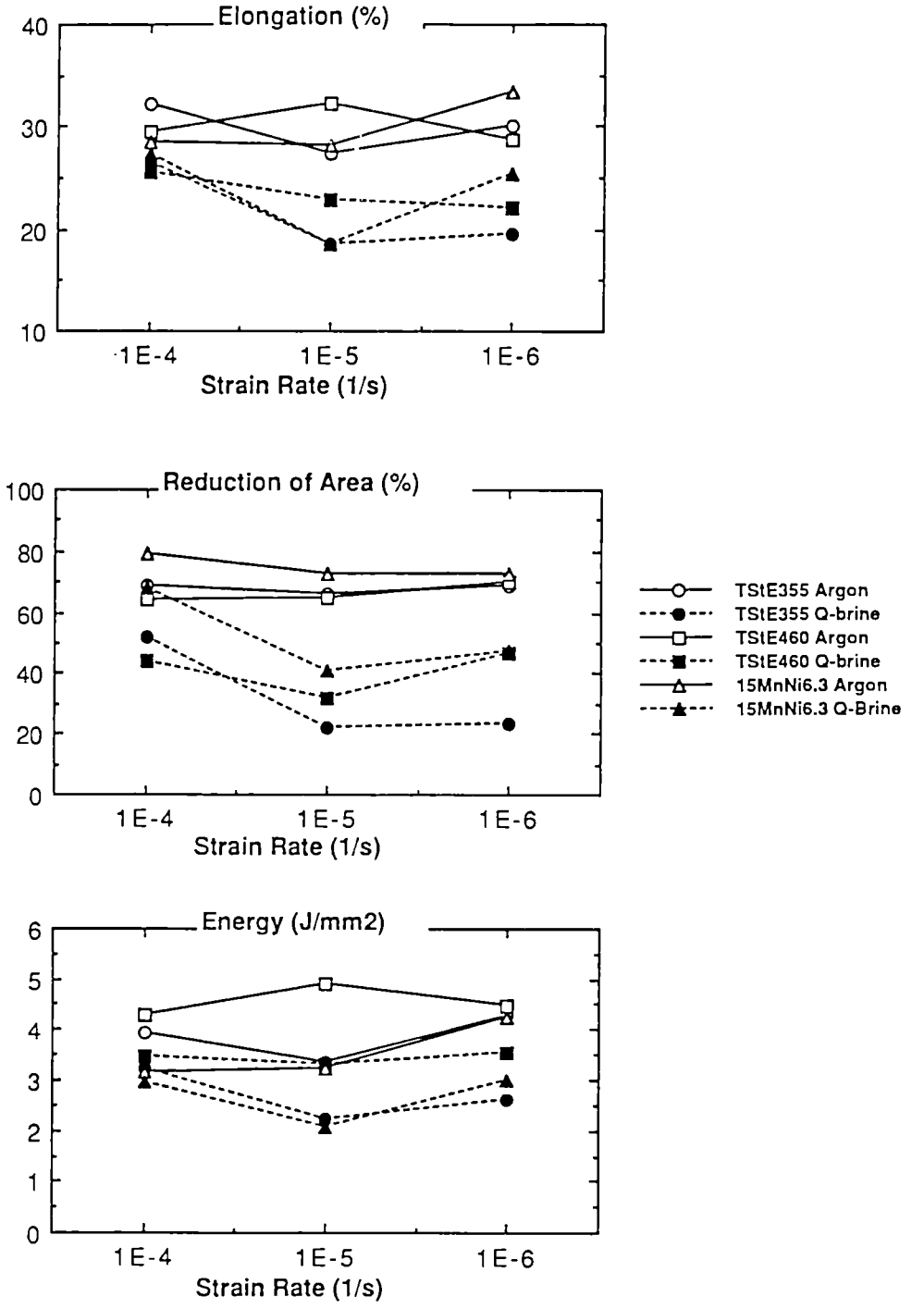


Fig.2: Elongation, reduction of area and energy versus strain rate for the TSt E 355, TSt E 460 and 15 MnNi 6.3 steels tested at 170°C and 13 MPa in argon and Q-brine.

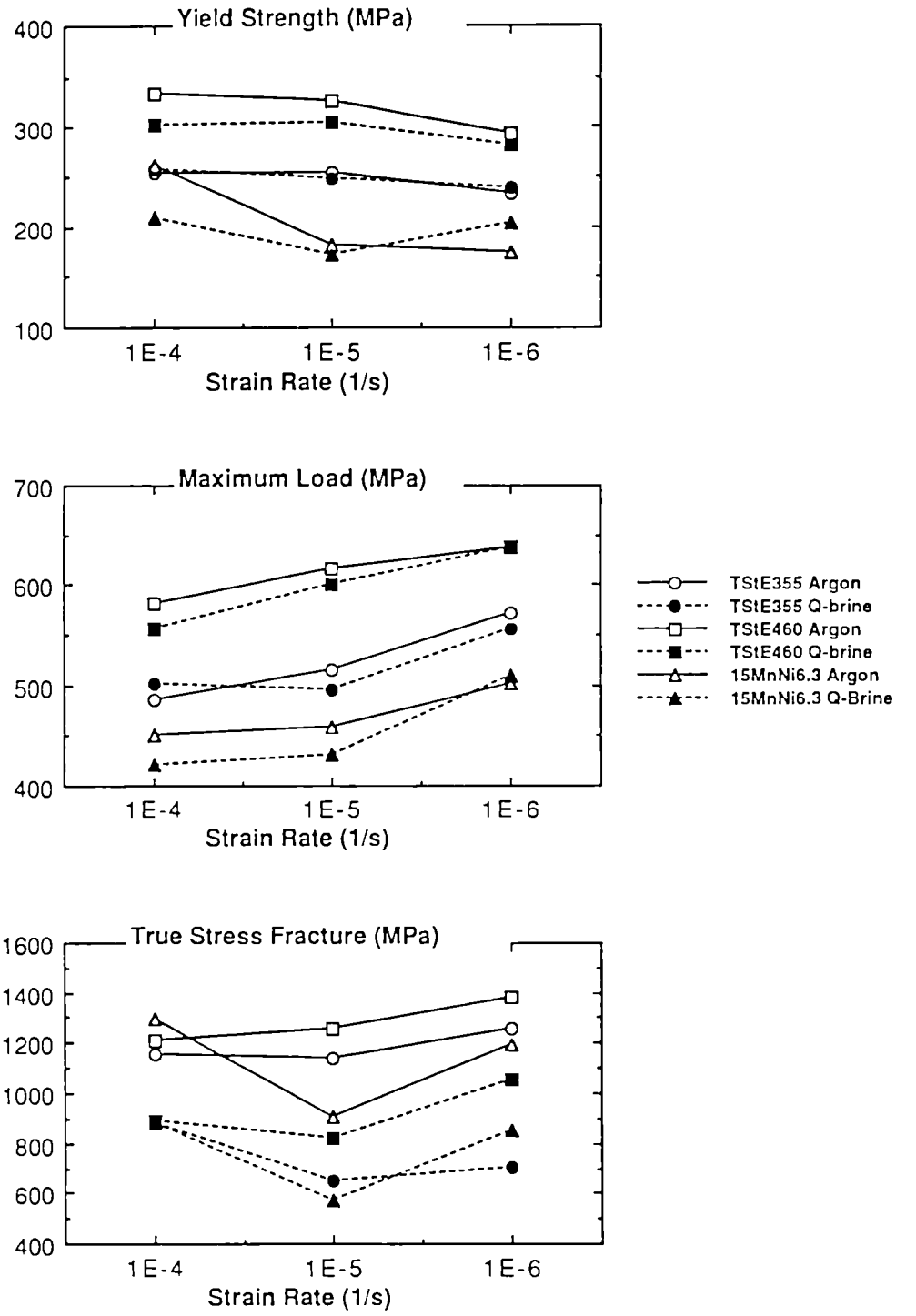


Fig.3: Yield strength, maximum load and true stress fracture versus strain rate for the TSt E 355, TSt E 460 and 15 MnNi 6.3 steels tested at 170°C and 13 MPa in argon and Q-brine

Fig.4: Extensive secondary cracking of the 15 MnNi 6.3 steel tested in Q-brine at 170°C, 13 MPa and 10^{-5} s^{-1}

Title :	Modelling and Testing of the Hydration of Backfill and Sealing Materials
Contractors :	SCK/CEN, CEA, UWCC, UPC
Contract N° :	FI2W-CT90-0033
Duration of contract :	from 01-07-91 to 30-06-94
Period covered :	from 01-07-91 to 31-12-91
Project leaders :	G. Volckaert (coordinator), B. Felix, C. Imbert, H. Thomas, E. Alonso

A. OBJECTIVES AND SCOPE

When considering compacted clay-based materials for sealing, the study of the hydro-mechanical behaviour of unsaturated materials becomes an essential point to be understood. It is also considered to use clay-based materials as backfilling around HLW packages. In this case their behaviour during saturation is further complicated by the thermal transient caused by the heat emission of the waste.

Elastoplastic models of the Cam-Clay type are neither able to describe irreversible volumetric strain (swelling or collapse) nor to describe the evolution of the mechanical property limits due to changes in the water content. In the case of partly saturated clay materials, it is necessary to take into account the appearance of suction phenomena which have a strong influence on the hydraulic, mechanical and thermal properties of the material.

The goal of this 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 by data transfer techniques and will be able to describe stress/strain behaviour, moisture migration and heat transfer.

In this project the CEA and SCK/CEN will be responsible for the main experimental work while the groups at the universities of Cardiff and Catalunya will perform 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 thus suction potential of swelling clay at room temperature. In these experiments the suction potential will be imposed.

3. Modelling

The first step will be to adapt the models to dens, 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 the adapted models will be coupled in a straight forward manner by means of data transfer techniques.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

An X-ray transparent oedometer has been designed and a prototype has been realized by the SCK/CEN. A first test with a medical X-ray tomograph at the University of Genth has been performed. Although the result of the test was positive, some adaptations of the design were necessary. An improved oedometer was realized and the equipment is now ready to start with experiments in which the progress of a hydration front can be followed in detail.

The CEA has studied how to adapt their oedometers to be able to perform experiments under controlled suction. With the osmotic method, the limit of the suction will be first 1.5 MPa. Later it is hoped to reach a value of about 5 MPa. At this time the apparatus has been designed but not yet realized. A prototype will be build as soon as possible. The adaptation of a triaxial cell is planned and will begin after the validation of the oedometers.

UPC and UWCC have already developed the theoretical formulation which combines on the on the one hand the thermo/hydraulical behaviour with soil suction and on the other hand the hydro/mechanical behaviour with soil suction. The software development for the extended models has been started. First scoping calculation with the existing models were performed.

Progress and results

SCK/CEN

Development of an X-ray transparent oedometer

As a medical computerized tomograph (CT-scanner) will be used, it is necessary to produce an oedometer transparent for 150 KeV X-rays. This means that an optimum between contradictory conditions needs to be found. On the one hand the oedometer cell needs to be made either thin walled or made of very light material but on the other hand it needs to be able to withstand high swelling pressures (up to 10 MPa). The result of the first test with a thin walled (5 mm) stainless steel cell, was negative. From this test and from discussions with specialist at the university of Genth, it was clear that a detailed image of the clay sample in the oedometer would be obtained if the sample was completely surrounded by a material with a density lower than the density of the clay sample. Therefore a new thick walled (25 mm) plexiglass cell was developed. This cell is placed in an aluminium frame and also all other steel parts were as much as possible replaced by aluminium. The sintered stainless steel filters were replaced by sintered quartz filters. For the test with this cell clay powder was uniaxial compacted in the cell to a density of 1.97 g/cm^3 and about 3 ml of water was injected at the bottom of the cell to generate a hydration profile. This test was positive and the tomographs gave a sharp image of the clay sample. Even the small pyrite particles in the clay sample could be clearly seen. Also the hydration profile could be clearly found back. From this test it was concluded that after calibration of the apparatus for the appropriate range of density, density variations as low as 1 % can be quantified. Tests with a uniaxial press have shown that the plexiglass cell can withstand a maximum load of 10 ton, so that it fulfils both conditions mentioned above. A second cell has been designed which allows a more precise control of the water injection.

Experiments with this cell will start next semester.

CEA

Design of an oedometer with suction control

Regarding the results provided by the different methods, the osmotic method is preferred to the counter-pressure method. The osmotic technique does not add a mechanical stress in the apparatus and some experience in suction control of clay with this method has been gained in a previous experiment.

It was decided to adapt the existing oedometers which previously provided some data on french clay. These data constitute a reference for the first results and validation tests. The oedometer samples are very thin to decrease the lateral friction. So applying a controlled suction at two faces of the clay, it is hoped to reach faster the equilibrium of the suction in the clay.

Methodology of the experiment

A non-saturated clay has an initial suction. When a mechanical stress is applied on it, the suction is modified. For the moment, the suction inside the sample during the experiment can't be measured without disturbing it. The only possibility is to apply a known suction.

So it is proposed to perform standard oedometer tests under controlled suction. Different values of suction can be tested under the same path of stress. Each step of loading must be maintained as long as the strain and the suction are not stabilized. For suction, it means that the flow of water becomes negligible. During such an experiment the vertical strain and inflow or outflow of water versus time need to be measured.

An other possibility is to modify the suction under a constant stress state. The decrease (or the increase) of the suction will be achieved by two or three steps. It is however not yet clear if such cycles of suction can be realised as a great difficulty will be the influence of temperature.

It is planned to realise and validate one or more oedometer cells. Some experiments will be performed at maximum suction to validate this device. At the same time, the development of a triaxial cell equipped with a system controlling the suction, will be studied.

UWCC

Evolution of research strategy, in terms of development of the formulation to be adopted

The current heat and moisture transfer model at UWCC has to be further developed to be applicable to dense, swelling clays. This means that in the first instance strain and deformation effects have to be included as independent variables.

To achieve this aim, and to render UWCC's model compatible with UPC's work, it was established that UWCC's approach, involving two variables, capillary potential and temperature, would have to be extended to a three variable formulation involving capillary potential, temperature and air pressure. This step was therefore considered first, for the case of soil as a rigid matrix.

The adaptation of this model to include deformation effects was then considered. Three types of soil constitutive relationships were clearly considered to be possible candidates for inclusion : an elastic model, a non-linear elastic model based on a state surface approach, as proposed by

UPC and an elasto-plastic model, also as proposed by UPC.

A strategy based on a modular approach to this problem was considered to be most applicable. Such an approach would allow an overall model of stress/strain behaviour to be developed, with the flexibility to accommodate any one particular constitutive relationship, as deemed both appropriate and actually feasible to implement.

Evolution of research strategy in terms of development of computer software

The overall objective of the "model development" work is the eventual production of software which can solve a theoretical formulation of thermo/mechanical/hydraulical behaviour of unsaturated soil. To this end, solutions are sought to four independent variables : temperature, capillary potential (soil suction), air pressure and deformation. To achieve this aim it has been decided to now proceed with the following steps :

- the development of a software frame work within which eventually this overall model can be accommodated
- the development of software which can solve either the hydro/thermal behaviour or the hydro/mechanical behaviour and provide solutions for temperature, capillary potential and temperature or deformation.

In this way, it is hoped that the overall problem, which is very complex in nature, can be talked in a step-by-step approach.

Model application to experimental work

During a meeting on the new in-situ test Bacchus2, concern was expressed regarding the boundary conditions on the inner surface of the annulus of buffer material, at its interface with the central filter. Discussions took place as to the importance of this boundary condition on the movement of moisture within the material, from the outer boundary. UWCC has carried out a sensitivity analysis of the problem, using their computer model for flow of water in unsaturated soil. In conclusion, it appears that the influence of the inner boundary on the overall moisture migration patterns is not significant within the context of the assumptions made and range of analysis performed. Even a very dry inner boundary condition only served to cause soil drying very near to the boundary itself and did not appear to influence moisture transfer in the majority of the flow domain.

The results achieved appear to suggest that the clay buffer, placed initially at 50 % saturation will take approximately seven months to become saturated. However, the assumptions made in determining material properties for the purposes of this investigation must be taken into consideration when assessing the accuracy of the results achieved from the numerical model.

UPC

Development of field equations

As a basis for the new code, a thorough review of the fundamental equations has been performed. This includes the motion of the fluid phase due to water potential and temperature gradients; the motion of the fluid phase due to water potential and temperature gradients; the motion of the gaseous phase including convective, diffusive and vapour components and the heat transfer associated with conduction and convective phenomena. Continuity equations for water, air and enthalpy have been formulated.

Basis for software development

The already operational water-gas-mechanical code NOSAT will be

maintained. In this code the mechanical description of partially saturated soil behaviour is kept relatively simple. Nevertheless, this description is well adapted to incorporate the results of common oedometer and isotropic tests (and in particular swelling tests). This code will experience relatively minor changes as required to solve specific boundary value problems in one dimension, plane strain or conditions of axisymmetry.

A new code will be developed with a number of features described later, which incorporates recent experience in handling this type of codes. The new program will feature the new elastoplastic constitutive models being developed and will certainly include heat balance capabilities. The field equations have already been discretized and programming has started.

Constitutive modelling of expansive clays

The modelling of expansive clays has two previous references in the work developed in the past at UPC :

- the description of volumetric deformation upon suction and stress changes by means of state surfaces;
- the development of an elasto-plastic model for partially saturated soils which may account for a moderate expansion of the soil.

Independently, a consideration of the microstructural features of active clays has led to the development of a two-structure model, mainly to describe internal water transfer mechanisms which are believed to be of significance in the long term behaviour of expansive clays. This double structure model relies in a state surface description of volumetric deformations.

The next natural step towards a more comprehensive description of expansive soils is to accept the elastoplastic framework as a desirable feature and to incorporate to it the double structure idea which is a significant characteristic of highly expansive materials. A qualitative model has been recently presented.

Design of experimental program

A test program has been designed to provide the necessary parameters for the mechanical model being used later on in the full scale simulation. In addition, the suction controlled tests will be most useful to validate the new constitutive model under development.

It should be noted that the results of these tests may also be interpreted and synthesized in terms of the state surface models. Therefore the program NOSAT may be used, at a first instance to perform simulation analysis of both the laboratory test results themselves and the full scale experiment.

Title:	Theoretical and Experimental Study of Degradation Mechanisms of Cement in the Repository Environment"
Contractor:	CEA, CEN-SACLAY - UNIVERSITY of ABERDEEN
Contract N°:	FI2W/CT90-0035
Duration of contract:	from 01.03.1991 to 28.02.1995
Period covered:	March 1991 - December 1991
Project leader:	R. ATABEK (1991) - E. REVERTEGAT (CEA coordinator) F.P. GLASSER (Univ. ABERDEEN)

A. OBJECTIVES AND SCOPE

The objective of the research programme is to determine degradation mechanisms of cement and concrete relevant to the repository environment. It is apparent that throughout the Community, repository environments are not completely quantified. There is, therefore, an urgent used to collect data on the performance of cement which are quantitative but not site-specific; which are applicable to a range of possible sites.

The studies will address time dependent changes in the internal constitution of cement based materials and quantify reaction kinetics and mechanisms, based on theoretical and experimental determination of calcium leaching. It will also determine the impact of ground water chemistries and backfills on cement performance.

Work is being undertaken on the basic thermodynamics and solution chemistry of cement systems. Working systems which model cement performance have been constructed. These give good agreement between predicted and measured values. The models are, however, chemically simple and do not enable us to take into account ageing factors, the complexity of ground water, chemistry and interactions between cement and backfill materials.

This research programme is coordinated with the studies carried out by AEA Harwell, RNL RISO and BAM Berlin within the framework of the EC Contract N° FI2W/0040 entitled: "The performance of cementitious barriers in repositories".

B. WORK PROGRAMME

Task 1 : Knowledge of cement paste attack mechanisms

- 1-a: experimental data acquisition for chloride, sulfate and carbonate attack
- 1-b: literature assessment

Task 2 : Verification of the $\sqrt{t}$ law of calcium oxide leaching :

- 2-a: study of commercial cement pastes with high water/cement ratio
- 2-b: study of long term synthetic phases and temperature effect

Task 3 : Modelling of cement paste degradation

Task 4 : Application to cement clay interaction

C-1 PROGRESS OF WORK AND OBTAINED RESULTS (University of Aberdeen)

State of advancement

The main part of the work has been devoted to task 3 and the related tasks 1b and 2b, which deal with the modelling of cement paste degradation. Globally the modelling can be divided into two parts; the first concentrates on the isothermal thermodynamics of the cement system in order to predict the stable hydrates. The second part deals with kinetics to give the time dependence of the processes described by thermodynamics. We have started to study the thermodynamic aspects of cement degradation because it relates closely to the model and it allows to make some predictions of the relative time dependence (an absolute time dependence is obtained when kinetics are added). However thermodynamic modelling is impossible to undertake without essential data on the existing stable phases (metastable phases are not taking into account for the long term modelling of cement degradation). The main part of the data has been found in the literature (task 1c) but others data have been generated experimentally (task 2b). From these data, the $CaO-Al_2O_3-SiO_2-CaSO_4-CaCO_3-CaCl_2-Na_2O-K_2O-H_2O$ phase diagram could be assimilated and applied. But it is impossible to understand directly this system and simpler phase diagrams have to be studied in a first step. The first phase diagram studied was $CaO-Al_2O_3-CaSO_4-H_2O$ at 25°C. This diagram predicts the result of the sulphate attack which can lead to formation of expansive hydrates (especially ettringite) that destroy the cement matrix. However even for this three component system, some problems are not yet solved due to the existence of solid solutions occuring for hydrates having the chemical formula $3CaO.Al_2O_3.3CaX.mH_2O$ and $3CaO.Al_2O_3.CaX.nH_2O$ ($X=SO_4$, 2OH, 2Cl and CO_3 in cement chemistry).

Progress and Results

Task 1b: Literature Assessment

Data useful for the thermodynamic modelling (solubility, stability, enthalpy of formation...) have been searched in the literature. Few papers relate phase diagrams to cement chemistry; the data are scattered but only the main data related to the $CaO-Al_2O_3-CaSO_4-H_2O$ system are reported here. For the system $CaO-Al_2O_3-CaSO_4-H_2O$ there are two main experimental studies, by Jones /1/ and D'Ans and Eick /2/. These studies define the stable hydrates; gibbsite (AH_3*), C_3AH_6*, ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$), gypsum ($CaSO_4.2H_2O$) and portlandite ($Ca(OH)_2$). Also the composition of solution at the four invariant points designated H2 (C_3AH_6-AFt-AH_3), E2 (AH_3-AFt-gypsum), F (CH-AFt-gypsum) and G (C_3AH_6-AFt-CH) had been determined. However some uncertainties exist concerning the stability or the metastability of monosulphoaluminate ($3CaO.Al_2O_3.CaSO_4.12H_2O$). Jones /1/ and D'Ans and Eick /2/ consider the monosulphoaluminate as metastable but this view is not shared by all authors /3/. These differences of interpretation are likely to be due to the existence of solid solutions occuring for hydrates having the chemical formula $3CaO.Al_2O_3.3CaX.mH_2O$ and $3CaO.Al_2O_3.CaX.nH_2O$ ($X=SO_4$ or 2OH in the $CaO-Al_2O_3-CaSO_4-H_2O$ system) /4/. Substitution of sulphate by hydroxyl and vice versa in both ettringite and monosulphoaluminate modify their relative stability and change their solubility product. The extent of solid solution has been recently studied /3-5/; AFm in the $CaO-Al_2O_3-CaSO_4-H_2O$ system, can be represented as a solid solution between $3CaO.Al_2O_3.CaSO_4.12H_2O$ and $3CaO.Al_2O_3.Ca(OH)_2.12H_2O$ (C_4AH_{13}*) by the chemical formula;

$$Ca_4\{Al_2(OH)_{12}\}^{2+}\{(1-x)SO_4.x(OH)_2.6H_2O\}^{2-} \text{ with } 0<x<0.5 \qquad (AFm,x)$$

The two end members of the solid solution are at 25°C; monosulphoaluminate (AFm,0) and hemisulphoaluminate (AFm,0.5). It is noticeable that the maximum value of x decreases with the temperature and no substitution occurs above 80°C.

AFt can be represented by a solid solution between $3CaO.Al_2O_3.3CaSO_4.32H_2O$ and $3CaO.Al_2O_3.3Ca(OH)_2.33H_2O$ by the chemical formula;

$$Ca_6\{Al_2(OH)_{12}.24H_2O\}^{6+}\{(3-1.5x)SO_4.1.5x(OH)_2.2H_2O\}^{6-} \text{ with } 0<x<1 \qquad (AFt,x)$$

A miscibility gap exists in the solid solution for x=0.5. Two important remarks can be made on these results; first, these solid solutions are synthesized in very particular conditions

(generally low temperature and calcium complexed in saccharide solution). Secondly these studies only deal with the crystallographic aspect of the solid solutions (no solubility data are given).
For what extent are these solid solutions relevant to cementitious systems? AFm solid solutions are frequently reported, but the system is generally not at the equilibrium and can promote metastable compositions. Also sulphate substitution by hydroxyl would occur preferentially at high pH (high OH^- concentration). If AFm has a domain of stability, the system is complicated and two new invariant points have to be considerated (See task 3). The system is even more complicated if both AFm,0 (monosulphoaluminate) and AFm,0.5 (hemisulphoaluminate) are supposed to be stable at 25°C. In this case 4 new invariant points are added to the system. Kapralik and Hanic /6/ give a reasonable hypothesis concerning the hydrates in equilibrium at these invariant points.

* In cement notation: C=CaO, A=Al_2O_3 and H=H_2O

** AFt = general term to design the solid solution formed by ettringite
AFm= general term to design the solid solution formed by monosulphoaluminate

Task 2b: Study of long term synthetic phases and temperature effect
Due to the uncertainties concerning AFm phase stability, some experiments have been carried out to determine its stability and solubility. AFm has been synthesized from a mixture of ettringite and C_3A. This indirect method has been used because direct synthesis (mixture of lime, calcium sulphate and aluminate solutions) appears to form mixtures of AFm with other hydrates (generally gypsum). Then AFm has been redispersed several times in water in order to determine its solubility. After each redispersion, solution and also the solid were analysed. After 6 redispersions, AFt is present with AFm without significant evolution of the composition of the solution (solubility product is constant). However this is not a sufficient result to confirm that AFm is metastable with respect to AFt, as this can represents the equilibrium between AFm and AFt (boundary curve). In order to evaluate if the solubility product of AFm varies with the extent of the substitution of sulphate by hydroxyl, AFm has been equilibrated in presence of CH and also in NaOH solutions (increase of OH concentration relative to SO_4). In both cases, AFm and CH were found but also a slight amount of C_4AH_{13}. The value of the solubility product slightly decreases (table 1). The presence of C_4AH_{13} should not induce this variation of the solubility product if the system is at a metastable invariant point (AFm-C_4AH_{13}-CH). AFt has also been redispersed in NaOH solutions to check if a similar variation of the solubility product occur. In these experiments, no other phases than AFt were found but the value of the solubility product decreases slightly as it is observed for AFm (table 1). Then the increase of x value in AFm,x and AFt,x induces a slight decrease of the value of the solubility product. However refinements of the XRD patterns are in progress to determine precisely the extent of the substitution.

Task 3: Modelling of cement paste degradation
The part of work done in this task concerns the construction of the $CaO-Al_2O_3-CaSO_4-H_2O$ phase diagram at 25°C. The phase diagram is calculated by determining the stable hydrates in minimising the free energy of the system. This is possible by solving a system of equations formed by the solubility product of the hydrates;

- Ettringite (AFt,0):

$$K_{sp1} = (Ca^{2+})^6.(Al(OH)_4^-)^2.(SO_4^{2-})^3.(OH^-)^4 = 2.803E\text{-}45$$

This value corresponds to an unsubstituted AFt; $3CaO.Al_2O_3.3CaSO_4.32H_2O$

- Monosulfoaluminate (AFm,0):

$$K_{sp2} = (Ca^{2+})^4.(Al(OH)_4^-)^2.(SO_4^{2-}).(OH^-)^4 = 3.715E\text{-}30$$

This equation corresponds to an unsubstituted AFm; $3CaO.Al_2O_3.CaSO_4.12H_2O$, although the experimental data used to calculate can correspond to a slightly susbstituted AFm (See Task 2b). AFm is taken into account during the calculation to determine if it can exist a domain of stability for monosulphoaluminate.

- Hydrogarnet (C_3AH_6):

$$K_{sp3} = (Ca^{2+})^3.(Al(OH)_4^-)^2.(OH^-)^4 = 2.160E\text{-}23$$

- Calcium hydroxide ($Ca(OH)_2$):

$K_{sp4} = (Ca^{2+}).(OH^-)^2 = 8.905E\text{-}6$

- Gibbsite (AH_3) (crystalline form):

$K_{sp5} = (Al(OH)_4^-) / (OH^-) = 3.993E\text{-}2$

The crystalline form is assumed to be stable compared to the gel form

- Gypsum ($CaSO_4.2H_2O$):

$K_{sp6} = (Ca^{2+}).(SO_4^{2-}) = 3.720E\text{-}5$

The values of the solubility product were calculated from data obtained in the literature (task 1b) or experimentally (task 2b). Congruent dissolution is assumed for each hydrate and the activity coefficients have been calculated using the Davies' equation.

The phase diagram can be drawn in three dimensions using total calcium, aluminium, sulphate concentrations in solution as axes (fig. 1). Each hydrate is in equilibrium with many compositions of the solution that represent a surface of equilibrium which is delimited by 4 boundary curves (intersection of surfaces of equilibrium i.e., two solids in equilibrium with the solution). The four invariant points (three solids in equilibrium with the solution) defined by Jones /1/ are also reported. The calculated compositions of the solution at these invariant points are close to experimental (table 2) and the sequence of the stable phases relative to the sulphate concentration is similar. This sequence can be divided into 7 segments;

1/ $0 \leq [SO_4] < 0.018$ mM/l
   stable phases: AH_3 - C_3AH_6 - CH

2/ $0.018 \leq [SO_4] \leq 0.03$ mM/l
   stable phases: AH_3 - C_3AH_6 - AF_t - CH

3/ $0.03 < [SO_4] < 11.4$ mM/l
   stable phases: AH_3 - AF_t - CH

4/ $[SO_4] = 11.4$ mM/l
   stable phases: AH_3 - AF_t - CH - gypsum

5/ $11.4 < [SO_4] \leq 15$ mM/l
   stable phases: AH_3 - AF_t - gypsum

6/ $15 < [SO_4] \leq 15.1$ mM/l
   stable phases: AH_3 - gypsum

7/ $15.1 < [SO_4] \leq 15.22$ mM/l
   stable phase: gypsum

From these results, pH at which AFt is stable are delimited by the pH at the invariant points G and E2; 10.4 and 12.55 respectively. In these calculations, AFm,0 is a metastable phase and thus does not appear on the phase diagram. However it is not yet possible to generalize this result for the entire range of solid solution AFm,x ($0<x<0.5$). What would be the modifications induced by a stable domain for AFm,x? The AFm,x surface of equilibrium would lie between C_3AH_6 and AFt surfaces of equilibrium and induce 4 new boundary curves and 2 new invariant points (fig 2). Then 9 segments instead of 7 have to be considered;

1/ AH_3 - C_3AH_6 - CH
2a/ AH_3 - C_3AH_6 - AFm,x - CH
2b/ AH_3 - AFm,x - CH
2c/ AH_3 - AFm,x - AFt - CH
3/ AH_3 - AF_t - CH
4/ AH_3 - AF_t - CH - gypsum
5/ AH_3 - AF_t - gypsum
6/ AH_3 - gypsum
7/ gypsum

and the sequence of the invariant points with the sulphate concentration would be;

X0; C_3AH_6 - AFm,x - CH
X1; AH_3 - C_3AH_6 - AFm,x
X2; AFm,x - AFt - C_3AH_6
R2; AFm,x - AFt - AH_3
F; AFt - gypsum - CH

E2; AFt - gypsum - AH_3

Another sequence is conceivable if $[SO_4]_{x1} > [SO_4]_{x2}$ but this one is less probable. Globally if AFm,x is a stable phase, the consequences for modelling are minor; affect only the results for sulphate concentrations below $[SO_4]_{R2}$ which is close to $[SO_4]_{H2}$=0.03mM/l /1/. Moreover if we consider the leaching of cement by pure water AFt and AFm,x would be transformed into C_3AH_6. Kapralik and Hanic /6/ consider that the two end members of the solid solution at 25°C ($3CaO.Al_2O_3.CaSO4.12H_2O$ (monosulphoaluminate; AFm,0) and $3CaO.Al_2O_3.1/2CaSO_4.\ 1/2Ca(OH)_2.12H_2O$ (hemisulphoaluminate; AFm,0.5)) as stable phases. The AFm,0.5 surface of equilibrium would be inserted between C_3AH_6 and AFm,0 ones. This would add two new invariant points and two new segments in the sequence of the sulphate concentrations. However it seems to us that it is preferable to consider a solid-solution with a varying solubility product.

The existence of solid-solution with hydrates having the general formula $3CaO.Al_2O_3.3CaX.mH_2O$ or $3CaO.Al_2O_3.CaX.nH_2O$ complicate greatly the system CaO-Al_2O_3-$CaSO_4$-H_2O and also in a quite similar way the system CaO-Al_2O_3-$CaCO_3$-H_2O. Then the next step will be to calculate the CaO-Al_2O_3-$CaCO_3$-H_2O and CaO-Al_2O_3-$CaSO_4$-$CaCO_3$-H_2O phase diagrams. Unfortunately another kind of substitution can occur when Al is substituted by Si. This substitution, where Si has a coordinantion of 6, is likely to occur in C_3AH_6 and ettringite. In this latter compound, the substitution of both SO_4 by CO_3 and Al by Si can lead to the formation of thaumasite ($[Ca_3Si(OH)_6]_2.(SO_4)_2.(CO_3)_2.24H_2O$) which is also reported as expansive and so destructive. It could be possible to have a solid solution between carbonated AFt and thaumasite, but data on these compounds are practically nonexistent and some experiments will be devoted to produce them.

C-2 PROGRESS OF WORK AND OBTAINED RESULTS (CEA, CEN-SACLAY)

State of advancement

Prediction of the alteration of concrete over 300 years period required the development of a model which integrates the problems of ionic diffusion in the pores of the material as well as kinetics of the dissolution and precipitation processes of the different hydrates. The first step of the problem is considered, i.e the degradation processes of an uncracked cement paste in contact with waters containing little or no salt. The experimental environment conditions are chosen, taking into account previous results /7/, to be representative of underground water chemistry.

The work carried out since the beginning of the contract was mainly devoted to prepare the samples and start the experiments. However the first experimental results obtained for Portland cement clearly show that the cement paste is leached in deionized water according to a diffusion process. The pore solution is in local equilibrium with the solid phases at every point of the paste. The cement paste attack can be modelled by a system of differential equations which are a function of $x/\sqrt{t}$ (x = distance from the surface, t = time). This system can be solved numerically by assuming that each component is only found in its majority species.

Progress and results

Task 1-a: experimental data acquisition for cement paste attack.

It is assumed that cement paste hydrates behave in the same way as those in concrete (no paste-aggregate reaction). The work done during this period has been devoted to prepare the samples and start the experiments with chloride and sulphate.

Experiments are carried out on cement paste disks (ϕ = 70 mm, e = 4 mm) submitted to various aggressive environments. The materials of concern within the scope of the study include Portland cement and blends of cement with slag and fly ash (cement named CLC), with a water/cement ratio of 0.38. The stability domain of the hydrates which precipitate or dissolve in the CaO-SiO_2-Al_2O_3 - corrosive ion system is determined as a

function of time. The aggressive environments are chosen to be representative of underground water chemistry; a pH of 8.5 is maintained constant over the test duration. Precise characterization of the corroded material is carried out through microstructure analyses, mercury porosimetry, mechanical properties, measurements of corrosive ion diffusion coefficient and depth of ion penetration.

The samples submitted to 1 and 3 months of chloride or sulphate attack ($[Cl^-]$ = 20 $g.l^{-1}$ or $[SO_4^{--}]$ = 10 $g.l^{-1}$) are under examination; preliminary results will be available in the early 1992.

Task 2-a: verification of the $\sqrt{t}$ law of calcium oxide leaching in the case of commercial cement pastes.

Systems containing mainly Portland cement will yield much free $Ca(OH)_2$ but after thorough maturation, blended cement systems will contain little or no free $Ca(OH)_2$. For a wide range of reasons, including the foregoing, it is less certain that $\sqrt{t}$ law of calcium oxide leaching will apply. The purpose of the experiments described below is to precisely supply the loss of Ca^{++} from cement pastes submitted to leaching tests. Various types of French commercial cements are tested. The temperature is fixed at 20°C and the water/cement ratio is 0.4 and 0.8 : this last value is chosen to accelerate leaching. Two types of environmental conditions are selected and maintained constant throughout the test: pH = 7 without and with chloride ($[Cl^-]$ = 20 $g.l^{-1}$). Two different methods are used: a) the weight loss of a cement cylinder is measured as a function of time using a hydrostatic balance; b) the hydroxide leaching from a cement cylinder is measured by maintaining pH in the solution equal to 7 by nitric acid addition.

The first results obtained in pure water for Portland cement pastes (water/cement = 0.4) clearly show that after a short period of time, leaching kinetics obey a $\sqrt{t}$ law which is characteristic of a diffusion process. As is clear from Figure 3, deviation from the $\sqrt{t}$ law at the beginning of the experiment is due to the carbonation of the samples. The leached ions are mainly hydroxides and calcium, and all the ions are released following a pure diffusion law. The analyses of the solid samples after leaching enable us to identify, as presented on Figure 4, an undamaged core delimited by a total dissolution of portlandite, followed by a succession of zones delimited by dissolution or precipitation fronts of the solid phases. Progressive decalcification of the C-S-H in the corroded zone is also observed.

Task 3 : Modelling of cement paste degradation.

From the experiments described previously, it can be concluded that ion leaching is governed by a diffusion process and that at any point of the paste, there is a chemical equilibrium between the liquid and the solid phases (local equilibrium). A simplified approach is used to solve by computered numerical methods the system of diffusion and chemical equilibrium equations.

It is considered that for a given value of CaO/SiO_2, the C-S-H is thermodynamically stable in a range of Ca^{++} concentration in the solution given by the curve presented on Figure 5 /8/. The thermodynamical equilibrium of the C-S-H is modelled by a series of C-S-H characterized by their CaO/SiO_2 ratio. In a first approximation the porosity and diffusion coefficients are assumed to be the same in the different zones. The solubility data used are those measured by the University of Aberdeen. Moreover the only solid phases taken into consideration are portlandite, AFt, AFm and C-S-H, and so, the calculated results are not directly comparable to the experimental results. However this approach allows to approximate the concentration profiles in the liquid and solid phases as a function of the variable $x/\sqrt{t}$ (where x = distance from the surface). Figure 6 gives the results obtained for the ion species in solution in connection with the solid phases existing in the different zones.

In the future, the model will be refined, taking into account porosity and diffusion coefficient variations.

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LIST OF PUBLICATIONS FROM THE REPORTED WORK

1. D. Damidot, M. Atkins, A. Kindness and F.P. Glasser "Sulphate attack on concrete: limits of the AFt stability domain", E-MRS, Strasbourg (1991), to be published in 1992
2. D. Damidot and F.P. Glasser "Thermodynamic investigation of the $CaO-Al_2O_3-CaSO_4-H_2O$ system and influence of Na_2O", submitted Cement Concrete Research
3. D. Damidot and F.P. Glasser "Sulphate attack on concrete: Prediction of the AFt stability from phase equilibria", submitted for 9th Int. Symp. Chem. of Cement, New Delhi (1992)
4. F. Adenot and M. Buil "Modelling of the corrosion of the cement paste by deionized water", submitted Cement Concrete Research

Table I. Composition of the solution and value of the solubility product for AFt and AFm

Experiment	[Ca] mM/l	[Al]	$[SO_4]$	[Na]	[OH]	log Ksp
AFm in water	4.93	1.6	0.013	0	8.2	-29.43
AFm + CH in water	17.31	0.063	0.004	0	34.5	-29.11
AFm in NH solution	0.54	1.97	0.079	375	373.95	-29.26
AFt in water	1.995	0.552	0.81	0	1.18	-44.55
AFt + CH in water	16.51	0.043	0.009	0	32.9	-44.31
AFt in NH solution	0.6175	0.311	0.91	53.48	52.5	-44.54
AFt in NH solution	0.55	0.451	2.20	503.8	500.1	-44.12
AFt in NH solution	0.351	2.035	4.084	997.5	991.5	-43.80

Table II. Composition of the solution at the different invariant points. (E) indicates experimental values obtained by Jones /1/ or Eick and D'Ans /2/ and (C) for calculated values

Invariant point	[Ca] mM/l	[Al] mM/l	$[SO_4]$ mM/l	[OH]mM/l	pH
G(C)	21.25	0.01	0.015	42.46	12.52
G(E)	21.46	0.025	0.107	42.68	12.53
H2(C)	5.04	0.386	0.03	9.63	11.93
H2(E)	3.495	0.09	0.375	6.15	11.78
F(C)	31.3	0.3E-3	11.4	39.8	12.47
F(E)	31.56	0.06	12.33	38.4	12.46
E2(C)	15.17	0.001	15	0.339	10.43
E2(E)	15.136	0.09	14.82	0.542	10.63

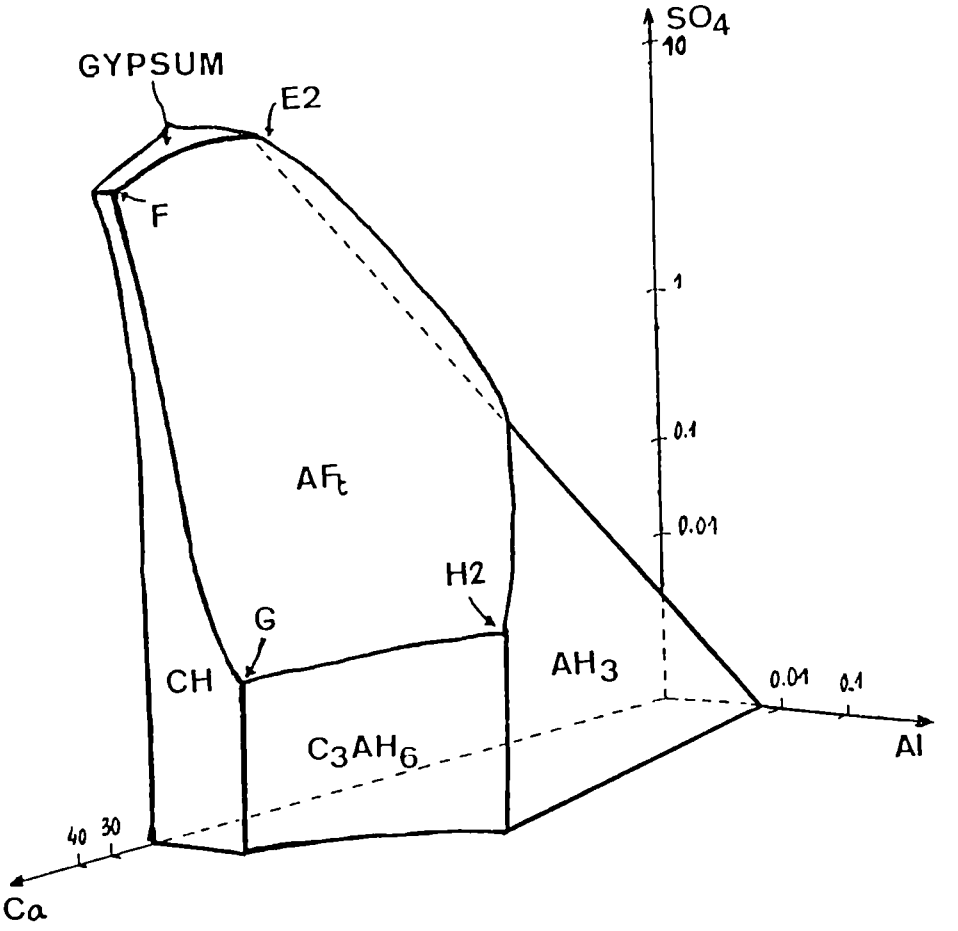


Fig. 1. $CaO\text{-}Al_2O_3\text{-}CaSO_4\text{-}H_2O$ stable system at 25°C.

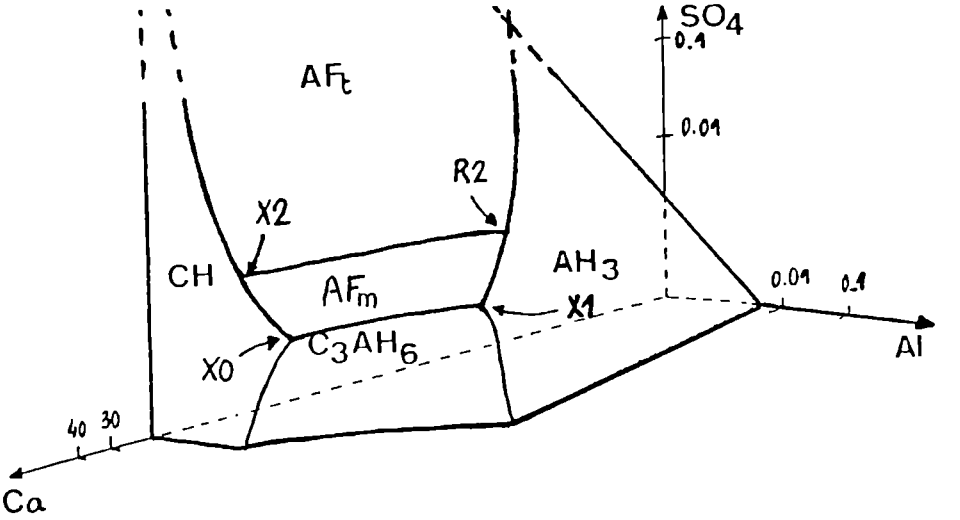


Fig. 2. Possible modifications of $CaO\text{-}Al_2O_3\text{-}CaSO_4\text{-}H_2O$ system at 25°C if AFm,0 is stable.

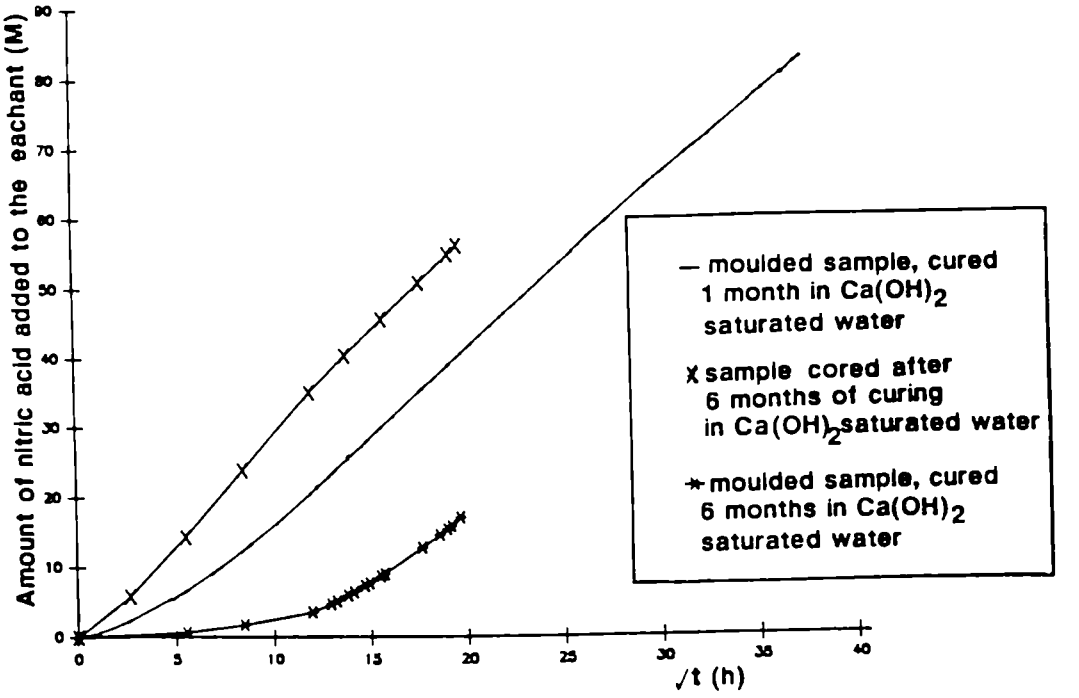
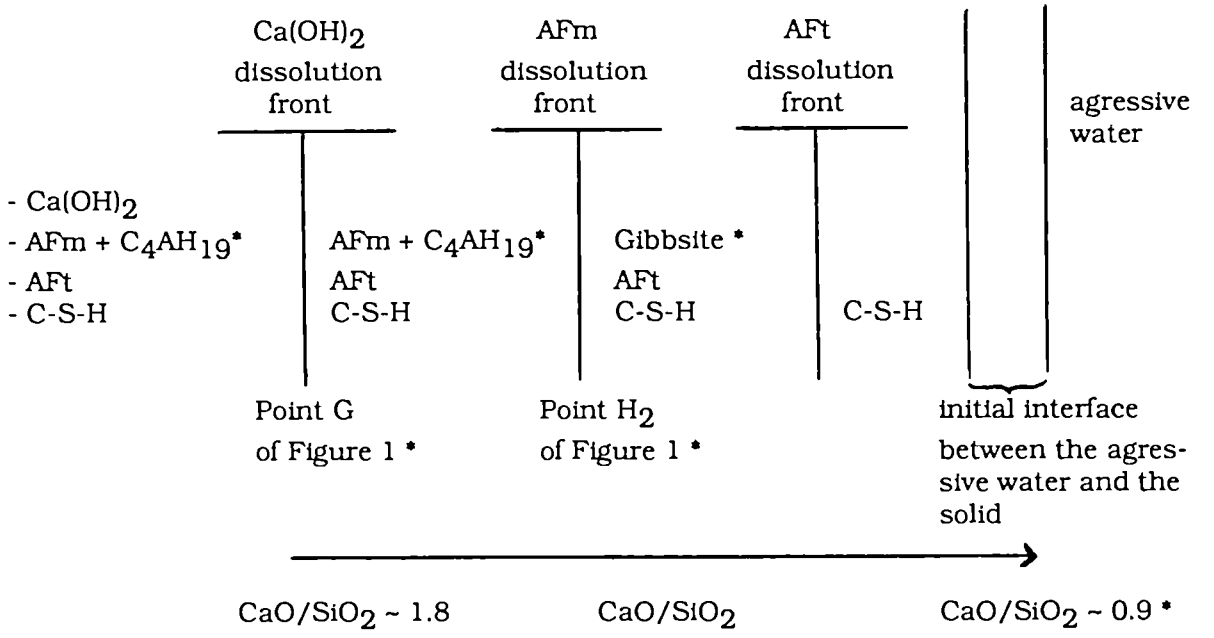


Figure 3. Study of leaching kinetic (Portland cement - w/c = 0.4)
Effect of sample carbonation



* Hypotheses to be confirmed

Figure 4. "Zoning" of the altered part of the cement paste, consisting of an assemblage of multi-mineral domains separated by frontiers

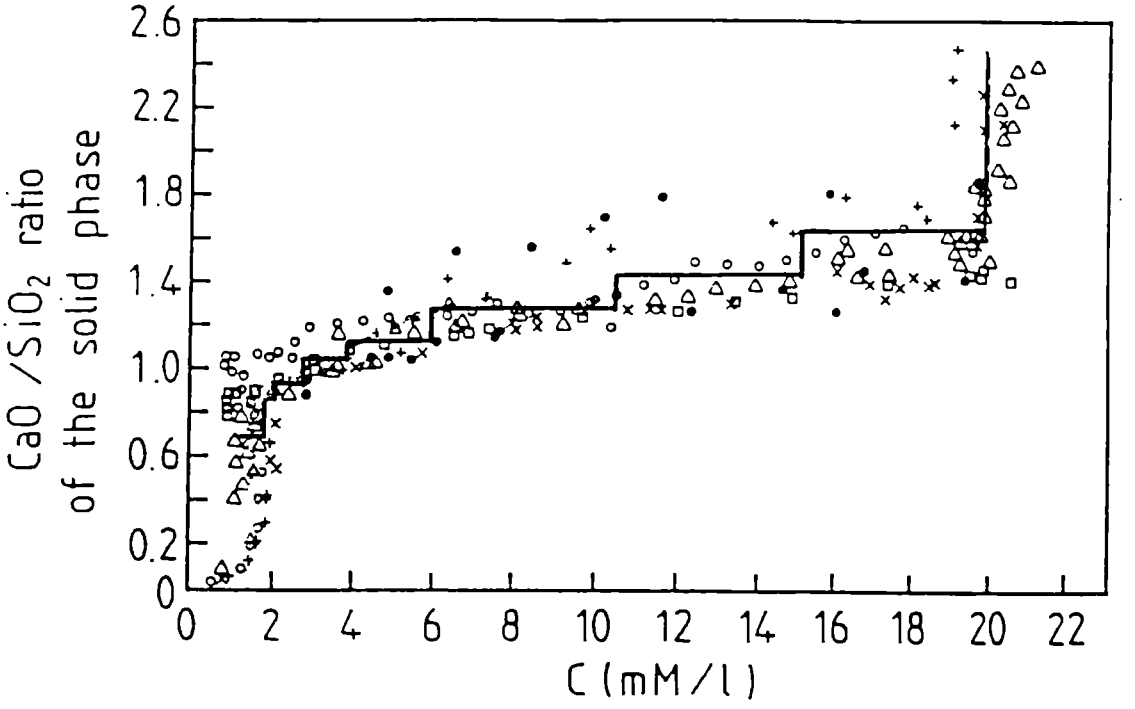


Figure 5. CaO/SiO2 ratio in C-S-H as a function of calcium concentration in solution

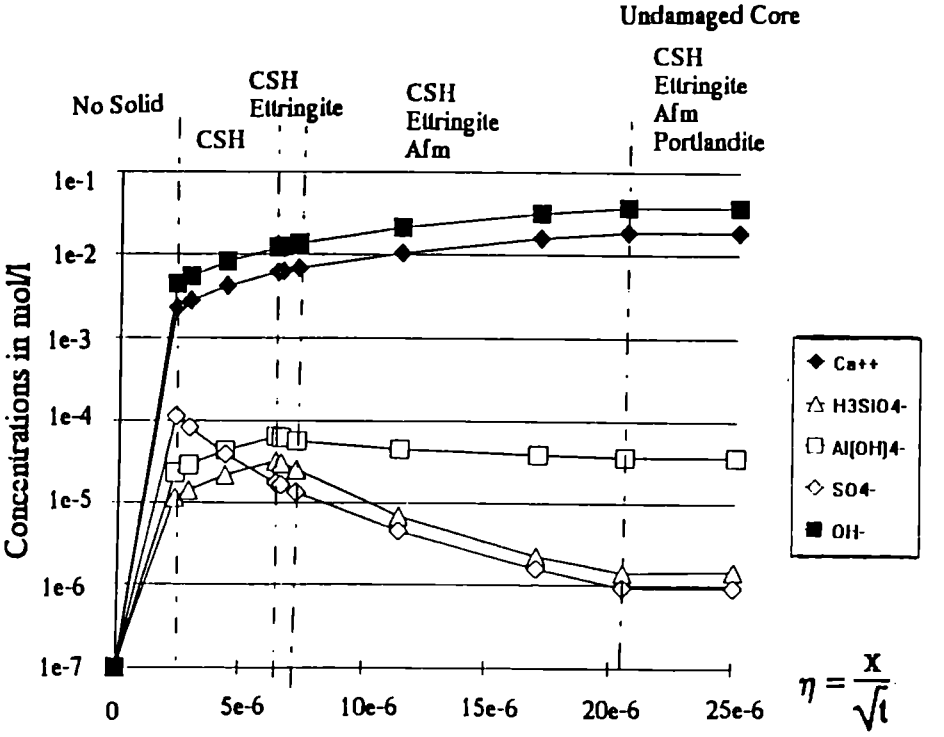


Figure 6. Concentration of the different ion species in solution as a function of the distance from the surface (calculated values)

Title	The Performance of Cementitious Barriers in Repositories
Contractor(s)	AEA Industrial Technology (co-ordinator)
	Riso National Laboratory
	Bundesanstalt für Material Forschung und Prüfung
Contract N°	FI2W-CT90-0040
Duration of Contract	from 1 May 1991 to 30 April 1994
Period covered	1 May 1991 to 31 December 1991
Project Leader	Dr A.W. Harris (AEA), K. Brodersen (RISØ), J. Göbbels (BMA)

A. 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 examinethe 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.

B. 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

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of Advancement

The contract was slightly late in commencing, the official start date being 1 May 1991. All tasks specified to begin at the commencement of the programme have been initiated and are progressing as expected. Task 3, the development of overall models of the behaviour of an inhomogeneous repository is intended to be the culmination of the programme and hence only the first sub-task has commenced.

Progress and results

Task 1 - Crack Healing

Sub-task 1.1 - Experiments on crack healing

An initial set of experiments dealing with the healing of cracks by bicarbonate-bearing water have been completed and a second set initiated. The resulting deposits have been investigated using chemical and microscopic means. The previously existing model of the crack-healing process is being extended to handle the data from these experiments.

Eight experiments were performed to examine crack closure due to calcium carbonate deposition from simulated groundwater flowing through cracks in hardened cement mortar specimens. A typical example of the change in composition of the out-flowing water is shown in Figure 1. The calcium concentration decreases from the high initial value, caused by the dissolution of calcium hydroxide from freshly exposed surfaces in the crack, goes through a minimum and then increases again when the crack walls have been covered by a layer of calcium carbonate. During the latter stage the bicarbonate ion has become the dominant anion in both the out-flowing and in-flowing solutions. The calcium concentration in the in-flowing solution is given by the horizontal line in Figure 1. The sodium and potassium concentrations are due to leaching from the crack walls.

The experimental results have shown that the tendency of the cracks to actually close depends mainly on the crack width. The closure of cracks with widths greater than 0.1 mm appears to be uncertain.

Some simple experiments on the flow of pure, carbon dioxide-free water through high porosity cement mortar have performed. A decrease in the hydraulic conductivity by a factor of about 10 was observed over a period of 60 days. This may possibly be due to the migration of the calcium silicate hydrate (CSH) phase within the specimen.

Task 2 - Cement-groundwater Interactions

Sub-task 2.1 - Diffusive Cement-groundwater Interactions

A literature survey has been initiated to assess previous work in the field of reactions between aggressive solutions and cement-based systems. Initial indications are that there has been considerable work on the behaviour of carbon dioxide, both in the gaseous and dissolved states, as would be expected due to interest in the process of carbonation. The remaining significant body of appropriate research has been concerned with the reaction between seawater and concrete. Seawater can be considered to be a reasonable simulant of the groundwaters expected in many areas. However, the impact of minor chemical species will be sufficient to give rise to considerable differences between the behaviour of seawater and real groundwaters. Previous work has been almost exclusively concerned with structural concretes; materials which differ considerably from proposed backfills.

The impact of the reaction layers formed by interaction with reactive groundwaters on the diffusion and sorption properties of cementitious materials is being assessed. Initial work will concentrate on the reaction between CO_2-bearing solutions and the Nirex reference backfill. A series of specimens are being subjected to CO_2-saturated solutions to form reaction layers. The initial exposures have now been completed and the impact of the reaction on diffusion and sorption will be assessed in the next stage of the task.

The diffusion of tritiated water will be investigated. This diffusant will used because previous work has demonstrated that it is not significantly sorbed by cementitious materials. A tin radiotracer will be used to determine the impact of reaction on sorption behaviour. Cementitious materials exhibit a strong sorption for this element and hence any significant changes in behaviour should be readily observed.

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.

An experimental apparatus for the simulation of long term water flow through materials has been designed and constructed. Relatively high pressure gradients are employed to force significant volumes of water or reactive solutions through small specimens. The ratio of total perfused water volume to specimen volume is of the order of 500. At the groundwater flow rates expected in repository situations, this represents a timescale of the order of millions of years. It is hoped that the experiments will demonstrate the propensity for the formation of preferential flow pathways due to inhomogeneities in the materials and the alteration in flow caused by reactions with aggressive solutions.

Initial experiments have been performed using the Nirex reference backfill grout and pure water. A typical variation in the pH of the perfusing solution with the volume of water passed is shown in Figure 2. A pH of approximately 12.5 is assumed to correspond to buffering by the dissolution of the portlandite (calcium hydroxide) phase in the material.

Sub-task 2.3 - Modelling cement-groundwater interactions

The interaction of groundwater and cement mineral phases during flow within the pore structure is being modelled. The initial models will be set up to simulate the through-flow experiments carried out under Sub-task 2.2. The models will be used to interpret the experimental data. In particular, it is expected that the groundwater-cement interaction will at some stage become limited by the formation of depleted-layers around mineral phases and the formation of reaction products. At this stage the pH buffering and calcium dissolution into the solution will deviate from expectations based on the absolute calcium content and calcium-silicon ratio of the material. It is hoped that this will lead to an assessment of the true buffering capacity of the material and the potential for the formation of preferential pathways.

Typical groundwaters will contain significant quantities of a number of species which can play a part in the formation of imhomogeneities, in particular dissolved carbon dioxide, which will form calcium carbonate, as considered in Tasks 1 and 2.1. In addition, the concentration of magnesium may be significant since the substitution of magnesium for calcium in the portlandite phase gives brucite. This is a relatively insoluble mineral which buffers the pH at a value significantly less than those given by calcium-bearing phases.

The volume change on the formation of brucite is negative, hence preferential flow pathways may develop in addition to the loss of pH. The rate at which brucite is deposited within the cementitious backfill may have significance in the assessment of repository conditions. In addition, the reaction will change the composition of the groundwater, producing a magnesium-free solution in the downstream part of the repository. Consequently, the timescale of the reaction with magnesium is important.

A simple calculation based on the rate of supply of magnesium indicates that the complete conversion of soluble portlandite to insoluble brucite will take 18.4 million years at a groundwater flow rate of 10^{-11} ms^{-1}, a value typical of the low groundwater flow-rate environment of a repository. This significantly exceeds the time required to completely dissolve the expected quantities of portlandite in the Nirex reference backfill and hence the period over which the downstream "reacted" groundwater composition persists will be significant. The timescale of the reaction between portlandite and the groundwater to form brucite is such that the complete conversion of the entire repository portlandite content to brucite is not likely and the impact of the reaction on pH buffering behaviour may not be significant.

The modelling of brucite deposition is continuing using the computer models of cement behaviour to provide a more realistic assessment of the consequences of the reaction and the required timescale. This information will be used as part of the report on groundwater compositions.

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 has been developed /1/.

The model assumes that the pH of the water exiting a crack will be conditioned by the diffusion of species from the material adjacent to the crack. Hence, the pH evolution will be governed initially by the water flow rate and the rate of diffusion and subsequently by the spacing of the cracks. The crack spacing will determine the length of time beyond which the backfill will be "exhausted". The distribution of pH within a crack is predicted to follow an error function. The model provides an analytical solution for the ratio of the time required for the pH to decrease significantly in the water exiting a crack to that required for the pH to drop in the water leaving a homogeneous repository, t_c/t_0. This ratio is given by;

$$\frac{t_c}{t_0} = \frac{\pi L D_i}{J S^2}$$

where L is the crack length, D_i the diffusion coefficent, J the water flow rate and S the crack spacing. The cracks are assumed to be oriented parallel to the direction of water flow. If the crack spacing is small, perhaps less than a metre, the ratio is close to or even greater than unity and crack flow may enhance the buffering behaviour. However, the inverse square dependence on crack spacing means that spacings of the order of 10 m may reduce the period for which the pH is buffered to a useful level by two or more orders of magnitude. This spacing would correspond to only a few or even a single crack through the repository.

The analytical model described above has shown that cracks may exert a significant influence on the evolution of pH of the groundwater exiting a repository and hence may affect the retention of radionuclides. The model will be used as the basis for a more detailed model which will incorporate the effects of reaction layers on the edges of the crack. It is expected that this model will have to be computerised to produce a realistic depiction of the situation.

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/1/ ATKINSON, A., Nirex Safety Study Report NSS/R287 (1991) (draft).

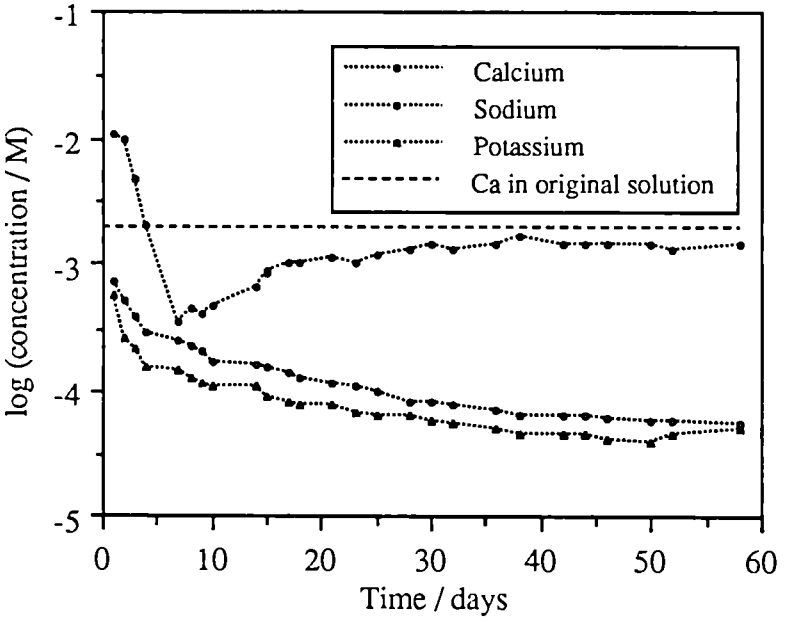


Figure 1 Variation in the composition of the synthetic groundwater after flow through a cracked cement mortar. Horizontal line represents the calcium concentration in the original solution.

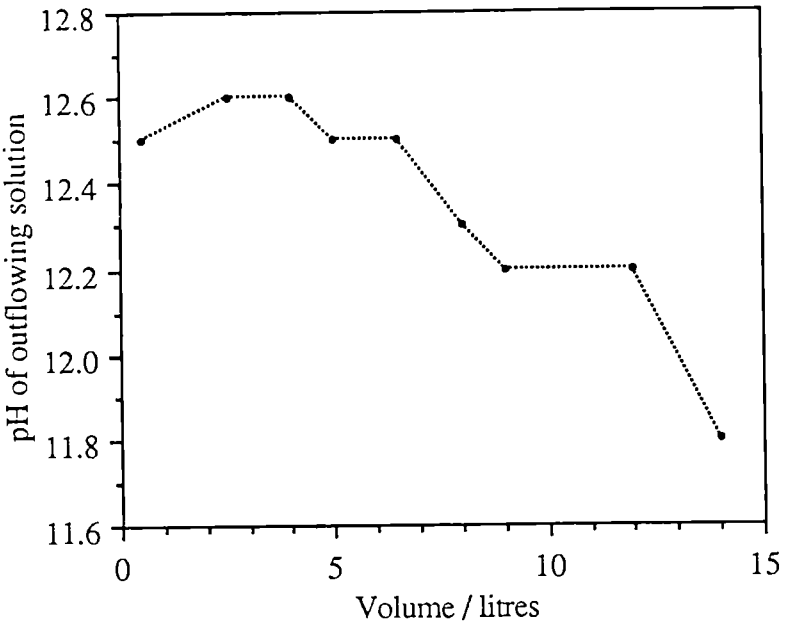


Figure 2 Measured variation in the pH of the solution after perfusion through the reference backfill grout.

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 01-10-91 to 31-12-91
Project leaders :	G. Volckaert (coordinator), C. Mayor, E. Alonso, P. Rivas

A. *OBJECTIVES AND SCOPE*

When considering compacted clay-based materials as engineered barrier in the direct environment of a HLW container, not only the hydromechanical performance needs to be studied but also thermal and hydrochemical evolution needs to be included.

The influence of temperature on the hydraulical, mechanical and chemical field, has been 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

A code to simulate multiphase flow under nonisothermal conditions will be developed and, on the one hand coupled to a chemical transport code and on the other hand to a elastoplastic model adapted to account for expansive soil 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 by heating of the central zone and flow of water in the clay barrier.

Model application

The thermo-mechanical and thermo-chemical models will be used in the interpretation of the above experiments and experiments carried out under complementary programs.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

In the field of thermo-mechanical modelling, a physical model incorporating all important phenomena in the behaviour of an unsaturated swelling clay, has been build up.

In the thermo-chemical literature compiling has started.

A first prototype cell has been constructed and validation tests have started.

Progress and results

UPC (main subcontractor to ENRESA)

The field equations describing the behaviour of an expansive clay barrier in a combined temperature, hydraulic pressure and stress field, have been formulated. Programming of the new code is at an early stage. The field equations have been discretized and the general organization of the program has been established.

On going work concerns the programming effort and the mathematical formulation of the model for expansive soils. It is hoped that the model will be ready for validation when first results of the thermomechanical laboratory tests become available.

CIEMAT

A prototype cell to perform thermo mechanical tests on high density compacted clay blocks has been designed and constructed. A first test to check the suitability of the system without hydration was performed. This includes the selection of thermocouples, interstitial pressure and moisture sensors, and the testing of the installation and heating procedure.

The program of triaxial tests on unsaturated clay consists of two phases : first test are performed at different moisture contents and in a second phase test with suction control will be performed. The selection and checking of a system for suction control based on the counter pressure method is ongoing.

SCK/CEN

The SCK/CEN has been involved in the coordination of this contract with other contracts in the same field such as e.g. contract FI2W-CT91-0098, the BACCHUS test (part B) and contract FI2W-CT90-0033, "Modelling and testing of hydration of clay backfilling and sealing materials".

Title:	Determination of Fissile Material by Neutron Transport Interogation
Contractors:	Forschungszentrum Jülich (KFA) SCK/CEN MOL
Contract No.:	FI2W/0010
Duration of Contr.:	from 01 Nov. 1991 to 31 Oct. 1995
Period covered:	1.11.91 to 31.12.91
Project Leader:	Dr. Reinhard Odoj
- for KFA:	Dr. Peter Filß
- for MOL:	Dr. Pierre Van Iseghem

A. Objectives and Scope

This research is concerned with non-destructive assay techniques for direct fissile material determination in high-density waste material mainly in waste drums. The starting point for further development is an assay system at the KFA /1, 2, 3/ for fissile material determination by active neutron interrogation with an Sb-Be neutron source. In this assay system the fission neutrons are discriminated from the source neutrons by their transport properties in hydrogeneous material. Under typical operating conditions the neutron count rate is proportional to the fissile material content of the investigated sample. The system thus directly determines the fissionable nuclides U-233, U-235, Pu-239, Pu-241. It needs a shielded site for operation. This type of Sb-Be assay system has detection limits between 1 mg and 1 g fissionable material depending on sample size and matrix composition /3/.
Neutron transport calculations were initiated at C.E.N.-S.C.N. MOL to obtain a theoretical understanding and further improvement of this assay system including neutron transport properties in the waste drums.
On the other hand a replacement of the Sb-Be neutron source e.g. by an Am-Li source and an effective recording of the passive neutrons could lead to an improvement and easier handling of the system. The aim of the improved assay system is in any case an easy and reliable estimation or determination of the fissile material content of various packages, mainly waste drums.

B Work Programme

B1 Checking and optimization of the barrel scanner with the Sb-Be neutron source by comparison with neutron transport calculations.

B2 Modification of the system for passive neutron counting capabilities.

B3 Active neutron interrogation with other neutron sources, in particular

- Sb-Be
- Am-Li
- Cf
- Am-Be

B4 Test and performance of the active/passive neutron assay system with actual samples, mainly waste drums from the nuclear fuel cycle.

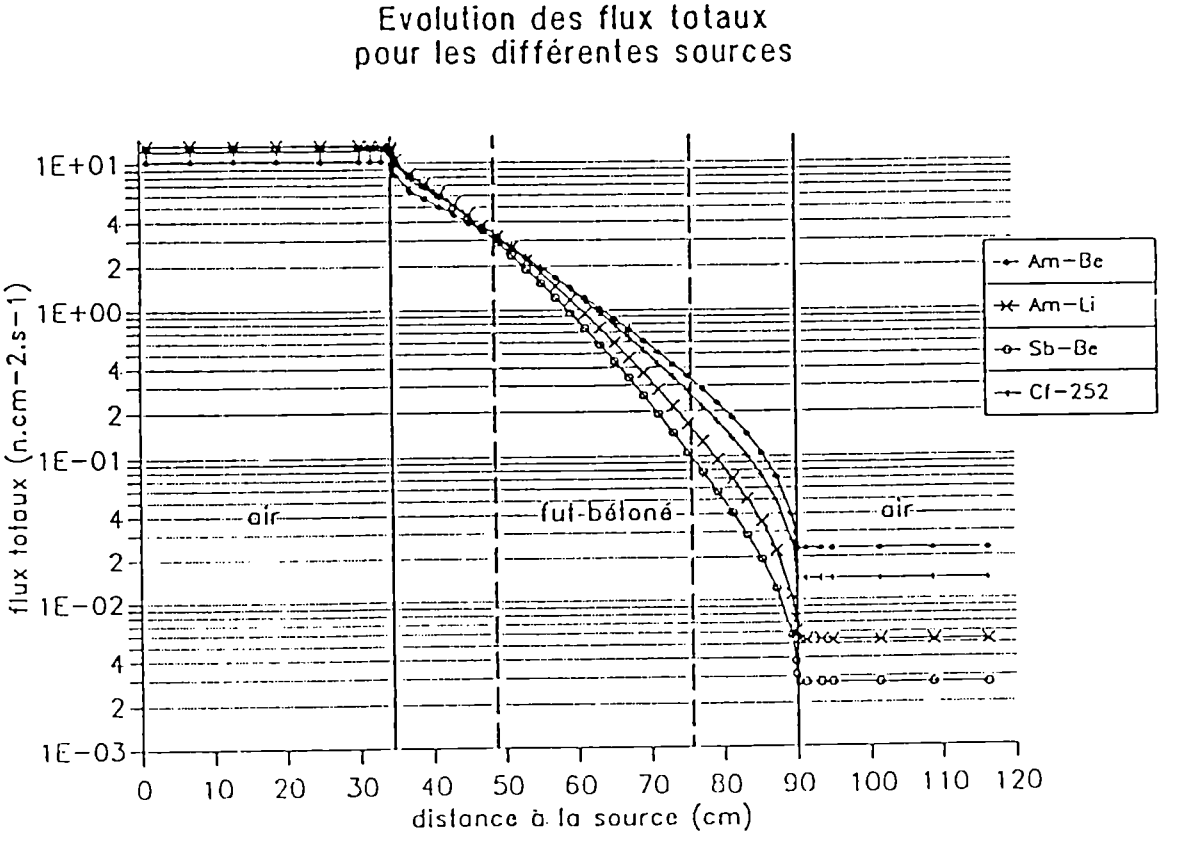


Fig. 1: Total neutron flux in a waste drum filled with concrete

C Progress of Work and Obtained Results

State of advancement

The project started in the second half of 1991 with experiments to characterize alternative neutron-sources and with an exchange of knowledge between KFA and MOL on neutron transport properties. The state of progress is in keeping with the contracted time schedule.

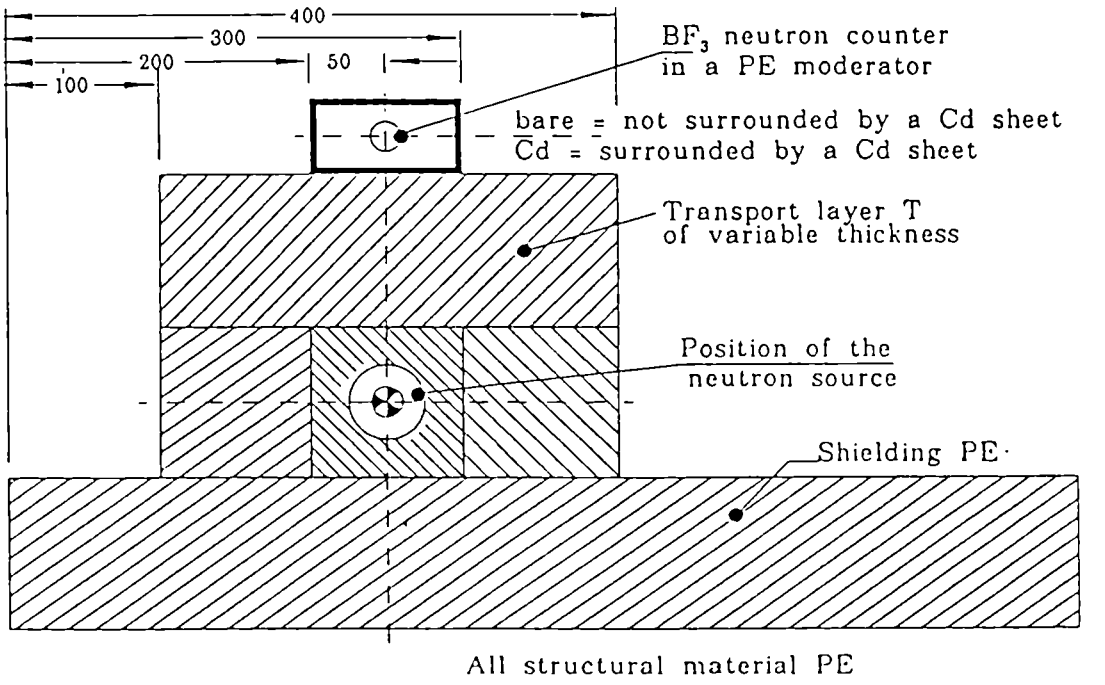


Fig. 2: Setup for the characterization of the thermal and fast neutron field surrounding a radioactive neutron source

Progress and Results

Experimental work with the Sb-Be source is presently hampered because the activation of Sb in a research reactor is in the moment not possible in Jülich at the

moment. Work is therefore currently focused on alternative neutron sources. The calculations at Mol indicate that the alternative neutron sources mentioned above are promising from the point of view of the total and thermal neutron flux in the waste drum /6/. This is shown in Fig. 1. The central neutron flux is higher for Am-Li than for Sb-Be.

Preliminary experiments were performed at KFA with the radioactive neutron sources Am-Li, Cf and Am-Be /7/ and PE as a transport medium.

The basic geometry shown in Fig. 2 was chosen to estimate thermal and fast neutron fluxes.

Table 1: Neutron count rate measured in Fig. 2 with different neutron sources and transport layers of thickness T

Neutron source and respective count rates	**T = 0 cm**	**T = 5 cm**	**T = 10 cm**	**T = 15 cm**
Am-Li source				
Z1 (s^{-1})	1070	185	24	5.3
Z2 (s^{-1})	327	29	4	1.5
Z3 (s^{-1})	743	156	20	3.8
Cf-252 source				
Z1 (s^{-1})	154	42	15	4.8
Z2 (s^{-1})	54	13	5	2.4
Z3 (s^{-1})	100	29	10	2.4
Am-Be source				
Z1 (s^{-1})	97	35	12	6.2
Z2 (s^{-1})	39	12	5	2.6
Z3 (s^{-1})	58	23	7	3.6

Z1 = bare counter = thermal + fast

Z2 = Cd surounded counter = fast neutrons

Z3 = Z1 - Z2 = thermal

These fluxes and their relation are very important for the operation of the neutron counter for fissile material detection and the suppression of the source neutron background. The results for the polyethylene geometry are presented in Table I.

This table shows that from the point of view of flux decrease the Am-Li source is similar to the Sb-Be source. Additionally it has a very high thermal neutron flux (Z3 at T=0) in the vicinity of the source. Combined with a low fast neutron flux at distant positions (Z2 at T = 15 cm), this is a promising prerequisite for the sensitive detection of fast fission neutrons according to the above mentioned assay principle. The fissile material signal is only disturbed to a minor extent by source neutrons which constitute the neutron background level. This kind of investigation therefore has a good chance of being successfully pursued.

List of Publications

/1/ Filss, P.; Jül-Report, Jül 2027 (1985)

/2/ Filss, P.; Journal of NIM 8 (1979) 74 - 79

/3/ Dierckx, R.; Eur. Report EUR 12609 EN (1990)

/4/ Warnecke, E.; Giller, H.; BfS Report ET 3/90 (1990)

/5/ R. Carchon; private communication (Code DIF-IV)

/6/ Mandoki, Robert; Optimisation d'un système de dosage du Pu-239 ...
I. S. I. B-Bruxelles /C.E.N. - S.C.K. - Mol (1990)

/7/ P. Filss; Nucl. Engineering and Design 131 (1991) 271 - 274

Title : Inventory and Characterization of Important Radionuclides for Safety of Storage and Disposal. Correlation with Key Nuclides which are Easy to Measure in Typical Waste Streams

Contractor : CEA Cadarache, ONDRAF/NIRAS, GRS-Cologne, ENEA-Saluggia
Contract No: FI2W-CT90-0034
Duration of contract : 01.05.1991 - 30.04.95
Period covered : May 1991 - December 1991
Project leader : A. Raymond, CEA-Cadarache - R. Swennen (ONDRAF)
W. Müller (GRS)

A. OBJECTIVES AND SCOPE

This contribution to the characterization of the radionuclide inventory of isotopes of critical importance for the safety of storage and disposal comprises a study of the main radioactive waste streams produced in each of the participating countries.

The study has three main objectives:
- checking and standardisation of existing analytical methods for application to real samples from the main waste streams,
- development of some new alternative analytical methods for long-lived beta-emitting nuclides,
- establishing of correlations for critical radionuclides to easily measurable key nuclides.

Only low- or intermediate-level wastes originating from both power plants or reprocessing plants will be considered in the framework of this contract.

Samples of each of the selected waste streams will be analyzed for both easy to measure key nuclides and critical isotopes as determined by the national safety assessments of each participant.

B. WORK PROGRAMME

B.1.
- working organization,
- review of the current situation of the participants,
- selection of the analytical techniques to be used and to be improved or developed,
- list of data to be collected and studied.

(FR-DE-BE-IT)

B.2.
- sampling and measurement of a major waste stream (FR-BE),
- theoretical study of potential correlations for nuclear reactors (DE),
- implementation of a data base (DE),
- from previously available results, collection of results and evaluation for the data base (DE)

B.3.
- realization of a non-destructive measurement system for gamma-emitters (IT)

B.4.
- test and calibration of the non-destructive measurement system

B.5. - inter-country comparison of analytical performances,
- collection of the results for the first selected waste stream,
- first correlation exercise,
- discussion of possible further improvements concerning the analytical methods, the list of isotopes, the number and the representativity of the samples.
(FR-DE-BE)

B.6. - inventory and characterization of the remaining selected waste outputs,
- input of the corresponding results into the common data base,
- theoretical investigations of correlations for the wastes of the reprocessing industry,
- calculation of the correlation factors,
- improvement of existing analytical techniques and development of some new ones
(FR-DE-BE)

B.7. - non-destructive and destructive measurement campaigns on the containers produced at the EUREX plant
(IT)

B.8. - evaluation of the results and discussion
(FR-DE-BE-IT)

B.9. - incorporation of the newly available results concerning some critical radionuclides,
- refinement of results for statistically non-significant or only slightly significant results,
- development of individual evaluation codes for each participant.
(FR-DE-BE-IT)

B.10. - appraisal of the results,
- writing up of the analytical methods,
- testing and improvement of codes for routine applications,
- final evaluation.
(FR-DE-BE-IT)

(FR-France, DE-Germany, BE-Belgium, IT-Italy)

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement :

The programme is progressing on schedule : task B1 is completed while tasks B2 and B3 have started.

Although included in task B5 the comparison of analytical methods has been initiated in 1991. Similarly, the development of new methods (task B6) started by carrying out a new procedure for I-129.

For practical reasons, the common data bank will be supplied by each contractor on a continuous mode and not waste stream by waste stream so that the correlation factors will be continuously updated.

This also means that tasks B5, B6 and B2 (in part) will be largely merged.

Although they were not included in the initial work programme, AEA Technology/Dounreay and ENRESA in Spain took a full part in it by attending the workshops and by starting experimental work similar to that of the original contractors.

The first measurement campaigns (task B.2) started during the second half of 1991 for CEA, ENRESA and AEA Technology.

PROGRESS AND RESULTS

The first 8 months of this programme were mainly devoted to launch if by setting up a working organization, finalizing the list of measurements to be carried out, reviewing the available analytical methods, creating the data banks, building some new equipments.

1. INTERNAL ORGANIZATION

The contractors decided to meet at least twice a year, preferably 2 or 3 weeks before each progress meeting of the working group WG3. A visit of installations related to the programme will be a full part of these meetings. If necessary, bilateral meetings of the contractors will be held at any time and the coordinator will be kept informed.

2. LIST OF MEASUREMENTS

The list of destructive analyses that will be carried out in the frame of this programme is summarized in table I. This list is not definitive but only minor changes are expected to occur during this contract. The list of radionuclides was established from the national safety assessments for each participating country.

Not all of these nuclides are presently attainable with the existing analytical techniques of the contractors.

So, the activity results for these isotopes will be progressively incorporated in the data bank as soon as the necessary analytical procedures become available, as it is expected from the development part of this programme.

The list of non-destructive measurements has been finalized too and mainly concerns the analysis of Cs-137 and of some other gamma-emitters in low/medium - level combustible/compressible wastes from reprocessing plants.

3. REVIEW OF ANALYTICAL METHODS

The analytical methods that should be used in the framework of this programme were reviewed and compared in terms of principles and of detection limits.

The last point, which is of paramount importance for this work, will be discussed in more details at the next workshop.

Concerning the principles of the methods, it was observed that many of the procedures having common steps, it should be possible to standardize them by the end of the contract.

4. DATA TRANSFER AND PROCESSING

An unique from sheet for collecting all experimental results related to this programme has been discussed and finalized (figure 1).

A first data base for storing and processing the results from destructive measurements was created and evaluated from previous data of the contractors while a second one is being created for non-destructive measurements.

Each contractor will be provided before the end of the programme with a software enabling him to compute his own correlation factors. In this respect, GRS established a data sheet listing the minimum PC-equipment necessary to run this software.

5. DEVELOPMENT OF NEW ANALYTICAL TECHNIQUES

A new and rapid procedure for the analysis of I-129 has been developed. This critical nuclide was extracted from acidic solutions by dicyclohexyl 18 - crown 6 in 1, 1, 2, 2 tetrachloroethane in presence of palladium, of potassium iodide and of sodium metabisulfite as reducing reagent. After stirring, the organic phase was separated and analyzed by X-ray spectrometry for I-129 (measuring line : 29,7 keV). After optimization of parameters a detection limit of 50 Bq/l was obtained in an intermediate-level effluent from the reprocessing industry, with a total preparation time limited to 35 minutes for a batch of 8 samples.

6. CONSTRUCTION OR MODIFICATION OF EQUIPMENTS

6.1. NON DESTRUCTIVE MEASUREMENT SYSTEMS

Both ENEA/Saluggia and AEA/Dounreay are building gamma-ray measurement systems for assaying 200 l - drums.

In the case of ENEA, it is a single germanium detector system with a rotative support for the drums and a scanning platform for the detector. AEA selected and built a computerized, segmented scanner system composed of 4 germanium detectors for the activity measurements, of 4 Eu-152 sources to correct for gamma transmission for each drum and of a conveyor. Now in operation, this system has a detection limit of about 80 kBq per drum for Cs-137 in a drum of density $0.2 g/cm^3$ and is capable of analyzing up to 20 drums per hour on a fully automatic mode.

6.2. SHIELDED HOT CELLS FOR SAMPLE PREPARATION (CEA)

Two shielded preparation cells for handling the most irradiating samples related to this programme have been modified or built at CEA/CADARACHE.

The first cell, which is a modification of the CALIMEDON hot cell (shielding : 21 cm of steel, area : 25 m^2; weight : 200 tons), will be used for the preliminary conditioning steps, consisting in :

- receptioning the primary filter cartridges in their transport container,
- dismantling these cartridges,
- sampling small portions (1 to 3g) of each analyzed filter using a specially built, remotely controlled cutting unit (under construction).

The second hot cell, which has been partly built for this programme, will be used for wet chemistry operations, consisting in :

- the solubilization of the small portions of filters coming from the CALIMEDON cell with simultaneous trapping of the volatile radionuclides.
- the sampling and the dilution of the resulting solutions for transfer to the analytical laboratories.

7. QUALITY CONTROL

It was decided that duplicated samples will be taken whenever possible and kept in each participating laboratory until the end of the programme as reserve samples; they will be used in the case of unexplained discrepancies for reanalysis.

8. VISIT OF INSTALLATIONS

Included in the workshops were the visits of the following installations :

- in Cadarache ("Department of waste management and disposal") :
  * the "LECC" Laboratory (non-destructive testing, lixiviation and preparation hot cells),
  * the radioanalytical chemistry laboratory,
  * the inductively-coupled plasma mass-spectrometry equipment.
- in Saluggia :
  * the EUREX reprocessing plant

TABLE I : DESTRUCTIVE MEASUREMENTS

Plant	Reactor type	Sample type	Number of samples	H-3	C-14	Fe-55	Ni-59	Ni-63	Sr-90	Mo-93	Zr-93	Nb-93m	Nb-94	Tc-99	Pd-107	Ag-108m	I-129	Cs-135	Alpha TRU	Pu-241	Gamma-emitters
Cruas	P	CF	3	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
Cruas	P	PR	3	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
Cruas	P	PC	2	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
Dampierre	P	CF	3	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
Dampierre	P	PR	3	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
Dampierre	P	PC	2	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
EDF 3	P	CF	3	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
EDF 3	P	PR	3	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
EDF 3	P	PC	2	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
Doel	P	CF	3	X	X		X	X	X				X	X			X	X	X		X
Doel	P	PR	5	X	X		X	X	X				X	X			X	X	X		X
Doel	P	EC	5	X	X		X	X	X				X	X			X	X	X		X
Doel	P	PC	2	X	X		X	X	X				X	X			X	X	X		X
Tihange	P	CF	3	X	X		X	X	X				X	X			X	X	X		X
Tihange	P	PR	5	X	X		X	X	X				X	X			X	X	X		X
Tihange	P	EC	5	X	X		X	X	X				X	X			X	X	X		X
Tihange	P	PC	2	X	X		X	X	X				X	X			X	X	X		X
Trillo	P	PR	3	X	X	X	X	X	X			X	X	X			O		X	X	X
Trillo	P	EC	5	X	X	X	X	X	X			X	X	X			O		X	X	X
Vandellos	P	PR	3	X	X	X	X	X	X			X	X	X			O		X	X	X
Vandellos	P	EC	3	X	X	X	X	X	X			X	X	X			O		X	X	X
Garona	B	PR	6	X	X	X	X	X	X			X	X	X			O		X	X	X
Garona	B	EC	3	X	X	X	X	X	X			X	X	X			O		X	X	X
Cofrentes	B	EC	6	X	X	X	X	X	X			X	X	X			O		X	X	X
EDF A	P	EC	2	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
EDF B	P	EC	2	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
EDF C	P	EC	2	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
EDF D	P	EC	2	X	X		X	X	X	O	O	X	X	X	O	O	X	O	X	X	X
Eurex		CW	15						X					X					X	X	X
Total:			**106**																		

Legend:

X	Analysed
O	Progressively included if planned methodology research successful
CF	Coolant filters
EC	Evaporator concentrate
PC	Primary coolant
PR	Primary resin
P	PWR
B	BWR
CW	Low-level compressible wastes

FIGURE 1

1. Form Sheet for the Data Transfer

- Name of Plant : _____
- Unit Number : _
- Kind of Plant : _
- Kind of waste : __
- Kind of Sample : __
- Density of sample : _.__
- Residual humidity : _.____
- Type of Data : _
- Dimension : _
- Source : _____
- Date of Sampling : __.__.__
- Date of Measuring : __.__.__
- Country : __
- Events
  Water Chemistry : ___
  Defects on Fuel Elements : ___

2. Form Sheet for the Data Transfer
Measurement Step (/)

H3 _._E___	Rb87 _._E___	Cs135 _._E___	U232 _._E___
Be10 _._E___	Sr90 _._E___	Cs137 _._E___	U233 _._E___
C14 _._E___	Zr95 _._E___	Ce141 _._E___	U234 _._E___
Na22 _._E___	Nb94 _._E___	Ce144 _._E___	U235 _._E___
Cl36 _._E___	Tc99 _._E___	Eu152 _._E___	U238 _._E___
Ar39 _._E___	Ru106 _._E___	Eu154 _._E___	Np237 _._E___
Ca41 _._E___	Ag108m _._E___	Eu155 _._E___	Pu238 _._E___
Mn54 _._E___	Ag110m _._E___	Pb210 _._E___	Pu239 _._E___
Fe55 _._E___	Cd113m _._E___	Ra226 _._E___	Pu240 _._E___
Co58 _._E___	Sb125 _._E___	Ac227 _._E___	Pu241 _._E___
Co60 _._E___	Sn126 _._E___	Ra228 _._E___	Pu242 _._E___
Ni59 _._E___	I125 _._E___	Th230 _._E___	Pu244 _._E___
Ni63 _._E___	I129 _._E___	Th232 _._E___	Am241 _._E___
Se79 _._E___	Cs134 _._E___	Pa241 _._E___	Am242m _._E___

Cm242 _._E___
Cm244 _._E___
Cm245 _._E___
Cm246 _._E___
Cm247 _._E___
Cm248 _._E___

Title : Inventory and Characterization of Important Radionuclides in Reactor and Reprocessing Waste

Contractor : GRS Cologne, AEA Dounreay, ENRESA Madrid
Contract No: FI2W-CT-91-0109
Duration of contract : October 1991 - September 1995
Period covered : - January - December 1991
Project leader : W. Müller, GRS - Germany (coordinator)

A. OBJECTIVES AND SCOPE

The study contributes to the characterization of the radionuclide inventories in different waste streams from nuclear power plants and from reprocessing plants. The study is meant as a complement to the existing CEC contract No FI2W-CT90-0034 entitled "Inventory of relevant radioisotopes - non-destructive determination by correlation with key nuclides".

The main objectives of the study are :

- checking and standardisation of existing analytical methods for application to real samples from the main waste streams,
- establishing of correlations for radiologically critical nuclides to easily measurable key nuclides.

For the following types of waste samples will be analyzed for both easy measurable key nuclides and other radiologically critical nuclides :

- evaporator concentrates from PWRs and BWRs,
- ion exchange resins from PWR primary coolant clean-up systems,
- ion exchange resins from BWR reactor water clean-up systems,
- solid low-level reprocessing wastes from the Dounreay facility.

Sample preparation and measurement techniques will be checked and optimised. For the measurement results and the parameters necessary for their interpretation data banks will be established and evaluated.

B. WORK PROGRAMME

B.1.
- review of the current situation of the participants,
- list of information to be collected and studied,
- final choice of the list of radionuclides to be measured.

B.2.
- sampling and measurement of a major waste stream,
- destructive measurement campaign on reprocessing wastes,
- establishing of the data bank for reprocessing waste data,
- development of mathematical and program tools,
- collection of available results from previous measurements and evaluation.

B.3.
- preparation of simulated waste drums,
- test of the measuring equipment with simulated wastes.

B.4.
- comparison of the test results with ENEA measurements,
- discussion of consequences for equipment calibration and interpretation of the results of routine assays.

B.5.
- collection of the results of the measurements campaign resp. the first waste stream,
- first correlation exercise,
- discussion of further improvements

B.6. - measurements of the remaining waste streams,
- recording of corresponding results in the data bank,
- improvement of analytical and mathematical/computational methods.

B.7. - routine assays of reprocessing waste drums with gamma scanner.

B.8. - interim assessment of the obtained results and necessary supplementary work.

B.9. - final evaluation of results,
- discussion of results and conclusions,
- development of individual evaluation codes for each participant.

B.10. - appraisal of the results,
- final documentation,
- testing and optimisation of codes for routine applications.

Title:	Construction and Testing of a Computer Tomography Assembly for Routine Operation
Contractors:	Forschungszentrum Jülich (KFA)
Contract No.:	FI2W-CT90-0009
Duration of Contr.:	from September 91 - August 1995
Period covered:	1.7.91 to 31.12.91
Project Leader:	Dr. Reinhard Odoj

A. Objectives and Scope

The product control institution (PKS) of the BfS located at KFA has been appointed to perform quality control of rad-waste packages for the licensing authorities prior to disposal in an underground repository. This can either be achieved by nondestructive and/or by destructive analysis of the waste packages. Fig. 1 shows the gamma scanner Gernod which is the most important NDA system for activity determination in large volume drums. The decisive criterion for acceptance is knowledge of the specific activity of the conditioned waste and the total activity of the waste package. Determination of the specific activity and total activity is straightforward in the case of a homogeneous waste matrix of densities between 0.1 and 3 g/cm3. It is strongly dependent on the μ/ϱ values of the transmitting matrix for the registered gammarays. In the case of shielded structures or inhomogeneous fillings, the calculation must include shielding factors which range from 1 for homogeneous filling to 20. A better estimation of the shielding properties by computer tomography is the aim of this contract. The objective is a direct measurement of the distribution of ϱ and μ/ϱ or μ in shielded structures and heterogeneous fillings of waste drums by attenuation measurement and computer tomography. The application of computer tomography (CT) to the scanner will be done in close cooperation with groups in KFA and BAM.

B Work Programme

B1 Modified scanner with active gamma ray screening capability
-addition of a gamma source
-addition of count rate measurement/evaluation for CT application

B2 Computer tomography for samples of uncommon composition and density distribution
-design of technical equipment
-suitable isotopic source
-software adjustment

B3 Comparative test measurements

C Progress of Work and Obtained Results

State of advancement

The project started in the second half of 1991 with

- considerations for an extension of the existing gamma scanner for inclusion of computer tomography
- tests for the application of existing software programs on this computer.

The literature survey led to a reconsideration of the optimum mechanical layout and the best kind of radiation source. The installation of the software is still underway because of difficulties with the different structure of the computers used.

Progress and Results

The basic gamma scanner is shown in Fig. 1. The geometry for passive gamma-registration and the formula used for evaluation are shown in Fig. 2 and discussed in detail in /1, 2/. These formulae show that knowledge of μ/ρ and the actual distances d and h are important for evaluation. They are to be obtained by computer tomography. In order to supply the necessary input data for transmission computer tomography a discretization of the barrel plane by screening is necessary (Fig. 3 /3/).

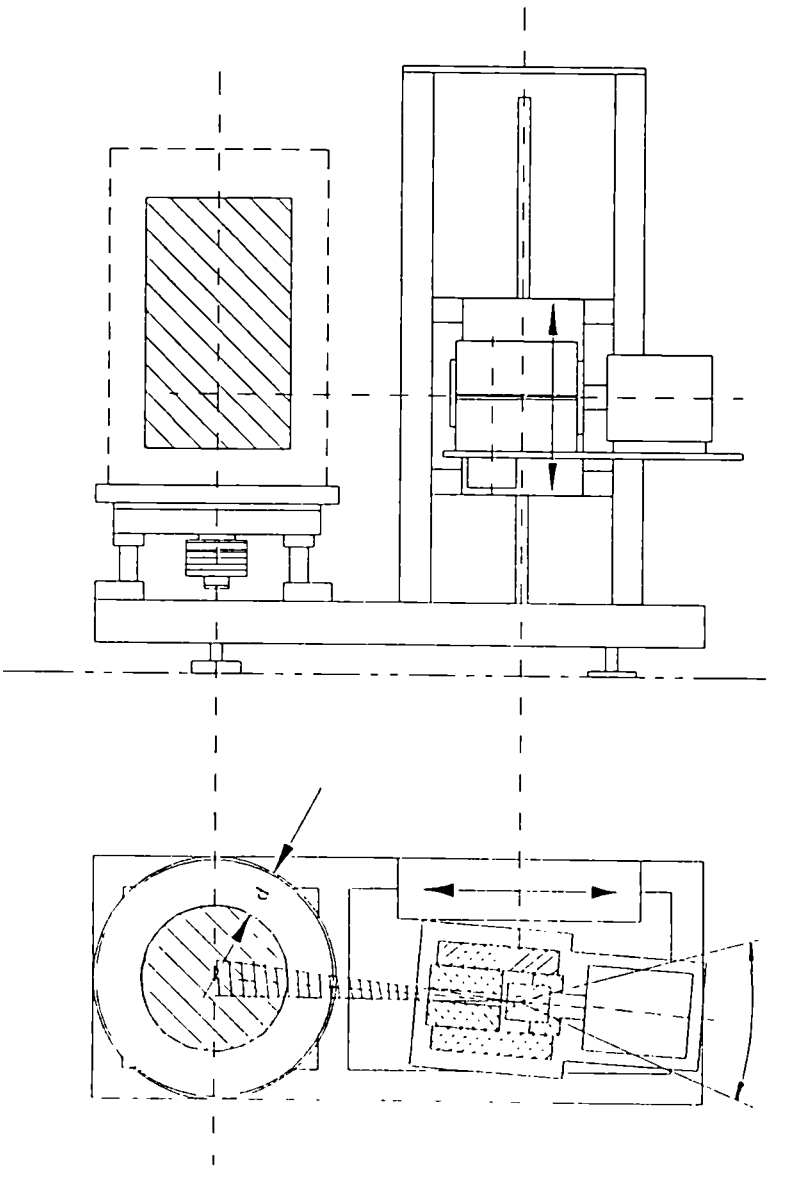


Fig. 1: The gamma scanner Gernod with its swivelling capability

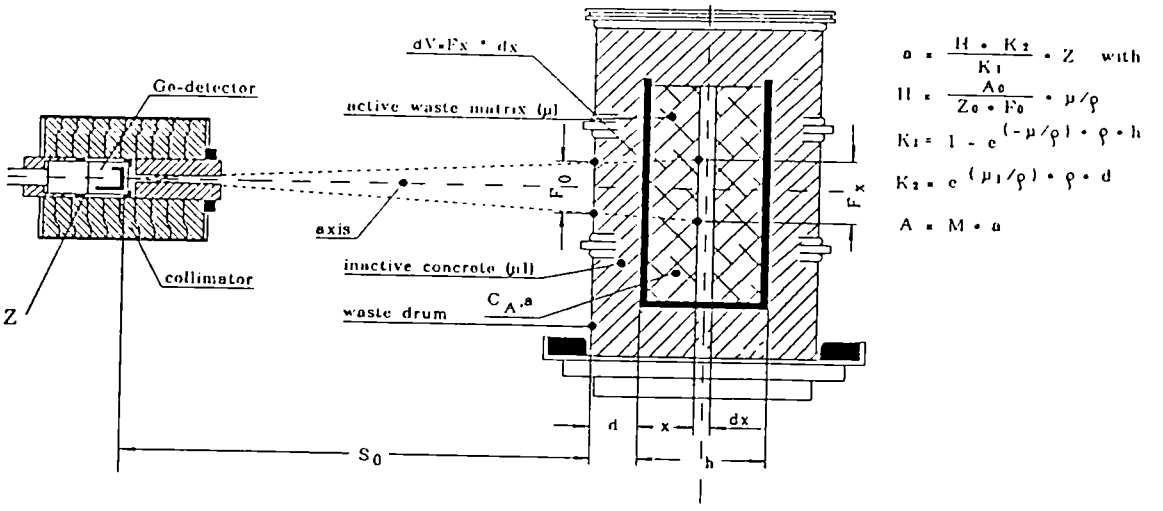
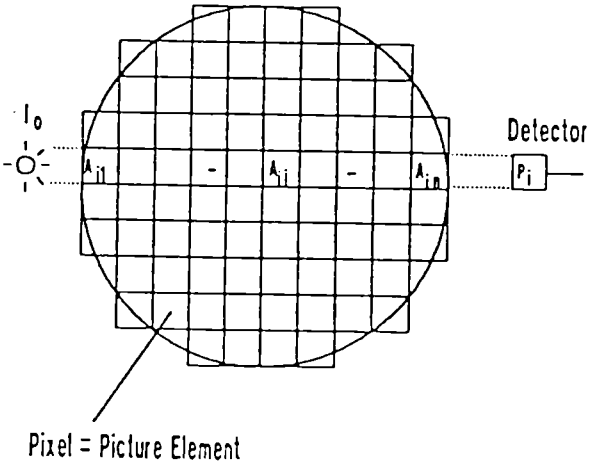


Fig. 2: Measuring geometry for Gernod and formula set for evaluation



I_0 - γ source

A_{ij} - activity (ECT) or

coefficient of absorption (TCT)

P_i - projection value (measurement)

Fig. 3: Discretization of the drum plane into pixel elements

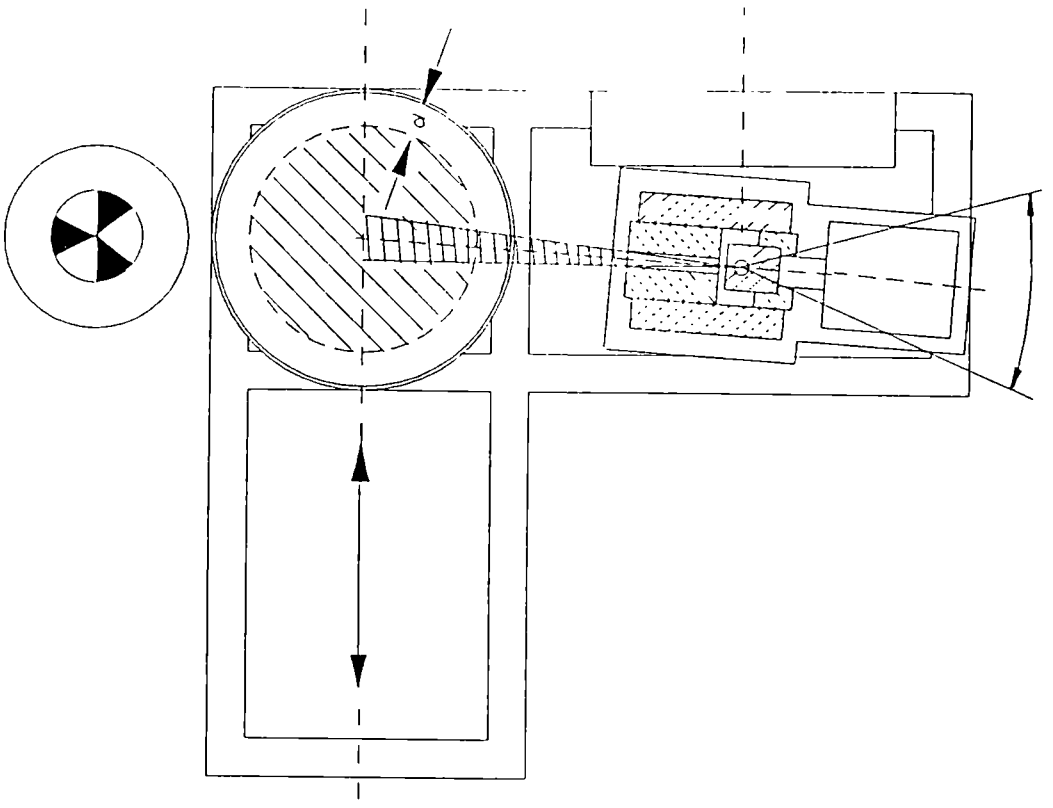


Fig. 4: TCT with translation and rotation

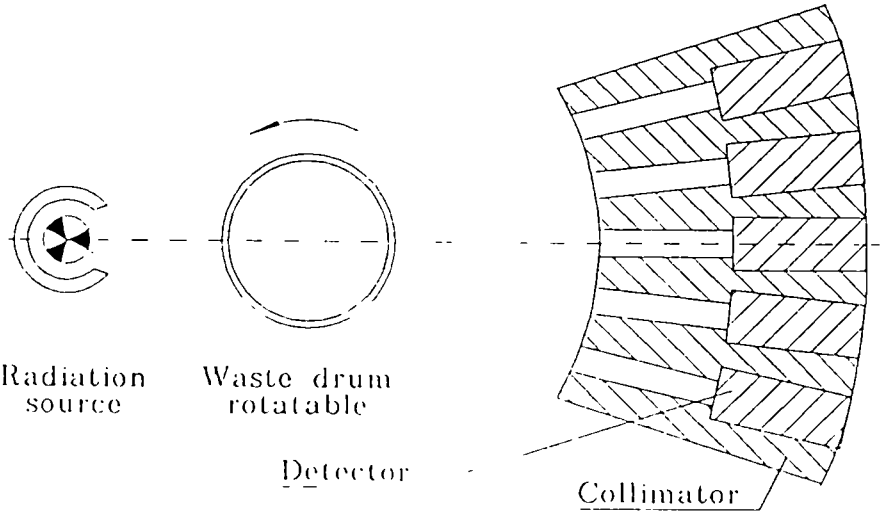


Fig. 5: TCT with a multidetector bench

This can either be achieved by translation and rotation as shown in Fig. 4 or by rotation in front of a multidetector system of the type shown in Fig. 5 (from /4/). Both possibilities are under consideration. A test facility with a sledge movement was constructed mechanically.

On the other hand work was started for the installation of the unfolding program (pixel elements, see Fig. 3) onto the Gernod scanner. It will probably be necessary to separate the PC for operation of the scanner and the PC for the unfolding process. If this is achieved, emission computer tomography (ECT) would be possible with the swivelling capability of the existing gamma scanner for planes of constant density. In order to test ECT, a multidensity drum is going to be prepared with holes for the insertion of radioactive samples.

References

/1/ Filss, P.; Kerntechnik 54 (1989) 198 - 201

/2/ Filss, P.; Ollig, H. in Odoj. R
Eur 13885 EN (1991)

/3/ Duwe, R.; Jansen, P.
NED 130(1991) 89 - 102

/4/ Reimers, P.; Goebbels, J.; Ketschau, A.
BAM 316-5691 UWA 5821/1 (1985)

Title: Behaviour of Low Level Radioactive Waste under Fire Accident Conditions

Contractor:	AEA Technology
Contract No:	FI2W/CT90-0014
Duraction of contract:	from 1st October 1991 to 30th September 1993
Period covered:	1st October 1991 to 31st December 1991
Project Leader:	Dr R P Bush

A. OBJECTIVES AND SCOPE

The objective of the work to be undertaken within this project is to provide information on the release of radionuclides from 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 will be used to enable the response of packaged LLW under various conditions to be predicted.

Little information relevant to this topic is available . The approach to the project (based on large-scale inactive tests, mathematical modelling, and small-scale active experiments) is similar to that used in a previous study of immobilised intermediate level waste, but will take 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

A literature review will be carried out 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

Mathematical models will be developed and validated for the thermal behaviour of LLW, including heat and mass transfer, gas diffusion and combustion phenomena.

1.2.3 Large-Scale Testing

Large scale thermal tests will be carried out on simulated LLW in two stages: 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.

1.2.3 Small-Scale Thermal Tests

Small-scale thermal tests will be made to determine the releases of radionuclides from radioactive samples of individual LLW components and mixtures, under conditions to be defined from the modelling work and large-scale tests.

C. PROGRESS OF WORK AND RESULTS OBTAINED

1. State of Advancement

In the first three months of this project, work has been limited to collecting information for the literature review, planning the work on mathematical modelling, and preparing specimens for the first tranche of full-scale tests. It is expected that the review and planning activities will be completed on target. Sufficient specimens of supercompacted 'pucks' of simulated LLW are available for the first phase of the large-scale tests. Detailed plans for the conditions and measurement schedules for these tests are being compiled.

2. Progress and Results

2.1 Literature Review

Information for the literature review is still being collected and assessed, particularly in the area of the physico-chemical properties of LLW components and how these might affect release mechanisms.

Only a relatively small amount of work has been published on the release of radionuclides from LLW materials. Most of this is not directly relevant to fire accident situations involving packaged LLW.

Some work has been published on the releases of uranium and plutonium from contaminated surfaces similar to those found in LLW, and from combustible materials. The experiments sought to simulate fires in reprocessing plants, rather than conditions relevant to fire accidents during waste management operations. This means that air flow rates in most of the experiments were relatively high, and the results indicate that these high flow rates were responsible for the dominant release mechanisms involved.

Releases from contaminated non-combustible surfaces are very dependent on air velocity, but no results are available under static conditions. For combustible materials contaminated with uranium oxide and uranyl nitrate, an air flow of 50-100cm/s increased the release fraction by a factor of over 100 compared to static conditions.

Other work with combustible materials shows that release fractions for uranium are very dependent on the nature of the substrate, but less dependent on the chemical form of the uranium contaminant. The release mechanism probably depends strongly on the physical and chemical processes occurring in the substrate material.

The release fractions measured for uranium and plutonium in all these studies are generally well under 1%.

Rather less published information is available on the release of fission products from LLW. In experiments on supercompacted trash, over-poured with mortar, release fractions for caesium and strontium of 0.2% and 0.01% respectively were measured, with waste temperatures reaching 400°.

The physical and chemical effects of supercompaction are likely to influence release mechanisms, but no measurements to evaluate such phenomena have been reported. Similarly, the effect of immobilisation on release fractions has not been studied systematically, although measurements have been made on some immobilised waste forms.

2.2 Preparation of Specimens for Large Scale Tests

Two waste compositions were selected for the preparation of specimen supercompacted 'pucks' for the initial large scale thermal tests. Waste 1 contained a high volume fraction of cellulose (present as paper towels) together with smaller amounts of plastic and rubber and a low level of metal. Waste 2 represents harder laboratory trash that has already undergone incineration. It contains no cellulose, but is about 30% by volume metal and glass together with a mixture of chlorinated and unchlorinated plastics and rubbers.

For each waste composition, six 200 litre drums have been filled with carefully prepared mixtures of components in a manner to give as homogeneous a product as possible. The waste was lightly compacted during drum filling to achieve the target density in each case. After filling and closing, the drums were supercompacted at a force of 2000 tonnes using a Hansa High-Force Supercompactor. A volume reduction factor of between 3 and 6 was obtained. No visible breach of contaminent occurred for any of the Waste 1 drums, but there were minor penetrations of two of the drums containing the harder Waste 2.

The pucks are now being stored for the large-scale thermal tests, to be conducted in 1992.

Title: NON-NUCLEAR NON-DESTRUCTIVE TESTING METHODS TO DETERMINE FREE WATER, GAS PRESSURE AND MATRIX LEVEL IN WASTE DRUMS

Contractor: Battelle-Institut e.V., Frankfurt am Main,
Federal Republic of Germany

Contract No: FI2W/CT90/0018

Duration of contract: Sept.1991 to Aug. 1995

Period covered: Sept.1991 to Dec. 1991

Project leader: J. Eisenblätter

A. OBJECTIVES AND SCOPE

The aim of the work is the further development of various non-destructive testing (NDT) methods to check for unwanted substances in complete packages filled with radioactive waste. In detail, the following properties are to be determined from outside:

- free water at the matrix surface,
- the matrix level, and
- the internal gas pressure.

The NDT methods to be applied were found to be suitable in a previous screening study (Contract No. FI1W/0227). These methods are: the acoustic impedance measurement, Lamb wave attenuation measurement, a pressure compensation method, and the analysis of cover resonances. Main objects of investigation are full-size 200 litre drums of 1.5 mm wall thickness (rolling hoop and rolling channel drums) filled with concrete to different levels.

B. WORK PROGRAMME

Task 1: Acoustic impedance measurement (AIM) for detecting matrix and free water levels

Task 2: Measurement of Lamb wave attenuation to determine free water and matrix levels

Task 3: Measurement of internal gas pressure using the pressure compensation method

Task 4: Measurement of internal gas pressure by cover resonance frequency analysis

Task 5: General work: Preparation of the test objects, information exchange, evaluation of the results, and reporting

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Because of some delay in the contract settlement with the German Ministry of Science and Technology, the work could not be started before November 1991. Besides some sonsiderations of the general design of a testing unit including all four NDT methods and besides sample preparation the work has concentrated so far on task 1 and 3 of the programme: AIM for detecting matrix and free water levels and the pressure compensation method for measurement of internal gas pressure.

Progress and results

Task 1: Acoustic impedance measurement (AIM) for detecting matrix and free water levels.

A small hammer is electromagnetically excited so that it periodically strikes the steel sheet. The reaction of the hammer is determined by means of a piezoelectric accelerometer applied to the hammer. The excitation system and the sensor are integrated in a probe head which is manually passed along the structure. The signal obtained is not only influenced by the steel sheet but also by the material behind the drums' wall, e.g. concrete, water, or air. The signal parameter best suited to discriminate between different filling materials was found to be the phase shift between excitation and AIM signal /1/. There was a good discrimination between matrix and either water or air. But the discrimination between water and air was rather poor.

For better discrimination an additonal vibration sensor should be provided which receives the sound generated by the hammer. Work has started to select and test appropriate air-borne and structure-borne sound sensors. The sensor selected has to be integrated later-on into the probe head. These experiments are not yet finished.

Task 2: Measurement of internal gas pressure using the pressure compensation method.

Overpressure inside a drum creates a deflection of the cover. External counterpressure exerted on the drum cover can compensate this deformation. In the device built in the previous project /1/, this counterpressure was exerted by a pressure plate loaded by a hydraulic cylinder. As this device is very heavy, it is planned to reduce its weight substantially and to make it easier to handle. Work has just started, thus no results are available up to now.

Task 5: General work.

Ten rolling hoop or rolling channel drums already existing at Battelle were prepared for the experiments.- Information exchange took place at the Task 3 - Progress Meeting at Nov. 20, 1991 in Brussels and at two visits at the quality control group of the KFA Jülich.

/1/ Eisenblätter, J., Schäfer, P., Weiß, R., Battelle Frankfurt
Report No. BF-R-40.047-4 (1990)

Title: Test for process control during treatment of low and medium radioactive waste in practise

Contractor: KEMA N.V., KFA Jülich, Laborelec
Contract No.: FI2W/CT90/0019
Duration of contract: 1 January 1991 to 31 December 1994
Period covered: January 91 - December 91
Project leader: H. Cornelissen (KEMA N.V., coordinator), R. Odoj (KFA), Mr. Roofhooft (Laborelec)

A. OBJECTIVES 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, tracability and the possibility for corrections of the system.

This research project referes 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 with 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

Subject 1: Process descriptions of waste treatment
Subject 2: Chemical characterization
Subject 3: Radiological qualification test methods
Subject 4: Mechanical and physical qualification tests
Subject 5: Validation of test methods and evaluation.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

As part of subject 1 in the research programme a study was made with respect to process descriptions in relation to waste pre-treatment, cementation, packaging, transport and preparation for storage of low and medium wet radioactive waste from nuclear power plants in Belgium, Germany and the Netherlands and the corresponding quality actions and requirements. Also literature survey was made of chemical and radiological characterization methods (subjects 2 and 3).

Progress and results

1. Process descriptions

For the Belgian, German and Dutch situation typical processes and approaches concerning cementation of low and medium level radioactive waste are described. A typical example of a waste treatment process is given in figure 1.

With respect to the Belgian situation the nuclear waste treatment system of the Doel power station is described with emphasis on liquid waste and encapsulation /7/. The main treatment process is evaporation although flocculation facilities are also available. Boric acid is recovered as much as possible. Non recoverable liquid effluents are devided in three main categories:
- chemical waste
- miscellaneous waste
- regeneration effluents.

The main types of solid waste are:
- filter cartridges
- ion exchange resins
- solids (equipment parts).

The routes followed by the different wastes are described. The formula's used to calculate the composition of concrete are also given. The formula's are based on pH, density and boron content. The aggregates are lime, cement, sand, gravel and concentrate from the evaporators.

In Germany the waste producers/conditioners must demonstrate that waste forms or waste packages of adequate quality are produced if certain operating conditions which have to be specified in a handbook, are observed. They have to show that the instrumentation is adequate and that the control measures assure the observance of the operating conditions so that the fulfillment of the acceptance requirements can be guaranteed. The acceptance requirements, specified for the "Konrad" repository include requirements on activity inventory, product properties and container/package properties. The product requirements (e.g. on cemented wastes) are dependent on activity inventory and/or container/package properties. Activity inventory and product properties are usually verified by a combination of analyses/tests at the primary waste, observance of certain process parameters and/or tests/checks at product samples. During examination of process and procedures for process qualification it has to be shown that fulfillment of the repository requirements is guaranteed by the combination/range of measures/methods determined for normal operation. Factors which probably can influence behaviour/state of setting are listed and discussed in /6/.

In the Netherlands two nuclear power stations are operated. In Dodewaard it concerns a 58 MWe BWR and in Borssele a 477 MWe PWR. For both power plants the treatment of low and medium radioactive waste is described in /1/. The wastes are cementated by in-line mixing at Dodewaard and by mixing in drum at Borssele. The cementated waste is packaged in 200 liter steel drums which for the Dodewaard situation are placed in concrete 1 000 liter containers. The transport and interim storage is organized by COVRA (central organization for radioactive waste). COVRA also defines requirements and procedures. Standard there are tests for process control during conditioning and qualification tests for the wastes to be cementated.

2. Chemical and physical characterization

Chemical and physical properties of liquid radioactive waste are of great importance for the quality assurance (QA) for storage and disposal of this waste in a cemented form /2/. In its final form, the following properties of the waste are mentioned to be of importance for quality assurance:

- solidity, like the strength of the matrix and the absence of cavities
- amounts of radionuclides present
- leaching behaviour of the various radionuclides from a package
- leaching behaviour of substances that may influence a disposal facility, like complexing agents
- the inflammability and possible release of burnable gases like hydrogen
- content of poisonous substances
- completeness of the fixation (no free liquid)
- exothermal reactions after cementation. A high temperature in the core of a matrix during hardening, may result in cracks in the cement matrix or decomposition of organic materials like anion exchangers.

Chemical characterization comprises an indication of the concentration of various substances which are present in the raw waste. Physical characterization consists of an indication of the magnitude of various physical parameters like temperature, density, water-cement ratio and electrical conductivity of that waste.

A number of substances can be mentioned that will decrease the setting of cemented waste. Some substances have a favourable influence on the cementation process or neutralise the bad influence of others. Additives to improve the processability are well known. With these additives the water content can be lower so more waste can be put into a container. Formation of free liquid can be prevented with special agents. The bad influence of borate can be reduced by addition of lime. Fixation of organic ion exchangers can be improved by addition of silica dust. Acids can be neutralised with lime; oil can be absorbed in vermiculite. This substance also improves the resistance against leaching. Fibres can be added to improve the strength, however, they must be corrosion-resistant against the highly alkaline pore water.

From the literature survey it can be concluded that there exists a lot of experience on the influence of chemical and physical properties of raw liquid waste on cemented product quality. An exact determination of the influences for general purpose is not very useful because there are many local differences in waste compositions, cements and certification criteria.

3. Radiological qualification

The radioactivity in LLW and MLW can have an negative effect on the physical properties of a cement matrix. Self-irradiation can influence the waste-form leachability, the compressive strength and the hardness depending upon the waste composition, the type of irradiation, the dose rate and the total dose. Radiolytic degradation can result in the production of gases which may pressurize the waste container /4/.

The radiological characterization of the raw liquid radioactive waste is preferable above immobilized waste. Therefore measurements have to be done before any LLW or MLW is mixed with other LLW or MLW, cement or additives. The measurements on the raw waste stream has to detect the homogenity of the radioactivity and the amount of radioactivity. It is not possible to measure online the specific radioactivity of all the relevant nuclides. Therefore the measurements will be concentrated on the gamma emitting nuclides Co-60, Cs-137 and Ce-144. These nuclides are called the "key nuclides". With the aid of scaling factors the specific activity of other relevant nuclides in the waste is calculated. Technical difficulties have to be solved in the development of an adequate gamma spectrometer system and the linking of all different hardware parts to one process control system.

It is evident that all measurements are influenced by the specific detection geometry and waste properties such as the density, mean atomic weight and specific activity.
Special interest is given at:
- detection of the key nuclides Co-60, Cs-137 and Ce-144
- permitted uncertainties (homogeneity, activity)
- dynamic range of the instruments.

It can be concluded that the online radiological characterization of LLW and MLW is in principle possible by assessment of the specific activity of key nuclides with gamma spectroscopy and the use of scalings factors for all other relevant nuclides. The method can be used to optimize the definition of the waste container.

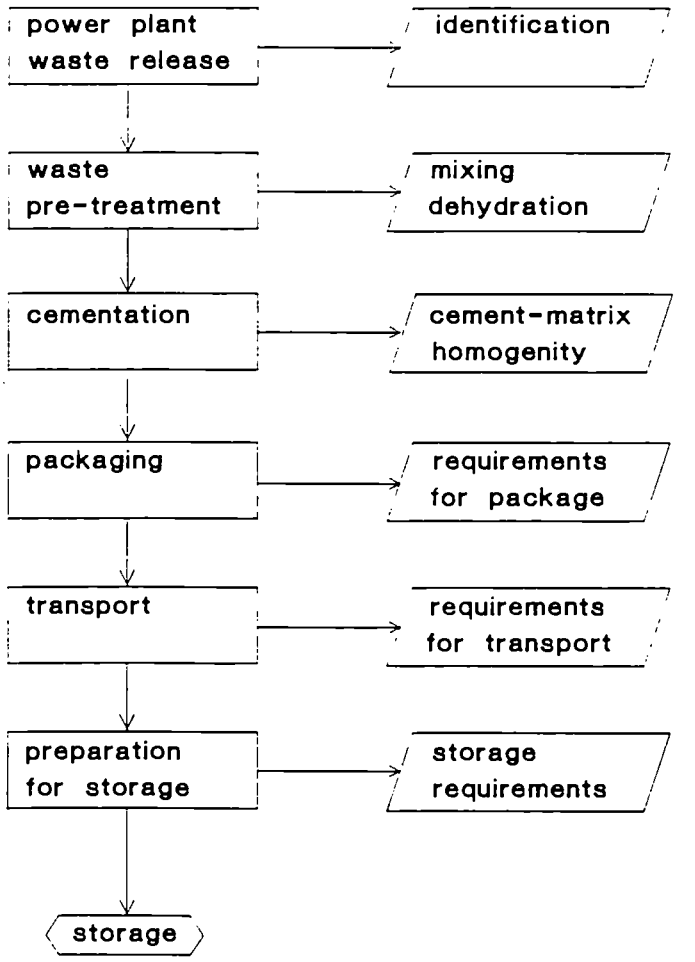


Figure 1 Example of radwaste treatment process and quality actions

List of publications

/1/ KEMA, 1991a (Cornelissen, H.A.W. and Vogelsang, H.W.J.). Process descriptions of radwaste treatment in the Netherlands. Report number 12376-CBP 91-678.

/2/ KEMA, 1991b (Boekschoten, H.J.C. and Bloem, P.J.C). Chemical and physical characterization of liquid radioactive waste in relation to its solidification: a literature study. Report number 12376-CMO 91-3051.

/3/ KEMA, 1991c (Cornelissen, H.A.W.). Tests for process control during treatment of low and medium radioactive waste in practice. Intermediate report 1. Process descriptions. Report number: 12376-CBP 91-903.

/4/ KEMA, 1992a (Velzen, L.P.M. van). Test for radiological characterization of low and medium radioactive waste during process control in relation with its solidification. Report number 12376-MOS 92-3626.

/5/ KEMA, 1992b (Cornelissen, H.A.W.). Tests for pocess control during treatment of low and medium radioactive waste in practice. Anual report 1. Process description and inventories of chemical and radiological characterizations. Report number:12376-CBP 92-21.

/6/ KFA, ICT/PKS report, 1991 (Odoj, R. and Wolf, J.). Cementation of radioactive wastes in Germany.

/7/ LABORELEC, 1991 (Roofthooft, R.). Nuclear waste treatment at the Doel power station.

Title : Establishment of Non-Destructive or Partially Destructive Test Procedures for Determining the Characteristics of Waste Containers

Contractor : CEA Cadarache
Contract No: FI2W/CT90/0021
Duration of contract : 1.10.91 to 30.9.95
Period covered : 1.10.91 to 31.12.91
Project leader : J. Misraki

A. OBJECTIVES AND SCOPE

In the frame of the low and medium wastes packages' characterization, this programme proposes to establish examination procedures relying on acquired experiences about real packages.
One of the main objectives is to limit to the minimum the destructive examinations; non destructive examinations having the advantage of not causing secondary wastes.

B. WORK PROGRAMME

After inquiries in various characterization laboratories in France, we propose to write assay procedures for the following :

B.1. - sampling methods for analysis (alpha, beta, gamma, ...),
B.2. - gamma scanning on packages,
B.3. - microorganism actions on embedded wastes (bitumen, cement),
B.4. - water content measurement in embedded wastes (Solo 40),
B.5. - radiolysis gas measurement,
B.6. - thermoluminescent dosimetry,
B.7. - tomography's applications on waste packages checking, (filling rate, homogeneity, bulk density, integrity of the package after aggressive assays, ...).

C. PROGRESS OF WORK AND OBTAINED RESULTS

C.1. Sampling methods for analysis

With the aim of establishing any standardization in the samples preparation, for analysis, in the low and medium activities wastes packages characterization, a first procedure heading :
General sampling methods for analysis (alpha, beta, gamma, ...) is presented.
It defines the preparation techniques useful in the manufacturing, applied to :

. physical, chemical and mechanical assays,
. scale 1 packages assays.

It applies to embedded wastes, in hydraulic binder, or polymer matrix. In every case, a dissolution procedure of the embedded wastes are proposed.

On the other hand, with regard to the size and the number of test samples to make, propositions are made to resolve various restraints that are imposed on the characterization assays.
Indeed, when the assays must be carried out in series, (e.g. mechanical resistance after thermal cycles or x-ray expositions) it is necessary that sample test sizes are compatible among themselves. This makes it easier, in particular, for direct comparisons between obtained results, without using corrective factors. On the economic and exploitation levels, this standardization reduces the multiplicity of necessary equipments (mould, coring tools, ...).
Lastly, a method for expressing results, packages identification and sample follow up is proposed. The detailed procedure will be sent to the members of Task 3 in the beginning of February 1992.

C.2. Gamma-scanning

The fundamental safety rules and technical specifications of radwastes management organisms ask, in the frame of waste packages characterization, to measure mass activity and the distribution of this in the coated wastes. This is the radioactive homogeneity determination. A non destructive method is applied in a routine way to the packages. A mobile installation called "MARCO" (Mesures d'Activité des Radioéléments dans les Colis de déchets) permits the checking of this feature. A detailed procedure will be sent to the members of Task 3 at the end of April 1992.

References

/1/ DRDD/SCECA/CA 90/05 Ind O Mars 1990
Evaluation, characterization and quality assurances of low and medium waste forms

/2/ DRDD/BECC 87/217 du 24 juin 1987
Recueil des fiches techniques "Caractérisation des Déchets FA-MA"

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 1.9.1991 to 31.8.1995
Period covered:	from 1.9.1991 to 31.12.1991
Project Leader:	Dr. Peter Reimers (BAM, coordinator), C.Lierse (TU) A. Jouan (CEA)

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 5 years. A new scanner particularly designed for waste drums goes into operation at TU Munich in theese days. 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 ndt-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 which fullfills 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 is to improve its knowledge about the vitrified HLW packages.
The previous methods of investigation were destructives ones and the glass blocks were always dissociated each other.
The purpose of this investigation is to develop a non-destructive tomographic examination method in order to appreciate the real status of the glass block in the metallic canister.
The principal defects which 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.

B. WORK PROGRAMME

The work programme comprises 3 main tasks correlated to the 3 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 consists of 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.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The state of advancement of the project is in due course of the contracted time schedule. The contract of the third partner TU Munich will start in April 1992.

Progress and results

At BAM the first version of a scanning programme for digital radiography (DR) with a multidetector system has been written and is in the test phase now.
Name of the programme: Schattenbild.c
Function of the programme: The programme builds a shadowgraph from the attenuation profiles measured by a computertomograph with a multi-detector array. Because the angular distance between the individual detectors is rather big (1°) it is necessary to move the object across the beam with step width = beam width.

Description of the programme:
-the measured intensity values are multiplied with a reference factor for each detector to calibrate the detector response
-the image parameters are read from the header of the data file
-the image size is calculated
-the number of twice measured intensity values is calculated
-the header of the image file is written
-main loop of the programme:
-the calibrated attenuation values are put together while the the twice measured values are skipped.
Further improvements:
It is planned to expand the scanning range in such a way that larger objects which exceed the diameter of one fan of 31 detectors can be X-rayed. This will be possible by adding one or more fans at either side of the zero fan. To avoid geometrical distortions of the projection image it is necessary to turn the obect by an adequate angle.

The linac detectors used up to now transferred the analogue output signal to a common AD convertor. Due to the necessary cable length of 15 m the signal to noise ratio was so bad that the dynamic measuring range was limited to 1:1000. To improve the situation it is planned to digitize the measuring signal immediately in each individual detector. Each detector is coupled to a separate controller by a digital data way. The controller can store and integrate output data until they are assumed by the DAC (data acquisition computer). Due to the high processing speed of the controller and the fast data transfer between detector and controller (250 kwords/sec) the linac can be operated with the highest frequency possible (800 Hz). By this means the measuring time will be shortened by a factor of 3. In the working period the printed circuit board layout was designed and the components ordered.

CEN VALRHO has fabricated 3 canisters with vitrified waste simulate on the R7 vitrification prototype at Marcoule.
- Block A (canister n° 71)
This block was fabricated with a very slow cooling control cycle (3 °C.h^{-1}) from 800 °C to 30 °C in order to obtain a monolithic glass block. It will be used as reference for leaching tests.
- Block C (canister n°67)
- Block D (canister n°72)
These two blocks were elaborated with the thermal scenario of an industrial vitrification facility (R7)
- Preheat empty canister for 3 hours at 650°C;
- Cast the first 200 kg melt;
- Cast the second 200 kg melt and switch off the preheater;
- Remove package from preheating furnace two hours after the second cast;
- Natural cooling.

The 3 canisters were sent to BAM for tomographic examination.

The various scenarios implemented to produce the blocks of glass are descibed in the following table 1.

table 1: Specification of the glass blocks to be investigated

N°block	Description		Experimental validation
A	monolithic bloc	easier investigation on cracks reference block for leaching	Static leaching
B	abundant molybdic phase	quantification of molybdic phase	Dynamic leaching
C	standard thermic scenario + consolidation treatment	effect of consolidation comparison with A block	Static leaching
D	standard thermic scenario + liquid impregnation	estimation of the water penetration in the cracks	/

Title: High Energy Accelerator Tomography (HEAT)

Contractor: AEA Technology Harwell, UK - BAM Berlin, Germany
Contract No.: FI2W/CT-90/0107
Duration of contract: January 92 - December 94
Period covered: 1 January 1992 to 21 January 1992
Project leader: Martyn Sené

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 it should provide discrimination against the low-energy background from the objects significantly improving the signal to background ratio in measurements. Secondly, the discrimination against background should also relax the detector shielding requirements. Finally, 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.

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. Set up Harwell linac tomography tests.
WP6. Harwell linac tomography tests.
WP7. Assess implementation of HEAT at BAM.

WP8. Transport counters to BAM and set up.
WP9. Demonstration of HEAT at BAM with simulated waste.
WP10. Assessment of technique and final report.
WP11. Coordination of project.

C.PROGRESS OF WORK AND OBTAINED RESULTS

With a start date for the contract of 1st January 1992 this report covers only a short period. Preliminary work has begun, however, on work packages WP1 (design of Cerenkov detectors) and WP4 (design and manufacture of collimators and bremsstrahlung convertor).

C.1 Design of Cerenkov detectors

As a first step towards design of the Cerenkov detector system electron bremsstrahlung spectra from a linac, hardened by transmission through typical waste packages, are being calculated along with gamma-ray intensities and spectra from representative high-level wastes. These represent respectively the signal and background in a Computed Tomography measurement. The preliminary calculations clearly show that, as expected, detectors intrinsically insensitive to lower energy gamma-rays will provide a susbtantially improved signal-to-background ratio over those sensitive across the whole range of gamma-ray energies.

Work has also started on modelling the expected response of a Cerenkov detector system to gamma-rays in the energy range from 0 to ~10MeV. The calculated response will be folded with the representative signal and background spectra described above to assess the discrimination of the detectors against the low energy background.

In many detectors the magnitude of the detector output is directly proportional, over a large energy range, to the total kinetic-energy of the ionising particles entering or produced in the material of the detector. Electrons from gamma-ray interaction in scintillators are a good example of this. In contrast the response of a Cerenkov detector to electrons exhibits a low energy threshold and a non-linear response up to an electron energy of several MeV. Calculations of the response of several candidate Cerenkov media to electrons in the energy range up to ~10MeV have been carried out and compared with previous work reported in the literature. When calculating the expected gamma-ray response the electron response has to be combined with modelling of the interaction of gamma-rays in the Cerenkov medium. Preliminary calculations have been carried out of the response of several Cerenkov media to gamma-rays taking into account Compton scattering and pair production interactions of the gamma-rays in the Cerenkov medium. To simplify these preliminary calculations approximate expressions for the electron/positron kinetic energy distribution following gamma-ray interaction were used in place of the full expressions.

The results, including the individual contribution of the two different gamma-ray interactions are shown for SF5 (lead) glass in figure 1. The calculations take into account the quantum efficiency of the photocathode of a typical bi-alkali photomultiplier (PMT) but ignore the effects of light collection from the Cerenkov medium by the PMT . The results clearly illustrate that the threshold and non-linear response for electron detection is reflected in the expected gamma-ray response.

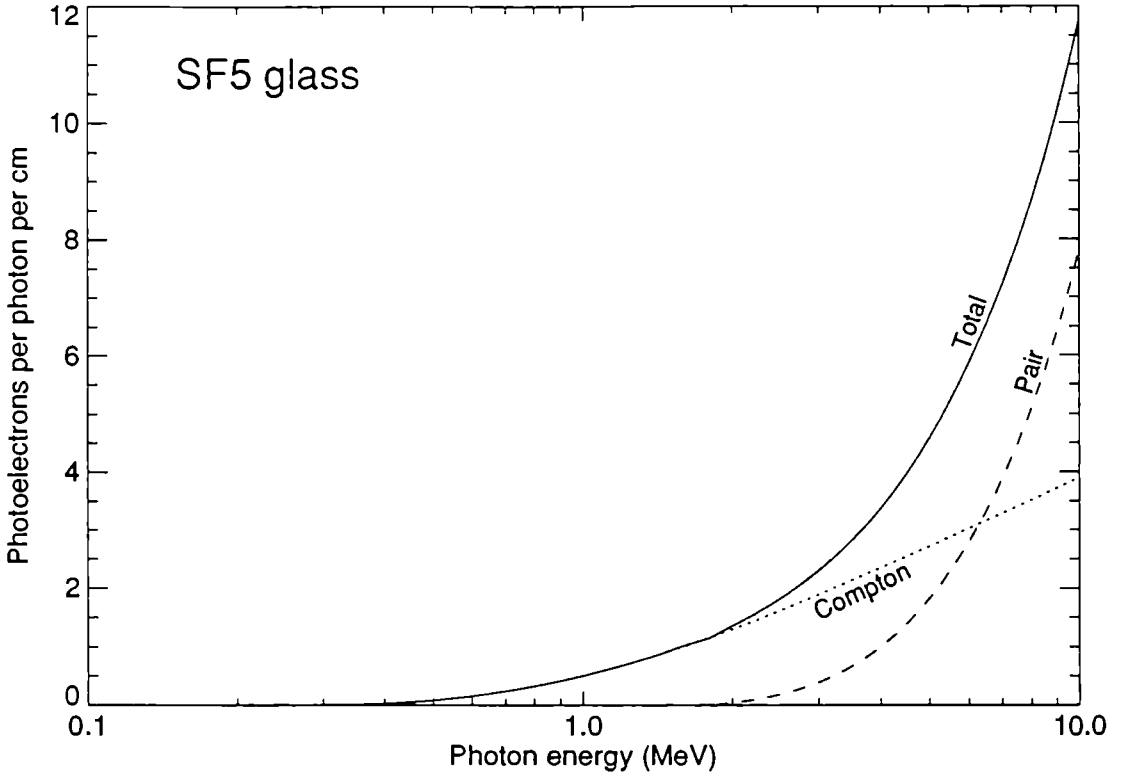


Figure 1: Calculated Cerenkov response of SF5 (lead) glass to monoenergetic gamma-rays using simple aproximations for Compton scattering and pair production interactions and assuming a light collection efficiency of 100%.

These preliminary calculations will be repeated using the more accurate electron/gamma-ray transport code EGS4. This will enable the effect of detector material, shape and size on the total light output to be investigated in more detail.

As design of the Cerenkov detectors proceeds the effects of light collection by the PMT from the Cerenkov medium and suitability of the overall detector geometry for computed tomography will also be taken into account. The selection of a photomultiplier or photodiode together with design of a suitable signal processing system will also be considered. Confirmatory measurements with laboratory sources and the Harwell electron linac HELIOS will be carried out at various stages of the design.

C.2 Design of the Collimators

Discussions are underway between Harwell and BAM to fix the gross features of the geometry of the tomography tests to take place in phase 2 of the programme. This will enable detailed design of the detector collimators to proceed. Important parameters are the bremsstrahlung radiator to collimator distance, the angular separation of the detectors and the range of opening area of the collimators. Compatability of the adopted geometry with the BAM tomography facility is also an important consideration so as to enable the demonstration measurements in phase 3 to be carried out with the minimum of modifications.

Part A3

Task 4

"Disposal of radioactive waste: Research to back up the development of underground repositories"

Topic 1	Research related to sites and their characterisation
Topic 2	Design, construction and operation of underground repositories
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

Topic 1 **Research related to sites and their characterisation**

FI2W/0046 Simulation of the effect of long-term climatic change on groundwater flow and the safety of geological disposal sites

FI2W/0049 Experiment on groundwater flow in a fracture for the validation of chemistry/hydromechanical transport of coupled models for fractured media

FI2W/0050 Experiments in 600m borehole in the Asse II salt mine

FI2W/0051 Evaluation of a self-consistent approach to fractured crystalline rock characterisation

FI2W/0063 INTERCLAY II - A coordinated benchmark exercise on the rheology of clays

FI2W/0075 Paleoclimatological revision of climate evolution and environment in western mediterranean regions

Topic 2 **Design, construction and operation of underground repositories**

FI2W/0048 Development of borehole seals for high-level radioactive waste (DEBORA Project)

FI2W/0064 The refinement of soil gas analysis as a geological investigative technique

FI2W/0072 Methodology studies on the sealing of boreholes

FI2W/0076 MEGAS: modelling and experiments on gas migration in repository host rocks

FI2W/0093 Gas pressure build-up in radioactive waste disposal : hydraulic and mechanical effects

Topic 3 **Radionuclide migration in the geosphere**

FI2W/0039 Continuation of the migration experiments (laboratory and in-situ)

FI2W/0065 CHEMVAL-2. A coordinated research initiative for evaluating and enhancing chemical models used in radiological risk assessment

FI2W/0071 OKLO-Natural analogue for transfer processes in a geological repository

FI2W/0079 Development of a model for radionuclide transport by colloids in the geosphere

FI2W/0080 Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment

FI2W/0081 Fundamental studies on the interaction of humic substances

FI2W/0082 Rock matrix diffusion as a mechanism for radionuclide retardation natural radioelement migration in relation to the microfractrography and petrophysics of fractured crystalline rock - Phase 1

FI2W/0083 Effects of humic substances on the migration of radionuclides: complexation of actinides with humic substances

FI2W/0084 Colloid migration in groundwaters: geochemical interactions of radionuclides with natural colloids

FI2W/0085 The role of colloids in the migration of elements

FI2W/0097 The role of colloids in the transport of radionuclides in geological media

Topic 4 Modelling in the presence of uncertainty and management of data in non homogenous systems

FI2W/0086 Study of coupling between "fractured medium" and "porous medium" flow models

FI2W/0087 Methods of handling non-homogeneities at different scales in radionuclide transport

FI2W/0088 The treatment of uncertainty in groundwater flow and transport modelling

FI2W/0089 Uncertainties in the modelling of migration

FI2W/0090 Unbiased guess, a concept to cope with fuzzy and random parameters

FI2W/0091 Review and development for modelling with uncertainty and variability

TASK Nr. 4 - DISPOSAL OF RADIOACTIVE WASTE: RESEARCH TO BACK UP THE DEVELOPMENT OF UNDERGROUND REPOSITORIES

A. Objectives

The overall aim of this task is to provide a theoretical and experimental basis as well as data bases, concepts or models for understanding the long-term behaviour of potential host rocks as natural isolation barriers in order to support the 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;
* rock mechanics laboratory and in-situ tests in host rock media and benchmark of codes 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 on the role of organic compounds, complexes and colloids (CoCo activities) on geochemical benchmark codes and development of 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.
Studies are also carried on 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.

* Geoforecasting studies to predict future climate changes and simulation of their effects on groundwater flow in the Netherlands as well as paleo-climatological revision during the last 2 million years in the Western Mediterranean regions.

Topic 2: Design, construction and operation of underground repositories

This topic is focused on support studies and experiments to projects of Part B of the programme on backfilling and/or sealing of boreholes in salt, clay and fractured crystalline rock. Various research efforts in the field of gas generation, gas release and migration through host rocks (in particular clay and salt) were grouped together in a coordinated project PEGASUS (Project on the Effects of Gas in Underground Storage facilities).

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
* geochemical modelling of radionuclide migration and 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.

Simulation of the effects of long-term climatic change on groundwater flow and the safety of geological disposal sites.

Contractor: University of Edinburgh, U.K.; Rijks Geologische Dienst, and Rijksinstitnut voor Volksgezondheid en Milieuhygiene, The Netherlands.

Contract No: F12W/0046

Duration of Contract: 42 months

Period Covered: 1st April 1991 - 29 February 1992

Project Leader: Professor G S Boulton, University of Edinburgh.

A: OBJECTIVES AND SCOPE

A1 Scope and background – Recent developments in glaciology, hydrogeology, geochemistry, geostatistics and mathematical modelling, together with enormously improved knowledge of subsurface geology in Europe and the resolution of palaeoenvironmental change, now make it possible to model, simulate and test complex environmental processes in the past and extrapolate them into the future. In making predictions about the future of radioactive waste repositories, models need to be stringently tested. Using them to simulate past events and testing them against geological evidence is a way, possibly the only way, of doing them.

A2 Aims of research and applications – To investigate the extent to which future environmental changes may affect groundwater flow in the vicinity of rock-salt radioactive waste repositories and the migration patterns of radionuclides after release into the geosphere.

A3 Degree of development of research. The programme involves the development of a coupled time-dependent, three dimensional, thermal/mechanical model of subglacial groundwater flow, and non-linear statistical approaches to modelling the future.

A4 Collaboration. There is a high degree of collaboration between the University of Edinburgh, the National Institute of Public Health and Environmental Protection (Netherlands), the Geological Survey of the Netherlands and the University of Paris-Sud.

B. WORK PROGRAMME

B1 Development of an ice sheet model to simulate Saalian glacial history in the Netherlands.

B2 Determination of the upper boundary conditions for groundwater flow and a consolidation/flow model.

B3 Simulation of the three-dimensional groundwater flow field within a supra-regional hydrogeological model extending from Denmark through Germany to the Netherlands.

B4 Acquisition of geological and hydrogeological data for the large-scale groundwater flow model.

B5 Applying and testing the subglacial groundwater flow model.

B6 Development of a site-specific model for the subrosion of salt.

B7 Testing the subrosion model at specific sites in the Netherlands

B8 Simulation of future changes.

C: PROGRESS OF WORK AND RESULTS OBTAINED

C1 *State of advancement*

The programme is proceeding according to plan and the milestones set for the first year in the original proposal have all been achieved. The main components of the programme in the first year have been:

C1.1 Development of the ice sheet model (EDIN). A time-dependent, thermo-mechanically coupled flow line model has been developed and applied to the supra-regional transect from Denmark to the Netherlands, so as to match inferred Saalian ice sheet history. The model computes subglacial melting rates and O-isotopic composition of the meltwater. A series of sensitivity tests have defined parameter values within which the ice sheet must exist.

C1.2 Groundwater flow model (RIVM) The groundwater flow model (METROPOL) has been applied to the Netherlands aquifer to compute the flow field, potential field and transit times for a given meltwater input from the ice sheet model. The sensitivity of the model to changing parameter values has been established.

C1.3 Collection of geological and hydrogeological data (EDIN, RGD). This has comprised two components. The first has been the estimate of the pattern of palaeoclimatic change in north-west Europe since the beginning of the Saalian stage needed to constrain the ice sheet and non-glacial recharge model. The second has been the description of the hydrogeology of the area of our supraregional model. This is now largely complete.

C1.4 Collection of data for model testing (EDIN, PARIS-SUD, RGD). The first set of geotechnical data has been collected and synthesised. Samples have been taken for geochemical analysis and are currently being analysed.

C2. *Progress and results*

C2.1 The development of the ice sheet model. The ice sheet model used in this study is time dependent and considers the three dimensional velocity and temperature fields within the ice mass. The model presently runs on the University of Edinburgh's parallel processing supercomputer.

A time dependent environmental signal is used to drive the model. This time series is derived from two sources, the SPECMAP global record and records of the sea surface temperatures from the N.E. Atlantic (Figure 1),and has been calibrated against the evidence of the local North European climate.

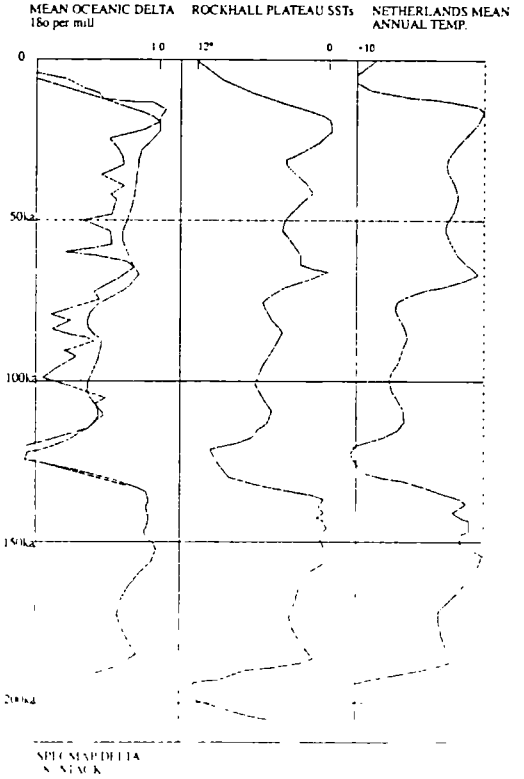


Figure 1. Climatic time series for the last 200 Ka. The mean ocean $\delta^{18}0$ curve is the one which starts at about 120 Ka. The curve for the Netherlands is the result of a linear correlation between the Rockall Plateau SST curve and sparse palaeoenvironmental data from the Netherlands. A more sophisticated version is in preparation.

This model has been used to study both the Weichselian and Saalian European glaciations. Extensive comparison of model output with geological evidence left behind by the Weichselian ice sheet has been performed. The Model has a 20 km horizontal grid size and its domain extends from Iceland to the Ural mountains, and from the North Pole to the Mediterranean. The following coupled processes are included in the model.

- isostatic deflection of the lithosphere under the ice sheet's mass;
- the evolving internal temperature structure of the ice sheet, including diffusive, advective and strain heating terms (Figure 2);
- the behaviour of the grounding line and the flow within ice shelves fringing the ice sheet (which has a significant role in determining the advance and retreat of the ice sheet's marine margin;
- the flow of ice by deformation within the ice mass, which is dependent on local temperature and stress fields.

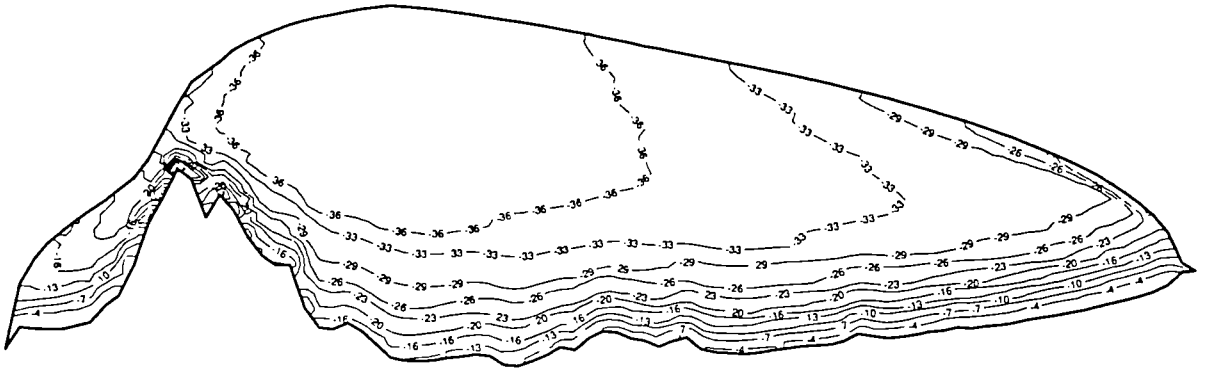


Figure 2. The modelled internal temperature for the Saalian ice sheet along the line of the supra-regional hydrogeological model (Figure 4) to the right, the Scandinavian mountains in the region of Gudbrandsdalen and to the edge of the western Norwegian continental shelf on the left. The bed is at the melting point in the left hand and right hand regions.

Output from the model includes time series of total volume, ice and water fluxes, and the recharge and isotopic composition of groundwater. The spatial distributions of ice thickness, isostatic deflection, basal stresses, basal melt rates, and basal temperatures can also be produced for any period during the model run.

In the present study this model is coupled with a groundwater model of the Netherlands during the Saalian glaciation. The ice sheet model is particularly appropriate for this use because:

(1) it has been successfully tested using the Weichselian glaciation in Scandinavia;
(2) it explicitly models the variables which lead to coupling with the groundwater system, namely basal melt rates, stresses and temperatures;
(3) the spatial pattern of these variables can be output from the model for the periods of interest.

The most efficient method of coupling the ice sheet and groundwater models is to mount both on the same mainframe computer. It is planned to exchange the groundwater and ice sheet models between EDIN and RIVM.

C2.2 Testing the ice sheet model.

In order to test the results of the ice sheet model with respect to the crustal response to ice loading, the pattern of advance and retreat of the ice sheet and of major changes in ice flow patterns, a comparison has been made with the evidence that has been left by these events in the geological record. In order to carry out these tests several sets of geological data have been collected.

- On the basis of the relative sea level curves that are available for a large number of locations influenced by the isostatic depression of the crust, a reconstruction has been made of the pattern of emergence of these areas after deglaciation.
- A remote sensing survey of Landsat Imagery has been carried out in order to map streamlined subglacial bedforms, (drumlins, flutes) in Scandinavia which can be used as paleo iceflow indicators. There are sets of these streamlined features which have been cut at an angle by subsequent sets of features. By carefully analysing these cross-cutting relations, a reconstruction of the changes in ice flow pattern has been made which are related to shifts in the positions in the major domes of the Scandinavian ice sheet.
- A detailed investigation has been carried out to reconstruct the former ice marginal position on the basis of a literature study and on remote sensing surveys. On the basis of several dating techniques (c^{14}, varve-chronology) rates of retreat and advance have been established for different parts of the ice sheets.

C2.3 Application of the ice sheet model to the Netherlands

After testing against plentiful data for the Weichselian glaciation of Britain and Scandinavia, the ice sheet model was applied to the Saalian glaciation, which extended over the Netherlands and the sites specifically to be identified as foci for this project.

Two simulations have been undertaken, forced by climatic patterns in which a snow line and a fixed mass balance distribution with its origin at the snow line varies firstly as the SPECMAP global O-isotope record and then as the Rockall Plateau SST curve for stage 6. However, the point along the curves at which European ice sheet initiation occurs is taken to be that which would cause an ice sheet to reach the known Saalian glaciation maximum in Central Netherlands. The magnitude of the local climatic cycle is taken from the palaeotemperature curve published by Zagwijn (1975), although the pattern is that given by the SPECMAP and Rockall Plateau curves

The glaciation of the Netherlands generated by this procedure is one of approximately 15,000 years duration. Model output comprises:-

- the tempo of ice sheet build up and decay;
- the time-dependent pattern of crustal loading and unloading;
- the crustal response to loading and unloading;
- the distribution of zones of subglacial melting and the rates of melting in time and space (Figure 2);
- the isotopic composition of meltwater.

The global eustatic sea level effect is computed from the SPECMAP O-isotope curve for stages 6-7-8 computed as in Boulton *et al* (1985). The pattern of relative sea level change through the glacial cycle is then determined by subtracting the isostatic from the eustatic component.

A series of sensitivity tests have been undertaken, as a result of which it was found that the extent and magnitude of basal melting was most sensitive to atmospheric lapse rate (Figure 3).

C2.4 The supra-regional hydrogeological model.

Modelling is being focussed along a 100 km wide swath stretching from S W Sweden to northern Belgium (Figure 4). It lies approximately parallel to the flow of the Saalian ice sheet and defines the principal aquifers as far as the edge of Fennoscandian basement rocks. The hydrogeological basement along much of the model is defined by the top of the Zechstein salt (Figure 4), which is overlain by a Mesozoic aquifer, a Tertiary aquitard and a Quaternary aquifer. A section along part of the transect is shown in figure . The geometry of all the major hydrogeological units has now been mapped and their known permeability/porosity characteristics have been compiled.

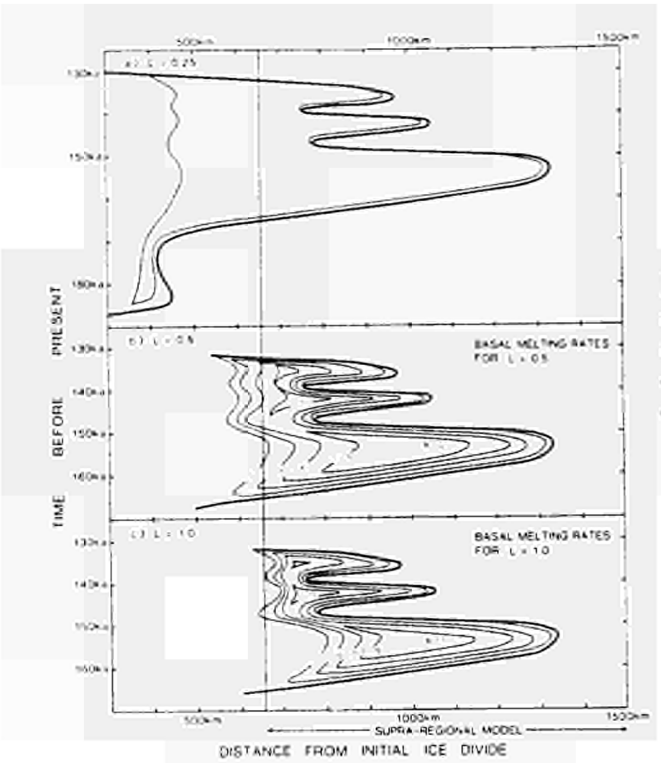


Figure 3. The rate of melting in time and space of the Saalian ice sheet along the flow line. The rates are non-dimensional and are computed for different lapse rates of °C/100 m.

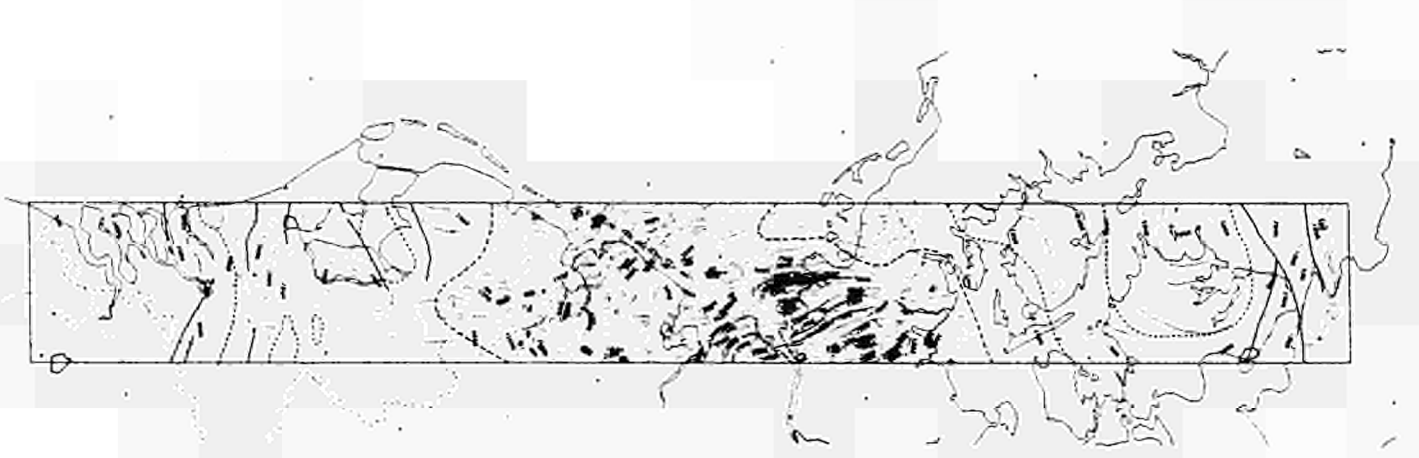


Figure 4. The supra-regional model showing the top of the Zechstein beds.

In the next phase of the testing and site-specific modelling, we anticipate a higher resolution characterisation of hydrogeological geometry associated with aquitards in the Quaternary sequence and in the vicinity of salt domes.

C2.5 The sub-glacial groundwater flow model

A simple geohydrological model has been constructed to investigate the influence of the choices made for the various boundary conditions and for parameter values on the main characteristics of groundwater flow underneath a glacier. This has taken the output from the ice sheet model along part of the supra-regional transect.

To obtain an idea of the sensitivity of this model to changes in boundary conditions, geohydrological parameters (like the hydraulic conductivity and porosity of the respective strata), and to the discretisation of the profile calculations have been carried out using the METROPOL-1 code from the METROPOL package, developed at RIVM.

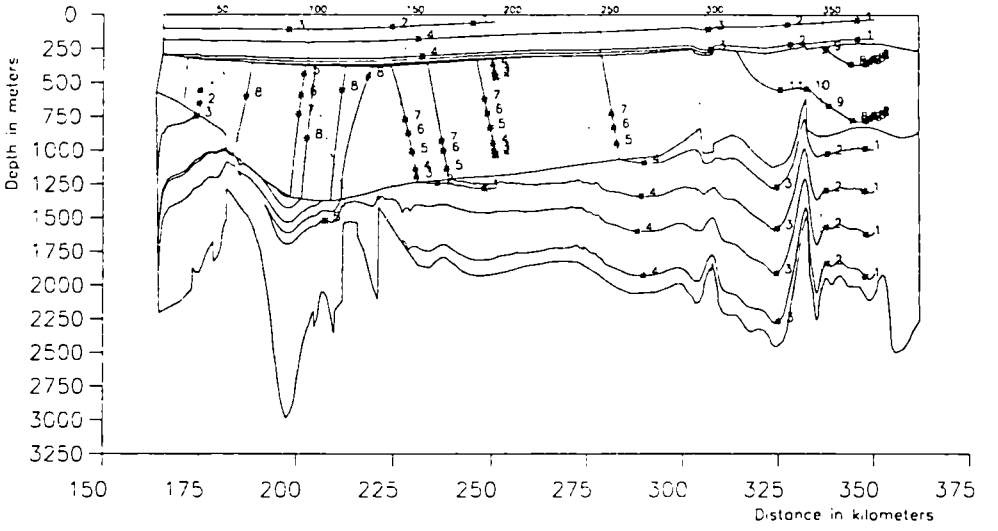


Figure 5. Modelled subglacial groundwater flow showing the head contours (dotted lines) and particle trajectories along part of the supra-regional model (Same horizontal scale as in figure 3). The top statum is the Quaternary aquifer, underlain by the Tertiary aquitard, the Mesozoic aquifer and the Zechstein aquiclude. Time markers along trajectories are in years (1 = 100 yrs; 2 = 500; 3 = 1,000; 4 - 2,500; 5 = 5,000; 6 = 7,500; 7 = 10,000; 8 = 25,000; 9 = 50,000; 10 = 75,000; 11 = 100,000).

C2.5.1 Discretisation of the profile

Two discretisations of the profile have been considered to investigate numerical sensitivity of the model. First a coarse mesh has been constructed, in which each stratum is represented by one layer of elements only. This coarse mesh consists of 1456 nodal points and 543 elements (181 * 1 * 3 in X, Y and Z-direction respectively). Later on this coarse mesh has been refined, such that each geohydrological stratum is represented by at least three layers of elements. This refined mesh consists of 4378 nodal points and 1980 elements (198 * 1 * 10 in X-, Y-, and Z-direction respectively.

A considerable number of cases that were investigated using the coarse mesh were also computed using the refined mesh. Where the overall picture of the groundwater system was nearly identical for the two discretisations used, the accuracy of the computations was increased using the refined mesh, which is clearly demonstrated by decreasing mass balance differences (from approximately 18% to 7% for the more complicated cases).

C2.5.2 Boundary conditions

A number of different boundary conditions have been considered to investigate the sensitivity of the model. Essentially these consist of either a no flow boundary, a prescribed head boundary, a prescribed flux boundary or a combination thereof.

At the right-hand boundary (Figure 4) two different situations were considered. First, the influx of the total of 4000m^3/m/yr of melt water was assumed to take place at the upper aquifer only, the lower aquifer and aquitard having no flow boundaries. In the second case the total meltwater influx has been distributed proportionally over both the upper and lower aquifer:

$$Q_j = \frac{k_j . D_j}{\Sigma k_i . D_i} . Q_{total}$$

The lower boundary is formed by the relatively impervious Zechstein evaporites, and consequently can be treated as a no flow boundary for all cases considered.

The left-hand boundary condition consists of a prescribed head at the lower aquifer, and no flow at both the aquitard and the at the upper aquifer. The value of the prescribed head has been varied between 0 and 5m.

At the top boundary a head is prescribed at the discharge area (from km 165 - km 172.5), no flow is assumed at the glacier edge (from km 172.5 - km 207), and a meltwater influx is prescribed at the remaining part of the upper boundary. The prescribed fluxes considered are either constant in the X-direction, or increasing from 0 to 2 cy/yr towards the North-East.

C2.5.3 Geohydrological parameters

Groundwater flow essentially is dictated by two geohydrological parameters: the hydraulic conductivity (k) and the effective porosity (N). Therefore, the sensitivity of the model to variations in parameter values has been investigated. For each parameter two cases were considered.

In the base case, hydraulic conductivities values for this parameter were chosen of 20, 0.1 and 2 m/d for the upper aquifer, the aquitard and the lower aquifer respectively. Moreover, all strata were supposed to be isotropic. A variant with anisotropy of the clays was introduced. This correction was made to compensate for major intersecting sandy layers within the dominantly clayey sequence. In X-direction the conductivity of these sandy sequences has been averaged, whereas in Z-direction the conductivity is dictated by the clays:

$$k_x = \frac{\Sigma k_i . D_i|_{sand}}{\Sigma D_i|_{total}}; \qquad \frac{1}{k_z} = \frac{\Sigma \frac{D_i}{k_i}\Big|_{clay}}{\Sigma D_i|_{total}}$$

For the effective porosities a correction of the values for both the aquitard and lower aquifer has been carried out. These values, which were 35 and 30% respectively in the base case, were changed into 15 and 5%. The value for the effective porosity of the upper aquifer remained unchanged (30%) throughout the investigations.

C2.5.4 Results

Particle trajectories reflect the groundwater velocity field in a clear and simple way, and, rather than looking into the computed velocity field, were used to investigate the differences between the various cases. Particle trajectories starting in the upper aquifer were not significantly affected by the choice of boundary conditions or parameter values. For those with starting points at the right-hand side of the model the corresponding residence times remained approximately the same; e.g. about 4,000 yr. However, when starting points were chosen at the right-hand side of the lower aquifer and the aquitard, important changes in both flow direction (sometimes even reversal of flow direction) and changes in residence times were observed in the various cases. Residence times for particles starting in the lower aquifer ranged between 6,000 and 70,000 yr, depending on boundary condition and parameter values, and for particles with starting points in the aquitard from approximately 33,000 to about 126,000 yr.

C2.5.5 Conclusions

As mentioned before, refinement of the mesh has only very little effect on the overall picture of the groundwater flow system (hydraulic heads and

particle trajectories of both meshes being approximately identical), but the mass balance of the fluid is improved strongly using the refined mesh.

The influence of the choice of boundary conditions in the recharge areas of the model (e.g. the right-hand and top boundaries) have a rather great influence on the flow system and also do have a great radius of influence. On the other hand the model seems rather insensitive to changes in the boundary conditions at the discharge areas (e.g. the left-hand and extreme left top boundary), and also the radius of influence is limited.

Introduction of a permafrost area in the upper aquifer strongly influences the local groundwater flow pattern. Furthermore, due to the decreasing transmissivity of that part of the aquifer, the gradient in hydraulic head increases influencing mainly groundwater velocities (increasing) and residence times (decreasing), whereas the flow direction remains unaltered.

Changing the geohydrological properties of the various strata obviously has a very important effect on the flow system. Diminishing the hydraulic conductivity of the aquitard, and introducing anisotropy causes the hydraulic head gradients to increase considerably, especially in the upper aquifer. Moreover, depending on the right-hand boundary conditions imposed, the head difference between the upper and lower aquifer at the right-hand side of the model also increases, causing increased vertical velocities in the Tertiary clays.

Finally, the influence of changes in porosity values has been investigated. As could be expected, this influence remains limited to the magnitude of the groundwater velocities, which increase proportionally to the decrease of porosity values. Consequently, the residence times decrease proportionally; however, the flow direction and hydraulic heads remain unaltered.

C3 *Some important conclusions*

- the water pressure head at the right hand side of the model varies from 350 m to 400 m.
- the upper aquifer carries most of the water discharge, with a net downward flow vector in the zone of melting and a strong upward flow beyond the glacier margin or beyond proglacial permafrost.
- the constriction of flow in the lower aquifer produced by the rise of the Zechstein surface at 225 km produces a net upward flow in this aquifer and through the overlying aquitard in a zone 75 km wide up-glacier of this point; strong upward and downward flows through the aquitard and the lower aquifer occur between 225 km and 175 km because of peaks and troughs on the Zechstein surface (note that several of these are a product of the 2D model which causes isolated Zechstein peaks to act like ridges transverse to flow); upward flow beyond the glacier or proglacial permafrost affects the whole post-Zechstein sequence.
- residence times of meltwater through the upper aquifer is relatively short, of the order of 4,000 years; in the lower aquifer they range from 6,000 to 70,000 years; and in the aquitard from about 33,000 to 126,000 years.
- extension of permafrost beyond the glacier margin lengthens the hydraulic pathway and therefore produces a larger pressure-head at the right-hand side of the model.
- Saalian glacial meltwater should still be retained in Quaternary and Tertiary aquitards
- explosive release of subglacial fluids may be important in generating certain classes of geological structure.

C4 *Testing the models*

Output from our models permits us to commence a programme of testing. Initially, this is concentrated in three areas:

- Large pre-consolidation gradients are predicted in aquitards as a consequence of high potential gradients. Appropriate tests are well underway.
- High potential gradients in clays should produce a fractionation effect in certain isotopes. This is being explored.
- Certain types of diapiric structure should be closely related to hydrogeological characteristics.

C5 *References*

(1) BOULTON, G.S. & DOBBIE, K. (in press). J. Glaciol. Consolidation of sediments by glaciers: relations between sediment geotechnics, soft-bed glacier dynamics and subglacial groundwater flow.

(2) BOULTON, G.S., GLASBERGEN, P., SLOT, T & BLESSING, K. (in prep.) Deep circulation of groundwater and hydrocarbons in overpressured subglacial reservoirs and its geological consequences.

(3) BOULTON, G.S., PAYNE, A., DONGELMANS, P., BROADGATE, M., Glasbergen, P., SLOT, T., de MULDER, E., WILDENBORG, T., BLESSING, G., & FONTES, J-C. .Simulation of the effects of long-term climatic change on groundwater flow and the safety of geological disposal sites.. 1st six-month progress report for the period 1 March-31 August 1991. Contract No: F12W-0046.

Oral presentations

(1) International Association for the Study of the Quaternary (INQUA) Beixing, 1991. Invited paper. Simulated futures in glaciated terrain and the problems of nuclear waste disposal.

(2) International Geological Congress, Kyoto, 1992. Invited Plenary Paper. - Predicting the future: the probability of future glaciations and their hydrogeological consequence and the implications for nuclear waste disposal.

Title : Experiment of groundwater flow in a fracture for the validation of chemistry/hydromechanical transport of coupled models for fractured media.

Contractor : BRGM/4S/GEG

Contract n° : FI2W-CT90-0049(DTEE)

Duration of contract : from 01/01/1991 to 12/31/1994

Period covered : from 01/01/1991 to 12/31/91

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. 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 equipement and qualification tests,
- choice of the sample and initial caracterization of the fracture,
- Tests of percolation (3 or 4 tests according to the necessary duration for each percolation),
- Presentation and interpretation of the results.

C - PROGRESS OF WORK AND OBTAINED RESULTS.

* State of advancement

At the end of this first year of work, the state of advancement is the following :

- the prototype has beeen designed
- all the plans have been realized
- the materials have been ordered
- the fracture which will be used for the percolations has been chosen.

The main task has been the conception of the prototype. This was done in concertation with the geochimists to avoid the problems of contamination of the fluid by elements existing in the various parts of the prototype.

Concerning the chosen fracture, we have already realized the casting of the voids and we are studying what method is the best solution to examine the microroughness of the fracture.

* Progress and results

1. Geometrical, mechanical, thermical and hydraulical hypotheses.

The rock samples are cylindrical and have a diameter of 120 mm and a "elancement" of 2. The fracture is perpendicular to the axis of the sample and is located at middle height. The axial stress will reach 15 to 20 MPa and the loading will be achieved by stage of constant value.

The temperature of the cell will be less than 80°C during the experiment of percolation with a possibility to reach 120°C. The temperature during the percolation of a fluid in the fracture is limited by the low internal overpressure inside the cell.

The fluid is injected in the plan of the fracture from the center of it (divergent radial flow). An injection HPLC pump will be used. A large scale of flows and pressures can be covered with changing the head of the pump. The fitting of the rotation speed of the pump will permit the variation of the flow for a given scale.

A tank for the recovering of the fluid will be put around the sample closed to the level of the fracture. It will be composed by 4 compartments of similar sizes. The fracture will be maintain in a satured state. The different flows will pour in the recovering circuit by the mean of thin-plate rectangular weirs.

The death volumes, as well at the proximity of the sample as in the recovering circuit will be minimized to reduce the response duration of the observations by chemical analyses of the percolated fluid.

2. Elements composing the test device.

The device is composed of :

- a loading frame equiped with a hydraulic jack to apply the axial loads and with an hydraulic device to control the pressure in the jack.

- a test cell certifying for the sample, a controled temperature during the tests of percolation and which will maintain an inert gaz atmosphere (low overpressure) around the sample.

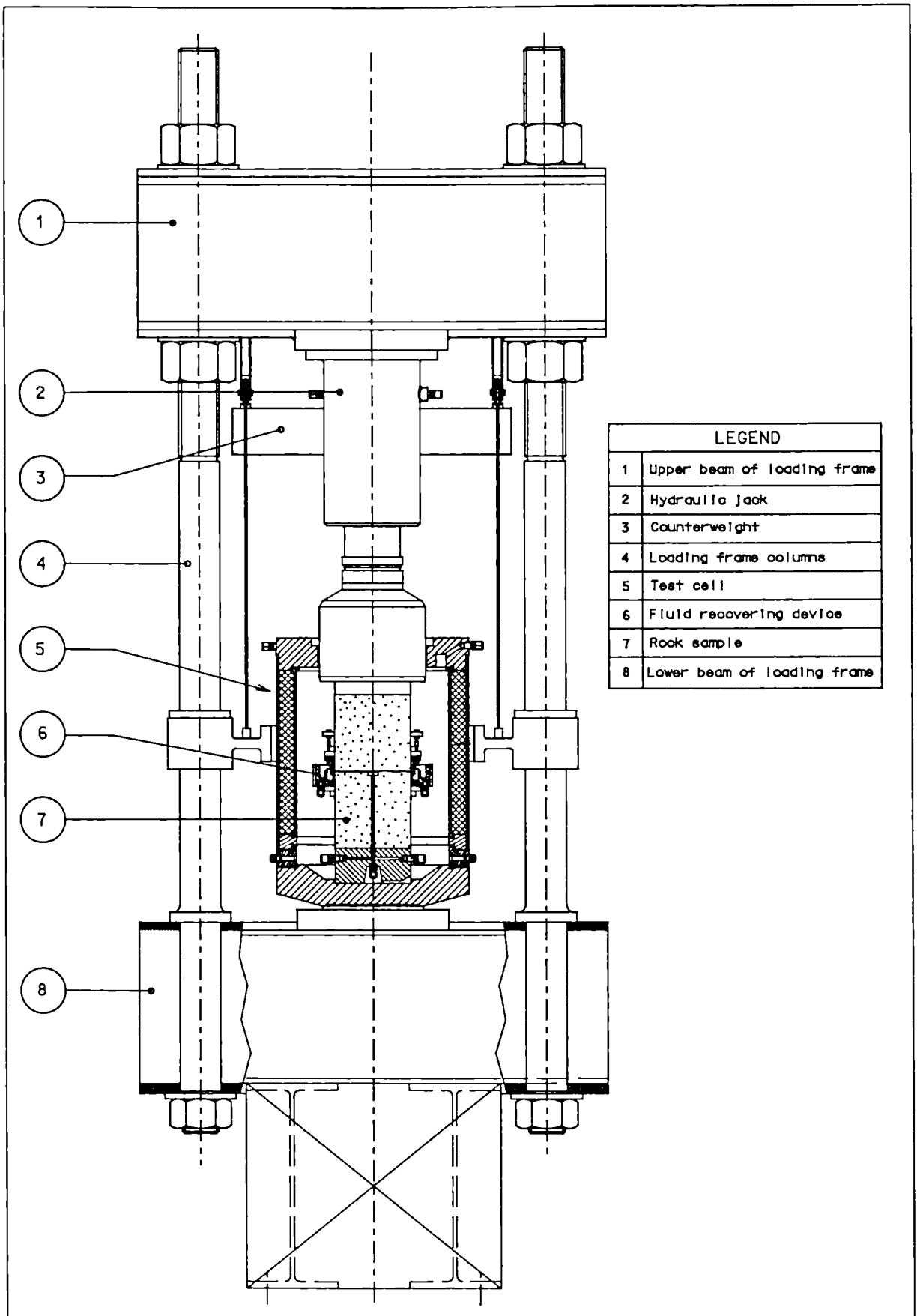
- a device for injection, controling and data acquisition which enables the monitoring during the test of various parameters (normal stress, normal displacement of the fracture, temperatures, pressures and injected or recovered flows) necessary for the interpretation of the test.

A global representation is presented figure 1 and the details of the equipment of the fracture is presented figure 2.

3. Description of the fracture.

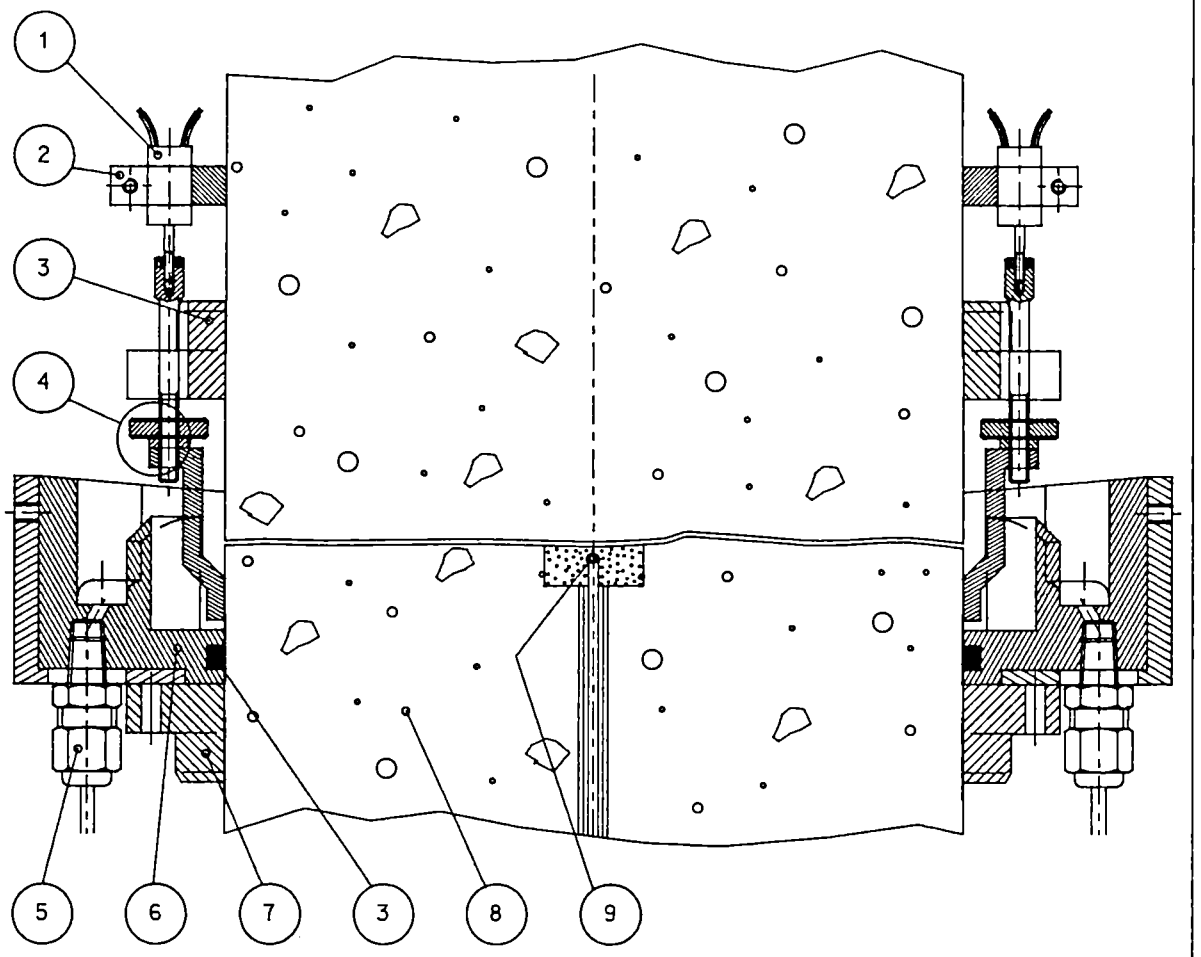
The chosen fracture is a tension fracture in a granite. The granite is a medium grey granite with a porphyroid trend. The path of the fracture is alternatively inter and intragranular. The mean aperture of the fracture is 250 to 300 μm. This fracture has been previously studied. In this study, the morphology of the fracture has been put in relation with the hydromechanical behaviour of the fracture. This knowledge will be important in order to prepare the tests of percolation and to understand the interaction between the fluid and the rock.

To prepare the study of the channels network in the fracture, the casting of the voids has been realized according to a protocole defined in previous works concerning the hydraulical behaviour of the fracture.



LEGEND	
1	Upper beam of loading frame
2	Hydraulic jack
3	Counterweight
4	Loading frame columns
5	Test cell
6	Fluid recovering device
7	Rock sample
8	Lower beam of loading frame

FIG.1 : GENERAL FRONT-VIEW OF THE EQUIPMENT



LEGEND	
1	Linear displacement transducer (LVDT)
2	Transducer support
3	Flange for sample positionning on lab rugosimeter
4	Setting device between transducer and sample
5	Fluid draining fitting
6	Fluid recovering tank
7	O-ring
8	Rock sample
9	Temperature probe

FIG.2 : DIAGRAM OF FLUID RECOVERING DEVICE (CROSS-SECTION) AROUND ROCK SAMPLE

Title:	Experiments in a 600m borehole in the Asse II salt mine
Contractor:	ECN
Contract No:	FI2W/0050
Duration of contract:	January 1991 to December 1992
Period covered:	January 1991 to December 1991
Project Leader:	ir. L.F.M. Hamilton/ir J.J. Heijdra

A. OBJECTIVES AND SCOPE

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 predict the in-situ measurements.

In this research programme 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 the borehole, i.e. at different salt pressures as soon as a 600 m deep borehole becomes available.

The obtained experimental results will be available to predict the behaviour of salt deposits and will give essential information to be used in safety assessment of disposal facilities of radioactive waste in rock salt, especially on the field of elastic behaviour and pressure dependency of creep.

B. WORK PROGRAMME

The tasks which need to be conducted during the contracting period are:

1. Maintenance of existing installed experimental equipment:
   The equipment is controlled by an electrical system that can be operated by remote and local control. The transducer signals from the experiments are collected by computers and transported to ECN. The system needs to be maintained.
2. Execution of the experimental programme:
   The VPD requires that parameters (pressures) are changed and thus requires operation by personnel. The convergence measuring devices have to be installed in the borehole before measuring and are removed afterwards.
3. Data collection and interpretation of results:
   The automatically collected experimental data will be interpreted and validated.
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 measurements performed in other programmes.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Measurements with the VPD have been started in March 1991. Although problems raised with the device as measurements proceeded, important information about the constitutive behaviour of the Asse II rock salt is obtained.

Based on earlier experiments, a set of constitutive parameters was found which described these experiments quite good. In order to account for the presence of micro-cracks and primary creep effects, the in-situ elasticity of the rock salt in this set has been assumed to be considerably less (by a factor of 3 to 4) than the values found in laboratory experiments on small salt samples. The VPD experiment, however, shows that the in-situ value appears to be significantly higher and does not differ much from values found in the laboratory experiments. This implicates that the set of constitutive parameters needs to be reconsidered and a renewed evaluation of all in-situ experiments must be performed.

A start has been made with the evaluation of the convergence measurements executed in the 300m hole previous to the VPD measurements which will be reported in the beginning of 1992.

Progress and results

During the first part of the measuring period of the VPD the expected response of the salt could not be measured. The response already was expected to be quite low since the experiments had to be performed in a 300 m deep borehole instead of the intended 600 m which decreased the response of the salt by a factor of about 10. Due to a small leakage of the system, probably coused by serious heat effects during the installation of the device, this small response was not found.

It was then decided to start with the measurements of the elastic response of the rock salt on pressure changes. This experiment performed quite good and gave interesting results. In subsequent pressure steps the response of the salt was measured during pressure build-up and pressure relief. During a second run, giving reproducible results, the device broke down suddenly. The leakage of the device was too high to measure with enough accuracy any response of the salt. Since the device is not retrievable it can not be repaired.

The measurements, however, are very interesting because the in-situ elastic behaviour appears to be higher than was expected based on previous in-situ experiments. Evaluation of the results has been performed and is currently being reported. The consequence of this will be that the set of constitutive parameters used thus far needs to be reconsidered. For the description of the convergence the implication is not that high.

The effort in this project during 1992 therefore will be focused on the reconsideration of constitutive parameters. Performance of convergence measurements in a 600m deep borehole will begin as soon as GSF has finished the drilling. GSF has modified the drilling rig and has started drilling a demonstration hole. The actual 600m deep borehole will be drilled in spring 1992.

List of publications

/1/ J. Prij et al.: Pre-test analyses for the HAW test field, Petten, ECN-R--91-001.

Title:	Evaluation of a self-consistent approach to fractured crystalline rock characterisation
Contractor:	Golder Associates (UK) Ltd
Contract No:	F12W/0051
Duration of Contract:	From 6/91 to 6/94
Period covered:	6/91 to 12/91
Project Leader:	M Brightman

A. OBJECTIVES AND SCOPE

The aims of the project are:

(i) to assess the errors in predictions of nuclide migration in fractured crystalline rocks resulting from the application of inappropriate interpretation techniques

(ii) to assess the impact of the "fractional dimension" approach on the results derived from hydrogeological testing

(iii) to develop a methodology for constructing fracture network models to incorporate field dimensional information directly

B. WORK PROGRAMME

1) provide a literature review of the impact of the application of "fractional dimension" interpretation on hydrogeological tests in fractured crystalline rocks

2) evaluate, present, and assess the impact of "dimensional" interpretation on some existing data sets

3) simulate "dimensional" results within a fracture network model

4) assess the available methods by which "dimensional" results would be incorporated explicitly into a fracture network model

5) demonstrate the impact of cylindrical flow versus variable dimension results on the output from a transport version of the fracture network model

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

1) Substantially complete
2) In progress
3) In progress

This project commenced during 1991 and progress to date has consisted of an initial literature review and preliminary "dimensional" hydrogeological test interpretation and simulation.

Progress and Results

A well documented and monitored set of pumping tests was required in order to evaluate the applicability of the approaches under consideration. In addition the fractures, fracture zones and faults throughout the experimental region needed to be well characterised. These criteria must be met if pumping tests interpretations are to be validated against numerical models, in the forward modelling sense.

The Large Scale Crosshole tests (LSCH Tests), which took place in the Swedish Stripa mine laboratory during 1989, fulfil the criteria outlined above. These were a series at constant rate tests with durations of days, for which drawdown and recovery information was recorded. One pumping test from the LSCH program was chosen for a more detailed analysis.

After allowing approximately 3 days for the hydraulic system to come to equilibrium, pumping was started but failed after a few hours. Following one day of recovery a constant flow rate of 2.9 ml/s was maintained for approximately 9 days. Finally, approximately 4 days of recovery data was recorded after the cessation of pumping.

Preliminary examination of the data indicates that equilibrium conditions are never achieved. Attempts may be made to impose a linear drift correction on the data but, as the effects of earlier events die away, this approach will bias the data. The approach here is not to attempt a drift correction, but to give more weight, when curve fitting, to late time and recovery data.

The data was first prepared by constructing log-log plots of drawdown versus elapsed time, and the semi-log derivative of drawdown versus elapsed time for each observational piezometer within the mine. Type curves were also produced and its semi-log derivative. Type curve matching was then used to infer values of hydraulic conductivity, specific storage and the fractional dimension parameter; these matches being made more certain by also matching to the semi-log derivative (see Figure 1). For comparison, matches to the Theis model, a special case of the generalised radial flow model with n=2, have also been made.

A table of results (Table I), together with a representative example (Figure 2), are shown below. It is observed that the dimension of flow varies throughout the period of pumping, generally increasing with the duration of pumping. There are a number of ways in which this effect can be interpreted. Firstly, early time data may be distorted by earlier hydraulic events so that anomalously low estimates of flow dimension are obtained. Secondly, the flow geometry may be different on differing scales. At early times the hydraulic 'pressure signal' will only have probed a small region in the neighbourhood of the pumped section, and pressure responses may well only be characterising a single, or small collection of fractures. In this case it is expected that the fractional flow dimension will be less than or equal to two; flow in a single fracture is constrained to be less than two-dimensional, by the geometry of the fracture and by recognising that, at early times at least, leakage into the solid matrix will be negligible. At late times, however, the fractional flow dimension is likely to governed by the large scale fracture network properties, such as connectivity and cross-connections. A third possible interpretation is that at late times leakage into the solid matrix is significant; this would have the consequence that inferred values of flow dimension would be larger than those obtained for flow within the fracture network alone. Finally, some combination of the above three explanations may be appropriate.

To account for significant leakage, and for 'fractional dimension' flow, methods for analysing pumping test data based on the fractal reservoir model must be sought. This is currently being investigated.

One way to minimise the effects of historical hydraulic events, is to analyse recovery information. A method already exists for analysing this type of data for the fractal reservoir model; for the generalised radial flow model, however, a method does not exist but is being developed as part of this project.

Table I Results of type curve matching to drawdown data from the LSCH test in borehole section C1-2

		Early time		Late time	
Borehole Section	Radial Separation	Diffusivity m2/s	n	Diffusivity m2/s	n
C4	26.31	1.7E-04	1	2.7E-03	3
C5-2	35.49	Not analysable		8.8E-02	>3
C5-1	80.89	Not analysable		2.3E-01	>3
N2-2	43.75	1.5E-02	1	4.7E-02	>2
D2-H	9.7	2.1E-06	1.5	1.5E-03	3
D5-B		Totally masked by drift			
W1-5	50	4.9E-02	1	2.0E-01	3
C3-1	31.57	1.1E-03	1	2.2E-02	3
C2-1	32.72	9.4E-06	1	3.3E-02	3

† Diffusivity only calculated. K and Ss determination requires knowledge of the extent of the flow region b

†† Dimension estimated as no clear matches

Figure 1 Type curves for various values of dimension of the generalised radial flow model.

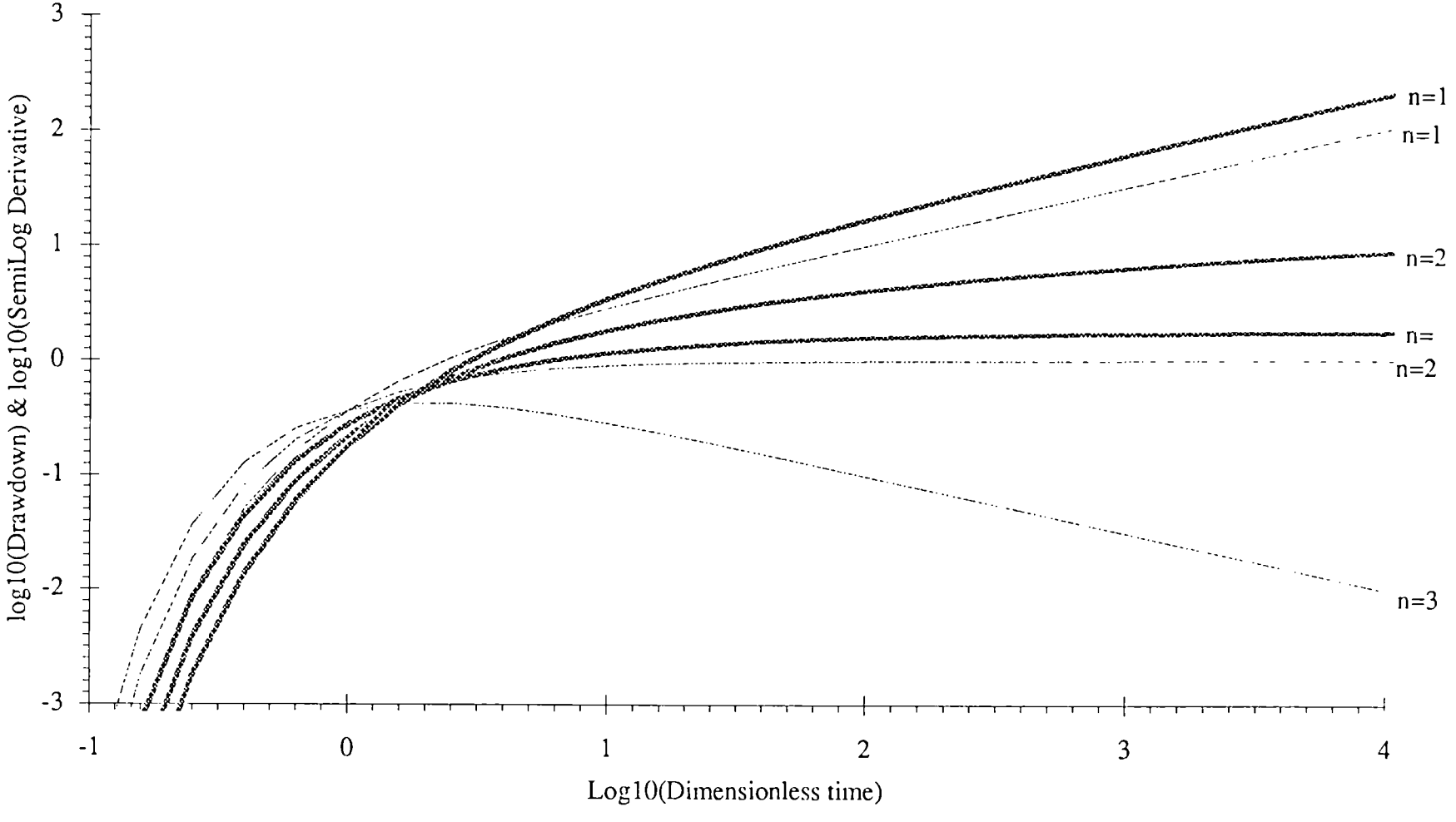
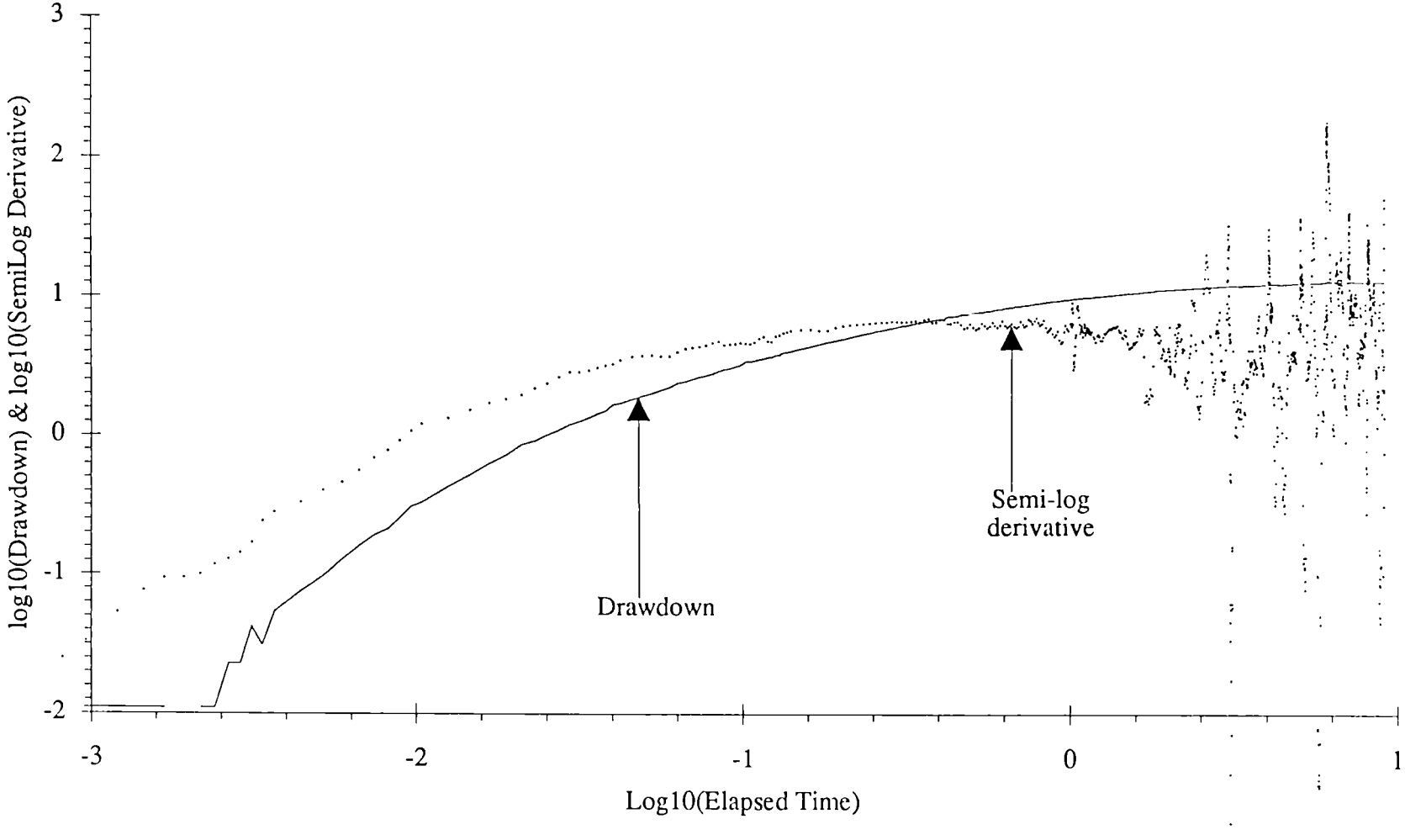


Figure 2 An example response (and its derivative) in borehole section C3-1 due to pumping in C1-2.



INTERCLAY II - A Coordinated Benchmark Exercise on the Rheology of Clays

Contractor:	WS Atkins Engineering Sciences
Contract No:	FI2W-CT91-0063 (SSMA)
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).

B. Work Programme

There are to be 3 principal stages.

In Stage 1 the basic ability of popularly used models and the computer codes which contain them will be briefly reviewed. The review will comprise a comparison both of the theoretical capabilities of the codes as described in their documentation and of their performance on 4 simple, somewhat hypothetical problems.

In Stage 2 it it intended to use well-controlled laboratory tests on reconstituted clays as a basis for a computational benchmark problem. Participants will be asked to replicate the measured laboratory behaviour as far as possible, in their calculations.

In Stage 3, "in-situ" behaviour will be modelled. Sources of well validated in-situ behaviour will be investigated in Stage 2, a suitable test selected and a benchmark formulated. The various "heater" tests planned by SCK/CEN at the Mol facility are strong candiates. If possible precise details of the actual in-situ behaviour will be withheld from participants so that their predictions are "blind".

In each stage, the work programe is broadly as follows:

1. The project team agrees, at plenary meetings, suitable benchmark problems to be solved by all participants.

2. The Coordinator prepares discussion documents, in co-operation with Steering Group, and circulates them to participants for comment.

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.

5. The Coordinator collects and compiles results and other data from participants and prepares draft reports for discussion at plenary meetings (approximately 6 monthly).

6. The Coordinator prepares and issues final definitive reports taking account of participants' comments.

C. Progress of Work

The formal start to the contract was 1 June 1991 and a 2 day plenary meeting of all participants was subsequently held in Epsom on 4/5 July 1991 /1/. The next such meeting was scheduled for Mol on 20/21 January 1992.

At the July meeting partners defined the programme of benchmarks for Stage I. Four problems were discussed and agreed in outline.

1. an axisymmetric 1-d approximation of a cylindrical (i.e. tunnel) excavation in clay under isothermal and isotropic conditions.

2. a two-dimensional, axisymmetric approximation of the progressive excavation of a cylindrical tunnel in clay, again under isotropic, isothermal conditions. Such approximations are relevant to deep repositories.

3. a plane strain representation of a shallow 'lined trench' repository founded on clay.

4. problem 1. extended to include a centrally located heat source.

In all cases interest centres on the ability of various conceptual models (and the codes in which they are implemented) to predict steady state behaviour.

Subsequently detailed specifications of Benchmarks 1 & 2 were drawn up, issued for comment and then finalised /2/. Partners are to submit their results to the coordinators for collation and presentation at the Mol plenary meeting.

Outline specifications for Benchmarks 3 & 4 were issued in December 1991 /3/ and are to be finalised at the Mol meeting.

The July meeting also considered suitable sources of experimental data for Stage II benchmarks. In the ideal suitable tests would satisfy the following criteria:

- well founded, reliable, accurately and comprehensively measured behaviour.

- thermal and mechanical loading

- known (prescribed?) boundary conditions

In practice it was recognised that only well-behaved laboratory tests would provide sufficiently comprehensive and authoritative data. Such tests, however, should be more than simple triaxial tests - i.e. a key feature is some form of stress variation. To date no suitable test has been located.

For Stage III, the project anticipates use of one or other of the in-situ heater tests at Mol. The planned ATLAS tests (to be installed in February 1992) have been designed with the requirement of the INTERCLAY project in mind. In addition the INTERCLAY partners are monitoring progress with the CACTUS programme.

In summary, although still in its early stages, the project is progressing satisfactorily.

References

/1/ INTERCLAY II Minutes of plenary meeting, Epsom, July 1991, WS Atkins Engineering Sciences.

/2/ INTERCLAY II - Specification of Benchmarks 1 & 2, October 1991 - WS Atkins Engineering Sciences.

/3/ INTERCLAY II - Outline Specification of Benchmarks 3 & 4, December 1991 - WS Atkins Engineering Sciences.

Table I - INTERCLAY II Participants

Coordinator:	WS Atkins	(UK))	
	GCG	(UK))	Steering Committee
	SCK/CEN	(B))	
	BRGM	(F)	
	CEA	(F)	
	EMP	(F)	
	ETSIM	(S)	
	G3S	(F)	
	GEODESIGN	(B)	
	ISMES	(I)	
	LGC	(B)	
	BNFL	(UK) -	Observer
	ENRESA	(S) -	Observer

Title:	Paleoclimatological Revision of Climate Evolution and Environment in Western Mediterranean Regions
Contractor:	ENRESA
Contract nº:	FI2W-0075
Duration of the contract:	48 months: June 1991 - May 1995
Period covered:	from June to December, 1991
Project leader:	Carlos del Olmo

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, scarce data is availale about past climate evolution in Spain and surrounding countries. This project is concerned with the study of climatological changes occured 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 the BRGM as an associated contractor. The work about climate evolution in Spain has been subcontracted to the Instituto Tecnológico y Geominero de España. The 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:

1) Synthesis of the environment in Spain over the last two million years. Period of Performance: June 1991 to April 1993.
2) Paleoclimatic and environmental study of Quaternary deposits in the Tajo Valley.
   Period of performance: June 1991 to April 1994
3) Study and dating of travertines in Spain as a paleoclimatic and paleoenvironmental index.
   Period of performance: June 1991 to April 1994
4) Climatic reconstruction of the last thousand years in Spain on the basis of dendrochronological series. Period of performance: June 1994 to April 1995
5) Paleoenvironmental reconstruction and construction of future evolution scenarios. Period of performance: June 1991 to April 1995.

C. PROGRESS OF WORK

State of advancement

Work over the six month period has proceeded as planned and no delays are foreseen for the time being. Task 1 is ahead of schedule, while tasks 2 and 3 are progressing as programmed. No progress has been made in tasks 4 and 5. Most of the effort during this period has been spent in defining the scope of work and coordinating among the different participants, preparing contractual agreements and selecting working groups from different public institutions in Spain.

Progress and results

Task 1. Synthesis of the environment in Spain over the last 2 million years.

A publication summaryzing all previous work will be ready by the beginning of 1993. The following chapters have been finished:

. Avian Fauna,
. Galcial and Periglacial Environments,
. Travertines,
. Neotectonics,
. Volcanism,
. Marine Vegetation
. Vertebrates and invertebrates,
. Small mammals
. Evolution of the Environment in Spain during Historic Periods.

The rest of the chapters are currently being written, and should be finished by the second quarter of 1992.

Task 2. Research on the Quaternary paleoenvironmental evolution of a sector of the Tajo Valley.

A definitive work plan has now been drawn up for this task. A section across the Tajo Valley between Tarancón and Talavera de la Reina will be studied because the highly developed terraces, represent much of the quaternary paleoenvironmental history of the area. Field work has begun ahead of schedule. Paleoenvironmental reconstructions and chronological approximations will be based on the following techniques: Pollen analysis, fauna and lithic industry studies, sedimentological analysis, magnetostratigraphy and thermoluminesce.

Task 3. Study and dating of travertines in Spain.

A definitive work plan for this task has also been completed. It will include the following phases:

1. Detection and surveying of the country's main travertine outcrops, via the existing bibliography, cartography and aerial photography.
2. Selection of a representative range of locations on the basis of altitude, latitude and longitude. The selection will be accomplished by aerial photography and field visits.

3. Sampling campaigns for geochronological and isotopic analysis and other possible support techniques (palinology, etc). The isotopic analysis will be performed both on travertines and on the shells contained therein.
4. Geochronological analysis using the U/th method and analysis of stable isotopes of carbon and oxygen.
5. Processing of the geochronological and paleoclimatic data obtained.

In addition, field sampling of the travertine deposits of the Iberian Mountain Range is almost completed.

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: from January 1991 to December 1994
Period covered: January 1991 - December 1991
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 shaft seals, drift seals, and borehole 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 only 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 to 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

The DEBORA-project was started in early 1991. The most important work during the year 1991 was the definition of the project requirements and the formulation of the detailed work programme.

Because the technical boundary conditions of a repository represent the most important basis for all further works, a compilation of these conditions has been made initially.

Progress and results

1. Compilation of the technical boundary conditions important to the design of HAW borehole seals.

The concept of the Federal Republic of Germany considers a disposal of high-level radioactive waste (HAW) in 300 or 600 m deep boreholes, respectively, drilled in the repository at a depth of approximately 800 m. The emplacement boreholes will have a diameter of 0.6 m and will have a spacing in the underground emplacement drifts of approximately 50 m. The cross-section of the emplacement drifts is assumed to be 6 x 6 m.

The dimensions of the HAW-canisters containing the vitrified HAW are specified by the French Cogema and the British BNFL, as these companies will reprocess the spent fuel elements from German nuclear power plants. The data of the HAW-canisters are summarized in Table I.

According to the waste specification given by Cogéma the dose rate at the canister surface at the time of waste conditioning amounts to 14 kGy/h. This dose rate is mostly generated by radionuclides with short half-life (e. g. Ru 106/Re, Cs 134 or Pm 147). Considering the radiation effects in salt (radiolysis, gas generation), only those radionuclides are of relevance of which the half-life is significantly longer than the period of interim storage of the waste canisters. In this regard Cs 137 and Sr 90 are of primary interest. In Table I a value of 4.8E15 Bq is given for the activity of Cs 137. The surface dose rate resulting from this value is in the range of 0.8 kGy/h. The thermal power of the waste canister amounts to 2.3 kW. Considering an interim storage of the vitrified HAW of 40 years, the dose rate would decrease to about 0.3 kGy/h and the thermal power to about 720 Watts/canister.

Besides the HAW-canisters, resulting from reprocessing of spent fuel elements, so-called Pollux canisters containing chopped unreprocessed spent fuel elements are considered for disposal in boreholes. The data of a Pollux canister are summarized in Table II. After an interim storage time of 40 years the Pollux canisters will have a surface dose rate lower than 0.1 kGy/h and a thermal power of about 235 Watts.

The waste canisters are welded leaktight to avoid any release of radionuclides. They will be stacked vertically in the disposal boreholes on top of each other.

2. Definition of the tasks of HAW borehole seals

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.

With regard to safety aspects during the operational phase of a repository, the specific objective of a HAW borehole seal is to shield the operating personnel from ionizing radiation.

In order to avoid explosive or toxic concentrations of gases in the

underground repository the release of thermally and radiolytically generated gases from the disposal boreholes is to be limited under simultaneous avoidance of the development of high gas pressures in the borehole.

With regard to the long-term safety, the borehole seal has to prevent the migration of radionuclides possibly leached from the waste matrix under altered repository conditions.

3. Analysis of events affecting the borehole seal

Events in the disposal boreholes and in the surrounding rock salt, for example mining of drifts or emplacement of canisters in a certain time sequence, may affect the conditions around the borehole seal. It has to be determined which of these events are of importance to the design and the quality of the seal.

Borehole convergence: due to heating of the salt and mining activities stresses are induced in the rock which lead to an increased convergence of the salt. Because of the reduction of the borehole volume, there will be an increase of gas pressure acting directly on the seal. If porous material is inserted into the annulus between canisters and borehole wall this pressure might be limited to acceptable values. The rates of convergence are to be determined with and without backfilling material under consideration of the thermomechanical conditions near the disposal borehole.

Borehole filling strategy: temperature, stress, and deformation fields around HAW boreholes are dependent upon the geometrical arrangement of the disposal boreholes and on the number of heat producing canisters brought into the borehole per time unit. Therefore, the borehole filling strategy has to be analyzed under consideration of the needs determined by repository operation.

Release of liquids and gases into in the HAW boreholes: it is known from earlier investigations that rock salt contains natural trace amounts of water and gases which are released into the borehole atmosphere as a result of heating and irradiation. Quantities and release rates are to be determined by model calculations in order to estimate the potential for corrosion of the canisters and the increase in gas pressure. For the calculations it is necessary to know the petrophysical parameters of the host rock, such as diffusivity, permeability, porosity, and internal surface. Concerning these parameters some investigations have been made in the past, but within this programme they have to be intensified.

Corrosion of waste canisters: liquids and gases from the salt can lead to corrosion of the waste canisters at elevated temperatures (200°C) and pressures. It has to be evaluated from literature if corrosion of the steel canister and of the glass matrix are of significance under normal or altered repository conditions. Also, the question has to be considered whether corrosion is an important source of gas production.

Release of radionuclides: from the waste matrix is possible if a canister is damaged by mechanical destruction or by corrosion and whether migration of the radionuclides through the air gap or the backfilling material and the borehole seal takes place. In order to evaluate whether the release of radionuclides might be of any significance, the potential source term as a function of canister and glass corrosion as well as possible mechanisms of transport have to be analyzed.

4. Performance of model calculations

An important item is the thermomechanical load on the HAW borehole seal. In the discussion on this loading, the filling strategy of the

borehole seemed to be an important aspect. The determination of an optimal filling strategy is a rather complicated problem. This can be demonstrated by some problems involved, such as the axial load carried by the waste canister and the possible need of a load carrying plug between a number of canisters. In order to avoid a confusing situation related to these problems, it was decided to try to determine by a numerical analysis which aspects of the filling strategy would have a large influence on the thermomechanical loading and which would have a small influence. Having identified the most sensitive aspects one can concentrate on these items for further research in this project.

The goal of the analysis is the determination of the sensitivity of the thermomechanical loading of the borehole seal with respect to the following aspects:

- the length of the borehole or the length of the canister stack, respectively
- the loading velocity
- the heat load
- the length of the seal
- the influence of the excavation of the gallery on the stress distribution in the surrounding rock

The first thermal and structural analyses have been made to determine the influence of the stack length on the area where the borehole seal is situated. Also, structural analyses have been made to determine the area around a gallery influenced by the excavation activities.

Influence of the stack length

From the different thermal analyses with varying stack lengths it could be concluded that the maximum deviation in temperature in the area of the borehole seal will be restricted to 10 K by assuming a stack length of 5 m as compared to larger stack lengths.

The maximum deviation of the stresses for the same stack length will be restricted to 2 MPa over a time period of 10 years. This deviation was calculated for a borehole without any backfilling and for a borehole which was backfilled with salt grit. Further analyses with a borehole backfilled with salt grit still have to be made to come to a final conclusion on the influence of the stack length on the area of the borehole seal.

Influence of the excavation of the gallery on the stress distribution in the surrounding rock

Analyses have been made to calculate the area around a gallery which will be influenced by the excavation of the gallery ifself. From these analyses it could be concluded that the influenced area will be restricted to a radial distance of 8 times the radius for a time period of 10 years. For a gallery of 6 x 6 m cross-section, which has been modelled in the analyses, this means that a distance of at least 25 m should be taken into account when a time period of 10 years has to be considered.

5. Elaboration of sealing techniques

As a preliminary result salt grit is considered to meet the objectives outlined in section 2 and to represent a possible material for the sealing of HAW boreholes. Salt grit will strongly decrease in porosity and permeability as a consequence of convergence of the rock salt especially at elevated temperatures. Values of its initial permeability are around 10^{-11} m^2 and those of its porosity are around 30 %. Salt grit in the Asse mine backfilled 60 years ago possesses values of permeability down to 10^{-14} m^2 and porosity down to 3 %.

Table I: Specification of the HAW-canister Cogema 7/86 /1/,/2/

Glass Product	[-]	SON 68
Burnup of Fuel	[MWd/t]	33,000
Cooling Time of Fuel Before Re-processing	[a]	4
Volume (Total/Glass)	[l]	180/150
Mass (Total/Glass)	[kg]	475/400
Canister Diameter	[m]	0.43
Canister Height	[m]	1.34
Canister Material		1.4833
Maximum Possible Stack		19
Activity		
After Vitrification		
Beta, Gamma	[Bq/Can]	2.8 E16
Alpha	[Bq/Can]	1.1 E14
Cs 137	[Bq/Can]	4.8 E15
Sr 90	[Bq/Can]	3.4 E15
Surface Dose Rate	[Gy/h]	
After Vitrification		
n		6.1 E-03
Beta, Gamma		800*
After 40 Years		
n		?
Beta, Gamma		300
Thermal Power	[kW/Can]	
After Vitrification		2.3
After 40 Years		0.72

* estimated under consideration of the Cs 137 content only

Table II: Specification of the POLLUX-Canister /2/,/3/

Burnup of Fuel	[MWd/t]	45,000
Volume (Total/Net Volume)	[l]	190/80
Mass (Total/Fuel Pieces)	[kg]	1130/390
Canister Diameter	[m]	0.43
Canister Height	[m]	1.34
Maximum Possible Stack		235
Surface Dose Rate	[Gy/h]	< 100
Thermal Power	[kW/Can]	
After 40 Years		0.235

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THE REFINEMENT OF SOIL GAS ANALYSIS AS A GEOLOGICAL INVESTIGATIVE TECHNIQUE

Contractor: Università "La Sapienza", Rome (Italy)
Contract No. FI2W-CT91-0064 (TSTS)
Duration of contract: April 1991 - March 1994
Period covered: April 1991 - September 1991
Project leader: S. Lombardi

SUMMARY

In the first six months, all the participants have carried out preliminary researches in order: to select test sites in the United Kingdom and in Italy; to set up the laboratories and to compare analytical methods. To this end, several surveys were performed in Italy and analytical experiences have been exchanged. Also, each participant has performed part of his own programme. In particular:

- Exeter University has set up a mobile laboratory equipped with a Leybold UL 400 ^4He analyzer;
- Rome University has carried out helium soil gas surveys in areas where clayey sequences outcrop. In both regional and detailed scale surveys, helium positive anomalies were found to correspond to regional fault systems. Further, an interpretative analysis of previous soil gas data using fractal scaling laws has been performed by INTERA as the main subcontractor of Rome University.

A. OBJECTIVES AND SCOPE

The present work consists of a multidisciplinary study aimed to optimize a set of investigation techniques for the siting of plants subject to environmental hazards. The study is based on the integration of sampling and analyses of soil gases with other investigation techniques. The main objects of the research are:

- the implementation of the analytical and sampling techniques in soil gas method;
- the study of gas permeability, gas diffusion and partitioning coefficients in various lithologies and soils in test sites, mainly clayey basins in Italy and in the United Kingdom;
- the study of soil gases as fault tracers and of gas flux within 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 diffusion;
-the creation of a data base in order to give mathematical models on gas generation and migration. Further, an assessment of the commercial value of the soil gas method will be carried out.

The participants to the research together with Rome University are: ISMES, Italy, coordinator F. GERA and Exeter University, U.K., coordinator P. GRAINGER.

B. PROGRESS OF WORK AND OBTAINED RESULTS

Foreword

In the first six months, all the participants have carried out preliminary researches in order: to select test sites in the United Kingdom and in Italy; to set up the laboratories and to compare analytical methods. To this end, several surveys were performed in Italy and analytical experiences have been exchanged. Also, each participant has performed part of his own programme and in succession, the work carried out by each participant is described.

B 1. Exeter University (P. Grainger, G. Duddridge).

As part of its programme Exeter University has set up a mobile laboratory as follows.

B.1.1 The vehicle. - A mobile laboratory for the field analysis of soil gases was first employed on the Faults in Clay contract from 1986 to 1989 /1/. The vehicle employed was a Renault Trafic T-1000 petrol-engined panel-van equipped with a Dupont 120 SSA ^4He analyser, liquid nitrogen dewar and storage cupboards. It was designed so that electrical power could be supplied from mobile generators or from a mains supply.

For the present contract work it was considered that a new mobile laboratory was essential. The old vehicle and ^4He analyser were both nearing the end of their useful lives and needing constant attention and repairs. Therefore a new mobile laboratory has been built. A simple panel-van was once again considered appropriate, but one with full standing head room for the laboratory area. It was considered essential to have both side-door and rear-door access to the laboratory area, for safety reasons. The type of vehicle chosen due to its economy and robustness was the Mercedes 208 diesel Panel Van giving a laboratory area of 3.3x1.68m. When equipped less than 50% of the 1 metric tonne payload capacity of the vehicle is exploited.

B.1.2 The He analyser - The old Dupont ^4He analyser employed a diffusion pump and a liquid N_2 trap. A good vacuum was often not achieved until several hours after start up and sometimes not until a full day had passed. This limited its usefulness in the field and accordingly a model with a turbomolecular pump was considered essential so that vacuum can be achieved in minutes. Improvements in the design of these having removed previous doubts about durability of such systems particularly in respect of transportation.

The analyser chosen was the Leybold UL 400 due to its good vacuum capabilities compared to the UL 100 portable model. The model

appeared to offer the best value for money and investigation suggested good back up and servicing from the manufacturer. A vacuum down to $2x10^{-11}$ mbar litres/second can be achieved even without liquid N_2 and it is anticipated that it will only be necessary to employ a small external trap, because gas samples are often water saturated. This is considered an advantage as carrying large quantities of liquid N_2 had been a limitation in the previous laboratory. Not only is it a potential safety problem but after losses from evaporation the pressurized dewar was found in practice to maintain supplies for only 3-4 days work.

B 1.3 Electrical fittings. - The electrical system is designed as a dual input system to operate from a mains supply or from generators. Those to be used are two Honda EB1900X petrol generators, rated at 1.5kW (mean), 1.9kW (maximum). The UL400 is able to run on the unsmoothed electrical supply from the generators, but a smoothing apparatus used is made by the Interpower Ltd., the UPS(UP500.230A). An internal battery generates an alternating voltage equivalent to that of the mains and the battery itself is kept constantly charged by the generator supply. It gives complete mains isolation and backup power for a limited period.

B. 1.4 Storage and additional features. - The laboratory area is fully fitted with storage cupboards for the soil gas sampling equipment. A sink is provided for general cleaning purpose. A twin battery systems is employed, both charged from the engine, with one dedicated to the low 12 volt circuit for lighting and water pump. The laboratory interior is lined and insulated and doors fitted with high security locks.

B.2 Rome University (Lombardi S.)

As part of its programme the University of Rome has carried out: soil gas surveys at different scales in areas where clay sequences outcrop; and an interpretative analysis of previous soil gas data using fractal scaling laws. The latter study has been performed by INTERA as the main subcontractor of Rome University.

B.2.1 Soil gas surveys. - The aim of the soil gas surveys was to acquire more information for test site selection. Furthermore, a large set of case histories will greatly add to: mathematical modelling of gas migration; validating the soil gas method for studying the permeability of clayey sequences toward gases; studying the commercial value of the soil gas method; etc...

The surveys were performed in areas characterized by different geological settings. More than 500 soil gas samples were collected. The

gas species studied are ^{4}He, ^{222}Rn and, in about 10% of the samples, major gas components including CO_2. The soil gases have been collected at a depth of about 0.5 m, extracting the gas from the pore space of the soil, using regular grids with a sampling density ranging from 2-3 up to 100 samples per square kilometre. The surveys were performed during the summer season, in very dry periods /2/. The gas samples, kept in stainless steel containers, were transported to the laboratory and then analyzed by mass spectrometry and gaschromatography. The ^{222}Rn was determined "in situ" by alpha-particle counting/3/. The interpretation of the results is still in progress. Nevertheless, two case histories will be described and compared afterwards as they seem self consistent. They refer to the helium soil gas distributions in two test sites characterized by different structural settings.

The first test site is located at Piano d'Asco, W of Tolfa Mt. (Latium), where pliocenic blue clays with a maximum thickness of 150m outcrop. This area and its surrounding plains has not been directly involved in the complex tectonics which gave rise to the Apennines. Nevertheless, it was influenced by several tectonic phases including a recent extensive one.

In a small zone, about 1 square kilometre, where no geological and morphological evidences of faults exist, 108 soil gas samples were collected and analyzed for ^{4}He. Helium was determined in order to study its behavior in a non fractured clay and therefore to provide results as a base reference data set.

In Table I and in Figure 1 some descriptive statistical data and the helium distribution are reported respectively. The helium results for this and the other area are given as difference (ΔHe) between helium in soil gas and the atmospheric helium (5220 ppb;/4/) taken as reference standard. In the following discussion, only positive values will be discussed as in this case a deep origin helium flux can be inferred.

It is possible to observe that helium values are relatively low if compared with those of other Italian areas, where the tectonics has been, and still is, particularly active. Most of the values are close to the reference standard or negative. Nevertheless, more than 25% of the soil gas samples gave positive anomalies with ^{4}He values above the mean value plus 1/2 standard deviation. Their distributions are interpreted to trend N-S, E-W and probably NW-SE directions, that is according to those of regional fault systems.

The second test site, Pisticci is located in the Bradanic Trough which represents the southern part of the Apenninic Foredeep.

In this area plio-pleistocenic blue-clays outcrop as a consequence of sedimentary and tectonic events which occurred from the Pliocene age. The first led to the fill up of a structural trough and to the deposition

of clayey sequences more than 1000m thick; the second to a rapid uplift related to the surrection of the Apenninic Chain.

The blue-clays can be defined as silty clays and are characterized by the presence of illite, kaolinite and smectite mineral groups. They have a very low permeability even if the presence of both thin sandy layers and a pervasive joint network locally influences the hydraulic conductivity of the clay body.

The plio-pleistocenic clayey sequences, covered by thin sandy-conglomeratic beds, are also intersected by major tectonic elements with preferential NW-SE and NE-SW trends.

In this area a regional soil gas survey has been performed. 246 soil gas samples were collected in an area of about 100 square kilometres, with a sampling density of about 2 stations per square kilometre. The observed helium data show a great range of values (Table I). As in the previous survey, most of the values are negative or close to the reference standard, but about 10% of the samples show values ranging from 1000 up to 21,000 ppb above the atmospheric helium. Positive high helium anomalies as the latter are found in Italy only immediately after seismic events or in areas where both deep oil reservoirs and active extensive tectonics exist (Vasto, Val D'Agri, Lombardi, unpublished data). In Pisticci both active tectonics and deep oil reservoirs exist. As in the previous survey, the positive highest anomalies are elongated according to those of the main regional fault systems of the area that is NW-SE and NE-SW (Figure 2).

The comparison between the results obtained in the two surveys seems to confirm that:

- the soil gas method can give information on the clay permeability to gases even in surveys at different scales: detailed (100 samples per square kilometre) and regional (2-3 samples per square kilometre);
- the tectonics has more control on the helium distributions in soils than the clay thickness.

B.2.2 - Interpretative analysis and representation of site data utilizing fractal scaling laws (INTERA, P. Grindrod, M.D. Impey). Many naturally occurring phenomena possess spatial structure which may be represented via nonlinear, fractal, scaling laws. The application of fractals in simulating and interpreting nature has become a popular area of scientific pursuit in recent years. This stems from two main advantages. First, fractals are represented, and often generated, from simple sets of rules which are iterated to produce structure. Such discrete formulation is ideally suited to numerical computation. Second, many areas of current scientific interest require a description, or model, of highly variable "rough", noisy, data sources. Statistical

fractals provide an easy way to measure and control variability, structure and nonsmoothness.

The key to defining statistical fractals is the specification of a scaling law. For example, a surface *z(x,y)* is a statistically self-affine fractal if it satisfies a relationship of the form

$$\gamma(h) \propto H^{2p}$$

where

$$\gamma(h)=<\{z(x_1,y_1)-z(x_2,y_2)\}^2> \text{ and } h=|(x_1-x_2,\ y_1-y_2)|$$

and p is some constant. Here the brackets <.> denote the spatial average over all pairs of points (x_1,y_1), (x_2,y_2) separated by a distance h.

Such surfaces are smooth if $p>1$ but are not smooth if $0<p<1$. In fact, for $0<p<1$, the fractal dimension of the "surface" (z(y), in (x,y,z) space is given by 3-p.

Within the project an investigation of the application and exploitation of fractals within the analysis and representation of soil gas data has been started.

For example, using the Vasto He data, provided by Rome University, we sought to estimate the fractal scaling relationship as follows. Firstly for all possible pairs of data points we calculated their distance of separation, h, and the square of the difference in their observed values. These were binned, on a log scale, so that an estimate of the mean value, $\gamma(h)$, could be made for each bin, along with standard deviations. On a log-log scale the relationship, $\gamma(h)$, was fitted to a straight line having slope 2p (Figure 3). In fact 15 bins were used for ln h values between 0.64 and 2.04, with bin widths 0.01. The number of pairs of data points within each bin was between 1,497 and 12,404.

The resulting fitted curve had slope

$$2p=0.42988$$

(standard deviation = 0.029). A χ^2 value for the fit was 15.45, giving a reasonable confidence of 27.9%.

As data becomes available, further analysis and mapping will be undertaken. Our aim is to validate the fractal conceptual model for soil gas distributions, prior to representing the soil gas data by fractal simulations.

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Table I

Survey	Mean	Std.Dev.	Mode	Val.Min.	Val.Max.	N.Samp.
P.d'Asco	30	102	0	- 221	242	108
Pisticci	570	3006	0	-1400	21010	264
Pist.R.	-28	247	0	- 879	949	246

Statistical descriptive parameters for helium results. In the third row the Pisticci results in a restricted range [-1000≤He≤+1000ppb] are given.

FIGURES

Figure 1 - Helium distribution in soil gas at Piano d'Asco. The dashed lines represent the alignment of the positive anomalies. The observed trends coincide with those of the local regional fault systems.

Figure 2 - Helium distribution in soil gas at Pisticci. The dashed lines represent the alignment of the positive anomalies. The observed trends coincide with those of the local regional fault systems.

Figure 3 - Vasto variogram.

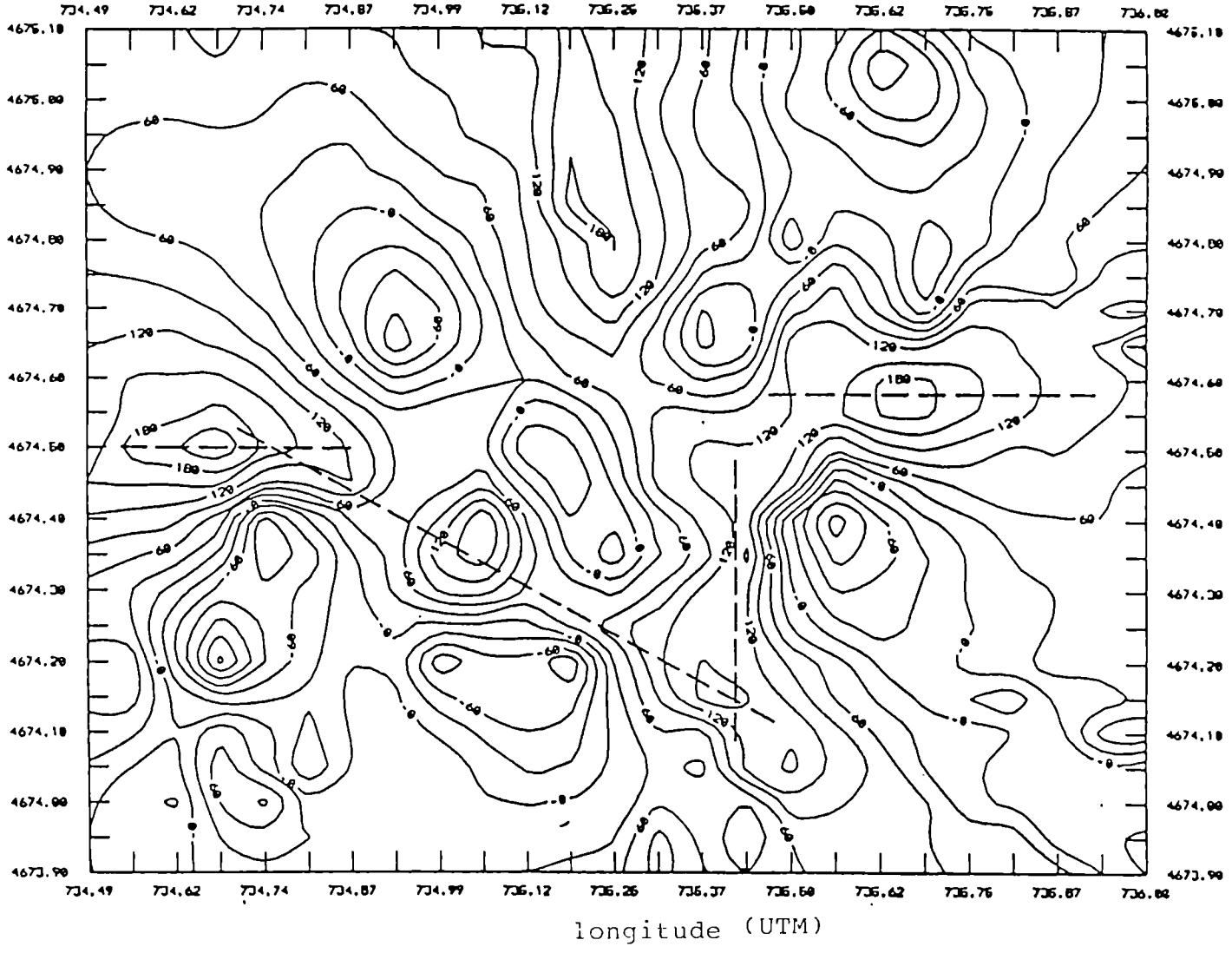

734.49
734.62
734.74
734.87
734.99
735.12
735.26
735.37
735.50
735.62
735.76
735.87
736.00
4675.10
4675.00
4674.90
4674.80
4674.70
4674.60
4674.50
4674.40
4674.30
4674.20
4674.10
4674.00
4673.90
latitude (UTM)
longitude (UTM)

Fig. 1

Fig. 2

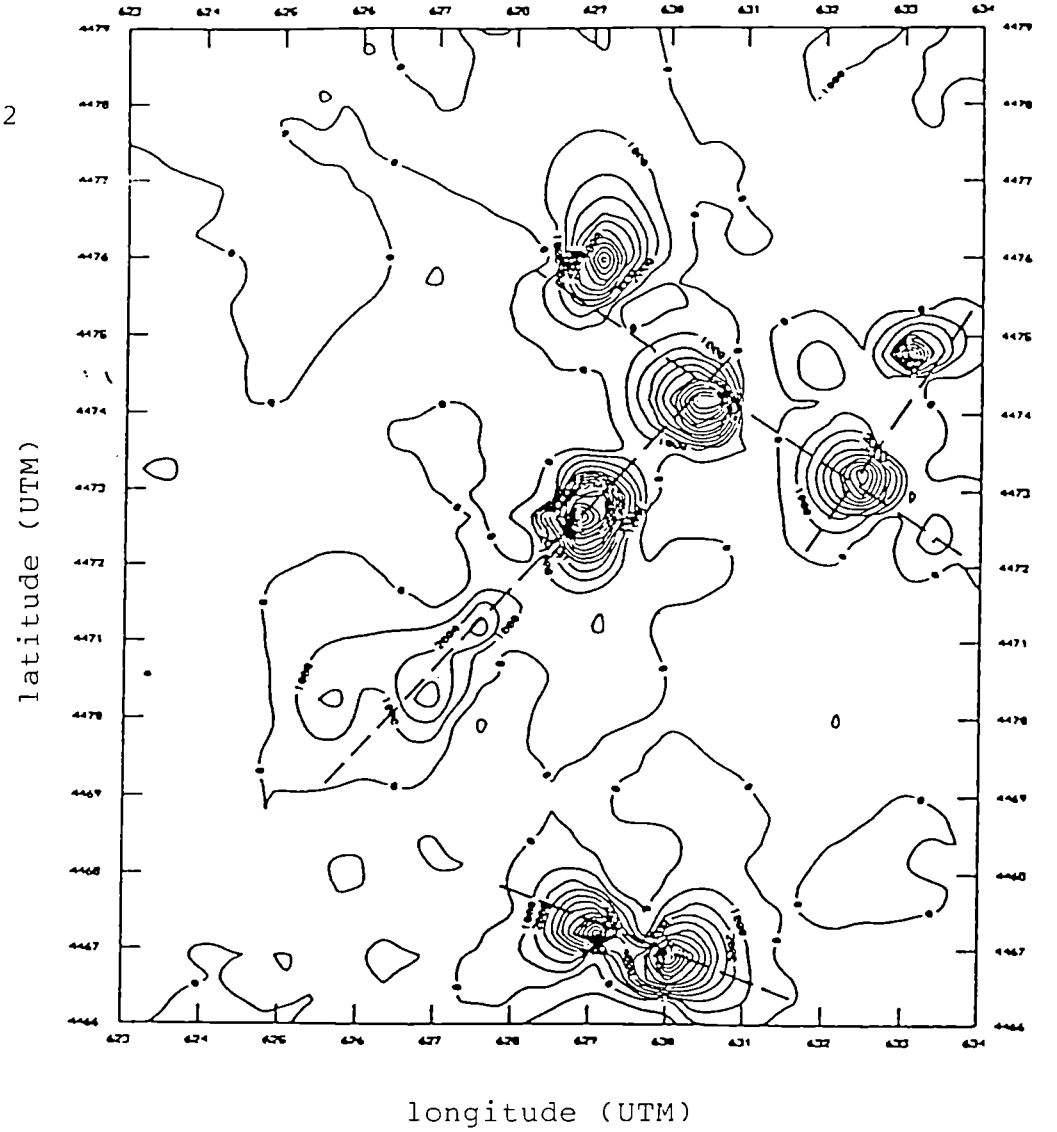
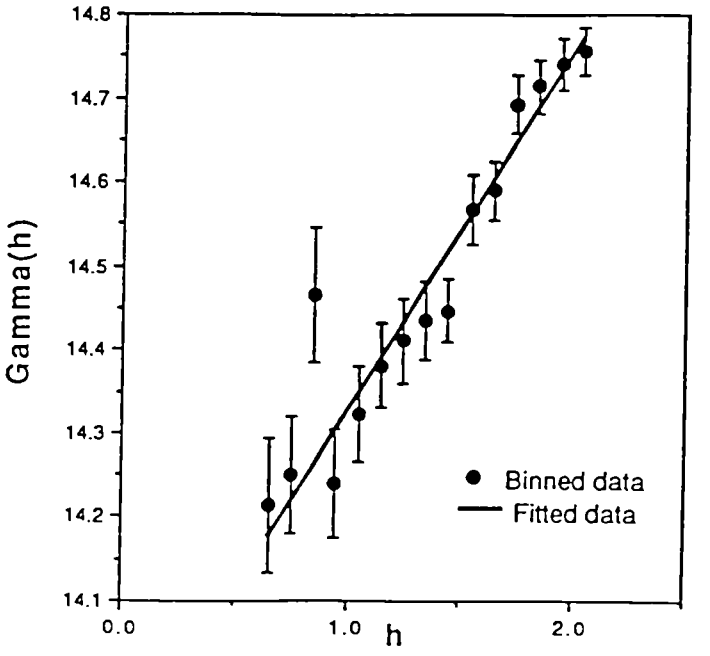

latitude (UTM)
longitude (UTM)

Fig. 3


Gamma(h)
h
Binned data
Fitted data
14.8
14.7
14.6
14.5
14.4
14.3
14.2
14.1
0.0
1.0
2.0

Title: Methodology studies on the sealing of boreholes

Contractor: BRGM, Department of Geotechnical Engineering
Avenue de Concyr, BP 6009, 45060 Orléans cedex 2, France

Contract number: F12W/0072

Duration of contract: October 91 to September 95

Period covered: 1.10.91 to 31.12.91

Project leader: J.F. Ouvry

A - OBJECTIVES AND SCOPE

The objective of the work is the design and implementation of an *in-situ* borehole sealing technique in crystalline rocks. The sealing or plugging of boreholes on or around a site for storing radioactive waste, usually is done by means of compacted bentonite, a bentonite grout, or a grout consisting of binders. It is proposed to manufacture a binder to which are added a bitumen emulsion, clay, and various other substances. A fracture will be identified in crystalline rock and will be sampled by means of drilling. Fissure space will be studied in the laboratory and data will be geostatistically processed. Water tests will be carried out to define the hydraulic behaviour of the fracture. Before and after injecting the special grout mixture into the fracture via one of the boreholes, tomography will identify the injection zone; core sampling of the injected fracture will enable to verify the quality of injection.

This contract combines a partnership composed of BRGM (F), the SIF Bachy company (F) and the Mott MacDonald Civil company (UK).

B - WORK PROGRAMME

1 - Bibliographic compilation and synthesis of earlier work.
2 - Laboratory tests to optimize the composition of the grout.
3 - Definition of an *in-situ* fracture by means of tomography, water tests and characterization of the fissure space from samples.
4 - Injection of the grout into the fracture, post-injection checks of penetration of the grout using tomography, and quality control of the injection through observation of core samples.

C - PROGRESS OF WORK AND OBTAINED RESULTS

State of progress

The progress of the work programme has been in three directions: bibliographic compilation and synthesis, selection of grout components and selection of the fracture. The bibliographic compilation (B.1) covers publications on plugging and sealing of boreholes, in the context of radioactive-waste storage, in Belgium, Canada, France, Italy, Sweden, the U.K. and the U.S.A. Some information is also available on the work carried out in Japan. Generally speaking, the North American and in particular Canadian (AECL) work remains relatively inaccessible, in spite of its importance.

The choice of grout constituents (B.2) led to selection of four cement types, two types of blast-furnace slag, microsilica, two types of lime and two commercial bentonites. The supply of superfine cement seems difficult and expensive. Commercial bentonites have a suitable grainsize, but their mineralogy is poorly known and may be variable; it is thus planned to buy 'FoCa' bentonite from Fourges-Cahaignes.

As experimental site (B.3), the Total Compagnie Minière uranium mine at Bernardan, northern Massif Central, France, was selected. Access is via a 3.5 m diameter decline and the local stress tensor is known from earlier work. After a short study, a fracture of satisfactory length was selected at 180 m depth.

Progress and results

Bibliographic compilation and synthesis (B.1, Programme of Work)

Today, the plugging or sealing of boreholes drilled to investigate the storage of radioactive waste, is done by emplacing plugs of compacted bentonite, or by injection of bentonite grout or cement grout.

In crystalline rocks such as granite it is recommended to use high-density compacted bentonite (>20 kN/m^3), whose hydration and swelling potential assure a perfect seal of the borehole. The use of calcic bentonite is planned in Sweden (Stripa), France (CEA) and Belgium

(CEN/SCK). Emplacement is by the introduction of perforated casing filled with dry and compacted bentonite. All types of boreholes can be plugged, regardless of inclination, deviation or diameter.

Injection tests with bentonite grout (Tixoton-Na) were carried out with a dynamic method for the Stripa project (1988-1991) in the Swedish mine of the same name. The results show that fissures with an average width of 0.1 mm can be injected, but that the injection in boreholes seems limited because of the rapid attenuation with depth, of the dynamic injection oscillations.

Injection with cement grouts has been planned for crystalline as well as sedimentary host rocks. In the tuff at Yucca Mountain (USA), the use of cement grout is particularly suitable in view of the physico-chemical compatibility between cement and the calcic nature of the tuff. In the Canadian Pinawa granite, injection tests of cement grout in a fracture zone (upper part of the granite) were carried out below access and ventilation shafts, but results are as yet unavailable. On the Harwell site (UK), tests of injecting cement grout into clay did not have the expected result, in particular because of lack of adhesion between clay and grout. Finally, research is being carried out in Japan and Canada on the use of super-fine cement, and is quite advanced at the University of Sherbrooke (Quebec) and AECL on the composition of the grout, its penetrability and its longevity.

Selection of grout components (B.2, Programme of Work)

The grout being developed by Bachy as part of the CEC contract, is primarily composed of:

- a bitumen emulsion;
- a clayed mineral phase that ensures stability of the grout;
- a binder, to be selected from cement, slag, or lime and microsilica.

The penetrability of such grout is largely related to its flow behaviour in a fracture (shear threshold, viscosity) and to the grainsize of its constituents. As of now, grainsize studies have led to the selection of:

- a superfine blast-furnace slag with a median diameter (d_{50}) equal to 2.65 μm and a d_{90} diameter equal to 6.54 μm;
- microsilica of d_{50} = 0.53 μm and d_{90} = 2.34 μm;
- micronized lime of d_{50} = 1.32 μm and d_{90} = 5 μm;
- commercial calcic bentonite of d_{50} = 2.95 μm and d_{90} = 6.36 μm (after 24 hours of hydration).

At the moment, the supply possibilities of superfine cement and FoCa bentonite are being investigated.

The proportions of the mixture will be fine-tuned on the basis of workability, rheology and penetrability of the grout, which will mostly consist of binder. The bitumen emulsion will be obtained with a high-energy turbine; the expected d_{50} of bitumen globules will be a few μm.

Concerning the longevity of the hardened grout, permeability and leaching tests in the laboratory will only provide information that is valid for the duration of the tests.

Selection of a natural fracture (B.3, Programme of Work)

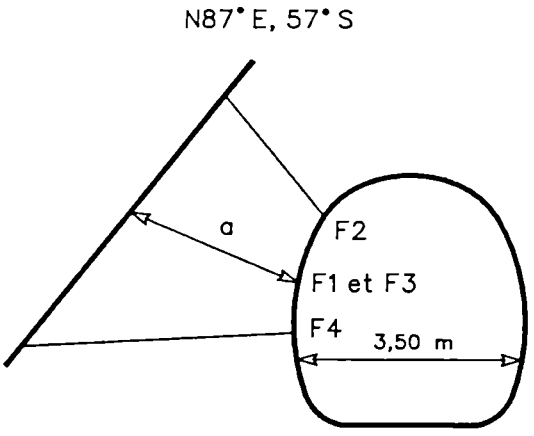
The Bernardan uranium mine in the northern Massif Central, France, operated by Total Compagnie Minière, was selected because of its accessibility and the fact that the local stress tensor is known from earlier hydraulic fracturing studies by BRGM (1). A natural fracture of sufficient length was found at 180 m depth, after a short review of fracture data; its trend is N 87° and its dip is 57° S.

The fracture plane will be obliquely cored in four places, as shown schematically on Figure 1. The fissure cavities of the four core samples will be studied in the laboratory with profilometry, according to a method developed by BRGM (2). Geostatistical processing of the results will enable to determine the geometrical characteristics of the fracture, such as opening and angularity.

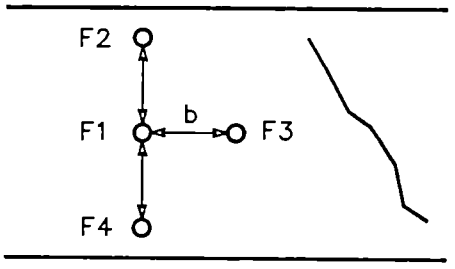
On the site, electromagnetic tomography will be carried out between the four boreholes, which should enable to define the extension of the fracture. Water-injection tests will then clean the fracture between the boreholes, after which it will be ready for injection of the grout.

List of publications

No publications as yet.



CROSS-SECTION



a = 5 m
b = 1 a 2 m
F1 a F4 : Ø 116 mm

ELEVATION

Figure 1 - Location of the fracture selected for grout-injection tests and schematic plan of the coring.

REFERENCES

1 - Burlet, D. - Détermination du champ de contraintes régional en France à partir de tests hydrauliques en sondages. Final Report of contract EN3G-0056-F(CD), 1990

2 - Gentier, S., Billaux, D. and Van Vliet, L. - Laboratory testing of a void of a fracture. Rock Mechanics and Engineering, 22, 149-157, 1989

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 :		from 01-03-91 to 31-12-91
Project leaders :		G. Volckaert (coordinator), P. Grindrod, S. Horseman, V. Fioravante

A. OBJECTIVES AND SCOPE

In a deep geological disposal facility there are several possible sources of gases 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. 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.

Within this project INTERA will perform the main modelling work. The SCK/CEN will be responsible for the gas reaction, diffusion and uniaxial flow and in situ experiments. BGS will perform geotechnically based triaxial gas flow experiments. ISMES will perform experiments at higher temperature.

B. WORK PROGRAMME

1. Chemical and diffusion experiments

Preliminary experiments have shown that Boom clay has a certain capacity to react with hydrogen. The intrinsic reaction rate, the reaction capacity of the Boom clay and the diffusion coefficient will be determined.

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

The in situ experiments 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 model.

C. *PROGRESS OF WORK AND OBTAINED RESULTS*

State of advancement

1. Chemical and diffusion experiments

A chemical reactor has been designed and is now under construction.

For the diffusion experiments the initial idea was to use a flow through diffusion set up. This technique however requires an accurate determination of the concentration of dissolved hydrogen which was found to be complex to integrate in the experimental set up. Therefore this idea has been abandoned and in stead it will be tried to use the in diffusion technique which only requires the measurement of the hydrogen consumption at the inlet side. For these experiments the same type of equipment as for the uniaxial breakthrough experiments will be used.

2. Geotechnical experiments : uniaxial

The uniaxial experiments are running as planned. The relative gas permeability has been determined for artificial Boom clay plugs with a dry density close to the in situ dry density.

Also a first series of gas breakthrough experiments could be performed. The breakthrough pressure varied between 0.9 and 2.9 MPa and a clear relation with the hydraulic conductivity could be demonstrated.

3. Geotechnical experiments : triaxial

The design of the experimental cells have been adapted to allow for gas injection. First experiments are planned to start in the next semester.

4. In situ experiments

A first injection experiment using an existing piezometer is planned for next semester.

5. Modelling

A review of available literature on transport and dispersal of gas through clays and of available two-phase flow codes has been made. For the situation of a repository in clay the new two-phase flow code TOPAZ was developed. Also a number of scoping calculations were performed using analytical models for a number of important phenomena in gas migration.

Progress and results

SCK/CEN

Relative gas permeability

To determine the gas permeability as function of the degree of saturation a series of gas flow experiments was carried out on artificial clay plugs with different degrees of saturation but with a dry density of 1.7 g/cm^3, which is the same as the in situ Boom clay. The plugs were made by uniaxial compaction of clay powder with a homogeneous water content. Clay powder with a homogeneous water content up to 9 weight % is produced using a climatic cabinet while wetter samples are produced by spraying a fine mist over a thin layer of clay powder. The prepared clay powder is directly compacted in the permeameter cell to avoid the transfer of the compacted sample and to avoid a gap between the sample and the wall of the cell. The press used to compact the samples has been equipped with a displacement transducer so that theoretically the density of the samples could be regulated with a precision better than 1 %. During the gas flow measurements special attention was paid to the stability of the degree of saturation of the samples. In all experiments the permeameter cell was blocked in a rigid frame equipped with a displacement transducer so that the

swelling of samples could be avoided or that potential shrinkage could be determined. In none of the experiments shrinkage was observed which confirms that the samples did not dry out. The pressure gradient over the plugs was controlled only by the inlet pressure, the outlet pressure was always the atmospheric pressure. The gas used up to now was Ar, in the future also He might be used. The gas permeability of about 40 clay plugs has been measured and the saturation range between 0 % and 95 % has been covered. The relative gas permeability of the Boom clay seems to become 0 at a saturation of about 90 %. At this saturation no continuous gas channels remain available and the gas breakthrough pressure becomes > 0. This point is called the "residual gas" point.

Breakthrough experiments

Natural clay plugs were prepared from either fresh Boom clay samples or well preserved Boom clay cores. The plugs were made using a lathe so that they have a very smooth surface and exactly the diameter of the permeameter. Directly after their preparation, the clay plugs are transferred to the permeameter cells which are of the same type as those used for the relative permeability experiments. The smallest volume change which can be measured by this system is 3 µl. First the hydraulic conductivity of the clay plug is measured and then gas is injected at the top of the clay plug at a pressure difference below 1 Mpa. The pressure difference is gradually increased until breakthrough occurs. In table 1 the results obtained up to now are summarized. From the breakthrough pressures maximum pore diameters were estimated. Figure 1 clearly shows that there is a relation between hydraulic conductivity and the breakthrough pressure.

BGS

Theoretical development

A literature search and an identification of possible gas migration mechanisms has been completed. A parameter evaluation with special reference to Boom clay has been performed. Parameters for Boom clay have been compiled under the following headings :

- index properties
- geotechnical and hydrogeological properties
- mineralogical and bulk geochemical properties
- hydrochemical properties

Were possible ranges have been assigned to the key properties to enable scoping calculations to be performed.

In order to assist in experimental design, simple scoping calculations have been performed on pore size, gas diffusion rates (1-D), gas solubility, capillary entry pressure, bubble pressures and the conditions that could lead to gas-fracturing. Based on those scoping calculations , a number of scientific conclusions have been drawn.

Using a parallel plate model for the clay fabric, the "average" pore size of the Boom clay is estimated to be in the range 8 - 12 nm. This compares with a van der Waals molecular diameter of 0.278 nm and a mean free path of 112.3 nm for hydrogen. Thus the "average" pores are of molecular size. During the diffusion of hydrogen through the clay pores, the collision of gas molecules with solid surfaces is likely to be important suggesting a Knudsen-type diffusion mechanism.

If we perform capillary entry pressure or bubble pressure calculations for pore sizes in the range 8-12 nm, it is found that the pressure of the hydrogen phase is exceeding high and might exceed the lithostatic stress,

at depth, in the clay.

It can be argued that gaseous phase flow in the clay will be accompanied by pore enlargement. Essentially, the clay fabric becomes locally deformed to accommodate the gas flux. The high pore pressure and low effective stress in a region of the clay subject to a gas flux will tend to produce localised increase in pore size. This is one of a range of mechanisms that require experimental examination. Also the application of hydrofracture theory to the problem of gas fracturing has been examined and a number of scoping calculations in this area have been performed.

Experimental design

The original proposed adaptation of a triaxial cell is believed to be to complicated for the planned experiments and is likely to lead to difficulties in sealing the sample and obtaining a gas-tight system. Therefore a more simple apparatus has been designed for gas migration experiments on 50 mm diameter specimens. The vessel is a factory-modified pressure vessel (Autoclave Engineering or High Pressure Equipments-HIP) rated at 70 Mpa. The vessel will be equipped with five ports : gas-in, gas-out, water-in, water-out plus a water pressurisation port. An optional "floating piston" is to be purchased to enable experiments to be performed on "remoulded" clay if this proves desirable. The internal dimensions of the pressure vessel are 75 mm internal diameter by 250 mm nominal internal length, allowing considerable flexibility in specimen size.

The test gas will be helium which provides a safe analogue of hydrogen in laboratory experiments.

Gas injection will use a syringe pump equipped for precise flow-rate or pressure control and capable of accurate volume-change measurements. Using a gas-water column, gas flow can be achieved by pumping water. Experiments are scheduled to start in May 1992.

ISMES

Experimental design

The experimental system is base on the HITEP apparatus which is basically an equipment for triaxial tests where a cylindrical soil sample is subjected to a selected stress-strain state and drainage condition and where the temperature of the sample can be controlled.

The modification needed to allow the HITEP for the tests on gases mainly concern the internal cell. Two ideas were chosen, called the "oedometer" and the "needle" solutions.

The working principle is the same for both solutions : the soil sample can be consolidated to a required stress level in k_o condition (i.e. lateral deformations are avoided); the gas is initially contained in an "input pressure chamber". During the test the gas migrates from the input chamber through the sample and it is collected to an "output chamber" which does not contain gas before the test.

In the first solution, two porous stones, which contain the sample, are connected to the gas chambers. The gas pressure is homogeneously distributed at the bottom of the sample so it should migrate through the soil following parallel flow lines (1 D flow problem).

In the second solution, the gas from the input chamber will be injected through the soil sample by a hollow needle placed along the axis of symmetry. In this case the gas migration becomes a three dimensional problem.

Although the second solution could be theoretically more difficult to

interpret than the first one, it seems to be practically easier to achieve. Therefore in the last period our efforts were devoted the cell for the needle solution.

A draft of the designed cell is reported in figure 2. The main features can be summarized as follows :

The gas, at the required pressure and temperature, is initially contained in two chambers. One of the two chambers (called input gas chamber) will be connected to the hollow needle during the test while in the other, used as reference, the pressure will be kept constant. The decay of the pressure measured by a differential transducer, allows a direct measure of the migration through the soil. The soil sample is constrained in a porous annular cylinder contained in a chamber called "output gas chamber". This chamber is filled with water and is used for the back pressure of the sample. If the gas goes through the soil sample then it will be collected in this chamber where the pressure will increase.

The sealing of the system has been tested and now the system will be further tested on sand samples at low stress states before the experiment on clay will start.

INTERA

Modelling

INTERA have made considerable progress on the mathematical modelling aspects of the MEGAS project. Two reports and the two-phase flow code TOPAZ have been produced.

The first report [1], is a comprehensive review of available literature on the transport and dispersal of gas through clays, with particular reference to hydrogen within Boom clay. A number of mathematical modelling issues were highlighted, including conceptual model uncertainty (two-phase flow and its alternatives); parametric uncertainty (saturation dependent processes); and the possible effect of (relatively) high gas pressures upon the structure of the Boom clay. The report suggests that both numerical two-phase flow and analytical interfacial displacement models should be considered in parallel. The report also highlights a number of issues (viscous fingering, clay elasticity) whose role in gas migration in Boom clay may be important, but is relatively poorly understood.

In addition the report reviews available two-phase codes capable of making repository scale calculations, and sets out the two-phase model encoded in TOPAZ. The code utilizes an essentially 1-dimensional model for the simultaneous flow of gas and water through a porous medium, which may be extended to 2 and 3 dimensions by using cylindrical or spherical coordinate geometry and corresponding symmetry assumptions. Input boundary conditions of constant gas flux or pressure at a constant gas saturation of unity are imposed, together with output boundary conditions of constant water pressure and water saturation of unity.

The second report [2] examines analytical mathematical modelling of a number of phenomena in gas transport and dispersal of gas in clay. The report presents models developed for gas transport and dispersal of gas in clay. The report presents models developed for gas dissolution and diffusion, reaction-diffusion, steady-state flux through saturated or partially-saturated clay plugs, and gas bubble growth. These models were used to provide initial estimates of the physical conditions to be encountered, both within the MEGAS experimental programme and within the ONDRAF/NIRAS repository scenario. These estimates represent initial "best guesses", to be added to and amended over the period of the MEGAS project.

List of Publications

G. Volckaert (SCK/CEN, Belgium), P. Grindrod, M. Impey (INTERA-SCIENCES, UK), V. Fioravante (ISMES, Italy), S. Horseman (BGS, UK)
MEGAS : MODELLING AND EXPERIMENTS ON GAS MIGRATION IN ARGILLACEOUS HOST ROCKS
In Proceedings of the NEA Workshop on Gas Generation and Release from Radioactive Waste Repositories
Aix-en-Provence, 23-26 September, 1991

Table I : Results of the breakthrough experiments

Plug height cm	Density kN/m^3	Orientation	Hydraulic conductivity m/s x 10^{-12}	Break-through pressure MPa	Maximum pore radius m x 10^{-9}	Flow 10^{-4} Nml/min
4.25	20.29	vertical	2.3	2	49	NA
5.255	20.17	horizontal	3.6	1.2	82	35
5.00	20.40	vertical	1.8	1.5	66	3400
4.71	20.24	NA*	2.1	0.9	110	460
2.765	20.38	vertical	3.4	2.2	45	7.1
5.00	NA	45 °	7.4	1.4	71	28
3.575	NA	horizontal	7.5	< 1.5	> 66	NA
3.20	NA	NA	3.3	2.4	41	2.2
3.995	20.82	artifical plug	1.5	2.9	34	1.1

* NA : not available

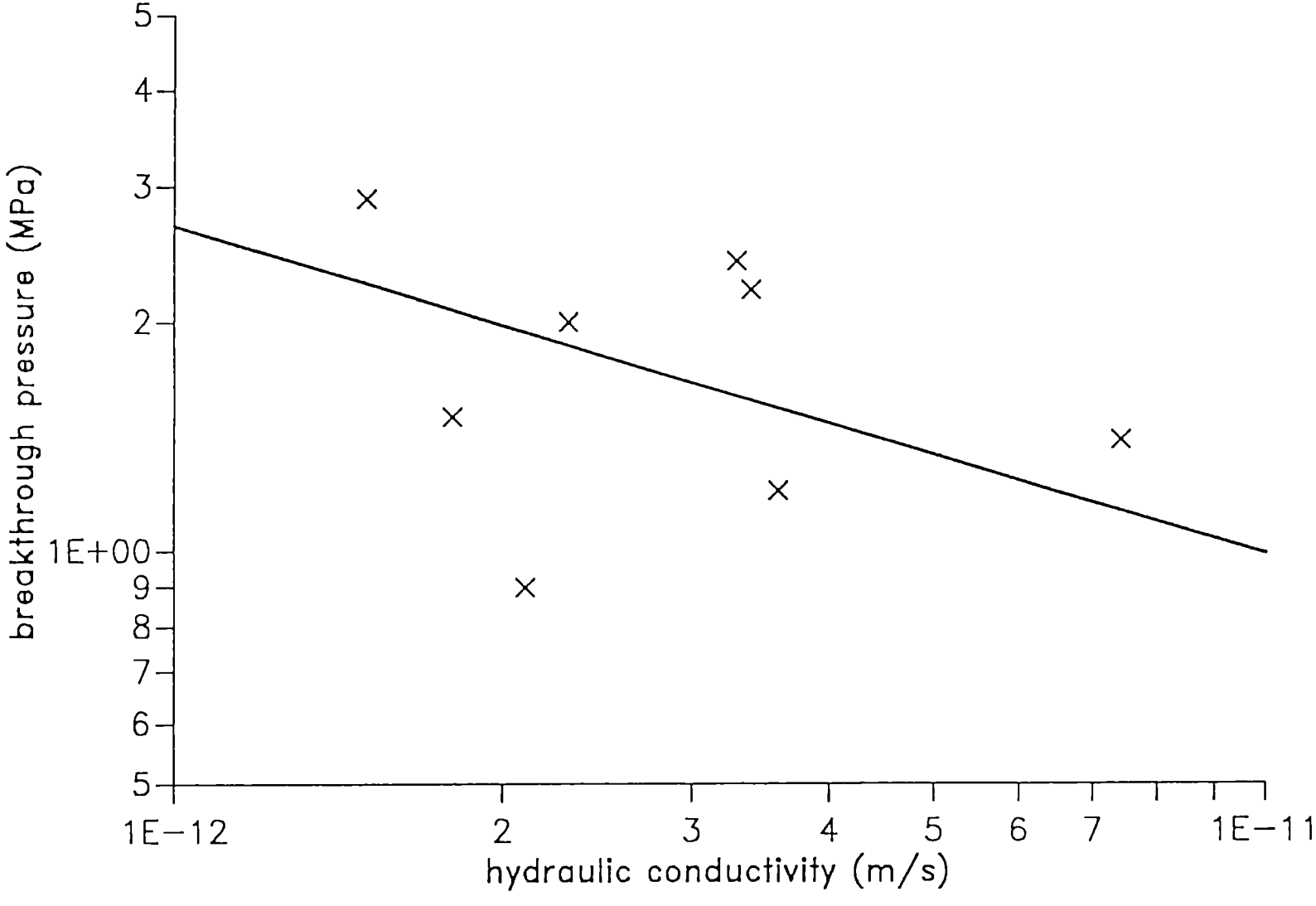


Figure 1 : Breakthrough pressure as function of hydraulic conductivity

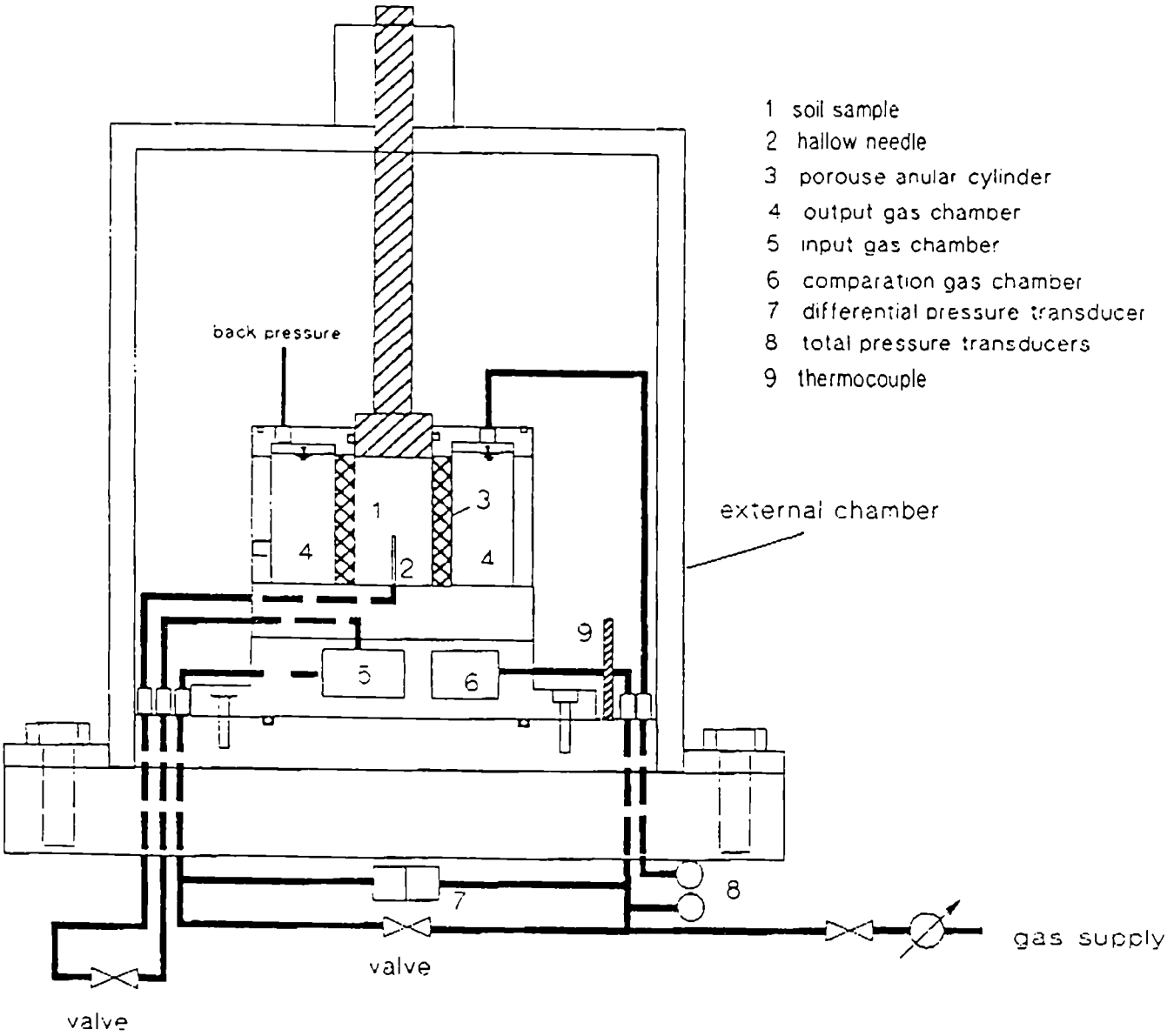


Figure 2 : Internal chamber "needle solution"

GAS PRESSURE BUILD-UP IN RADIOACTIVE WASTE DISPOSAL : HYDRAULIC AND MECHANICAL EFFECTS

Contractor: GEOSTOCK, France
Contract N° : FI2W/0093
Duration of contract: July 1 1991 - June 30 1995
Period covered: July 1991 - December 1991
Project Leader: P. COLIN

A. Objectives and scope

The specific aim of this study is to evaluate the consequences 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 the 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 simulators used in the oil industry. A sensitivity study will then be performed. The mechanical modelling using new theoretical developments for fracture initiation and propagation through the bifurcation theories will be carried out with the cooperation of the French Institute of Petroleum (IFP); the scientific adviser is Pr Dragon from ENSMA in Poitiers (France).

B. Work programme

1. Phenomenology review : inventory of two phase flow phenomenology applied to gas migration from a radioactive wastes repository.
2. Laboratory experiments : limited number of investigations (threshold pressure, capillary pressure, relative permeability, etc) on some representative host rock core samples.
3. Two phase flow modelling : suitability of existing reservoir codes, simulation of gas pressure build up (isothermal flow, and in thermal conditions), in porous and fissured medium.
4. Mechanical developments and modelling : theoretical works for the elaboration of a new criteria for fracture initiation and propagation.
5. Conclusions.

C. Progress of work and results obtained

State of advancement

The main activity during this six months period (July - December 1991) is essentially related to the phenomenology to be considered for the simulation of gas migration throughout a radioactive waste repository, to the elaboration of a data base and to a first modelling activity on a simplified geometry.

PROGRESS AND RESULTS

1. Phenomenology involved in gas migration (step 1)

Gas generation rates

The gas produced from corrosion and radiolysis is mainly hydrogen. The gas flow rate is a dimensioning parameter for the ensuing pressure build up. The information available in the literature related to gas generation has been reviewed. It is concluded that the volume liberated may be two or three orders of magnitude greater than the repository volume; anyhow some further contacts will be taken (ANDRA, ENRESA, ONDRAF, and other partners) in order to more clearly assess the knowledge on the possible gas volume generation mechanisms and flow rate history with time.

Molecular diffusion

The first phenomenon expected is the dissolution of the gas into the surrounding water, the quantity dissolved depends on the solubility, pressure and temperature. The molecular diffusion is a possible phenomenon for gas migration but the quantity of gas evacuated by diffusion is expected to be low because of the low diffusion coefficients (in the range of 10^{-9} m^2/s).

Migration - fracturation

If the gas production is such that a gas phase is formed, the gas migration is controlled by the threshold pressure (P_T), and the permeability-capillary pressure (kr-Pc) properties of the backfill and the host rock.

The situations where fracturation may occur are analyzed. If the gas pressure (P_{gas}) reaches P_{frac} then :

- If $P_{frac} < P_T$ then the flow occurs mainly in the fractures, leading to accumulation, then an extension of the fracture network,
- If $P_{frac} > P_T$ then the gas flows through fractures and toward the matrix.

This research will be focused on fracture initiation in step 4.

Two phase flow modelling

Conventional two phase flow numerical codes used for the simulation of oil reservoirs may be suitable for the simulation of a non wetting phase (gas) displacing a wetting phase (water), through a radioactive waste repository in isothermal conditions. The thermal effects may be simulated with thermal simulators.

Such a flow can be described by a system of coupled equations in time and space. The equations used to solve this problem are :

- Continuity equation : mass balance for each component (1)
- Darcy's law for multiphase flow (2)
- Relative permeability (kr) equations (3)
- Capillary pressure equation (Pc) (4)
- Relationship between the saturations (5)

It is recalled that the flow is described assuming Darcy's law. This might be questionable in very low permeability media like clay due to the pore size distribution. To our knowledge there is no simulator which takes into account non-Darcy flow.

The relations (3) and (4) can be determined either by appropriate laboratory experiments or, if not available, with empirical models establishing the expression of kr and Pc versus phase saturation (Corey or Grant models).

The numerical resolution of the above equations on a discretized geometry, often uses a finite difference method with an IMPES scheme (Implicit in Pressure and Explicit in Saturation) or fully implicit scheme giving less numerical dispersion.

The molecular diffusion process is not taken into account by classic two phase flow models, though it appears that the numerical dispersion due to the discretization in space is important and can be described by an equation which is similar to the one describing the diffusion mechanism. Another solution would be to use finite elements models.

Our scope of work (step 2) comprises experimental investigations which have not been carried out during the relevant period (no representative core samples available).

2. Two phase flow modelling (step 3)

Choice of a representative data set

Due to the deficiency of measurements concerning kr-Pc data, some empirical properties have been set for a typical clay host rock. The intrinsic permeability is $k = 4.5\ 10^{-13}$ m/s.
Some correlations were used in order to build the kr-Pc curves, both phase saturation dependent.
The threshold pressure P_T was derived using the intrinsic permeability / P_T correlation.

The kr(Sw) equation was derived from Corey equations using the pore size distribution obtained from the Leverett J function.
Figures 1 and 2 show the capillary pressure and relative permeability curves for a hypothetical clay host rock.
The other PVT parameters necessary for a two phase flow simulation have been derived from standard data tables for hydrogen gas and water.

Preliminary results

A simple 3D model has been run in order to test the physical validity of the data set and get some order of magnitude of the pressure response for hypothetical gas flow rates. The geometry consists in a clay host rock 200 m thick, whose top is at 600 m depth, separated by two permeable sandstone layers 100 m thick. The rock properties are assumed to be isotropic and homogeneous.
The models used are PC-BOAST2 (in the preliminary phases of the simulation work) and SCORE which is a large size model developed by French oil companies Elf Aquitaine and Total-CFP, by Gaz de France and IFP.
The preliminary results indicate that the order of magnitude of the pressure build up is 6 MPa, for a constant gas flow rate ($qg = 1000\ Nm^3$/year) over a period of time of 5000 years (see figure 3).
The horizontal distance concerned by the gas migration is dependent on the clay effective (or kynematic) porosity : the horizontal distance is 100 meters for a kynematic porosity of 15% (see figure 4) and 150 m for kynematic porosity of 3%. The vertical migration is of the same order of magnitude.
Those results are indicative and based on conservative and maybe non realistic assumptions : simplified geometry, no backfill materials, non representative gas flow rates, isotropic and homogeneous conditions.

3. Further actions

- Perform a limited number of laboratory investigations (kr-Pc);
- Simulations on conceptual near field geometries in order to test the efficiency of backfill-type candidates regarding gas pressure build up;
- Influence of different kr-Pc correlations;
- Thermal simulations in order to quantify the influence of a steam phase.

FIGURE 1

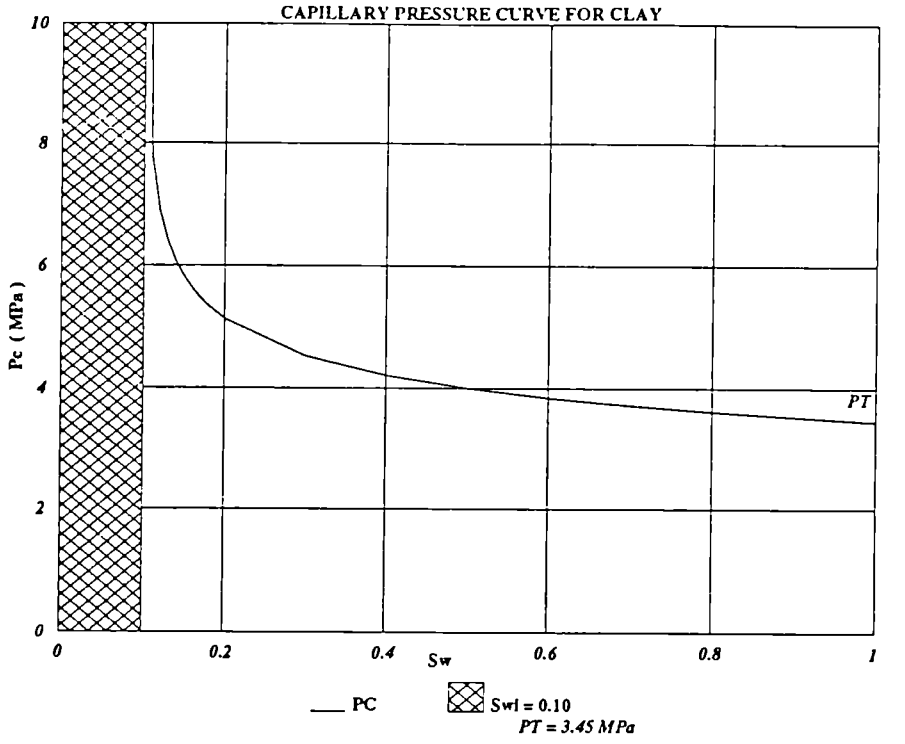
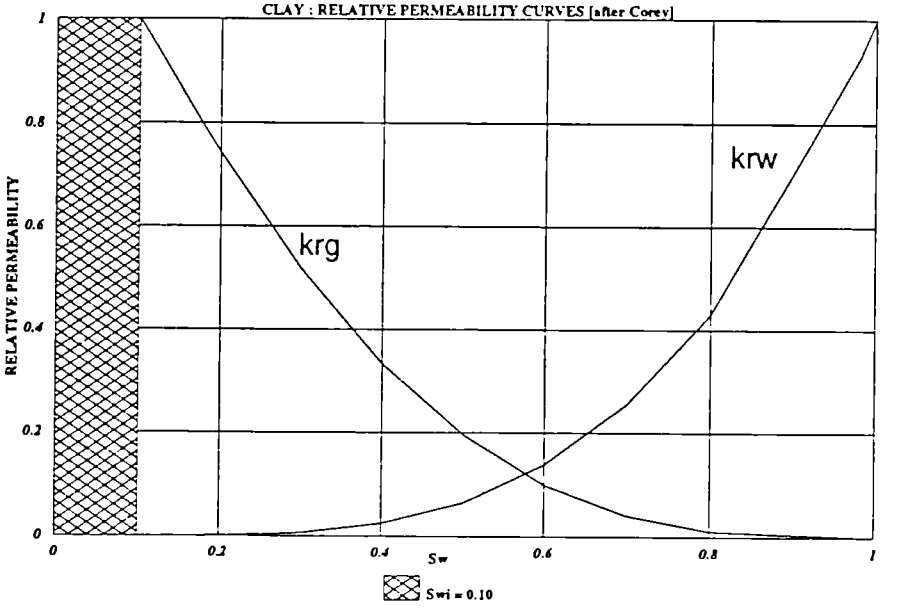


FIGURE 2



GEOSTOCK

Contract CEC-FI2W/0093

FIGURE 3

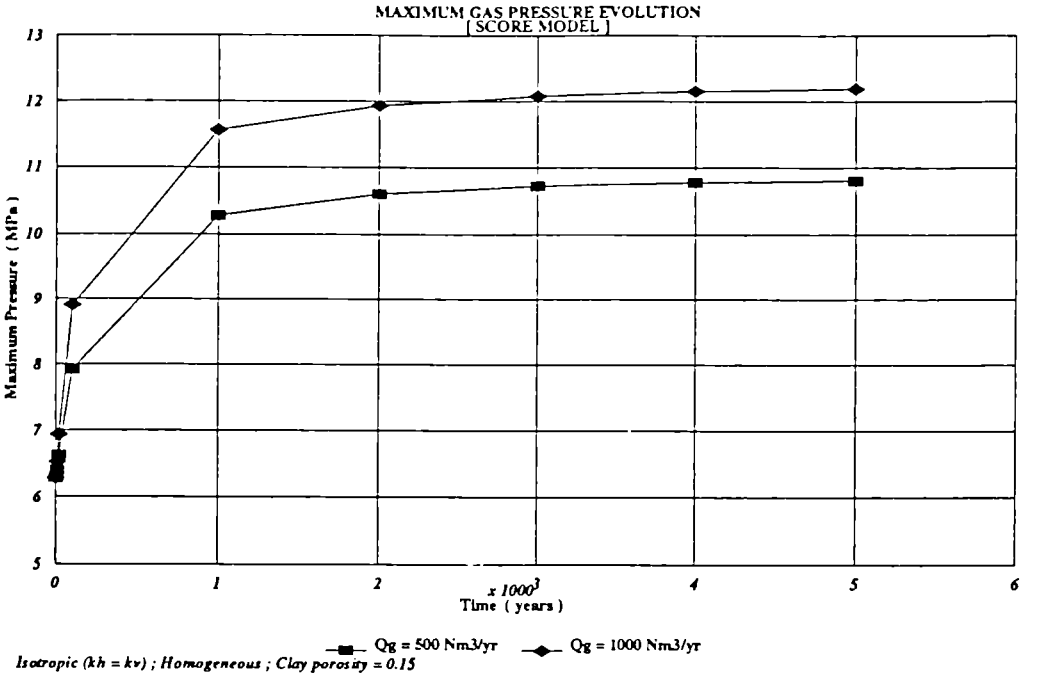
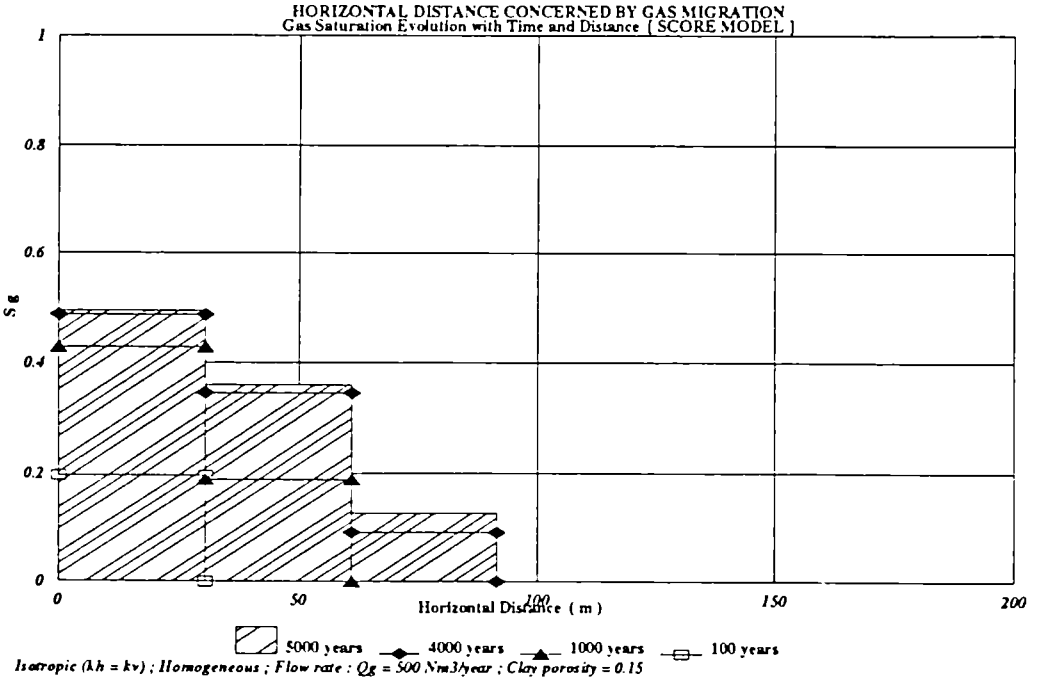


FIGURE 4



GEOSTOCK

Contract CEC-FI2W/0093

Continuation of the migration experiments (laboratory and in situ)

Contractor : ONDRAF/NIRAS, Brussels. Belgium

Contract N° : FI2W/0039

Duration of contract : September 1991 - August 1995

Period covered :September 1991 - December 1991

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/diffusion experiments in the laboratorium 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, ^{135}Cs, ^{237}Np) and possibly critical radionuclides (^{75}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 ^{3}H and ^{134}Cs were started previously and are regularly monitored.
   Additional tests with Am, Tc and H are planned.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

1. Lab-experiments

   Four new ^{75}Se migration experiments were started (2 diffusion and 2 percolation). Two of them were stopped after 8 and 11 months and are currently being analysed (^{75}Se counting of the clay slices and parameter determination).

   One ^{235}Np percolation experiment was stopped after 3.25 years. ^{235}Np counting of the clay slices is in progress.

   Two new mixed ^{14}C - ^{131}I flow-through diffusion experiments were started to study CO_3^{2-} migration. One previously started $^{14}CO_3^{2-}$ experiment was analysed and the migration parameter values were obtained.

2. In_situ

   The HTO injection experiment is sampled every 4 months. The measured results coincide very good with theoretical predictions.

   A new HTO injection experiment in a 3D piezometer configuration is in preparation. The experiment will actually be started in the second half of 1992.

Progress and results

1. Lab-experiments

   Four new migration experiments with ^{75}Se were started. For two of them $^{75}SeO_3^{2-}$ was equilibrated with a Boom clay slurry for 40 days, reducing SeO_3^{2-} to HSe^-. The slurry was dried and compacted and this clay slice was used as ^{75}Se source in 1 diffusion and 1 percolation experiment. For the other two experiments an Amicon filter, on which metallic ^{75}Se was precipitated, was sandwiched between two clay plugs (percolation experiment) or contacted with one side of a clay plug (diffusion experiment).

   The two Boom clay reduced ^{75}Se experiments were ended after 8 (diffusion experiment) or 11 months (percolation experiment). The ^{75}Se counting of the clay slices and the determination of the migration parameters ηR and D are actually in progress. The observation that no percolated ^{75}Se could be detected in the down stream reservoir of the percolation experiment indicates a strong retardation of the added ^{75}Se. The ^{75}Se profile in the clay plug should confirm this. These results will be available beginning 1992. The termination of the two metallic ^{75}Se experiments will completely depend on these results.

   One ^{235}Np percolation experiment was terminated after 3.25 years (3 other Np migration experiments, 2 diffusion and 1 percolation, are still running). The ^{235}Np counting of the clay slices is currently in progress. The analysis and parameter values will become available early 1992.

Two new mixed ^{14}C - ^{131}I flow-through diffusion experiments were started to study the migration behaviour of $^{14}CO_3^{2-}$. Carbonate is one of the more probable carriers of ^{14}C in the Boom clay. The first ^{14}C - ^{131}I experiment will be terminated in January 1992.

A previously started ^{14}C flow-through experiment was analysed. The migration parameters ηR en D were determined from the cumulated activity collected in the down stream reservoir, yielding $\eta R = 0.15$ and $D = 7.4\ 10^{-11}\ m^2.s^{-1}$. This value for the apparent dispersion constant D is only a factor 3 lower than D values for the non-retarded HTO or I, indicating a very minor retardation of $^{14}CO_3^{2-}$.

Two percolation experiments for measuring the mobility of dissolved organic matter in Boom clay were started. Migration of Boom clay organic molecules is studied by alternately percolating undisturbed clay cores with synthetic clay water (i.e. without organic matter) and real clay water. By monitoring the effluent and analysing the percolated organic matter the migration parameters can be obtained. Final results are expected mid 1992.

2. In_situ experiments

The HTO injection experiment in the multiple piezometer CP 1 (started February 1988) is running as foreseen. The sampling intensity has been reduced from once every 2 months to once every four months. The new HTO concentration measurements coincide very good with the theoretical migration predictions.

A new HTO injection experiment in a 3D piezometer configuration is in preparation. Three multiple piezometers are actually being installed and the exact relative position of each piezometer is accurately measured. After Boom clay convergence around the piezometers the HTO solution will be injected (second half of 1992).

The in situ ^{134}Cs percolation experiment (started July 1987) is sampled regularly but no ^{134}Cs has been detected so far in the percolated liquid.

List of publications

The paper "Migration of radionuclides in Boom clay - The interaction of safety assessment needs with experimental studies" (De Preter P., Put M., De Regge P.) was presented as a poster at the Migration '91 conference, Jerez de la Frontera, Spain.

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CHEMVAL2: A COORDINATED RESEARCH INITIATIVE FOR EVALUATING AND ENHANCING CHEMICAL MODELS USED IN RADIOLOGICAL RISK ASSESSMENT

Contractor/Coordinator: WS Atkins Engineering Sciences, Epsom, UK

Contract No: FI2W/0065

Duration of Contract: May 1991 - December 1994

Period Covered: May 1991 - December 1991

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 chemistry 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, G Ouzounian)
b) Ionic Strength Effects: GSF-IfH, Germany (H Lang)
c) Organic Complexation: LUT/Atkins ES, 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.

The exact scope and nature of work to be carried out will be as agreed at Plenary Meetings of CHEMVAL participants to be held throughout the Project.

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of Advancement

During the first seven months of the Project, working groups have been established for all technical activities. These will undertake data collation and model verification tests in the first half of 1992 - the latter defined by the Technical Coordinators. As with the earlier phase of CHEMVAL, more demanding validation exercises will be considered only when the new models have been verified adequately but searches for suitable laboratory and field experiments have already begun. In the case of coupled chemical transport modelling, where most of the codes to be used have already been tested to some extent, the situation is more advanced. Bespoke column experiments at AEA Winfrith and CEA Grenoble have been commissioned allowing a methodology for predictive migration modelling to be specified.

Draft status reports on each technical area have been prepared. These will be combined and published as a single EUR series document in April 1992. Thus, at the end of 1991, Stage 1 of the Project is nearing completion.

Progress and Results

The structure of the CHEMVAL2 Project is shown in Figure 1. Atkins ES 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 Atkins ES 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

BRGM, under contract to ANDRA, are responsible for a programme of work aimed at assessing the effects of elevated temperatures on the speciation and solubility of radioelements in groundwaters /4/. In order to make this assessment, improvements to a number of computer programs used previously in CHEMVAL will be required. Implementation of code changes is the responsibility of individual participants but formal verification of the enhanced programs will be addressed within CHEMVAL.

The thermodynamic database will also need to be extended to account for changes in formation constants (log ß) and solubility products (K_{sp}) as temperature rises in the range of 5-200°C. On the basis of available data, BRGM/ANDRA have recommended use of the Van't Hoff equation for all temperature corrections in view of its simplicity and the potential to compile a comprehensive, consistent data set. Data collation is underway and a series of verification tests have been formulated.

b) Ionic Strength Effects

The existing CHEMVAL Database accounts for activity coefficient (γ) corrections using the Davies Equation. This was deemed essential during the previous CHEMVAL contract owing to the limited timescale available and the need to adopt a consistent method throughout. Extension of CHEMVAL modelling activities to more saline waters is the responsibility of GSF-IfH who have carried out a brief review of available methods /5/. The latter range from the idealised Debye-Hückel theory for very dilute solutions to the heavily-fitted Pitzer virial expansion algorithms which have been applied to fused salts. Within CHEMVAL2, emphasis is being placed on salt concentrations up to 1 $moldm^{-3}$, encompassing seawater and virtually all

natural groundwaters. A work programme has been proposed involving the direct comparison of several alternative γ correction methods on a limited number of well defined experimental data sets. A preferred method for CHEMVAL2 will be selected at that time on the basis of data availability and compatibility with CHEMVAL objectives.

c) **Organic Complexation**

The problems associated with quantifying complexation of trace elements by high molecular weight organic matter (humics) were highlighted during the original CHEMVAL Project. The theoretical basis for most extant models is weak and few if any have a real predictive capability. Essentially, therefore, 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 Atkins ES. Following a detailed review of the literature /6/, three approaches have been advanced as meriting more detailed consideration; the simple ligand-binding model of Sposito and Mattigod, as incorporated in the GEOCHEM code, the continuous distribution (statistical) approach of Perdue and Lytle and the electrostatic site-binding model of Tipping. Collation of data to parameterise the Tipping model has begun.

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 the field. The coordinators for this area of research are AEA Harwell and the British Geological Survey. A review of sorption models of varying complexity has been undertaken /7/, with emphasis on data availability and the applicability of each approach to predictive modelling studies. The current status of eight computer programs has also been addressed though it is unlikely that all will feature in verification/validation exercises.

A three stage work programme is envisaged, comprising:

- code verification using standardized data
- predictive modelling of uptake onto pure (monomineralic) phases
- modelling uptake onto natural substrates.

Outline verification tests have been distributed as part of the first stage of this work.

e) **Co-precipitation**

Solubility limits based on equilibrium precipitation-dissolution are often used to establish source term concentrations for radiological assessment and also to estimate maximum concentrations of transported 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 co-precipitation on ubiquitous minerals such as calcite and amorphous iron oxides /8/. Test cases will then be defined to calibrate the chosen models. An appraisal of relevant data is now being carried out, including parallel research on radionuclide - $Fe(OH)_3$ co-precipitation at the Polytechnical University of Catalonia. In view of the need for substantial code development, detailed verification studies will not commence until 1993.

f) **Coupled Chemical Transport Processes**

A limited verification of six coupled codes was completed successfully during the first CHEMVAL Project /3/. However, no predictive validation studies were feasible within available timescales and comparisons with experiment were restricted to back-fitting published column data. A more exhaustive verification has been proposed for CHEMVAL2 whereby eight codes will be evaluated against analytical solutions /9/. The results of this work will be published in Autumn 1992. Problems encountered previously with poorly specified experimental data have been addressed by commissioning column studies designed specifically for testing coupled models. Two separate column investigations are already underway dealing with, respectively; uranium migration through intact sandstone cores (at AEA Winfrith) and Cs, Sr transport through packed sediments (at CEA Grenoble). Similar experiments on $Ca(OH)_2$ - rock interaction and high temperature clay alteration may be added, depending largely on progress in related technical areas.

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/4/ FABRIOL, R. and OUZOUNIAN, G., CHEMVAL2 Project: Modelling the Effect of Elevated Temperatures on the Speciation and Solubility of Radioelements in Groundwaters (Draft) (1991).

/5/ LANG, H., CHEMVAL2 Project: Modelling Radioelement Speciation and Solubility in Saline Waters (Draft) (1991).

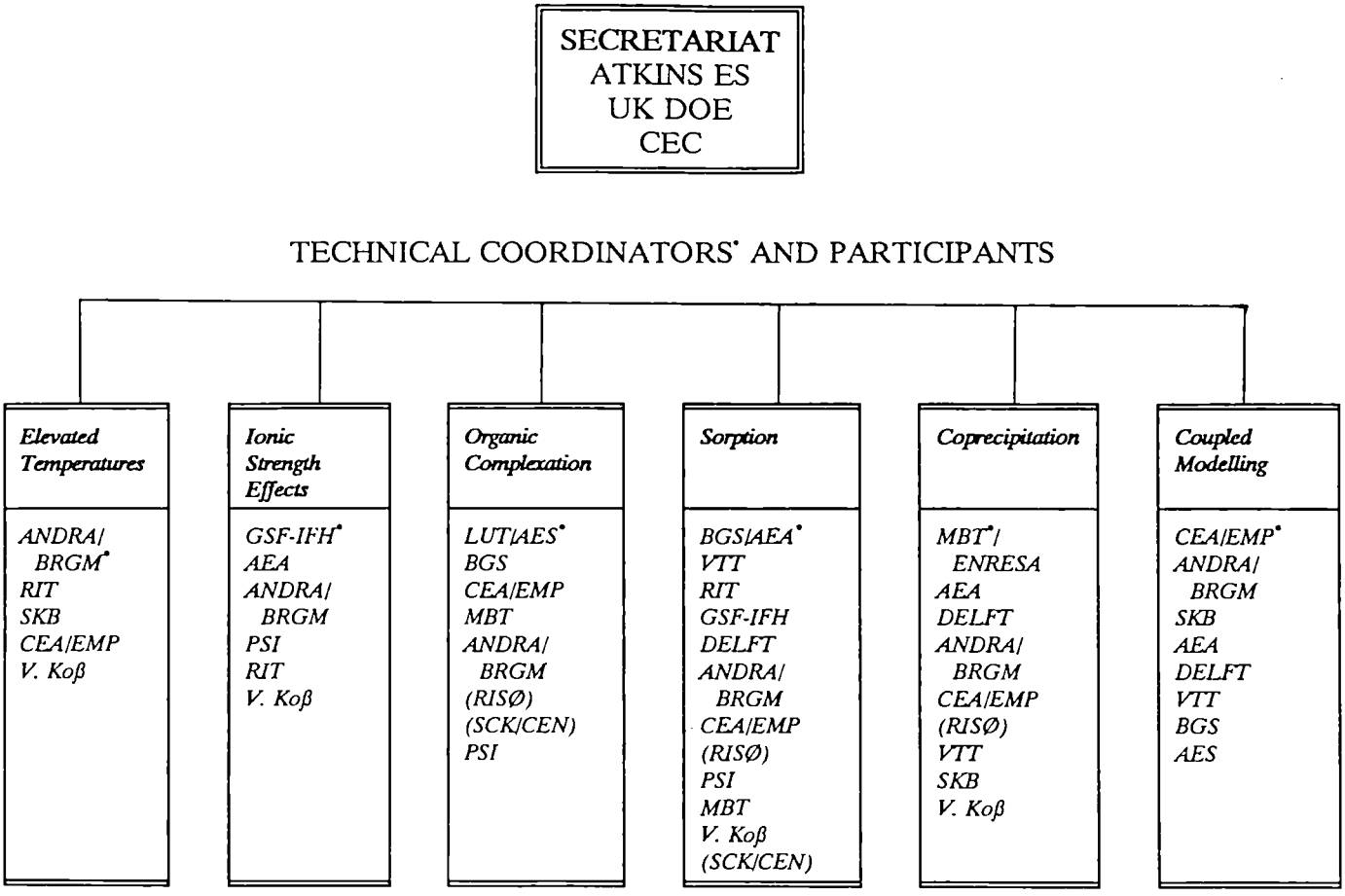
/6/ WARWICK, P. and READ, D., CHEMVAL2 Project: Approaches to Simulating Metal Complexation by High Molecular Weight Organics (Draft) (1991).

/7/ TWEED, C. and CRAWFORD, M., CHEMVAL2 Project: The Characterization and Modelling of Sorption Processes (Draft) (1991).

/8/ BRUNO, J., CHEMVAL2 Project: The Simulation of Trace Metal Co-precipitation (Draft) (1991).

/9/ MADE, B. and JAMET, Ph., CHEMVAL2 Project: Modélisation Couplée Chimie/Transport (Draft) (1991).

Figure 1. Organisation of the CHEMVAL 2 Project



Title : Oklo, natural analogue for transfer processes in a geological repository
Contractor : C.E.A./ I.P.S.N.
Contract : N° FI 2W CT 0071
Duration of contract : 4 years (january 1st,1991 to december 31st, 1994)
Period : 1991 (1st year of contract)
Project leader : Mrs Chapuis, C.E.A./ I.P.S.N.

The Uranium ore body in Oklo is a unique subject in the world, as natural fission reactions occurred there two billion years ago. It provides opportunities for the study of natural analogy with deep radioactive waste disposal, specially radionuclide mass transfer processes to the surface.

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).

2°- Study and characterization of the source term (mostly in CEA laboratories).

3°- Studies on the geochemical systems ruling the migrations, implying collaboration between CEA laboratories and other institutions: CREGU (Centre de REcherches sur la Géologie des matières premières minérales et énergétiques, formerly "de l'Uranium", Nancy), Centre de Géochimie de la Surface (CNRS, Strasbourg), and Ecole Nationale Supérieure des Mines de Paris (ENSMP, Centre de Géologie Générale et Minière and Centre d'Informatique Géologique, Fontainebleau).

4°- Modelling : Part of the modelling will take place in each laboratory involved, but the final coupling of models will be the responsibility of IPSN and ENSMP.

GEOLOGICAL SETTING

The Oklo uranium ore body lies on the south-western margin of the precambrian sedimentary basin of Franceville. The deposits are sedimentary, in a sandstone layer 3 to 6 meters thick, at the top of the conglomerate and sanstone 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 mean dip is 40° to the East at the open pit and decreases to the East and South-East, deeper in the underground works (Zone de plateure = flat-seam zone).

The uranium originates from erosion of the Chaillu basement to the south-west, and maybe from the leaching of overlying volcanic ashes. The uranium precipitated in hydraulic fracturation corridors, at a reduction front determined by the presence of mature organic matter.

1.- THE OPEN PIT :

From the present original ground level (450 m above sea level approx.), the mineralised layer was first mined as an open pit down to a level of 300 m. This is where natural reactors 1 to 9 were discovered. It is now an almost straight excavation, 1000 m long, 350 m wide and 150 m deep, with the major axis running north-south.

The western side of the quarry shows the upper surface of the Francevillian A sandstones, backing onto the Mounana "basement-window" (a small horst of the Chaillu granite, to the east of the Chaillu chain proper). It is on that sedimentary surface that the structural forms are easiest to make out, from north to south: the Crochon (small hook), the North dome, the Dressant (rise), the Cuvette (bowl or basin) and the South dome.

The sandstones are non-metamorphised and still show ripple marks, older than 2 billion years old. Strong dissolution marks can also be seen on the surface of the sandstones, where the reactors once stood.

The eastern side of the quarry was stoped at different levels as the mining progressed. It cuts into alternations of mudstones with some coarse breaks, of organic-rich schists and of dolomite and sandstone "complexes". A large dolerite dyke cuts East-West across the quarry, 3/4 length from the north.

The mineralised layer can no longer be seen in the open pit, as the ore has been entirely mined out, the only exception being a token of reactor n° 2, preserved in a steel compartment anchored at mid-heigth to the side of the north dome.

2.- THE UNDERGROUND WORKS:

The underground works started in 1974. the main way-shafts and a well have been sunk in the wall sandstones, as the access works avoid the FB shales of the roof as much as possible.

In the central part of the deposit, mining is by downward stoping, supported by concrete. From a crosscut, a drift is driven to the wall of the layer, i.e. a gallery (3 x 3.5 m cross-section) is made in the ore in contact with the FA sandstones, to the north and south edges of the workable deposit. From this drift, a series of percussion drillings in the roof, up to the base of the FB shales, radiometrically measure the ore concentration and thickness of the mineralised layer.

When drifting is finished, the return phase begins, i.e. from the drift all of the workable layer is knocked down in 4 m cuts. Each of the crosscuts is then cemented,along with the corresponding section of the drift, so that the slice being mined is progressively replaced by a bed of concrete parallelepipeds about 3.5 m high and 4 m wide. The cohesion of this concrete bed is increased by an iron brace.

When a slice has been fully mined, drifting begins on the layer immediately below,in the shelter of the concrete layer laid in the mined slice. The joints from the concrete passes are staggered from one slice to the next. Usually, a number of superimposed working areas are opened when a section is being mined.

In the outer areas of the deposit, where concentrations are lower, mining proceeds differently :

- the "North Extension" (to the north of the "Crochon"), where the layer was subvertical, was mined by upward stoping, using hydraulic backfill (waste rock) ; the next drift was then driven above this. The mining in that area is now finished.
- the northern halo of the Oklo core deposit,where the dip decreases to the east from 50 to 25° is mined by the pillar-and-room method, without backfilling, with a recovery from 50 to 60 per cent. This method will also be applied in the Okélobondo-plateure (flat-seam) area, to the south-south-east of Oklo proper.

The ore obtained by these methods has a much lower mine cost price because no concrete is used. It is also less expensive to process (lower sulfuric acid consumption, owing to the absence of alkaline solutions introduced by the concrete). Apart from the need to identify the batches properly and separate them for processing, there is no difference in terms of mining between ore from the reactors and that with a normal isotopic ratio.

3.- THE REACTORS:

The natural fission reactors are characterised by very high uraninium concentrations (from 20 to 60% by weight), closely correlated to Uranium-235 depletion (down to 0.265% of total U).

On the spot, they can be identified by two facies :

-. The "pile" (reactor core) facies, referring to an ore ranging from compact Uraninite to Uraninite nodules packed in a clayey matrix, totally devoid of quartz.

-. The reactor-clay facies, referring to a lens of clayey gangue isolating the core of the reactor from the over- and underlying sandstones.

The properties of the clays vary according to the recent (i.e. tertiary to present) weathering of the surroundings of the reactor to which they are associated: the gangue of reactors 1 to 6, which were quite shallow, was soft and plastic, while that of the deep-seated ones is compacted to an indurated shale. The mineral composition of these clays also appears to be different, whith Kaolinite being observed only whith the shallow reactors, while organic matter is most abundant in the deeper zones.

Up to now, 16 numbers have been allocated to reactor zones in the Oklo mine, but some numbers (11, 12, 14) appear to be void. Some more, which have not been reached yet by the works, but are known by exploratory coring, are designated by their borehole number, in the Okelobondo area, close to the south-east of Oklo. An isolated one in known below the Bangombé plateau, close to the Moanda manganese deposit, about 15 kilometers from Oklo.

Reactors numbered 1 to 9 and 15 have been mined out. There is at present no specific mining of the remaining reactors, as there is no market for depleted Uranium. The present accessibility of the reactors is thus 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 Unanium, of which 40 % have already been taken. A circulation drift is currently being mined in the direction of the lower levels of this reactor (D81), though it is still questionable whether it will actually be continued that far.

-. 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 SD38.

-. Reactor 16 was discovered in may 1991, at level 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. As drift D75N is intended for ventilation, we can expect an easy access to the reactor for some time.

-. 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 "Bangombé" (rather than "Bagombé") reactor is located a few kilometers to the south-east of the town of Moanda, itself 20 kilometers south of Mounana and the Oklo deposit.

FIELD SURVEY AND SAMPLING

1.- PRELIMINARY :

In april, 1989, a rescue mission had taken place, in order to avoid the loss of valuable, and as yet undeciphered, scientific information, for the mining company was working out all the depleted Uranium available, as they had a market for it at the time.

During that mission, wall face surveys and sampling have been conducted in forewinning drifts D73S in reactor zone 10 and SD37 in reactor zone 13. Small diameter cores were taken from reactor 10 (total length 23.03 m) and from reactor 13 (8.59 m).

Furthermore an additional coring program in reactor zone 10 was defined, to be carried out, in larger diameter, by the exploration team of the mining company. This was done during summer and fall the same year (cores SF82 to SF85, overall 90 m approx.).

2.- ROUTINE:

From september 1989 on, we have kept in Oklo a standing mission, *i.e.* a post-M.Sc. student has been appointed each year to follow the progress of the mining works, do the necessary surveys and some sampling, and advise us on the need and best periods for more specialised field missions or for orders of heavier work from the COMUF company.

Because of the shrinking market for depleted uranium, the year 1990 did not bring much on the reactor zones, despite the thoroughness with which the drifting works in the Okélobondo area have been followed. On the other hand, 1991 has been marked by coring through the $OK84^{DIS}$ zone and by hte discovery of zone 16, which has also been sampled in the same way.

THE SOURCE-TERM

The work undertaken with the Ionic Probe since 1989 bear on zone 10 and Zone 13.

The U/Pb ratios have made it possible to confirm two important times in the history of the bearings: 1970 Mega-annum (Ma) for the fission reactions (zone 10) and 750 Ma for the major lead mobility episode, probably linked to the emplacement of the dolerite dykes.

1.- ZONE 10 :

The reactor-core facies boundaries have been accurately drawn, thanks to measurements done on numerous wall-face and borehole samples. The reactor spreads from level 144 above (slice D65) to level 118 downslope (slice D82). Upslope, the observed depletion remain rather moderate,, with 235 U/ 238 U ratios from 0.670 to 0.725 % (atom %). Lower down more importantdepletions are observed, with 0.562 % in core SF84 and 0.46 % at level 91.65 in core SF29,an exploratory borehole the study of which had already begun before the present program.

2.- OTHER ZONES

Reactor Zone 13 shows several peculiar features: It is an uraninite layer, from 20 to 30 cm thick, about 5 m wide and only 12 m from top to bottom, which rests directly on the sandstones, with the only intercalation of a very thin bed of black clay and organic matter. The richest uraniferous layer reaches a density of 7, and it reaches a depletion ratio ($^{235}U/^{238}U$) of 0.46 %.

Despite a similar facies, zone 16 does not seem to quite reach the same depletion in Uranium-235 ($^{235}U/^{238}U = 0.65\%$).

New UF_6 isotopic measurements done on samples from old exploratory boreholes in Bangombé have confirmed the presence of a reactor zone there (BA145, 11.60 m: $^{235}U/^{238}U = 0.6552$; $BA145^{DIS}$,11.20 m: $^{235}U/^{238}U = 0.6983$ in atoms %).

THE GEOCHEMICAL SYSTEMS

1.- PETROGRAPHICAL FACIES

The petrographical and mineralogical facies of the deep reactors zones are similar to those of the earlier-discovered ones (1 to 9), apart from a few specific features, very much related to the lack of supergene weathering

The rocks surrouding the reactor zones are sandstones. They are made up of quartz, some biotite grains, less feldspar and few accessory minerals (zircon, uranium oxides, titanium oxides, organic matter). The claey fraction is made of ferrous chlorite and illite, and calcite is present as fissure infillings.

The reactor-clay facies shows areas of cryptocristalline magnesian chlorite, with a few corroded quartz grains. Secondary minerals (coffinite, zircon? ,uraniferous titanides) develop from primary accessory minerals. Apatite may also be met.

In the reactor-facies, the main mineral phases are Uranium oxide and white micas.

By comparison to reactor zones 1 to 9, kaolinite remains very scarce in the deep reactors, except in one borehole above zone 10.

2.- RETENTION BY CLAYS

The study of the retention of fission products by phyllosilicate minerals has progressed when enriched uranium has been evidenced in the acid leaching residue of a clay sample from the roof of reactor zone 10.

The uranium linked to the cristalline lattice of the chlorite is enriched ($^{235}U/^{238}U = 0.01051$), while the uranium extracted with the soluble fraction, which was only adsorbed on the surface of the clay particles, is depleted ($^{235}U/^{238}U = 0.00681$).

Plutonium-239 created during the fission reaction was mobilized by the contemporary reducing fluids. It was then trapped by the crystallisation of the chlorite and decayed on the spot to Uranium-235, thus causing the observed enrichment. The half-life of ^{239}Pu (24400 years) gives an estimate of the maximum time elapsed between the nuclear reaction and the chlorite crystallisation.

3.- RECONSTRUCTION OF ANCIENT FLUIDS

The study of trace elements contents in hydrothermal minerals in the vicinity of the reactor zones has been undertaken, with the aim of using these elements as tracers of the fluids which were circulated in the bearings. The analyses are done mainly by neutron activation.

The minerals studied are sulphides (pyrite and galena), in order to observe chalcophilous fission products. A simultaneous examination of the contents in arsenic, antimony, cobalt,nickel,molybdenum and silver shows that the samples gather into well-defined clusters. This can be explained in different ways:

- either it shows the evolution of an initial fluid, which undergoes differentiation through interaction with the surrounding rocks: but the monotonous surrounding sandstones argue against this interpretation;
- or it shows the circulations of different fluids in the sandstones and fissures, most probably also at different times in the history of the bearings.

MODELLING THE PRESENT MASS-TRANSFER

We hope to follow directly the water circulations resonsible for the transfer of elements,and to characterize the geochemical system which rules these transfers, by identifying natural tracers of the reactor zones in the environment.

The first stage of this task has been the compiling of an hydrogeological synthesis, taking into account all the available information on :

- the morphological and topographical frame,
- the geological frame, including the general structure, the stratigraphy, the rock fracturation and geometry of the levels with a potential hydraulic role,

- the hydrological frame, including the meteorology, the runoff, the position of the water occurrences in boreholes or in the underground works,

- the hydrochemical frame, with an inventory of all the analyses done to-date.

These data have made it possible to propose a diagramatic hydrogeological section, and to launch a preliminary hydrodynamic modelling.

We will now proceed with the sampling and hydrochemical and isotopical analyses of the waters, in order to identify an active geochemical system involving some reactor zones end products, and do *in situ* test and measurements to obtain the quantitative information necessary to the validation of the hydrogeological diagramatic model proposed.

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	01/10/91 - 31/12/91
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 series of codes going 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 test of the code against the laboratory experiments performed in 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

Task one, about the literature survey has been performed during these first three months of the contract.

The general literature survey has been firstly carried out by all the partners, while final compilation was organized in five different chapters, emphasizing aspects of colloid science which are of special interest for modeling purposes. Each partner is now in charge of writting one of these chapters, compiling all the previous findings.

Progress and results

The literature survey is summarized below, the division in chapters corresponds to the one of the progress report which will be provided in march 1992. On the basis of simple hydrodynamics, a first operational model has been developed which simulates transport of colloidal metal oxides through a fractured medium. Experimental results are not yet available.

Chapter 1 " GENERAL KNOWLEDGE ON COLLOIDS "

The general knowledge of the colloidal particles is the main basis of the study.

- Definition of colloids, origin of these particles and list of possible colloids (clay minerals, oxides and hydroxides, organic colloids) /8/. The colloids will be refered as either "intrinsec colloids" (if colloid consists essentially of compounds of the considered element) or "carriers colloids" (if colloids are built up of compounds of other elements).

- Evidence of colloids in different natural groundwater systems

- Physical and chemical properties :

  size, density, diffusion coefficients
  surface charge, existence of a diffuse double layer
  sorption processes and sorption capacity.

Chapter 2 " EVIDENCE OF MIGRATION OF COLLOIDS IN GEOSPHERE "

First, some sampling techniques and analytical methods are given, because experimental work generally involves sampling of water and subsequent analysis of water samples.

Then, the attempts already made to evaluate colloidal transport by studying data from natural analogues have been studied. The following field-experiments performed with the aim to study colloids are described :

- Nevada Test Site /2/.

- Los Alamos National Laboratory : long time leakage from an existing low-level nuclear waste site /9/.

- River Glatt and Chernobyl : studies of surrounding groundwater after radioactive fall-out from the reactor accident /10/.

- Natural analogue in Alligator Rivers in Australia /7/.

- Chernobyl : an attempt to evaluate colloidal transport has been performed in Switzerland in connection with the fall-out of radioactive elements from the reactor accident.

- Morro de Ferro in Brazil : thorium transport.

- Alligator Rivers Analogue Project : sampling and characterization of colloids.

Chapter 3 " LABORATORY EXPERIMENTS "

One of the most complete experimental study of the migration of fine particles taken as reference is that of Khilar an Fogler /3/.

The apparatus used for laboratory experiments, the specific measures and methods will be described.

The different elements of the experiments, which permit to divide the laboratory experiments planned in different steps are then emphasized :

- Porous medium constituted of laboratory columns packed with successively glass beads, sieved alumina grain and sand.

- Colloidal particles calibrated (latex) an then clay (kaolinite - bentonite) in pure form.

The experiments protocols are then given, they will include :

- response of clean media to small pulses
- response of clean media to step inputs
- response of a column loaded with colloids

Chapter 4 " INTERACTION MECHANISMS "

First the behaviour of colloidal particles will be compared to the one of dissolved species. Then the main transport and retention mechanisms are described:

- Transport mechanisms of brownian particles : advection, diffusion through Brownian motion and sedimentation.

- The main processes which bring particles into contact with the surface of the solid medium are given : sedimentation, direct interception and brownian diffusion. The different sites for retention are described /6/.

- The attachment mechanisms : retention of colloids is governed by physico-chemical interactions with the walls of the medium /1/. The retention forces include Van der Waals forces - attractive - and electrostatic forces - attractive or repulsive - described in parallel with double layer.

- Chemical interactions between colloids, and between colloids and solid medium (porous or fractured) are summarized.

- Interactions between colloids and the solute are studied.

An overview of the parameters which may influence these interactions is given : the particle charge, the characteristics of both colloids and medium, the characteristics of the solution are the parameters which define the relative importance of each process /5/.

Chapter 5 " MODELLING "

A description of the modeled system will be given : the geological characteristics of the surrounding of a waste, the hydrological regime, the porous and fractured media are precised /4/. The aims of assessments models are summarized.

The transport equations and the different model available for interactions (linear adsorption isotherm, linear adsorption isotherm with a maximum adsorbed mass, and Langmuir isotherm) are described, expliciting the parameters involved and the possible initial and boundary conditions to use.

Transport is divided in two stages : porous and fractured media. For each of these media the studied areas are :

- Characteristics of the media (permeability, ...)
- Model for water flow
- Mass transport phenomena and governing equations.

Analytical solutions for special conditions are first given. Then both numerical methods to solve the transport equations and results obtained with existing codes are described.

List of publications

A working document had been presented by each of the partners during the third project meeting :

Lee van der J., Radionuclide migration in the geosphere : modeling transport of colloids, Fontainebleau, Sept. (1991)

Cayeux de M.D., Development of a model for radionuclide transport by colloids in the geosphere, bibliography survey, INTAKTA Rep. 5501-1, Oct. (1991)

Weerd van de R., Development of a model for radionuclide transport by colloids in the geosphere, RIVM, Oct. (1991)

Hlavacek M. and Rodier E., current bibliography report on the migration of radionuclides in soils, LSGC, Apr. (1991)

Hernandez A., Bibliographic review on the area of colloid studies in geologic environments, CIEMAT, Oct. (1991)

References

A list of more than 120 references is already available, corresponding to the work compiled by all the partners. Only the main references are given in this paper, they are the following :

/1/ BONANO E.J. AND BEYELER W.E., Transport and capture of colloidal particles in single fractures. Scientific basis for nuclear waste management VIII, (Ed. JANTZEN C.M., STONE J.A. and EWING R.C.) pp 385-392. Materials Research Society, Pittsburgh, (1985)

/2/ BUDDEMEIER R.W., HUNT J.R., Transport of colloidal contaminants in groundwater : radionuclide migration at the Nevada Test Site. Alied Geochemistry, Vol. 3, pp 535-548, (1988)

/3/ KHILAR K.C. AND FOGLER H.S., Reviews in Chemical Engineering, colloidally induced fines migration in porous media, (Dordrecht, The Netherlands, pp 41-108, (1983)

/4/ MARSILY G DE, Quantitative hydrogeology : groundwater hydrology for engineers. Academic Press inc., London, 440p, (1986)

/5/ MARSILY G. DE., Radionuclide migration in the geosphere : an overview. Radiochimica Acta 44/45, pp 159-164, (1988)

/6/ MCDOWELL-BOYER L.M., HUNT J.R., SITAR N., Particle transport through porous media, Water Resour. Res., n°22, 13, pp 1901-1921, (1986)

7/ SEO, T., Uranium distribution in the colloidal and solute phases at the koongarra Uranium deposit, Alligator Rivers Analogue Project, Progress Report 1, june 1990 / August (1990)

/8/ STUMM W. AND MORGAN J.J., Aquatic Chemistry An Introduction Emphasizing Chemical Equilibria in Natural Waters, John Wiley & Sons, New York, (1981)

/9/ TRAVIS B.J. AND NUTTAL H.E., Analysis of colloid transport, Proc. of the Symposium Scientific Basis for Nuclear Waste Management IX, MRS Symposia Proc., Vol 50, pp 737-745, (1985)

/10/ VON GUNTEN H.R., WABER U.E., KRÄHENBÜHL U., The reactor accident at Chernobyl : a possibility to test colloidal-controlled transport of radionuclides in a shallow-aquifer, Journ. of Cont. Hydrology, 2, pp 237-247, (1988)

Title: Characterization and validation of natural radionuclide migration processes under real conditions on the fissured granitic environment
Contractor: ENRESA (Coordinator)/CIEMAT, CIMNE, AEA, BGS and CEA/IPSN
Contract nº:FI2W-CT91-0080(RZJE)
Duration of contract: 24 months from March 1st, 1991 to February 28, 1993
Period covered: March 1991 to December 1991
Project leader: Julio Astudillo

A. OBJECTIVES AND SCOPE

The objective of the project is the characterisation of natural radionuclide (U, Th, and they desintegration products) migration processes in a fractured granitic environment and validation of models describing these processes.

In situ studies will be 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 have been planned to study the same phenomena under controlled conditions.

Finally, the identified processes will be modelled and 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, and JRC/CEC-Ispra co-operates with the Project participants. The Project is scheduled to run for four years, in two two-year phases. Phase 1 was initiated on 1st March 1991, and 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

II. Geochemical characterisation: Hydrogeochemistry (physicochemical and ionic phases). Groundwater colloidal phases studies (sampling, characterisation and transport). Groundwater mixing and circulations patterns. Fissure filling characterization. Hydrothermal and weathered transformation

III. Migration studies: Natural radionuclide distribution. Mobilization/retention processes (laboratory). In situ migration experiments

IV. Hydrogeological characterisation: Assessment of borehole conditions. Design and construct wirelines straddle packer testing system. Transmissivity and head measurements. Define numerical models. Design crosshole interference tests in selected fractured zones.

V. Modelling studies: Development of 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

Several critical activities were initiated or completed in the first nine months of the Project.

- Overall Project objectives were reviewed and agreed and a set of interim objectives developed, directly related to the needs of safety assessments for radioactive waste disposal systems.

- An integrated programme of field and laboratory work at the site was developed; this programme will serve as a useful Project management tool and will help ensure needed co-ordination takes place.

- Basic geological and geophysical mapping of the site has been completed.

- A preliminary set of conceptual models for groundwater flow at the site has been developed on the basis of available geological and hydrological information.

- Eighty percent of the drilling programme has been completed.

- The delays in the drilling programme have afforded the opportunity for a detailed review of borehole locations and borehole management to ensure that appropriate information is collected, which will meet the needs of all participating organisations.

- Preliminary sampling for hydrogeochemical studies for ionic and colloidal phases has been completed in boreholes S-1 and S-7 (gallery).

I. Characterisation of the physical environment

I.1. The Site

The experimental site of "El Berrocal " is situated 92 Km to the southwest of Madrid near the village of Nombela (Toledo), in the southeastern part of the Sierra de Gredos, Central Mountain System. The El Berrocal granite is of late Hercynian age, and has intruded through the older granodiorites which are the dominant rock in this area. The 22 Km^2 granitic intrusion contains a uranium-rich quartz dyke that was extensively mined some 30 years ago. The main access gallery has a length of about 80 m and intersects the quartz dyke at 46 m.

In the earlier phase of work (1989-1990), 30 m of new gallery was excavated and 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 (Fig. 1). Seven further shallow boreholes were drilled in the gallery (S-3, S-6, S-8, S-10) and two deeper boreholes (AT-1, AT-2) 150 m to the south of the gallery, as shown in Fig. 1. The local topography and major fractures are illustrated in Fig. 2.

I.2. Drilling programme

At the start of phase 1, it was planned to drill a set of 200-250 m deep boreholes at the locations (numbered 13-17) indicated in Fig. 3. Drilling was to have commenced by 1st July 1991. Initiation of the drilling programme was delayed until mid-August, at which time drilling was started at one borehole position, No. 16. Borehole 17 was to have been used by the team from CEA/IPSN for the testing of their downhole logging tools.

The delay in the drilling programme provided an opportunity to reconsider the location of the boreholes in view of the developing ideas concerning the hydrological regime at the site. It was considered that the initially proposed configuration may not provide sufficient information on the three-dimensional flow field needed to distinguish between the alternative conceptual models, because most of the boreholes were more or less aligned along a supposed north-south down-slope hydraulic gradient. Consideration is now being given to repositioning borehole 17 slightly closer to boreholes 14 and 16, and to positioning a new borehole to the east of borehole 16 (perhaps by 50-100 m).

At the moment, four boreholes have been finished (S-13, S-14, S-15, S-16). The core obtained are transported to Nombela for storage and the fractured, fresh and altered granite are studied. A preliminary infilling mineralogical reconaisance is also performed.

I.3. Geotectonic characterization

Geological mapping

Basic geological and geophysical mapping of the site has been completed. Three major systems of fractures have been identified, based on Landsat images, aerial mapping, field mapping on the surface and within the gallery, and studies of rock cores from the S boreholes (Figs. 1-2). The dominant fracture system trends N-110°-E and may have a profound influence on the local pattern of groundwater flow and the distribution of springs at the site, but this cannot be proved with the data at hand. Other important influences on local groundwater flow may be the variable local topography (Fig. 2) and the presence of the old mine workings, which were excavated in four levels at depths up to 60 m but are now thought to be flooded.

II. Geochemical characterization

The main activities performed during this reporting period are in relation with the borehole and cores drilled in the gallery in the last project. The results obtained have been used to prepare the study in the deeper boreholes.

II.1. Colloid studies

General characterization of colloids

Particulate matter in groundwater from boreholes S-2 and S-7 was sampled (without the use of packers) and mineralogical, geochemical and scanning electron microscopy analysis of colloids conducted. This work aims at understanding the physical characteristics and radionuclide sorption capacity of colloidal material present at the site. Preliminary results indicate that:

- The particulate matter in borehole S-1 is rich in clay minerals (e.g. chlorite and sericite) and contains relatively high concentrations of SiO_2, Al_2O_3, organic matter and the trace elements Zn, Cu, Ba and U.

- The groundwater in borehole S-7 below 45 m depth has a relatively low redox potential, high pH, high sulphide content, and low Zn, Cu and U content, and

- The colloidal particulate in the same groundwater is rich in silica, clay minerals and organic material.

Colloid sampling in fractured zones

A new sampling of colloids has been performed by AEA-HARWELL in boreholes S-1, S-2 and S-7 using selected fracture zones, isolated with a packer system.

II.2. Fissural filling studies

Hydrothermally altered clay-rich material associated with the primary fracture system (trending N-100°-110°E) has been sampled at 13 locations in the access gallery and mineralogical and geochemical analyses conducted. This work will provide information on the uranium-retention capacity of the clay-rich material as a function of the mineralogical and chemical composition. Preliminary results indicate that:

- illite is the primary clay mineral present,
- the high uranium concentrations cannot be explained by the adsorption effect of clay minerals alone; rather, most uranium is probably in the form of fine-grained UO_2 rich materials
- some uranium is apparently in a readily soluble form, and
- the high thorium concentrations can be explained by the presence of fine-grained, unaltered thorium-rich accessory minerals from the granite or the precipitation of thorium as $ThSiO_4$ or $Th(OH)_4$ jointly with the clay minerals.

III. Migration studies

III.1. Natural radionuclide distribution

Altered granite associated with the same fracture system has been sampled at seven locations in the access gallery and mineralogical and geochemical analyses conducted. This work will provide information on the mineralogical and spatial distribution of uranium in the rock and on the hydrothermal alteration processes that have occurred. Preliminary results indicate that:

The altered granite is a highly tectonised and hydrothermally-altered version of the normal El Berrocal granite, and the effects of these processes have led to intensive cataclasis of the granite, sericitisation of albite, potassium-feldspar and chloritised biotite, an increase of free quartz, filling of the fractures with iron-oxyhydroxides and quartz, an increase in Fe_2O_3, MgO, K_2O (CO_2 + H_2O^- + H_2O^+), Rb, Li and U concentrations and a decrease in FeO and Na_2O concentrations.

III.2. Mobilization/retention processes (laboratory)

Following the ongoing activities in column migration experiments, in collaboration with JRC-ISPRA a set of preliminary batch K_d (U-233) and column migration tests (using tritium and U-233) with crushed granite samples and water from the site has been completed. This work has studied the effect of pH on K_d the variation in K_d with the addition of organic matter to the liquid phase, and the migration of tritium and U-233 under dynamic conditions. Preliminary results indicate that:

- K_d decreases significantly with increasing pH, implying that uranium adsorption decreases as solubility increases.
- K_d decreases with the addition of organic matter, probably for the same reason (although the exact reason is unclear), and
- dynamic column tests on crushed granite lead to uranium K_ds very much lower than those in the batch sorption tests, owing to the importance of kinetic effects.

III.3. In situ migration experiment

A preliminary study of the hydraulic conexion between boreholes S-1 and S-7 has been performed by JRC-ISPRA to plan a stable isotope migration test. The fracture zone was isolated by packers in borehole S-7 and ground water was pumped from borehole S-1. Results are under interpretation.

IV. Hydrogeological characterization

IV.1. Assessment of boreholes and protocols for borehole management

During this period of the project a series of protocols for borehole management was prepared by BGS, concerning:

. Hydraulic testing during drilling
. tracers for drilling fluid (note that artificial tracers have not been used in drilling the first borehole - it is planned, however, to use such tracers in drilling the next vertical borehole),
. temperature and conductivity logging for localisation of zones of inflow, and
. development of boreholes after drilling in order to minimise mixing of groundwaters.

The hydraulic tests performed during the drilling of the first two boreholes were not satisfactory and have been rejected for the other boreholes.

A preliminary instrumentation for hydraulic head measurement and to avoid mixing of groundwaters has been undertaken in the boreholes when finished.

IV.2. Preliminary Conceptual Models for Groundwater Flow

Development of an initial set of alternative conceptual models for the site is of high priority because the range of possible alternatives will have a potentially important bearing on the field investigation programme and the exact position of the phase 1 (and Phase 2) boreholes. Three potentital end-member conceptual models for flow, based on control by topography, major fracture zones and the location of old mine workings, have been outlined by CIMNE and discussed by the PCC (Fig. 4). However, the real flow field may well reflect a complicated combination of the three models. Close attention will be paid in the coming months to the relationship between the alternative conceptual models for groundwater flow at the site and the experimental programme needed to distinguish between the possible alternatives. Borehole locations were reviewed in July 1991 and a further review will be made in late September 1991, after initial results from Phase 1 drilling work are obtained.

V. Modelling

The main objectives of the work are:

. To develop a stochastic formulation for flow and transport in fractured media by superimposing a three-dimensional continuum on a two-dimensional medium (high-permeability fracture zones), and

. to implement such a formulation in a computer code (called TRANSIN-III) able to analyse real cases and, specially, to apply this code to the El Berrocal site.

In the current reporting period, attention has been focused on three areas:

. Existing physical, hydrogeological and hydrochemical data from the site have been compiled and reviewed, as a starting point for development of an initial conceptual model(s) for groundwater flow at the site.

. Relevant literature on the stochastic formulation of flow and transport models has been compiled and reviewed and various theoretical methods tested, as a starting point for development of the formulation outlined above.

. Two (of eight) envisaged improvements to TRANSIN have been made, involving (i) incorporation of a leakage coefficient that is allowed to vary temporally (as well as spatially) and (ii) reprogramming to allow hydraulic conductivity to vary as a function of saturated thickness of the aquifer for the cas of uconfined flow.

D. LIST OF PUBLICATIONS

MARIN, C., HERNANDEZ, A. (1991) "Uranium mobilization around a fissure" El Berrocal batholith (Third International Conference on Chemistry and migration behaviour actinides and fission products in the geosphere. Jerez (Spain), 1991)

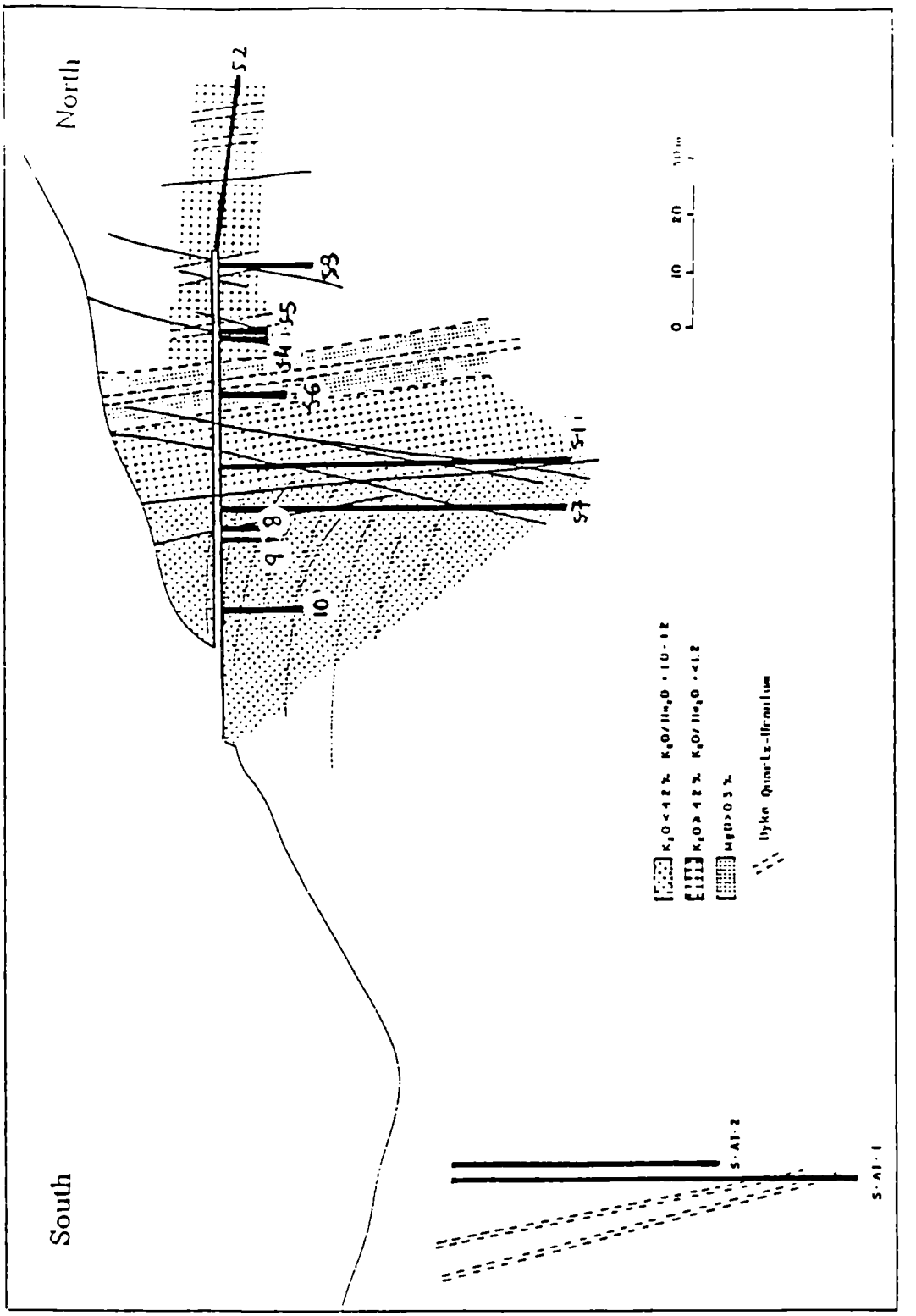
GUTIERREZ, M., BIDOGLIO, G., AVOGADRO, A. (1991) "Studies on hydro-geochemical controls of neptunium and selenium migration in granite columns (Third International Conference on Chemistry and migration behaviour actinides and fission products in the geosphere. Jerez (Spain), 1991)

PEREZ DEL VILLAR, L., DE LA CRUZ, B., PARDILLO, J., COZAR, J. (1991) "An approach to the calculation of U (Rh) mineralogical distribution in the fres granite from El Berrocal pluton" EB-CIEMAT (91-)-26. TOPICAL REPORT

GUTIERREZ, M., BIDOGLIO, G., AVOGADRO, A., MINGARRO, E., D'ALESSANDRO, M. (1991) "Experimental Investigation of radionuclide transport through Cored Granite Sampled" Radiochimica Acta 52/53, 213-217 (1991)

PEREZ DEL VILLAR, L., DE LA CRUZ, B. (1989) "Caracterización mineralógica y geoquímica del granito sano y alterado de El Berrocal (Gredos). STUDIA GEOLOGICA SALMANTICENSIA XXVI, 1989, UNIVERSIDAD DE SALAMANCA

FIG. 1 Structural zonation and borehole positions (thick solid lines) in the El Berrocal granite. As an indication of vertical scale, note that boreholes S-1 and S-7 have a depth of approximately 60 m.



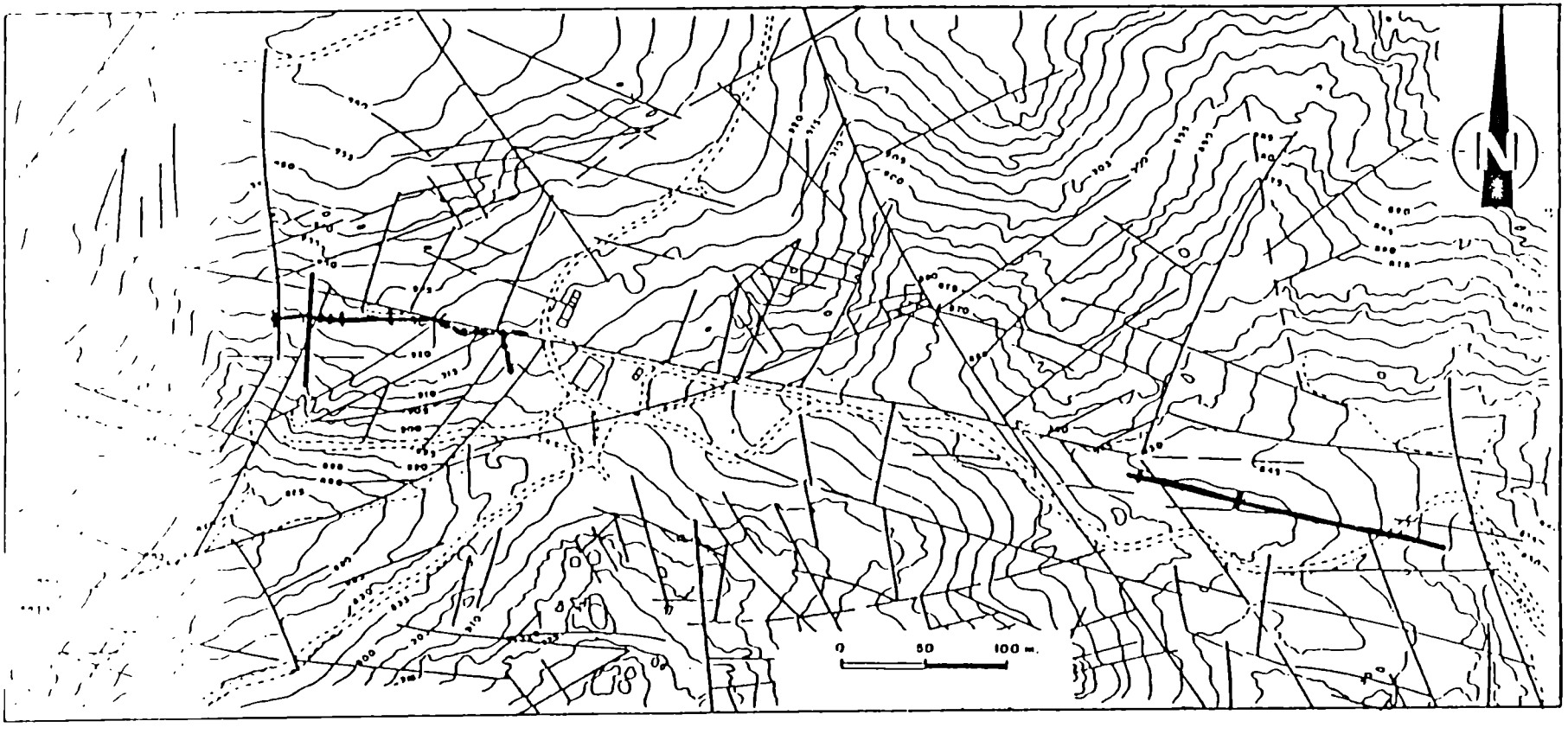
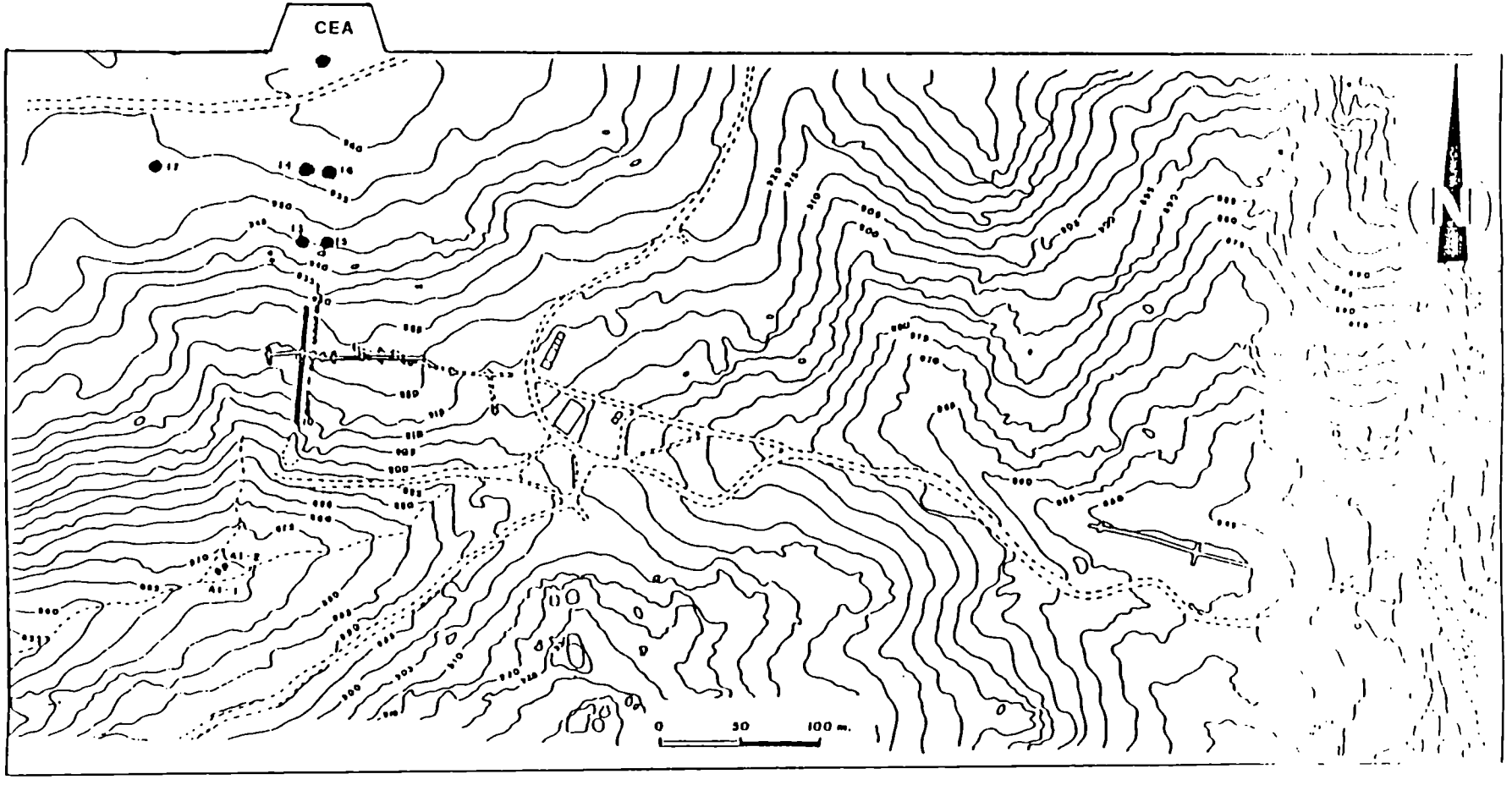


FIG. 2 Topographic map of the site, showing the major lineaments that have been mapped, and the position of the old mine workings (thicker lines). Studies are focused around the western mine workings and the N-S-aligned access gallery.

FIG. 3 Proposed borehole locations (13-17, plus CEA) for the Project. Moderate repositioning of one or more boreholes is under discussion (see text). Boreholes 13 and 15 will be inclined 20°-30° toward the gallery; the others will be vertical.



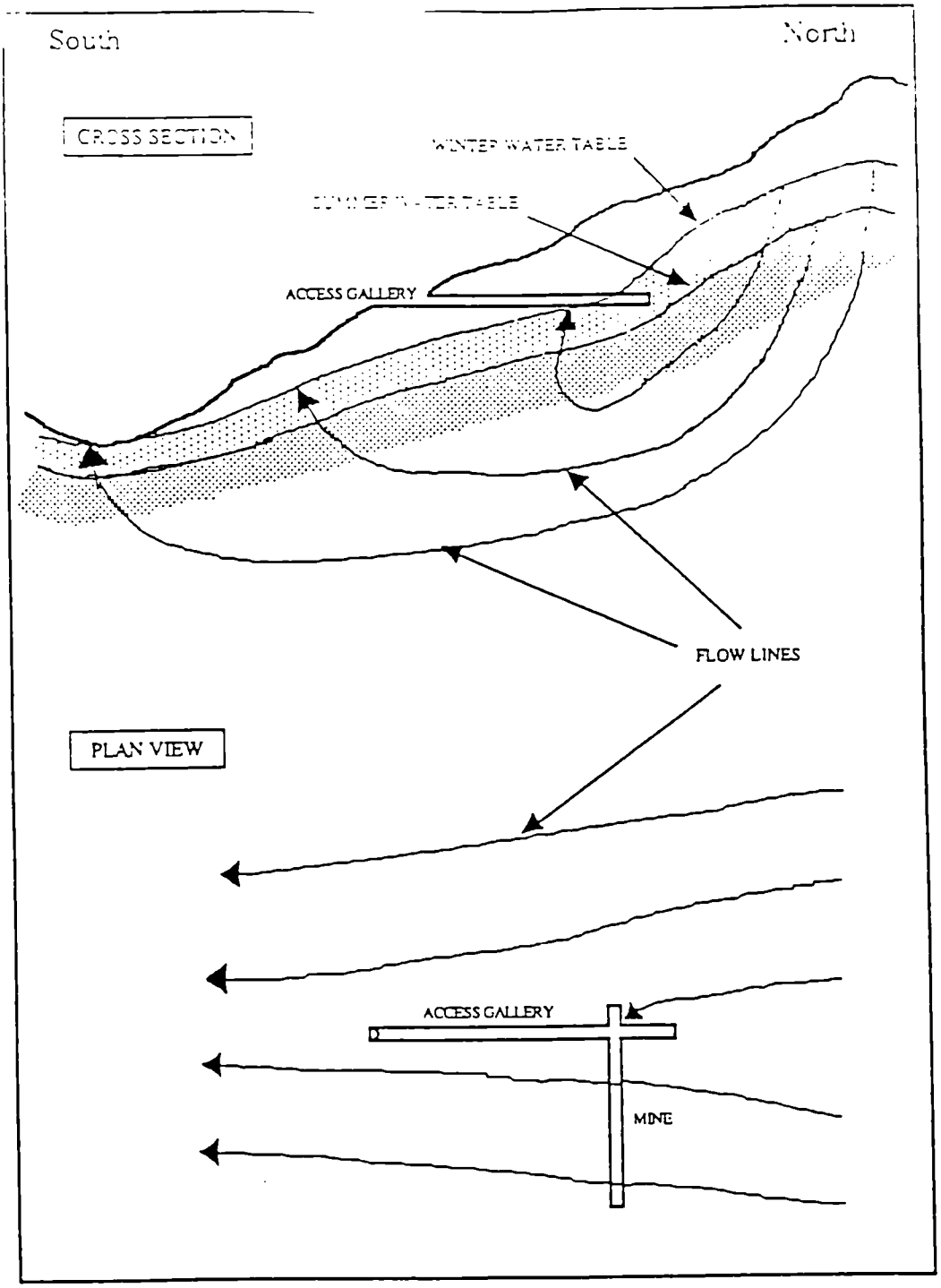


FIG. 4a Preliminary 'end-member' conceptual models for groundwater flow at the site, based on primary control by topography (Fig. 4a), major fracture zones (Fig. 4 b), and the location of mine workings (Fig. 4 c). This figure shows a N-S-aligned cross-sectional view and a corresponding plan view of the basic conceptual model, a groundwater flow system controlled primarily by topography, with minor effects of the mine superimposed.

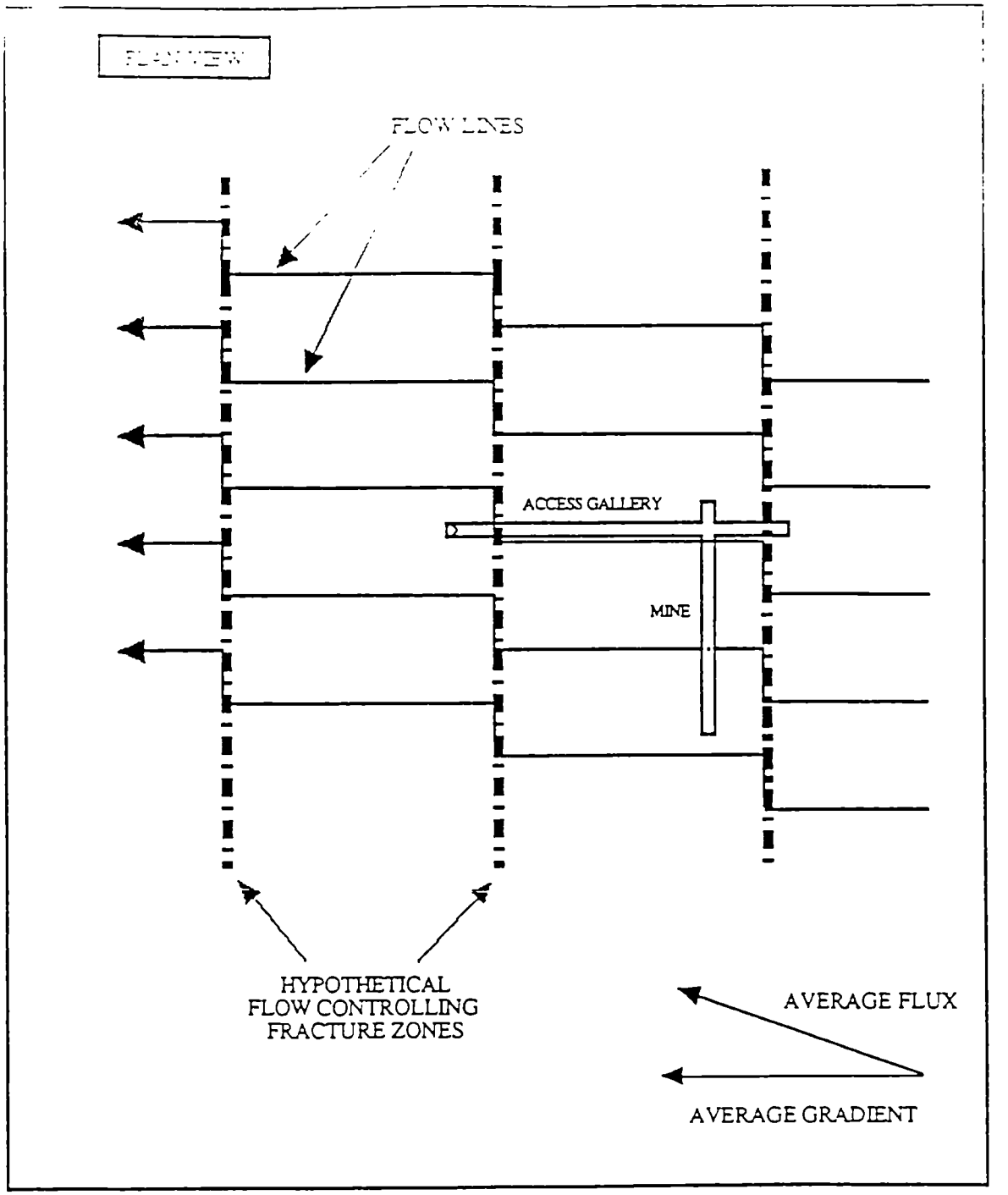


FIG. 4b Preliminary 'end-member' conceptual models for groundwater flow at the site, based on primary control by topography (Fig. 8a), major fracture zones (Fig. 8b), and the location of mine workings (Fig. 8c). This figure shows a schematic plan view of a groundwater flow system along a topographic gradient, but influenced strongly by the position of major fracture zones.

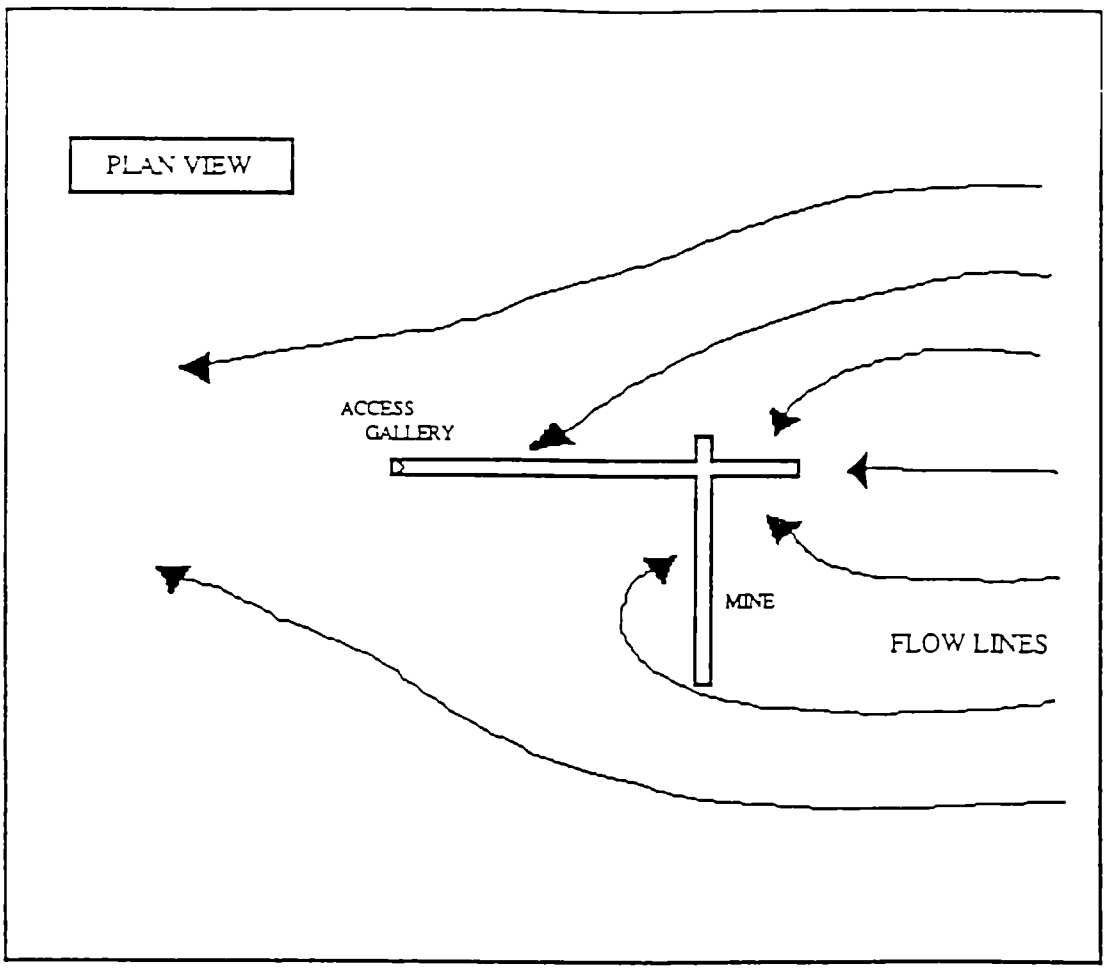


FIG. 4c Preliminary 'end-member' conceptual models for groundwater flow at the site, based on primary control by topography (Fig. 8a), major fracture zones (Fig. 8b), and the location of mine workings (Fig. 8c). This figure shows a schematic plan view of a groundwater flow system along a topographic gradient, but influenced strongly by the position of the access gallery and the old mine workings.

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:	01-06-1991 - 31-12-1991
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

Within the period 1991-06-01 - 1991-11-30 the first part of the research project, i.e. the preparation of labelled humic material has been approached. Labelling has been carried out using either iodine isotopes or C-14.

In the case of C-14 labelling two approaches have been followed: 1° methylamination of a small fraction of the available carboxylic acid groups in humic acids and 2° enzymatically incorporation of C-14 labelled phenol into the humic acid skeleton. In both cases high incorporation rates of the label into the humic materials have been obtained. Thus methylamination gave labelling yield up to ca. 80%, whereas quantitative incorporation of the phenol label was obtained.

Preliminary results of the use of these labelled organics, for example in transport studies have been reported.

Progress and results

1. Carbon-14 labelling

Two strategies for C-14 incorporation have been examined.

Carbodiimides, such as 1-ethyl-3-dimethylaminopropylcarbodiimide have been used in protein chemistry as cross-linking agents and in the determination of carboxylic acid functionality. Reaction at carboxylic acid groups produces an o-acylisourea intermediate which in turn reacts with a nucleophile. When an amine nucleophile is present an amide is produced with the liberation of a proton and a urea as byproducts, regeneration of the carboxylic acid occurs when water is the attacking nucleophile. We have studied the reaction using C-14 labelled methylamine hydrochloride as the amine nucleophile.

Functional group analysis of commercially available sodium humate (Aldrich) provides a figure for total proton capacity of 3.14 meq/g of humic material of which 0.2 meq/g is attributable to carboxylic acids. When as the free acid the total capacity is raised due to protonation of the carboxyl groups leading to a value of 4.7 meq/g for carboxyl content. C-14-methylamine hydrochloride was used as supplied at a specific activity of 1.48 GBq/ mmol, hence an incorporation of 35 kBq/mg of humic acid would correspond to 2.3×10^{-8} moles of methylamine per mg of humic acid or less than 0.5%consumption of the available carboxylic acid groups. This labelling has been obtained at 80 % yield.

This reduction in carboxyl functionality is unlikely to significantly reduce the metal binding capacity of the humic acid, in which carboxylic acid groups are thought to play a predominant role.

The second method considered for C-14 labelling of humic materials involves

the enzymatically mediated incorporation of C-14 phenol. A proposed production route for humic substances involves polymerisation of simple monomeric species such as hydroxyphenols originating from the decomposition of plant components. Based on this assumption, incorporation of other phenolic compounds might be achieved without significant alteration to the humic material.

Such incorporations can be achieved with humic acid and C-14 phenol in solution by the presence of enzymes of the peroxidase group and hydrogen peroxide. The uptake of phenol is dependent on the initial concentrations of the enzyme, phenol and hydrogen peroxide. Horseradish peroxidase (HRP) was found to be the most efficient of the enzymes studied and at [HRP] > 2.5 eu/ml (virtually) quantitative phenol incorporation was achieved with initial concentrations of phenol, humic acid and hydrogen peroxide of $< 5 \times 10^{-4}$M, 935 mg/L and 1.6×10^{-3} M, respectively. This corresponds to a < 5% increase in mass of the humic acid and the use of much lower levels of phenol are envisaged in future work in order to minimise disruption to the humic acid molecules. Using this technique, however, very high specific activity labelling may be achieved. If the above conditions are used with carrier free phenol at 1.85 GBq/ mmol specific activity (readily obtainable), the resulting labelled humic acid will have an activity of ca. 1MBq/mg. Phenol incorporation as high as 10% by weight has been achieved. However, the resulting samples were found to contain "poly-phenol", resulting from an enzyme mediated oxidative polymerisation of phenol, as a major impurity.

2. Iodine labelling

Two methods for radioactive iodine incorporation into humic materials have also been developed.

The first, in an analogous reaction to phenol incorporation, employs an enzymatically mediated process, using Horseradish peroxidase, lactoperoxidase or chloroperoxidase and hydrogen peroxide. This reaction is thought to mimic reactions in soil catalysed by extra-cellular enzymes which lead to the iodination of humic substances in nature and are believed to be responsible for the formation of organohalogens of non-anthropogenic origin in the soil. Lactoperoxidase is commonly used for protein iodinations.

In an attempt to optimise labelling conditions the effect of $[I^-]$, [HA] and [Enzyme]/$[H_2O_2]$ have been studied. However it was not possible to raise the labelling efficiency above 35-40% of the initially applied iodide. This is thought to be due to the equilibrium established between the species and the relatively small number of sites potentially available for iodination. The reaction is thought to lead to iodine incorporation via electrophilic aromatic substitution and proposed humic acid structures indicate only a few "free" aromatic hydrogens.

The second iodination method also relies on electrophilic aromatic substitution

brought about by the action of the oxidising agent Chloramine-T on sodium iodide (sodium [I-125] iodide, Amersham), another reaction widely used in protein chemistry. In proteins iodination is primarily directed to the phenolic side chain of tyrosine residues although reaction at histidine, tryptophan and sulphydryl groups may also occur.

Initial studies on I-125 labelling with Chloramine-T indicated quantitative uptake of the added iodide, however the resulting label was not stable and gradual release of activity was observed. A stable iodinated material has now been produced by the addition of the reducing agent sodium metabisulphite. A significant reduction in yield is seen with ~ 35% of the initial activity bound to humic acid and 20 % bound to fulvic acid labelled similarly. The reducing agent returns any oxidised iodine species to the iodide and hence causes the removal of any iodine loosely bound to the humic material via electrostatic attraction. A stable sample of fulvic acid with a specific activity ~ 37kBq/ mg has been produced.

3. Stability of the labelled material

The stability of the labelled humic and fulvic materials and their transport behaviour has been assessed in the laboratory using glass columns (80mm long, 26mm diameter) packed with sand which were eluted with groundwater taken from the same site as the sand. The speciation of the eluted materials was determined by gel chromatography.

Labelled materials produced by three of the techniques have been investigated, the enzymatic incorporation of iodine was not studied further due to the poor pH stability of the label.

List of publications

1) Pia Lassen, Mette Poulsen and Lars Carlsen,*Enzymatically mediated incorporation of phenol in humic acids,* Finnish Humus News, **3** (1991) 221
(The paper was presented at the 3rd International Nordic Symposium on Humic Substances in Turku/Åbo, Finland, aug. 1991)

2) L. Carlsen, P. Lassen, J.V. Christiansen, P. Warwick, A. Hall and A. Randall *Radiolabelling of humic and fulvic materials for use in environmental studies,* submitted for publication in Radiochim.Acta.
(The paper was presented at the Migration '91 conference in Jerez, Spain in october 1991).

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.

Contractors:	University of Exeter (UK), University of Oviedo (E), Commissariat à l'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 - 28.02.93.
Period covered:	01.03.91 - 31.12.91.
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 distances 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 focussed on the El Berrocal study site in Spain. Delays in the drilling of new boreholes and hydrogeological testing at the site have led to delays in the distribution of sample material to project participants, and much of the work carried out to date has been concerned with technique development, the setting up of new laboratories, instrument calibration, and preliminary investigations using samples from previous studies at El Berrocal. The work undertaken can be described under the following headings:

1. Field sampling, sample preparation and sample distribution (Oviedo);
2. The assessment of confocal laser microscopy for the study of microcrack networks in rocks (Oviedo);
3. Petrographical characterisation of the El Berrocal granite using stereological and digital image processing techniques (Oviedo/Oxford);
4. Mercury porosimetry (Besançon);
5. Microfissure studies by optical fluorescence microscopy (Besançon);
6. Uranium series investigations (Exeter);
7. Geochemistry, including an interlaboratory/intertechnique comparison in relation to uranium analysis (Exeter/CEA Fontenay-aux-Roses);
8. Uranium series diffusion modelling (Liverpool).

Towards the end of the reporting period, new core material was obtained from El Berrocal (borehole S-16) and sample preparation for the wide range of studies to be undertaken in the project is now well advanced.

Progress and results.

1. Field sampling, sample preparation and sample distribution.

Several cores from the El Berrocal study site have been provided by the Centro de Investigaciones Energéticas, Medio Ambientales y Tecnológicas (CIEMAT) in Madrid (from boreholes S-1, S-7 and, more recently, S-16). One core from borehole S-16 (37.85 - 38.50 m) has been cut longitudinally and distributed for (1) geochemical/uranium disequilibrium studies, (2) petrophysical determinations and (3) mercury porosimetry.

Additionally, oriented cores, 42 mm in diameter and about 150 mm long have been drilled in three different locations inside the mine adit. 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 collected from the mine adit.

2. Assessment of confocal laser microscopy for the study of microcrack networks in rocks.

Preliminary studies of the three-dimensional microfractographic network of the El Berrocal granite have been undertaken by the University of Oviedo under laser scanning microscopy in confocal mode (LSM-CM). This technique has been selected as the most appropriate for observing and evaluating the open rock microfractography at the microscopic level; that is, the interconnected fissure network through which diffusion takes place.

In particular, the direction and dip of the fissures, their connectivity and tortuosity, can be more accurately evaluated for a better interpretation of the contribution of each family of fissures to the channelling of radionuclide migration through the rock matrix.

A number of commercially-available microscopes (Zeiss, Leitz, Bio-Rad) have been evaluated. A decision on which instrument to employ in the study will be made during 1992.

3. Petrographical characterisation of the El Berrocal granite.

Stereological studies and digital image processing techniques.

To assess the usefulness of the parameters selected to characterise the petrographic components of the El Berrocal granite, a preliminary petrographic study has been carried out in Oviedo using two different methods: digital image analysis and stereology. In each case, both mineral grain properties (volume percentage (Vv), mineral affinity (θ) and fractal dimension (D) of grain boundaries) and fissure characteristics (specific surface, orientation, fissure classification and fractal dimension) have been analysed. The stereological studies have been supported under sub-contract by the University of Bern (CH).

Acoustic microscopy.

Polished thin sections of El Berrocal granite have been studied under acoustic microscopy at the University of Oxford. The images obtained make possible the detailed identification of intergranular structures in the rock-forming minerals (very fine cracks, grain and sub-grain structures, etc.).

Physical properties.

Some physical properties (open porosity, void index, water content after 2 and 5 days and under saturation) have been measured in Oviedo following ASTM and ISRM standards and recommendations, in the different slices parallel to the fracture prepared from the core from borehole S-16, to see if there exists any variation as the fracture is approached.

Measurement of Vp in relation to distance from the fracture.

The velocity of longitudinal waves (Vp) has been measured in Oviedo in the core from borehole S-16 before cutting. The measurements have been carried out in 'virtual' slices 11 mm thick parallel to the fracture, and in four directions (45° from each other) normal to the core axis. After cutting the core, Vp has been measured along the core axis in each of the slices prepared for the determination of physical properties. Preliminary interpretation of the results suggests that Vp decreases with increasing distance from the fracture.

4. Mercury porosimetry.

In the absence of new drill core from El Berrocal, preliminary tests have been carried out at the Laboratoire de Microanalyses Nucléaires (LMN), University of Franche-Comte, Besançon (F), on granite blocks from El Berrocal and a sample preparation procedure has been established. Difficulties have been experienced with the new core samples owing to their

small diameter (83.4 mm) and the need to conduct a large number of measurements at different distances from the fracture.

For the mercury porosimetry, the sample dimensions have been constrained by the limitations of the porosimeter which was designed by the LMN for analysis of low-porosity materials. Different sample geometries and dimensions have been tested to determine the optimum for granite samples: cylindrical samples with axes parallel to the fracture, 11 mm in diameter and 26 mm in length, in batches of three (results presented in Table I); and parallelepiped samples, 22 x 26 x 10 mm in dimensions with the 22 x 26 mm face parallel with the fracture (Table II). For the new sample cores, cylindrical samples, 24 mm in diameter and 16 mm in length with axes perpendicular to the fracture will be used, and a standardised experimental procedure is now being established for samples of this type.

Porosities for the cylindrical samples were found to vary between 1.23 and 1.38%; in the parallelepiped samples, porosity varied between 1.35 and 1.74%. In each case, the highest porosity value was obtained from the sample nearest to the fracture. For the cylindrical samples, a decrease in porosity with increasing distance from the fracture of 0.015% per cm was observed; for the parallelepiped samples, the variation with distance from the fracture was more erratic. Samples are injected with mercury at pressures of up to 200 MPa, corresponding to pore diametres of 0.006 μm.

5. Microfissure studies by optical fluorescence microscopy.

Thin sections of El Berrocal granite, 40 μm thick, impregnated with fluorescent resin, have been studied in Besançon using fluorescence optical microscopy. The feldspars appear highly altered; quartz grians show intragranular and intergranular cracks and the mica sometimes shows a loss of cohesion between grains.

The angle of dip of the cracks in quartz with respect to the vertical axis of the core was also measured on approximately 100 linear crack segments. The results show an anisotropy with a dominance of cracks around 45°. These measurements are continuing using a computerized system to speed up the procedure.

6. Uranium series disequilibrium investigations.

Uranium series investigations are being carried at the Earth Resources Centre, University of Exeter, out to determine the key activity ratios U-234/U-238 and Th-230/U-234 in a series of rock slices taken from each sample core. A new Canberra alpha spectrometer, complete with System 100 multi-channel analyser (MCA), quadruple detection chambers, software package, new vacuum pump and IBM 30-286 computer, have been installed, and early work has concentrated on calibrating the new system, ensuring its reliable operation, and checking spectra against those obtained on a pre-exisiting system used in an earlier study /1/. Results show uranium isotopic ratios to be satisfactorily reproducible. The uranium disequilibrium work is being supported under sub-contract by the Harwell Laboratories of AEA Technology (UK).

7. Geochemistry.

Major and trace element geochemistry is being determined in Exeter and at the CEA's Centre d'Etudes Nucléaires de Fontenay-aux-Roses using a range of techniques, including: inductively coupled plasma atomic emission spectrometry (ICP) and X-ray fluorescence spectrometry (XRF) for a wide range of major and trace elements; neutron activation analysis for a range of trace elements including uranium, thorium and the Rare Earth Elements; and volumetric analysis for Fe(II). Infra-red spectrometry using a Siemens IFS25 instrument will also be employed to provide information on the molecular structure of sample powders, notably of hydrated solids for which the technique is particularly suitable.

Uranium concentrations are also provided by the alpha spectrometric analysis of uranium and thorium isotopic ratios. These values, along with those obtained in Exeter by X-ray fluorescence spectrometry (XRF) for a series of El Berrocal samples studied during a previous investigation /1/, are compared with uranium values obtained this year by neutron activation at Fontenay-aux-Roses in Table III. The neutron activation values are plotted against the XRF values obtained for sample EB1F in Figure 1. The results represent an interlaboratory/inter-technique comparison which forms part of the quality assurance work being undertaken in the project. Despite some scatter, the correlation between the different techniques and the two laboratories is generally good.

8. Uranium series diffusion modelling.

Assumptions and Model.

The data being acquired in the various studies described above will provide the input for a mathematical diffusion model being developed by the University of Liverpool (UK). Models of the migration of uranium from fracture water into the wall zone of crystalline rock, developed for the El Berrocal project, assume:
(1) that uranium diffuses through the connected porosity of the rock; and
(2) that it is retarded by sorption onto and into alteration minerals near the fracture.

It has been assumed, fairly safely, that connected porosity and constrictivity decrease with distance from the fracture, but that tortuosity increases away from the fracture. Similarly, it is known that the sorptive mineral concentrations decrease away from the fracture. So far, in the models developed to simulate the known distribution of excess uranium (that is, in excess of the concentration in the fresh rock) it has been assumed that the petrophysical parameters discussed above change (decrease or increase) linearly with distance from the fracture. However, for simplicity, it has been assumed that the sorption factor Kd (the ratio of sorption, in millimoles, per unit mass of rock to the concentration in solution) is constant with fracture distance. The one-dimensional diffusion-retardation differential equation has been solved by finite difference methods assuming a constant concentration of U in the fracture water from the start of migration. For thorium (i.e. Th-230, the daughter of U-234), it has been assumed that there is no diffusion and, therefore, that the concentration change depends only upon its radioactive growth and decay.

Results.

In the absence of El Berrocal data, the simulations have been compared with other published fracture profiles with the following results:
(1) U 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 m3/kg) from laboratory batch and other experiments;
(2) Neither U-234/U-238 nor Th-230/U-234 activity ratios can be simulated with any degree of confidence by assuming simple diffusion and sorption processes alone. However, these simulations have only been able to make use of general rock property and alteration mineral variation, and very little of the data are site specific; that is, the data input into the simulations do not correspond, as yet, with the published U-series variations. Further simulations will be attempted upon receipt of the site-specific data from El Berrocal.

List of publications.

HEATH, M. J., MONTOTO, M., RODRIGUEZ -REY, A., RUIZ DE ARGANDOÑA, V. G., and MENENDEZ, B. (1991). Rock matrix diffusion as a mechanism for radionuclide retardation: evidence from uranium disequilibrium, geochemical and petrophysical studies of El Berrocal granite, Spain. Proc. 3rd Int. Conf. on Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere - Migration '91. Jerez de la Frontera (Spain), 21-25 October, 1991.

Reference.

/1/ MONTOTO, M., HEATH, M. J., RODRIGUEZ-REY, A., RUIZ DE ARGANDOÑA, V. G., CALLEJA, L. AND MENENDEZ, B. (1991). Natural analogue and microstructural studies in relation to radionuclide retardation by rock matrix diffusion in granite: final report. Report to Commission of the European Communities (Contract No. FI1W-0143).

TABLE I. Mercury porosimetry results for cylindrical samples of El Berrocal granite sample GREBK.

Sample No.	Mass (g)	Volume (cm3)	Distance from fracture (cm)	Porosity (%)
GREBKCA	18.77	7.352	1.05	1.38
GREBKCB	19.05	7.312	2.55	1.33
GREBKCC	18.47	7.274	4.16	1.27
GREBKCD	19.05	7.359	5.80	1.34
GREBKCI	18.96	7.458	6.97	1.27
GREBKCG	18.86	7.417	9.70	1.23

TABLE II. Mercury porosimetry results for parallelepiped samples of El Berrocal sample GREBK.

Sample No.	Mass (g)	Volume (cm3)	Distance from fracture (cm)	Porosity (%)
GREBKP1	14.53	5.761	0.45	1.74
GREBKP2	14.55	5.730	1.50	1.44
GREBKP3	14.99	5.990	2.62	1.40
GREBKP4	14.89	5.900	3.75	1.47
GREBKP5	15.32	6.140	4.85	1.35
GREBKP6	16.06	6.310	6.07	1.40
GREBKP7	14.02	5.550	7.17	1.52
GREBKP8	13.99	5.468	8.20	1.52

TABLE III. Comparison of uranium concentrations (ppm) determined by X-ray fluorescence spectrometry (Exeter), alpha-spectrometry (Exeter) and neutron activation analysis (CEA, Fontenay-aux-Roses).

Sample No.	Distance from fracture (mm)	U (XRF)	U (Alpha sp.)	U (NA)
EB1F.0X	-2.5	119	105	104.5
EB1F.0	2.5	46	39	42.4
EB1F.1	13.5	26	22	29.2
EB1F.2	29.5	25	24	21.8
EB1F.3	43.0	16	12	13.5
EB1F.6	81.0	20	18	17.9
EB1F.8	123.0	22	19	20.4
EB3.0	2.5	22	20	21.2
EB3.1	13.0	19	19	20.2
EB3.2	26.0	17	19	18.3
EB3.4	52.0	16	18	16.6
EB3.7	106.0	14	15	18.2
EB3.11	198.0	14	14	20.3

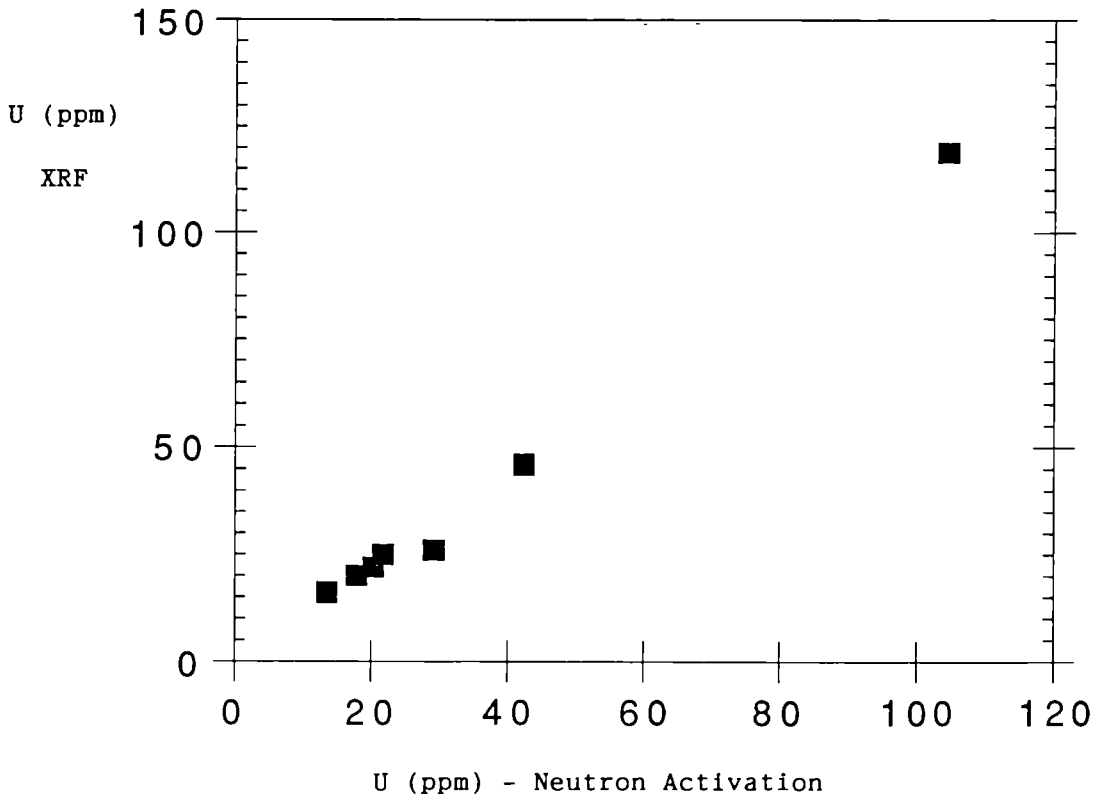


Figure 1. Comparison of uranium concentrations obtained by neutron activation analysis and X-ray fluorescence spectrometry, El Berrocal sample EB1F.

Effects of Humic Substances on the Migration of Radionuclides: Complexation of Actinides with Humic Substances

Contractor: Institut für Radiochemie, Technische Universität München

Contract No.: FI2W/CT91/0083
Duration of contract: July 1991 - June 1994
Period covered: July 1991 - December 1991

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 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 laboratoriers 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)

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. A study has been conducted by KUL and TUM to determine an effective ligand concentration of a given humic acid. This is a parameter being used for the evaluation of the complexation constant of a metal ion for the bulk polyelectrolytes like humic or fulvic acid. Time resolved laser fluorescence spectroscopy (TRLFS) is further developed for its application to the humate complexation study of trivalent metal ions by CEA-FAR, JRC-Ispra and TUM. Effect of humic acid on the interaction of metal ions with inorganic colloids is examined systematically by JRC-Ispra. The humate complexation of Np(V) is studied by UM in the metal ion concentration range of 10^{-14} mol/L. This study is of experimental significance for understanding the effect of metal ion concentration on the humate complexation.

Progress and results

1 Complexation reaction of actinide ions with reference and site specific humic acids.

For the present study, humic and fulvic acids from three different sites and a commercial humic acid from Aldrich Co. are used. They are 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 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 own 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 the 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)		Under investigation		
Aldrich HA(III)		Under investigation		
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		Under investigation		
Podzol-B HA			5.4	

1): pH=7/10

1.1 Experimental techniques

TUM

UV-spectroscopy is applied for the study of the Am(III)-fulvate complexation with a relatively high concentration of Am (10^{-5}/ 10^{-6} mol/L). Time resolved laser fluorescence spectroscopy (TRLFS) is used to investigate the Cm-fulvate complexation at low metal ion concentrations (10^{-7}/ 10^{-8} mol/L) with a low loading of the fulvic acid ligand. By energy transfer from humic or fulvic acid molecules to metal ions, the fluorescence yield of the Cm-complexes is enhanced. By selective excitation at different wavelength, the spectroscopic speciation of Cm^{3+} and Cm-complex is optimized.

CEA-FAR

TRLFS is applied for the study of the humate complexation of Cm and Dy. Further development of this technique by coupling with a dye laser to allow variation of the excitation wavelength is in progress.

UM

A three step-laser-resonance-ionization mass spectroscopy sytem is used for the detection of actinides in the femtomol concentration range. This detection system is coupled with

the electrophoretic ion focusing which is used for the separation of the NpO_2^+ ion from the complexed form. Other separation techniques are being developed.

KUL

The ion exchange technique has been used for the actinide complexation study over several years. For the present programme a number of ion exchangers have been compared. Additionally a dialysis membrane technique is applied.

JRC-Ispra

TRLFS is applied for the study of the competitive reaction between Eu(III) and Cr(III) with humic acid.

1.2 Results of the complexation study

TUM

The fulvate complexation of trivalent actinides with Gohy-573 FA is investigated at pH=6.0 and I=0.1. The metal ion concentration is varied from nmol to µmol in order to examine whether the degree of loading of the fulvic acid influences the complexation behaviour. The species involved are quantified by spectral peak deconvolution. The concentration range of the investigated metal ions and the fulvic acid are:

	[An(III)]		[FA(III)]	
Am-fulvate	5 - 46	(µmol/L)	15	(µmol/L)
Cm-fulvate	56 - 78	(nmol/L)	0.076 - 47	(µmol/L)

The loading of the fulvic acid with Cm(III) or Am(III) varies from approximately one percent to a level of saturation. No variation of the complexation constant with the degree of loading is observed. The complexation constant is found to be: $\log\beta_{(An(III)\text{-fulvate})} = 5.86 \pm 0.11$. The complexation constant for the fulvic acid is somewhat lower than that for the corresponding humic acid ($\log\beta = 6.27 \pm 0.07$ [1])

CEA-FAR

The experimental range of the metal ion concentration is between $3x10^{-8}$ and $2x10^{-6}$ mol/L and pH between 4.2 and 6.9 at a constant ionic strength of 0.1. The experimental method is based on measuring the total fluorescence intensity as a function of the humic acid concentration at the constant metal ion concentration. The quantification of the humate complex and the free metal ion is made by analysing the fluorescence titration curve.

The effective ligand concentration, expressed as a complexation capacity, and the complexation constant are evaluated by computer fitting of the fluorescence titration curve. The complexation capacities determined by CEA-FAR are found to depend on both pH and total metal ion concentration:

	pH				
	4.2	4.7	5.2	6.1	6.9
Concentration (in mol/L)	Complexation capacity (in mmol/g HA)				
[Dy]=$2x10^{-6}$	0.7 ± 0.1[1)]		0.7 ± 0.1[2)]		1.0 ± 0.1[3)]
[Cm]=$5x10^{-7}$	0.5 ± 0.1	0.5	0.50 ± 0.05	2.0 ± 0.3	1.5 ± 0.1
[Cm]=10^{-7}	0.10 ± 0.02	0.20 ± 0.05	0.30 ± 0.05	0.5 ± 0.1	0.60 ± 0.05
[Cm]=$3x10^{-8}$	0.040 ± 0.003				

1): pH=4; 2): pH=5; 3): pH=6

The complexation constants evaluated by taking the complexation capacity into account are found to be independent of pH. This is in agreement with the observations of TUM [1,8] and KUL. However, the complexation constants determined by CEA-FAR are found to vary significantly with the metal ion concentration:

Metal ion:	Am[1)]	Dy	Cm	Cm	Cm
[M(III)] (mol/L)	$3x10^{-5}$	$2x10^{-6}$	$5x10^{-7}$	$1x10^{-7}$	$3x10^{-8}$
logß (L mol^{-1})	7 - 7.5	7.6 ± 0.1	7.4 ± 0.2	8.4 ± 0.5	9.5 ± 0.5

1): from [9]

UM

The Np(V)-humate complexation is studied at a Np-concentration of approximately 10^{-14} mol/L. The humic acid concentration ranges between 5 and 20 mg/L (appr. 25 and 100 µmol/L) and pH between 3 and 7 at constant ionic strength of 10^{-3}. A considerable variation of the complexation behaviour with both pH and humic acid concentration is observed. Comparison of these results with the published data from TUM [5] is difficult, because the loading capacity of humic acid for Np(V) in the pH range and at given ionic strength is unknown. However, the following calculation is made for comparison:

	UM (this study)	TUM [5]
	[Np] ≈ 10^{-14} mol/L, pH = 5, I = 10^{-3}	[Np] ≈ 10^{-4} mol/L, pH = 6-9, I = 0.1
logß(Np(V)-HA):	3.7 ± 0.4[1)] / 5.0 ± 0.4[2)]	3.66 ± 0.02

1): assuming 100% loading capacity
2): corrected for a loading capacity of 5 % estimated from Ref. [5] for pH 5 and I=0.1

KUL

The effective ligand concentration of humic acid is determinded directly by the complexation capacity with Eu(III). This is compared with the exchange capacity of Cobalt-Hexamine and the degree of ionization by direct pH-titration. The results obtained by these methods differ from one another. The complexation capacity is found to vary with pH. This is in agreement with the results from TUM. One example for the pH dependent complexation capacity of humic acid (Aldrich HA(III)) is given for Eu(III):

pH:	3.15	3.50	4.50	6.00
Complexation capacity: (meq/g HA)	2.38 ± 0.06	2.95 ± 0.18	4.14 ± 0.18	5.39 ± 0.17

KUL has determined the complexation constants for Eu(III) by ion exchange technique [10,11] using three different ion exchangers at pH 3.6 to 6.0 and at the ionic strength 0.01 and 0.1. The number of humic acid ligands involved in the Eu-humate complexation reaction is evaluated to be 1.18 ± 0.19. For this reason KUL concludes that only one type of binding occurs. The complexation constants are shown to be independent of pH and ionic strength:

	pH / ionic strength	logß (L mol^{-1})
Dialysis method:	3.5 / 0.1	(7.33 ± 0.58)
Ion exchange method: (Lewatit CP-3050)	3.6 / 0.1	6.83 ± 0.21
	4.5 / 0.1	6.62 ± 0.26
	4.5 / 0.01	7.14 ± 0.13
	6.0 / 0.1	6.92 ± 0.06
	mean value:	6.88 ±0.22

2 Competition reactions with cations in natural groundwaters

JRC-Ispra has studied the competition reaction between Cr(III) and Eu(III) with humic acid (Gohy-573 HA) at pH=5.5 and ionic strength of 0.1. Cr(III) is bound to the humic acid to a same extent as Eu(III). The complexation constant derived for Cr(III) is logß(Cr(III)-HA) = 6.3. This confirms that the magnitude of the complexation mainly depends on the oxidation state of the metal ion [12,13].

3 Influence of humic substances on the interaction between actinides and inorganic colloids

The colloidal properties of humic acid and amorphous silica or γ–alumina as well as

mixed systems of humic acid with these inorganic colloids are investigated by JRC-Ispra. The size, the zeta potential and the sorption of humic acid on these inorganic colloids are examined. The colloid generation of Am(III) and Np(V) in these mixed systems is studied.

The size of humic acid is found to increase with decreasing the pH and increasing the humic acid concentration. The pH effect is explained by decreasing repulsion between the humic acid molecules due to charge neutralization through proton association of functional groups. Between pH 10. 5 and 5, the zeta potential is found to change from ≈ -32 to ≈ -20 mV reflecting that at pH 5 ≈40 % of the carboxylic groups of humic acid are proton associated [1]. In contrary to humic acid, γ-alumina shows an isoelectric point in the investigated pH range (at pH=8.8) with a negative charge at higher pH and ≈+30 mV at pH 5.

The sorption of humic acid on γ-alumina is investigated by two different experiments. With increasing humic acid concentration the zeta potential of γ-alumina progressively resembles that of humic acid. With 25 ppm humic acid and 200 ppm alumina, the zeta potential of γ-alumina at pH 5 changes from +30 to 5 mV (cf. -20 mV for pure humic acid). Furthermore, between pH 4 and 8 ≈90 % of humic acid is sedimented with γ-alumina colloids by ultracentrifugation. Above the isoelectric point of γ-alumina the fraction of sorbed humic acid is found to decrease (≈80 %) due to charge repulsion. The sorption of humic acid on amorphous silica is found to be less pronounced but have a stronger pH dependency than the γ-alumina.

The sorption of both Am(III) and Np(V) on the inorganic colloids is found to change with addition of humic acid. The influence of humic coating on the sorption of Am is stronger than that of Np. This reflects the higher strength of the Am-humate interaction compared to the Np-humate. The sorption of Am on pure silica colloids increases steadily from ≈20% at pH 5 to ≈90% at pH 9, whereas adding as little as 1 ppm humic acid to 1200 ppm amorphous silica 80-100% of Am is sorbed. The sorption of Np(V) on amorphous siclica is realtively low (<10%) below pH 8. Above this pH the sorption increses and reaches a maximum of ≈70% at about pH 10. Between pH 7 and 9, the addition of humic acid leads to an increased sorption of Np by 15 to 30 % relative to pure silica colloids. These results clearly demonstrate the affinity of humic acids for inorganic surfaces and its strong influence on the actinide sorption behaviour.

4 Validation of the results in natural aquatic systems by comparison of calculation with spectroscopic experiment

Work on this task is scheduled to start in the second year of the research programme.

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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:	May 1991 - December 1991
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 for 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

B.1 Sampling of groundwaters, colloids and sediments under well controlled conditions (TUM, AEA, GSF)

B.2 Characterization of colloids, groundwaters and sediments (TUM, AEA, GSF)

B.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)

B.4 Transport process study by scaled column experiments (TUM, GSF, AEA, Atkins)

B.5 Synthesis and theoretical interpretation (Atkins ES)

B.6 Liaison with related studies within the MIRAGE programme (e.g. calculation tool)

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The sorption of actinide ions with high electric charges ($Z \geq 3^+$) onto groundwater-colloids can be considered as generation of "pseudocolloids" of actinides, which play an important role for the subsequent migration processes of the actinides in the geosphere [1, 2]. The study of this subject has been started in the second phase of the CEC-MIRAGE project [3]. For the quantitative description of colloid-associated radionuclide migration in a given aquifer system, precise knowledge on the generation of pseudocolloids and their migration processes is indispensable.

For the present study, groundwater samples and sediments have been collected in May 1991 from four boreholes of Gorleben aquifer systems, which are geologically and chemically different. The sampled groundwaters were submitted to parallel ultrafiltration using filters of different pore sizes to estimate the size and quantity of natural colloids. The groundwaters, ultrafiltrates and sediments are characterized for their chemical composition and physical properties. Trace elements of higher oxidation state ($\geq 3+$) in groundwaters are found to be strongly sorbed on humic colloids. Column experiments for the transport process study are being prepared in close collaboration among participants. Preliminary tests on hydraulic properties, break-through characteristics and scaling factors of the sediment columns are in progress.

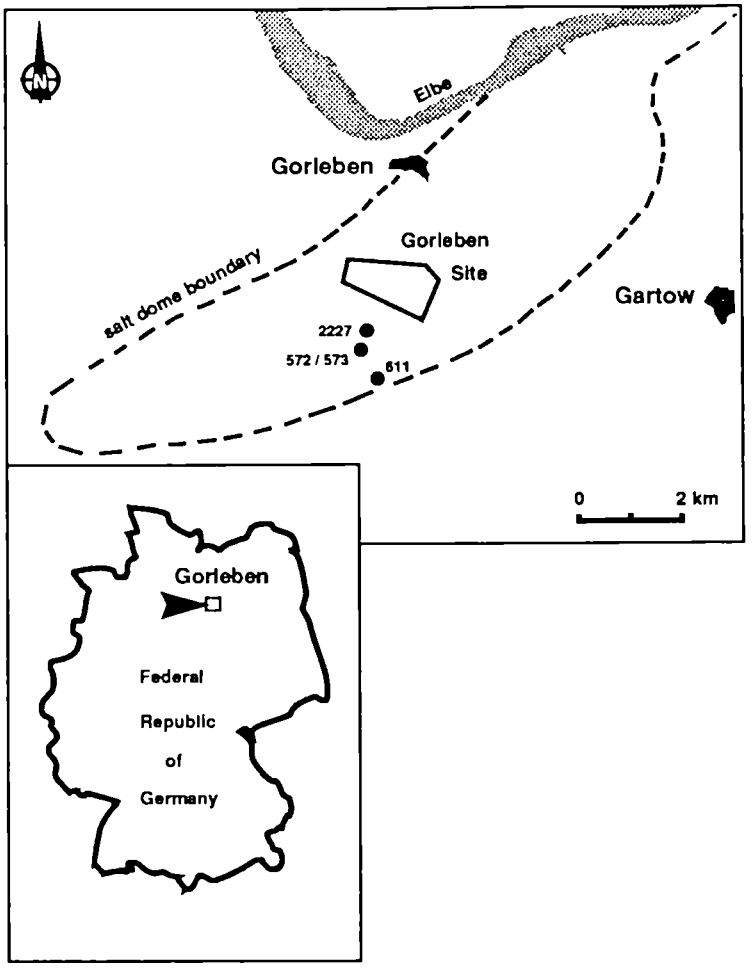
Progress and results

1 Sampling of groundwaters, colloids and sediments

Groundwater

Selected aquifer systems from the geological site foreseen for the future German nuclear waste repository at Gorleben were sampled between 13. - 17. May 1991. Groundwater samples were collected from boreholes Gohy 572, Gohy 573, Gohy 611 and Gohy 2227 (Fig. 1). These boreholes intersect at least three different aquifers. The geological cross section of the salt dome and the nature of the overlying sediments (not shown in this report) indicate a hydrological connection between groundwaters from boreholes Gohy 573 and Gohy 2227. The sampled aquifers are situated within sand, silt, marl and clay overlying a salt dome with a volume of approximately 8×10^{10} m^3 [4]. Gohy 572 and Gohy 611 correspond to shallow Pleistocene sand and silt aquifers with low salt content, whereas Gohy 573 and Gohy 2227 are intersecting a relatively deep and saline aquifer with glacial intercalations of lignite. The groundwater collected from boreholes Gohy 573 and Gohy 2227 are, therefore, rich in organics. Before sampling, the boreholes were flushed by pumping off three times of their water volume. The sampling was carried out anaerobically (N_2 + 1% CO_2) to minimize contamination by oxygen. It is

Figure 1: The location of the Gorleben sampling site



known, however, from earlier work that the sampling even under anaerobic conditions causes somewhat change in the redox potential of groundwater. For this reason, during the pumping procedure measurements are made for pH, Eh, T, O_2, HCO_3^- and electrical conductivity immediately after sampling and for pH, Eh, O_2 directly in situ. Each participating group (TUM, AEA, GSF) collected 2 x 50 L of unfiltered groundwater from each borehole for laboratory analysis. The groundwater samples were stored anaerobically in Al-containers with a special inner coating to prevent surface reactions during transportation and storage. Additional samples were collected by GSF for determination of the isotopes ^2H, ^3H, ^{13}C, ^{14}C and ^{18}O. These groundwater samples were stored in nitrogen flushed polyethylene and stainless steel containers.

Colloids

Colloid concentrates and ultrafiltrates were sampled in the field anaerobically (N_2 + 1% CO_2) using an Amicon DC10LA ultrafiltration system with a 1µm prefilter and a 10,000

molecular weight (MW) (approximately 1.5 nm) cut-off hollow fibre in a tangential flow filter cartridge. Details of the Amicon DC10 LA ultrafiltration system are given elsewhere [5]. 20 L of colloid concentrate were produced out of 500 L of prefiltered groundwater giving a concentration factor of about 25 and a colloidal size distribution between 1 µm - 1.5 nm. Samples of 20 L ultrafiltrate (fraction passing through 10,000 MW) were also collected. The hollow fibre cartridge was washed in turn with 0.1 M NaOH to remove organic material sorbed onto the filter and 0.1 M HCl to remove all remains. All washes were combined, acidified with HNO_3 and reserved for analysis.

Sediments

Sediments were collected from three of the four boreholes, namely from drill cores stored at the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) at Hannover, F.R.G. The sediment samples are corresponding to boreholes and filter depths from where the groundwater have been collected. The sediment samples available for characterization are listed in Table 1.

Table 1: Sediment samples from drill cores of boreholes Gohy 573, Gohy 611 and Gohy 2227

Sample	Borehole	Depth below surface [m]	Lithology
Gohy 573-1	Gohy 573	135.5 - 136.0	fine-grained quartz sand
Gohy 573-2	Gohy 573	136.0 - 136.5	medium-gained quartz sand
Gohy 573-3	Gohy 573	136.5 - 137.0	lignite
Gohy 611-1	Gohy 611	18.0 - 19.0	med.-coarse gr. quartz sand
Gohy 611-2	Gohy 611	19.0 - 21.4	med.-coarse gr. quartz sand
Gohy 2227-1	Gohy 2227	129.6 - 130.0	fine silt, sand, marl
Gohy 2227-2	Gohy 2227	130.0 - 130.5	silt, sand
Gohy 2227-3	Gohy 2227	130.5 - 131.15	lignite

2 Characterization of groundwaters, colloids and sediments

Different analytical tasks, coordinated and distributed to the participating laboratories are:

- Chemical composition of groundwater and colloids (TUM, AEA)
- Chemical and mineralogical composition of sediments (TUM),
- Size distribution and population quantification by SEM/TEM, LPAS and ultrafiltration (TUM) and PCS technique (AEA),
- Provenance of colloids by isotope analysis (GSF, AEA),
- U-series disequilibrium study on colloids, groundwaters and sediment surfaces (AEA).

2.1 Experimental techniques

To characterize the composition of various colloid size fractions, the unfiltered groundwater samples are passed through flat bed membrane filters with nominal cut-off pore sizes of 1000 nm, 450 nm, 100 nm, 30 nm (Nuclepore and Sartorius filters), 2 nm and 1 nm (Amicon filters). Major, minor and trace elements in groundwaters and thus filtered ultrafiltrates are determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) at TUM and AEA. The concentrations of anions are analyzed by high performance ion chromatography (HPIC) and additionally some elements by atom absorption spectroscopy (AAS) at TUM. The concentration of dissolved organic carbon (DOC) is measured by catalytical thermal decomposition with IR-detection and optical absorption by UV/VIS spectroscopy at TUM. The chemical compositions (major, minor and trace elements) of sediments are analyzed by X-ray fluorescence analysis (XRFA) and neutron activation analysis (NAA) [6] at TUM. Mineralogical studies (thin-section microscopy, X-ray powder diffraction) are carried out at the department of mineralogy at TUM. The concentrations of U, Th and lanthanides present in groundwater samples are analyzed by isotope dilution/ alpha spectrometry [7] and ICP-MS at AEA and by NAA and ICP-MS at TUM. The partition of the activities of the longer-lived isotopes from the natural decay series between the colloid and solution phases are measured at AEA using isotope dilution/ alpha spectrometry. The ^{226}Ra concentrations in the 1 µm prefiltered water are determined using a radon emanation technique [7] and the $^{228}Ra/^{226}Ra$ activity ratios are determined by γ-spectrometry at AEA. Photon correlation spectroscopy (PCS) is applied at AEA to characterize the size distribution of the naturally occurring colloid population in the unfiltered Gorleben groundwaters. Colloid concentrations in various colloid fractions after ultrafiltration are determined by photoacoustic detection of light scattering (PALS) [8] at TUM. ^{3}H concentrations in the groundwaters are determined radiometrically at GSF after synthesis of propane in a proportional counter after electrolytical enrichment of ^{3}H. ^{14}C contents are determined by liquid scintillation counting after synthesis of benzene from CO_2 which was extracted from the acified groundwater samples; results are given as percent modern carbon (pmc). ^{2}H, ^{13}C and ^{18}O analyses are performed by mass spectrometry at GSF.

2.2 Chemical composition of groundwater and colloids

Chemical and physical characteristics of the the groundwaters are summarised in Table 2. The depth profile of aquifers varies from 21 m to 137 m below surface. The geological cross section of the salt dome and the nature of the overlying sediments (not shown in this report) indicate that between boreholes Gohy 573 and Gohy 2227 groundwater should be hydrologically connected. However, the chemical and physical properties of these two groundwaters differ significantly and hence do not support this assumption. The salinity, given as an electrical conductivity ($\mu S\ cm^{-1}$), generally increases with the

Table 2: Characterization and analysis of the selected groundwaters from the Gorleben site: physical parameters and concentrations of ions and DOC (analysis at 450 nm prefiltered sample)

	Gohy 572	Gohy 573	Gohy 611	Gohy 2227
Depth below surface [m]	70.2 - 73. 2	134.0 - 137.0	21.0 - 24.0	128.0 - 130.0
Color	transparent	brown	transparent	brown
pH	8.9* / 8.0	8.2* / 7.6	8.4 * / 7.1	7.8* / 7.5
Eh [mV]	17* / 119	-32* / -87	-90* / 31	-136* / -141
O_2 [$\mu g\ L^{-1}$]	n.d.	5.4*	20.5*	14.5*
HCO_3^- [$mg^{-1}L$]	310* / 299	490* / 480	64 * / 77	488* / 453
Conductivity [$\mu S\ cm^{-1}$]	540* / 568	1910* / 2010	200 * / 214	4300 */4550
Σ cations [meq L^{-1}]	6.10	19.5	2.34	44.3
Σ anions [meq L^{-1}]	5.82	20.3	2.31	44.9
DOC [mgC L^{-1}]	15.9	98	0.1	80

* field measurement; n.d. = not detectable

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 [9], is observed as a composite of humic and fulvic acids, which are loaded with various metal ions through complexation 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. DOC concentrations in filtrates decrease gradually with decreasing pore size of filter (Table 3). At the smallest pore size of about 1 nm, between 80.5% and 95.7% of DOC are filtered. The numbers in Table 3 show that DOC concentrations in the filtrates at 1000 nm, 450 nm and 100 nm are not different significantly. From these data and according to results obtained from earlier work [10] 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.

Concentrations of trace metal ions in filtrates from parallel filtration at different pore sizes were determined by NAA and ICP-MS. As a typical example, the average concentrations of natural lanthanides, U, Th, Hf and Zr analyzed in filtrates of Gohy 573 are given in Table 4. It is known from earlier work [10, 11] that trace elements of higher oxidation

Table 3: DOC concentrations [mgC L^{-1}] measured in filtrates from parallel filtrations at different pore sizes

	1000 nm Nuclepore	450 nm Sartorius	100 nm Nuclepore	30 nm Nuclepore	2 nm Amicon YM10	1 nm Amicon YM2
Gohy 572	15.2± 0.9	15.9±0.9	14.9±1.1	15.2±0.3	14.2±0.8	1.3±0.2
Gohy 573	95.7±1.3	97.8±1.1	70.4±1.5	33.7±0.7	27.7±0.8	4.1±0.2
Gohy 611	n.d.	0.1±0.3	n.d.	n.d.	n.d	n.d
Gohy 2227	80.7±1.9	79.8±1.8	79.9±0.3	54.3±2.0	40.9±1.1	15.7±0.6

n.d. = not detectable

Table 4: Concentrations [µg L^{-1}] of trace elements in filtrates of the groundwater Gohy 573 from parallel ultrafiltration at different pore sizes. Analysis by NAA and ICP-MS (TUM)

	1000 nm Nuclepore	450 nm Sartorius	100 nm Nuclepore	30 nm Nuclepore	2 nm Amicon YM10	1 nm Amicon YM2
La	5.42	5.30	1.66	0.13	0.19	0.04
Nd	5.42	5.01	1.68	0.19	0.07	0.02
Sm	1.28	1.21	0.48	0.13	0.05	< 0.05
Yb	1.13	1.05	0.48	0.18	0.06	0.03
Th	3.11	2.82	0.85	0.07	n.d.	0.002
U	0.96	1.02	0.43	0.029	0.097	0.030
Hf	1.21	1.22	0.58	0.164	n.d.	0.039
Zr	134	130	67.5	21.7	3.17	1.13

n.d. = not detectable

state (≥ 3+) are in general preferentially associated with humic colloids. Between 99.3% of REE and 96.9% of uranium is filtered on the smallest pore size of about 1 nm suggesting that the trace elements listed in Table 4 are almost quantitatively associated with humic colloids. Neutron activation analysis (NAA) of the filter cakes is in progress.

2.3 Chemical and mineralogical composition of sediments

The chemical composition of the sediment samples from drill cores of boreholes Gohy 573, Gohy 611 and Gohy 2227 (analytical data not listed in this report) show marked differences in concentrations of SiO_2, Al_2O_3, Fe_2O_3 and K_2O, which are main

components of quartz, feldspar and clay minerals. This is supported by mineralogical studies, on which the lithological description of the sediment samples is given in Tables 1 and 5. The lowermost lignite found in borehole Gohy 573 is overlaid by relatively pure quartz-sand, whereas the lignite of borehole Gohy 2227 is covered by sediments with a higher portion of clay (marl).

The contents of heavy metal elements analyzed by NAA of borehole samples Gohy 573 and Gohy 2227 are given in Table 5. In the case of borehole Gohy 573 the concentrations of lanthanides and other metal elements in the lignite are ten times higher than those of the quartz-sand. Such an effect is not observed for borehole Gohy 2227, where the lanthanides and other metal elements are equally distributed between lignite and overlying sand and marl. One explanation might be the different sorption behaviour of the overlying sediments due to different amounts of clay. Another reason could be different sources of the lignites found in Gohy 573 and Gohy 2227 although these two boreholes should be hydrologically connected due to the general hydrogeological model. The high concentrations of humic colloids determined in corresponding groundwater samples of boreholes Gohy 573 and Gohy 2227 are most likely related to these glacial lignite intercalations. For this reason a more detailed characterization of the lignites is desired.

Table 5: Contents of REE and other metal elements in drill core sediments from boreholes Gohy 573 and Gohy 2227. Elemental concentration by NAA in [mg kg^{-1}]

Sample,Gohy:	573-1	573-2	573-3	2227-1	2227-2	2227-3
Depth [m]:	135.5-136.0	136.0-136.5	136.5-137.0	129.6-130.0	130.0-130.5	130.5-131.2
Lithology :	quartz-sand	quartz-sand	lignite	sand/marl	sand, (marl)	lignite
La	2.39	7.62	22.0	13.5	10.9	8.20
Ce	5.91	6.32	50.0	78	23	19
Nd	3.50	7.30	30.0	n.d.	12.0	12.0
Sm	0.38	0.45	5.05	2.31	1.81	2.90
Yb	0.24	0.25	3.20	1.21	0.88	7.62
Lu	0.03	0.04	0.40	0.16	0.11	0.34
As	0.89	0.78	6.30	10.6	5.53	6.57
Co	0.76	1.09	10.0	19.4	9.90	2.29
Hf	1.00	1.03	10.2	3.10	2.20	0.99
Th	0.80	0.86	6.92	4.30	3.40	1.60
U	0.29	0.38	2.80	1.41	1.20	0.57
W	0.90	0.72	40.0	169	169	1.22

2.4 Colloid size distribution and population quantification

The particle counting made by PCS technique at AEA for the unfiltered groundwaters of boreholes Gohy 573 and Gohy 2227 indicates that the particle populations are different within these two samples. Quantification of colloidal particles in various filter fractions are being further determined by the more sensitive PALS technique at TUM and the results will be reported later.

2.5 Isotope studies

Determination of the isotopes ^{2}H, ^{3}H, ^{13}C, ^{14}C and ^{18}O are in progress at GSF. The following are first results on groundwater and DIC (dissolved inorganic carbon). Measurements on DOC (dissolved organic carbon) have to be confirmed by repeating the sample preparation and subsequent isotope determination in parallel at two laboratories (GSF and AEA). Emphasis will be given to the very careful preparation and sample treatment under controlled conditions to avoid any contamination. For this purpose TUM will provide a glove box with pure argon atmosphere.

The ^{3}H results obtained so far at GSF are expressed as TU (Tritium Unit). 1 TU corresponds to a $^{3}H/H$ ratio of 10^{-18} or to an activity concentration of 0.118 Bq/kg water. ^{2}H and ^{18}O results are given as ‰ deviations (δ-values) versus SMOW (Standard Mean Ocean Water) with a twofold standard deviation of 1‰ and 0.15‰, respectively. The ^{13}C results are given as ‰ deviations versus PDB (Pee Dee Belemnite) standard with a twofold standard deviation of 0.4 ‰. ^{14}C contents are expressed as percent modern carbon (pmc). 100 pmc correspond to 95 % of the NBS oxalic acid standard.

The tritium (^{3}H) concentrations of all samples show not detectable or very low values with the exception of Gohy 611 (8.0 ± 0.7 TU). The tritium model age calculated at GSF according to the piston flow model is below about 40 years for the sample of groundwater Gohy 611 and above 40 - 50 years for all other samples. The aquifer from which Gohy 611 was collected is only between 18.0 - 21.4 m deep. For this reason, infiltration of surface-water into the aquifer is most likely. The detectable but very low tritium concentration of sample Gohy 572 could be interpreted either as relatively young water or as an admixture of a small amount of young water to older water.

The $^{14}C_{DIC}$ contents in the groundwater samples are low. They range between (3.7±0.8) pmc for Gohy 573 and (5.2±1.1) pmc for Gohy 572. Based on these values and after preliminary geochemical corrections by means of the computer programme PHREEQE [12] ^{14}C model ages were calculated by GSF for Gohy 572 (approx. 18,000 years), Gohy 2227 (approx. 19,000 years) and Gohy 573 (approx. 22,000 years). The calculated ages correspond to maximum ages because of possible dilution of ^{14}C in the groundwater samples (e.g. by oxydation of fossil organic matter within the aquifer) or

reduction of ^{14}C by isotope exchange processes with the aquifer matrix. In the case of mixture of groundwaters of different ages, the ^{14}C model ages are meaningless.

The $\delta^{13}C_{DIC}$ values appear normal, with one exception of Gohy 572, as expected for groundwaters which have been evolved in carbonate containing aquifers. The relatively high $\delta^{13}C_{DIC}$ value of groundwater sample Gohy 572 (- 4.1‰) is possibly the result of methanogenesis and/or carbon exchange processes in the aquifer.

The $\delta^{2}H$ and $\delta^{18}O$ values are characteristic for usual recent groundwaters in this area and are not influenced by water-rock interactions or evaporation. Because the preliminarily calculated ^{14}C model ages of the groundwaters correspond to Pleistocene age whereas the stable isotopes ^{2}H and ^{18}O show no influence of such a cold climatic period, all groundwaters are possibly of Holocene origin (younger than about 10,000 years).

The well verified data on the isotopes ^{2}H, ^{3}H, ^{13}C, ^{14}C and ^{18}O in both groundwater samples and colloid fractions may facilitate establishing the provenance of colloids in Gorleben aquifer systems.

2.6 Disequilibrium study of U/Th-decay series

^{238}U and ^{232}Th isotopes of prefiltered (1 µm) groundwaters Gohy 572, Gohy 573, Gohy 611 and Gohy 2227, colloid fractions and ultrafiltrates, which were produced in the field during the sampling campaign, were determined at AEA. Due to a failure of the in-situ ultrafiltration no confirmed data are available for this report.

3 Generation of pseudocolloids of radionuclides

The generation mechanisms of pseudocolloids are studied with the radiotracers of Am(Eu) for M(III); Pu(Th) for M(IV); Np for M(V) and U for M(VI). Experiment on generation mechanisms (ion exchange, sorption) is in progress at TUM. This study includes reversibility and kinetics of generation mechanisms as well as concurrent reactions. Emphasis is given to the partitioning of radionuclides among groundwater, colloids and sediments.

4 Transport process study by scaled column experiments

Column experiments are designed in close collaboration among all participants (TUM, AEA, GSF, Atkins). The participants agreed upon groundwater from borehole Gohy 2227 for the column experiments, because this groundwater has been well characterized during earlier work and because it contains substantial amounts of humic colloids. The

sand used for the column experiment was sampled from the sediments overlying the Gorleben salt dome and is comparable with the pleistocene quartz-sand of borehole Gohy 2227. Estimation of microstructure parameters (sediment surface, pore size distribution) of the sand is in progress at GSF. The hydraulic properties (dispersivity, flow rate etc.) of the sediment-groundwater system are characterized by GSF using ^{3}HHO and $^{82}Br^{-}$ tracer experiments before, during and after the column experiments. A pilot study is established by GSF and TUM using Eu(III) as an injected migrant in the presence and absence of $^{125/131}I$-marked humic colloids. The humic colloids will be extracted from groundwater Gohy 2227 and will be provided by TUM. This will be used for the assessment of the radionuclide migration behaviour (break-through characteristics) within a scaled sand-groundwater system in the presence of natural humic colloids.

5 Synthesis and theoretical interpretation

A comprehensive review of extant organic complexation models has been carried out by Atkins, with the objective of identifying suitable state-of-the-art codes for adoption and enhancement. Such a model should have the following capabilities:

- simulation of both cation and anion binding,
- treatment of amphoteric nature of humic substances, allowing reversibility if uptake to be considered,
- treatment organic-inorganic interaction in terms of whole system speciation,
- representation of colloid transport.

In addition, a centralised Gorleben database has been developed, containing both generic and site-specific data.

List of publications

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[2] Kim, J.I.: Actinide Colloid Generation in Groundwater, Radiochim. Acta **52/53,** 71 (1991)

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[4] Physikalisch-Technische Bundesanstalt (ed.): Grundkenntnisse über die Salzstockentstehung. PTB aktuell 5, Braunschweig (1981)

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[9] 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)

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[11] 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)

[12] Parkhurst, D.L., Thorstenson, D.C., Plummer, L.N.: PHREEQE-A Computer Program for Geochemical Calculations, U.S. Geol. Survey, Water Resources Investigations, 80 - 96 (1980)

Title: The role of colloids in the migration of elements.
Contractor: Risø National Laboratory, Denmark.
Contract N°: FI2W/0085.
Duration of contract: from 1/5 1991 to 30/6 1994
Period covered: 1/5 1991 to 31/12 1991.
Project leader: B. Skytte Jensen.

A OBJECTIVES AND SCOPE

The objectives of the present investigation is to quantify the behaviour of colloids under varying chemical conditions by means of suitable laboratory experiments. The aim is to derive thermodynamic equations, which may be used for the modelling of their fate in natural systems.

Numerous studies of selected aspects of colloid behaviour have been reported in literature. However, most of these studies are too specific to be of interest for the present study.

Colloids may be of almost any composition, their peculiar behaviour being a consequence of their large surface and the increased importance of their specific interface chemistry.

To narrow the field of interest, the study will focus on humic acids, whose importance in natural systems is well recognized.

Only one humic acid, purchased as sodium humate from Aldrich-Chemie, D-7924 Steinheim, Germany, will be studied. Despite the fact that humic acids isolated from different places deviate in composition and probably also in structure, it is expected that they exert a similar overall behaviour although not identical interaction constants.

B WORK PROGRAMME

1 To collect useful information on humic acid behaviour, which can support the present investigation.

2 To study and quantify flocculation processes induced by the addition of polyvalent cations in competition with other ions.

3 To follow the distribution of trace elements (R.E.) Between flocculate and solution. If possible the amount of cations bound to dispersed humic acids will also be determined.

4 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.

5 If the suggested model is not found satisfactory, an empirical expression describing the behaviour of the selected humic acid will be derived.

C PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Literature search is progressing with the identification of several recent and important papers on humic acid structures, properties and behaviour.
A stock solution of the selected humic acid is being characterised and a qualitative reaction pattern established.
The planning of the first experimental work, which will start immediately, is finalised.

Progress and results

1 The at present favoured model for humic acids describes them as aggregates of smaller units bound together by groups of polyvalent ions like Fe^{3+},Al^{3+},Ca^{2+} etc. The aggregates are assumed to possess poly-electrolytic properties.
A stock solution of the selected sodium humate has been dialysed for 14 days to remove impurities of neutral salts. During this process was observed the continuous leaching of coloured components, which could be the result of a depolymerisation reaction in the humate solution, a reaction which therefore could be reversible.
The pH of the dialysed stock solution is measured to 6-7.

2 It has been observed that the humate solution does not form a visible precipitate with a one molar NaCl solution, but does so in a saturated solution.
Flocculation occurs with the addition of magnesium and calcium salts, in which respect the latter is more effective.
By saturation with gypsum or calcite, the former solid with a larger solubility product provokes flocculation, whereas it could not be observed with calcite.
After isolation of the calcium induced flocculate, it could be 're-dissolved' in both pure water and in a one molar NaCl solution, which demonstrates the reversibility of the flocculation process.
A complete elemental analysis of the humate solution is in progress. The preliminary results indicate a molweight pr. functional group about 200, which corresponds well to some substituted benzoic acid. The analysis for possible soluble anionic species, which is not yet available, is crucial for the interpretation of the observed 'neutral' pH.

3 The distribution of rare earth elements between flocculate and solution (suspension ?) as a function of solution composition will be followed by ICP-MS. It has not yet been possible to find a filter which removes the dispersed colloids quantitatively, wherefore the determination of the distribution of elements between solution and dispersed matter might be impossible. The search for alternative separation methods continues.

4 Both modelling approaches are available, but their implementation awaits
5 experimental data.

Title:	The role of colloids in the transport of radionuclides in geological media
Contractors:	CIEMAT, CEA, CNRS, GSF, INFM, INTERA, Nantes University
Contract n°:	FI2W/0097
Duration of contract:	from October 1, 1991 to September 30, 1993
Period covered:	October - December 1991
Project Leader:	CEA, V. Moulin

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 (association of radionuclides with colloids) to 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*.

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 will be conducted either with model inorganic colloidal suspensions or with mineral monoliths as macroscopic surfaces of colloids. Dynamic experiments will be performed using well-defined packings of both synthetic and natural minerals (major constituents of granite, such as those found at "El Berrocal"). Moreover, a particular attention will be devoted to the *organic coatings* (in static and dynamic conditions). These studies will provide data directly usable by migration models. These models will be developed to predict colloid transport under conditions relevant to geological disposals.

This programme will be carried out in collaboration with the different partners of this contract: CIEMAT (Madrid), CEA (Fontenay-aux-Roses), CNRS (Orsay), GSF (Münich), INFM (Padova), INTERA (London), Nantes University.

B. WORK PROGRAMME

B.1. Colloid properties

B.1.1. Colloid characterization

B.1.2. Application to a site

B.2. Sorption mechanisms

B.2.1. Association of radioelements with colloids: formation of pseudocolloids; organic coating study

B.2.2. Interaction of colloids on mineral surfaces

B.3. Transport mechanisms

B.3.1. Transport experiments in geological systems

B.3.2. Transport experiments in model systems

B.3.3. Modelling

C. PROGRESS OF WORK AND RESULTS OBTAINED

State of advancement

The main emphasis of work in this period (Oct-Dec 91) has involved:

* the characterization of natural colloids present in "El Berrocal" aquifers. This has been achieved through scanning electron microscopy after concentration by ultrafiltration for the determination of composition and size distribution of colloids, and also through photon correlation spectroscopy for the colloid size distribution.

* the sorption mechanisms of cations onto fine particle suspensions (model colloidal particles such as silica and muscovite mica) and on mineral monoliths (silica, muscovite mica) as a macroscopic equivalent to particle surfaces in order to identify processes occurring between particles and cations.

* the effect of organics coatings on the transport of cations. A novel procedure has been developed to coat well-defined packing particles (silica) with humic substances.

* the identification of data needed for the modelling of colloid transport into porous media.

Progress and results

1. Colloid properties

1.3. Application to a site

The preliminary results obtained on colloids found in "El Berrocal" aquifers indicate the presence of particles with sizes ranging from 100 nm to 1000 nm, constituted of alkaline feldspars, quartz, clay minerals, Al oxi/hydroxides and organic residues /1/.

2. Sorption mechanisms

Experiments have been carried out in order to identify the mechanisms governing the formation of pseudocolloids (association of radionuclides with colloids). The sorption of uranium (VI) onto model synthetic colloids, namely silica and muscovite mica particles, has been studied by batch experiments as a function of pH and ionic strength. Parallelly, the sorption of U(VI) and Th(IV) onto mineral monoliths (silica, mica) has been investigated by RBS (Rutherford Backscattering Spectrometry). These two complementary approaches lead to compatible data and provide a better understanding of sorption processes /2/.

3. Transport mechanisms

3.2. Transport experiments in model systems

The effect of organic coatings is investigated through transport experiments with radioelements associated or not with colloids in model systems (silica packings). A procedure has been developed in order to create an organic coating (humic acids) on well-defined packing particle of silica. Affinity columns have been realized on dextran silica and on pure silica. The

procedure permits to select the functional group of the organic molecules which will be linked to the silica surface (through a covalent bonding). By this way, the role of particular chemical functions of humic acids (carboxylic, phenolic) in the transport of radiolements would be studied /3/.

The preliminary results obtained with americium on these affinity columns indicate a great influence of pH on the elution curves showing affinity differences between the speciation forms of Am and the support.

3.3. Modelling

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 /4/, 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.

List of Publications

/1/ P. GOMEZ and V. MOULIN, Study of colloidal particles present in groundwaters of "El Berrocal" (Spain), Radiochim. Acta, submitted.

/2/ G. DELLA MEA, J.C. DRAN, V. MOULIN, J.C. PETIT, J.D.F. RAMSAY and M. THEYSSIER, Scavenging properties of inorganic colloids toward heavy elements, Radiochim. Acta, in press.

/3/ A. BIORET, J. PIERI, J.P. DURAND and F. GOUDARD, Relative affinity of speciation forms of americium on humic acid columns. Anal. Biochem., submitted.

/4/ P. GRINDROD., R.C. BROWN and N.D. GEALY, Colloid migration and dispersion within saturated media: a modelling perspective, Draft, Intera Technical Report I2421-1, 1992.

Title : Study of coupling between "fractured medium" and "porous medium" flow models

Contractors: CEA/IPSN*

Contract n°: FI2W/ CT 91/0086 (SMA)

Duration : 01/08/91 - 31/07/92

Period covered: from 01/08/91 to 31/12/91

Project leader: M. GOMIT (CEA/IPSN) - MM. GOBLET, de LOPE (CIG/ENSMP)**

A- OBJECTIVES AND SCOPE

The objective of the present study is to investigate the use of the coupled model from a methodological point of view. Modelling of fractured medium in the framework of the safety analysis of a deep geological disposal for radioactive waste generally relies on two families of models :

- the Equivalent Porous Medium model relies on the assumption that properties of the fractured medium (hydraulic conductivities, porosity,...) can be averaged in a meaningful manner on rock volumes which can be regarded as small on the regional scale of interest ;
- the Discrete Fracture Model seeks to represent each fracture of the medium, or at least a statistically equivalent set of fractures, and to describe more accurately the flow in the fractures.

In the framework of contracts with the CEA/IPSN, the CIG/ENSMP, has developed and applied two numerical tools :

- the FRACAS model /1/ is a Discrete Fracture Network (DFN) model describing flow, mass transport, heat transfer and hydromechanical interrelations in a network of disk-shaped fractures (Beacher model) ;
- the TRISEC code is an Equivalent Porous Medium (EPM) model which solves in three space dimensions the equations for flow and heat transfer on a variety of finite elements.

B- WORK PROGRAMME

A numerical tool based on the connexion of the FRACAS and TRISEC models has been developed by CIG/ENSMP for CEA/IPSN. Our approach is to apply this coupled model at the scale of a real site with data as close as possible to "real life". The aim of these evaluations is to see whether a distance exists from which the DFN perturbation is no more visible, and how this distance depends on the "coupling radius".

* Commissariat à l'Energie Atomique - Institut de Protection et de Sûreté Nucléaire

** Centre d'Informatique Géologique - Ecole Nationale Supérieure des Mines de Paris

C- PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The first step has been the coupling of these models (FRACAS + TRISEC). The main problem was the transition between the randomly distributed channel exits on the coupling shell and the ordered finite element mesh.
The coupled model is tested on a representative site in three dimensions using a realistic geometry and the data available at typical sites, for example Fanay-Augères for the fracture statistics.

Progress and results

.Description of the coupled EPM-DFN model

The basic problem in connecting an DFN model to an EPM model is the transition between the random structure of the former and the ordered structure of the latter.
More precisely, a volume of a simple geometrical form will be defined inside which a DFN will be generated. The one dimensional bonds in which flow takes place intercept the external shell of the DFN zone at a number of points. The connexion consists then in equating pressure and flow rate at each side of the limit. However, since the region not modelled by a DFN model must be discretized in finite elements, the continuity conditions are more accurately written if the finite element mesh has nodes which coincide with the bond exits. The connexion problem consists therefore of three stages :
- construction of a mesh using the bond exits as basic nodes,
- formulation of the continuity equations,
- solution of a global set of equations.

The first task is accomplished by a Voronoï - Delaunay procedure, which creates a triangulation on each face of the coupling shell, with the bond exits as nodes. Since the triangulation may not be sufficiently regular for a finite element code to use it, additional nodes are automatically introduced to satisfy a user - supplied regularity criterion (see figure 1). A two-dimensional mesh of triangles is thus built on the coupling shell. This mesh serves as support for the construction of a three dimensional mesh of 6-node elements extending until the outer limit of the studied domain. The construction of this 3D - mesh is itself automatic (see figure 2).
The continuity of pressures and flow rates is then expressed on each node which is connected to a DFN bond. Additional nodes receive a zero flow condition which focusses the flux towards the "active" nodes. These continuity equations lead to an assembling procedure merging the DFN and EPM linear systems into a single global, sparse system of equations for the pressures of the finite element nodes and at the DFN nodes.
This global system is solved with a preconditioned conjugate gradient solver. The numerical tool just described has been developed during the period 1989-1991 in the framework of a contract with IPSN/DAS/SAED. It solves the equations of flow in a domain of simple geometry (parallelepiped) for classical boundary conditions. Further developments considered imply the extension of the particule tracking

technique used in the DFN model to the EPM model, to allow a characterization of flow lines and transit times.

. Main steps of the study

The normal use of this type of model would be to adopt the DFN approach in the near-field, up to a scale where the transition to EPM can be done smoothly. This implies several requirements :
- there should exist a Representative Elementary Volume (REV) of such size as to be small compared to the total modelled domain. The volume modelled with DFN should be much greater than this REV ;
- the Equivalent Porous Medium would not be homogeneous, but should reflect the heterogeneity of the DFN.
If these conditions were met, relatively smooth conditions might exist at the interface between DFN and EPM. The behaviour of DFN, while reflecting the local heterogeneity, would however be relatively independent of the size of the zone devoted to DFN (the "coupling radius").
If on the contrary, the "coupling radius" is not sufficiently large for smooth properties to emerge, either because no REV exists or because it is too large, both the behaviour of the DFN under the boundary conditions created by the EPM and the behaviour of the EPM perturbed by the DFN will depend on the "coupling radius".

. Proposed Approach

The synthetic site to be modelled will have a simple but realistic geometry, i.e. a recharge zone and natural outlets. A regional circulation will thus be created around the repository position. Data from real sites will be used for fracture statistics : presently the fracture distribution measured at Fanay-Augères is used, but the distribution of conductivities is shifted towards lower values to reflect a more realistic situation (in a repository candidate site). Large scale hydraulic conductivity is described by the same kind of distribution as was used for the PAGIS exercise for example (values obtained from the Auriat site).
A domain of varying size, centered around the repository, will be modelled by DFN. This domain is a sub-zone of a realization on a larger volume, in order to sample the same distribution.
On this structure, steady state flow is computed. Various indicators of behaviour are computed :
- flow at the outlets,
- distribution of head and flux on shells of growing radius between the coupling shell and the outermost boundary ;
- distribution of head and flux inside the DFN ;
- in a later stage, transit time from the repository to various points might be computed (this is subsequent to the development of a global particle tracking algorithm).

. Present status and further steps of the study

A mesh has been built and preliminary flow calculations done. The procedure for evaluating the model behaviour at several distances from the repository is being tested. We expect the first comparative results betwen different coupling radius to be available at the end of April 1992. An analysis of these results will permit us to decide the further orientation to be followed.

D. REFERENCES

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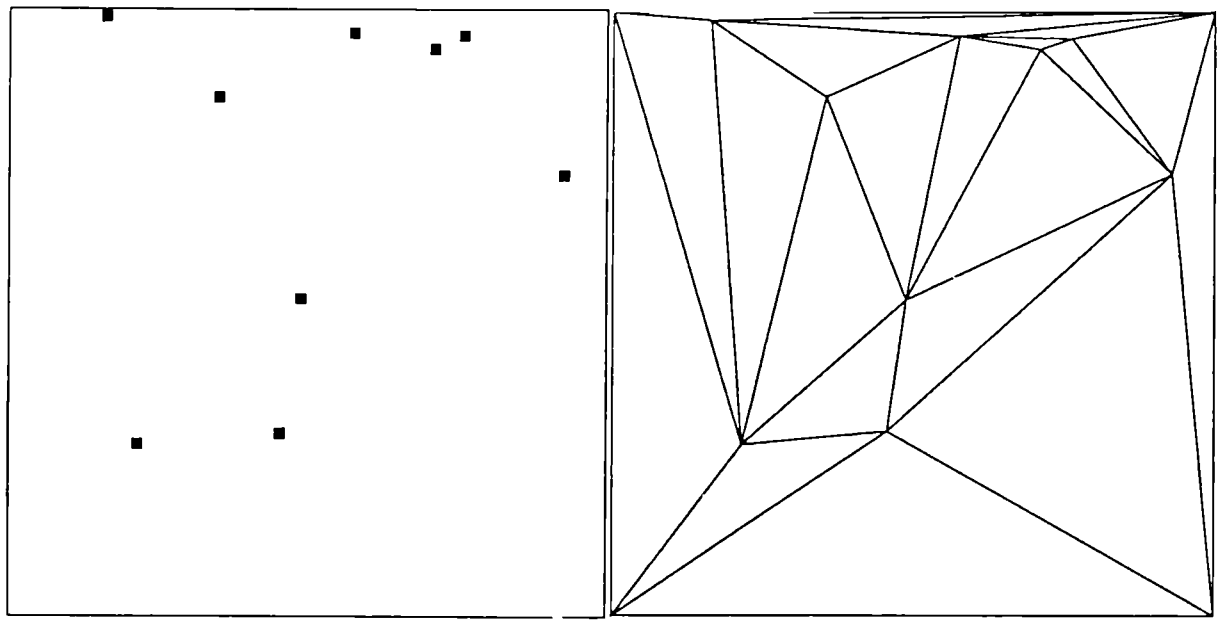
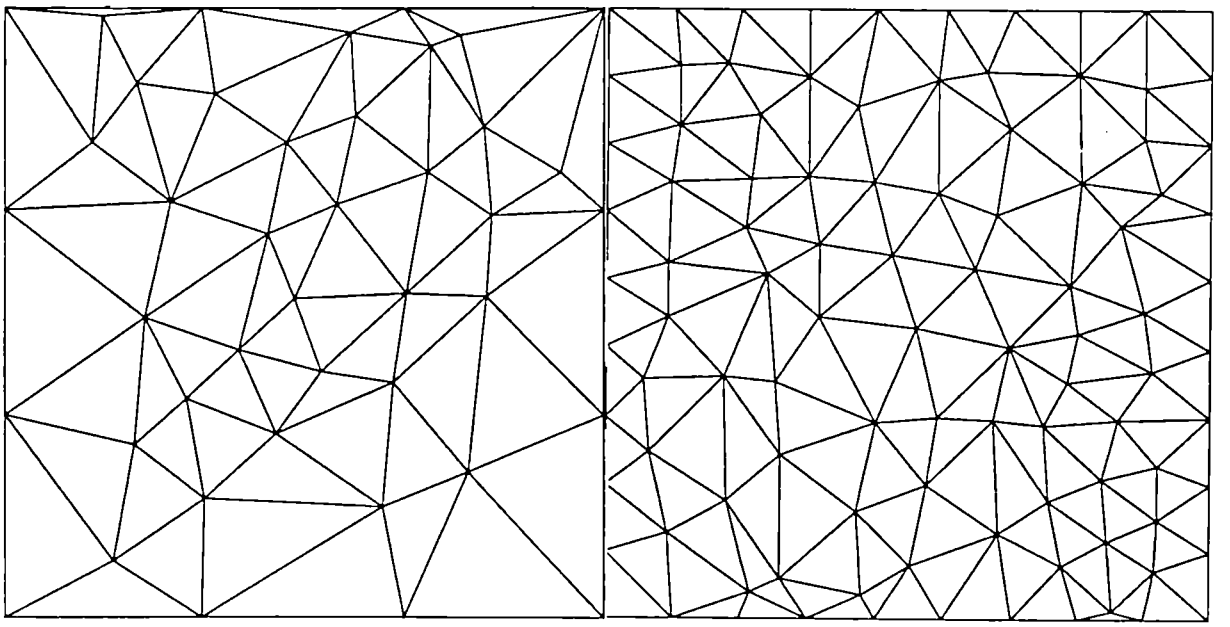


1a 1b



1c 1d

Figure 1 : Representation of face of the coupling shell showing the channel exits (1a), the raw mesh (1b) and successive refinements (1c and 1d)

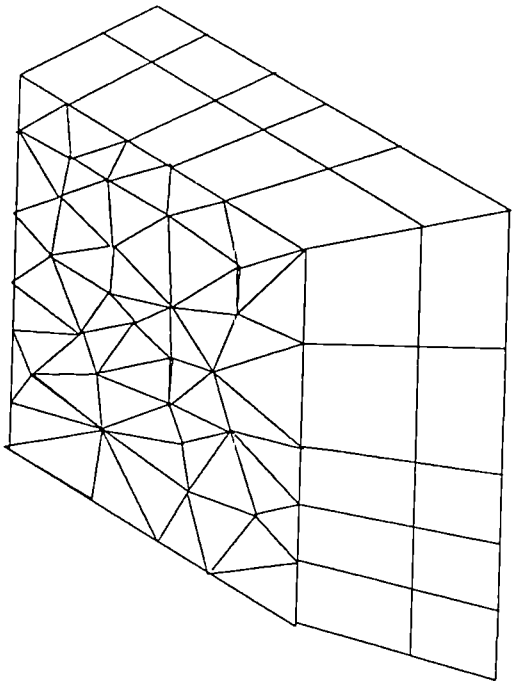


Figure 2 : Construction of a 3D mesh from a 2D triangulation

Title:	Methods of Handling Non-Homogeneities at Different Scales in Radionuclide Transport
Contractor:	Electrowatt Engineering Services (UK) Ltd
Contract No:	FI2W/0087
Duration of Contract:	1st September 1991 - 30th August 1992
Period Covered:	1st September 1991 - 31st December 1991
Project Leader:	Professor M M R Williams

A. OBJECTIVES

To develop a working set of equations to describe the transport of radionuclides in media with randomly varying material properties. To apply these equations to some well-defined geometrical situations and to highlight the deficiencies in current practice, much of which uses the classical advective-dispersion equation. To review the past work in the field. It is expected that the new equations will be applicable to practical situations in assessing the containment efficiency of waste repositories.

B. WORK PROGRAMME

1. State of advancement

2. Progress and results

    2.1 Review of past work
    2.2 A new approach to radionuclide transport

3. References

C. PROGRAMME OF WORK AND OBTAINED RESULTS

1. STATE OF ADVANCEMENT

The main advance since the start of the work programme has been the completion of a review of past papers relevant to the transport of radionuclides in fractured rock. In particular, we have examined the early work of Taylor which laid the foundations of dispersion theory and the later work of Saffman in which geometrical models of capillaries were introduced. Finally, the most recent developments in which the advection-dispersion equation has been treated as a stochastic differential equation has been assessed and reviewed. The conclusions of this work have already been issued as a formal report to the Commission.

Work has also begun on the development of a set of equations to describe radionuclide behaviour based upon a completely new approach which uses the ideas of kinetic theory and introduces a fictitious marked particle which is tracked through the random matrix. Such an approach was introduced due to the intractability of the more conventional stochastic approach and the difficulty of applying it to complex practical situations.

2. PROGRESS AND RESULTS

Progress has been made on two points: (1) the completion of the review of past work as mentioned above and (2) the development of a new approach based on the transport equation of kinetic theory.

2.1 REVIEW OF PAST WORK

In order to obtain a clear picture of the state of the art in the field of radionuclide transport and to highlight the limitations and areas where further work is needed, a comprehensive review of the theoretical background to dispersion was carried out. This commenced with the early work of Taylor [1] on diffusion by continuous movements. Using relatively simple (but at the time very novel) procedures, Taylor was able to show that the mean square distance travelled by a marked particle in a fluid in time T was of the form

$$\langle X^2 \rangle = v^2 \left\{ 2AT - 2A^2 \left(1 - e^{-T/A}\right)\right\}$$

where v is the particle velocity and A is a measure of the rate at which the motion at time T forgets its initial behaviour at T = 0. A is called the correlation time and is a fundamental parameter in stochastic processes. Taylor continues in this seminal paper to define the correlation coefficient

$$R(\xi - t) = \langle U(\xi)\ U(t) \rangle$$

of a turbulent fluid and to deduce the following remarkable result

$$D(t) = \frac{1}{2}\frac{d\langle x^2\rangle}{dt} = \langle u^2\rangle \int_o^t d\xi\ R(\xi)$$

thereby defining the diffusion coefficient D in terms of R.

Later, Taylor [2] deduced a working advection-dispersion equation for soluble matter entrained in a solvent flowing slowly through a tube. This formed the basis of the work of Aris [3].

Saffman [4, 5] introduced a theory of dispersion which regarded the medium as a random array of capillaries, then by statistical averaging and use of Taylor's ideas of correlation functions, he obtained expressions for the longitudinal and transverse dispersion coefficients. Saffman's work highlighted the importance of the molecular diffusion coefficient in bounding some otherwise infinite integrals. However, this is probably one of the unsatisfactory aspects of Saffman's work in that it is difficult to accept that molecular diffusion, which in many practical situations is a very small effect, could play such a crucial role in determining the mechanical dispersion. Nevertheless, Saffman's expressions have led to good agreement with experiment and so form a useful milestone on this difficult journey.

Mention should also be made of a contribution by Brenner [6] on dispersion resulting from flow through spatially periodic porous media. Brenner bases his approach on the general ideas of Taylor and Aris. However, he notes that since porous media are often modelled geometrically by so-called capillary models of the interstitial space, it may be expected that the Taylor-Aris theory would play a central part in correlating experimental observation of dispersion in porous media. In general, this turns out not to be the case and most theories of dispersion in such media tend to be less rigorous and employ a priori, indeed ad hoc, random walk or mixing cell assumptions to a marked particle, rather than a fundamental application of the advective-dispersion equation at the local level within the interstitial fluid. Brenner then develops his theory assuming that the medium is spatially periodic since he believes that we should not confuse complexity with randomness. He also notes that microscopic examination of porous media indicates a periodic nature. The outcome of Brenner's work, which is extremely complicated, leads to an expression for the dispersion coefficient in terms of the structure of the medium and the solution of an intra-cell boundary value problem.

Brenner also gives some persuasive arguments as to why the molecular diffusivity plays an important role in dispersion analysis.

The final part of our review paper covers the more recent work of stochastic differential equations. In this theory, the classical advection-dispersion equation is taken to represent the radionuclide transport. However, the parameters within that equation are regarded as being random in nature. Thus, for example, in the work of Gelhar et al. [7], the equation is written

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x}(uc) = \frac{\partial}{\partial x}\left(D_L \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial z}\left(D_T \frac{\partial c}{\partial z}\right)$$

This describes net motion in the x-direction but with some dispersion in the x and z-directions. Such a situation can arise in a statistical medium. Now generally, it may be assumed that $D_L = \alpha_L U$ and $D_T = \alpha_T U$, where α_L and α_T are the dispersivities or dispersion lengths.

Since U depends on the hydraulic conductivity k, which in turn depends upon the random interstitial geometry of the medium, we may regard U as spatially random i.e. $U = U(z)$ is a random function of the transverse direction z. It may also be a function of x, but in a stratified medium the dominant variation will be on z. Thus the transport equation becomes a stochastic differential one. Gelhar et al. apply perturbation theory to solve the equation and after some effort show that, for long times, the mean concentration C obeys an equation of the following form

$$\frac{\partial \bar{c}}{\partial t} + \bar{u}\frac{\partial \bar{c}}{\partial x} = \left(A(t) + \bar{\alpha}_L\right)\frac{\partial \bar{c}}{\partial x^2}$$

where A(t) is a term that depends on the correlation function of the hydraulic conductivity. The important point is that the equation is of the classical advective-dispersive type but with a time dependent dispersion coefficient. This result goes some way to explaining the scale-dependent behaviour of the dispersion coefficient that has been noted by experimentalists.

The review discusses further papers dealing with stochastic advective-dispersion equations all of which lead in general terms to the same conclusion as Gelhar et al.

2.2 A NEW APPROACH TO RADIONUCLIDE TRANSPORT

In order to avoid the complications inherent in the stochastic procedure described above, we have devised a new approach based on the kinetic theory and in particular by analogy with neutron transport. An angular concentration $C(\underline{r}, \Omega, t)$ is introduced which is the concentration of marked particles in a given direction Ω, with Ω defined by the orientation of cracks and fissures in the rock.

Using arguments from neutron transport [8], we can deduce the following equation for C

$$\left[\frac{\partial}{\partial t} + v\,\underline{\Omega}\,.\,\nabla + v\,\Sigma\,(\Omega) + \lambda\right] C(\underline{r},\Omega,t) =$$
$$f(\Omega) \int d\Omega'\; v\Sigma\;(\Omega')\; C(\underline{r},\,\Omega',t) \;+\; S(\underline{r},\Omega,t)$$

Physically, this equation describes the motion of a marked particle within the rock matrix. We assume that it travels unhindered in a direction Ω for a mean distance $1/\Sigma(\Omega)$ and then encounters a branching point where the crack subdivides into several different directions. The probability that the particle will move in a new direction Ω is given by $f(\Omega)$. The distributions $\Sigma(\Omega)$ and $f(\Omega)$ are given by the rock geometry.

Calculations with this equation show that it reduces to the classical advective-dispersion equation under certain limiting conditions and leads to explicit expressions for the dispersion coefficient and the mean flow velocity in terms of averages over Σ and f. Work is currently in progress to obtain numerical and analytical solutions of this new transport equation.

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THE TREATMENT OF UNCERTAINTY IN GROUNDWATER FLOW AND TRANSPORT MODELLING

Contractor:	AEA Decommissioning & Radwaste, Harwell Laboratory, UK
Contract No:	FI2W / 0088
Duration of Contract:	1 April 1991 to 31 March 1995
Period Covered:	1 April 1991 to 31 December 1991
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 an important role 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 is 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 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 which 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 the 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

State of Advancement

Task 1.1: Mathematical models which can be used to represent a site have been reviewed. Of these, Indicator methods appeared the most promising and are being investigated further. The basic idea of the approach (for the simple case of a sand / clay formation) is to define an Indicator Random Function I(x) such that, I(x) = 1 for x in sand, I(x) = 0 for x in clay. Various statistical properties of I, can then be considered. One of these, the variogram, contains information about the correlation structure of I(x) and so about, say, the connectivity of the clay features. Many of the techniques of geostatistics can then be applied to qualitative information such as 'rock type', which is more likely to be available. The Gorleben site has been identified as suitable for testing this method. Although this data set is not generally available the Gesellschaft für Reaktorsicherheit (GRS) have agreed to supply the data. Initial test calculations to investigate the usefulness of the proposed method have begun. Much of the work which has been performed to date has consisted of setting up initial test versions of the required software.

Task 2.1: Methods for the treatment of uncertainty have been reviewed. Methods based on an adjoint sensitivity analysis have been selected for more detailed investigation. This approach will be coded into the AEA Technology groundwater flow code NAMMU.

Progress and Results

Task 1 - Site Characterisation (subtask 1.1)

Choice of method: An initial review of methods which can be used to represent a site in a numerical model was carried out. Approaches such as Boolean models, fractal models and various types of 'numerical rock' model were considered. The aim was to choose the most promising method for further investigation. Ideally, the chosen method should enable both qualitative and quantitative data to be used, should allow conditioned parameter fields to be generated, should give a natural framework for the treatment of uncertainty and should allow a natural description of the connectivity of geological units. Most methods satisfy some of the criteria listed above. However, Indicator methods appear to satisfy all of them. This approach was therefore adopted for further investigation.

Indicator methods have been used for several years in mining studies and are finding increasing application in the water resources and petroleum industries /1,2,3/. The basic idea

of the approach can be illustrated by the example of the Binary Indicator case. Consider a sand / clay formation. Define an Indicator Random Function I(x) such that

$$I(x) = 1 , \quad \text{for x in sand,} \quad I(x) = 0 , \quad \text{for x in clay.}$$

Various statistical properties of I, such as the mean and variance can be considered. In particular an Indicator variogram

$$\gamma(h) = E \{ (I(x+h) - I(x))^2 \} ,$$

can be defined. Where E{ } indicates expected value. $\gamma(h)$ contains information about the correlation structure of the random function and so in this case about, say, the connectivity of clay features. Using this statistical framework makes it possible to apply many of the methods of analysis used in geostatistics. However unlike 'standard' geostatistics the Indicator approach allows these methods to be applied to qualitative information such as 'rock type', which is more likely to be available at a site. It would be possible, for example, to use the techniques of Kriging to carry out stratigraphic interpolation (i.e. construct geological cross sections).

Choice of Site: It was then necessary to select a suitable test case for the method, preferably using data from a real site so that the work is more relevant to real assessments and would give a more immediate indication of the usefulness of the approach. Several site data sets were considered. The Gorleben site, which consists of a sedimentary sequence overlying a salt dome, was identified as suitable for use in this project, in part because the data set contains a considerable amount of lithological information. Although this data set is not generally available in the public domain the Gesellschaft für Reaktorsicherheit (GRS), Cologne, with whom AEA Decommissioning & Radwaste have had a good working relationship for many years, have agreed to supply the Gorleben data set for use in this project. GRS have access to the data because of their participation in the INTRAVAL project and simply require that the results of the calculations be reported to the INTRAVAL Gorleben working group.

Initial Tests: Initial test calculations were then carried out to investigate the usefulness of the proposed method. These calculations are at a preliminary stage. Much of the work which has been performed to date has consisted of setting up initial test versions of the required software. In particular, a simple code has been written to transform the petrographic data for the site, supplied by GRS in electronic form, into a form suitable for use in a variogram

estimation code. It would be expected that Indicator variograms would be anisotropic, reflecting the anisotropy of the geological structure, and so a variogram estimation code has been written which allows for this. Experimental Indicator variograms have been computed (Figures 1 and 2). It can be seen that the vertical variogram shows a clear correlation structure in the data set, whereas the horizontal variogram is quite 'noisy'. Further investigation of the effect of the choice of parameters in the variogram estimation procedure is being carried out. An initial version of a code to carry out Indicator Kriging has been written and is currently being tested.

Task 2: Treatment of Uncertainty (subtask 2.1)

The aim of this task is to investigate methods for the treatment of uncertainty in groundwater flow and solute transport calculations. The initial stages of this work involved surveying the literature and reviewing available approaches. Particular attention was paid to novel approaches (e.g. /4,5/) and their usefulness for assessment type calculations. Methods based on an adjoint sensitivity analysis have been selected for more detailed investigations. This approach will be coded into the AEA Decommissioning and Radwaste groundwater flow code NAMMU.

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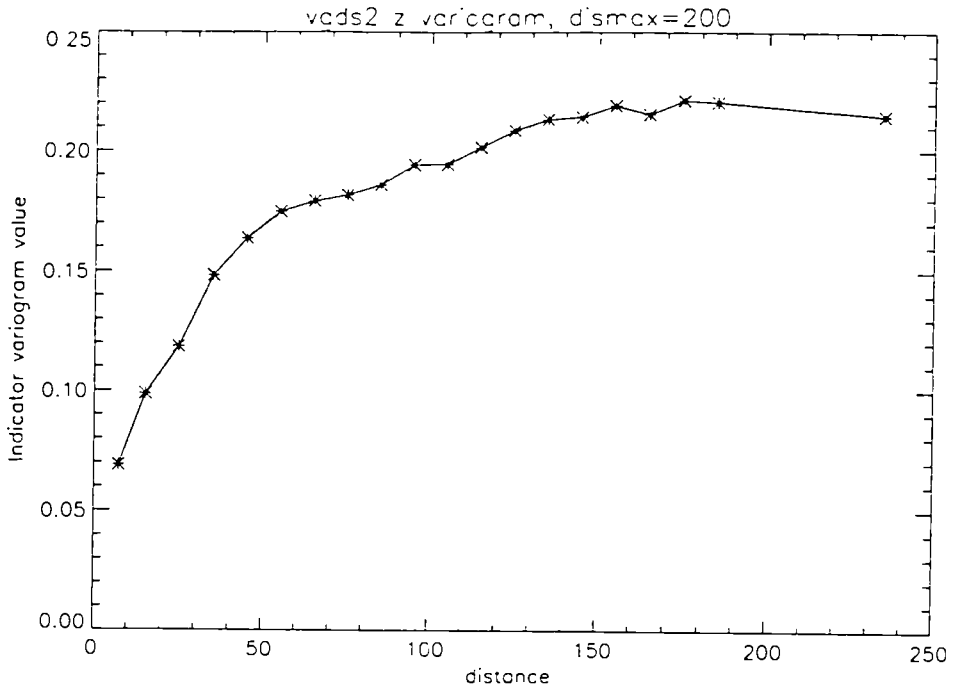


Figure 1: Indicator variogram in the vertical direction, calculated from the Gorleben site data.

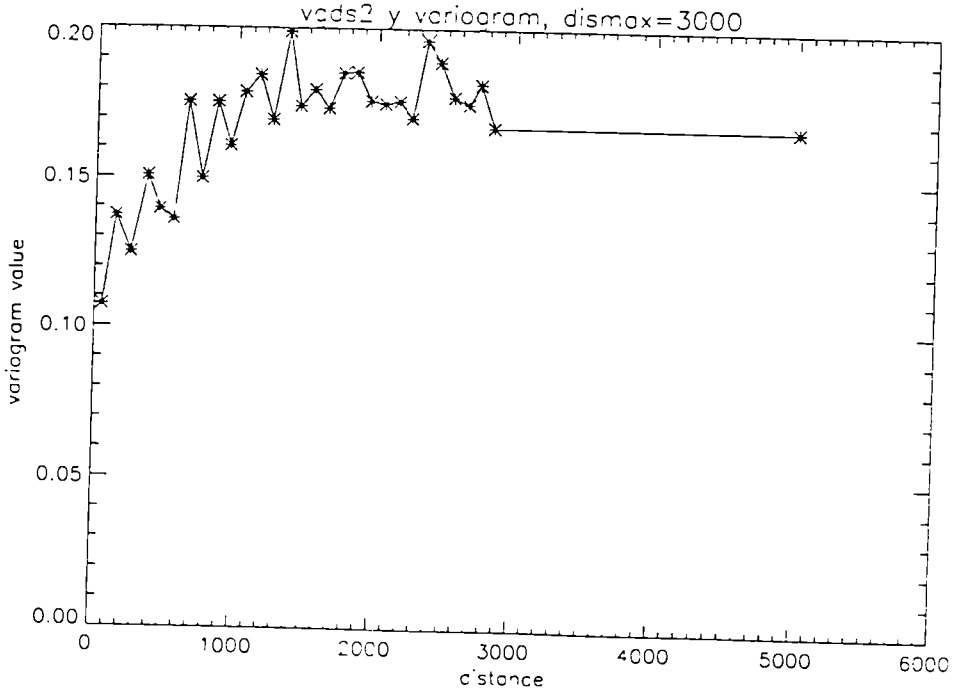


Figure 2: Indicator variogram in the horizontal direction, calculated from the Gorleben site data.

Title: Uncertainties in the modelling of migration.
Contractor: Risø National Laboratory, Denmark.
Contract N°: FI2W/0089.
Duration of contract: from 1/9 1991 to 1/9 1994.
Period covered: 1/9 1991 to 31/12 1991.
Project leader: B. Skytte Jensen.

A. OBJECTIVES AND SCOPE

The objectives of the present investigation is to estimate the uncertainties to be ascribed to the results of modelling calculations of diffusion and convection calculations. Especially the uncertainties which are the consequences of the possible presence of unidentified heterogeneities in a given formation will be considered. Numerous other sources add up to the final uncertainty, like poorly understood and characterised geochemistry, but contrary to the first type of uncertainties, such problems may in principle be solved by intensive and well planned laboratory experiments.

Several related attempts aiming at decribing the dispersion to be expected, when migration proceed through a complex of fissures, have been reported, although measures of the expected uncertainties have not been explicitly stated.

Only recently has attention been paid to the uncertainties to be ascribed to migration modelling, wherefore the relevant tools have not been firmly established yet. Several approaches are possible mostly related to experimental work in the field or the lab. In the present investigation, computer-experiments alone will be used as the tool.

B. WORK PROGRAMME

1 To develop an algorithm which will be used for creating two- and three dimensional 'synthetic' geological formations with inhomogeneities whose positions are selected at random.

2 To develop a mass-conserving algorithm which can handle diffusion in heterogeneous media in both two- and three dimensions.

3 To develop methods for analysing for the variability in migration lengths and effective diffusion coefficients etc.

4 The effect of inhomogeneities on dispersion in two-dimensional plugged flows will be illustrated by means of conformal mapping.

5 Networks, in which the permeabilities of paths are randomly generated, will similarly serve as a model for three-dimensional migration in fissures, and a program will be developed which can handle network flows, solve for potentials, fluxes, particle migration lengths and plugged flow dispersion.

6 The calculated results will be compared with experiences from field and lab work.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

No-flow systems.

The main efforts made during the reference year have been the development of programs to create 'formations' with randomly positioned inhomogeneities in two- and three dimensions. Methods for determining effective porosities have been developed.

Similarly a program for calculating three-dimensional diffusion in the above 'formations', where diffusion coefficients vary with position, has been developed and used. It has been found, that only three-dimensional calculations are realistic approximations to lab and field experiments.

Flow-systems.

Methods for visualising plugged-flow dispersions in two-dimensional systems with inhomogeneities have been developed.

A network model in which permeabilities of path sections are randomly generated is being developed for estimating uncertainties and dispersion effects due to convection in fissured formations. Preliminary calculations have indicated the usefulness of model.

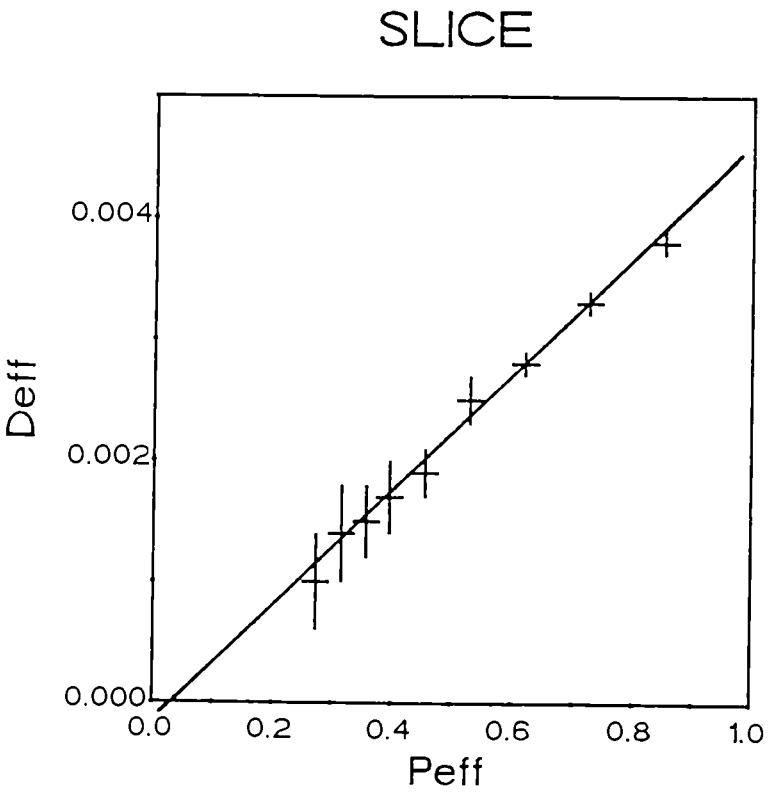
Progress and results

1 The algorithm for positioning inhomogeneities in two- and three-dimensional arrays was easily accomplished. By scanning the resulting arrays the effective porosity could be determined. As expected would several positions coincide with increasing numbers of obstacles, and random clustering would also occur generating variations in sizes of inhomogeneities, as would be expected in real systems. Real systems will in most cases not be random, but display different more or less ordered structures generated by geological processes. To study these effects diffusion experiments have been done in a few ordered arrangements of the inhomogeneities.

2 A simple mass-conserving explicite finite difference algorithm for calculating diffusion in inhomogeneous media has been developed. After several hundred iterations the total amount of the diffusing species is up to 99% of the added amount, depending somewhat on the size of the iteration steps.

In calculations performed until now is demonstrated a linear relationship between the effective three-dimensional diffusion coefficient and the effective porosity of the medium. The uncertainties to be ascribed to the mean effective diffusion coefficients increase rapidly with decreasing porosities, see fig. 1.
In this presentation the 'sampling technique' is made similar to an often used slicing method used with laboratory columns.
With other 'sampling techniques' simulating elution, pumping, scanning etc., the results may be, that the mean effective diffusion coefficients do not deviate drastically from the data in fig. 1, but the uncertainties might well be appreciably larger.

Fig.1.



In the case of two-dimensional diffusion the mean effective diffusion coefficient show a larger decrease with a decrease in the effective porosity, approaching zero at porosities around 0.3.

In the one-dimensional case it is obvious, that a single non permeable inhomogeneity will completely block for any diffusion beyond its position.

4 By means of conformal mapping it is possible to illustrate two-dimensional flow around corners, obstacles etc. as well as the associated convective dispersion phenomena. A few examples will be shown, which demonstrate possible implications for real three-dimensional flows.

5 Networks, in which the permeabilities of local paths are randomly generated, will serve as a model for a three-dimensional migration in fissured structures. Based on its analogy with electrical circuits, a program will be developed, which can handle network flows, solve for potentials, fluxes, particle migration lengths and velocities ultimately allowing for an estimate of convective flow dispersions. Preliminary modelling exercises have shown it to be feasible.

6 Finally the implications of the calculations in relation to lab and field investigations will be discussed.

Title :	Unbiased Guess, a Concept to Cope with Fuzzy and Random Parameters
Contractor :	BRENK SYSTEMPLANUNG
Contract N° :	FI2W-CT91-0090
Duration of contract :	from 01.06.1991 to 30.09.1994
Period covered :	from 01.06.1991 to 31.12.1991
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 first part of our work we have compiled the principle drawbacks using probability or fuzzy theory in risk analysis and decision making dealing with the transport of radionuclides from a radioactive waste repository. Furthermore, we started our investigations how information theory may help to overcome some of these difficulties.
We state the four principle difficulties in handling uncertain knowledge :

- Identification of the kind of characterization of the decision-relevant quantities (i.e. dose) which the decision maker really wants to know (probability, possibility or something else) and definition of adequate characterizing functions;
- Interpretation of the values of the characterizing functions (what does a possibility of 0.83 mean ?);
- Development of a mathematical formalism to handle these characterizing functions;
- Development of an unambiguous formalism to derive the characterizing functions (pdf's, basic assignments) of the parameters for a given uncertain information.

A method for the unambiguous choice of the characterizing function of the parameters seems to be a generalized Maximum Entropy Method, the Method of Unbiased Guess. Some measures of uncertainty are compiled, whose maximisation or minimisation may lead to a useful strategy in defining the characterizing functions.

Progress and results

Uncertainties in risk analysis dealing with the transport of radionuclides from a radioactive waste repository arise from the uncertainty about the relevant processes (⇒ equations), uncertainty of the material properties (⇒ parameter) and uncertainty about the initial and boundary conditions. The usual way of describing these uncertainties is the use of pdf's (probability density functions). However, the application of this strategy to transport phenomena at a specific site may become somewhat doubtfully when using it to transfer knowledge from one site to another. Probability is defined as the relative frequency, that a randomly chosen event will be part of a well-defined set. In the case of a radioactive waste repository the meaning of this quantity is limited, because firstly one has only one choice (so the relative frequency may not be an appropriative quantity), and, secondly, the sets are not well-defined.
Another well-defined characterizing function is the (crisp) possibility of the occurrence of a special value for the decision-relevant quantity. This characterizing function is, like the probability, principly measurable and therefore

objective. In practice, however, the possible values for the decision-relevant quantity normally cover a wide range due to the necessarily conservative estimations of the possible range for each of the parameters, so that they are not very useful.
One way to overcome this difficulty is the introduction of fuzzy ranges for the values of the parameters. In these fuzzy ranges the possibility of the parameter values are not known. As a result, the possibility distribution of the decision-relevant quantity has a sharper shape. Another way is the introduction of new characterizing functions such as "degree of relevance" or "degree of conservativity". The problem in both cases is, that the occurring characterizing functions can not be measured in nature, so that their interpretations are subjective (What does a possibility of 0.83 or a degree of conservativity of 0.5 mean?).
A formal language that allows the introduction of such descriptions is the fuzzy theory. But the discussion above shows, that at the point, where fuzzy theory shows practical advantages, the subjectivity starts. But at this place it should be realized, that the apparently objective description in terms of probability are actually subjective as well. When an expert uses values of some parameter to estimate a distribution function, this function may be called a "pdf", but it isn't in the sense of the definition at a (measurable) relative frequency. In reality this distribution function is somewhat like a "degree of evidence" of a special value to occur. For this reason we believe, that at a given state of uncertain knowledge, the introduction of fuzzy theory does not necessarily mean the introduction of additional subjectivity compared to handling the uncertainty in terms of probabilities, because the application of statistical methods to nonstatistical uncertainties is subjective itself.
From the above we state the four principle difficulties in handling uncertain knowledge :

1. Identification of the kind of characterization of the decision-relevant quantities (i.e. dose) the decision maker really wants to know (probability, possibility or something else) and definition of adequate characterizing functions;
2. Interpretation of the values of the characterizing functions (what does a possibility of 0.83 mean ?);
3. Development of a mathematical formalism to handle these characterizing functions;
4. Development of a unambiguous formalism to derive the characterizing functions (pdf's, basic assignments) of the parameters for a given uncertain information.

The first two points are subjective and have to be done by the user of the formalism.
The mathematical formalism to handle uncertain information (point 3) can be constructed by using fuzzy theory. A very interesting approach in combining fuzzy quantities with classical probability is the method of basic probability assignments (short: basic assignments). P(X) denotes the set of all subsets of a basic set X. For $A \epsilon P(X)$ the basic assignment m(A) can be viewed as the degree of evidence of a given information indicating that a unknown event may be part of the set A :

$$m: P(X) \rightarrow [0,1] \;\; ; \;\; m(\varnothing) = 0 \;\; ; \;\; \sum_{A \epsilon P(X)} m(A) = 1$$

Are all of the available informations related to single elements x_i of X ($x_i \epsilon X$), then the basic assignments can be viewed as a (classical) pdf :

$$m(A) = 0 \text{ for all } A \neq \{x_i\} \;\; \Leftrightarrow \;\; m(\{x_i\}) = p(x_i)$$

Since ambiguity in the available information concerning the compilation of model parameters represents the main obstacle for a consent about the results, it seems very promising to develop an unambiguous formalism to derive the characterizing functions (pdf's, basic assignments) of the parameters (point 4).

A method successfully used in classical probabilistics is the Maximum Entropy Method : Given a set of restrictions (= informations) for a unknown pdf. Chose from the set of all pdf's fulfilling the given restrictions that pdf with the maximum Shannon Entropy I(p) :

$$I(p) = - \sum_{x \epsilon X} p(x) \log_2 p(x)$$

This method of choosing the "most likely" pdf can not be proofed, but it has been applied with overwhelming success to many fields, such as physics, medicine and economics.
We propose the generalisation of that method to fuzzy theory. This method can't deliver an objective interpretation of fuzzy theory, but it may be used as an unambiguous formalism to convert unspecific information to former defined basic assignments. Appropriate measures of uncertainty to be maximized may be the following:

measure of "Dissonance in evidence" E(m) with

$$E(m) = - \sum_{A \epsilon P(X)} m(A) \log_2 Pl(A) \;\; ; \;\; Pl(A) = \sum_{A \cap B \neq \varnothing} m(B)$$

measure of "Confusion in evidence" C(m) with

$$C(m) = - \sum_{A \epsilon P(X)} m(A) \log_2 Bel(A) \;\; ; \;\; Bel(A) = \sum_{B \subseteq A} m(B)$$

measure of "Nonspecifity in evidence" V(m) with

$$V(m) = - \sum_{A \epsilon P(X)} m(A) \log_2 |A| \;\; ; \;\; |A| = \sum_{x_i \epsilon A}$$

Further we propose to investigate the applicability of a generalised measure of Entropie, which can be viewed as a generalisation of the Shannon Entropy:

$$G(m) = - \sum_{A \epsilon P(X)} m(A) \log_2 m(A)$$

Review and development for modelling with uncertainty and variability

Contractor: Intera Information Technologies, Environmental Division;
University of Bristol, Information Technology Research Centre;
Université Libre de Bruxelles, IRIDIA.
Contract Number: FI2W/0091
Duration of contract: from 1 May 1991 to 30 April 1993
Period covered: 1 May 1991 to 31 December 1991
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 (ITRC).

B. Work Programme

B.1 Review

This phase consists 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 will be defined to cover the types of uncertainty and techniques identified as being most important in the first phase of the project. The aim is 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 is on recommendations for novel methodologies which could be used to address important issues. These will be based on the experience gained in the trial applications of the previous phase.

C. Progress of Work

C.1 General

During the period covered by this progress report, the project has focused on the first phase of the work programme. There has been a significant effort by the collaborators to understand each others areas of expertise. In particular, the university participants had no previous experience of radioactive waste disposal issues, and have dedicated much time to learning about the issues involved.

Each of the collaborators has completed a review of methods available which could be applied. This work is summarised in the following subsections.

From this, major areas to be addressed in the later phases have been identified and work on these has begun. The areas to be addressed are as follows:

- Fuzzy calculations. Intera will develop a demonstration code to demonstrate how fuzzy numbers can be passed through typical assessment calculations in a manner similar to probabilistic safety assessment codes.
- Scenario Analysis. Intera will develop a methodology for handling scenario generation and screening with fuzzy concepts. This will be demonstrated on a realistic site and disposal concept.
- Expert systems. ITRC and IRIDIA will develop codes which demonstrate how project information can be stored and retrieved electronically. The scope for using fuzzy concepts for the manipulation of the stored knowledge base will be examined from the separate perspectives of the two groups. Intera will act as experts, helping to capture the appropriate knowledge from a project. The recently published SKI Project-90 documentation has been identified as source for a demonstration application of this work.
- Cellular automata and fuzzy classification. ITRC will pursue the idea of using a fuzzified cellular automata to model spatial variability in transport calculations.
- Improvements to FRIL. ITRC will identify improvements required in the user-interface to the FRIL code. FRIL is a fuzzy inference language and will be used in the ITRC approach to the expert systems topic discussed above. The improvements will be made by FRIL Systems Ltd.
- Development of Pulcinella. IRIDIA will continue development of the Pulcinella code, including interfacing to expert system software. Pulcinella will be used in the IRIDIA approach to the expert systems topic discussed above.

C.2 Progress at Intera (P.C.Robinson)

A review of types of uncertainty and techniques for their treatment has been completed and is summarised below.

Uncertainty begins with regulations, although in many cases this is actually ambiguity which could be removed. Some regulations are genuinely 'fuzzy' and this could be viewed as giving an advantage in terms of flexibility and practical use for all parties. Regulations which purport to address the uncertainty issue are, unfortunately, often ambiguous, making it unclear which approach (if any) is to be preferred.

In treating uncertainties in the future evolution of a site, the scenario approach is often used. Assigning probabilities to these scenarios is difficult, but can be formalized by using a simulation approach. A new 'fuzzy' approach to Scenarios is suggested as a topic for further study.

An important type of uncertainty involves the specification of

conceptual models. Historically, there has been a tendency to focus attention on a single, 'best' description of the system to be modelled. Often, the uncertainty that is suppressed by making such a choice is reintroduced in an ad hoc fashion by widening the ranges of parameters in the chosen description. Thus conceptual model uncertainty and parameter uncertainty become confused.

In order to eliminate some alternatives, experimental work is used to validate particular models. An illustration of one difficulty in this approach is given; models which agree at small scales give divergent results when applied on a larger scale. The issue of conceptual model uncertainty is increasingly being recognized in national and international projects. The INTRAVAL project and proposed PSACOIN Level 2 exercise both address this issue.

Models used in assessment calculations are often simplified considerably from research models. Simplifications can be made by excluding processes, by reducing dimensionality, by averaging and by linearizing equations. Generally the exclusion of processes is justified on the grounds of conservatism, but whenever possible averaging is claimed to be realistic. It is pointed out that many simplifications are made so commonly that they are often not recognized as such. In a comprehensive assessment they should be recognized and justified.

The issue of risk dilution through uncertainty is addressed. It is concluded that this is an inevitable consequence of using a maximum expected dose criterion.

Uncertainty caused by numerical or coding errors has received much attention in international studies. These ensure that such errors are minimized. Data input errors are more likely to go unnoticed, and careful Quality Assurance is required to avoid them.

Approaches to uncertainty used within the radioactive waste field are discussed, as are approaches to uncertainty in other disciplines. The general conclusion is that the issue of uncertainty is recognized in many disciplines, but is tackled in a less sophisticated way than in radioactive waste disposal. Some approaches to design under uncertainty in the chemical and process industries appear applicable to repository design work.

Alternative approaches to handling uncertainties are considered. Of these, the fuzzy set concept is clearly applicable and is discussed further below. Voting theory offers a cautionary tale when trying to rank options. The use of fractals to model spatial variability is also seen as worthy of serious study. A section on performance measures shows that measures other than the maximum expected value are less prone to risk dilution.

Fuzzy Sets versus Probabilistic Approaches

Of all the novel methods and applications reviewed during the course of this study, the only contender for widespread application in the radioactive waste disposal field is fuzzy sets. We have used this term rather loosely to mean approaches based on characterizing parameter uncertainty, future evolution uncertainty and other types of uncertainty in terms of membership functions rather than probability distributions.

It must be admitted that there is not a consensus as to where fuzzy methods may be preferable to probabilistic methods. The difficulty in choosing the best method is fundamentally a philosophical one. If we put aside genuinely stochastic processes, where probability theory is clearly the correct approach, then how should ignorance, or lack of complete knowledge, be characterized and manipulated?

It is generally accepted that the starting point must be a measure of

degree-of-belief in some assertion (parameter value, conceptual model, etc.). The Bayesian probability approach then asserts that probability theory can be used to manipulate these degrees-of-belief, characterized as subjective probability distributions. Indeed, it is sometimes claimed that probability theory is the only theory that can do this correctly. Of course, this depends on which axioms one considers must be satisfied and so only moves the debate back one level.

In the fuzzy approach the degrees of belief are interpreted as membership levels for a fuzzy set, and the rules of fuzzy arithmetic are used to manipulate these. It is noted that the fuzzy combination rules used throughout this study (min and max) are not the only possible rules but are generally accepted and have been used for definiteness.

It is also noted that, as far as computational cost is concerned, there is very little difference between probabilistic and fuzzy approaches.

Thus to distinguish between the approaches it is pertinent to attempt to answer a number of simple questions:

- How are uncertainties characterized, and how should this characterization be interpreted?
- If only a range for a parameter can be defined, how is this treated?
- If an assertion can be broken down into a set of assertions, which must all hold for it to be true, how can this be dealt with?
- If alternative sets of assertions can lead to a common overall assertion, how is this handled?
- How, in practice, are the uncertainty characterizations elicited?
- Can the uncertainty characterization of irrelevant parameters influence the result?

These questions are answered in the review report. It is concluded that the fuzzy approach is practicable and a demonstration code to illustrate its application is being designed.

C.3 Progress at ITRC, Bristol (J.F.Baldwin, T.P.Martin and Y.Zhou)

The first phase of the CEC-funded MUNVAR project (modelling uncertainty and variability) includes a review of methods and tools for handling uncertainty in safety assessments. At the kick-off meeting (May 9th 1991), it was agreed that participants would analyze the PSACOIN level-E model /1/ and highlight areas where work is needed on the handling of uncertainty. We have examined the level-E model, concentrating on aspects which involve uncertainty. Various new approaches to the management of uncertainty have been proposed in research areas where the Bristol AI Group has expertise.

In conventional geosphere models, there are a number of parameters where probabilistic values are taken with apparently little or no justification. If it is necessary (say) to model the failure rate of canisters, it may be appropriate to use probability; however, factors such as retardation coefficients and base retardation coefficients seem to be using probability distributions to hide a great deal of uncertainty both in the relation of the mathematical model to reality, and in the actual parameters fed into the model from experiment (such as rock porosity). Most of the other parameters described by pdfs fall into the category of combining several sources of uncertainty into a rather arbitrarily determined pdf, whether or not the uncertainty is probabilistic in nature. This may be a case where the choice of mathematical model is governed by historical factors rather than necessarily being the most appropriate choice.

Fuzzy sets have been examined as an alternative to pdfs /2/, and have the advantage that a range of possible values is treated, with an

automatic sensitivity analysis included. Fril /3/ was used in these calculations, calling existing routines written in Fortran via the Fril foreign language interface. Further work is under way to improve the efficiency of computation involving fuzzy sets in Fril /4/, as well as enhancing the representational power of the language.

We are interested in cellular automata as a means of modelling systems that have traditionally been tackled using partial differential equations, as this may lead to easier methods of handling fuzzy parameters. We have examined a cellular automaton which solves Burgers equation, a nonlinear diffusive wave equation. The example was chosen as a simple test case to gain experience, not because of the relevance of this particular partial differential equation

In a system which is modelled accurately by a standard pde such as the diffusion equation, there may be uncertainties in the values of various parameters (eg values taken from experimental data), and in initial values and boundary conditions. It is common to treat this uncertainty using probabilistic methods, typically by defining probability distributions to represent the uncertain values. Since it is not always possible to carry probability distributions through a calculation, a method such as Monte Carlo simulation is generally used and the calculation is repeated with many combinations of values from the different probability distributions. However, it is not always clear that probabilistic methods are the most appropriate.
If the underlying source of uncertainty is not random, it may be better to use fuzzy set theory and possibility theory to model uncertain values. Several authors have proposed methods of incorporating fuzzy numbers into differential equations, although few have actually been applied to real problems. Shaw /2/ examined various methods proposed in the literature and found that none were satisfactory within the fuzzy framework, as additional assumptions were needed about the evolution of uncertainty. An alternative approach was proposed in which the differential equation is treated as a mapping from input values to output, and this mapping is fuzzified in the usual way using the extension principle. This was illustrated in a practical system by examining fuzzy diffusion, in which both the initial amount of material and the diffusion coefficient were known only fuzzily. The method is particularly suited to exactly solvable systems where the inverse of the mapping may be determined; in other cases, it is necessary to use a sampling approach which detracts somewhat from the utility of the method.

We are examining methods of incorporating fuzzy values into the cellular automaton model, concentrating initially on a system that models the diffusion equation. Several fuzzifications have been investigated, and the work is being extended to investigate flow through porous media where parameters are known only fuzzily. This is seen as a promising research area which should reinforce existing work using partial differential equations, but may lead to more efficient calculations where fuzziness is involved.

Mass Assignments

Pdfs are often elicited from experts or groups of experts by interviews, panel discussions, etc. This leads to some sort of consensus view, in which the experts knowledge is forced into a particular framework because of computational convenience, not because pdfs are necessarily the most natural way to represent the knowledge. An alternative approach to representing and computing with incomplete and uncertain knowledge is to use mass assignments, which subsume both probability and fuzzy set theory, and enable evidences to be combined and conditioned within a rigorous theoretical framework. The knowledge representation employed is similar to

that of Shafer /5/ but the combination method is not that of Shafer-Dempster, and far more reasonable results are obtained in cases where the use of Shafer-Dempster leads to problems.

A theory of evidential reasoning /6,7/ has been developed using mass assignments, which incorporates such reasoning methods as logical deduction, induction, abduction, non-monotonic inference, probability logic and fuzzy logic. Most practical problems are resolved using a combination of these methods. This theory allows incompleteness in the specification of the probability distributions required if probability theory were to be used and also unifies the fuzzy and probabilistic approaches to uncertainty. Mass assignments can be combined using meet and join operations, and updated with additional information in the form of mass assignments.

Let $\mathbf{M}$ represent all mass assignments over a frame of discernment F. $\langle \mathbf{M}, \vee, \wedge \rangle$ is an algebra with idempotence, commutativity, associativity, absorption, distributivity properties of a Boolean algebra. Full complementation properties are not satisfied. The algebra is thus a pseudo Boolean Algebra. Statements involving both fuzzy sets and probabilities can be represented in mass assignment form and used for many applications such as fuzzy and probabilistic control and databases, memory based reasoning, non-monotonic and probabilistic logic and expert systems.

Memory-based Reasoning

When an expert is consulted on the value of a particular parameter, the formulation of a best estimate is related to the experts past experience of similar situations. For example, consider an aeronautical engineer who is given a proposed design and asked to comment on some feature of it such as its stability at high speed. The experts answer will be based on a considerable amount of background knowledge including the (known) behaviour of a number of objects under wind tunnel testing, under actual flight testing, and under computer simulation. By reasoning with heuristic fuzzy rules such as

> ' object 1 showed property X under conditions Y and Z; the new design is fairly similar to object 1 in certain relevant aspects, and will therefore react in a similar way',

the expert performs a very complex interpolation procedure involving comparisons of the new design to known designs, and is therefore able to reach an estimate. This process clearly involves a great deal of uncertainty and a step in the direction of automating this complex interpolation is under investigation. In its most basic form, a query is answered by reference to similar cases in a data base. For example, if the query is concerned with the classification of an object with known feature values, then objects are found in the database which have similar feature values to that of the given object.
The classification of the given object is then determined by reference to the classification of the chosen examples. For more general queries of a more complicated form than simple classification, a transformation is necessary to view the answering of the query as a comparison with points in a vector space. This approach shares many properties of general behaviour to that of neural nets. Both approaches are robust to noisy data, can fill in for missing information etc.

We are concerned with classification and pattern recognition queries. The general approach to case based reasoning is to fuzzify the data for each of the examples to provide a means of generalization of the data provided and hence allow an interpolative method of answering the query. This fuzzification is done by introducing a set of labels for each feature space. A feature value which can be a point value for a given example is then expressed as a fuzzy set over these labels. The labels themselves can

be fuzzy sets on the feature space.

Overall Control

Many of the proposed areas of research represent extensions of the Fril system or have already been implemented within Fril as parts of other research programmes. Fril is a logic programming language with a built-in mechanism for handling many different types of uncertainty. It combines a dialect of the complete Prolog language with a support logic reasoning mechanism, for representation and reasoning with uncertainty in a logic programming environment. This generalisation of logic programming includes probabilistic reasoning using support pairs and approximate matching of fuzzy concepts by semantic unification.

The inference rule for support logic reasoning is based on a natural generalisation of the theorem of total probability. Evidences obtained from different viewpoints can be combined together to focus the inference, and provide feedback for the reasoning process. The support logic calculus characterises laws for negation, conjunction and disjunction along a particular proof path, and combination laws for multiple evidences from different proof paths. Additionally, the rule-based approach of Fril allows straightforward representation of declarative knowledge with uncertainties expressed using the support logic formalism, whilst also allowing procedural code to be written.

FRIL has been used to model a very broad range of applications in artificial intelligence, with particular emphasis on knowledge engineering or expert systems. Fuzzy sets and fuzzy arithmetic can be carried out in Fril, as discussed by . The Fril system is extendible and extra code written in any conventional language such as C, Fortran, Pascal, etc can be incorporated into the system and accessed as an integral part of Fril. In addition, various modules are available within Fril to aid in program development and in modelling of other forms of uncertainty such as mass assignments, The language thus forms a natural choice as the overall manager of an integrated package involving modules implementing the ideas discussed above.

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C.4 Progress at IRIDIA, Bruxelles (V.Poznanski and P.Smets)

Initially, a thorough survey was made of the existing methods for eliciting and subsequently inferencing with expert opinions within PSA. The chief finding of this survey was that, with the exception of the work already performed by Bristol, only conventional probabilistic means for

safety assessment have been used successfully.

Also, nonstandard methods for handling uncertainty were examined, with a special emphasis on the particular specialities of IRIDIA concerning the transferable belief model (TBM). Various ways of eliciting and applying belief function theory were examined.

Another area examined in detail was the possibility of applying AI techniques to the PSA domain. Expert systems, non-monotonic logic and reason maintenance systems were explored.

Consideration was then given to how existing methods of belief assessment and elicitation for probabilities could be carried over into other domains. Two promising methods have been examined. The first requires a rich source of probabilities but enables belief functions to be elicited accurately. The second is less formally adequate, but enables various different belief representations to be elicited from experts who do not necessarily have the necessary means of expressing their intuitions. This latter method uses a paired comparison model.

Belief functions were applied to problems that had been previously considered from only a probabilistic viewpoint. We concluded that the TBM is often more convenient to manipulate, and where it yields results that differ from probability theory, they can be argued to be more intuitive. A novel means of belief combination, known as the cautious Dempster rule of combination, has been considered as a means to combine non-independent expert opinions; it may even be used to detect which aspects of experts' opinions are independently obtained. Finally, we detailed a method by which expert opinions of differing reliability can be combined within the TBM; a principled means of weighting these opinions using discounting factors was explained.

Within the logical domain, it has been shown how expert system techniques, such as the employment of logical knowledge representations can be useful for representing both deep and shallow knowledge. The depth analogy refers to the degree of superficiality of the knowledge. Deep knowledge would involve detailed information about a particular domain and the world in general. Within PSA, this would include knowledge about geology, transport models, physics etc. On the other hand, shallow knowledge might provide simple representations of information within, say, a report without understanding the concepts which it described in any depth. Both shallow and deep systems can be represented using a logic supported by a deductive engine.

It has also been shown how reason maintenance technology, along with the use of quantified degrees of certainty, can be used to represent expert opinion and subsequently revise it if it proves to be inconsistent. A logical knowledge representation which allows the expression of default assumptions and quantified degrees of uncertainty has been designed. It is an extension of existing first-order logics.

Finally, we have considered how existing belief support tools can be extended to cope with the logical problems associated with expert systems. It has been considered how a logic can automatically generate the graph structures used by the MacEvidence, TresBel and Pulcinella belief support systems at IRIDIA.

We intend to represent some information available in the SKI Project 90 report as FOPC rules and build a suitable inference engine to answer queries. The resulting database will undoubtedly contain only shallow information, but can be extended in a number of ways. It should be possible to deepen the information content or add some of the AI technologies mentioned above.

Part A3

Task 5

"Method of Evaluating the Safety of Disposal Systems"

Topic 1 Complements to the previous evaluations

FI2W/0008 Global dispersion models for I-129 and C-14

FI2W/0016 Performance assessment of the geological disposal of spent fuel in a clay layer

Topic 2 Sensitivity studies

FI2W/0017 EVEREST : EValuation of Elements Responsible for the Equivalent doses associated with the final STorage of radioactive waste

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.

Global Dispersion Models for I-129 and C-14

Contractor:	National Radiological Protection Board, Chilton, UK
Contract No:	FI2W/CT90/0008
Duration of contract:	from 1 January 1991 to 31 December 1992
Period covered:	1 January 1991 to 31 December 1991
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 deliver significant collective doses to the world's population over long timescales, if released 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

Significant progress has been achieved on tasks B.1 and B.2. Work has started on task B.3. The gathering of information is a continuous process and therefore work on tasks B.1 and B.2 will continue at a lower pace, concurrent with the remaining tasks of the project. Several models for predicting the global circulation of stable carbon and carbon-14 have been identified. Some have been implemented on the NRPB computer system and comparison runs have been carried out. Available models for predicting the global circulation of iodine-129 are based upon a model developed at Oak Ridge National Laboratory (ORNL), USA. Two versions of this model have been implemented on the NRPB computer system and comparison runs have been carried out.

Progress and results

B.1 Identification and implementation of available models

Searches of bibliographic computer data bases and consultation with individuals and organisations revealed eleven models for predicting the global circulation of stable carbon and/or of carbon-14. Four models were selected for implementation on the NRPB computer system and two have been implemented in the present reporting period. The four models selected for implementation are those of Cannell and Hooper/1/, Nair/2/, NCRP/3/ and Bush *et al.*/4/. These models were chosen to reflect a range of different complexities, both in general terms and in terms of the modelling of the marine and terrestrial environments. The models of Cannell and Hooper and of Bush *et al.* have been implemented on the NRPB computer system. The models were solved using the NRPB COMA program which uses a matrix inversion method for solving systems of coupled linear first order differential equations. Predictions of stable carbon and carbon-14 distribution between the different environmental compartments were obtained for both models. The runs for stable carbon were performed using the estimated current distribution of this element. The runs for carbon-14 were performed by placing the estimated current global inventory, 9.25 10^{18} Bq, in one of the compartments of the model. In both cases the distribution up to 5 10^{5} years in the future was predicted. Results for both models were similar: for carbon-14 the final distribution was 94% in the oceans, 4% in the terrestrial compartments and 2% in the atmosphere. About the same final distribution is observed for stable carbon. The Cannell and Hooper model also incorporates a compartment representing fossil fuel reserves. Table I gives the distribution of stable carbon in this model as a function of time. It can be seen that the fossil fuel compartment empties in about 10 000 years as a result of the burning of fossil fuels. The models of Nair/2/ and NCRP/3/ are currently being implemented.

Literature searches and consultations with individuals and organisations have revealed only two available models to predict the global circulation of iodine-129. The first was developed by Kocher at Oak Ridge National Laboratory (ORNL)/5/ and subsequently revised/6,7/. The second was developed at NRPB/8/ by revising the first version of the ORNL model. Both models have been implemented on the NRPB computer system. The implementation of the ORNL model was checked by comparing the results of test cases (a 37 GBq release into the land atmosphere compartment for 1 year and for 50 years) with those published by Kocher, with good agreement being obtained. Table II gives the predicted inventories in the ORNL model compartments for the release over 1 year. It can be seen that in this case the iodine is rapidly transferred from the atmosphere to the soil and ocean mixed layer. After about 10 000 years most of the iodine is in the deep ocean and eventually, at about 1 million years after the release, most of the iodine is in the ocean sediments. Two

methods of solution for the NRPB model were compared. One using the COMA software and the other using the FACSIMILE software/9/. The latter solves the differential equations by a time-stepping technique. The results of both solution methods on test cases were in close agreement.

B.2 Review of data on important processes and parameter values

The data on important processes and parameter values have been obtained principally at the same time as information on the available global circulation models. In the case of carbon, estimates by various researchers of the inventories of stable carbon in the different parts of the environment, agree closely with each other. Estimates of fluxes are also in fairly good agreement, although there is a variation of over two orders of magnitude in the estimated fluxes between the atmosphere and the terrestrial biosphere. The most common means for calculating doses to man from carbon-14 is by assuming that the specific activity of carbon-14 in man's intake of carbon is the same as that in the environment.

As part of a general review of parameter values for the global circulation of iodine-129 the concentrations of stable iodine in different parts of the environment have been reviewed. The values obtained are generally in good agreement with each other except in areas where significant variation might be expected, for example, in river water. Information on the origin of iodine in soil is also being collated since some measurements indicate that the iodine in soil is derived from sedimentary rocks and not, as is often supposed, from the marine environment/10/.

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Table I. The distribution of stable carbon as a function of time, predicted by the model of Cannell and Hooper

Time y	Atmosphere Pg C	Ocean Pg C	Biomass Pg C	Soils Pg C	Fossil fuels Pg C
0	725	37000	560	1400	10000
0.5	726	37000	560	1400	9998
5.0	732	37020	564	1398	9984
50	741	37210	574	1411	9900
500	770	39060	597	1473	9048
5000	870	45650	675	1667	3679
50000	882	46430	684	1689	0.45
500000	882	46430	684	1689	0

1 Pg = 10^{15} g = 10^{12} kg

Table II. ORNL model. Inventories in each compartment following a release of 37 GBq (5.65 kg) of ^{129}I to the land atmosphere compartment over 1 year.

Year after start of release	Inventories (g) in compartment :				
	1	2	3	4	5
0.1	$2.5\ 10^{1}$	$2.4\ 10^{2}$	$2.7\ 10^{1}$	$2.7\ 10^{2}$	$3.8\ 10^{-4}$
1	$3.9\ 10^{1}$	$2.8\ 10^{2}$	$8.0\ 10^{2}$	$4.5\ 10^{3}$	$7.8\ 10^{-2}$
10	$3.4\ 10^{-2}$	$2.7\ 10^{-3}$	$5.5\ 10^{2}$	$4.7\ 10^{3}$	1.3
100	$2.5\ 10^{-3}$	$1.0\ 10^{-3}$	$3.8\ 10^{1}$	$4.6\ 10^{3}$	3.3
1000	$2.9\ 10^{-3}$	$8.8\ 10^{-4}$	$4.5\ 10^{1}$	$3.8\ 10^{3}$	2.7
10000	$5.3\ 10^{-3}$	$4.5\ 10^{-4}$	$8.6\ 10^{1}$	$4.7\ 10^{2}$	$3.3\ 10^{-1}$
100000	$4.7\ 10^{-3}$	$3.2\ 10^{-4}$	$7.5\ 10^{1}$	$2.3\ 10^{1}$	$1.7\ 10^{-2}$
1000000	$9.5\ 10^{-4}$	$6.6\ 10^{-5}$	$1.5\ 10^{1}$	4.7	$3.4\ 10^{-3}$
	6	7	8	9	
0.1	$4.4\ 10^{-2}$	$2.2\ 10^{-9}$	$3.6\ 10^{-4}$	$7.2\ 10^{-6}$	
1	$1.9\ 10^{1}$	$1.3\ 10^{-5}$	$7.5\ 10^{-2}$	$1.5\ 10^{-3}$	
10	$3.5\ 10^{2}$	$3.9\ 10^{-3}$	1.6	$3.1\ 10^{-2}$	
100	$9.5\ 10^{2}$	$1.6\ 10^{-1}$	$1.6\ 10^{1}$	$3.3\ 10^{-1}$	
1000	$1.7\ 10^{3}$	2.9	$9.2\ 10^{1}$	2.9	
10000	$5.0\ 10^{3}$	$8.0\ 10^{1}$	$2.1\ 10^{1}$	$1.1\ 10^{1}$	
100000	$4.5\ 10^{3}$	$1.0\ 10^{3}$	$8.2\ 10^{-1}$	1.8	
1000000	$9.1\ 10^{2}$	$4.5\ 10^{3}$	$1.7\ 10^{-1}$	$1.3\ 10^{-1}$	

Index to compartments :

1 Ocean atmosphere 2 Land atmosphere 3 Ocean mixed layer
4 Soil 5 Terrestrial biosphere 6 Deep ocean 7 Ocean sediments
8 Shallow subsurface 9 Deep subsurface

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 28 February 1994
Period covered :	from 1 March 1991 to 31 December 1991
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 (e.g. PAGIS and PACOMA), 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. Adaption 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 activities carried out in 1991 have been focused on the data collection. The radionuclide inventories of the selected spent fuel types have been calculated. The repository concept has been adapted to the spent fuel characteristics.

The methodological aspects are worked out in parallel with the corresponding EVEREST developments.

Progress and results

Detailed lists of the radionuclide inventories (Table I) and of the thermal outputs (Figure 1) of the various considered spent fuel types have been prepared.

A repository concept has been developed which allows for the placement of containers, in which four spent fuel assemblies have been packed, in the centre of disposal galleries. The thermal output from the spent fuel repository is higher and the thermal dissipation period lasts much longer than it is the case for the disposal of the high-level waste which results from the same nuclear programme. As a consequence the minimum total surface of the spent fuel repository is estimated to be about 3 km^2 for a cooling time of 50 years, whereas a surface of only 1 km^2 is needed in the case of a high-level waste repository. The considered repository concept, which consists of 10 parallel disposal galleries, is shown in Figure 2.

A review of the catalogue of features, events and processes, which has been drawn up for reprocessing waste types, has indicated that for what concerns the methodological aspects attention should be given to the near field phenomena which include here the release of radioactive gases after corrosion of the cladding material and to the extent of the thermal field which is much more influential than in the case of high-level waste disposal. Criticality problems are not expected in the case of spent fuels which have been burned up to the level they were designed for.

Table I Radionuclide inventories of the considered spent fuel types

	UOX 33 (Bq/tHM)	UOX 45 (Bq/tHM)	MOX 45 (Bq/tHM)
H-3	2.37E+13	2.95E+13	2.99E+13
C-14	2.63E+10	3.14E+10	2.42E+10
Cl-36	1.37E+06	1.90E+06	2.01E+06
Ca-41	3.37E+07	3.96E+07	2.95E+07
Co-60	2.41E+14	2.77E+14	2.30E+14
Ni-59	2.54E+11	2.53E+11	2.09E+11
Ni-63	3.35E+13	3.90E+13	2.94E+13
Se-79	1.52E+10	2.04E+10	1.94E+10
Rb-87	8.12E+05	1.06E+06	9.04E+05
Sr-90	2.52E+15	3.22E+15	2.73E+15
Zr-93	7.39E+10	9.83E+10	8.95E+10
Mo-93	1.36E+09	1.83E+09	1.68E+09
Nb-94	5.18E+10	7.11E+10	7.06E+10
Tc-99	4.86E+11	6.29E+11	6.31E+11
Pd-107	3.84E+09	5.93E+09	8.20E+09
Sn-126	2.77E+10	3.91E+10	4.35E+10
I-129	1.15E+09	1.58E+09	1.72E+09
Cs-135	1.45E+10	2.36E+10	2.95E+10
Cs-137	3.50E+15	4.70E+15	4.70E+15
Sm-147	1.37E+05	1.55E+05	1.61E+05
Sm-151	1.22E+13	1.54E+13	2.08E+13
Eu-154	2.65E+14	4.38E+14	4.84E+14
Cm-248	4.22E+03	4.58E+04	1.01E+06
Pu-244	1.11E+04	3.22E+04	1.62E+05
Cm-244	4.69E+13	1.60E+14	9.31E+14
Pu-240	1.89E+13	2.17E+13	3.73E+13
U-236	1.01E+10	1.26E+10	9.79E+09
Th-232	2.86E+00	4.07E+00	3.10E+00
U-232	6.76E+08	1.46E+09	1.51E+09
Cm-245	3.99E+09	1.79E+10	1.63E+11
Pu-241	3.61E+15	5.20E+15	7.74E+15
Am-241	2.95E+13	4.49E+13	7.46E+13
Np-237	1.16E+10	1.75E+10	1.56E+10
U-233	3.19E+05	4.82E+05	4.74E+05
Th-229	1.53E+03	6.36E+03	6.33E+03
Cm-246	7.93E+08	4.47E+09	5.04E+10
Pu-242	5.60E+10	1.04E+11	2.32E+11
Am-242m	2.49E+11	4.97E+11	1.54E+12
U-238	1.17E+10	1.16E+10	1.15E+10
Pu-238	8.27E+13	1.69E+14	3.10E+14
U-234	1.31E+09	2.62E+09	5.34E+09
Th-230	3.41E+04	6.80E+04	1.55E+05
Ra-226	2.95E+01	6.08E+01	1.54E+02
Cm-247	2.01E+03	1.59E+04	2.74E+05
Am-243	5.19E+11	1.23E+12	4.37E+12
Pu-239	1.15E+13	1.33E+13	1.75E+13
U-235	7.51E+08	6.23E+08	7.14E+08
Pa-231	1.06E+05	1.00E+05	1.18E+05

(UOX : uranium oxide fuel; MOX : mixed oxide fuel;
33 : burn up equal to 33 GWd/tHM)

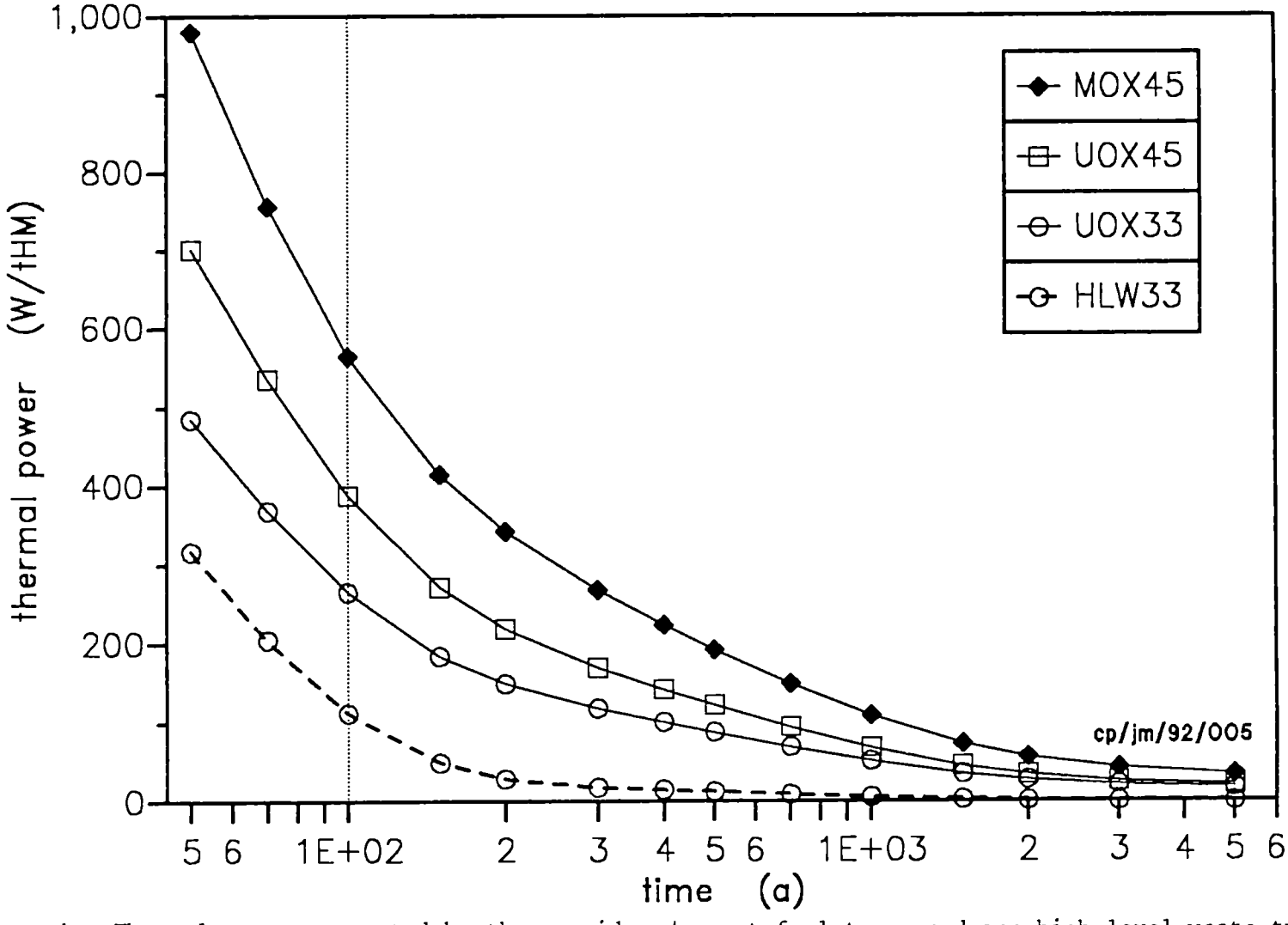

Figure 1 : Thermal power generated by the considered spent fuel types and one high-level waste type (MOX : mixed oxide fuel; UOX : uranium oxide fuel; HLW : high-level waste which results from the reprocessing of uranium oxide fuel; 33 : burn up equal to 33 GWd/tHM)

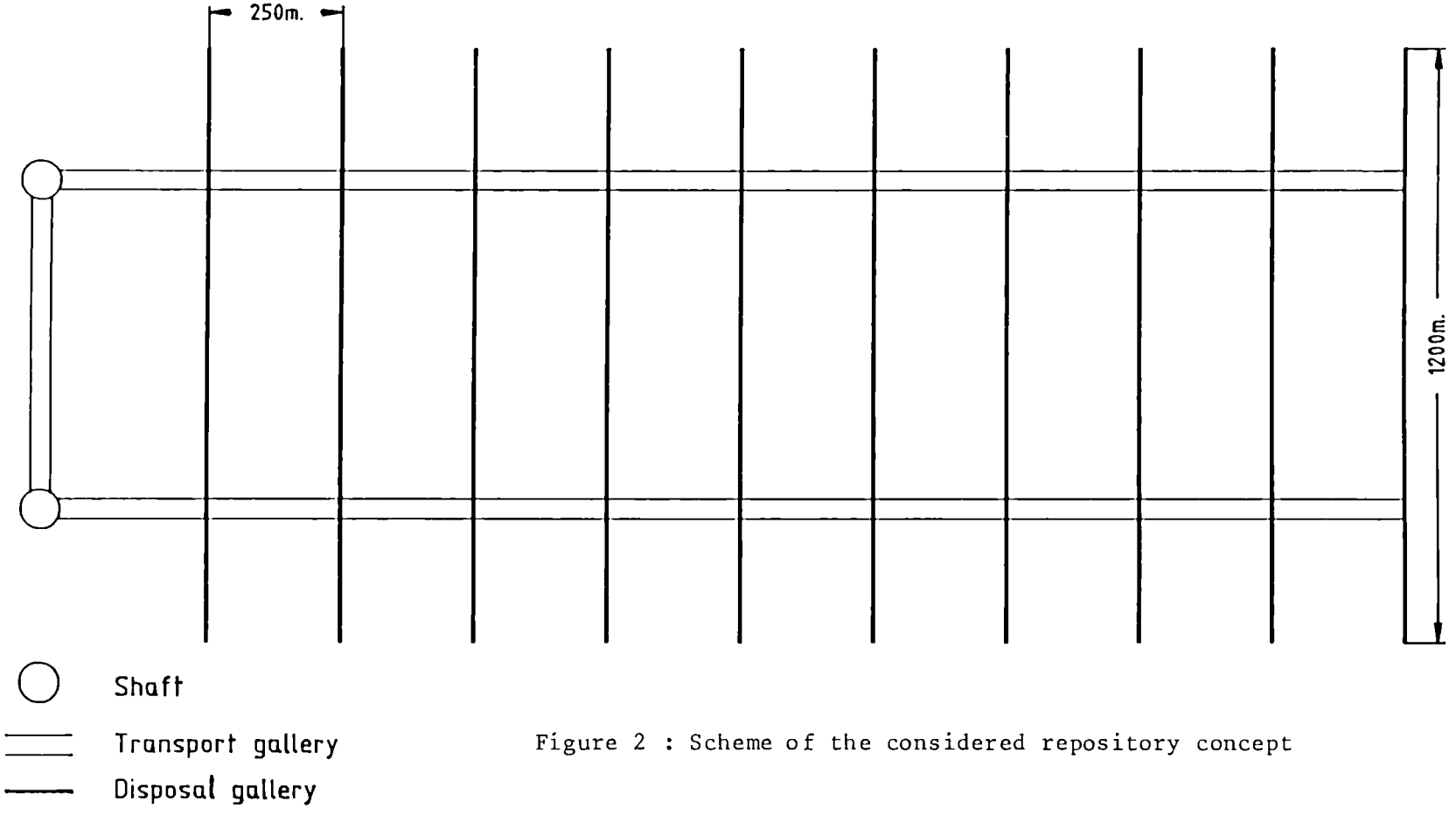

Figure 2 : Scheme of the considered repository concept

Title : "EVEREST :EValuation of Elements Responsible for the Equivalent doses associated with the final STorage of radioactive waste".
Contractors: CEA/IPSN* - CEA/ANDRA* - CEN/SCK**- GRS°- ECN°°
Contract n°: FI2W/ CT 90-0017
Duration : 01/04/91 - 30/09/94
Period covered: from 01/04/91 to 31/12/91
Project leader: Mrs BRUN-YABA (CEA/IPSN coordinator) - M. LARUE (GRS) - M. MARIVOET (CEN/SCK) - M. PRIJ (ECN) - M. RAIMBAULT(CEA/ ANDRA)

A- OBJECTIVES AND SCOPE

The general objective is the evaluation of the sensitivity of the radiological consequences associated with deep nuclear waste disposal with regard to the different elements in the performance assessment, for the following geological formations: clay, granite and salt and for HLW and MLW.
This work will be realised in four phases 1- methodology elaboration, 2- model description and data collection, 3- calculations, 4- interpretation of results.

B- WORK PROGRAMME

B.I- Methodology -this phase will be divised in four steps: identification of main features controlling the radionuclide transfered to the human environment, scenarios,definition of calculations to be performed and reflexion on differents approaches and techniques of sensitivity analysis.
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 sensitivity analysis calculations for normal and altered selected scenarios for each site.
B. IV- Result interpretations:the final phase will lead to a hierarchized list of the important elements (scenarios, phenomena, RN..)for each site in order to define priorities for the future R&D programm.

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C- PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

On the basis of an exchange of informations and viewpoints, the working group 1 created to identify "the questions to be solved" has established a first list of features,events and processes to be taken into account for clay, granite and salt.
On the basis of this list, the working group 2 "scenarios" has defined a list of important scenarios to be considered in the EVEREST project for each specific formation .
For the third step of the methodology phasis "techniques and approaches of S.A" the stage of exchange and reflexion is not completed.

Progress and results

B.I Methodology phasis -

The primary objective of the Working group 1 was to establish a preliminary list of questions to be solved in view of the identification of the most relevant processes and phenomena that could be a potential cause of significative changes on the radiological consequences.
The objective of the Working group 2 "scenarios" was to define a selection procedure of scenarios on the basis of this preliminary list and to give for specific formation, a list of important scenarios to be be taken into account within the EVEREST project. It appeared at the different meetings that two different approaches have been used for the identification of the scenarios within the national programmes of performance assessment.
A first approach considers that the disposal system is separated into barriers . The selection procedure consists in the establishment of an exhaustive list of FEP's which might influence the state of the barriers or the release and transport of radionuclide. These FEP's are classified into primary and secondary FEP's.
A primary FEP's attacks or bypasses one or more of the barriers and defines the state of the repository. A secondary FEP only influences the transport of the radionuclides for a given state. Two states of the barriers are defined: present or bypassed. The three main barriers are the waste forms plus engineered barriers, the host rock and the aquifers.
The second approach considers the three differents systems, near-field, geosphere and biosphere as a whole system without prejudging the role that can play each barrier. The selection procedure begins by listing initiating and independent events or situations which might occur after the repository closure. The second step is to consider the associated secondary events with their corresponding processes in order to build scenarios. The last step aims at defining enveloppe scenario to restrict their number.
Although the selection procedure are different, several elements common between the two approaches have led after discussions to a common list of relevant scenarios for each formation.(Cf Tables I to III)
Two levels of treatments of these scenarios can be apply :

- TT: Total Treatment of the scenario including radiological consequences.

- TP: Partial Treatment of the scenario , only a qualitative evaluation will be carried out.

A final report on the scenario selection procedure and the detailed description of selected scenarios will be made for the beginning of january 1992, on the basis of contributions from each contractor.

B II- Model description and data collection.

A draft document on radionuclide inventories for several kind of fuel, standard, high burn-up fuel and MOX has been presented. These inventories led to some remarks and need to be verified before the final inventory document can be published.

D- REFERENCES

CLAY SCENARIOS

N° SCENARIO			PROCESS		
IPSN ANDRA	CEN/SCK		CEN/SCK	IPSN	ANDRA
1	1	Normal evolution (including Würm type glaciation)	TT	TT	TT
2	3	Riss type glaciation (--> erosion, hydrogeology)	TP	TP	TP
3	4	earthquake/neotectonics (inner geodynamics) Belgium : near field effects France : fault activation	TT	TP	TP
4	10	Exploratory drilling	TP	TP	TP
5	2	Exploitation drilling	TT	TT	TT
6	4	Geologic barrier by passed Belgium : non detected faults France : sand lenses	TP	TP	TP
7	5	Sealing failure	TT	TP	TP

TABLE I

GRANITE SCENARIOS

		ANDRA	IPSN
1	Normal Evolution	TT	TT
2	Altered natural evolution (Riss glaciation,...)	TT	TP
3	Sealing defect	TP	TP
4	Undetected fault	TT	TT
5	Exploitation of water (associated with a detected and conductive fault)	TP	TT

TABLE II

SALT SCENARIOS

N° Scenario				PROCESS priority			
GRS	ECN	IPSN ANDRA		GRS	ECN	IPSN	ANDRA
1	1A	1	Normal Evolution . diapirism . subrosion . glaciation	TT or TP		TP	TP
1	1B, 1C,	2	Altered Evolution (natural)	TT or TP	1	TP	TP
2	2A 2A 2C.. 2G	3	Water intrusion . anhydrite vein . sealing defect	TT	2	TT	TT
2	2B	4	Water intrusion + brine pocket	TT		N	N
3	4B	5	Solution mining (salt consumption)	TT or TP		TT	TT
3	3	6	Solution mining (abandonned cavity)	TT or TP		TT	TT
3	4C	7	Conventional mining	TT or TP		TP	TP
3	4A	8	Reconnaissance drilling	TT or TP		TP	TP

TABLE III

PART B

CONSTRUCTION AND/OR OPERATION OF UNDERGROUND FACILITIES OPEN TO COMMUNITY JOINT ACTIVITIES

Project B1 "The underground facility in the Asse Salt Mine (FRG)"

FI2W/0002 The HAW project : test disposal of highly radioactive canisters in the Asse salt mine

FI2W/0006 Retrievable emplacement experiment with ILW and spent HTR fuel elements in the Asse salt mine

FI2W/0068 In-situ investigation of the long-term sealing system as a component of a dam construction

FI2W/0069 Active handling experiment with neutron sources

Project B2 "The underground facility HADES in the argillaceous layer under the Mol Site (B)"

FI2W/0001 Characterization of the clay under thermal loading for underground storage - CACTUS project

FI2W/0003 Preliminary demonstration test for disposal of high-level radioactive waste in clay (PRACLAY, CERBERUS, Mine-by-test)

FI2W/0096 Completion of the corrosion programme in Boom clay (in-situ experiments)

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 facility 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 acvtivities were already started at the Asse salt mine (FRG) and in the underground facility at Mol (B). The research in the Asse salt mine concerned mainly the preparation of the test disposal of simulated vitrified HLW (HAW) project. In the underground facility at Mol a test Drift was excavated and various lining systems tested. Moreover, a combined heating/radiation experiment (CERBERUS) was initiated and corrosion loops for testing of corrosion behaviour of potential container materials were installed.

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) which had already started during the previous programme are now being continued.
Additional research projects are being initiated as described below. New facilities scheduled in France (Project B3) and in the United Kingdom (Project B4) have not yet started.

Project B1: The underground facility at the Asse salt mine (FRG)

At the facility at Asse the Commission supports experiments involving emplacement of simulated high-level waste, the test emplacement of genuine medium-level waste, the long-term sealing of galleries in salt, and monitoring the effects of neutron and gamma sources in a salt environment.

The first HAW project concerns test disposal of 30 radioactive canisters simulating vitrified high-level waste in six 15m deep boreholes. Handling equipment has been developed and manufactured and is now being tested. Electrical heaters installed in two additional boreholes since November 1988, provide data on the thermo-mechanical behaviour of the salt. In parallel irradiation experiments are being carried out on salt samples at irradiation facilities at Saclay (F) and Petten (NL) to investigate both radiolysis effects and radiation damage phenomena.

The MAW/REV project concerns in a retrievable emplacement experiment with intermediate level waste and spent fuel (HTR fuel) elements. Six 200 litre drums with cemented cladding hulls, fuel hardware and dissolved sludge from the WAK-Karlsruhe reprocessing plant and four 220 litre stainless steel canisters with 950 spherical spent fuel elements are to be emplaced for a maximum of five years in three unlined boreholes.

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.

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.

Project B2: Experiments at the HADES underground facility at Mol (Belgium)

In the 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 horizonal mini-tunnels in clay. It will feature a full scale simulation, over a length of 20m of the cross sectional configuration of the waste environment, complete with heat generation (electrical heaters).

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 the CACTUS project, the near-field thermo-hydro-mechanical behaviour of clay around boreholes with high-level waste is being investigated using electrical heaters.

Finally, the in-situ tests on the corrosion behaviour of potential canister materials, already started in the previous programme, are being continued.

THE HAW PROJECT: TEST DISPOSAL OF HIGHLY RADIOACTIVE CANISTERS 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-C(MB)
Duration of Contract: from May 1990 to December 1991
Period covered: January 1991 - December 1991
Project Leaders: T. Rothfuchs, L. Vons, M. Raynal, J. C. Major

A. OBJECTIVES AND SCOPE

For a number of years research and development activities have been carried out in the Asse salt mine for the final disposal of high-level radioactive waste (HAW) in salt formations. The heat producing waste has been simulated so far by means of electrical heaters and also cobalt-60-sources. In order to improve the final concept for HAW disposal in boreholes drilled into salt formations, the complete technical system of an underground repository is to be tested in a full scale test facility.

To satisfy the test objectives thirty highly radioactive canisters containing the radionuclides Cs 137 and Sr 90 in quantities sufficient to cover the bandwidths of heat generation and gamma radiation of real HAW, will be emplaced in six boreholes located in two test galleries at the 800 m level in the Asse salt mine. The duration of testing will be approximately five years.

For handling of the radioactive canisters and their emplacement into the boreholes, a system consisting of six transport and storage casks of type Castor-GSF-5, two above ground/underground shuttle transport casks of type Asse-TB1, an above ground transfer station, an underground transport vehicle, a disposal machine, and of a borehole slider will be tested.

The scientific investigation programme is based on the estimation and in situ observation of the thermal, radiation-induced, and mechanical interaction between the radioactive canisters and the rock salt. Accompanying laboratory investigations will be carried out at Braunschweig (FRG), Petten (NL), Saclay (F) and Barcelona (E).

B. WORK PROGRAMME

B.1 In-Situ-Activities
B.1.1 Completion, Testing and Maintenance of the Handling System for the Radioactive Canisters
B.1.2 Emplacement of the Radioactive Canisters and Periodical Retrievability Tests
B.1.3 Maintenance of Instrumentation: Electrical Heaters, Gap Monitoring System, Data Collecting System etc.
B.1.4 Irradiation Experiments in the Dummy Canisters
B.1.5 Performance of a Radiological Measuring Programme
B.1.6 Thermomechanical and Geochemical Analysis
B.2 Laboratory Activities
B.2.1 Radiolysis Effects in Salt
B.2.2 Geochemical and Petrophysical Characterisation of Salt Samples
B.2.3 Development, Calibration, and Testing of High-Dose Measuring Systems
B.2.4 Gamma Fields and Gamma Spectra Calculations
B.3 Desk Studies
B.3.1 Development of a Post-Test Plan
B.3.2 Description of the Mineralogical and Geochemical Properties of the Underground Test Field

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The test disposal of highly radioactive canisters in the Asse salt mine will be performed in view of the planning, design and licensing procedure for a HAW repository in Germany.

In 1991 the final approval of the canister handling system by the mining authority has been achieved. Since late 1988 two preceding electrical reference tests are in operation in the heater boreholes A1 and B1. Laboratory investigations on radiolysis effects in salt are underway since beginning of the project. The results obtained until the end of 1990 were already reported in /1/, /2/, /3/.

Progress and results

1. In-Situ-Activities

1.1 Completion, Testing and Maintenance of Handling Systems for the Radioactive Canisters

Early in 1991 the above ground transfer station was adapted to the modified version of the Castor GSF-5 casks and equipped with an improved radiation shielding. A test with a 3.3 TBq Co 60 source revealed final shortcomings which were corrected.

The radiation shielding of the underground components was also examined and the required improvements were carried out. These measures have, however, not been totally completed to date. After their completion a test using a stronger radioactive source is planned.

The load bearing device for handling of the Asse-TB1 casks failed in late 1990. In order to continue the cold training a chain suspension was developed and licensed alternatively. However, in order to make a remote handling of the casks possible, an improved load bearing device is under contruction. In May 1991 a trial emplacement and retrieval process was demonstrated for representatives from the Mining Authorities and their expert, the Association for Technical Inspection (TÜV) Hannover. This demonstration showed that the emplacement system requires no alterations and that retrieval of all test sources can be performed within 45 hours. An additionally required partial demonstration of the emplacement procedure at borehole A4 was carried out at the end of the year. The entire transport and disposal system has, therefore, been successfully subjected to an acceptance test in the sense of the necessary licensing according to the Mining Act.

In respect of the preparation of the transatlantic transport of the radioactive canisters from the USA to Germany a US-validation of the international type B(U)-license for the transport cask GNS-12 is necessary. This validation is available since November 1991.

1.2 Emplacement of the Radioactive Canisters and Periodical Retrievability Tests

Due to a delay in the licensing procedure the emplacement of the radioactive canisters could not be performed and has been postponed.

1.3 Maintenance of Instrumentation: Electrical Heaters, Gap Monitoring System, Data Collection System

Installation of the canister guiding system (CGS) is completed and the boreholes are ready to accept the radioactive canisters.

The gap monitoring system (GMS) is continuously operated in the borehole B1. High quality of the measured tube deformation demands for regular calibration. The calibrations are performed monthly. At the end of 1991, the evaluated deformation reached about 0.3 mm on the radius. The maximum allowable ovality is 4 mm.

The heaters in the boreholes A1 and B1 are operated at constant power which corresponds to the decay heat produced by the radioactive canisters. Heater power supplies are maintained regularly to assure correct heater operation. At the end of 1990 some problems in the power supplies operation begin to emerge. The problems could be solved by installing new coal brushes and changing the position of the variac trafo's in such a way that they are less vulnerable for pollution.

Borehole A1 has been equipped with special instrumentation to monitor the salt pressure and the tube deformation. This instrumentation is calibrated regularly by ECN. After the salt pressure build up at the beginning of the experiment the maximum salt pressure on the liner tube has been reached. Since then a small relaxation is observed with a slow pressure decrease in time. To enhance the deformation and to make it easier measurable, the liner in hole A1 has a thinner wall relative to the liner in other holes. Short after the experiment was started, the magnitude of ovality has reached about 0.5 mm on the radius. Since then it remains at this value. Also orientation of the ovality main axis stays unchanged, pointing roughly towards the east.

In a large number of the experimental positions, temperature is sensed by means of shielded thermocouples. Up to the end of 1991 some of the signals are lost due to the thermocouple malfunction. This occurs more frequently at the outer surface of the liner in borehole A1.

The data collection system (DCS) has operated well in the period until the end of 1991. Nevertheless, a number of problems in communication with ECN and GSF computers are recorded in 1990. The software modification, that has been performed, improved the situation slightly. In June 1991 decision was made to split the communication task from the control and data management tasks and transfer it onto a separate computer. A MicroVAX 3100 computer will be installed to take the communication task over from the PDP 11/24 computer now in the use.

1.4 Irradiation Experiments in the Dummy Canisters

Preparation of the salt samples and sample holders necessary for these experiments was terminated in 1990. The irradiation will only be started after emplacement of the radioactive canisters. Together with all partners the test plan /4/ for the irradiations was prepared.

1.5 Performance of a Radiological Measuring Programme

The radiological measuring programme comprise measurements of gamma dose rates and doses in the above ground transfer station, in the dummy canisters, and in the surroundings of the emplacement boreholes. The measurements can only performed in connection with the emplacement of the radioactive canisters.

1.6 Thermomechanical and Geochemical Analysis

Already at the end of 1987 most of the instrumentation for monitoring stresses, stress changes, rock displacements, temperatures and gas release had been installed. The set of instruments at the heater boreholes A1 and B1 was connected to the DCS in summer 1988, and the instruments at the remaining emplacement boreholes in summer 1989. From then onwards the complete data set is being monitored continuously.

The salt walls of the heater boreholes A1 and B1 have reached temperatures of about 225°C after approximately 300 days of heating and are rather constant since that time.

Stress measurements using straingaged stressmeters are conducted to investigate specific stress components developed in the pillar in the region between the test sites A1 and B1. The vertical stress component and the horizontal stress component measured are about 15 to 16 MPa and are nearly constant since July 89.

Since five years the vertical stress component measured at the Monitoring Station already installed in 1985 for long term observation of stress components shows a constant value of 20 MPa. The radial measuring Glötzl pressure cells, installed in borehole adjacent to the heater boreholes A1 and B1 at a depth of 12.1 m and a distance of 7.5 m to them indicate actually an in situ stress of 10 MPa to 11 MPa, as measured already 1990.

The displacement measurements consisting of room closure and extensometer measurements, were continued. The vertical convergence rate in the gallery A of the experimental area actually ranges between 12 mm/yr an 19 mm/yr; the corresponding horizontal convergence rate ranges between 14 mm/yr and 19 mm/yr. In gallery B the vertical convergence rate actually ranges between 13 mm/yr and 18 mm/yr the horizontal rate ranges between 17 mm/yr and 23 mm/yr. At test site A1 the horizontal and the vertical convergence rate are equal, whereas at site A4 the horizontal convergence rate is 19 % higher than the vertical one. For sites B1 and B4 the horizontal convergence rate is 24 % resp. 32 % higher than the vertical ones. Comparing the results with those as measured in 1990 a decreasing tendency of the convergence rate on the whole by about 6 % to 20 % is being observed.

Twelve sensitive tiltmeters have been installed by the Institut de Physique du Globe de Paris (IPG) in three locations around the HAW test field to survey the movements of salt. Except for 2 units, the measurements carried out in 1991 are satisfactory and confirm the previous results. They are homogeneous with modelling and with other geomechanical measurements. The magnitude of the values measured at the location close to heater borehole A1 is much higher than at the two other stations. The inclination rate is slowly decreasing without any asmytotic state of evolution. Heating 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.

Seismic velocities, close the heater borehole B1, decreased slightly after the start of the heating, indicating weak microfracturing. In the walls of the gallery, weak microfracturing did develop more continuously.

An important aim of the HAW experiment is the use of the measurements for the validation of thermomechanical codes. The validation process adopted at ECN is a stepwise approach. The first step is formed by the pre-test analyses which have been performed before the start of the experiment. The second step is a confrontation of the pre-test results with the experimental data. The final step is the evaluation which can also contain some new predictions of the behaviour with a better model.

The pre-test analyses, performed at ECN are finalized in 1990 and reported in /5/. The analyses have been made with plane strain models for the pillar, axi-symmetric models for the boreholes and a three dimensional model for the central part of the HAW test field. The programmes used are TASTE and ANSYS for the temperature analyses while ANSYS and GOLIA-FAME have been used for the deformation annd stress analyses.

In 1991 most of the work was devoted to a furhter elaboration of several assumption in the pre-test analysis. In /6/ an analysis is presented on the influence of the number of (heated) boreholes. It is concluded that the maximum thermally induced compressive stresses in the field with two rows of four boreholes can accurately be determined with a model based on two rows of an infinite number of boreholes. This implies that the maximum thermally induced stresses reported in /5/ fairly correspond with those to be expected in the HAW fields once loaded completely. For the development of the compressive stresses for longer time periods the analyses /6/ show that the boundary conditions have a large influence on the evolution of the stresses. Based in this finding a full three dimensional model has been set up of the HAW test field with only two (electrically) heated boreholes.

In /7/ the influence of a relatively short heater-interruption on the liner load in the two types of boreholes (type A and B) has been analyzed. Directly after the interruption the temperature and compressive stresses drop significantly. It appeared that 20 days after the restart of the heaters the maximum temperatures and the maximum liner load accurately correspond with the values in the uninterrupted operation of the heaters.

To better understand the measuring result of a Glötzl pressure cell an analysis has been performed in which the time dependent (isothermal) behaviour of the cell is investigated /8/. It is concluded that the time between drilling of the borehole and the emplacement of the Glötzl influences the behaviour of the measured pressure for a very long time period. It needs more than 300 years before the pressure on the cell equals the lithostatic pressure in the field. Thus the measuring result of the Glötzl cell cannot be considered to represent directly the stresses in the field. The behaviour under heated conditions needs more detailed analyses. Although the analyses have been made for a Glötzl the same conclusions hold for other types of pressure cell in a creeping type of rock.

During the experiment with the electrically heated boreholes, (small) ovality of the cross section of the lining was measured. Causes of this ovality are variations in the pressure of the heated salt on the liner and bending of the liner due to the deformation behaviour of the salt around the galleries and the heated boreholes. In /9/ analyses have been reported on the amount of ovality caused by bending or by pressure variations. It was concluded that the expected amount of bending cannot be the cause of the ovality while pressure variations of 1 to 2 MPa can cause ovalities as measured.

The activities of IfT in regard of thermomechanical analysis concentrated in 1991 on finite element calculations for the constant heated borehole A1 and its surrounding. An axisymmetric model of the borehole was used and the time dependent fields of temperatures, displacements, and stresses are obtained for a time period of ten years after the beginning of heating. The measured and calculated temperatures agree very well while the agreement between the measured and calculated stresses and deformations is less good. It is likely that these discrepancies are caused by the somewhat stiff model because of the axisymmetric formed gallery and the neglection of primary creep. In the case of the stress measurements it is concluded (as has been done by ECN, see above) that the stress gage installation technique possibly results an insufficient contact of the gage to the rock mass thus resulting too low measurement values.

In the framework of the gas release measurements gas samples were taken from the available 48 boreholes and analysed. A mechanical gas sampling device, featuring a sampling syringe, a manometer and a valve manifold, was successfully employed. This newly built device allows to withdraw smaller sample volumes than previously possible. In most cases a plateau value had established for the various gas concentrations. However, with a few exceptions very low gas concentrations were observed in the unheated boreholes. In summer 1991 all boreholes were rinsed with N_2 in order to reduce the partial pressure of the various other gas components. Samples were taken immediately following, one day later and at increasing time intervals afterwards. By the end of 1991 the old plateau values of the gas concentrations have in some cases already been reached. It is hoped that the diffusion range of gases in rock salt can be derived from such investigations.

Additionally to the in situ measurements laboratory investigations have been carried out for the IfT to determine the adsorption enthalpies of CO_2 and CH_4 on salt crystal surfaces. Such data are not available in the literature, but are required as input data for gas release models. These models will be used to predict the fate of the gases around an emplacement borehole. The enthalpy for CO_2-adsorption on a (100) NaCl-surface is about 29 kJ/mol, while the experiments with CH_4 have not yet been completed.

2. Laboratory Activities

2.1 Radiolysis Effects in Salt

In the frame of the French laboratory investigations on radiolytic gas formation and liberation from Asse salt, improvements in irradiations procedures have been necessary to obtain higher dose rates in Osiris facility: 100 kGy/h have been reached, inducing however an increased temperature (150°C). By the end of year 1991 most of the irradiations scheduled in the programme were completed. Analyses confirm or focus that radiolytic gas production is mainly governed by parameters such as small grain size, high integrated doses or composition of ambient gases. Conclusions are that investigations should be carried out to improve detection of reactive gases which recombine quickly after irradiation stops. Additional analytical methods were successfully investigated to shorten the analysis delay (Fourier IR spectoscopy). Next studies should also emphasize on the effect of higher doses such as those accumulated in 100 years in rock salt surrounding vitrified wastes in a repository. All experimental and analytical data available up to date have been evaluated.

Radiation damage development has been studied in the same samples as will be used in the dummy canisters (see also section 1.4) in the HAW test field by means of irradiations performed in the gamma irradiation facilities (GIF) of the high flux reactor (HFR) at Petten.

Irradiations which took place at 100 °C, variable dose rate (240 to 40 kGy/h) up to 350 MGy and in unpressurized samples produced stored energy values congruent with calculations performed using the modified Jain-Lidiard model. Another set of irradiation experiments took place at 100 °C, 15 kGy/h and up to 45 MGy total doses and in samples either pressurized (200 bar) or unpressurized. These experiments are nearer to repository conditions than ever was the case before and showed that the efficiency of gamma-rays in producing damage is higher than calculated using the modified Jain-Lidiard model at low total doses (up to 4 MGy/h) but lower at higher doses (45 MGy). This is thought to be related to energy requirements for colloid nucleation, to colloidal induction time

and to sample heterogeneities either previous to irradiation or produced by it.

Modification of the Jain-Lidiard model to introduce these observations is in progress as well as new irradiation experiments under the same circumstances except for dose rate (now 4 kGy/h) which is even nearer to repository conditions as in the previous experiments.

2.2 Geochemical and Petrophysical Characterisation of Salt Samples

The geochemical characterization of salt samples irradiated at a dose rate of 15 kGy/h in the HFR-Petten and their radiation damage as well, have been almost completed:

Water content determinations and fluid inclusions analyses at the University of Barcelona have been completed while the determination of the chemical composition of the rock salt is still in progress. Microstructural observations on PLL samples have been completed and the results are shown in Table I.

PLL samples are salt samples from the Sallent Mine (Spain), BHA and BHP from the Asse Mine (Germany) and PP and SS are synthetic rock salt samples. Basically, water is present is intergranular form and for some samples (PLL mainly) as fluid inclusions. Average composition of fluid inclusions for PLL samples, both irradiated and non-irradiated, compare as indicated in Table II. Basically, radiolysis does not cause any variation in the chemical composition of brine. PLL samples irradiated at a dose up to 420 kGy do not present any feature of grain boundary migration and are completely white up to a dose of 260 kGy. Samples irradiated between 6 and 48 MGy are blue coloured and barely any grain boundary migration was observed. It can be concluded that, despite their water content, very few migration of grain boundaries has taken place in PLL samples. This fact suggests that other parameters should be taken into account like the impurity content and others that seem to be still unknown.

Colloidal sodium determinations performed by light absorption have been completed while by measuring H_2 coming from dissolved salt is in progress. The colloidal sodium determination results are shown in Table III.

Table I: Water Content Data of Samples Irradiated in the HFR-Petten

	PLL	BHA	BHP	PP	SS
Water Cont. Range (%)	0.06-1.31	0.09-0.15	0.07-0.26	0.07-0.12	0.05-0.13

Table II: Composition of Fluid Inclusions in PLL Samples

Non Irradiated	Na^+	Mg^{2+}	K^+	SO_4^{2-}	Cl^-
AVERAGE	2.92	1.12	0.30	0.08	6.16
DEVIATION	0.28	0.25	0.06	0.02	0.29
Irradiated					
	Na^+	Mg^{2+}	K^+	SO_4^{2-}	Cl^-
AVERAGE	3.03	1.25	0.31	0.08	6.21
DEVIATION	0.13	0.05	0.03	0.01	0.06

Table III: Colloidal Sodium Determination Results of Samples Irradiated in the HFR-Petten

DOSE	F-CENTERS	COLLOIDS
20 KGy	10E-5 - 10E-6	< 10E-6
260 KGy	10E-5	< 10E-6
420 KGy	10E-5 - 10E-6	< 10E-6
6.6 MGy	10E-5	10E-4
26 MGy	10E-5	10E-4
48 MGy	10E-5	10E-4

(Order of magnitude expressed in molar fraction)

It is considered that the small variations of colloidal sodium content are probably related to the chemical composition. On the other hand, F-Centers concentration seems to keep constant.

Concerning the petrophysical characterization of salt samples an extensive rock mechanic programme on rock salt from the test field has been carried out in the IfT rock mechanic laboratory in Braunschweig during the past year. Using a technique recently developed by GSF, 43 triaxial dilatancy tests have been conducted. Dilatancies, as measured in volumetric strain, between -0.0028 and 0.0294 were observed. The failure curve of rock salt under triaxial extension seems to correspond with the isoline of no dilatancy. The still continuing data analysis aimes for an empirical dilatancy law. A series of 42 uniaxial creep tests on small rock specimen has been completed in 1991, allowing the analysis of 23 steady-state, 22 transient and 3 accelerated creep phases. Transient creep analysis is becoming more important as its contribution towards the overall creep deformation process is recognized. A new transient creep model, targeted to calculate steady-state creep rates from a short transient creep phases, is being developed.

2.3 Development, Calibration, and Testing of High-Dose Measuring Systems

CEA/ANDRA has developed two separate dose measuring systems, respectively based on ion chamber detectors and thermoluminescent solid state dosemeters, aiming to record dose rates in various locations of the test field as well as in the above ground transfer station. The first is completed and partly delivered at Asse, partly stored in Saclay. The second systems, which has needed intense development works for high temperature applications, is also completed.

The solid state dosimetry system developed at GSF-Institut für Strahlenschutz (ISS) which is based on the combination of quartz and LiF is applicable to measure doses up to 50 MGy as well as to estimate the irradiation temperatures.

In order to improve the performance characteristics of dosemeters and to obtain an efficient evaluation procedure, a low level experiment using a 9 GBq Co 60 and a 16 GBq Cs 137 source has been carried out in emplacement borehole B3 in the HAW test field. In the case of the Cs 137 the measurement was performed with the radiation source in an empty as well as in a glass filled dummy canister. Absorbed dose rates at the outer surface of the borehole liner were measured. The results of the measurements obtained with the measuring systems of CEA and ISS were in good agreement. Similar experiments were performed in the Morsleben mine with higher activities. The tests showed, that the handling procedures developed for the measurements are ready for operation.

2.4 Gamma-Fields and Gamma-Spectra Calculations

CEA in Saclay/France performed dose calculations to give a predictive map of gamma dose distribution in the salt surrounding the emplaced radioactive canisters. Preliminary analysis determined which radiative transition may have significant effect and have to be considered: one gamma transition for each Cesium and Strontium plus Bremsstrahlung for the latter were thus pointed out. 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). An additional (custom-usable) software permits to obtain the result at any point in salt and for any kind of loading or arrangement of the radioactive canisters (Fig. 1).

Also the ISS performs calculations of dose distribution around the emplacement boreholes, using Monte Carlo methods. Preliminary results of height profiles of dose rates in air and gamma spectra in the surrounding of an emplaced canister and at various locations in salt were derived. For the low level experiment (see section 2.3) with a dummy canister containing a small Cs 137 source calculations were performed for the two experimental arrangements. The calculated height profiles of dose rates for both arrangements are given in Fig. 2.

3. Desk studies

3.1 Development of a Post-Test Plan

During the year 1991 the tables of contents for the post-test plan itself and for a work plan according to the post-test plan were developed. The main chapters of the post-test plan are dealing with the documentation of the observed test conditions, with the post-test analyses of the thermal and radiological impacts, with the corrosion of materials and with a final evaluation of the handling procedures of the radioactive canisters. Furthermore, plans will be developed to evaluate the applied measuring methods and the validation of numerical computer codes.

3.2 Description of the Mineralogical and Geochemical Properties of the Underground Test Field

The chemical analyses on about 90 further rock salt samples were completed. The mineral contents were calculated and correlated with the mineral contents for the x-ray measurement. The correlation is very good. In the frame of a subcontract a special analytical survey was conducted for the investigation of rare earth elements both in halite and sulfate components of 41 samples from the Staßfurt rock salt. The concentration ranges from 4 ppb to 1851 ppb, with an average of 117 ppb. The concentration of the element fluorine in representative borehole samples ranges from 30 ppb to 850 ppb, with an average of 400 ppb. The microscopical study on thin sections yielded some interesting results. The scanning electron microscopic study of the void and the intergranular space was started and will be continued. Also finished was the analytical part of the textural characterisation of the test field.

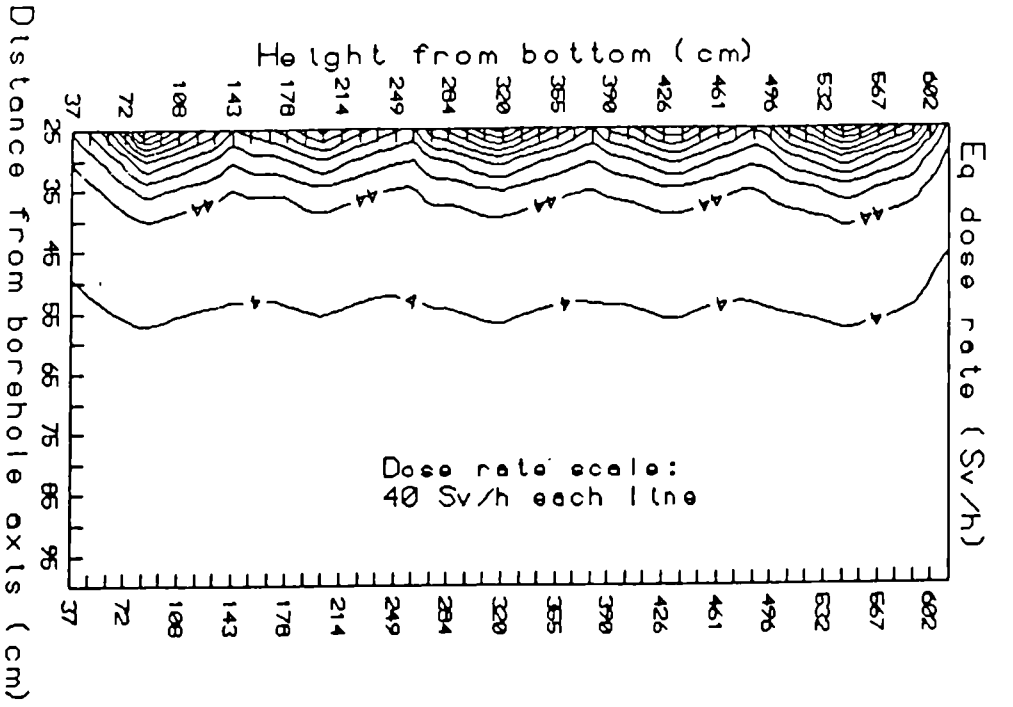

Fig. 1: Predictive calculations of equivalent dose rate in the salt at emplacement borehole A3

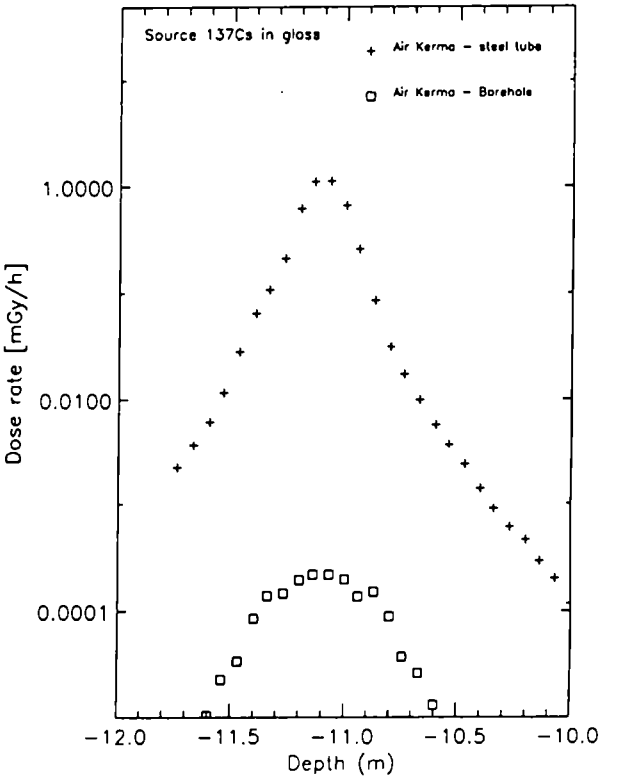

Fig. 2: Hight profiles of the dose rates at the outside wall of the steel liner and in a borehole at r = 73 cm in the salt for the case "Cs 137 source in glass", normalised to 16 GBq source activity.

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Title:	Retrievable Emplacement Experiment with ILW and Spent HTR Fuel Elements in the Asse Salt Mine
Contractors:	Forschungszentrum Jülich GmbH (D) and Forschungszentrum für Umwelt und Gesundheit GmbH (D)
Contract N°:	FI2W/0006
Duration of contract:	July 1990 - December 1992
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Project leaders:	D. Niephaus and K. Wieczorek

A. OBJECTIVES AND SCOPE

In the Federal Republic of Germany, radioactive waste with perceptible heat generation is to be finally disposed of in vertical boreholes 300 m deep in a final repository in a salt dome. The final disposal technology for ILW and spent HTR fuel elements has been developed in the framework of the MHV Project. In the subproject "Retrievable Emplacement Test" of this project six 200-l drums with cemented cladding hulls, fuel hardware and dissolver sludge from LWR reprocessing, and four canisters with spent HTR fuel elements are to be emplaced for five years in unlined boreholes in the Asse mine.
Apart from demonstrating that these wastes can be safely handled under real mining conditions, the objective of this programme is above all to demonstrate that during storage no circumstances arise which could cast doubt upon safe operation of the boreholes. In addition, it will be possible for the first time so study the effects of gas release from wastes into a final repository borehole.
Work will be done by KFA, Jülich and GSF, Braunschweig under coordination of KFA.

B. WORK PROGRAMME

1. Preparation of the experiment
1.1 Coordination of work between the partners, GSF and KFA
1.2 Assembly, installation and test of components
1.3 Licensing
1.4 Installation of radiation protection instruments
1.5 Staff training for emplacement and retrieval

2. Implementation of the experiment
2.1 Coordination of work between the partners, GSF and KFA
2.2 Transport of the waste packages to the Asse mine
2.3 Emplacement of the waste packages in three boreholes
2.4 Measurement of dose rate, temperature, gas composition and borehole convergence
2.5 Maintenance of equipment
2.6 Radiation protection measurements
2.7 Staff training for retrieval

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

The retrievable emplacement test with ILW (fig. 1) and spent HTR fuel element packages (fig. 2) will take place in three vertical boreholes, 10 meters deep and with a diameter of 1 meter, in the test drift EV on the 800-m level of the Asse salt mine. The drift was driven, the boreholes were drilled and partially instrumented, and the main components were fabricated in parts during previous phases of the project.

During the reference year 1991, installation of the borehole internals and fabrication of all components have nearly been completed. Inactive system tests have successfully been performed to check the interactive function of all major handling components.

Due to delay in the licensing procedures, the emplacement of the waste canisters could not be performed during the reporting period and has been postponed to 1993.

Progress and results

1.1 Coordination

In compensation for services in the field of staff training which were not possible during the reference year, GSF has agreed to provide additional engineering services for the installation of equipment at the Asse mine.

1.2 Assembly/installation/test of components

Manufacturing of the components for transport, handling, emplacement and retrieval of the waste packages has been continued and nearly completed during the reference period. The second AVR shipping cask for transport and handling of HTR fuel elements packed in a canister was assembled. The switchgear and control equipment of the shaft house crane assembly has been completed, and the new trolley with its 10-t/720 kp hoist has been finished. Moreover, the switchgear and control equipments of the three underground crane assemblies have been completed.

Prior to their installation at the Asse mine all major components have to be tested in interaction for proper functioning within the scope of inactive system tests. Two out of three system tests, simulating the reloading of a 200-l drum from a CASTOR shipping cask into an E2 transfer cask and simulating the package emplacement in and retrieval from a borehole were successfully completed.

The gas monitoring and analysis equipment, which will serve to supervise and analyse the borehole atmospheres during test disposal was installed and tested, as planned, in one of the two instrument containers on the test drift EV.

Transport and handling of the canisters with spent HTR fuel elements will be carried out using a type-B licensed AVR shipping cask. Prior to each off-site transport the leak tightness of the canister closure must be demonstrated. For this purpose, a plug replacement and leak testing unit was installed and cold-tested in a KFA Hot Cell. A second unit of almost equal design is currently under construction and will be installed in the "Hot Cell" at Asse.

The installation of the borehole internals (figure 3 shows, as an example, the internals of borehole EV2) has been completed. The last completely instrumented storage rack was

lowered in borehole EV4, and the measurement and power supply cables of the storage racks in the boreholes EV2 to EV4 were laid to the instrument cabinets and wired.

Another item in the field of installation was to put the above ground fault monitor into operation. With this unit, safety relevant data like heater temperatures and gap sizes between the storage racks and the borehole walls in the emplacement boreholes will be monitored.

1.3 Licensing

Operational planning licences pursuant to the Federal Mining Act, a licence pursuant to § 9 of the Atomic Energy Act, transportation licences in accordance with the road/railway traffic law, and nuclear materials safeguards pursuant to the Verification Agreement are required for the emplacement experiment.

In compliance with the requirement of the Goslar Mines Inspectorate, which is the regulatory authority for licensing the experiment under the Federal Mining Act, a status report was drafted during the period under review. The report describes all components, installations and experimental facilities in their overall correlation as well as the experimental results obtained so far. It is a prerequisite for further operational planning licences and for the statutory licensing procedure under the Atomic Energy Act.

1.4 Installation of radiation protection instruments

The concentration of gaseous radionuclides (H-3, C-14, Kr-85), the local dose rate and the local dose must be measured at various locations in the test drift EV. Installation work was continued with respect to radiation protection. The equipment for transferring the safety-relevant data to the data collection system of the radiation protection department above ground was completely installed.

1.5 Staff training for emplacement and retrieval

There has been no progress under this and the following headings during the reporting period.

List of publications

/1/ BRÜCHER, H.; NIEPHAUS, D.; BARNERT, E.; KROTH, K.; 2nd Annual conference on High Level Radioactive Waste Management, Las Vegas, Nevada/USA, April 28-May 3, 1991, Proceedings Vol. 1 pp 340 - 346.

/2/ BRÜCHER, H.; CEC Report EUR 13985 (1991) pp 121 - 127.

/3/ NIEPHAUS, D.; CEC Report EUR 13985 (1991) pp 128 - 140

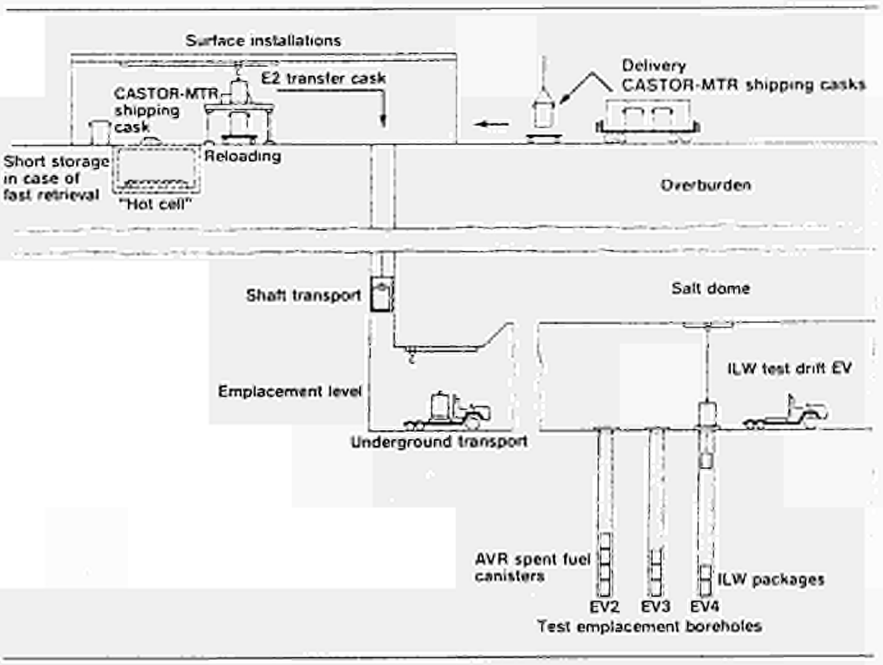

Fig. 1: Handling of ILW packages for the Retrievable Emplacement Experiment

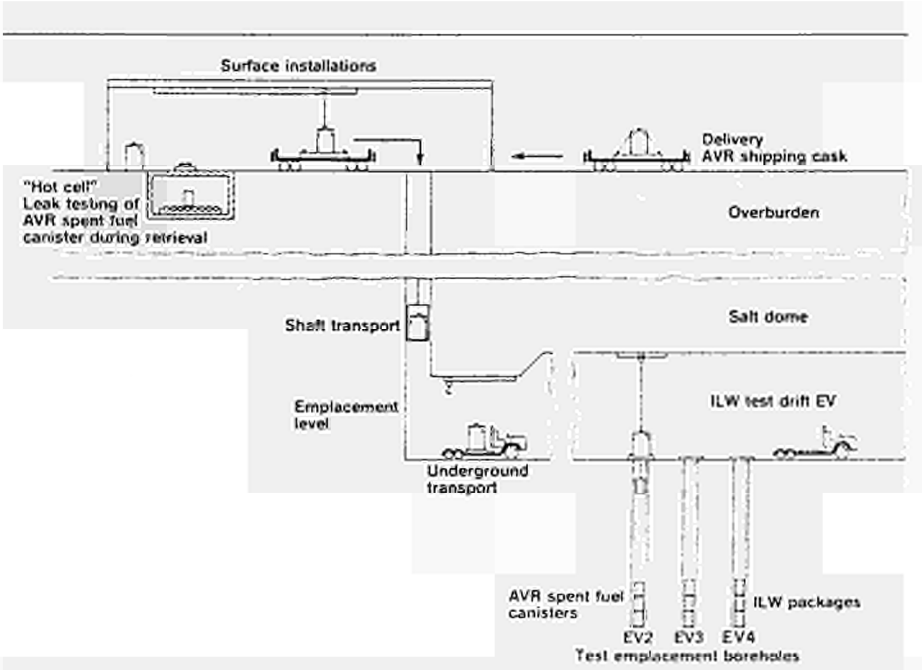

Fig. 2: Handling of spent HTR fuel elements packages for the Retrievable Emplacement Experiment

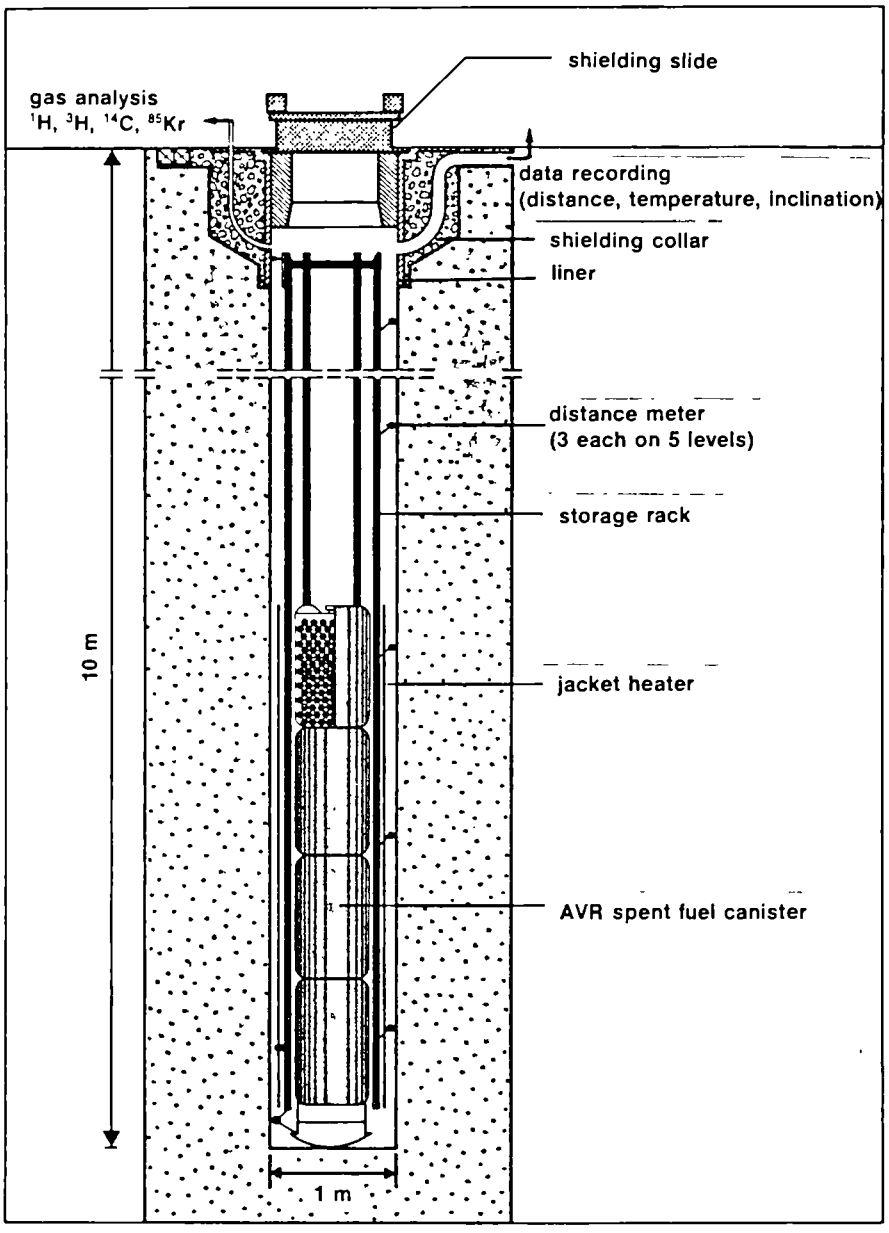

Fig. 3: Vertical cross section of borehole EV2 for the Retrievable Emplacement Experiment

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:	01.04.91 - 31.03.95
Period covered:	01.04.91 - 31.12.91
Project Coordinator:	W. Bollingerfehr

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 /1/. 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 functioning (tightness) over long time periods (up to approximately 500 years) via model calculations.

The long-term evolution of permeability and porosity will be considered, investigating the chemical stability and the petrophysical behaviour.

The state of the art on calculations and codes for multiple-phase flow will be analyzed, adequate mathematical models and computer codes developed and verificated.

B. WORK PROGRAMME

According to the Technical Annex of the contract, the work programme consists of the following items:

performed by 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

performed by 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

performed by 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

Up to the end of the year 1991 DBE finished the planning work for the long-term seal components and the construction work for the 1 : 1 scale test in the Asse Mine (see item I/1.). The preparation of the test field has been started by installing the connection pipe for pressurization. GSF has developed the scientific investigation programme, designed the instrumentation for the in situ test and planned the laboratory tests and the test on large scale boreholes according to the item I/1 and I/2. The pressure unit for applying gas pressure has been designed, manufactured and installed in the test field. Laboratory tests on construction materials have been performed.

In order to collect geochemical data ANDRA investigated the physico-chemical and petrophysical characteristics (item II/1) of the component of the long-term seal (briquettes). The solubility of materials in fresh water and brine have been measured and laboratory dynamic experiments with laboratory percolation test through different assemblages of briquettes have been performed (item II/2 to II/4). The design of the pilot test in the Amelie Mine has been finished and the preparation of the test field is going on (item II/5). In the field of geochemical and petrophysical modelling an overview of the development of recent geochemical model on application on thermodynamic codes are performed (item II/8 and II/7). Considering modelling of petrophysical characteristics of briquettes assemblages a review on "dissolution of solid and porous materials by fluids" was achieved. A literature study for analysation the state of the art on calculations and codes for multiple-phase flow has been done (item III/1). It has been proven that a large number of codes deal with topics strongly related to the hydromechanical behaviour of salts. None of them appeared to address precisely all required mechanism. That is the reason why preliminary work of mathematical modelling is underway (item III/3). The planning of laboratory experiments has been started (item III/2).

Progress and results

1. Requirements and design basics for the long-term seal in situ test in the Asse Mine

The repository relevance for the separate test of the long-term seal can be achieved, regarding some basic demands as

- contribution towards the mechanical integrity of the entire dam construction
- similar mechanical behaviour as the surrounding rock salt
- long-term corrosion resistance against brines and gases
- low permeability at the outset of functioning, corresponding to the surrounding rock salt
- mechanical stability and decreasing permeability up to a time period of 500 years

Besides that a simple mining and construction technique is requested.

In order to determine the long-term seal permeability the time dependent permeability evolution of the surrounding rock salt and the interface of the construction and the rock salt as well as that of the construction itself has to be described.

Regarding the transfer of the expected test results to an entire dam construction some additional design criteria had to be considered, mainly:

- corresponding dimension of the long-term seal in the separate test and in the dam itself
- corresponding flow conditions
- designing of the pressure chamber considering rock mechanical stability and avoiding rock arching

2. Results

2.1 Design and construction of the long-term seal test construction

Based on the fundamentals listed up in chapter 1 the components for the in situ test were developed and designed /1/. Figure 1 shows the conceptual design of the long-term seal test construction, which mainly consists of

- a pressure chamber
- the actual long-term seal
- an observation chamber and
- a static abutment

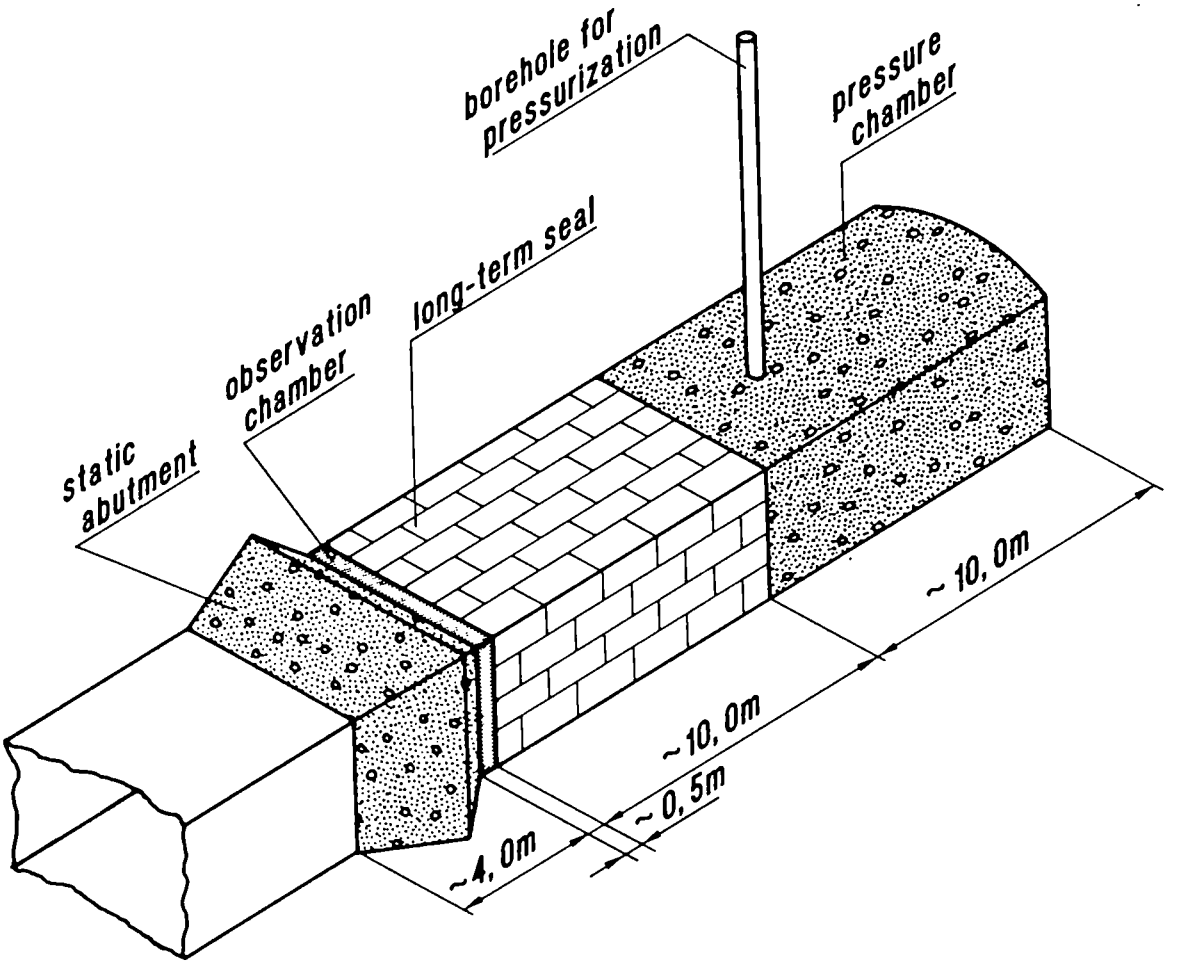

Figure 1: Conceptual design of the long-term seal construction

The design of the pressure chamber took into account the correspondence to the dam construction as well as criteria derived from test conditions and the operational safety of the Asse Mine. The long-term seal itself consists of a salt briquettes brickwork jointed by special mortar. The salt briquettes are made of highly compacted fine grained rock salt and have dimensions of 240 mm in length, 115 mm in width and 71 mm in height. Figure 2 shows the bond of the brickwork which is jointed full faced without continuous upright joints and joints of the bed.

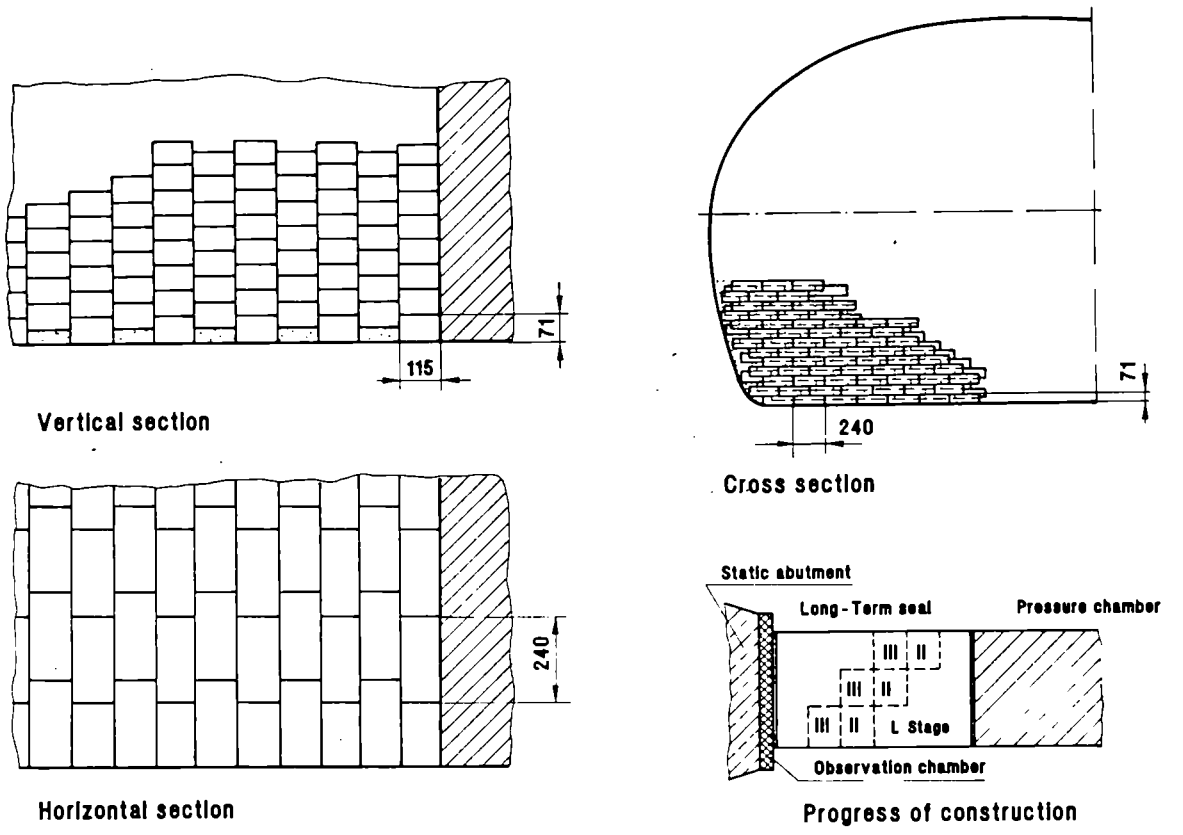

Figure 2: Long-term seal - design of salt briquettes brickwork

The observation chamber as well as the static abutment (see Figure 3) were designed with respect to the appropriate requirements, especially those derived from the test procedure, rock mechanical and constructional conditions.

A welded steel plate construction will be used for the observation chamber. The steel plate construction manufactured in 11 segments will be bolted at the construction site and arranged as a box-type construction. The observation chamber with a depth of 0,5 m consists of steel plates with 30 mm in thickness. Figure 4 shows the frontside of the chamber as well as details of the box-type construction. The static abutment consists of a concrete construction with steel reinforcement. It has a length of 4 m and the shape is similar to an asymmetric double cone. For controlling reasons of the test device in the observation chamber an access through the abutment has been designed with 2 m in height and 1 m in width.

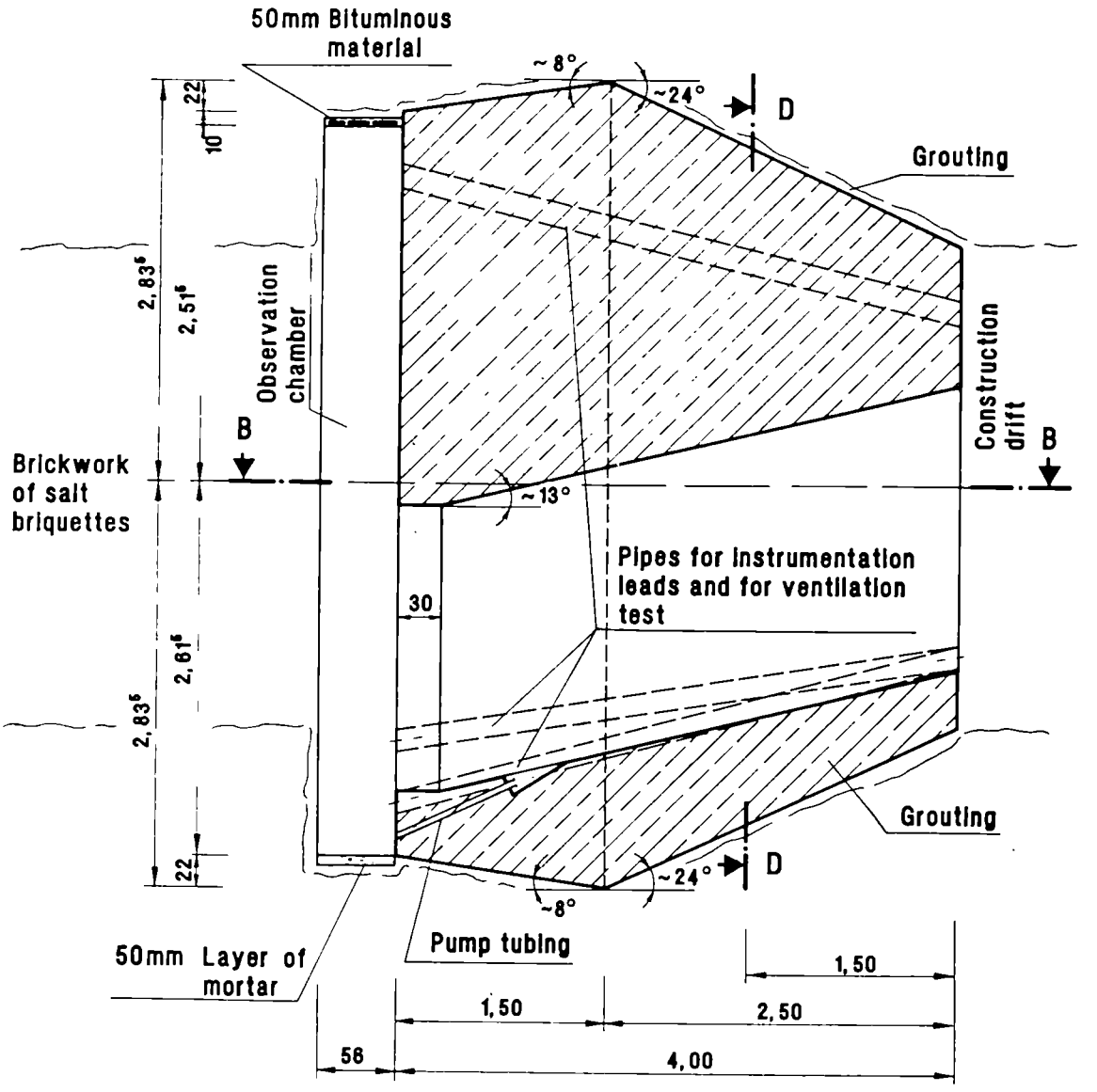

Figure 3: Static abutment and observation chamber - vertical section

The construction work of the total long-term seal test construction will be devided into the following steps. After installation of the tubing for pressurization and excavating the test drift, in a first step the in situ instrumentation of the pressure chamber will occur. The second step is the backfilling of the pressure chamber with basalt gravel in order to reduce the volume of air in the chamber itself. Hand in hand with the building of the salt briquettes brickwork the instrumentation of the long-term seal itself will be performed. At the end of this brickwork the observation chamber has to be arranged by its 11 segments as a box-type construction. The last component in constructing the long-term seal is the static abutment, produced of concrete B 25 with steel reinforcement.

Due to technical problems during the installation of the tubing for pressurization a time delay of nearly 4 months is obvious and invariable. That means that the test program using gas first will start in summer 1992 instead of spring 1992.

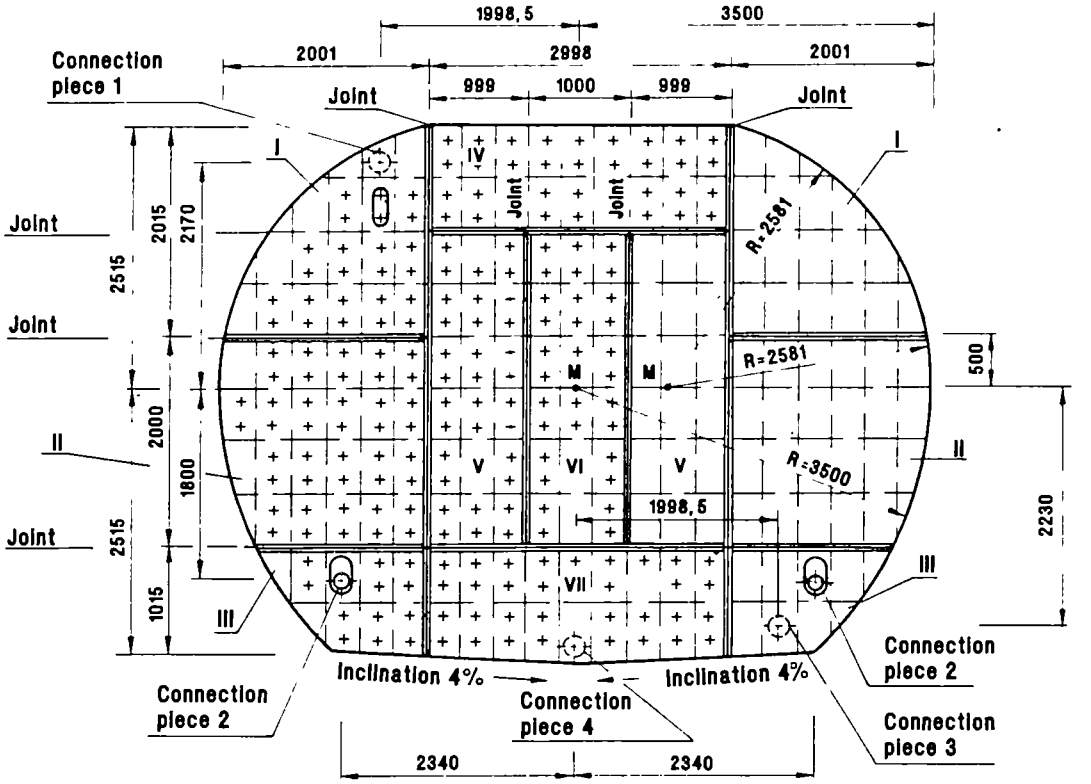

Figure 4: Observation chamber - frontside of the salt briquettes brickwork

2.2 Scientific investigation program including laboratory- and in situ-tests

Basing on the objectives of the long-term seal project GSF developed a scientific investigation programme which will give answers

- to the tightness of long-term seal component of a dam and
- its functioning over long time periods.

The programme /2/ consists of preliminary laboratory tests, large scale in situ-tests and the test of the long-term seal in the Asse Mine. Laboratory investigations on drilling cores from rock salt as well as on building materials have been performed with regard to their permeability and porosity. As a result the permeability of rock salt has been determined in a range between 10^{-16} and 10^{-22} m^2. First investigations using different gases showed an influence of molecular weight and gas adsorption on the permeability. The permeability of salt concrete specimen strongly depends upon storage temperature and humidity as past measurement have shown. Further investigations are planned and will be performed in 1992.

In addition to that large scale in situ-tests in boreholes have been designed. General aim is to determine the permeability of the inserted salt briquettes brickwork versus rock convergence. The layout of the borehole, its backfilling with a salt briquettes brickwork and the planning of necessary instrumentation have been performed.

The third and most important step developing the investigation programme has been done. Analogous to the investigation of the test dam, the procedure for the separate test of the long-term seal was devided into two phases: Test with medium gas first and test with fluids, using saturated brine, second.

A detailed time table for the several steps of testing has been developed; the layout of the instrumentation as well as the devices for pressurization for different measurement methods has been finished. As a result of this planning work figures 5 and 6 show the different cross sections for geotechnical and permeability measurements.

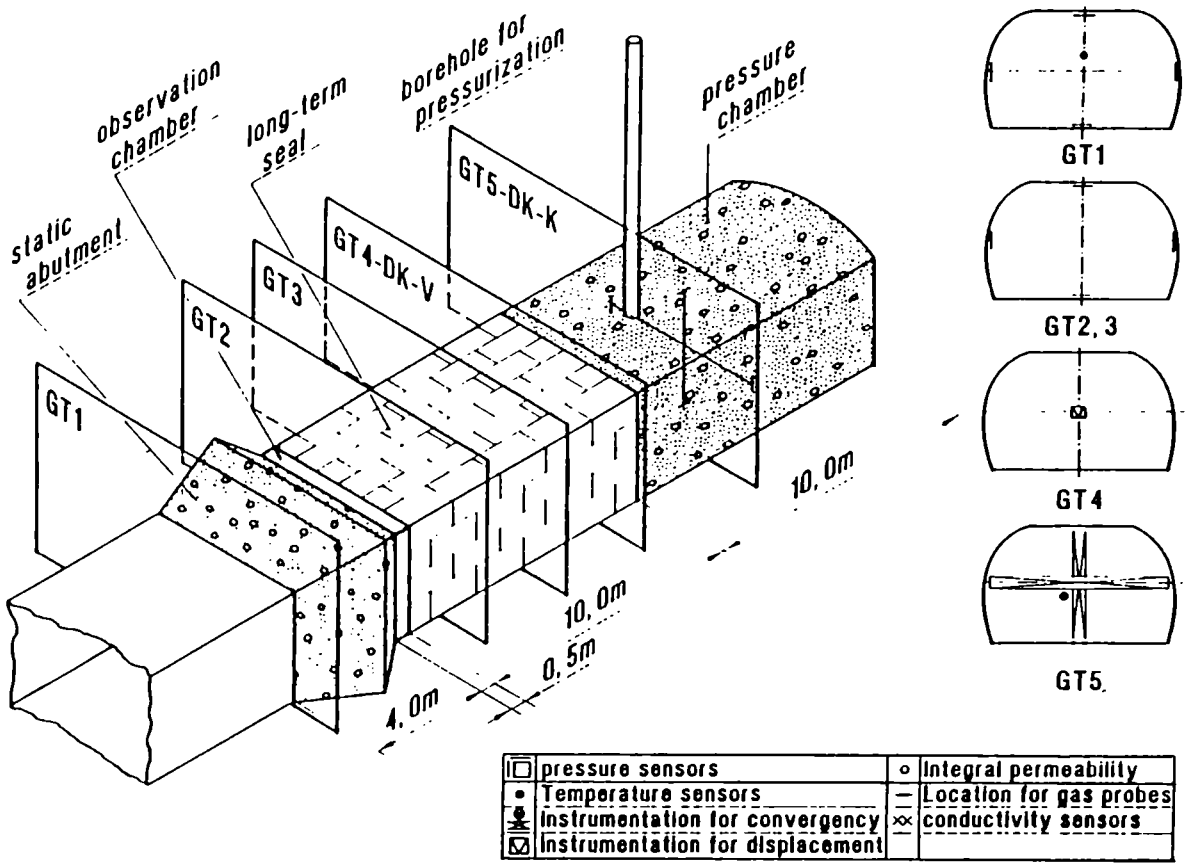

Figure 5: Cross section for geotechnical measurements

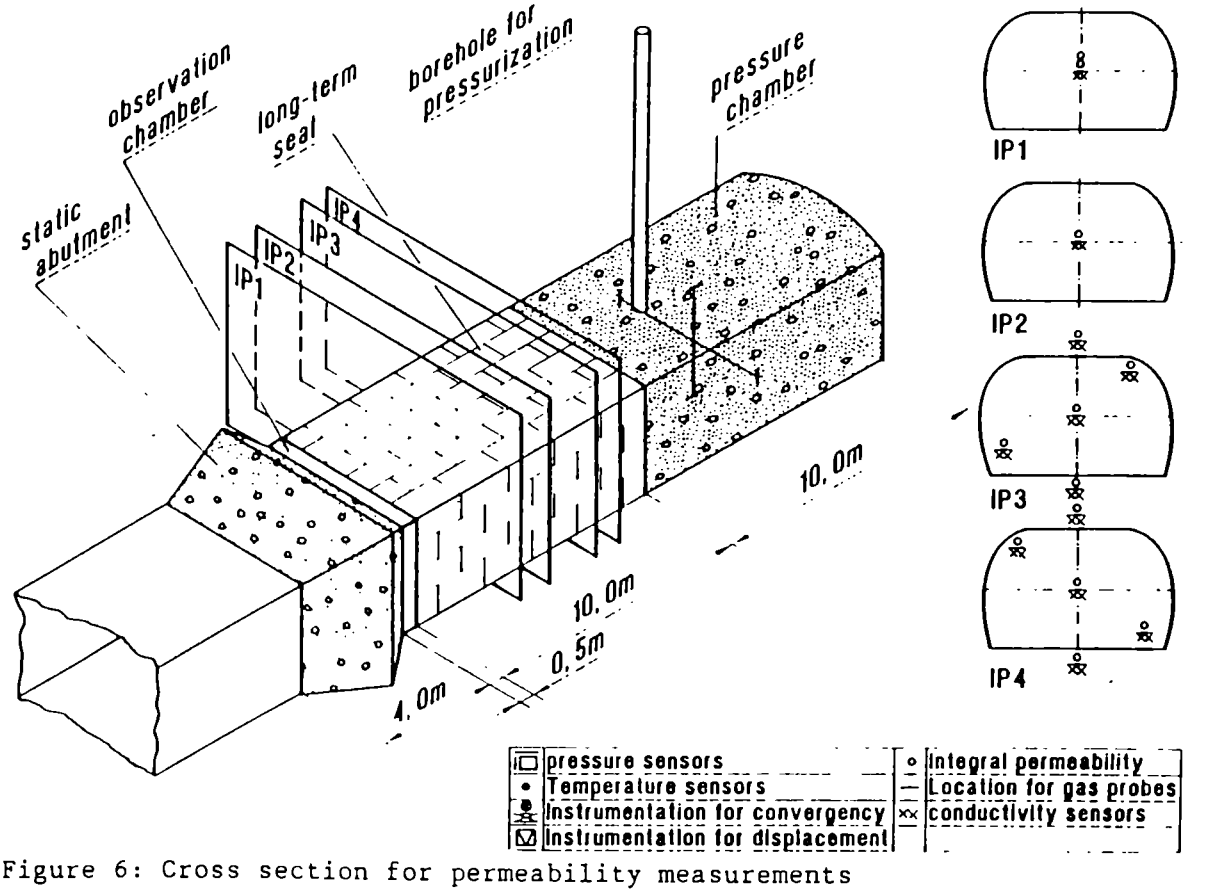

Figure 6: Cross section for permeability measurements

The long-term functionality of the long-term seal must be evaluated and extrapolated beyond the short test period via model calculations /3/. For this purpose the long-term seal was simulated in a flow model in a first step. Using the computer programme ECLIPSE, as a finite-difference-programme, it is expected to calculate various model variants in order to predict the long-term permeability of the long-term seal. Figure 7 gives an impression of the discretization of the test field in the Asse Mine.

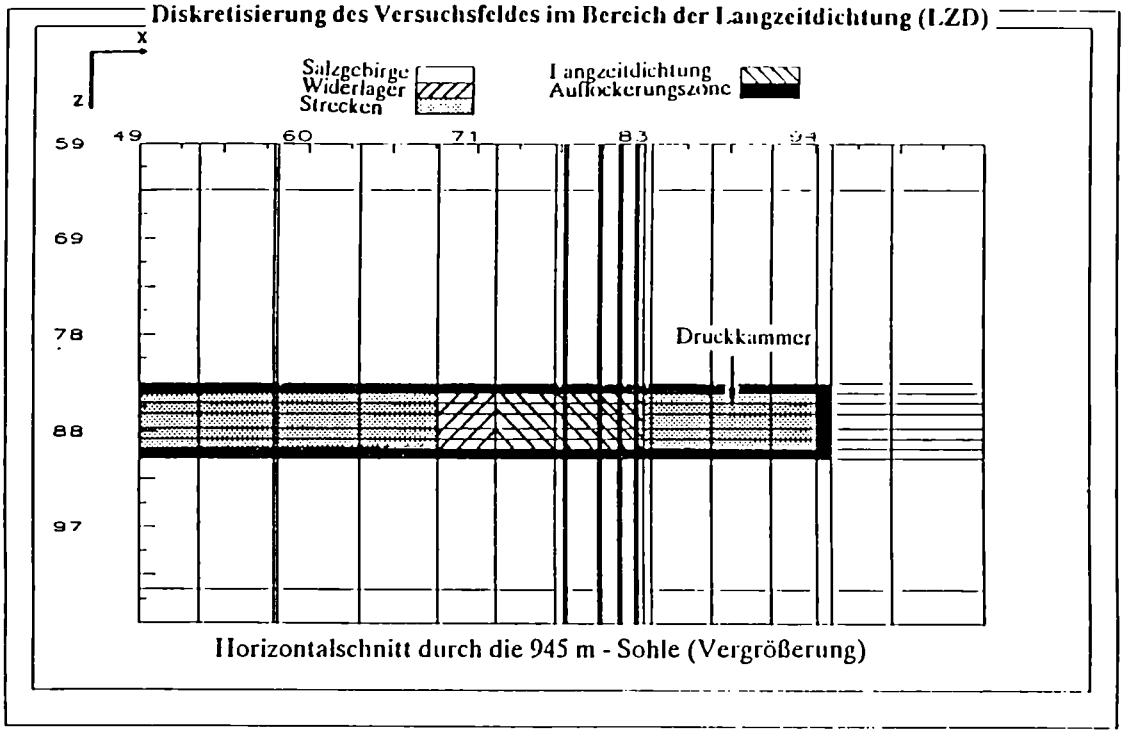

Figure 7: Discretization of the test field in the area of the long-term seal, horizontal section through the 945 m level (Magnification)

2.3 Investigation of the geochemical and petrophysical behaviour of the long-term seal

In order to evaluate and model the evaluation of permeability and porosity for the long-term seal ANDRA is involved in a geochemical and petrophysical investigation programme /4/. The geochemical evaluation is examined on the main components of the long-term seal: rock salt briquettes and salt mortar. Especially dissolution and precepition experiments are performed under the effect of presence of brine. Laboratory as well as a pilot test in the Amelie Mine will be performed.

In 1991 ANDRA concentrated the activities in collecting geochemical data. For this purpose physicochemical and petrophysical characterization of the salt briquettes have been performed. Figures 8 and 9 show in a three-dimensional diagram the result of the chemical analysis of the salt briquette surface and the density distribution of the briquettes.

Besides solubility measurements of the briquettes, laboratory dynamic experiments with laboratory percolation tests through assemblages of briquettes have been designed. In order to prepare the pilot test in the Amelie Mine the design of the test has been finished and the excavating of the test room is going on.

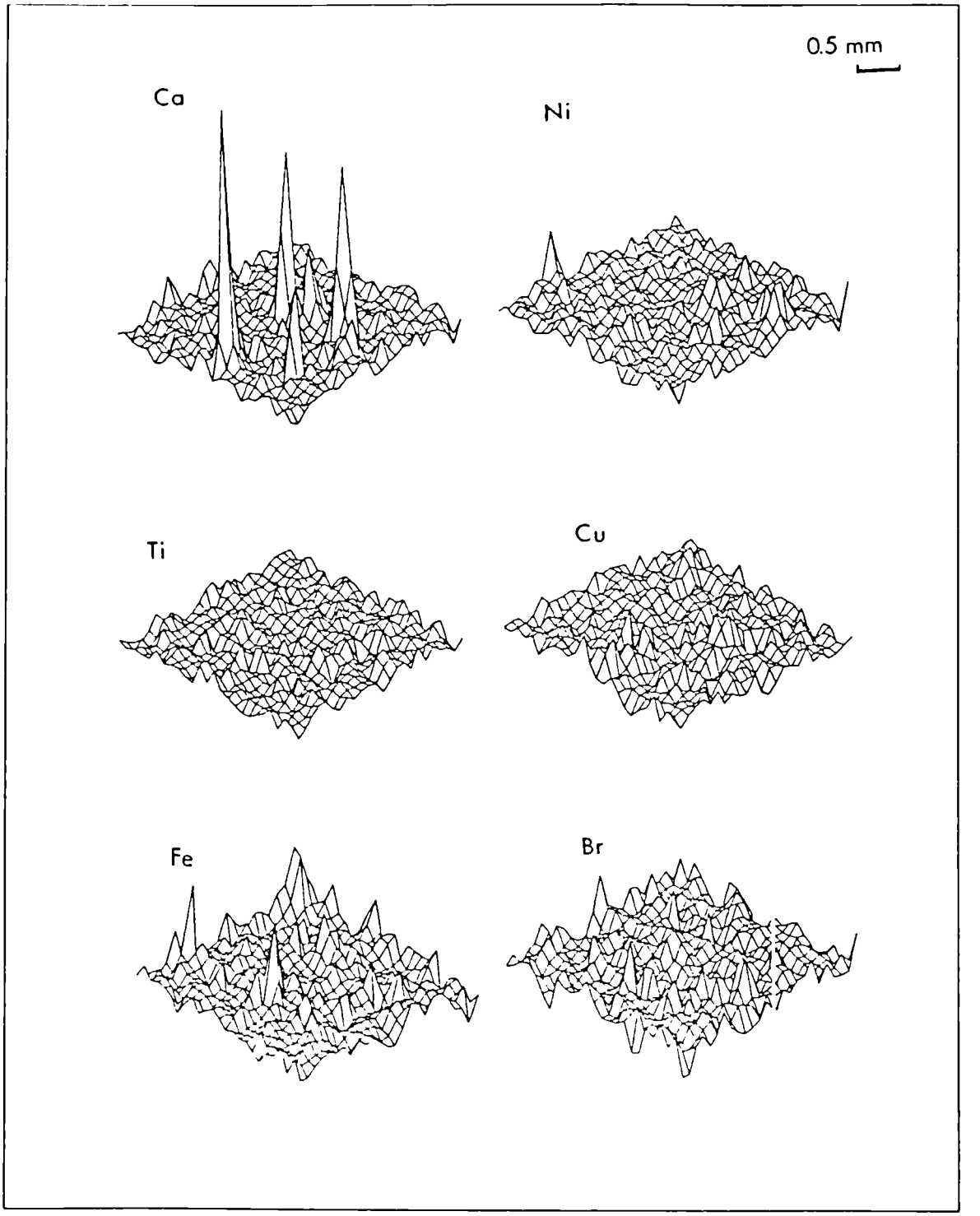

Figure 8: 3 D-Diagram, chemical analysis of a salt briquette surface

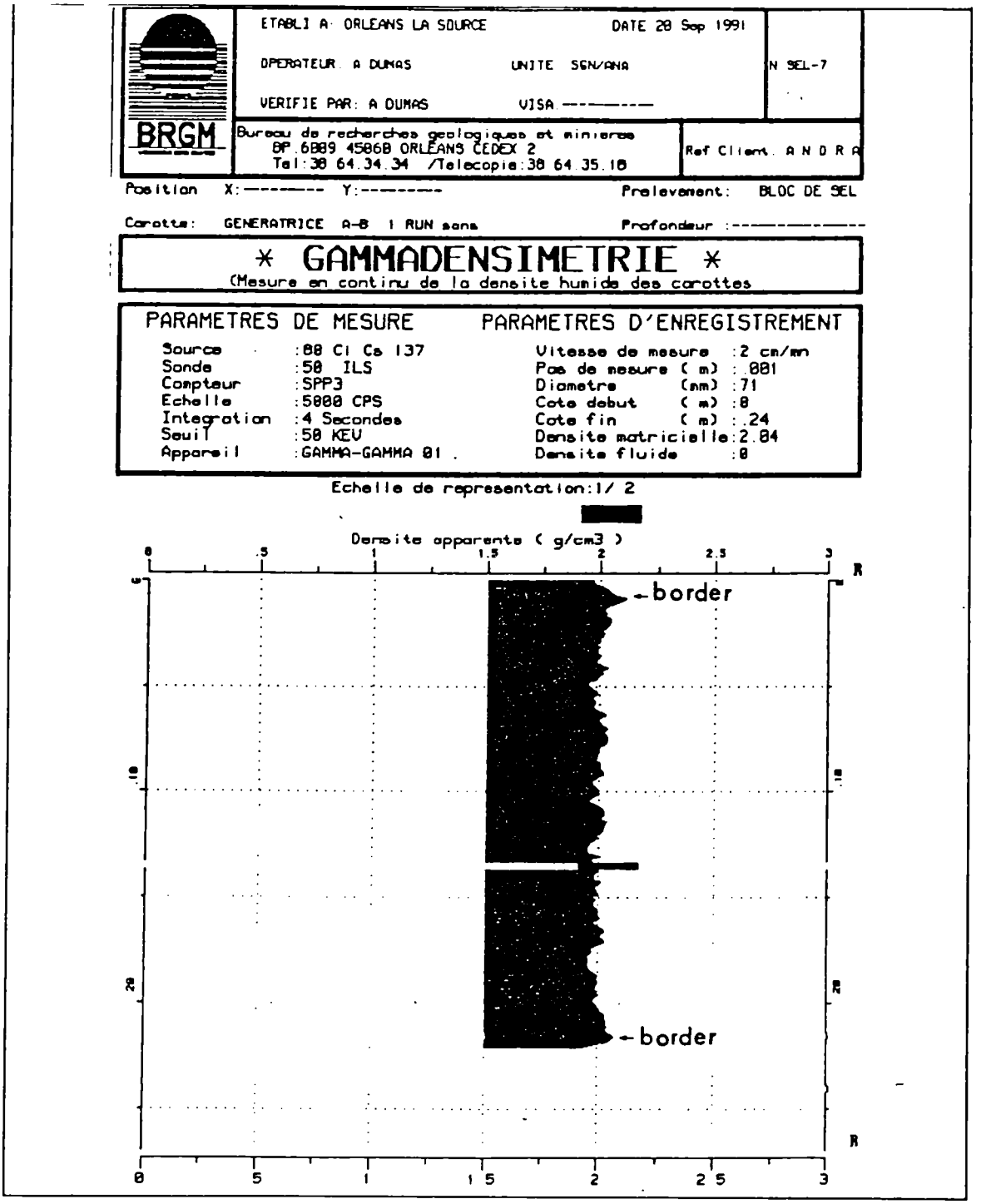

Figure 9: Gamma densimetry measurement of a salt briquette

The general aim of codes calculations in order to model geochemical behaviour is to predict the chemical equilibrium and water-rock interactions in a complex electrolyte solution in the quinary system. In 1991 ANDRA performed an overview of the development on recent geochemical model and on application of thermodynamic codes to the calculation of the saturation indexes of minerals in Amelie Mine brines.

The approaches to model petrophysical characteristics of briquettes assemblages are based on the study of transport properties as permeability and their evolution with reaction advancement. This method requires knowledges and description of geochemical dynamic experiments. Up to now a review on "dissolution of solid and porous materials by fluids" has been achieved and two experiments far from equilibrium were performed in order to enhance free and forced convection phenomena.

2.4 Modelling and validating multiple-phase flow phenomena

The main objective of ENRESA's research program in the context of the investigation of the long-term seal construction is to model and validate the effects of multiple-phase flow through the components of the long-term seal.

In a first step a state-of-the-art review has been performed. As a result it was found that there is not a well-established approach to the simulation of coupled hydromechanical problems in saline media /5/. Hence, fundamental mechanisms have been thoroughly studied so as to provide the basis for the planned laboratory experiments and modelling respectively.

A large number of codes deal with topics strongly related to the hydromechanical behaviour of salts. None of them appears to address precisely all required mechanisms. This implying specific code development leads to preliminary work of mathematical modelling, which is underway.

Activities related to laboratory experiments for determining the brine permeability of rock salt and granular aggregates will begin in 1992.

List of publications

/1/ Bollingerfehr, W., Engelmann, H. J., Stockmann, N., Miehe, R. and Yaramanci, U., 1991, In situ investigation of long-term sealing as a component of a dam construction, In: Proceedings of a Workshop 'Pilot tests on radioactive waste disposal in underground facilities', Braunschweig, 19. - 20. Juni 1991 (in preparation)

/2/ Stockmann, N., Flach, D., Klarr, K., Miehe, R., Schmidt, M. W. and Yaramanci, U., 1991, Das geowissenschaftliche Untersuchungsprogramm für den Dammbau In-situ-Versuch, In: Proceedings zu 'Dammbau im Salzgebirge', Peine 5.-6.12.1990

/3/ Miehe, R., Brewitz, W., Flach, D., Klarr, K., Jockwer, N., Schmidt, W., Stockmann, N. and Yaramanci, U., 1991, Untersuchungen zur Funktionsfähigkeit der Dammbaukomponente Langzeitdichtung, In: Proceedings zu 'Dammbau im Salzgebirge', Peine 5.-6.12.1990

/4/ Ouzounian, et. al., Evaluation and modelling of the long-term evolution of permeability and porosity of a sealing system in a salt environment under the effect of the presence of brine, In: Proceedings of a Workshop 'Pilot tests on radioactive waste disposal in underground facilities', Braunschweig, 19. - 20. Juni 1991 (in preparation)

/5/ Olivella, et. al., Hydromechanical behaviour of saline media, In: Proceedings of a Workshop 'Pilot tests on radioactive waste disposal in underground facilities', Braunschweig, 19. - 20. Juni 1991 (in preparation)

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:	01.04.91 - 31.12.91
Project Coordinator:	K. D. Closs

A. OBJECTIVES AND SCOPE

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

Up to now, items (1) and (2) of the work programme were dealt with. Work started in April 1991 by laying down the boundary conditions for the Monte-Carlo-calculations between DBE and ANDRA/CEA and getting the computer codes run. DBE calculated the neutron dose rates without and with backscattering for the POLLUX-cask in underground drifts for various parameters: fuel length within the cask, drift geometry, cask position within a drift. Moreover, the influence of air on backscattering was investigated. Preliminary calculations on dimensioning the shielding cask to be used later on in the demonstration test in the ASSE mine were also performed. First results were obtained by ANDRA/CEA for the POLLUX-cask for one drift geometry and one cask position. In general, the agreement between the DBE results and the ANDRA/CEA results is satisfactory. Some minor discrepancies still have to be discussed in more detail.

Progress and results

1. BASIC ASSUMPTIONS

The activities up to now mainly concentrated around the POLLUX-cask which was designed in the Federal Republic of Germany for direct disposal of spent fuel. It will be disposed of in drifts of a repository located in a salt dome. Such a cask can hold 8 PWR fuel elements which corresponds to 4.27 t of heavy metal (HM). For calculating the neutron source strength, the following fuel parameters were assumed: initial enrichment 3.6%, burn-up 45 GWd/tHM, cooling time 10 years.

For the DBE calculations, the Monte-Carlo-programme MORSE/SGC-S was used to calculate the dose rate of casks with radioactive sources. The necessary data were taken from the library files EURLIB-IV and VITAMIN-C with 171 neutron groups. Calculations for the dose rate and shielding thickness of a shielding cask with Cf-252 neutron sources were carried out with the programme ANISN.

For the ANDRA/CEA calculations, the neutron dose rate for the POLLUX-cask was calculated using the three dimensional neutral particle transport code TRIPOLI-2. This code solves the Boltzmann equation by a Monte Carlo method which takes into account exactly energetical transfers and anisotropies of collisions. The macroscopic total cross section library ENDF/B4 was used.

The geometry of the POLLUX-model is assumed to be rotation-symmetric and cylindric with several material shells to slightly simplify the complex structure. The model used in the calculations as well as the position of the various detectors for which the calculations were performed is shown in Fig. 1. Zone No 2, for example, represents the spent fuel; zones No 6, 7 and 11 the outer shielding made of nodular cast iron GGG 40.3.

Later on, a demonstration test will be performed in the ASSE mine to compare experimental and calculated neutron dose rates. Since a POLLUX-cask is too large and too heavy to be handled in the ASSE mine, a smaller shielding cask has to be designed which will use a Cf-252 neutron source and which should simulate the actual radiological situation as well as possible. Very preliminary design calculations for the shielding cask

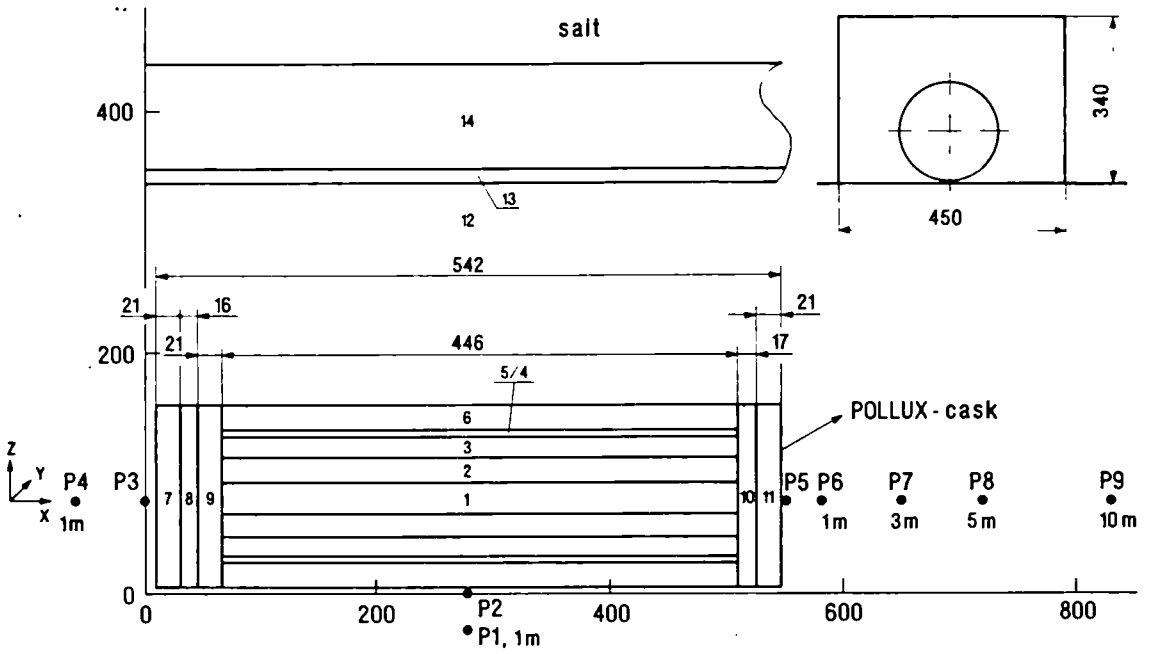

Fig. 1: Geometry of a POLLUX-cask in a disposal drift and detector positions (P1-P9), general lay-out

were performed, using the geometry and materials combination shown in Fig. 2. The overall length was varied between 1.35 and 1.79 m, the length of the line source lq between 0.6 and 1.04 m. Also l_o and l_d were slightly modified for the various calculations.

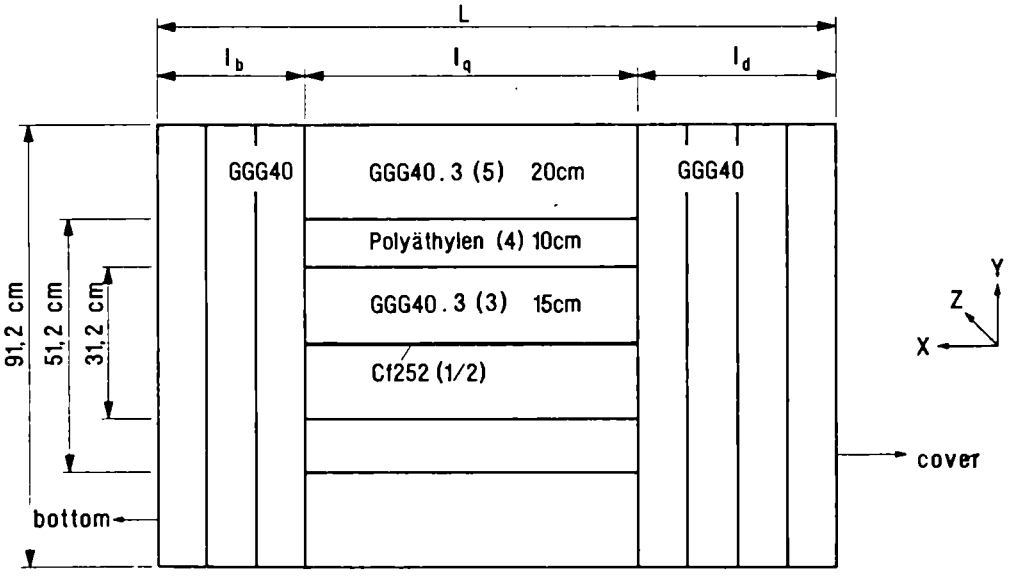

Fig. 2: Shielding cask with a Cf-252 line source

2. RESULTS

2.1 Predimensioning of Shielding Cask with Cf-252 Neutron Source

The neutron dose rates with (Ds) and without (D) salt environment for different cask geometries have been calculated to predimension a shielding cask with appropriate Cf-252-neutron sources which is going to simulate a POLLUX-cask with spent fuel. Preliminary results are shown in Fig. 3.

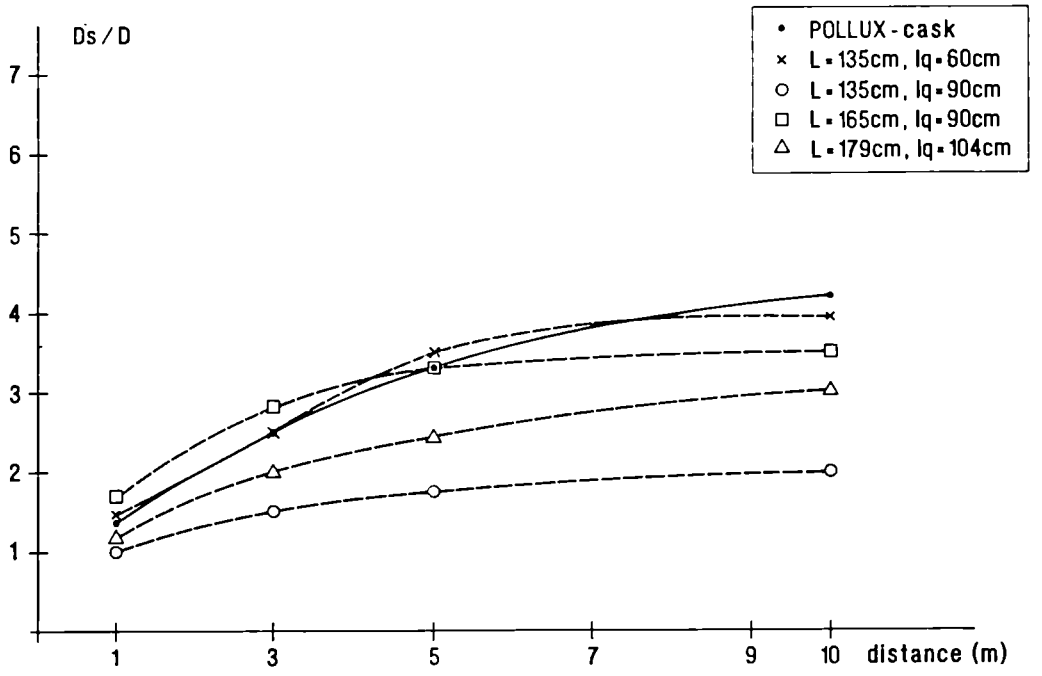

Fig. 3: Neutron dose rate ratios Ds/D for POLLUX- and shielding casks as a function of the distance

As shown in the figure, a shielding cask with a Cf-252-source optimized in cask geometry and source length is capable of simulating the radiation field around a POLLUX-cask very well. More detailed calculations are necessary for designing the shielding cask.

2.2 Influence of air

All preliminary calculations did not take into account the air surrounding a POLLUX-cask within a disposal drift. There were some doubts whether neutron scattering by air might have an influence on the overall result. To estimate the amount of air scattering, two runs were carried out with 10 m and 20 m thickness of air around a POLLUX-cask.

The results are shown in Fig. 4. At a distance of 5 m, for example, the direct neutron dose rate (i.e. without air scattering) is 3.9 µSv/h. Air scattering increases the dose rate to 4.3 µSv/h for 10 m and 20 m thickness of air, respectively. Since the absolute value due to air scattering amounts only to 0.5 µSv/h, which means an increase by only 10%, it was decided not to take into account air scattering for all future calculations.

2.3 POLLUX-cask in drifts

Lying down all details of the POLLUX-cask with respect to geometries, materials, materials composition etc. was an iterative process. The final model for the POLLUX-cask is shown in Fig. 5.

Zone 1, the structural material zone which simulates the compacted fuel assembly hardware contains 321,6 kg stainless steel and 69,8 kg Inconel. The fuel zone 2 is subdivided into an active zone which holds the UO_2 fuel and the Zircaloy cladding and the inactive fuel zone 2 a which

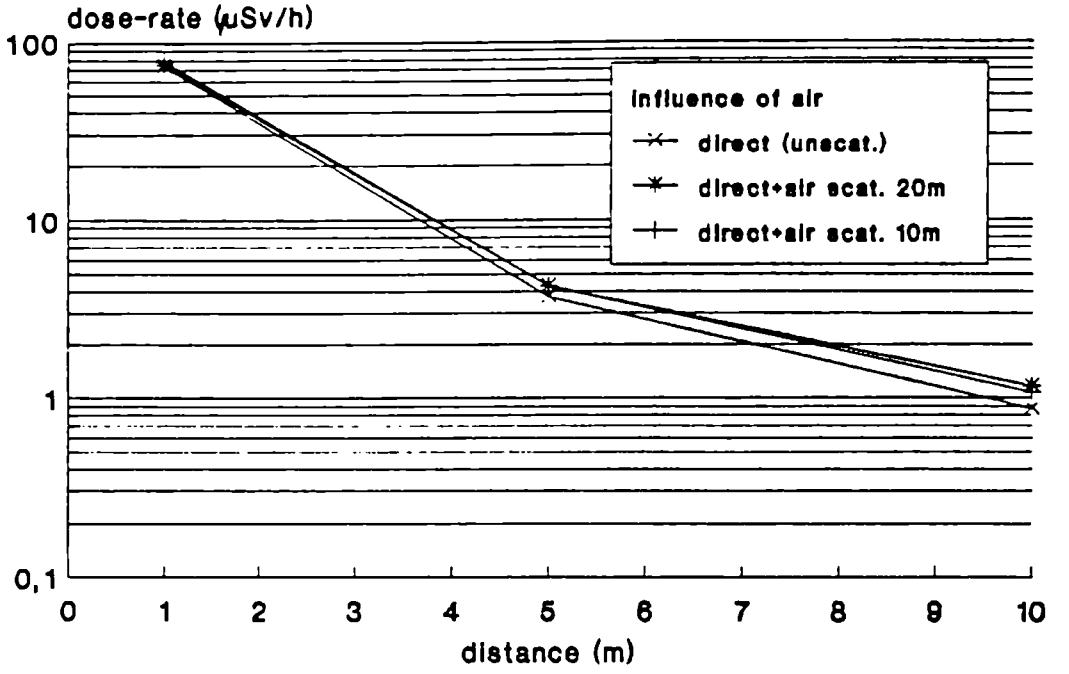

Fig. 4: Influence of air scattering for 10 m and 20 m thickness of air around a POLLUX-cask

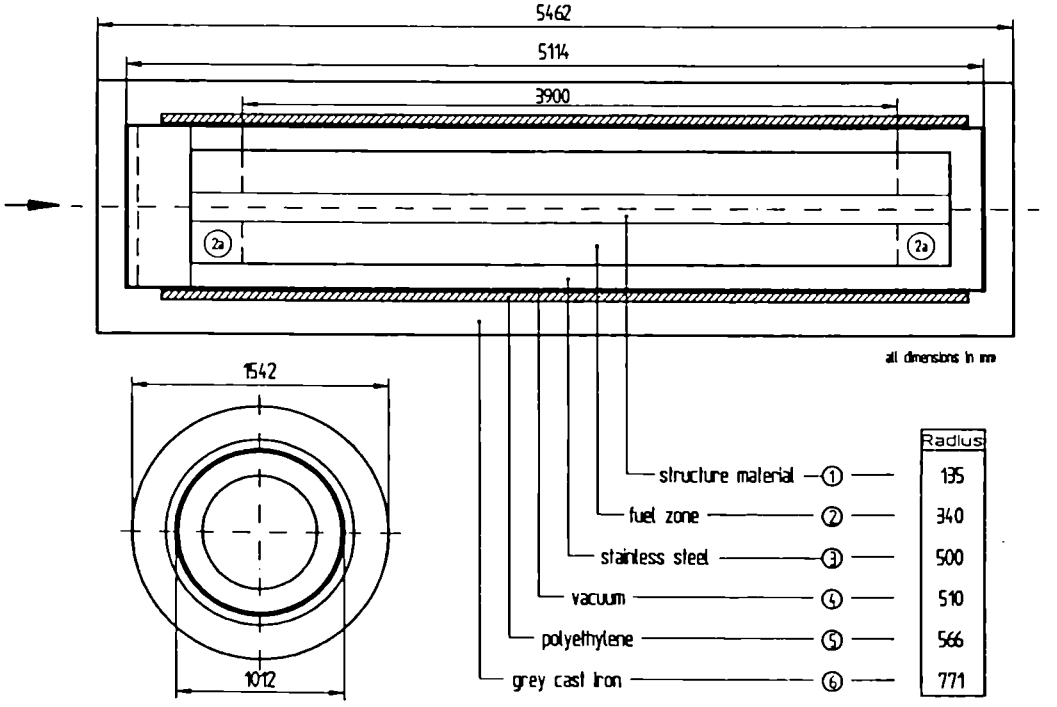

Fig. 5: Final model of POLLUX-geometry

contains only Zircaloy cladding. The stainless steel zone 3 consists of the steel 15 Mn Ni 63, and zone 6 of nodular cast iron GGG 40.3.

The results of the DBE calculations with the final POLLUX-geometry are shown in Fig. 6 and 7 for two drift geometries and two positions of the POLLUX-cask within the drifts. The emplacement drift is 4.5 m wide and 3.7 m high, the transport drift 7.0 m wide and 4.3 m high. As far as the position of the POLLUX-cask within the drifts is concerned, calculations

were performed for the POLLUX-cask lying on the floor of the drift (ground) and positioned at a height of 1.5 m.

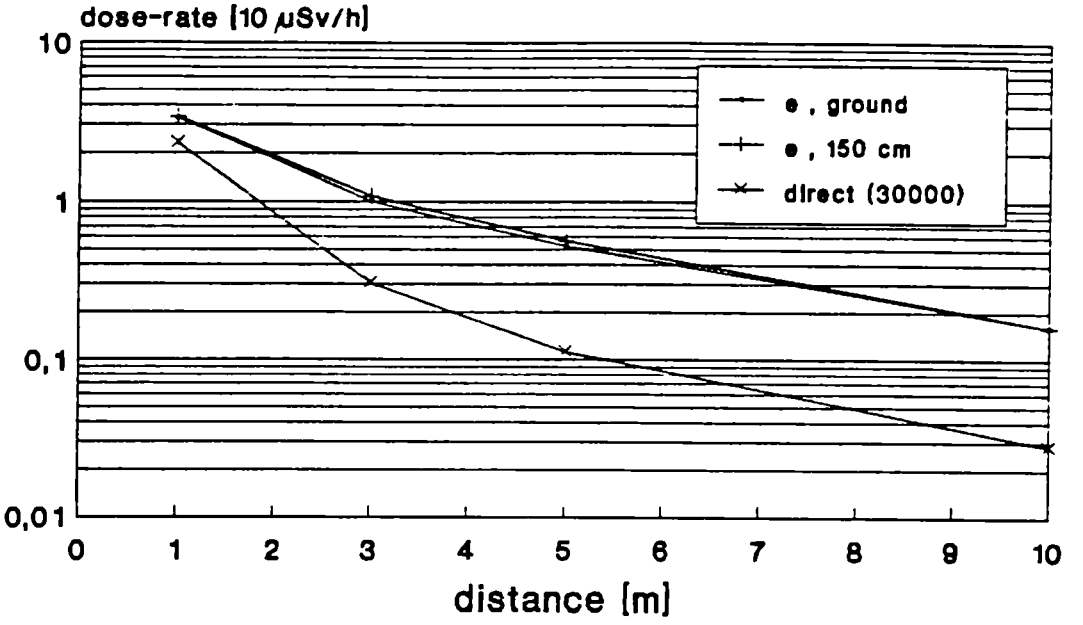

Fig. 6: Dose-rate of the final POLLUX-geometry in the emplacement drift (DBE)

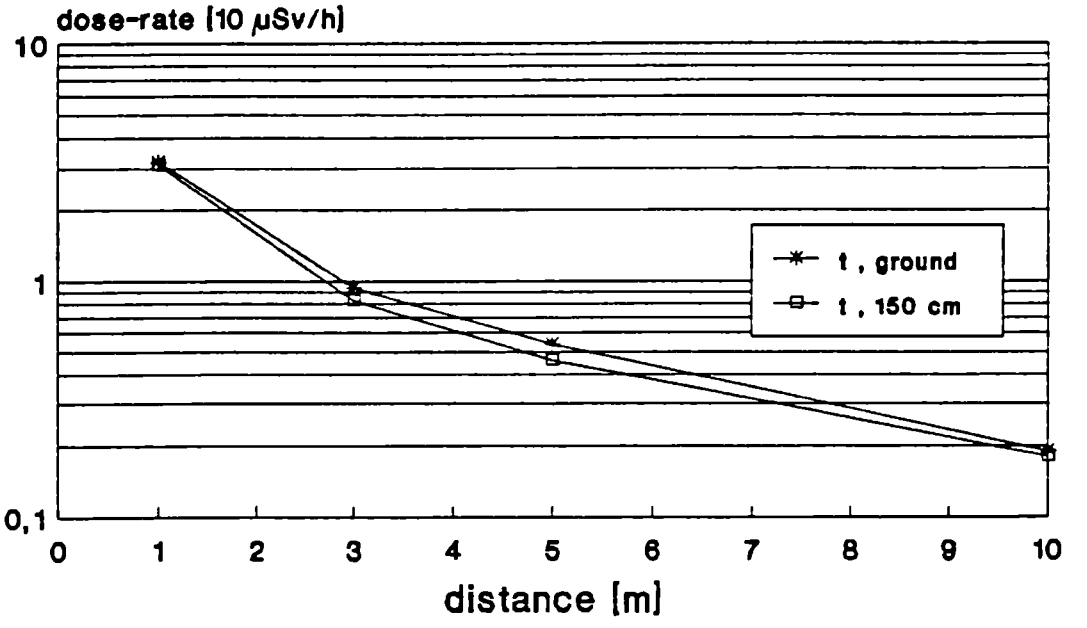

Fig. 7: Dose-rate of the final POLLUX-geometry in the transport drift (DBE)

Discussion of the results have not been finished yet, but it seems, that both parameters, namely drift dimensions and position of the cask within a drift do not have a large influence on the overall result. On the other hand, as can be seen from Fig. 6, the overall neutron dose rate during handling high level waste in a repository might be increased by a factor of 4 to 5 due to neutron backscattering. The number 30.000 in Fig. 6 means that 30.000 neutrons were be treated in the Monte-Carlo run.

ANDRA/CEA performed similar calculations for the POLLUX-cask as DBE, but with only one drift geometry (disposal drift) and one cask position within the drift (1.5 m). Their results are depicted in Fig. 8. The distribution of the dose rate versus the distance ρ of the source can be represented by a function of $1/\rho^2$. The presence of the salt all around the POLLUX-cask and the backscattered neutron phenomena increase the dose rate at some calculation points. Near the POLLUX-cask, in the calculation point P3, the source part is preponderant and the salt has a weak influence. On the radial axis, in the points P1 and P2 (not shown here), the salt has the same weak influence because of the short distance between the cask and the salt wall. On the azimuthal axis, for the points P4 and P´7 to P´9, the part of the backscattered neutrons depends on the calculation point and is the highest five meters further in the Point P ´8. At this calculation point the ratio Ds/D is 9. It is interesting to notice that in the point P 8, the opposite point on the bottom side, this ratio is just 3 because of the higher proportion of direct neutrons. To limit the standard deviation between 10% and 15%, a total of 50000 neutrons (approximately 100 batchs of 500 neutrons) have been simulated for each configuration by ANDRA/CEA.

The absolute value of the neutron dose rates in the ANDRA/CEA calculations are very similar to the DBE calculations. Please note, that points P 4, P'7, P'8 and P'9 in Fig. 8 correspond to 1, 3, 5 and 10 m in Figures 6 and 7. Minor discrepances with respect to the surface neutron dose rate still have to be discussed in more detail.

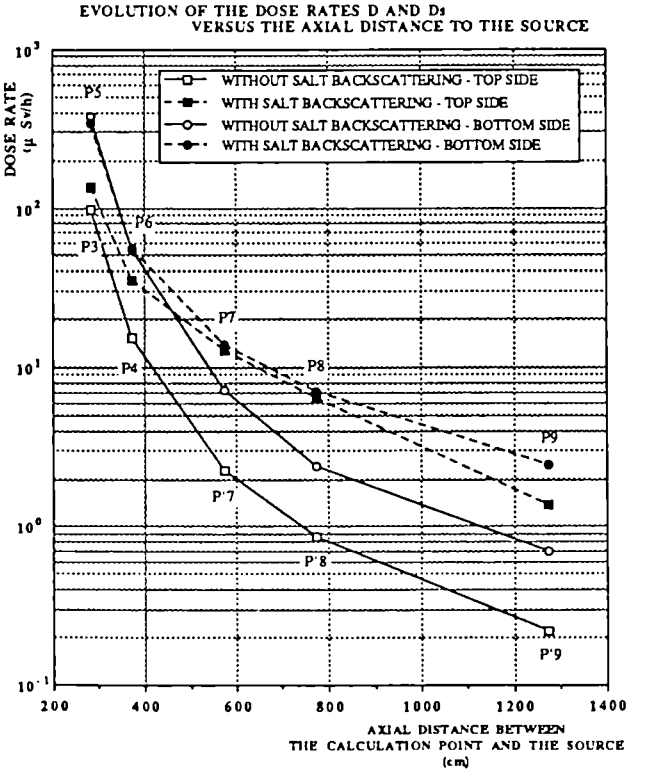

Fig. 8: Evolution of the dose rate D and Ds versus the axial distance to the source

3. CONCLUSION

From the work performed up to now and the first results obtained, the following conclusion may be drawn: The Monte-Carlo programmes used are suited to meet the envisaged objectives for the calculation of scattered and unscattered neutrons. There is a strong dependence between the amplication factor Ds/D and the source distance. A competition between two terms exist: the direct contribution to the total dose rate coming from the POLLUX-cask directly, and the backscattered neutrons contribution coming from reflection phenomena on the drift wall.

List of publications

H.-J.Engelmann, M.Khamis, J.Lempert: „Berechnungen der Neutronendosisleistungen einschließlich der Rückstreuung eines POLLUX-Behälters in den Strecken eines Endlagerbergwerkes". Tagungsband Jahrestagung Kerntechnik 1991, S. 221-224.

M.Khamis, K.D.Closs, J.M.Potier: "The Active Handling Experiment with Neutron Sources (AHE)". EC Workshop on "Pilot Tests on Radioactive Waste Disposal in Underground Facilities", Braunschweig, 19.-21. June 1991.

CHARACTERIZATION OF CLAY UNDER THERMAL LOADING FOR UNDERGROUND STORAGE
(Mol, Belgium)

"CACTUS" PROJECT

Contractor : CEA/ANDRA, Fontenay-aux-roses, France
Contract n°: FI2W-0001-F (CD)
Duration of contract : from september 1990 to march 1993
Project Leaders : M. Raynal, F. Plas, B. Vignal

A. OBJECTIVES AND SCOPE

The aim of CACTUS project is to study near field thermo-hydro-mechanical couplings in deep clay around a borehole waste emplacement, under thermal loading. This is of major importance for predicting the behaviour of radioactive waste storage, particularly as regards the irreversible phenomena due to the effect of heating on stresses and pore pressure. The experiment is planned to include a number of tests conducted in separate boreholes at Mol underground facilities, with identical heating probes but different types of thermal loadings and backfilling materials (Figure 1).

B. WORK PROGRAMME

1. CACTUS ONE : Emplacing of a prototype heater with backfilling material and heating after hydro-mechanical equilibrium. It was planned as a preliminary test.

2. CACTUS TWO : Emplacing of a heater with backfilling material and fast heating.

3. CACTUS THREE : Emplacing of a heater without backfilling material then heating after "creep" and hydro-mechanical equilibrium.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Prototype CACTUS 1 probe was installed in may 1990 then heated in september 1990. During november 1990, the heating was accidentally stopped due to an insulation fault. This electrical problem was solved. Heating restarted in march 1991 and is still going on. It is planned to stop at the beginning of 1992 to obtain two heating-cooling cycles. A third cycle is planned with higher thermal loading.

The CACTUS 1 incident resulted in re-designing the CACTUS 2 probe. The changes increased the cost and manufacturing time. Moreover, the probe body has been damaged during a leak test which delayed the trials. The probe was later successfully completed and CACTUS 2 was set in place in December 1991.

The success of CACTUS 1, which was initially intented as a prototype, and the increase in costs and lead time subsequent to the incidents which occured with CACTUS 1 and CACTUS 2 now compromise the completion of CACTUS 3.

Progress and results

CACTUS 1

The first complete CACTUS 1 heating cycle has greatly contributed to understand the irreversibility of the phenomena caused by the heat loading. Three phases require analysis:

(1) Before heating, the peripheral instrumentation (piezometric equipment, Glötlz cells, temperature probes and gama-neutron apparatus) has made it possible to accurately observe and establish the behaviour of the clay under isothermal conditions. During digging the borehole, a drop in the pore pressures and stresses was particulary observed, i.e hydro-mechanical expansion of the clay. After emplacement of the probe, the pore pressures and stresses re-established a new state of equilibrium as the clay closed around the probe and the backfilling material.

(2) When the probe was heated, the pore pressures immediately increased. This however began to dissipate while the temperatures continued to rise, tending towards a state of initial equilibrium. This is because the Boom clay, of which permeability is very low, first reacts under undrained conditions (Figure 2). The total stresses (radial and orthoradial) increased in correlation.

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. This behaviour may reflect temperature consolidation, well-known in clay environments.

(3) When heating stopped, it was found that the clay did not return to its initial state but remained slightly denser in the vicinity of the probe. The heating would thus have caused irreversible deformations of the clay (Figure 3).

The second heating-cooling cycle now in progress will make it possible to assess the elastic or plastic nature of the behaviour of the clay established after the first cycle.

CACTUS 2

The first results of CACTUS 2 (before heating) would appear to indicate behaviour similar to that of CACTUS 1, but developing more rapidly. This may be partly due to the conditions of emplacement and the properties of the backfilling material, which are slightly different. Finally, it is planned to began heating the probe without waiting for equilibrium to be re-obtained.

Publication

(1) PICARD J.M, 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

References

(1) PICARD J.M. : Essai thermo-hydro-mécanique dans une argile profonde (essai CACTUS), Rapport d'avancement n°1, Commission of the European Communities Mars 1991

(2) PLAS F. : Essai thermo-hydro-mécanique dans une argile profonde (essai CACTUS), Rapport d'avancement n°2, Commission of the European communities Octobre 1991.

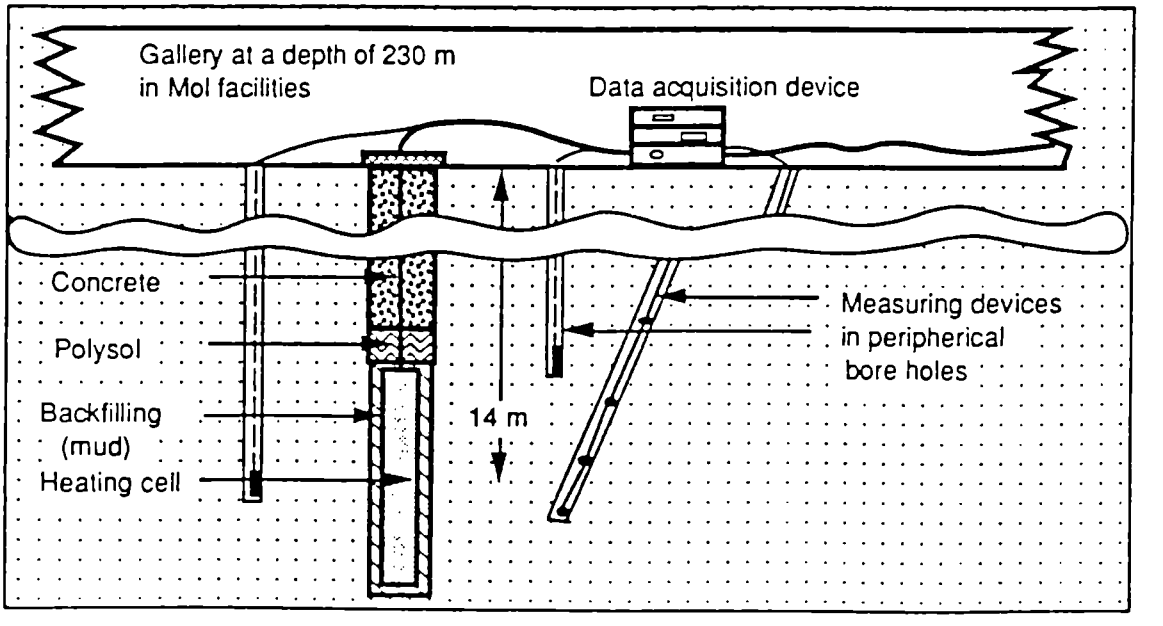

Figure 1 : Sketch map of CACTUS in-situ test

A: borehole digging
Probe emplacement
B: Start of the heating
C: End of the heating

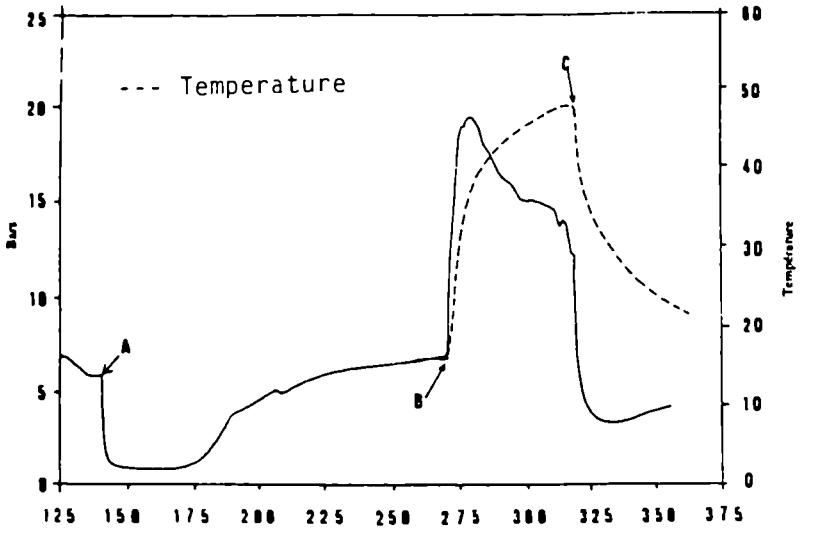

Figure 2 : Exemple of Boom clay pore pressure evolution
(H = 12.6 meters and R = 0.6 meter)

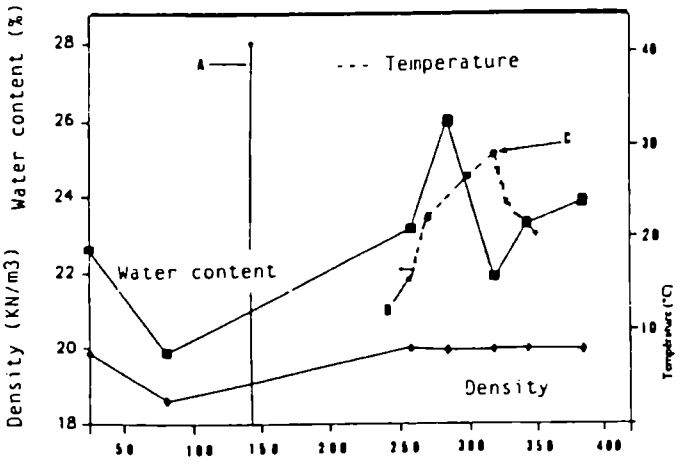

Figure 3 : Evolution of Boom clay water content and density
(H = 15 meters and R = 0.9 meter)

PRELIMINARY DEMONSTRATION TEST FOR DISPOSAL OF HIGH LEVEL RADIOACTIVE WASTE IN CLAY (PRACLAY / CERBERUS / Mine-by-Test)

Contractor : ONDRAF/NIRAS, Brussels, Belgium

Contract N° : FI2W/0003

Duration of contract : 01-07-90 / 31-12-94

Period covered : 01-01-91 / 31-12-91

Project leader : J. Van Miegroet

A. OBJECTIVES AND SCOPE

1. PRACLAY aims at demonstating the constructive and operational soundness of the Belgian Disposal Facility for High Activity Vitrified Waste in the Boom clay layer, 230 m under the surface in North-Belgium with the following four steps :

a) excavate a mini-tunnel similar, except in length, to the contemplated disposal galleries, using the industrial techniques that would have to be dealt with for the full-size repository.
b) erect and support a large connecting chamber of the type needed at the intersection between main and disposal galleries.
c) install and operate a dummy gallery geometrically identical, except in length, to an actual disposal gallery (fig. 1 and 2).
d) monitor the thermal and mechanical behaviour of the clay layer, gallery concrete lining, filling material and metal shroud surrounding the dummy waste.

2. CERBERUS investigates the near-field effects produced by a combined heater and radiation source emplaced in the Boom clay.

3. the Mine-by-Test monitors the short and long term mechanical behaviour of tunnelled structures in Boom clay.

All three tests are being carried-out in the Underground Laboratory operated by the CEN/SCK at Mol (Belgium).

B. WORK PROGRAMME

1. PRACLAY
   - Carry the engineering work needed for detailed design of the experiment
   - Review the multiple experience gathered in the Boom clay with the needed monitoring devices
   - Erect a large connecting chamber
   - Establish the detailed instrumentation program
   - Excavate the mini-gallery and install the equipment (dummy waste, instrumentation, ...)
   - Operate and monitor the experiment
   - Proceed with interpretation of results
2. CERBERUS
   - Follow-up/monitoring of the near-field effects
   - Overall interpretation/evaluation at end of programme
3. Mine-by-Test
   - Follow-up/monitoring of the long term behaviour of the Test Drift and surrounding argillaceaous host rock.

C. PROGRESS OF WORK AND OBTAINED RESULTS

- State of advancement

1) PRACLAY has proceeded along three lines :
   a) design/selection and justification of the demonstration experiment main features
   b) gathering of technical information needed for selection and installation of the monitoring and heating equipment
   c) comparative assessment of the available technologies for excavating the repository galleries and erecting their lining. Extrapolation to PRACLAY.
2) CERBERUS /Mine-by-Test are both in the midst of their operational and monitoring phases.

- Progress and results.

1. PRACLAY

1.1. Design/selection and justification of the demonstration experiment main features

1.1.1. Gallery diameter

Some serious consideration was given, at an early stage of the repository and PRACLAY design phase, to an excavation mode that would have limited the amount of ground work to little more than the external volume of the metal shroud, by relying on the micro-tunneling techniques and associated pipe-jacking methods that have been extensively developed over the last few years.
It has since been concluded that such methods were not likely to succeed in view of the visco-plasticity of the clay material and the rapid convergence it will experience soon after the drilling, under the geostatic pressure prevailing 230 m under the surface. In view of the obvious advantages of the "micro-tunneling" solution (minimal reshuffling of the clay layer ; minimization of the amount of foreign materials and of the subsequent interferences with both waste and clay ; reduced cost), such conclusion is clearly subject to revision if and when sufficient technological progress (with improved low-friction drilling fluids for example) will have been made.
For the time being however - thus for PRACLAY - it has been decided to proceed with a 2 meter wide, concrete-lined tunnel featuring, from centerline to wall, first the protective metal shroud (0.5 m O.D.), then the annular region "rebuilt" with an adequate backfill (fig. 1 and 2).

1.1.2. Thermal design of the experiment

- Objectives

While a broad consensus now exists to consider that the mechanical behaviour of the Boom clay at ambient temperature has been adequately understood and modelled, dealing with a superimposed thermal load is much more of a challenge.
Monitoring the clay layer around PRACLAY wil provide a rare opportunity to better calibrate the calculation tools being developed now. Besides, in view of the critical importance of PRACLAY for the repository safety demonstration, the most severe temperatures to be experienced in the clay over the whole heat-emitting life of the canisters will be simulated.

- Discussion and selection of the thermal features

a) radial limitations

It has been clear since the first days of PRACLAY that the unescapable time-limitations of the project (the most significant results are to be available by the end of the decade) will only permit an approximate simulation of the extreme temperature distribution : the thermal energy supplied to the clay during the heating phase will indeed be restricted to a tiny fraction of the heat generated by the actual waste ; moreover, the experiment life-time will have to be subdivided into one heating and one cool-down phase as both will generate valuable information for the mathematical modelling : as a result, no more than 3 years will be available for the heating phase, limiting thus the region of valid simulation to a narrow annulus behind the concrete lining.

Having in mind, on the other hand, that the material in direct contact with the lining outer face will have been heavily rearranged by the excavation works, it sounds reasonable to keep the first meter of clay out of consideration for a sensible monitoring of the hydro-thermo-mechanical behaviour.

Combining those conflicting requirements, one comes to the conclusion that, with the linear power of the actual canisters (347 w/m), no single region of the clay layer satisfies the requirements for close simulation of the extreme temperature field and sufficient representativity of the monitored material.

It has thus been decided to uprate (by 30 %) the linear power in order to achieve, by the end of the 3 year heating phase, within the first meters beyond the heavily rearranged zone, temperature levels similar to the maxima experienced during the heat-generating life of the actual canisters (table I).

The degree of uprating has been limited to 30 %, in spite of the obvious desirability of an even higher value, to keep the temperatures and temperature gradients of the near-field components (shroud, backfill, concrete lining) from exceeding too significantly their expected maximum values : some amount of overshooting* was however found acceptable, even desirable, in view of the demonstrative capability to be derived from the experiment

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the overshooting also extends to the temperature gradient within the clay inner layers : a degree of water overpressure might thus be anticipated.

Temperature increase in clay (°C)				
Radial distance from gallery centerline (m)	2	3	4	5
- after 1 year	51	35	25	18
- after 2 years	65	49	37	29
- after 3 years	74	57	45	37
- maximum increase to be simulated	69	58	51	45

Table I : Space/time dependence of the temperature distribution within the clay for 30 % upgrading of the linear power (450 w/m - gallery of infinite length).

b) axial limitations

Obvious limitations also affect the representativity of the axial temperature distribution : PRACLAY's limited length indeed generates significant end effects that tend to obscure the global picture : table II lists the temperature increases after 3 years of heating, at 2 meters from the gallery centerline, for various distances from the gallery mid-length and a variety of heating device overall lengths.

Temperature increase in clay (°C)				
Axial distance from mid-length of heating device (m)	0 (mid-length)	5	10	15
heating device overall length :				
10 m	43	27	n.a.	n.a.
20 m	54	50	29	n.a.
30 m	57	56	51	29
infinite	69	69	69	69

Table 3 : temperature increases in the clay, 2 meters from gallery centerline, after 3 years of heating. (linear power = 347 w/m).

End effects are indeed extremely significant over the first five meters of each of the investigated configurations ; the next five meters are also affected, however to a much lesser extent. It has therefore been decided to install a 20 meter long heating device, the central 10 meters of which will supply the information needed for the validation of the mathematical models.

c) Conclusions

Based on the above discussion, a number of "thermal" features of the PRACLAY experiment have been selected as follows :

- Linear power : 450 w/m (30 % more than in the disposal facility)
- Heating length : 20 m (with a 10 m central region featuring a "flat" temperature profile)
- Distance from main gallery to heat source front end : 5 m
- Total length of the test gallery : 30 m
- Heating phase : 3 years, cool-down : 2 years

Moreover, the vast majority of the instrumentation to be installed in the clay will operate in the so-called "monitored region", a 10 meter long, 2 meter thick clay annulus, centered on the gallery centerline, between the 2 and 4 meter radii.

1.1.3. Backfill

Based on an extensive analysis of the state-of-the art, the following conclusions have been reached, for the near-field shielding of heat-emitting waste :

a) the following properties are considered important :
   - extensive knowledgeability of material ("familiarity")
   - high swelling capacity for the sealing of voids
   - low compressibility
   - low permeability
   - simple and inexpensive technical methods for preparation and application
   - low corrosion potential on the waste and its immediate environment
   - sufficient thermal conductivity
b) smectite-rich argillaceous materials, with their high swelling potential, are seen as very promising
c) dry, precompacted blocks of sand/bentonite are expected to satisfy the above criteria.

1.2. Gathering of technical information needed for selection and installation of the monitoring and heating equipment

The need to keep the PRACLAY monitoring system reliably operational for a number of years develops into a set of very severe requirements for the measuring devices upon which such monitoring will have to rely : it was thus found appropriate to first carry an extensive investigation of the nature, type, main features, installation and operational problems associated, for a number of in-situ experiments bearing some similarity with PRACLAY, with the various types of instrumentation that come into consideration for the planned demonstration. Such screening was carried-out by the Mol Nuclear Research Center (CEN/SCK) and has resulted in a report whose conclusions are being used to select, on a preliminary basis, the

most promising equipments, some of which will be further tested in lab and/or in situ. A similar effort was devoted to the screening/selection of the heating devices. Both reports have been made available as part of the Jan 1 - June 30, 1991 Progress Report.

1.3. Comparative assessment of the available technologies for excavating the repository galleries and erecting their lining. Extrapolation to PRACLAY

In reference to the stated objective of the PRACLAY demonstration i.e. to make use, as much as praticable, of the very same industrial techniques that would be dealt with for the full-size repository, the first part of the comparative assessment carried-out by the engineering offices of TRACTEBEL S.A. was devoted to identification of those "industrial" techniques, by successively focussing on

- lining installation procedure (segment erection vs pipe-jacking)
- excavation rate
- needed overdrilling
- magnitude of the unsupported length in front of the lining
- lining stiffness
- lining material
- life-time of the lining
- design of gallery crossings.

Among the most important conclusions :

- pipe-jacking is not practicable in view of the major friction forces developing on the pipe from the yielding clay
- excavation rate should not be less than 2 meter/day while higher rates do not yield significant advantages
- some amount (min 1 cm) of radial overdrilling is recommended
- unsupported length at gallery front end should not exceed 1 meter.

In a second step, several modes of construction of the PRACLAY gallery featuring, within the limits allowed by the Underground Facility, a variable degree of conformity toward the optimum identified for the repository, have been investigated in cooperation with a couple of commercial Organisations active in this field : some of them display an attractively high degree of representativity allowing for close simulation of, a.o. lining design, lining emplacement, digging mode, crossing support structure and erection mode. The analysis ends up with a series of recommendations for an optimized location and mode of construction of the PRACLAY gallery incorporating most of the features that need to be demonstrated for the final repository.

2. CERBERUS

The combined heater (2 x 370 watt) and radiation source (Co-source producing 300 Gy/h) is in operation since 1989 and simulates the effects of a Cogema HLW-canister after 50 years of cooling time.

The monitoring programme centers on measurement of :

- the radiation level, with an ionisation chamber and $CaSO_4$/LiF dosimeters (once a month) ;
- temperature (measurement frequency based on temperature variations) ;
- in situ permeability coefficient (once every 3 months) ;

- total stress and pore-water pressure (measurement frequency based on pressure variations) ;
- the pH/Eh and detection of radiolysis effects in the near-field (presence of radiolysis products like H_2, O_2 and H_2O_2).

The code validation effort and other interpretations deal with
- the computer model DOSEGEO : radiation and dose-rate measurements performed in the near-field of the test ;
- the heat transfer model MPGSTN : temperature measurements and heat transfer parameters before and after the heat and radiation treatment ;
- the hydraulic field evolution to link the hydrological changes (fractures ...) to the shifts in radiation intensity and temperature ;
- the mathematical interpretation of the total and interstitial pressures with the code TEMPPRES : relation between the temperature and induced effective stress ;
- the pH and Eh measurements.

3. Mine-by-Test

Periodic measurements (manual and automated) are being performed on an array of measuring devices and sensors, viz. 6 piezometers nests ; 5 pore pressure sensors ; 34 load cells ; 42 total pressure cells ; convergence measurements in 7 rings and at the front ; topographic and triangulation campaigns.

- List of publications

1. The PRACLAY project
J. Van Miegroet (ONDRAF/NIRAS)
Workshop on "Pilot Tests on Radioactive Waste Disposal in Underground Facilities"
Braunschweig (Germany) June 19-21, 1991
2. The HADES project - Ten years of civil engineering practice in a plastic clay formation
D. De Bruyn, B. Neerdael (CEN/SCK)
Proc. Internat. Conf. on Civil Engineering in the Nuclear Industry
Windermere (UK), 20-21 March 1991
3. The HADES project at Mol ; Geomechanical behaviour of Boom clay
B. Neerdael, D. De Bruyn, R. Mair, R. Taylor
Workshop on "Pilot Tests on Radioactive Waste Disposal in Underground Facilities"
Braunschweig (Germany) June 19-21, 1991
4. The CERBERUS test
L. Noynaert, G. Volckaert, P. Meynendonckx, R. Beaufays, A. Fonteyne (CEN/SCK)
Workshop on "Pilot Tests on Radioactive Waste Disposal in Underground Facilities"
Braunschweig (Germany) June 19-21, 1991

FINAL ARRANGEMENT OF DISPOSAL GALLERY (AXIAL LAYOUT)

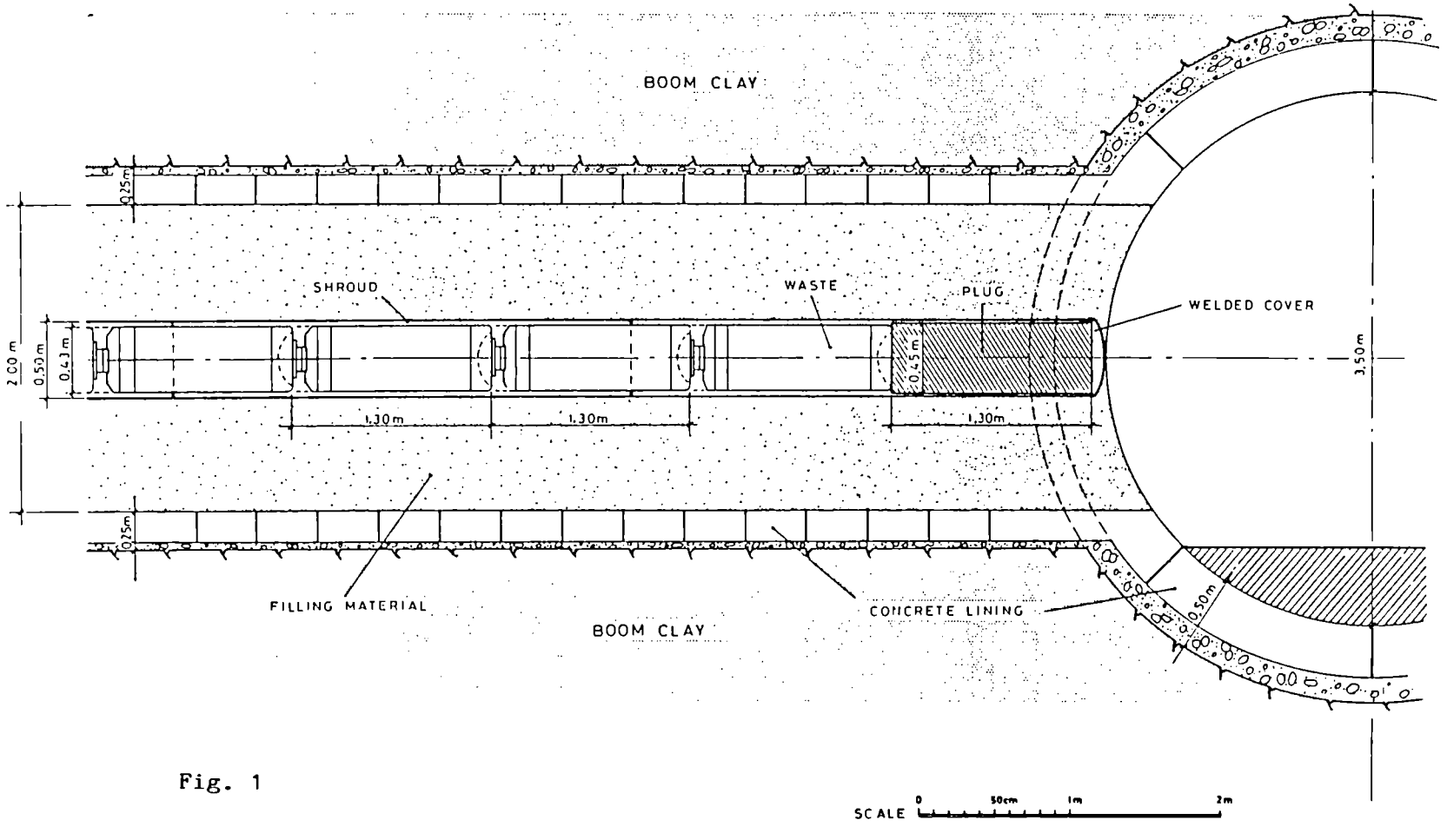

Fig. 1

FINAL ARRANGEMENT OF DISPOSAL GALLERY (CROSS-SECTION)

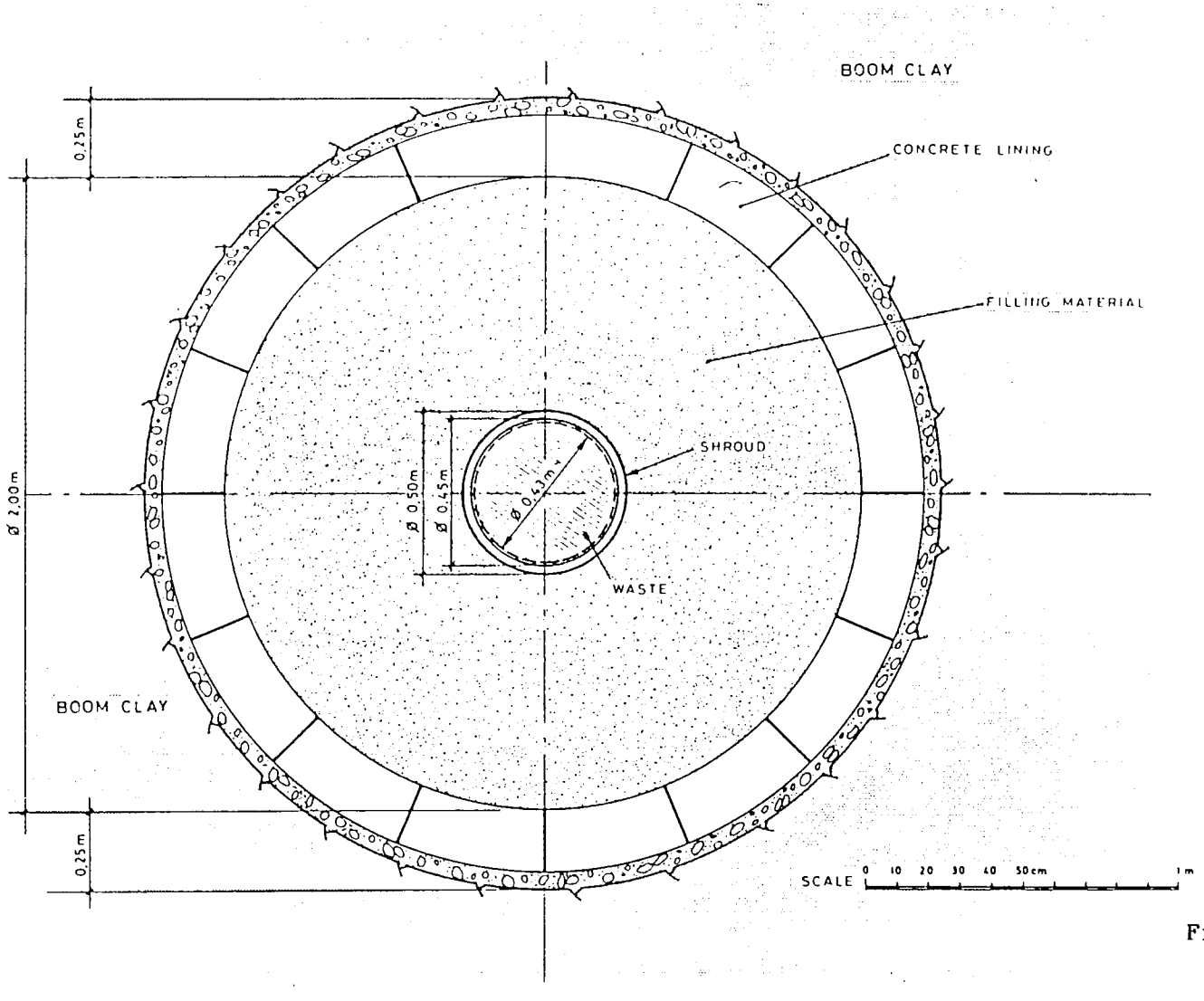

Fig. 2

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 :	01-01-91 / 31-12-91
Project leaders :	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 in 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 consists in on measurement of :

- dose-rate;
- temperature;
- pore water pressure;
- total stress;
- pH/Eh;
- radiolysis effects.

The codes involved in the validation trials are :

- the DOSEGEO model which allows to compute the dose-rate around a shielded γ source;
- the heat transfer model MPGSTN;
- the thermo-hydro-mechanical model TEMPPRES.

Investigations on thermal and hydraulic conductivities are also foreseen.

C. *PROGRESS OF WORK AND RESULTS OBTAINED*

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. $CaSo_4$: Dy , LiF and perspex dosimeters were also used. The values measured are compared with the results obtained with the DOSEGEO model.
The main results are :

- the values measured using the ionisation chamber are in good agreement with the computed ones;
- a good agreement also exists with the $CaSo_4$: Dy dosimeters for dose-rates of max. 125 Gy/h;
- at dose-rates greater than 125 Gy/h, the $CaSo_4$: Dy dosimeters measurements systematically differ from the results obtained by the ionisation chamber and the DOSEGEO model (more than 20 %);
- the perspex dosimeters values are 3 times the expected ones, probably indicating a calibration problem;
- the LiF dosimeters results are not reproducible;
- no modification of the attenuation of the γ radiation can be observed as a function of time.

* thermal field

The results are that :

- in the CERBERUS near field, the thermal conductivity reaches 1.6 W/m°C and the thermal diffusivity 25.0 m^2/y;
- for the temperature range investigated, 16 - 120 °C, the heat transfer parameters remain constant;
- the temperature at all thermocouples and Pt100 probes can be simulated with 5 % maximum error by using the MPGSTN code.

* hydrological field

- the pore water pressures are very sensitive to any temperature variation;
- the raise of pore water pressure can generate cracks, as one can conclude from the following table, comparing the value of the hydraulic conductivity measured before and during the heating phase of the test for the screens PSW3002 and PSE2742 :

Sensor	T_0 (°C)	k_0 (E-12 m/s)	T_t (°C)	k_t (E-12 m/s)	k_t/k_0 obs.	k_t/k_0 cal.
PSS2742	16.5	2.40	50	4.26	1.78	1.93
PSE2742	16.5	2.53	82	10.50	4.20	2.86
PSE3262	16.5	(3.74)	80	8.07	(2.17)	2.80
PSW3002	16.5	2.25	92	11.20	5.06	3.15

* thermo-hydro-mechanical field

  - the first simulation using the TEMPPRES model and the best available parameters for the behaviour of the Boom clay at high temperature was performed. It indicates that the general trends of the pore water pressure evolution can be reproduced, but the maximum value occurs later and the pore-water pressure is generally overestimated in the simulation.

* chemical field

  - the system used up to now, to perform the pH and Eh measurements has been modified in order to reach the equilibrium in a shorter time so as to perform the measurements at a higher frequency;
  - the following phenomena have been observed *in situ* :
    the Ph decreases from 8.5 to 6.4;
    the Eh still remains reducing (-202 mV versus SHE);
    the conductivity decreases from 2790 to 2244 µS.cm;
    decrease of the total number of anions and cations;
    decrease of SO_4^{2-} and Na^+;
    increase of K^+ and Cl^- (KCl bridge);
    increase of Si and B (due to clay or electrodes).

* list of publications

The CERBERUS Test
L. Noynaert, G. Volckaert, P. Meynendonckx, R. Beaufays, A. Fonteyne
Workshop on "Pilot Tests on Radioactive Waste Disposal in Underground Facilities"
Braunschweig (Germany) June 19-21,1991

MINE BY TEST

Title :	Mine by Test
Contractor :	ONDRAF/NIRAS, Brussels, Belgium
Contract N° :	FI2W/0003
Duration of contract :	01-07-90 / 31-12-94
Period covered :	01-01-91 / 31-12-91
Project leaders :	ONDRAF/NIRAS : J. Van Miegroet
	CEN/SCK : B. Neerdael, D. De Bruyn

A. OBJECTIVES AND SCOPE

Follow-up and monitoring of the long term behaviour of the concrete lined part, also called *Test Drift*, of the HADES Underground Research Facility, of its terminal shotcreted front and of the surrounding clay mass.

B. WORK PROGRAMME

Manual and automated measurements are performed systematically and periodically on :

- one settlingmeter and one inclinometer device installed above the *Test Drift* before the construction phase;
- 6 piezometer nests, 5 pore water pressure cells and one multiple point extensometer in the clay mass around the *Test Drift*;
- 34 load cells between concrete liners and 42 total pressure cells imbedded in these liners;
- diametrical convergence measurements of 7 instrumented rings;
- one multiple point extensometer installed from the end front and 15 reflectors installed on its shotcreted cover support.

Validity and reliability of the measurements are assured. Analyses of the collected data are interpreted by way of simple elasto-plastic models.

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 around the *Test Drift* show a slow stabilization of the measurements :

- inclinometer and settlingmeter measurements, which aimed to monitor displacements during the construction and immediately afterwards, were definitely stopped in 1989;
- total pressure on the lining ranges from 1.6 to 2.3 MPa (from load cells measurements);
- the lining average convergence amounts 1.1 %;
- after 4 years, the shotcreted end front has been displaced over the free margin without support between the end cask and the last concrete rings. Fracturing in the shotcreted shell is observed now.

Comparison between pressure and deformation on the different measuring sections show a good agreement of the convergence - confinement curves; an average lining stiffness of 200 MPa is deduced, corresponding to an equivalent lining elasticity modulus of about 700 MPa.

Comparison between direct measurements of the lining pressure (by way of pressure cells) and calculated ones (from load cells measurements) show that pressure cells measurements are systematically lower than those of the load cells (from 40 to 65 %), but that the pressure build up is similar.

Measurements of the displacements in the clay mass above the *Test Drift* (settlingmeter and inclinometer devices installed before construction) were compared to those, at the same distance of the gallery axis, of the extensometer installed during the construction : the delayed convergence (the displacement after installation of the lining, measured by the second device) is only a small part (from 5 to 8 %) of the total one. This is confirmed by the comparison between the clay wall displacement (inferred from the first type of devices) and the lining diametrical convergence.

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 : July 1991 - December 1991

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 the ongoing corrosion experiments.
2. Design, construction and installation of the new corrosion loops.
3. Overcoring and retrieval of the different tubes at due time.
4. Analysis of the metallic and waste form samples and of the surrounding clay-core.

C. PROGRESS OF WORK AND OBTAINED RESULTS

State of advancement

Tube n° 1 was overcored in September '91 and the different samples (metallic, waste forms and surrounding clay) were prepared for analysis.
The mass losses of the samples of tube n° 4, which was retrieved in November '90, were determined. Samples were prepared for the different surface analyses, which are currently in progress.
The concept of tubes 5b and 10 was revised and adapted to avoid problems of water accumulation in the tubes. The construction of both new tubes is finished. Tube 5b will be installed before mid '92 and tube 10 before end '92.

Progress and results

Tube n° 1 (installed October '85 ; 170 °C ; type 1, i.e. all samples are in direct contact with the clay) was overcored and retrieved in September '91. The unforeseen presence of old freezing tubes, which were emplaced during the excavation of the gallery, caused problems during overcoring. The clay core surrounding the C-steel samples was lost during the first overcoring effort.
The metallic samples (C-steel, ferritic and austenitic steel, Ni- and Ti-alloys) and the waste form samples (glasses, concretes) were ultrasonically cleaned and prepared for mass loss determination and surface analyses. Analyses by SEM-EDXA and EMPA on both types of samples are currently in progress.
The clay core surrounding the studied samples was sampled and the elemental analysis of the clay samples will be carried out in the near future.

Tube n° 4 (installed October '85 ; 13 °C ; type 1) was overcored and retrieved in November 1990.
Mass losses of the different samples were determined. The results for the waste form samples of tubes 1 and 4 are summarized in Table I. The main observation for the tests at ambient temperature is the complete absence of corrosion for most samples. In most cases even a minor weight gain is observed, indicating the formation of precipitates on the sample surfaces. The data at 170 °C on the other hand show very large corrosion of the samples, in so far that some of them were desintegrated.
The mass loss results for the metallic samples are given in Table II.
These data show that only C-steel corrodes at measurable rates. The average corrosion rate at clay temperature is about 4 times lower than at 90 °C (7.68 ± 0.45 um.j^{-1}). However, there is virtually no further increase of the average corrosion rate between 90 °C and 170 °C (8.59 ± 0.86 um.j^{-1}). The mass losses for all the other metallic samples are within or just above the accuracy limits of the experimental method.

Two additional tubes have been constructed. Tube 5b will be installed during the first half of '92. Tube 5b (type 2 ; i.e. all samples are in contact with Boom clay water saturated atmosphere) will be operated at 90 °C. Due to previous difficulties with the type 2 tubes (water accumulation caused overloading of the heating devices) the new tube 5b will be equiped with a semi-automatic He gas flow system to continuously remove the accumulated water. The design and construction of the new type 2 tube and the gas flow system were finished and they can be installed in the first half of '92. Before this, it is planned to test the gas flow system on an empty tube for about 2 months.
Tube 10 (type 3 ; i.e. part of the samples is in direct clay contact and the other part is in a concrete atmosphere) has also been constructed together with a gas flow system. The same testing procedure as for tube 5b will be applied to this system. The installation of tube 10 is foreseen late '92.

Table I Mass losses for the waste forms after in situ exposure at either 13 °C (tube 4, 5 years) or 170 °C (tube 1, 5 years)

Waste form		Mass loss ($g.m^{-2}$)	
		13 °C ; 5 years	170 °C ; 5 years
Glasses	SON 68	- 3	2435
	SON 58	54	disintegrated
	SON 64	7	disintegrated
	SAN 60	- 16	1063
	SM 58	0.3	disintegrated
	SM 513	3	177
	UK 209	- 7	1772
Glass ceramic			
	SAN 60 (700 °C ; 10 days)	- 11	1139
	SM 58 (800 °C ; 10 days)	136	3280
	C31.EC	- 8	not measurable*
TRUW candidate			
	FLK 77	38	- 201
	UWG 124	14	not measurable*
Glasses in contact with metallics			
	SON 68 / C-steel	- 36	not measurable*
	- / Hastelloy	- 19	not measurable*
	- / Ti	- 22	not measurable*
	SAN 60 / C-steel	- 41	- 78
	- / Hastelloy	- 24	not measurable*
	- / Ti	- 7	- 21
	SM 58 / C-steel	- 53	- 413
	- / Hastelloy	- 26	- 24
	- / Ti	- 26	- 27
Concretes			
	CPA 55	- 111	not measurable*
	gallery lining	23	not measurable*

Samples were covered with a sticky fixed clay layer

Table II Relative mass losses after chemical etching and average overall corrossion rates of canister/overpack materials exposed in situ in direct contact with clay

Tube 4, 13 °C, 5 years

Material	Mass loss (10^{-1} g.m^{-2})	Corrosion rate (um.y^{-1})
C-steel	742 ± 635	1.89 ± 1.62
Ferritic steel		
1803 MOT	6.9 ± 1.7	0.02 ± 0.0
Austenitic steel		
AISI 316	1.3 ± 4.0	0.0 ± 0.01
UHB 904 L	4.2 ± 9.2	0.01 ± 0.03
Inconel 625	0.3 ± 1.2	0.0
Hastelloy C4	- 13.8 ± 2.3	0.0
Ti/0.2 Pd	6.9 ± 10.6	0.03 ± 0.06
IMI 115	10.3 ± 6.4	0.05 ± 0.03

Tube 1, 170 °C, 5 years

Material	Mass loss (10^{-1} g.m^{-2})	Corrosion rate (um.y^{-1})
C-steel	3235.5 ± 325.1	8.59 ± 0.86
Ferritic steel		
1803 MOT	57.1 ± 11.8	0.15 ± 0.04
Austenitic steel		
AISI 316	5.1 ± 7.2	0.01 ± 0.02
UHB 904 L	- 10.2 ± 2.6	- 0.03 ± 0.01
Inconel 625	- 25.6 ± 1.2	- 0.06 ± 0.00
Hastelloy C4	- 32.2 ± 7.9	- 0.08 ± 0.02
Ti/0.2 Pd	- 33.7 ± 6.3*	- 0.15 ± 0.03*
IMI 115	- 17.6 ± 9.0	- 0.08 ± 0.04

* Samples possibly wrongly identified

ANNEX: List of organisms and companies participating in the programme during 1991

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(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
BATTELLE	BATTELLE Institut e.V. Am Römerhof 35 D-6000 FRANKFURT-am-MAIN
BERTIN & CIE	Bertin & Cie Centre de Bayonne Z.I. F-40220 TARNOS
BGS	British Geological Survey Kingsley Dunham Centre UK-KEYWORTH, NOTTINGHAM NG12 5GG

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
ELECTROWATT	Electrowatt Engineering Service Ltd. UK-Brandford BD1
ENEA-Casaccia	Ente per le Nuove tecnologie, l'Energia e l'Ambiente CRE-Casaccia Via Anguillarese 301 I-00060 S. MARIA di GALLERIA
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
GCG	Geotechnical Consulting Group Ltd Queensberry Place 1a UK-LONDON SW7 2DL
GEODESIGN	Geodesign S.A. Rue Pierre d'Aspelt 7 L-1142 LUXEMBOURG
GEOSTOCK	Soc. Française de Stockages Géologiques Geostock Rue Eugène et Arnaud Peugeot 7 F-92563 RUEIL-MALMAISON Cédex
GESSS	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
GRS	Gesellschaft für Reaktorsicherheit mbH Schwertnergasse 1 D-5000 KOELN 1
GSF-IfT	GSF-Forschungszentrum für Umvelt und Gesundheit GmbH Institut für Tieflagerung Theodor Heuss-Straße 4 D-3300 BRAUNSCHWEIG
IA	INTERATOM GmbH Friederich-Ebert Straße D-5060 BERGISCH GLADBACH 1
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
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
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
MBT	Halesa-MBT SAE Parc Tecnológic del Valles E-08290 CERDANYOLA
McAvoy Bayley	McAvoy Bayley 36 Grosvenor Gardens UK-LONDON SW1W OEB

NERI	National Environment Research Institute DK-4000 ROSKILDE
NRPB	National Radiological Protection Board Chilton, Didcot UK-OXFORDSHIRE OX11 ORQ
NUCLECO	NUCLECO Società per l'Ecoingegneria Nucleare SpA Via Anguillarese 301 I-00060 ROMA
NUKEM	NUKEM GmbH Postfach 1313 D-8755 ALZENAU
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
SGN	Société Générale pour les Techniques Nouvelles S.A. Rue des Herons 1, Montigny le Bretonneux F-78182 ST. QUENTIN EN YVELINES Cédex
SIEMENS (KWU)	Siemens AG - KWU P.O. Box 1001 00 D-5060 BERGISCH GLADBACH 1
SIFBACHY	Soc. Sondages Injections Forages de Bachy Rue Ste Claire Deville-lez-Colonnades 4 F-92563 RUEIL-MALMAISON
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