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INSTITUTE FOR
TRANSURANIUM
ELEMENTS

ACTIVITY REPORT
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Institute for Transuranium Elements (ITU)

The mission of ITU is to protect the European citizen against risks associated with the handling and storage of highly radioactive elements. ITU's prime objectives are to serve as a reference centre for basic actinide research, to contribute to an effective safety and safeguards system for the nuclear fuel cycle, and to study technological and medical applications of transuranium elements.

Institute for Transuranium Elements

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

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Institute for Transuranium Elements

Activity Report
2002

Institute for Transuranium Elements

Foreword

2002 was the last year of the Framework Programme 5. Towards the end of the year we were busy with extensive preparations for the new Framework Programme 6 starting in 2003. A distinctive feature of this new programme is the major emphasis on the enlargement to include the Candidate Countries in the EU.

Challenges for the Institute in the future are to further enhance its scientific excellence and reputation, to develop its competence in the nuclear fuel cycle and address nuclear energy and related issues, and to open our doors for the many scientists and engineers in the Candidate Countries to work with us and participate in making a true European Research Area.

The increasing importance worldwide of developing sensitive analytical techniques in the nuclear field is underlined by this year's review article "Recent advance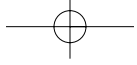s in analytical methods of safeguarding nuclear material". ITU's competence in this domain is well recognised and has been high-lighted by a number of features in the year 2002; for example, the success-ful exercise at the Turkish-Bulgarian border with regard to the smuggling of nuclear material.

The inauguration of the minor actinide laboratory (in Sept. 2002) allows ITU to play an important and unique role in Europe's efforts in partitioning and transmutation. The long-term aim of such programmes is to reduce the radiotoxicity of nuclear waste from tens of thousands of years to hundreds of years. Important progress has been made with the pyrochemical separa-tion of Am from the lanthanides, as described in a Highlight. Other High-lights describe the simulation of radiolysis effects in "old" spent fuel and the very high natural transmutation level in an aged curium oxide sample.

Many other highlights of the year's activities, including just a sampling of our many visitors, are described in the following sections. Two efforts resulted in being recognised in the Best Papers category at the JRC Award ceremony in December 2002. First, the observation (in collaboration with university of Jena) of photofission in thorium using an ultra-high-power laser. Second, the discovery (in collaboration with Los Alamos National Laboratory) of superconductivity in a series of plutonium compounds. Both these breakthroughs open fascinating fields of study, and underline the intellectual interest in this part of the periodic table.

I thank all the Institute staff for another successful year, and look forward to more exciting developments in 2003 as we start the 6th Framework Programme.

Finally, it is a great pleasure on behalf of all the staff to thank my predecessor, Roland Schenkel – now JRC Deputy-Director General in Brussels – for all his hard work in 2002 and for many years prior to that for ITU.

Gerard Lander
Director

Scientific Objectives

In the frame of the FP5 EURATOM programme and in line with its mission, the Institute for Transuranium Elements responds to the concerns of the European citizens by performing customer driven research and basic and exploratory research related to its core competences. The research areas in 2002 are described briefly below.

Management of spent nuclear fuel and highly active nuclear waste

The two approaches for spent nuclear fuel management favoured by the Member States of the European Union are studied at ITU:

– intermediate storage with subsequent conditioning for final disposal and
– intermediate storage with subsequent reprocessing before final disposal in geological formations.

The behaviour of irradiated fuel under conditions of direct long-term disposal requires further investigation with regard to the basic processes involved. Safety relevant data on the corrosion and dissolution behaviour of waste under realistic conditions and over a time period of 60-200 years are of utmost importance to determine the radiotoxic potential and assess the consequences of storage over extended periods of time.

The lowering of the radiotoxicity of highly active waste by reducing the quantity of actinides and other long-lived radioactive elements is another objective addressed in this research programme.

ITU is developing a partitioning and transmutation programme in close cooperation with its European, Japanese and US partners. The first goal of this activity is to define and experimentally assess the advanced reprocessing methods for commercial fuels of the first stratum, and both aqueous and pyrometallurgical partitioning techniques for fuels and targets for actinide transmutation in the multi-recycling strategy.

The second goal of this activity is to define and characterise the most suitable materials for transmutation of transuranium elements, in order to assess the technical feasibility of P&T. This objective requires further investigation on the manufacturing of fuels and targets for irradiation testing, and their material properties, including their reprocessing ability.

The third, technically connected, objective of this programme is to define, fabricate and characterise matrices for the conditioning and long-term storage (up to their final disposal) of minor actinides and long-lived fission products.

Safety of nuclear fuel

Due to the extended use of nuclear fuel in existing reactors, ITU studies the behaviour of nuclear fuels under high burn-up or accident conditions. Data-bases are needed on the properties for UO_2 (at burn-up >100 GWd/t) and MOX (at burn-up > 50 GWd/t) such as: high-temperature thermophysical properties, melting point behaviour of high burn-up fuel and corium, high temperature mechanical properties, swelling and gas release under transient conditions, RIM effect investigations, etc. This contributes to a better use of energy resources, and to an overall reduction of nuclear waste and transport requirements.

Modelling is an integral part of safety studies and ITU maintains and develops the TRANSURANUS fuel perform-

ance code. This code is presently extended with new data for MOX and UO_2 at high burn-up and in transient conditions. Training of users is a very important task and special attention is given to scientists from Candidate Countries. Through participation in PHEBUS, the reactor meltdown simulation project, ITU gains new insights into the behaviour of melted fuel rod bundles and of aerosol deposits in the primary circuit.

ITU contributes also to the development and use of advanced fuels in order to improve fuel safety and reduce civil and military stockpiles of plutonium.

Nuclear safeguards and non-proliferation

Preventing proliferation of nuclear material is a world-wide task shared by the European Commission's Euratom and the International Atomic Energy Agency (IAEA) inspectorates. They are responsible for implementing safeguards measures to control the use of nuclear materials within the European Union and world-wide.
As a long-time partner, ITU continues to provide analytical assistance and expertise on plutonium handling facilities, such as reprocessing or MOX fuel fabrication plants. As the Commission's Analytical Reference Laboratory in safeguards, ITU develops new analytical tools to analyse and characterise different nuclear materials. ITU fulfilled its commitment for designing and installing an *in-situ* laboratory for safeguards measurements and continues to operate the On-Site Laboratory at BNFL's Sellafield reprocessing plant and the Laboratoire sur Site at Cogema's La Hague plant.

ITU is closely involved in the international efforts to detect clandestine

activities and to combat the illicit trafficking of nuclear materials. ITU's activities in this area are co-ordinated through participation in the P-8 International Technical Working Group. Together with IAEA, ITU contributes to the development and implementation of a model action plan for the seizure of nuclear material in the future Member States of the European Union. The ITU nuclear materials databank is continuously extended by integrating data received from industry in the Member States, from Russia, Ukraine and from Candidate Countries.

In the areas of illicit trafficking of nuclear materials, illicit waste dumping and environmental impact of radioactive releases ITU improves the selectivity, sensitivity and accuracy of detection and measurement methods to better identify the origin of the materials.

Radioactivity in the environment

There is a need for validated analytical methods dedicated to traces and ultratraces of actinide elements in environmental samples. ITU is developing analytical methodology for isotopic determination of actinides in particles (fission tracks) to provide the scientific community, dealing with radioactivity in the environment, with the necessary assessed analytical protocols. Special attention is given to the development of separation and preconcentration techniques for improving the limits of determination of actinide elements in various matrices. This research is carried out in collaboration with institutional research centres and universities from Members States and Candidate Countries.

Maintaining and acquiring competence in basic actinide research

Any technological problem solving or improvement process requires a thorough understanding of the basic phenomena. Typically an evolution from macroscopic to meso- and microscopic investigation is required and a coupling between the different disciplines and scales of research within one institute is of vital importance.

ITU scientists aim at developing an understanding of these properties, including the electronic structure of actinides and actinide compounds and four major research topics are developed:

Preparation and characterization of actinide elements and compounds: Concerning fuel cycle safety actinide research contributes to the basic understanding by the structural studies of actinide compounds in both, polycrystalline and single crystals forms. ITU activity aims at providing these materials for both internal and external "customers".

Material Science: Present systems (safety, optimisation of lifetime and burn-up), future systems (new concepts and new processes), fuel behaviour under irradiation, intermediate storage, long-term storage, targets for transmutation, waste management, etc require material science data on actinides and actinide-containing products. ITU scientists aim at developing a profound understanding of thermophysical and thermodynamic properties of refractory nuclear materials.

Investigation of the solid state physics of actinides: From a theoretical point of view, expanding the knowledge on 5f elements is a task of ITU as these elements possess magnetic and superconductive properties not expected using the description of f orbitals derived from the properties of 4f (lanthanides) elements.

Surface and Interface Science of Actinide materials: Many processes in the nuclear fuel cycle are dependent on the behaviour of actinide elements in different chemical and physical forms. Of particular interest are phenomena at the interface (fuel-cladding interactions, lixiviation of spent fuel in intermediate or final disposal…). Therefore tailor-made thin films, clusters of atoms or multi-layers of actinides are studied at ITU.

With the creation of the *Actinide User Laboratory*, ITU supports the scientific community by giving access to its facilities to host scientists. Particular attention is given to training the next generation of scientists, especially those from Member States and Candidates Countries, which lack nuclear installations suitable for training.

Health and nuclear medicine

As a consequence of the Institute's experience in radiochemistry in general and radionuclide separation in particular, quality controlled, safe and reliable separation techniques have been developed for the isolation of specific radionuclides, for application in nuclear medicine. The high interest in the cancer-cell killing potential of such radionuclides (when coupled to specific targeting carriers) caused ITU to embark on dedicated production processes for such radioisotopes, the development of high performance radionuclide generators and on the efficient chelation of the compounds. ITU also continues to support the execution of clinical trials with these products and fosters the ability for widespread use of such new therapeutical treatment (known as alpha-immunotherapy).

Highlights 2002

Discovery of Superconductivity in Plutonium-Based Compounds

In 1911, the Dutch scientist Heike Kamerlingh-Onnes discovered superconductivity in the simple metal mercury [1]. It took more than 50 years until a theory could be established to explain the basic properties of this new thermodynamic state (BCS-theory). Its main ingredients are the pairing of charge carriers with opposite spin and momentum (Cooper pairs) below the transition temperature T_c into the superconducting state, the opening of an excitation gap in the band density of states and the Meissner effect, i.e., the superconductors' ability to expel an externally applied magnetic field from its interior. Superconductivity still is one of the most fascinating phenomena in solid-state physics.

During the past two decades, solid-state physics has evolved in a climate of discovery in which many of the fundamental rules are questioned by materials with unexpected properties. These "emergent properties", such as high-temperature superconductivity [2], heavy fermion superconductors [3], the coexistence of magnetism and superconductivity [4], etc, arise in complex materials in which electrons develop different states of organisation and correlation. Many of these unusual electronic ground states are encountered in f-electron materials, and are linked to the idea of hybridisation between the f and ligand electron states. How these properties evolve with the progressive filling of the 5f-shells remains an open question, but a key feature for their understanding. However, until recently, no equivalent compounds with transuranium elements were known.

Recently, Los Alamos National Laboratory and ITU-Karlsruhe reported in a joint paper the discovery of superconductivity above 18K in plutonium based compounds, i.e. $PuCoGa_5$ single crystals [5]. This new compound displays evidence for bulk superconductivity as illustrated in Fig. 1. Furthermore at this same temperature, a step-like transition in heat capacity is observed, from which we infer a γ (a measure of the conduction electron contribution to the low-temperature heat capacity) of 77 mJ/mol-K^2. This value of γ is enhanced relative to that expected for normal metals and is suggestive of heavy fermion behavior. More surprisingly, an unexpected large value of the upper critical field H_{c2} was inferred from field-dependent resistivity data yielding an estimated upper critical field of 740 kOe. The rather high transition temperature (for a metallic system) and the corresponding large upper critical field observed would make this material of tech-

Fig. 1 *Evidence of bulk superconductivity in $PuCoGa_5$ as observed by magnetic susceptibility and resistivity measurements. A transition to zero resistance, coincident with full-shielding diamagnetism, is observed near 18.2 K.*

nological importance for applied superconductivity (to be compared with e.g. Nb_3Ge, $T_c = 23.1K$, $H_{c2} = 230$ kOe), if it did not contain plutonium.

From these data, one is led to the conclusion that the superconductivity in $PuCoGa_5$ may be unconventional. In such a scenario, the nearly order-of-magnitude-higher T_c compared to that of rare-earth [6] analogous compounds would be attributable to increased hybridisation consistent with predictions for models of magnetically mediated superconductivity.

This discovery is complemented with the observation of similar properties in another Pu-compound of the same type, $PuRhGa_5$ obtained at ITU [7], with slightly lower critical parameters. As shown in Fig. 2, the $PuRhGa_5$ undergoes a transition into superconducting state around 8.6 K. A relatively large value of the upper critical field of 210 kOe was also inferred from resistivity measurements in an applied field.

$PuCoGa_5$ and $PuRhGa_5$ are two new Pu-based superconducting compounds with critical temperatures above 18 K and 8 K, respectively. The two compounds display very similar properties of type-II like superconductors. They provide the first series of superconducting compounds found in transuranium based compounds and are a noticeable advance in solid-state physics. We suggest that the mechanism of superconductivity is unconventional. As a result, the transuranics may represent a promising field for supercon-
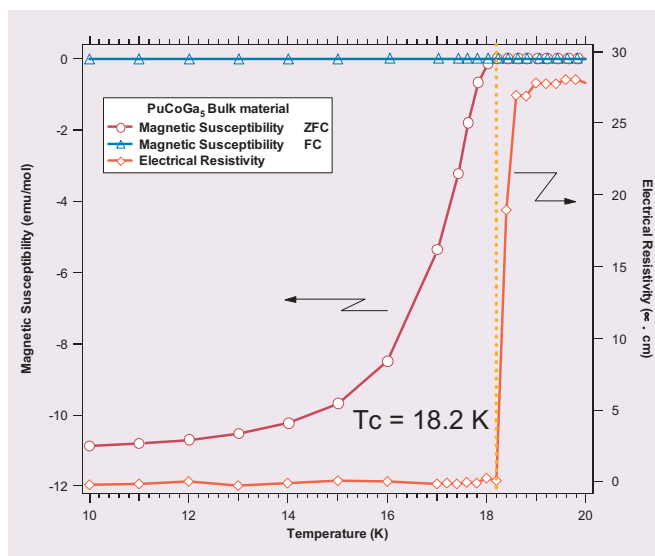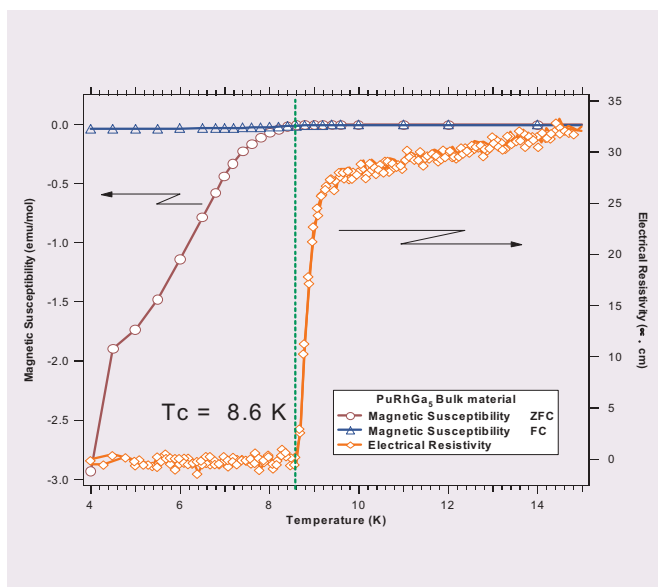
Fig. 2   Evidence of bulk superconductivity in PuRhGa$_5$ as observed by magnetic susceptibility and resistivity measurements. A transition to zero resistance, coincident with full-shielding diamagnetism, is observed near 8.6 K.

ductivity. The observed superconductivity results directly from plutonium's anomalous electronic properties and as such serves as a bridge between two classes of spin-fluctuation-mediated superconductors: the known heavy-fermion superconductors and the high-T$_c$ copper oxides. The crucial question to answer is whether the superconductivity in this system can be placed within the magnetically mediated superconductivity? "The picture that is emerging may well be of historic importance. As well as there being something magnetic about superconductivity, there is also something superconducting about magnetism" (cited from [8]).

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Contact: Franck Wastin · tel.: +49 7247 951 387 · fax: +49 7247 951 599 · wastin@itu.fzk.de

Laser Induced Nuclear Reactions in Actinides

Introduction

A new technique is presented for investigating nuclear reactions based on the use of very high intensity laser radiation. These studies may be used to identify reactions of interest in transmutation [1,2,3]. Through collaboration with the Institute of Transuranium Elements, the Universtiy of Jena, the Universities of Glasgow and Strathclyde, Imperial College, AWE Aldermaston and the Rutherford Appleton Laboratory (RAL), an investigation of nuclear reactions is underway using the high intensity laser radiation. By focusing the laser spot very high laser intensities in excess of 10^{19} W.cm^{-2} are produced. Under these conditions, matter in the focal spot is turned into a hot dense relativistic plasma with a temperature of several MeV. These resulting photons and particles can then be used to induce nuclear interactions in target materials. The results of the recent experiments performed with the VULCAN and Jena lasers are described here.

Laser Induced Photo-Fission of Actinides

Laser induced fission of metallic uranium was first demonstrated [4] with the VULCAN laser in 2000 in a collaboration involving ITU. In the latest experiments, laser induced fission of thorium has been demonstrated with the high repetition rate tabletop laser at the University of Jena. [5] and the VULCAN laser at RAL [6]. The experimental set-up is shown schematically in Fig. 1.

The gamma spectrum (Fig. 2) shows a number of signatures of typical short-lived fission products (with half-lives from 30 minutes to several hours).

In Fig. 3, results of the time resolved fission product decay from the fissioning of Th are given.

Following the successful work on ^{238}U and ^{232}Th, similar fission experiments are planned on ^{237}Np, ^{242}Pu, ^{235}U, and ^{233}U.

Laser Induced Heavy Ion Fusion

In the recent experiments at RAL, it has been demonstrated for the first time that light ions such as protons (and C, Al etc.) can be produced in a converter foil and that these ions can be directed onto a target and result in nuclear reactions (see Fig. 4) [6].
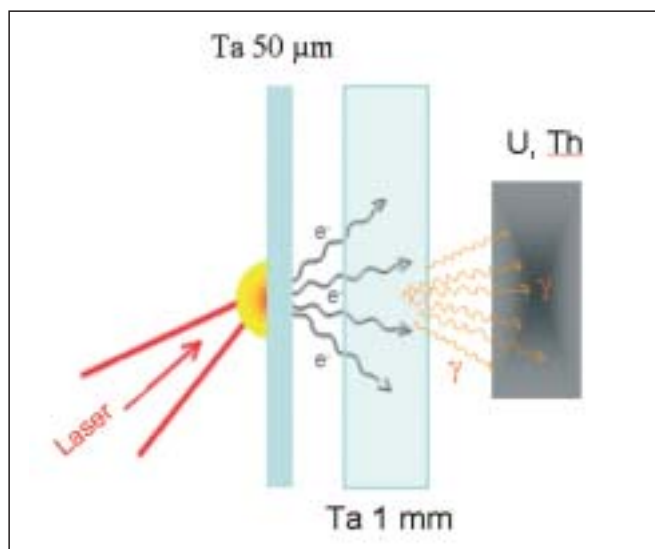
Fig.1 Set-up of the experiment. The laser beam is focused onto a Ta target where it generates a hot plasma on the surface. Electrons accelerated in this plasma enter the second part of the target (Jena setup), which serves as a bremsstrahlung converter. It is this bremsstrahlung which gives rise to photo-fission. The samples of U and Th are positioned directly behind this source of γ-radiation. In the RAL set-up, the laser is focussed directly onto the thicker Ta converter.

Fig. 2 γ-spectrum of the laser irradiated uranium (RAL results). Emission from a range of fission products (^{134}I, ^{133m}Te, ^{92}Y, ^{138}Cs, ^{135}I) with mass numbers around 90 and 130 is clearly visible.

Fig. 3 Decay characteristics of fission products from brems-strahlung induced fission of ^{232}Th. The deduced half-lives are in good agreement with literature values. Symbols indicate experimental data.

Of particular interest is the generation of protons. If the proton energy is high enough (depending on the laser intensity) then other nuclear reactions should take place, e.g. (p,xn), (p,f) and spallation. A maximum proton energy of 50 MeV has been reported for previous measurements [6], but following an increase in the laser intensity with the new Petawatt laser at RAL, a maximum proton energy of 250 MeV could be expected. The number of fast protons ranges from 10^{12} to 10^{13} per pulse with a transformation of approximately 12% of the laser energy into fast ion energy.

Heavy ion beams were generated from primary targets of iron, aluminium and carbon. Secondary target material consisted of aluminium, titanium, etc. The heavy ion "blow-off" fused with the atoms in the secondary target creating compound nuclei in highly excited states. The compound nuclei then de-excited to create fusion products in the secondary target foils.
Future experiments will be extended to actinides with a view to studying transmutation reactions through fusion and spallation.
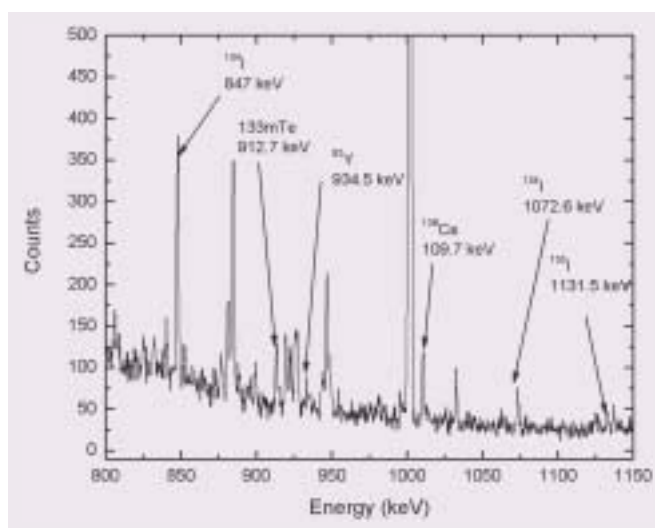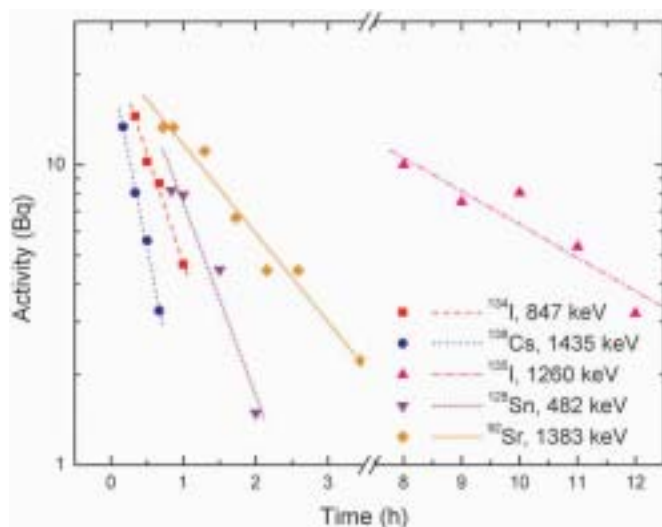

Fig. 4 Setup of the heavy ion fusion experiments. The laser is focused onto a primary target (Al, C or other), where it generates a hot plasma on the surface. Heavy ions accelerated in the plasma are blown-off into the second-ary target (Al, Ti, Zn, or other) inducing a fusion reaction.

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Contact: Joseph Magill · tel.: +49 7247 951 366
fax: + 49 7247 951 591· magill@itu.fzk.de

First Pyrochemical Separation of Minor Actinides from Lanthanide Fission Products by Electrolysis

Partitioning and transmutation (P&T) offers the possibility to reduce the long-term radiotoxicity of nuclear waste. In P&T scenarios long-lived radionuclides, especially actinides are repeatedly recovered and transmuted in dedicated reactors. Essential for successful P&T concepts is therefore the efficient recovery and multi-recycling of actinides. The fuel (or targets) used in such reactors will be significantly different from the commercial fuels of today as it will contain major quantities of (minor) actinides, probably in inert (U-free) matrices, and reach very high burn-ups. For such fuels, traditional reprocessing (aqueous) is not likely to be suitable and new pyrochemical separation techniques are under development. Pyrochemcial reprocessing uses a molten salt phase as solvent and the separation of different elements is normally carried out by electrochemical methods, such as electrolysis, electrorefining or by reductive extraction.

One of the key issues in partitioning is the selective recovery of minor actinides (Am, Cm). This necessitates that Am and Cm can be selectively separated from lanthanides (Ln) which is, due to the chemical similarity between these elements, a very difficult task to carry out. Existing methods are based on multistep reductive extraction in which actinides and lanthanides are separated between a molten salt and a molten metal phase (e.g. Bi). At ITU simplified separations of MAs from Ln, based on electrolysis, are being developed. The choice of cathodic material onto which MAs are deposited during electrolysis is essential. Two characteristics must be taken into account; a high stability of the formed deposit and enough difference in reduction potentials between MA and Lns to allow a selective electrochemical reduction and thus an efficient separation. Molten Cd and Bi have been widely used as cathodic materials due to the formation of stable MA-Cd or MA-Bi alloys. However, the selectivity of the MA recovery seems to be limited due to the small difference in reduction potentials. Solid Al, on the other hand, offers both formation of stable MA alloys and a relatively large difference in reduction potentials, see Fig. 1. This opens the possibility to accomplish an efficient and selective MA separation by electrolysis.
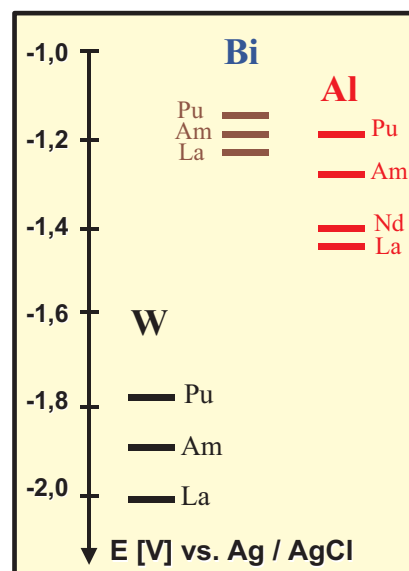
Fig. 1 Reduction potentials of some actinides and lanthanides on different cathodic materials. The differences in reduction potential is used in separation by electrolysis. Reduction potentials become, in general, more positive and compressed when the element is alloying with the cathode (e.g Bi and Al). This compression makes separation more difficult. On the other hand, W as an inert cathode material allows the pure deposited element to redissolve in secondary reactions (less stable deposit).

The feasibility of Al cathodes in MA separations has been demonstrated in experiments in which Am have been separated from Nd by electrolysis in molten chloride salt. First an $AmCl_3$- containing salt was produced by chemical oxidation of Am metal by addition of $BiCl_3$ and Nd was added to the salt melt as a chloride. The separation tests were carried out in a LiCl-KCl melt at 460°C using a plutonium rod as anode and aluminum foam as cathode, see Fig. 2.

Fig. 2 Al foam cathode (left) and the Pu metal anode (right).

A major advantage of a foam cathode is the large surface area for contact with the melt. During the electrolysis Am^{3+} is reduced and alloyed with Al and the Pu metal is oxidised on the anodic side, see Fig. 3.
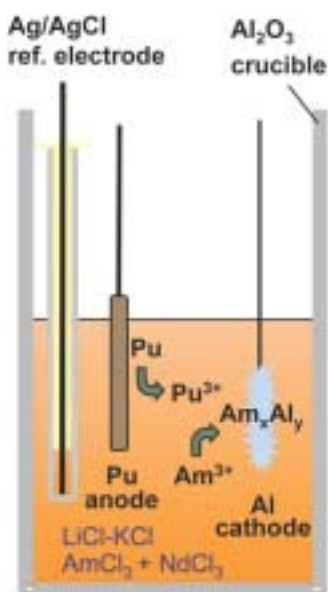
Fig. 3 *Set-up used for separation of Am by electrolysis onto Al foam cathodes. During the electrolysis of Am^{3+}, the Pu metal anode is oxidised to Pu^{3+}, i.e. it is dissolved which causes an increased concentration of Pu in the melt. At the end of the electrolysis, as the concentration ratio of [Am]/[Pu] is decreasing, mixed Am-Pu-Al alloys are expected to form.*

At the end of the first electrolysis, a salt sample was taken to analyse the Am, Pu, and Nd concentrations. A fresh Al foam cathode was then introduced in the same melt and a second electrolysis was carried out under the same conditions.
The results concerning the salt composition, before and after the two electrolyses, are summarized in Fig. 4.

It can be seen that Nd is not reduced during the electrolysis since its concentration is constant. However, the Am concentration is decreased and the Pu concentration is increased in both electrolyses. Nevertheless the Pu increase is somewhat less than predicted. This is due to the simultaneous deposition of Pu and Am as Pu^{3+} is more easily reduced than Am^{3+}.
After the experiment the Al cathode was removed from the salt melt and prepared for surface analysis. Using SEM-EDX,

see Fig 5, it could be concluded that a stable Am-Al alloy had been formed during electrolysis. Nd, on the other hand, was not detected. This proves for the first time that the difficult separation of MAs from Ln by electrolysis in a salt melt is possible.
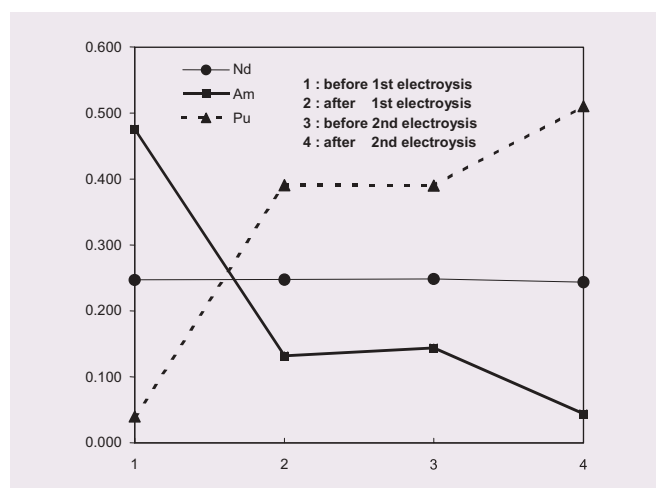
Fig. 4 *Concentration of Am, Nd and Pu in the salt melt before and after electrolysis.*
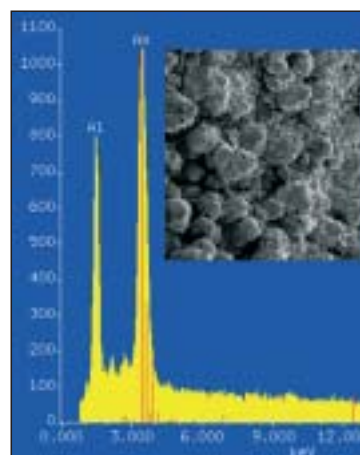
Fig 5. *SEM image of the Al cathode surface after electrolyis. The deposits were analysed using EDX (graph) and clearly indicate the formation of an Am-Al alloy.*

**Contact: Rikard Malmbeck · tel: +49 7247 951 417
fax: +49 7247 951 561 · rikard.malmbeck@itu.fzk.de**

Radiolysis Effects at Low α-Radiation Rates

If one considers the chemical properties of the customary LWR fuel, strong reducing conditions are expected in the existing or planned European geologic repositories for high-level radioactive waste. Under such conditions, fresh UO_2, the presently most-used fuel, is chemically stable even in permanent contact with water. Yet, radiolysis effects on water – especially due to α-radiation of actinides – are produced near the spent fuel, which may produce oxidising conditions locally. In fact, though production of oxidant reactants by radiolysis is accompanied by a corresponding number of reducing species, molecular hydrogen is normally formed as a primary product of water radiolysis so that, being inactive, an excess of oxidising species is finally expected in the spent fuel environment.

The radiation field of available – comparatively "hot" – spent fuel is dominated by gamma and beta radiation fields, however, after several hundreds of years only α-radiation is expected to be effective. Therefore, in order to single out the effects of α-radiolysis on the corrosion behaviour of spent fuel, UO_2 pellets containing short-lived α-emitters (^{238}Pu and ^{233}U) were produced. Specimens of UO_2, UO_2 containing 0.1 $^w/_o$ and 10 $^w/_o$ of an oxide constituted mainly of ^{238}Pu, as well as UO_2 containing 10 $^w/_o$ and 1 $^w/_o$ ^{233}U were fabricated by a sol-gel method which guarantees an intimate mixing of the α-emitters with the UO_2 matrix.
The leaching behaviour of samples simulating, the α-activity of fresh up to very old spent fuel (after centuries of storage) was studied in deionized water under un-aerated conditions. Enhanced uranium dissolution was always observed in the presence of α-emitters (Fig.1).

The specimen subjected to the strongest alpha-activity (10 $^w/_o$ ^{238}Pu) was eventually covered by a thick, yellow crust of Studtite [$UO_2|O|(OH)_2$] – $3H_2O$. The samples with lower α-activities (0,1$^w/_o$ ^{238}Pu, 1 and 10$^w/_o$ ^{233}U) were leached under the same conditions. In these samples, instead of Studtite, precipitation of Schoepite [$UO_2 \cdot n(H_2O)$, n<2] was observed. This can be attributed to the lower concentration of oxidant reactants (OH$^-$, H_2O_2,…) since for the low-activity samples the radiolytically produced peroxide content is far below that needed to precipitate uranium peroxide.
A dependence of the fuel dissolution on alpha-activity was measured under relatively low surface area volume conditions, whereby saturation conditions are apparently not yet reached (Fig. 1). However, the enhancement factor for uranium dissolution at a given α-activity seems to be rather

constant for sufficiently long experiment times. A log-log plot of this factor is shown in Fig. 2 as a function of the spent-fuel decay time during storage. It can be seen that the leaching effect is *not* proportional to the fuel radioactivity, a tendency to saturation being clearly indicated by the slope of the curve.
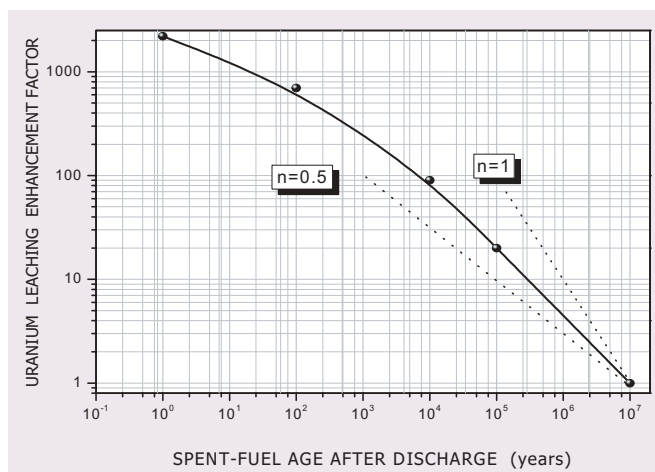
Fig. 2 Enhancement factor in cumulative leaching of alpha-doped uranium dioxide as a function of alpha specific activity (pure UO_2 corresponds to unit). The abscissa shows the age of a spent fuel corresponding to the various activities.

It must be stressed that these accelerated dissolution experiments are aimed at singling out and characterizing the effects related to the radiolytic process, possibly seen as the key mechanisms which could potentially alter the chemical stability of the waste in contact with groundwater. The radiolytic effects are highlighted by adopting "simple" experimental systems, which do not consider the totality of factors and parameters expected to affect the long term behaviour of spent fuel in a geologic repository. In a repository, multiple agents, both natural and engineered, will contribute to contrast the dissolution-enhancing influence of radiolysis, and will ultimately inhibit significant corrosion levels of the spent fuel to occur. These beneficial factors (e.g. the hydrogen overpressures, the presence of reducing species in the water and in the multiple containment barriers, the backfill materials selected to minimize transport of radionuclides, to mention only some among them) are the subject of separate studies, with the final aim of reaching a synthetic, comprehensive view of the whole issue of spent fuel behaviour during final storage.

Contact: Vincenzo V. Rondinella · tel.: +49 7247 951 279
fax: +49 7247 951 199 · rondinella@itu.fzk.de
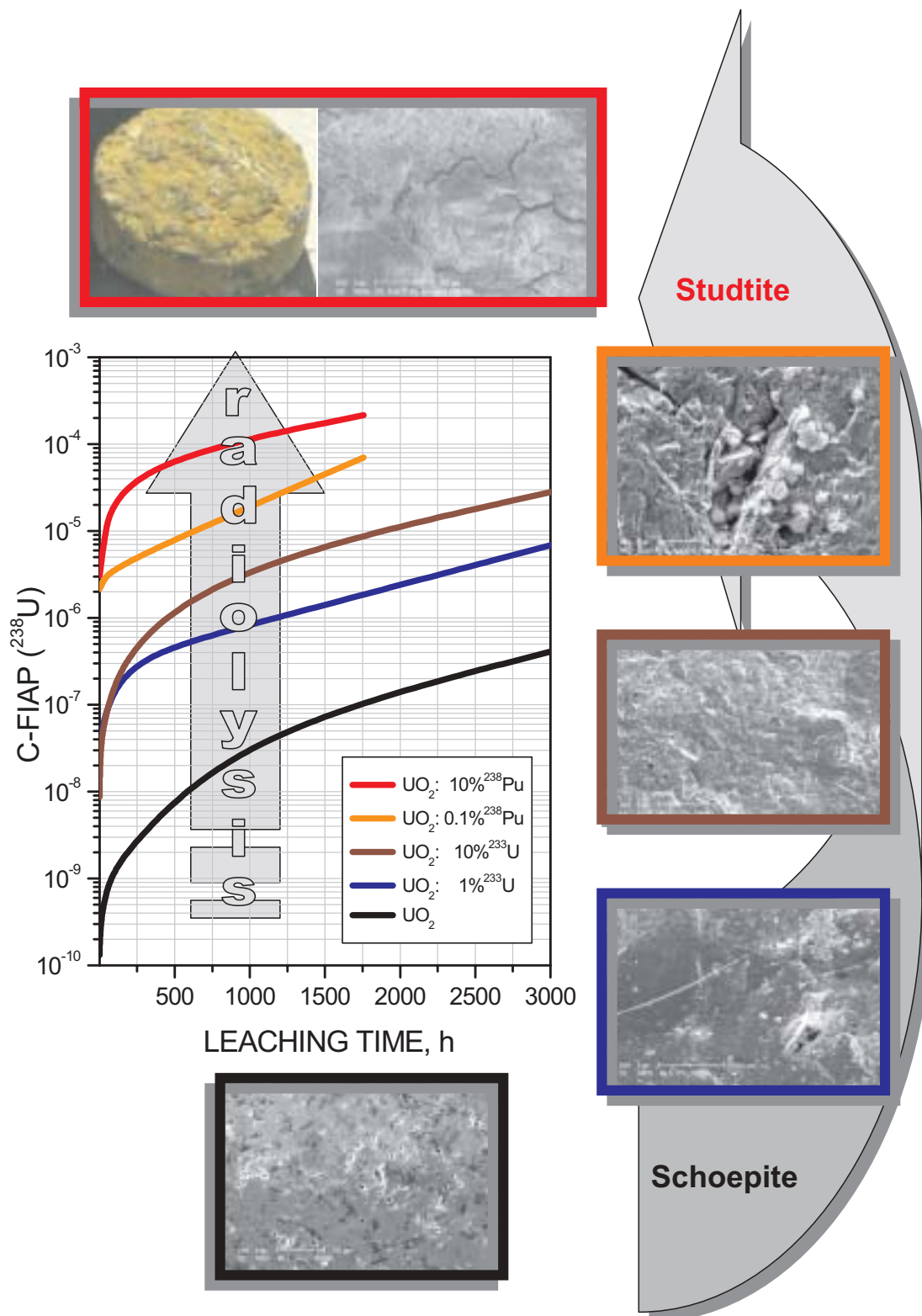
Fig. 1 *The plot shows the fraction of initial uranium inventory found in the aqueous phase (FIAP) as a function of leaching time in pure uranium dioxide and in uranium dioxide samples containing different concentrations of alpha-emitters. The micrographs show the morphology of the corrosion phases as the oxidation due to radiolysis products increases.*

Effects of Extreme Self-Damage in Curium Oxide

α-radiation damage in nuclear fuel and, more generally, in actinide compounds is receiving increasing attention due to a number of technological problems caused by self-induced changes in the physical properties of highly radioactive materials. In this context, we reported (TUAR-2001) that accumulation of α-damage and of accompanying large amounts of helium in plutonium oxide pellets resulted, under ambient conditions, into a microscopic disruption of the sintered structure.

Recently, ten years old $^{244}Cm_2O_3$ particles of approximately 1 mm size have been analysed and submitted to helium release and Knudsen-effusion tests. As the half-life of ^{244}Cm is 18 years, approximately 55 to 60% of the initial curium had decayed into ^{240}Pu producing an equal atomic fraction of helium.

Now, even for a small inert atom like helium, concentrations of this order of magnitude are hardly conceivable in the form of gas-in-solid; therefore, some form of bubble precipitation was expected to occur. Yet, the experiment showed that much more dramatic changes took place in the sample during ageing.

The microscopic observations of the sample, as well as the thermal annealing experiments on helium release reveal drastic restructuring phenomena. The initial granular structure has totally disappeared, and, though still geometrically compact, the sample consists of an intricate, spongeous agglomeration of small globular particles of sizes of the order of a few microns (Fig. 1).
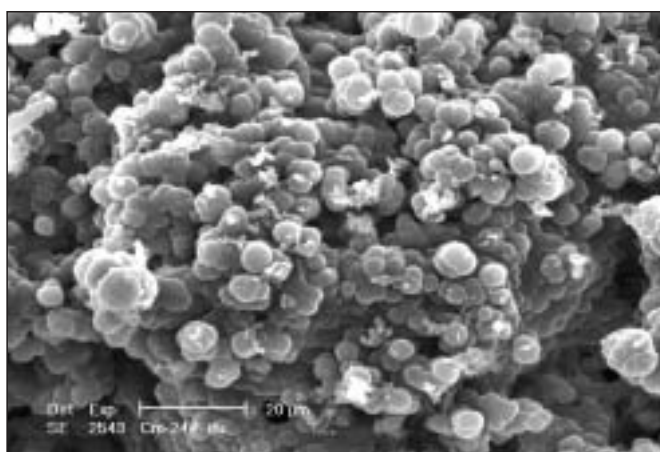
Fig. 1 Bulk structure of the oxide showing globular microscropic grains.

This structure appears to be stable up 1600-1700 K; above this temperatures a densification process starts.
Surprisingly, a number of morphologically diverse phases are formed during production of α-damage. Some of them are preserving traces of the original grains (Fig. 2),
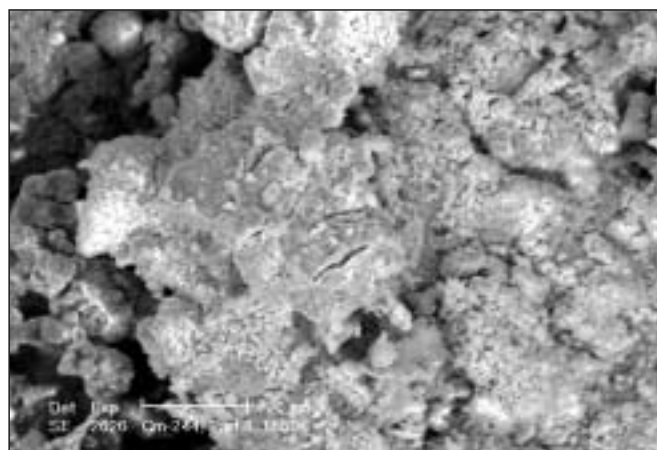
Fig. 2 Micrograph showing restructuring with traces of the original grain morphology.

others, formed on the sample outer surface, assumed coral-like configurations consisting of groups of regularly arranged platelets which often display a pronounced pine-tree dendrite shape (Fig. 3).

This phase, however, does rapidly disappear at temperatures above 850 K. While the "cauliflower" structure of Fig. 1 was
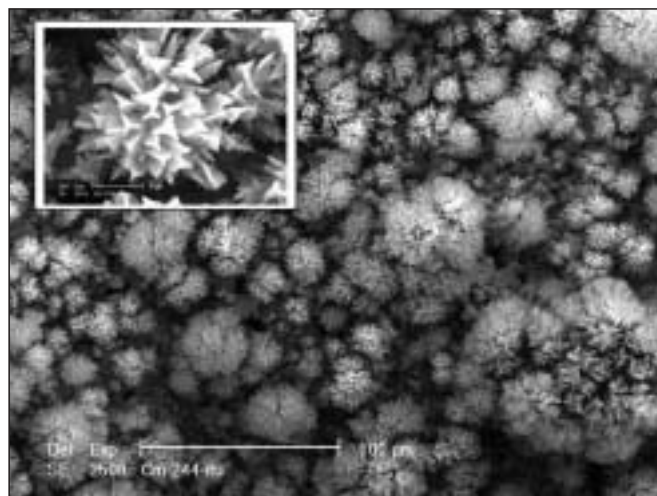
Fig. 3 Surface features of the curium oxide sample. Colonies of dendritic crystals are formed, likely due to re-deposition of recoil atoms. The inset shows a magnification of the dendrites.

formed by a process which probably treads the steps of the high burn-up fuel restructuring (RIM effect), the dendrites can only originate from re-deposition of vaporised atoms produced by energetic recoils and sputtering events.

Helium release during a thermal annealing at a constant heating rate of 40 K/min exhibits two peaks at, respectively, 700 K and 850 K (Fig. 4), very low temperatures indeed, if one considers the values of the activation energy for diffusion in actinide oxides.

However, the most striking result concerns the total fraction of gas, which was retained in the sample, amounting to less than 1% of the helium created. This means that a long range migration of He did take place at room temperature, implying an effective diffusion coefficient of the order of 10^{-15} -10^{-14} $cm^2 s^{-1}$, *i.e.,* at least of one order of magnitude larger than that of fission gas produced in pile by radiation enhancement at ratings of ~10^{13} fission cm^{-3}.

Contact: Claudio Ronchi · tel.: +49 7247 951 402
fax: +49 7247 951 198 · ronchi@itu.fzk.de
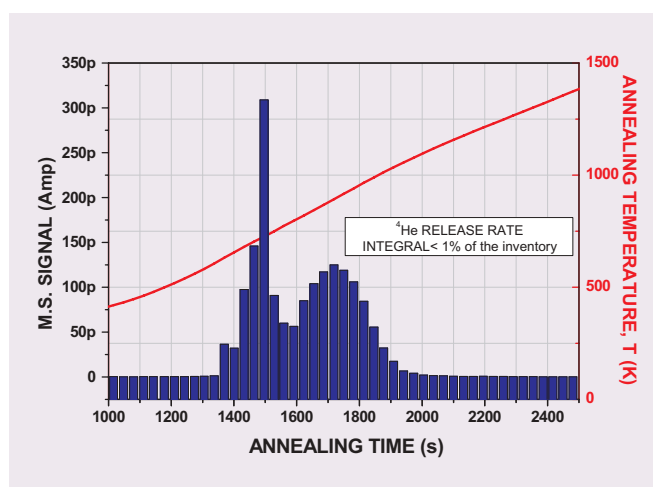
Fig. 4 Helium release rate during laboratory annealing of the aged curium oxide sample. Release occurs in two stages. The most striking result is that the total amount retained in the sample, and completely released during laboratory annealing corresponds to less than 1% of the helium amount created by curium decay.

Combating Illicit Trafficking of Nuclear and Radioactive Materials

Combating illicit trafficking of nuclear material is part of an international effort to prevent the proliferation of nuclear weapons and to protect the citizens against the hazard associated with illegal and unsuitable transport of these materials. After the events of 11 September 2001, also the threat of nuclear terrorism has to be seen in this context. With the assistance of the Institute for Transuranium Elements (ITU) and funded through the EC programmes PHARE and TACIS, a response action plan based on the recommendation of the International Technical Working Group (ITWG) had been implemented in the Czech Republic, Bulgaria, Hungary and Ukraine.

Since about 6 years, ITU has been involved in the international effort to combat illicit trafficking of nuclear materials. Its leading role in this area is based mainly upon its infrastructure, installations and experience to handle and analyse nuclear materials of all types in relevant quantities. Following the previous experience, ITU is currently executing a series of dedicated projects with the candidate countries to the European Union.

In the framework of its Technical Co-operation Project RER/9/060 on physical protection and security of nuclear materials, the International Atomic Energy Agency (IAEA) established a collaboration with ITU.

Three joint training workshops for law enforcement services and radioanalytical laboratory experts on combating illicit trafficking of nuclear and/or radioactive materials were organised at ITU in the year 2002. Representatives from Turkey, Cyprus, Azerbaïdjan, Estonia, Latvia, Lithuania, Kazakhstan, Romania, Slovenia, Bulgaria, Hungary, Malta, Poland, Czech Republic, Slovakia, Armenia, Belarus, Georgia, Russian Federation, Tajikistan and Ukraine participated in the training sessions. Technical experts from customs, criminal police or intelligence services and scientists from (radio)analytical laboratories followed a series of lectures and practical exercises to:
● categorise on-site radioactive and nuclear material by hand-held instruments
● and to familiarise radioanalytical experts with nuclear forensic techniques to characterise nuclear material and be able to write expert reports according to ISO standards.

Speakers from the IAEA, Bundeskriminalamt Wiesbaden, ESO Luxembourg and DG Enlargement Brussels completed the program with their presentations.

In some of the candidate countries, demonstration exercises were organised in order to test the interaction of the different services involved and to identify weak points in the national response plan (see Fig. 1).

Fig. 1   Health physicist measuring a suspect car after it had been cordoned off by a border guard officer (exercise in Hungary, November 2002)

The car was supposed to carry out a legal transport of radioactive material, yet the investigations revealed a second, hidden source containing plutonium. The material was categorised on the spot by scientists from the national expert laboratory.

In another exercise, for the first time ever, the scenario involved the bilateral co-operation of two countries in the field of combating illicit trafficking by responding commonly to the detection of material at the Kapikule border crossing point between Bulgaria and Turkey. Hidden radioactive and nuclear material (actually stemming from a real seizure) was found in a car entering Turkey. After a confirmation measurement (to ensure that it was not an excercise) and application of classical forensics (see Fig.2), a Bulgarian expert team was called to the crime scene in order to categorise on the spot the seized material using mobile equipment provided by ITU in the framework of a previous PHARE project. A common expert report, signed by both sides, was released to support legal prosecution.

The projects on combating illicit trafficking carried out by ITU are embedded in a close international and inter-institutional co-operation, they reflect a comprehensive approach to effectively fight illicit trafficking of nuclear and radioactive material.

Fig.2   A specialised police squad performing classical forensics examination of the seized material

Fig. 3   The joint Turkish/Bulgarian team with external observers from IAEA, ITU and Europol.

Contact: Pascal Daures · tel.: +49 7247 951 289 · fax: +49 7247 951 99 289 · daures@itu.fzk.de
Klaus Mayer · tel.: +49 7247 951 545 · fax: +49 7247 951 99 545 · mayer@itu.fzk.de ;

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Recent Developments in Analytical Methods for Safeguarding Nuclear Material

K. Mayer, H. Ottmar, P. van Belle, S. Abousahl, M. Betti, G. Tamborini, M. Wallenius, A. Morgenstern

1. Introduction

In the Euratom Treaty (Chapter 7, Article 77), the signatory states entitle the Commission to verify that nuclear material is not diverted from its intended (peaceful) use. On a world-wide scale, the common will of the international community to prevent the proliferation of nuclear weapons has been expressed in the Non-Proliferation Treaty. Verification of compliance with the treaty obligations is a key element of these treaties and is achieved by the implementation of Safeguards. Techniques which have been applied for Nuclear Material Safeguards range from seals to surveillance, from checking records to verification of plant design, from following material flows to verifying inventories of nuclear material. In the light of the experience gained in Iraq after the Gulf War and in North Korea, the need arose to establish capabilities for detection of undeclared activities or for verifying their absence.

The backbone of any safeguards system is measurements. On the one hand, measurements allow to accurately quantify the amount of nuclear material present in a certain facility, on the other hand measurements enable to reveal clandestine nuclear activities. The Institute for Transuranium Elements has been involved for many years in the development and application of measurement techniques for safeguards and has been providing scientific/technical support to DG TREN (Euratom Safeguards) and to the International Atomic Energy Agency (IAEA). In particular the recent safeguards challenges related to the large reprocessing plants, to particle analysis, to alternative nuclear materials, to illicit trafficking and to advanced fuel cycles have triggered significant development work at ITU. In the following we will describe the most prominent research and development activities and outline how the results obtained may contribute to make safeguards more effective and more efficient.

2. Methods for Accountancy Verification

Traditional Safeguards is based on a nuclear material accountancy, which is established by the user or owner of the material. This accountancy is subject to independent verification by the safeguards authorities. The verification is achieved by checking the records but, more importantly, by physical verification, i.e. through verification measurements. These measurements need to be accurate (in view of the large amounts of material handled in modern facilities) and results have to be provided in a timely manner (in order to enable early detection and to increase the deterrent effect). The methodological approach and the techniques used have to take this into account.

The most accurate measurements for accountancy verification are traditionally performed on samples of nuclear materials withdrawn by the safeguards inspectors from the process or storage area of a nuclear facility. The necessary measurements to be carried out on those samples, which normally involve the determination of the uranium and/or plutonium element concentration and the isotopic composition of both elements, have been made for a long time exclusively off-site in remote safeguards analytical laboratories. Only recently dedicated on-site laboratories became operational in the large reprocessing plants of La Hague and Sellafield for a timely execution of the analytical measurements on site [see sections 2.1 and 2.2].

A significant portion of the recent development work at ITU for analytical measurements applied to accountancy verification has been closely linked with the on-site laboratories, which represent a novum in the safeguards practice. In this context particular attention has been, and is being paid, to special measurement issues related to the use of radio-metric measurement techniques, which are playing an increasingly important role in the measurement technology for safeguards.

2.1 Streamlined methods for reprocessing plants

The uranium and plutonium accountancy verification at the input of large-scale reprocessing plants represents a key issue in safeguards. Existing safeguards agreements impose a 100% control on the dissolver solutions, where the true uranium and plutonium content in the spent fuels can be exactly determined for the first time after fuel unloading from a reactor. The resulting large number of these very special (highly radioactive) verification samples called for efficient analysis techniques and procedures to ensure their timely analysis at a high accuracy level in the on-site laboratories. Existing measurement techniques such as the radio-

metric techniques of K-edge densitometry and X-ray fluorescence analysis, incorporated in the so-called Hybrid K-Edge Densitometer (HKED), and the classical method of Isotope Dilution Mass Spectrometry (IDMS) had to be further streamlined and improved in terms of enlarged operational simplicity, automation and reliability to meet the requirements for effective on-site control [1].

For the on-site laboratory at La Hague increased operational simplicity for the radiometric HKED measurements has been achieved through measurements performed directly on the original sample containers as used for posting the input solution samples from the respective plants to the laboratory. Increased measurement capacity and timeliness of the measurements has been realized through the incorporation of a sample changer specially designed for reliable operation in a corrosive hot cell environment (Fig. 1). The advanced measurement technology has also been provided to the Nuclear Material Control Center (NMCC), Japan for joint use with the IAEA in the forthcoming on-site laboratory in the new reprocessing plant at Rokkasho.
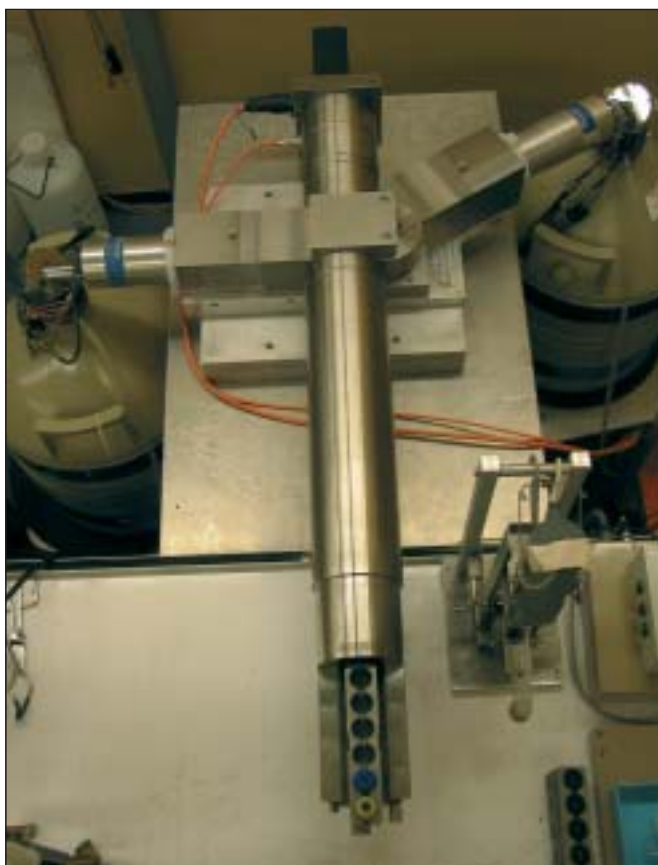
Fig. 1   Hybrid K-Edge Densitometer (HKED) with sample changer for Rokkasho

Fully robotised sample treatment procedures including improved U/Pu/fission product separation, alpha spectrometry of the U and Pu fraction, and filament preparation for mass spectrometry were set up to automate the sample preparation for IDMS to a high degree [2-4]. During initial routine operation occasional problems have been encountered, however, with the very high dilution factors (up to 40000) imposed for radiological safety reasons in order to reduce the dose rate for the spiked input samples to be transferred from the hot cell to the robotised glove-box. This problem has been recently overcome through the implementation of a simple and efficient fission product separation procedure carried out inside of the hot cell, which eliminates the need for any sample dilution. This modification has considerably increased the operational reliability of the IDMS measurements, which serve as reference method and for quality control for the routine HKED measurements.

2.2 Plutonium assay by neutron coincidence counting

Passive neutron coincidence counting (PNCC) is one of the most important nondestructive assay techniques in safeguards for the measurement of plutonium. It is widely used for the verification of the plutonium content in large items containing up to several kilograms of plutonium. By contrast, in the on-site laboratories PNCC is employed for the determination of the plutonium content in small PuO_2 and MOX samples typically containing only about 0.2-2 g of plutonium. Continuous research work is ongoing at ITU with the aim to upgrade PNCC to a validated accurate analytical technique for the determination of small quantities of Pu.

Improved methodology

The plutonium assay of small samples by PNCC relies on the correct interpretation of the observed neutron coincidence rate. This interpretation is complicated by the phenomenon of neutron multiplication due to induced fission, which cannot be neglected even for small sample sizes. The magnitude of the neutron multiplication depends on numerous sample parameters. Neutron transport codes such as MCNP are in principle capable of modelling in detail the neutronic processes occurring in given samples, but are too time-consuming for routine application. Therefore a computer program has been developed following a heuristic approach. The program initially relies on guidance from detailed modelling of specific cases by MCNP populating a data bank. Once a sufficient variety of sample cases has been treated by MCNP, interrogation of the data bank and interpolation of its data can replace the time-consuming modelling by MCNP [3].

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Determination of fundamental constants

The main emitter of spontaneous fission neutrons in reactor-grade plutonium materials is ^{240}Pu. The primary quantity commonly measured by PNCC is a ^{240}Pu-effective mass which takes into account the contributions from the three spontaneously fissioning plutonium isotopes ^{238}Pu, ^{240}Pu and ^{242}Pu:

$$m_{240eff} = \gamma_{238} \times m_{238} + m_{240} + \gamma_{242} \times m_{242}.$$

The coefficients γ_{238} and γ_{242} are required to proportion appropriately the contributions from ^{238}Pu and ^{242}Pu relative to ^{240}Pu to the observed coincidence rate. The γ values depend on the spontaneous fission half-life, the neutrons released per fission and other parameters. An experimental program has been carried out to determine these γ constants with much higher accuracy than previously available [4]. Tab. 1 compares the new coefficients determined for two different neutron coincidence counters (a combined neutron-gamma counter developed at ITU and the Harwell N95 counter) with previous values.

Tab. 1 Results for the new coefficients γ_{238} and γ_{242}.

Coefficient	OSL-Counter		N95	Previous Values
	GW=64μs	GW=88μs	GW=88μs	
γ_{238}	2.707 ±0.011	2.714 ±0.010	2.718 ±0.010	2.52…2.57
γ_{242}	1.658 ±0.005	1.667 ±0.003	1.664 ±0.003	1.66…1.71

Detection of ^{244}Cm

The plutonium assay by PNCC can be seriously biased due to potential interferences from traces of ^{244}Cm. Because of its very high spontaneous fission rate compared to that of plutonium, the ^{244}Cm concentrations in a plutonium sample must be limited to the sub-ppm level in order to avoid notable bias effects in a plutonium assay made by PNCC. An analysis procedure has been developed to determine quantitatively traces of less than 10 ppb of ^{244}Cm in plutonium [5]. The method combines two ratio measurements: a gamma-spectrometric measurement of the ^{241}Am/Pu ratio made on the original plutonium sample, and an alpha-spectrometric measurement of the ^{241}Am/^{244}Cm ratio made after the separation of plutonium by means of extraction chromatography. The method has been designed for easy integration into existing robotized sample treatment procedures applied for the routine IDMS analyses of plutonium samples.

2.3 Calorimetry

Calorimetry represents an alternative to PNCC for the non-destructive assay of plutonium. It is independent of neutron multiplication and matrix effects and therefore does not require modelling for data evaluation. Advanced calorimeters using thermopile technology for heat flow measurements are capable of measuring precisely the typical amount of heat ($\cong$ 10 mW) produced by gram-sized samples of reactor-grade plutonium. The high degree of achievable measurement reproducibility ($\cong$ 0.1%) is illustrated in Fig. 2, which shows the results of repeated measurements performed during 2002 at ITU with a commercial small sample calorimeter on a 11 mW plutonium sample.
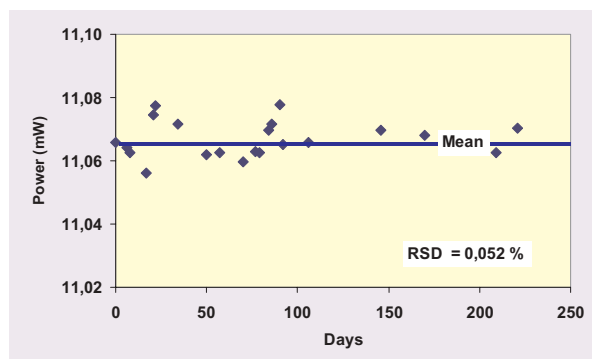
Fig. 2 Reproducibility of heat measurements with a small sample calorimeter.

The conversion of the measured heat into the corresponding amount of plutonium requires the knowledge of the accurate isotopic composition of the measured plutonium. In particular, the abundance of the isotope ^{238}Pu, which may contribute up to 60-70 % to the produced heat, must be known accurately. This abundance can be determined by three different techniques: mass spectrometry (if the absence of ^{238}U can be assured), alpha spectrometry, and high-resolution gamma spectrometry. A comparative study and performance evaluation for the ^{238}Pu abundance determination in support of the calorimetry measurements is under way.

2.4 Uranium inventory verification with COMPUCEA

ITU provides continuous in-field measurement support to Euratom and IAEA safeguards during the physical inventory verification in different European uranium fuel fabrication plants. The 'COMPUCEA' measurement technique (Combined Product Uranium Concentration and Enrichment Assay) employed in the on-site verification measurements is based on a simplified variant of the K-edge densitometry technique for the determination of the uranium concentration, and on passive gamma spectrometry for the ^{235}U abundance

measurement [6]. Substantial improvements both in measurement methodology and in instrument software for data evaluation, quality control and user interaction have been recently made, which helped to further increase the reliability and accuracy of the in-field measurements. The progress made has become manifest from the results of the recently conducted inventory campaigns.

3. Strengthening Safeguards

As pointed out above, traditional safeguards aims at verifying the correctness of declaration of a plant operator or a state. The lesson learned from the Iraqi experience calls for additional measures that allow to verify the completeness of such declarations. Measurement methodologies have been and are being developed at ITU for revealing clandestine production of weapons grade uranium or plutonium (through particle analysis), for checking the termination of production of weapons materials (through age determination) and for verifying that no alternative nuclear materials such as neptunium are separated from spent fuel solution.

3.1 Particle analysis

In the aftermath of the Gulf War, the capability of analytical chemistry to reveal ongoing undeclared nuclear activities by the analysis of environmental samples was demonstrated [7, 8]. The IAEA launched the "93+2" programme and demonstrated in field trials the effectiveness of environmental sampling in routine nuclear inspections. More recently, this methodology has been implemented in the "Additional Protocol" as complement to the existing safeguards agreements [9,10]. Euratom Safeguards joined these investigations through their High Performance Trace Analysis (HPTA) programme. In this framework, ITU played

an important role actively participating in the sampling during the field trials and by implementing new techniques able to detect nuclear activities by the characterisation of microparticles [11-15]. It was the first civil laboratory in Europe to develop such technologies and entered in the Network of the Analytical Laboratory of IAEA for particle analysis. Environmental sampling comprises samples outside a facility (biota, water, soil) and inside the facility (swipe samples). Emphasis was given to the analysis of particles stemming from swipe samples collected inside and outside nuclear facilities, in particular to uranium enrichment plants.

The main method used at ITU for the characterisation of individual micro particles containing fissile material is based on secondary ion mass spectrometry (SIMS). The measured isotopic composition allows one to identify the enrichment of the material, the process used for the enrichment as well as the starting material employed (natural or reprocessed uranium).

Uranium swipe samples analysis

The analysis aims at determining the range of uranium enrichments produced in a particular facility. The samples are handled in a clean laboratory class 100-10. Particles are transferred from the cotton swipe by ultrasonic removal to a polished graphite planchet for further instrumental analysis. Scanning Electron Microscopy combined with Energy Dispersive X-ray detection (SEM-EDX) is used after sample preparation to measure the elemental composition of micrometer-sized particles. To search for uranium containing particles the samples are scanned automatically by SEM using the backscattered mode. From these analyses, the number of uranium particles deposited on the planchet, together with their elemental composition and their coordinates are obtained (Fig. 3).
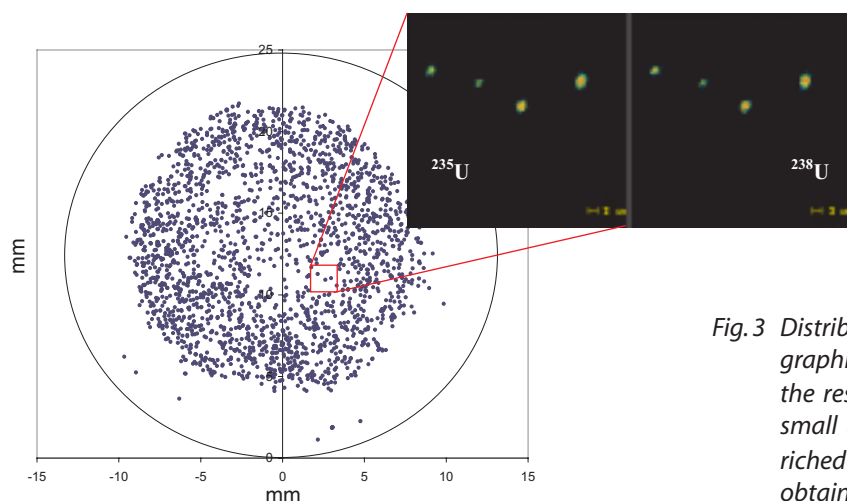

Fig. 3 Distribution of uranium particles (blue dots) on a graphite planchet detected by the automated SEM and the respective mass distribution of ^{235}U and ^{238}U on a small area containing only few particles of highly enriched uranium (isotope abundance in ^{235}U of 50%) as obtained by the SIMS.

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Subsequently, the sample is transferred to the SIMS instrument for measuring the isotopic composition of the particles of interest (using an electron multiplier pulse-counting detector) or for producing spatially resolved images for each isotope (using an imaging detection system). This is achieved by bombarding the particles on the planchet with O^{2+} ions, which then leads to the release of ions from the surface of the particles, the so-called secondary ions. These secondary ions from individual particles are then mass analysed and detected (Fig. 4).
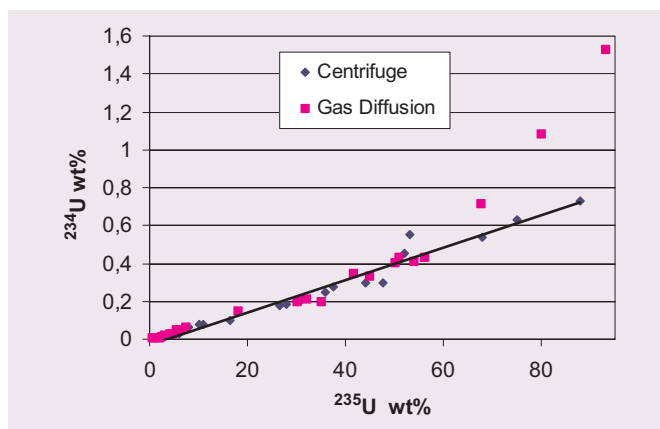
Fig. 4 The isotope abundance of ^{234}U plotted vs. ^{235}U as measured in particles from two different uranium enrichment installations. The results indicate that different separation processes are used in these two facilities

The isotope abundance of ^{235}U and ^{238}U in tens to hundreds of particles is measured; the results obtained reflect the range of enrichments that are produced in a given facility. These are then compared to the declaration of the plant operator. The isotopic composition, in particular the abundance of the minor U isotopes (^{234}U and ^{236}U) allows to recognise the feed material used (natural or reprocessed uranium) and the physical process used for the enrichment (gaseous diffusion or centrifuge enrichment).

Analysis of swipe samples from hot-cells

The main purpose of the analysis of samples from hot cells is to verify the absence of undeclared operations, such as Pu separation. The samples may contain U, Pu, other actinides and fission products. Due to their dose rate, they cannot be handled in the clean laboratory; the sample preparation is carried out in a "clean glove-box". Fig. 5 shows the SIMS results obtained from the analysis of particles taken in two different locations inside a hot cell facility.
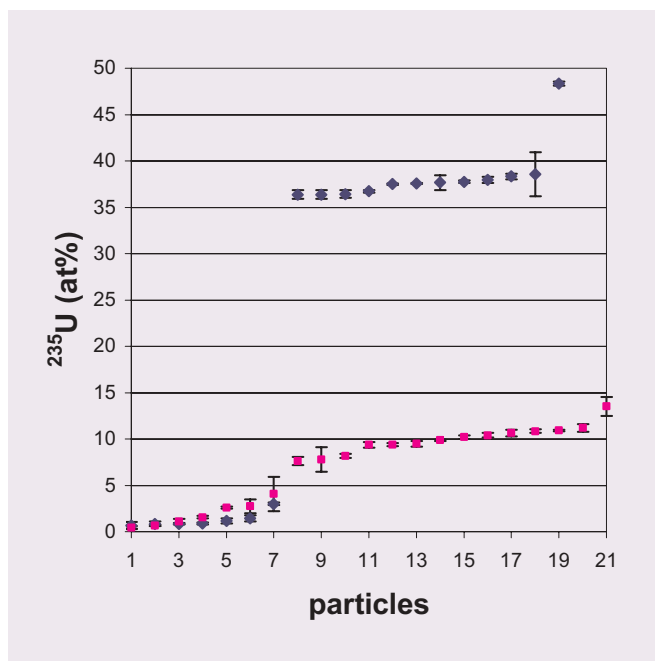
Fig. 5 ^{235}U abundance in particles found in samples from hot cells taken at different locations (represented by different colours). There are clearly two different populations of particles containing low enriched uranium and highly enriched uranium, respectively.

Two populations of particles were identified: the first one is centred in the region of low enriched uranium while the other one contains around 37% of ^{235}U. The isotope abundance of ^{236}U lies in the region betwen 0.3 and 0.4%, indicating fuel with low burn-up. The SEM analysis and the related EDX spectra of some of the particles revealed the presence of Al associated with U. The U isotopic ratio results together with the detection of Al clearly identify the particles as fuel from a Materials Test Reactor.

Uranium oxide control particles

In order to calibrate the measurement instruments, to establish traceability to the SI system (the international system of measurements and units) and for quality control, standard particles with a well-known content of uranium and certified isotopic composition are needed. Since such particles are not commercially available, it was decided to produce them at ITU. Monodisperse uranium oxide particles have been produced starting from certified standard reference materials of different uranium isotopic composition [16] by the aerosol generation method. The morphology of these particles was studied by scanning electron microscopy
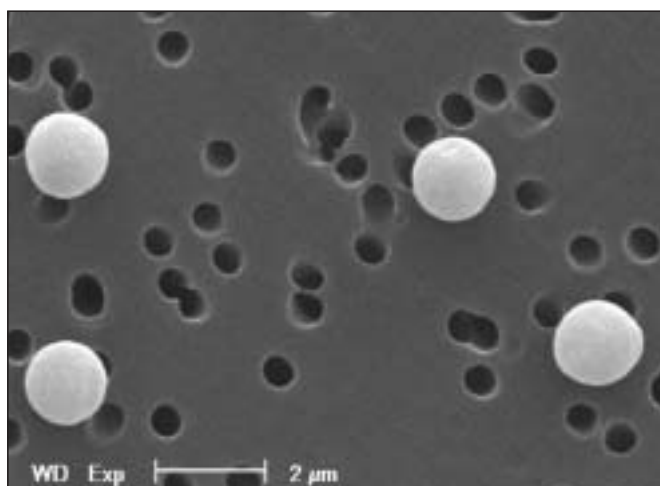
Fig. 6 SEM image of four monodisperse uranium oxide particles on a Nucleopore filter

(see Fig. 6). Secondary ion mass spectrometry was used to verify the isotopic composition of the produced particles.

Fission Track method

This method is an alternative to the previously discussed SEM-EDX technique. The fission track method is used at ITU for the identification of particles containing fissile isotopes after extraction of the particles from the swipe. The samples are irradiated with neutrons in a TRIGA reactor at the
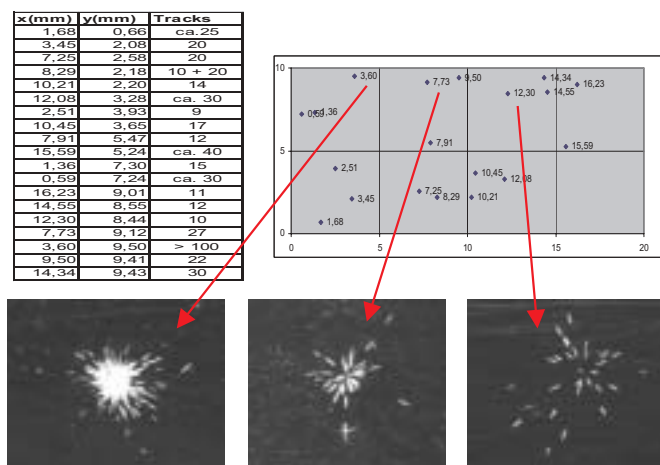
Fig. 7 Fission tracks observed on a portion of a swipe sample. The three particles are of similar size, yet the increasing number of tracks (bottom left to right) indicates increasing enrichment

University of Mainz. The neutrons induce fission and the fission fragments create "tracks" in a thin film that covers the sample (see Fig. 7).

The number of tracks is counted under an optical microscope, as indicated in the table. Assuming that the particles consist of pure uranium oxide and are of similar density and diameter as compared to the standard (monodispersed) particles, their enrichment can be estimated from the number of the tracks observed. The particle morphology can then be investigated by SEM and their isotopic composition is measured by SIMS.

3.2 Age determination

Work on the age determination of nuclear material was started in 1998 at the ITU in the context of nuclear forensics. The age is a very important parameter that allows to conclude on the origin of the material, i.e. its place and date of production. However, age determination can also be useful in safeguards (additional protocol) and in view of a fissile material cut-off treaty (FMCT). The "age" corresponds to the time that has elapsed after the last chemical separation or purification of the material. It makes use of the fact that uranium and plutonium isotopes decay into daughter nuclides following the law of radioactive decay. After a separation the concentration of daughter products is assumed to be zero. Yet they grow in at the rate of their parents' half-lives and the age can be determined from these time dependent parent/daughter ratios, i.e. for plutonium ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U and ^{241}Pu/^{241}Am, and for uranium ^{234}U/^{230}Th and ^{235}U/^{231}Pa [17].

The age determination was established first for bulk plutonium materials and validated using standard reference materials of known ages. The ages of three different Pu/U parent/daughter pairs were determined by isotope dilution thermal ionisation mass spectrometry (ID-TIMS). The results were compared to the age obtained from an independent method, i.e. the ^{241}Pu/^{241}Am-ratio by gamma spectrometry. Then the method was applied to samples from cases of illicit trafficking, with isotopic compositions varying from reactor-grade to weapons-grade plutonium, and with ages from 2 to 40 years. The ages obtained were consistent for all four parent/daughter ratios, thus demonstrating the reliability of the results [18].
Next the Pu age determination methodology was extended to particles using SIMS. Age determination of particles can be applied, e.g. for swipe samples from hot cells to reveal the production period. Standard reference materials of known ages were used to correct for the differences in ionisation

Review Article

yield of Pu and U [15]. A comparison of the results for Pu age determination obtained by three different techniques is shown in Fig. 8.

Fig. 8 Difference between experimentally determined ages of plutonium samples and their reported ages. Three different methods were applied: Thermal ionisation mass spectrometry (TIMS), gamma spectrometry and secondary ion mass spectrometry (SIMS).

Age determination of uranium is significantly more difficult, because uranium isotopes are very long lived, therefore the amount of in-growing daughter products is extremely small. An appropriate methodology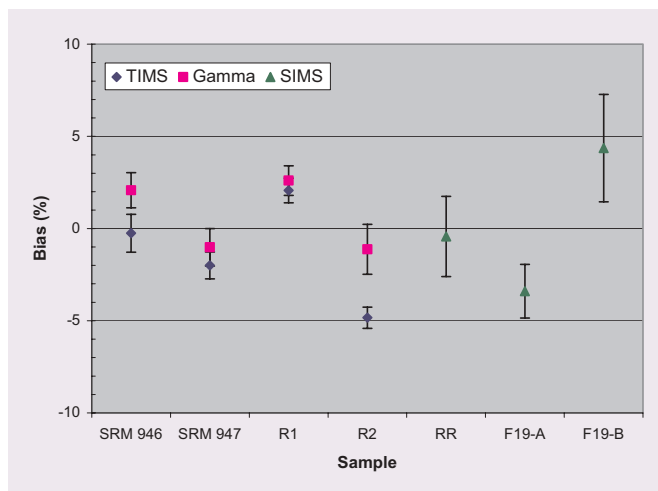 was first developed and validated for highly enriched uranium (HEU) [19]. The decay products were separated after having added a spike. The amount of daughter nuclide was accurately quantified using isotope dilution mass spectrometry for ^{230}Th and alpha spectrometry for ^{230}Th and ^{231}Pa. Very recently the method was extended to low enriched and to natural uranium, aged between 20 and 60 years.

3.3 Methods for control of alternative nuclear material

Recent discussions on the proliferation potential of neptunium and americium have led the IAEA to take some actions towards a possible control of these alternative nuclear materials (ANM). Presently efforts are mainly being focused on neptunium since the proliferation risk associated with americium is somewhat lower. One of the measures currently being considered for ANM control involves the establishment of methods for "flow sheet verification" (FSV) to gain assurance that ANM are not being separated during repro-

cessing. While representing mainly a qualitative verification approach, FSV nonetheless may have to be supported by supplementary measurements for direct analysis of neptunium.

Under normal plant operating conditions about 99 % of the ^{237}Np inventory entering the plant with the input solution of the dissolved spent nuclear fuels should finally end up in the high level liquid waste (HLLW). Key measurements for the control of ^{237}Np based on an input-output balance therefore would have to be carried out on these two relevant process solutions. The flow and distribution of Np in a reprocessing plant are shown in Fig. 9.

Experimental tests carried out at ITU have proven that the energy-dispersive K-XRF (X-ray fluorescence) technique incorporated in the HKED (Hybrid K-Edge) will be able to provide a direct determination of the ^{237}Np concentration in the HLLW stream at given typical concentration levels of about 1 g ^{237}Np/l without any prior sample treatment. The same analysis, however, will not be possible in input solutions, due to a strong uranium interference. Therefore two independent analytical methods for the analysis of ^{237}Np in input solutions have been developed and tested. Both methods were designed to add minimum costs to already existing safeguards measures applied for the control of the main nuclear materials uranium and plutonium, and to make use of the underlying instrumentation to a maximum extent [20].

Based on commercially available UTEVA resin, a method has been developed (not shown in Fig. 9) for the separation of uranium, plutonium, neptunium and americium from the input solution. The method yields recoveries of approx. 90% allow direct loading of separated fractions on filaments or α-targets for subsequent analysis by thermal ionization mass spectrometry and α-spectrometry. The separation method has been implemented successfully on a fully automated robot system that is in use for routine analysis of uranium and plutonium in samples originating from safeguarding activities of MOX fuel production and reprocessing input streams. If required, additional analysis of neptunium and americium can be made.

Additionally, a method was developed to extend the use of the available HKED instrumentation to the analysis of ^{237}Np in spent fuel solutions. It consists of selective chromatographic extraction of neptunium and plutonium using TEVA resin followed by determination of the ratio of [Np]/[Pu] on the column by high-resolution gamma spectrometry. Knowing the concentration of plutonium from routinely performed K-edge densitometry and X-ray fluorescence measurements, the concentration of Np can be evaluated. The method has been tested on simulated solutions and successfully validated on spent fuel of known [Np]/[Pu] ratio [21].
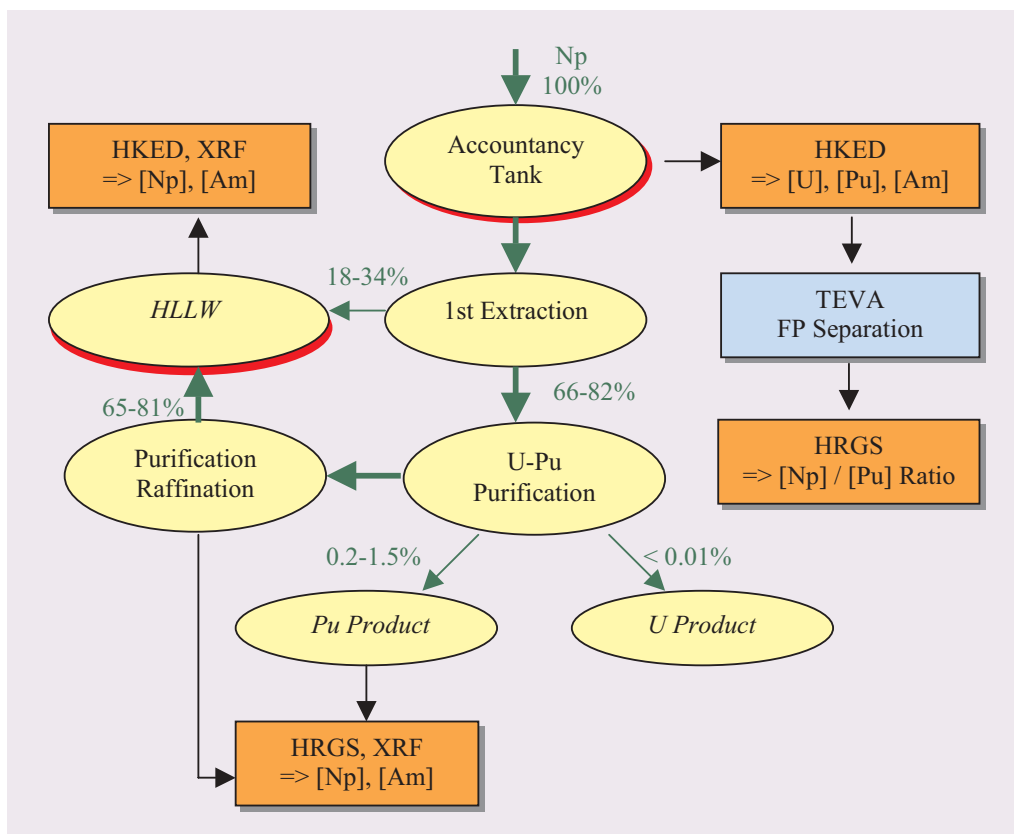
Fig. 9
Illustration of the flow of neptunium in a reprocessing plant with proposed scheme of sample measurements for Np control (HKED: Hybrid K-Edge Densitometry, XRF: X-Ray Fluorescence, HLLW: High Level Liquid Waste, HRGS: High Resolution Gamma Spectrometry).

4. Safeguards for Advanced Fuel Cycles

There is an increasing interest in advanced fuel cycles in which long-lived minor actinides will be partitioned and transmuted into less hazardous products [22]. It is logical that those advanced nuclear processes will also call for appropriate measurement technologies for the assay of major and minor actinides, both for the purpose of process control and for safeguards. However, it is also reasonable to anticipate that the verification measurements for safeguards in those fuel cycles, which offer by their very nature some inherent proliferation resistance [23-24], will not demand utmost measurement accuracy as required and achieved for the U-Pu verification measurements in the conventional fuel cycle.

4.1 Application of radiometric techniques

Radiometric assay techniques are attractive options for a variety of control measurements to be performed in advanced fuel cycles. Among the radiometric techniques developed and utilized for safeguards in the conventional fuel cycle the techniques of X-ray fluorescence analysis (XRF), passive neutron coincidence counting (PNCC), high-resolution gamma spectrometry (HRGS) and calorimetry show the most promising potential for applications in minor actinide assay. None of the techniques will be generally applicable for all possible measurement situations, but they will be able, either individually or in combination, to offer straightforward measurement solutions in most instances. Tab. 2 lists some pertinent information on the respective techniques and their potential application. The quoted minimum amounts of element/isotope needed for analysis were chosen to assure a measurement precision of 5 % or better.

4.2 Measurement examples

The ongoing research and development work for pyrochemical reprocessing conducted at ITU requires continuous and timely analytical support for a quantitative assessment of the separation processes and for the establishment of a material balance. This offered the opportunity for demonstrating the usefulness of several radiometric techniques for quantitative major and minor actinide analysis [25].

Tab. 2 Application of radiometric techniques for minor actinides.

Technique	Element/ isotope measured	Isotope contribution to response*	Minimum amount for assay	Application
K-XRF	Np Am Cm	- - -	50 μg 70 μg 100 μg	Any sample type in liquid form with mass fractions of analyte ≥ 0.02 %.
PNCC	Cm	^{244}Cm. 90-95% ^{246}Cm: 5-10%	200 ng	For any type of Cm-containing samples (liquid or solid) with Pu/Cm ratios $\leq$ 1000
HRGS	^{237}Np ^{241}Am ^{243}Am	- - -	500 μg 10 ng 100 ng	Liquid samples for absolute measurements. Low FP content for ^{237}Np assay.
Calorimetry	Am Cm	^{241}Am: 98% ^{243}Am: 2% ^{244}Cm: 99% ^{243}Cm: 1%	5 μg 200 μg	Refractory MA fuels for transmutation. Combined with PNCC/HRGS for interpretation.

* For typical MA isotopic composition in spent LWR/FBR fuels

Three of the above mentioned radiometric techniques (XRF, PNCC and HRGS) have been so far applied for the analysis of a variety of process samples taken from the electrorefiner and liquid-liquid extraction processes. The respective process samples were typically available in small amounts of $\cong$ 100 mg, either in the form of eutectic salt or in metallic form with Cd, Zr or Bi as major metallic matrix constituents (Fig. 10). Substantial development work for measurement and for data analysis was needed to correctly interpret the measurement responses obtained with the different radiometric techniques from this type of samples.

Curium was determined by passive neutron coincidence counting. Detailed neutron transport calculations, using
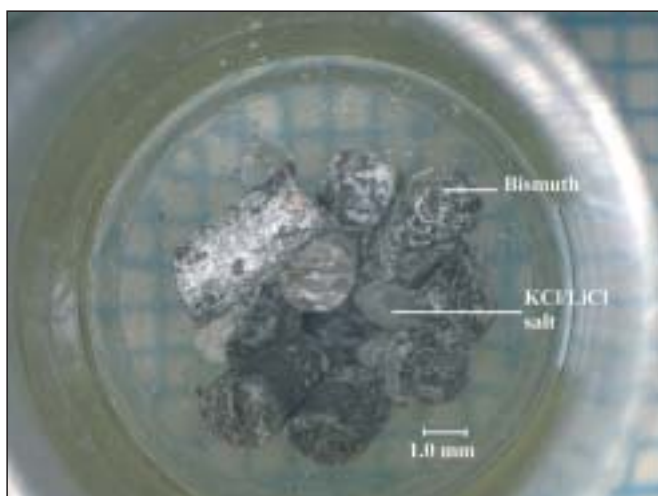
Fig. 10 Typical bismuth and salt samples taken from the pyro-processing facility at ITU.

MCNP, were performed to relate the detector response of the sample to the response of a ^{240}Pu neutron calibration source. The typical amount measured is about 100 to 400 ng ^{244}Cm.
New analytical procedures had to be developed for the absolute determination of the ^{241}Am and ^{243}Am mass fractions in the process samples by means of HRGS. For this purpose two separate spiking methods were established for routine use. The first is based on the use of a large uranium spike. The second uses a much smaller plutonium spike. ^{241}Am and ^{243}Am are quantitatively determined by gamma spectrometry against the 63.29 keV gamma ray from ^{234}Th (a decay product of ^{238}U). The typical amount measured is about 1 to 50 ng of ^{241}Am and ^{243}Am, respectively.

Furthermore, analysis software and measurement procedures for the energy-dispersive X-ray fluorescence (XRF) analysis needed to be adapted, optimised and developed. An example of an XRF spectrum and its deconvolution was given in the ITU Activity Report 2001, p. 15. This technique allows a multi-element analysis, in which the ratios between the actinides present in the solution are determined. Only a single absolute measurement of one of these actinides is then required to determine the absolute quantity of the others. The typical amount measured was about 0.4 to 1 mg for each actinide.

5. Summary and Outlook

In the last decade the safeguards world has been faced with new and important challenges. These have been taken up by the safeguards authorities and their mission has been

amended accordingly. The scientific-technical problems were addressed by research institutes among them also the Institute for Transuranium Elements and appropriate solutions have been or are being developed. Highly accurate measurement techniques were developed and further improved for an efficient verification of the declared amounts of nuclear material. As outlined above, emphasis is put on measurement methodologies that allow cost effective and timely execution of verification measurements. Furthermore, methods for the analysis of individual particles were developed and implemented in order to verify the completeness of declarations through environmental measurements. Future development work will be oriented to improve detection capabilities by improving particle recovery, enhancing the capability for the identification of relevant particles and increasing the precision of the measurement of minor isotopes. Nuclear forensic analysis and the fight against illicit trafficking will certainly remain in the focus and research on appropriate detection methods, testing, qualification and validation of measurement instruments needs to be intensified. ITU is taking a leading position in this area and will continue its efforts in the development of respective analytical methodologies and compilation of relevant information on nuclear materials. The development of new fuel cycle technologies, in particular methods for dry reprocessing, for advanced fuels and for partitioning and transmutation need to be addressed in view of their proliferation potential and safeguardability [26, 27]. Appropriate measurement techniques are under development at ITU.

Through its specific research and development programme, through the significant support to DG TREN (Euratom Safeguards) and through the European Commission's support programme to the IAEA, the Institute for Transuranium Elements contributes to ensuring that illegal activities involving nuclear material are prevented, deterred or detected.

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Visitors and Events at ITU

January

To strengthen the relations with the local authorities, ITU welcomed five mayors from the surroundings. ■ Paul Rübig, Member of the European Parliament (MEP) visited ITU in his function as member of the committee on Industry, External Trade Research and Energy to become familiar with the Institute's research activities. ■ Max Metzger visited ITU for the first time after being appointed new German member of the JRC Board of Governors.

February

Prof. Fortov, member of the Russian Academy of Sciences and former Russian Minister for Research, discussed at ITU the continuation of collaboration between ITU and the Institute of High Energy Density in Moscow.

March

The 8th "Winter Atomiade", organised in the "Black Forest" by ITU was attended by 250 participants from different research institutions in Europe. ■ Following a proposal of Rolf Linkohr, MEP and Axel Fischer, Member of the German Bundestag, a seminar in Berlin was organised on Partitioning and Transmutation (P&T). Dr. G. Heusener, Forschungszentrum Karlsruhe, Prof. C. Rubbia, Ente per le Nuove Tecnologie, Italy, Dr. R. Pellat, Haut Commissaire à

l'Energie Atomique, France, and Dr. J.-P. Glatz and Prof. M. Leroy from ITU gave a comprehensive overview of P&T.

April

Dr. K. Schwaiger, MEP and rapporteur for the 6th Framework Programme, discussed at ITU the Commission proposals for the JRC Euratom specific programme. ■ Prof. Šucha, participant of the Board of Governors, presented the main Slovakian activities in the nuclear field and expressed the wish for collaboration between Slovakian scientists and ITU. ■ ITU's director Dr. Roland Schenkel is appointed Deputy Director General of the JRC with specific responsibility for nuclear activities.

May

The Japan Atomic Industrial Forum Inc., the Central Research Institute of Electric Power Industry and ITU jointly organised in Karlsruhe a Workshop on the Nuclear Fuel Cycle System for the 21st Century. More than 50 experts from all over the world discussed directions for future nuclear energy systems development, including the closed fuel cycle or waste management. The necessity for international co-operative research and development was stressed and proposals for pure and applied research were examined.

June

The 3rd Alpha-Immuno-Therapy Symposium organised by the German Cancer Research Institute, the Universities of Heidelberg and Düsseldorf and ITU, focussed on the therapeutic use of alpha-emitting radioisotopes for killing cancer cells. About 100 physicians, physicists, chemists and engineers from all over the world met in Heidelberg to discuss both progress and challenges involved in the field of Alpha-Immuno-Therapy.

July

In the framework of a Joint Research Centre supported project with the Romanian Ministry for Water and Environmental Protection and the Romanian Ministry of Interior a demonstration exercise on combating illicit trafficking of nuclear material took place in Bucharest, Romania.

September

For the first time ITU participated in the "open day" of the German Research Centre Karlsruhe (FZK), more than 3.000 visitors took the opportunity to inform themselves. ■

ITU inaugurated a new laboratory to foster innovative solutions for nuclear waste management, the "Minor-Actinide-Laboratory". The new facility has been especially conceived to manufacture and characterise the most suitable materials for the transmutation of long-lived elements and will be

one of the major infrastructures within the European Research Area. About 80 guests from Europe and Japan attended the inauguration and the signing of a "Memorandum of Understanding" with the "Commissariat à l'Energie Atomique" (France) in order to implement a European network in this field. ∎

Kaoru Samejima, executive vice-president of the Central Research Institute of the Electric Power Industry, Japan visited ITU to strengthen the collaboration between the Institutes.

October
Within the collaboration between the IAEA and ITU, an international conference on advances in destructive and non-destructive analysis for environmental monitoring and nuclear forensics took place in Karlsruhe. The need and interest for collaboration between law enforcement and nuclear forensics scientists was a key item during the discussions. 120 participants from more than 40 countries took part.

November
Prof. G. H. Lander is appointed new director of ITU. After his studies at Cambridge (UK), Gerry Lander's career spanned working in the USA at Argonne National Laboratory and Grenoble, France at the Institute Laue Langevin. He was director of the Intense Pulsed Neutron Source at Argonne, leaving to come to ITU to lead the basic actinide research effort. ∎ MEP Yves Pietrasanta, visited ITU as Vice-Chairman of the Committee on Industry, External Trade, Research and Energy. ∎

The „Commission Nationale d'Évaluation" (CNE) is the panel of high level experts reporting to the French Parliament, in charge of possible future solutions for nuclear waste manage-ment. CNE visited ITU to monitor its activities in this field. ∎ The Advisory Group of ITU discussed the Institute's programme and strategy for the 6th Framework Programme. ∎

ITU largely participated in the 6th Framework Programme Launch Conference in Brussels. Actinide Research, Nuclear Safeguards, Illicit Trafficking, Alpha-Immunotherapy and the Transuranus Code were the main topics, presented by ITU colleagues.

December
A joint farewell- and welcome-party for ITU directors Dr. R. Schenkel and Prof. G.H. Lander was celebrated with all staff and many guests from research and politics. The former director Prof. J. van Geel transmitted his best wishes.

Basics

Facts & Figures

There were 67 publications in peer-reviewed journals and 88 in conference proceedings. The high number of technical reports (72) reflects the involvement in competitive activities and ITU's engagement in training of young scientists (PhD's & Post-Docs). In 2002, 2 patents were applied for, and 5 were granted. More detailed information can be found in annex I.
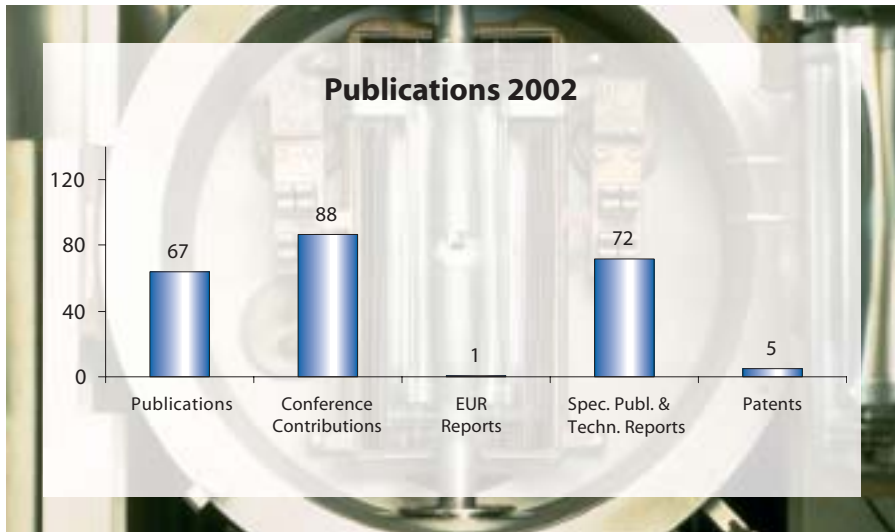
In addition to a statutory staff of 215, a total of 24 research fellows and visiting scientists were present at ITU in 2002. This category of staff is of vital importance to transfer knowledge to a new generation of European scientists. Additionally, ITU makes its facilities, materials and experience available to universities, research centres and other organizations throughout Europe to implement further its educational and training role.

Publications 2002

Publications	67
Conference Contributions	88
EUR Reports	1
Spec. Publ. & Techn. Reports	72
Patents	5

Distribution of the staff at ITU (Dec. 2002)

Scientific staff (Cat A)	54
Technical staff (Cat B)	107
Support staff (Cat C/D)	54
Post-doc	12
PhD	10
Visiting scientsts	2
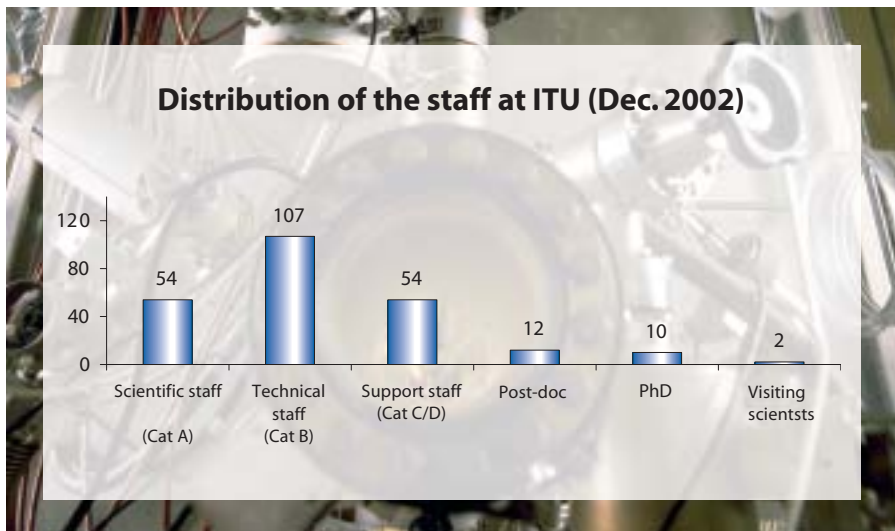
Two major categories of activities are performed in the Institute. The first category is the so-called institutional projects, which covers activities carried out on behalf of the European Commission. With the exception of Alpha-Immunotherapy financed by the EC programme "Serving the Citizen" all other activities are supported by the Euratom budget.

**Institutional budget
Overall Volume in 2002 : 37.2 M€**

- Safeguards Research and Development 36%
- Alpha-immuno-therapy 4%
- Basic Actinide Research 30%
- Spent Fuel Characterisation in View of Long-term Storage 7%
- Measurement of Radioactivity in the Environment 1%
- Partitioning and Transmutation 10%
- Safety of Nuclear Fuel 12%
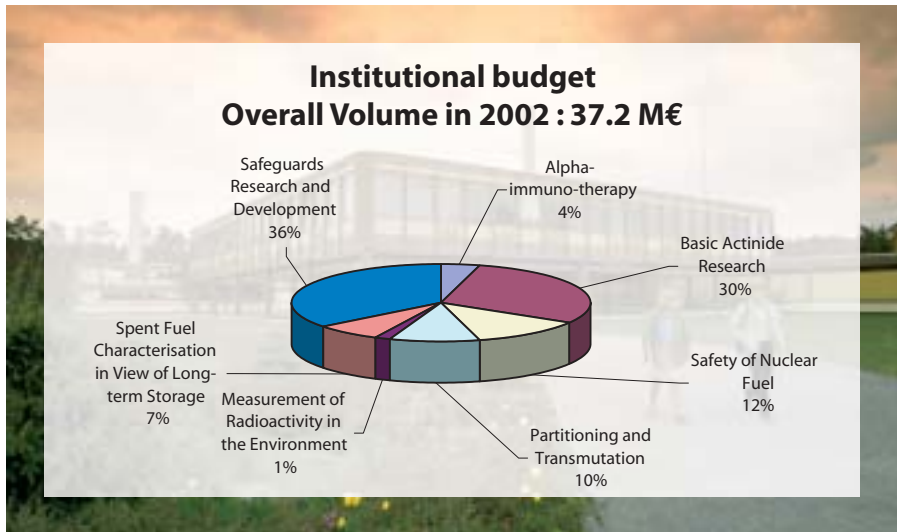
The second category is the so-called competitive activities: Third Party Work, Shared Cost Actions and Support to other Directorates of the Commission. The repartition of this income to the various institutional projects is indicated.

**Competitive budget assigned to institutional activities
Overall Volume in 2002 : 7.2 M€**

- Safeguards Research and Development 42%
- Basic Actinide Research 2%
- Safety of Nuclear Fuel 33%
- Spent Fuel Characterisation in View of Long-term Storage 5%
- Partitioning and Transmutation 18%
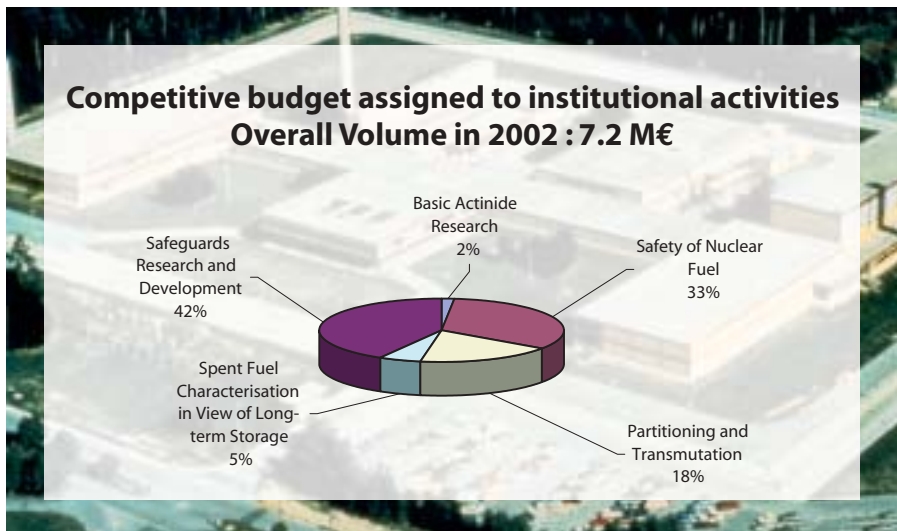
Income generated from competitive activities continued at a high level in 2002. The large increase in billed vs. signed for the Third Party Work is explained by the execution of major parts of contracts signed with industrial partners in previous years.

**Competitive Activities in 2002
Billed versus Signed**

M€

	Third Party Work	Shared Cost Action	Support to Commission	Total

- BILLED
- SIGNED

Benchmarking and Total Quality Management

In agreement with the general quality approach of the Joint Research Centre (JRC), and according to the quality system of the Institute, a new self-assessment has been conducted in 2002. With the scoring method developed by the European Foundation for Quality Management (EFQM) the results correspond to a total of 414 points, which is higher than in 2001 (391 points). EFQM was founded in 1988 by major European companies to develop a European framework for quality improvement along the lines of total quality management. The EFQM methodology was adapted to the needs of the JRC by the JRC Quality Group. A first outcome of the scoring workshop (see Fig. 1) was the decision to reinforce the communication on the follow-up actions.

The overall score increase was not true for all elements, which may reflect the fluctuations in the assessment team composition, but can also be attributed to a change in the organization of the scoring workshop. The better score for the criteria "Customer results" and "Key performance results", compared to the preceding years, was due to the

efforts made since 2-3 years in the definition of indicators and the collection of data, *e.g.* through the customer satisfaction surveys. The score for "Customer results" had an important impact on the total. Compared to 2001, there is a slight improvement in the criterion "Policy and strategy", the period of preparation of the 6th Framework Programme intensifying its visibility. The benchmarking was consolidated, both at ITU and at JRC level.

Two external audits of the quality system of ITU were achieved in 2002: in March in the frame of a competitive action, and in April for the confirmation of the certification according to the norm ISO 9001:2000. Around 20 internal audits were performed. They are managed with the support of "QM Intra", the Quality Management software installed on the ITU internal network, where a catalogue of audit questions has been included. The field of the internal audits has been extended, covering now specifically the safety management of the Institute. In 2003 safety management will be subject to horizontal audits, as well as financial procedures. This was partly an answer

to a development at JRC level, as was the nomination of a "complaint officer" in charge of collecting and evaluating the complaints from outside or inside of ITU, and of following corrective actions. All processes are described in "QM Intra", which is accessible to the staff. The definition of indicators will be completed in 2003.

A staff satisfaction survey was organized JRC-wide, with the active participation of the ITU representative in the JRC Quality Group. The results for the Institute were generally good, but they revealed some areas for improvement, namely in internal co-operation, management of change, procedures and management tasks. The management team has started the analysis and developed corrective actions:

- The development of a common leadership culture will continue, focussed on the aspects of communication, empowerment and teamwork. It started with a two-day workshop in September with the leaders of ITU. The management practices of the Institute were analysed and possible improvements identified. The staff was informed on the output of the workshop. The next step in this continuous process, is the decision of the co-ordination group on explicit actions. A second workshop is foreseen in 2003 to review and to support the whole development.
- In order to increase the mutual understanding within the JRC and to improve synergies ITU will organize seminars with invited JRC speakers.
- The Quality office shall integrate the different aspects of the quality system to simplify procedures and to avoid duplications.

Fig. 1   Self-assessment 2002, the scoring workshop

Organization Chart of ITU

Director
Gerard LANDER

Tel: +49 7247 951 350
Fax: +49 7247 951 591
E-mail: gerard.lander@cec.eu.int

Scientific co-ordinator
Maurice LEROY

Tel: +49 7247 951 386
Fax: +49 7247 951 591
E-mail: maurice.leroy@cec.eu.int

Programme office
Jean-François BABELOT

Tel: +49 7247 951 437
Fax: +49 7247 951 591
E-mail: jean-francois.babelot@cec.eu.int

Hot Cell Technology
Jean-Paul GLATZ

Tel: +49 7247 951 321
Fax: +49 7247 951 561
E-mail: glatz@itu.fzk.de

Materials Research
Claudio RONCHI

Tel: +49 7247 951 402
Fax: +49 7247 951 198
E-mail: ronchi@itu.fzk.de

Nuclear Fuels
Didier HAAS

Tel: +49 7247 951 367
Fax: +49 7247 951 566
E-mail: dhaas@itu.fzk.de

Nuclear Chemistry
Klaus LÜTZENKIRCHEN

Tel: +49 7247 951 424
Fax: +49 7247 951 596
E-mail: Luetzenkirchen@cec.eu.int

Actinide Research
Gerard LANDER (f.f.)

Tel: +49 7247 951 350
Fax: +49 7247 951 591
E-mail: gerard.lander@cec.eu.int

Nuclear Safety & Infrastructure
Werner WAGNER

Tel: +49 7247 951 330
Fax: +49 7247 951 502
E-mail: wagner@itu.fzk.de

Management Support
Jean-Pierre MICHEL

Tel: +49 7247 951 352
Fax: +49) 7247 951 590
E-mail: jean-pierre.michel@cec.eu.int

January 2003

PROJECTS

itu

**Institute for
Transuranium
Elements**

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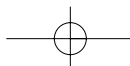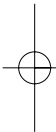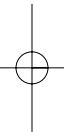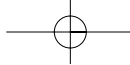
1. Targeted Alpha-Radionuclide Therapy ("Alpha-immuno-therapy")

Introduction

Cancer is one of the main health problems and of growing importance. The treatments available today, even though often effective, cannot permanently cure the majority of cancers. This is typically true for cancers that have spread around the body from the initial tumour site. New kinds of treatment therefore need to be developed.

Targeted Radionuclide Therapy is such a new kind of cancer treatment. It combines new developments in molecular biology and in radionuclides that are new for medical applications. Alpha-emitting radionuclides seem particularly promising.

Principles of Targeted Alpha-Radionuclide Therapy

Some biomolecules, like monoclonal antibodies or specific peptides, can selectively target particular cancer cells: They will find these cells, even if spread around the body, and bind to them.
If an alpha-emitting radionuclide is attached to such a biomolecule, the alpha particle produced during its radioactive decay can kill one or a few targeted cancer cells along its trajectory (Fig 1).

Alpha particles have a high linear energy transfer (LET) and short range in tissue: they release their high energy, and therefore create damage, over just a few cell diameters. They can therefore destroy tumour cells, with minimal damage to surrounding healthy tissue.

Targeted therapy seems particularly attractive for disseminated cancers, such as blood-borne and micro-metastatic tumours, or residual tumour cells that may remain after surgery, external beam radiotherapy or chemotherapy.

R&D activities at ITU

The *global aim* of the group is to contribute to a faster development and applicability of targeted alpha-radionuclide therapy of cancer in Europe and worldwide. Indeed,

ITU has specific and sometime unique competencies in some of the areas involved.

This is done in close collaboration with many external partners (see Tab. 1) and will probably also involve technology transfer to SMEs in the near future.

New collaborations were developed in 2002, in particular with a centre in Australia, which is probably the most advanced for clinical trials in some kinds of cancer, particularly melanoma.

An ITU/Targeted alpha-radionuclide therapy website was created end 2002 (http://ituwebpage.fzk.de/alpha_therapy/index.html).
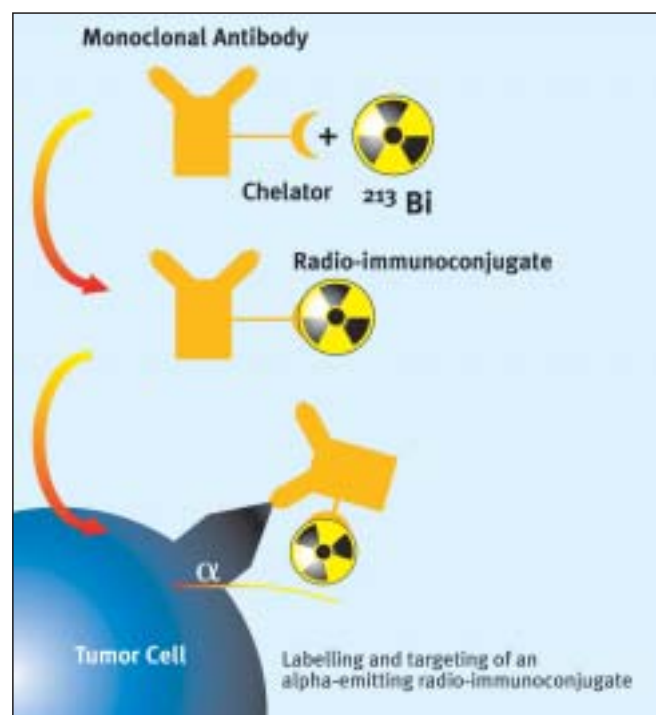
Fig. 1 The typical radioactively labelled biomolecule, to be injected, has 3 components: a monoclonal antibody, peptide or metabolite, targeting tumour cells; an alpha-emitter (typically Bi-213 or Ac-225) and a chelator linking the two.

Projects

Tab. 1 External collaborations

Partner	Cancer type or collaboration subject
Leukemia service, Memorial Sloan-Kettering Cancer Center, New York (USA)	Acute myeloid leukaemia (AML); Prostate cancer
Medical Scitec Australia Pty Ltd, Sydney (Australia)	Melanoma and prostate, pancreas, breast and ovarian cancer
INSERM U.463, Nantes (F)	Multiple myeloma
Department of Hematology, Oncology and Clinical immunology, University of Duesseldorf (D)	B-cell malignancies
Department of Hematology/Oncology, University Hospital, Heidelberg (D)	B-cell malignancies
Radiological diagnosis and therapy, German Cancer Research Centre (DKFZ), Heidelberg (D)	B-cell malignancies and other cancers
Department of Hematology, University of Ghent (B)	B-cell malignancies
Virga Jesse Hospital, Hasselt (B)	B-cell malignancies
Nuclear medicine department, University of Marburg (D)	Solid cancers
Radiological chemistry, Institute of nuclear medicine, Basel (CH)	Glioma, glioblastoma
Clinic of neurosurgery, Kantonsspital, Basel (CH)	Glioma, glioblastoma
Nuklearmedizinische Klinik, Technische Universität München, Munich (D)	Stomach cancer
Radioimmune & Inorganic Chemistry Section, ROB CCR, National Cancer Institute, Bethesda (USA)	Chelation Chemistry. Pancreatic and Ovarian Cancer, and many others
Forschungszentrum Karlsruhe, Karlsruhe (D)	Isotope production
Chelatec, Nantes (F)	Chelate for Bi and Ac
MAP Medical Technologies Oy (FIN)	Clinical grade chelated monoclonal antibodies
MediCity Research Laboratory, University of Turku (FIN)	Inflammation imaging

Activities at ITU essentially concern:
- Development of alpha-emitter production: Bismuth-213 (Bi-213), Actinium-225 (Ac-225), Radium-223 (Ra-223)
- Ensuring safe use in hospitals: radionuclide generators, training
- Labelling of biomolecules: chelator development, chelation
- Supporting pre-clinical research and clinical trials in Europe, USA and Australia
- Radiobiology: mechanisms of radiation effect, individual radiosensitivity

Development of Alpha-emitter production and radionuclide generators for pre-clinical and clinical studies

Alpha-emitters are one of the key components. Pre-clinical research and clinical trials suffer from limited availability of alpha-emitters worldwide. Only ITU and ORNL (USA) can currently produce those mainly used today (Bi-213, Ac-225) in reasonable quantity and of high enough quality and purity.

Because of its short half-life (46 min), Bi-213 must be produced at the place of utilisation. It is a daughter product of Ac-225 (10 days half-life). Ac-225 is currently obtained by extraction from Th-229.

A user-friendly radionuclide generator was developed for safe, reliable and efficient use in hospitals. It allows eluting Bi-213 from the Ac-225 placed in the generator. 19 such generators containing Ac-225 (activity of 350 mCi in total) were produced and shipped to collaborators in 2002.

To further simplify use and improve reliability and efficiency, an automated generator has also been developed, and a first prototype built in 2002. It is being tested (Fig. 2).

To tackle the limited availability problem, ITU is developing and has patented other production methods. The irradiation of Ra-226 with protons in a cyclotron to produce Ac-225, as developed with the Forschungszentrum Karlsruhe (FZK), seems particularly interesting: Ra-226 (p, 2n) Ac-225. A new target design was developed and partly tested in 2002.

Fig. 2 Automatic Bi-213 generator (prototype)

Discussions are in progress with SMEs for the technology transfer of this Ac-225 production methodology, including the radiochemistry know-how, and for collaboration on further R&D.

Work continued on other potentially interesting alpha-emitters, such as Ra-223. The new chemical separation method needed for its production and developed in 2001 works well. Development is in progress of a new calixarene-based chelator for labelling biomolecules with Ra-223 (see below).

Labelling of biomolecules

These molecules are typically monoclonal antibodies or peptides. They need to be radioactively labelled with the alpha-emitters. Labelling is done via a chelator, which must have two specific sites, *i.e.* be "bifunctional", one binding the radionuclide and the other to the biomolecule. To be appropriate, this labelling, or coupling, must be fast (compared to the half-life of the alpha-emitter), stable, including in physiological medium *in vitro* and *in vivo*, and occur in strict conditions that do not degrade the biomolecule (for instance at room temperature).
ITU is involved in chelator development and testing, improvement of chelation procedures and chelation of biomolecules for pre-clinical or clinical research.

In 2002, work continued on the two recently developed chelators for Ac-225, HEHA (patented) and OTEC (patent application filed in 2001). Their structure formulae are in the activity report 2001 (p. 36).

Connection of HEHA to monoclonal antibodies was shown to work well. Stability constants and stability in most physiological media were found to be acceptable, but were lower in the presence of human serum, and currently too low for *in vivo* applications. Further experiments should help clarify and hopefully solve this problem.
OTEC, which has good chelating properties, was further studied, and in particular different schemes for its synthesis (in progress) to find an appropriate one.

For Ra-223, a calixarene crown ether was shown to be a good chelating agent and the synthesis of a bifunctional compound is now in progress. *In vitro* and *in vivo* stability tests should follow.

An improved procedure was developed for labelling a peptide, a Substance-P analogue provided by the Basel partner, with Bi-213 and Ac-225. This should facilitate the use of this labelled peptide for pre-clinical and clinical research.

Pre-clinical and clinical collaborations

ITU is supporting the pre-clinical and clinical studies, carried out in the laboratories or hospitals of the partners, by providing radionuclides, new chelators, training, know-how and occasionally specific equipment (*e.g.* for installation of alpha-emitter hot laboratory in hospitals), labelling biomolecules or performing preliminary test experiments (*e.g.* on cell lines).
Studies in 2002 were performed on cells *in vitro*, in animals or within clinical trials in patients.

In vitro studies showed a relative radioresistance to alpha-immunotherapy (AIT) of some multiple myeloma (a kind of cancer) cell lines. This could at least partly be overcome by combining AIT with some of the various chemotherapeutic agents that were tested, thus improving the therapeutic efficacy. Moreover the bone marrow toxicity of AIT could be limited by using non-myelotoxic chemotherapy or low dose chemotherapy.

AIT was found to be significantly more effective in inducing apoptosis (programmed cell death), compared to gamma irradiation with equivalent absorbed doses, in lymphoid cell lines. This was also true for tumour cells from patients with chemotherapy-responsive chronic lymphocytic leukaemia, but not from chemotherapy-resistant ones.

Projects

In order to try and obviate for the insufficient penetration in solid and less-vascularised tumours of the relatively large antibody molecules, various smaller constructs (of single chain antibody fragments, scFv) were tested functionally and their efficacy shown in mice. Radiolabelling procedures of these "fragile" constructs still need improvement and preclinical animal experiments are planned for 2003, which should provide the prerequisites for subsequent clinical trials in lymphoma patients.

Spread in the peritoneal cavity of gastric cancer cells is associated with a poor prognosis and no effective therapy exists. A subgroup of these diffuse-type gastric cancers expresses a mutated form of E-Cadherin (a cell adhesion molecule). Bi-213-labelled monoclonal antibodies against this mutated form were shown to selectively target and induce death of the tumour cells *in vitro*. The therapeutic efficacy *in vivo* in mice as compared to the toxicity supports the idea of a loco-regional therapy of this kind of peritoneal carcinomatosis and should therefore be tested in clinical therapeutic trials.

A phase I clinical trial, the first one in Europe, included 9 patients suffering from refractory B-cell malignancy (Non-Hodgkin's Lymphoma) up to now. It allowed performing pharmacokinetic measurements and dosimetric calculations. It also showed that the treatment is feasible and safe (after 1 year observation) and showed encouraging clinical results. Further dose escalation steps should therefore start soon.

A phase I/II clinical trial for acute myeloid leukaemia was initiated in the USA and 13 patients studied up to now in this trial (31 in total for trials with Bi-213). Clinicians are very optimistic due to some complete or partial remissions obtained with the highest dose tested. Dose escalation continues.

Radiobiology

A project started in 2002, with the aim to better understand the effects of alpha, beta and gamma irradiation at the molecular level, to characterise the differences between these three types of radiation on normal and tumour cells and to find predictive factors for a response to alpha-immunotherapy in patients with leukaemia/lymphoma. For this, ITU acquired the equipment for a cellular and molecular biology laboratory. Preliminary results, in collaboration with the universities of Düsseldorf and Ghent, seem to show differences at molecular level between alpha and gamma irradiation on leukaemic lymphocytes, which are cell-type specific.

Organization of the 3rd international Alpha-Immuno-Therapy Symposium

This 3rd symposium was co-organized by ITU and its Heidelberg (DKFZ and university) and Düsseldorf (university) partners, as a continuation of the first Alpha-Immuno-Therapy Symposia organized by ITU in Karlsruhe in 1997 and 2000. It took place in Heidelberg on 3-4 June 2002 and aimed at further fostering the development of this new therapeutic approach, by bringing together world experts in the various concerned disciplines, from physics to oncology.

This fully international symposium was very successful according to many participants and speakers. It had double the number of attendees of the previous meeting (about 100), including from some companies. This shows the increasing interest and number of researchers and clinicians involved in this kind of therapy.

An abstract book was produced and distributed at the symposium. And for further dissemination of results, these abstracts and the speakers' presentations are available on CD and on the ITU/Targeted alpha-radionuclide therapy website.

Contact (1.): Christos Apostolidis · tel.: +49 7247 951 389 fax: +49 7247 951 99389 · apostolidis@itu.fzk.de

2. Basic Actinide Research

Introduction

The object of actinide research is the understanding of chemical bonding in, and the solid-state physics properties of, the actinide metals and their compounds. Our level of knowledge of actinide metals and compounds is far inferior to that of the rest of the periodic table, mainly because of the difficulty of handling transuranium materials, but also because of the inherent difficulty of understanding the behaviour of the *5f*-electrons. Their spatial extent and tendency to interact with electrons on ligand sites give actinide materials a complexity unique in the periodic table. Experiments and theory are performed with a view to improved understanding rather than applications. The long-term impact may be viewed in terms of a database for fuels development, for the treatment of waste, and as a contribution to our knowledge of materials in general.

First and foremost in our tasks is the preparation of materials, both in polycrystalline and single crystal form. A second major task is to develop measurement capabilities that can be used both to characterise the material and reveal interesting properties. Since many laboratories are now unable to work with transuranium elements (and sometimes not even with uranium), we have undertaken to construct a „User's laboratory" in Karlsruhe, which is funded by the European Commission (DG RTD) for external users from December 2001 for 28 months.

Following the characterization and initial measurements, usually at ITU, the further understanding of the basic properties often requires the use of other measuring techniques that are available only at large facilities (*e.g.* neutrons, synchrotron X-rays, and muons) or to perform specialised measurements at other laboratories. In most cases the samples must then leave ITU, and for this aspect we have developed a large number of different capsules. Encapsulation and transportation are then arranged by staff at ITU.

Another important aspect of the work is the training of students and postdoctoral candidates, and we have ~ 6 attached to the group at any one time: This helps to sustain and spread the knowledge of actinide science. The progress of our work is documented in papers in the open literature, conference reports, seminars, and review chapters.

2.1 Actinide User Laboratory

The Actinide User Laboratory established at ITU-Karlsruhe is selected as a user facility to participate in the Access to Research Infrastructures action of the Improving Human Potential Programme (IHP) which supports access to our actinide facility for selected users teams. The User Laboratory is open to all researchers of the European Union and Associated States, on a proposal review basis performed by a panel composed of internal and external experts. It aims to increase the awareness and expertise in basic actinide physics and chemistry in offering access to research teams not disposing of such facilities in their own organizations or country. Students are encouraged to participate in the programme and do part of their Ph. D. at the ITU. In this sense this programme ideally complements our institutional activities on actinide research by increasing networking and the number of researchers in this field.

The programme started in 2002. Two calls for proposals were made and submitted projects were assessed in February and October. Almost 180 operating days were allocated to 19 projects granted involving 25 users. Fig. 2.1 gives the number of proposals as a function of the teams' home institution country. At the end of 2002, 9 projects were accomplished. Fig. 2.2 gives the repartition of submitted proposals by type of science.
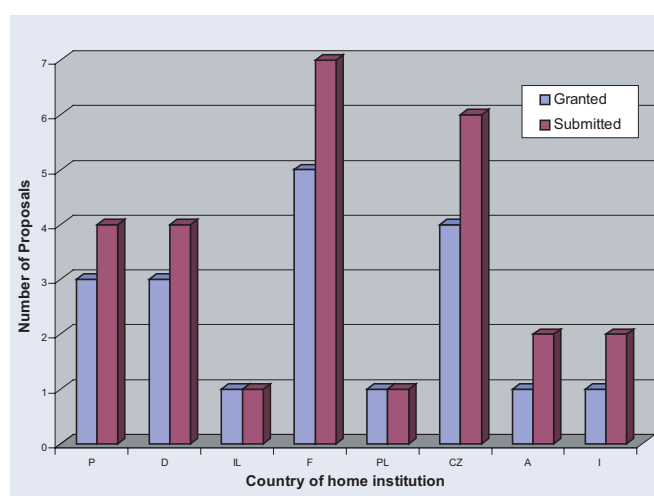
Fig. 2.1   Proposals for participation in the Actinide User Laboratory from the EU and Associated States.

Projects
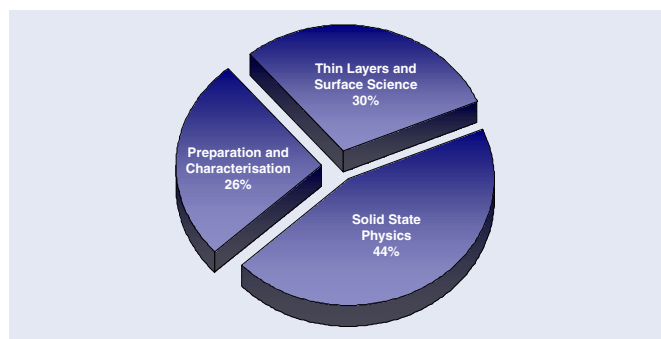
Fig. 2.2   Breakdown of proposals submitted to the Actinide User Laboratory by scientific discipline

2.2 Preparation and Characterization

Our main objectives are to provide well-defined samples for solid-state physics studies and other material research programmes for both internal projects and collaborations with external organizations, and to investigate new classes of materials. These activities cover sample preparation, annealing and single-crystal growth studies, characterization by powder or single crystal X-ray diffraction, and encapsulation of specific samples for internal or external investigations.

Compounds and alloys synthesis: Overview 2002

Complementing the systematic investigations of binary systems with transuranium elements, previously reported for the neptunium systems with silicon and germanium [1], we have completed this study with the investigation of the corresponding plutonium systems, *i.e.* Pu-Si and Pu-Ge systems. A detailed description of the Pu-Si system is given in this report.

Following the discovery of unconventional superconductivity behaviour in UGe_2 [2], URhGe [3] and more recently in $PuCoGa_5$ [4], we have undertaken a systematic investigation

Tab. 2.1   Samples prepared, characterized and encapsulated in 2002 for the indicated measurements.

Measurements	Laboratories	Compounds	Form
Neutron Scattering	ILL-Grenoble, ISIS (RAL)	UPtGe, UCoAl	SC AcM
Magnetism	ITU-Karlsruhe	Ternary gallide compounds (most of these samples were encapsulated as as-cast and annealed samples: $AnTGa_5$ (An : U, Np, Pu, Am, T = Co, Rh, Ir). Pu_2TGa_8 (T = Co, Rh)	AcM, SC
		Userlab: UFe_4Al_8, $NpFe_4Al_8$	AcM, SC
		Binary systems : PuSi, $PuSi_2$-x ($ThSi_2$ and AlB_2 type), Pu_5Si_3, Pu_3Si_2, $PuGa_3$ and $PuGa_2$	AcM
		Solid solution of interesting compounds: $(U_{1-x}Np_x)_2Rh_2Sn$, x = 0.8, 1; $(U_{1-x}Np_x)Ge_2$, x = 0.1	AcM
		Ternary systems: NpRhGe, PuRhGe, $Pu_4Ru_7Ge_6$	AcM
Magnetoresistivity	ITU-Karlsruhe	$AnTGa_5$ (An : Np, Pu, Am, T = Co, Rh, Ir). Pu-Si : PuSi and $PuSi_2$ (AlB_2 and $ThSi_2$ type) $NpPd_2Ge_2$, NpRhGe, $Pu_4Ru_7Ge_6$, $NpFe_4Al_8$	AcM
Diffusion	CEA- Cadarache	$(U_{1-x}P_x)O_2$, x = 0.05, 0.12, 0.2,0.3, 0.4, 0.5, 0.8, 0.95	SC
Pyrometallurgy	ITU-Karlsruhe	^{243}Am, Pu	AcM
Surface Science Photoelectron spectroscopy	ITU-Karlsruhe	Pu, PuSi and $PuSi_2$	P
High-Pressure Resistivity	ITU-Karlsruhe	NpSe, NpS, $PuCoGa_5$, $PuRhGa_5$	SC AcM
Laser Induced Nuclear Physics	ISIS RAL	Tc	AcM
EXAFS	SSRL-Stanford	UN, UO_{2+x}, x = 0.05, 0.08, 0.12, 0.17, 0.2	P
AcM = arc melting SC = single crystal P = powders, polycrystalline sample			

of these classes of materials. On one hand, solid solutions of $(U_{1-x}Np_x)Ge_2$, pure NpRhGe and PuRhGe compounds were prepared and characterized. These new compounds are isostructural to their uranium counterparts. On the other hand, our main effort was directed towards the 1:1:5 plutonium compound first to elucidate the crystal structure of this material and second to investigate the An-T-Ga ternary system, reported below.

To conclude this overview, a list of samples prepared, characterized and encapsulated in 2002 is given in Tab. 2.1.

The An-T-Ga ternary system

Ternary intermetallic 1:1:5 compounds, MTX_5 where M is Ce [5] or Pu [4], T is a transition metal such as Co or Rh, and X is In and Ga, is one of the richest family in the physics of unconventional f-electrons properties. From the structural point of view, it is interesting to observe that this system is related to UGe_2, which becomes superconducting in the ferromagnetic state [2]. Indeed these two systems crystallise with similar crystal structures made of simple cubic $AuCu_3$ building unit blocks. Analysis of as-cast (direct synthesis) $PuCoGa_5$ samples have shown the stability of this phase to be very narrow, and we have investigated the Pu-Ga binary and Pu-Co-Ga ternary phase diagram around the 1:1:5 stoichiometric ratio. The results are illustrated in Fig. 2.3.

Adding a third element in the binary Pu-Ga system leads to a large variety of different compounds crystallising with related crystal structures. For less than 10% change in the starting composition near 1:1:5, at least 3 distinct compounds can be obtained. On the one hand, this observation shows that all these phases are stoichiometric compounds. On the other, it highlights that the pure 1:1:5 phase is the richest gallium resulting from an equilibrium with pure gallium metal, and explains why large single crystal can be grown by the flux technique. We were also able to determine the relationship of the distinct neighbouring phases in the An-T-Ga system.

The study of these ternary systems allowed many new ternary phases to be isolated. All crystal structures displayed are related to each other and are built of common $AuCu_3$ blocks types along the c axis. This simple observation suggests that this crystal unit plays a crucial role in the particular physical properties observed.

References
[1] P. Boulet et al., J. Alloys Comp. 337 (2002) 44
[2] S.S. Saxena et al., Nature 406 (2000) 587
[3] D. Aoki et al., Nature 413 (2001) 613
[4] J. L. Sarrao et al., Nature 420 (2002) 297
[5] H. Hegger et al., Phys. Rev. Lett. 84 (2000) 4986

Contact (2.1-2.2): Franck Wastin • tel.: +49 7247 951 387 fax: +49 7247 951 599 • wastin@itu.fzk.de
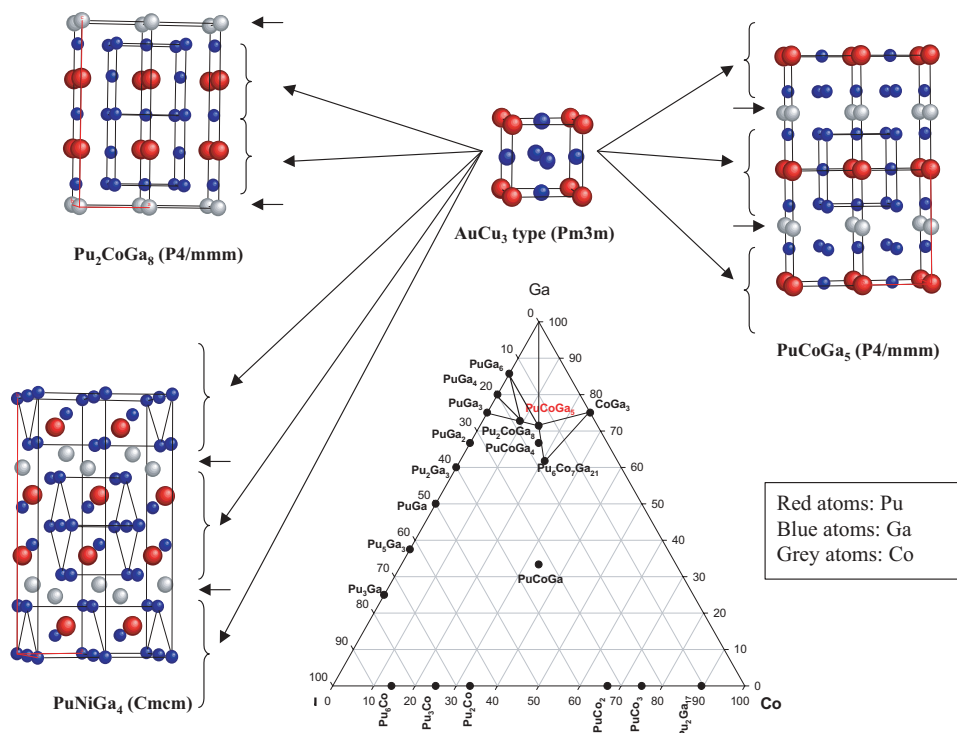

Red atoms: Pu
Blue atoms: Ga
Grey atoms: Co

Fig. 2.3
Partial isothermal section at 850 °C of the ternary phase diagram Pu-Co-Ga. The structures of main ternary phases observed are displayed, highlighting their common $AuCu_3$ type building blocks and the cobalt layers.

Projects

2.3 Solid State Physics

Investigation of plutonium binary systems

The electronic and magnetic behaviours of binary pluto-nium-silicon systems were investigated by magnetisation and electrical resistivity measurements. The compounds forming in the Pu-Si system crystallise in many different structures and reveal a large diversity of magnetic and electronic properties (Tab. 2.2).

Fig. 2.4 displays the magnetic susceptibility (more precisely M/H) of the 5 Pu systems measured from 2 K to 300 K. Pu_5Si_3 is a temperature-independent paramagnet, as expected from the small Pu-Pu distance, well below the Hill limit. $PuSi_{2-x \, (x = 0.3)}$ is a slightly enhanced paramagnet and obeys a modified Curie-Weiss law over the whole temperature range. PuSi orders ferromagnetically at $T_C = 76$ K with a saturation moment $\mu_{sat} = 0.34 \, \mu_B$/Pu atom. Above the Curie temperature, PuSi follows a modified Curie-Weiss law with an effective moment close to the Pu^{3+} free ion value.

The two other systems are more puzzling: $PuSi_{2-x \, (x = 0.4)}$ and Pu_3Si_2, exhibit two successive magnetic transitions of the ferrimagnetic and antiferromagnetic types at 160 K and 70 K, 24 K and 16 K respectively. The magnetisation in the ordered state is small (about 50 times less than in PuSi) and does not saturate at H = 7 T. In the paramagnetic state, both compounds follow a modified Curie-Weiss law. The relevant parameters are listed in Tab. 2.2. It can be noted that i) the paramagnetic Curie temperatures are rather close to
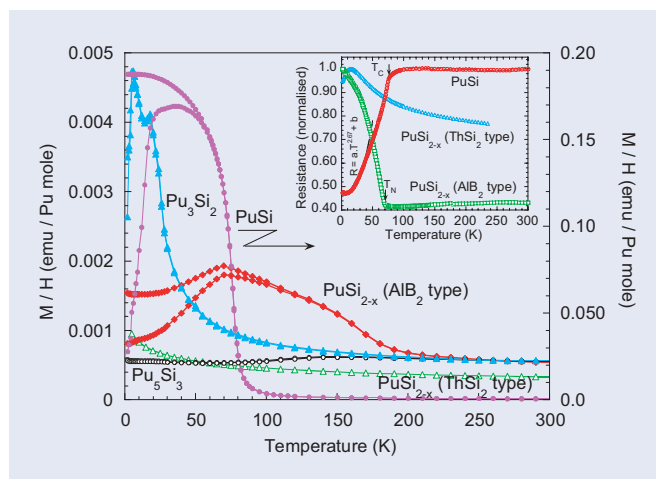
Fig. 2.4 *Zero-field cooled and field-cooled "Magnetic sus-ceptibilities" obtained at H = 1 T for PuSi and Pu_3Si_2 and at H = 7 T for Pu_3Si_2 and the two $PuSi_{2-x}$. (inset) Electrical resistivity as a function of temperature for three of the Pu-Si compositions.*

the ordering temperatures for PuSi and $PuSi_{2-x \, (x = 0.4)}$, ii) the effective moments of all compounds – except PuSi – are much reduced compared to the value of the free ion, iii) the constant term χ_0 is particularly high for $PuSi_{2-x \, (x = 0.4)}$ and Pu_3Si_2.

Fig. 2.4 (inset) shows the electrical resistivity measured from T = 1.8 K to T = 300 K for PuSi and the two $PuSi_{2-x}$ com-pounds. The curve of PuSi displays a plateau down to

Tab. 2.2 *Magnetic properties of $PuSi_x$ binary compounds as inferred from SQUID measurements. "Ferro" stands for "Ferromagnet", "Ferri" for "Ferrimagnet, "AF" for "Antiferromagnet", "Para" for "Paramagnet" and "TIP" "Temperature Independent Paramagnet".*

Compound	$PuSi_{2-x \, (x = 0.3)}$	$PuSi_{2-x \, (x = 0.4)}$	PuSi	Pu_3Si_2	Pu_5Si_3
Structure type	$ThSi_2$	AlB_2	FeB	U_3Si_2	W_5Si_3
Space Group	$I4_1$/amd	P6/mmm	Pnma	P4/mbm	I4/mcm
Pu Sites	4a	1a	4c	2a, 4h	4b, 16k
Pu-Pu (Å)	3.97	3.87	3.63	3.41	2.72
Pu-X (Å)	3.03	3.03	2.92	2.93	2.83
Density (g/cm³)	9.0	9.0	10.4	11.5	12.2
Magnetism	Para	Ferri / AF	Ferro	Ferri / AF	TIP
Ordering temperature (K)	-	160 / 70	76	24 / 16	-
Paramagnetic Curie temperature (K)	-58	142	79.3(5)	7.0(3)	-
Saturation moment (μB)	-	*not saturated*	0.34(2)	*not saturated*	-
Paramagnetic moment μeff (μB)	0.54(5)	0.33(6)	0.72(5)	0.57(5)	-
χ_0 (10^{-6} emu/mol)	230(5)	455(8)	356(4)	460(5)	-

T ~ 90 K and then a sharp decrease. A slight slope break occurs at the Curie temperature T_C = 76 K and at low temperature a $T^{2.67}$ dependence is observed. The paramagnet $PuSi_{2-x}$ ($ThSi_2$ type) exhibits a resistivity maximum at T ≈ 15 K, whereas the antiferromagnet $PuSi_{2-x}$ (AlB_2 type) reveals a sudden increase at the Néel temperature T_N ≈ 70 K. Such a sharp increase of the resistivity at low temperature below T_N was previously observed in NpBi, NpS and NpSe and ascribed to the opening of gaps [1].

Reference
[1] J.M. Fournier et al., Handbook on the Physics and Chemistry of Rare Earths, eds. K.A. Gschneidner et al., 17 (1993) 514-517

Investigation of Np_3Si_2 by SQUID and Mössbauer spectroscopy

In order to better understand the role of the 5f-states we have characterized the magnetic properties of the Np_3Si_2, which crystallises in the U_3Si_2 structure (space group P4/mbm) with two distinct neptunium sites (2a and 4h) coexisting with a population ratio 1:2 [1]. SQUID measurements give the bulk magnetic behaviour, whereas the ^{237}Np Mössbauer effect gives detailed microscopic information about the state of the ion in the solid. From the magnetisation curves as a function of field and temperature (Fig. 2.5) it is clearly seen that Np_3Si_2 orders ferromagnetically at low temperature, with a saturated moment μ_{sat} = 1.30 μ_B / Np atom.
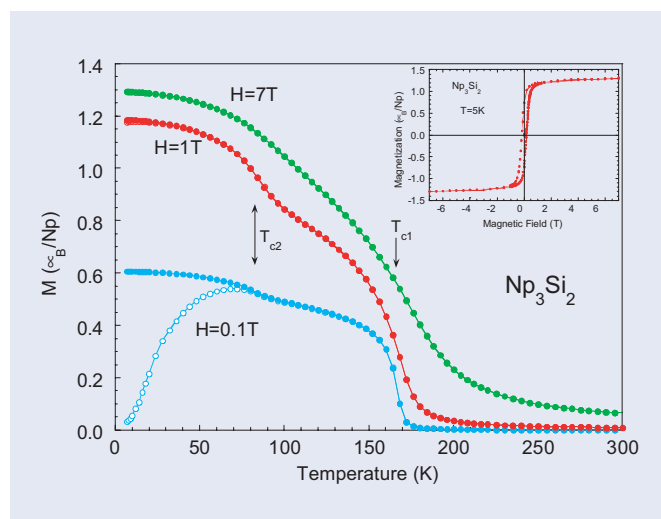
Fig. 2.5   Magnetisation of Np_3Si_2 in various fields. Both zero-field cooled (open circles) and field-cooled (full circles) are shown. The inset shows the hysteresis loop at T = 5 K.

However, this happens through a two-step transition: a first ferromagnetic transition is observed at T_{C1} = 166 K and a second one at T_{C2} = 82 K. This suggests that the two Np ions order at different temperatures in the lattice. Moreover, it can be estimated that the magnetisation of the first step represents 74 (± 10)% of the second (final) step. In this model, it would then suggest that the 4h Np site is the first to order (which would give 66% of the total magnetisation after the first step).

Because the Lamb-Mössbauer factor in Np_3Si_2 decreases rapidly as the temperature increases, Mössbauer spectra cannot be obtained above about 50 K. The spectrum recorded at 4.2 K reveals a complex pattern, in particular the external lines are not symmetric (see Fig. 2.6).
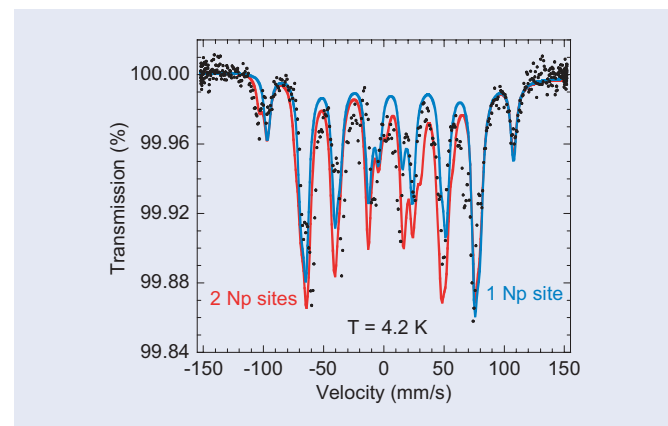
Fig. 2.6   Mössbauer spectrum of Np_3Si_2 recorded at 4.2 K. The experimental points are represented in black, the simulations assuming respectively 1 and 2 Np sites in blue and red continuous lines, respectively.

A correct fit of the experimental spectrum requires a complex distribution of Np sites (hyperfine field), further complicated by the existence of 2 distinct crystallographic Np sites (implying different quadrupolar interactions). For simplicity, we show here two simulations assuming only one or two distinct Np sites. The simulation with one Np site clearly does not reproduce the spectrum, particularly the intensities of the inner lines and the outer line around –105 mm/s. The model with two Np sites is much better; it assumes the presence of two distinct neptunium sites with different quadrupolar interactions and population ratio 2:1, as expected from the crystallographic structure. Moreover, this model also assumes the existence of two distinct isomer shifts, suggesting that the two Np sites may have different

Projects

charge states (Np^{3+} and Np^{4+}), and two distinct hyperfine fields, indicating that the two Np sites carry different ordered moments, 1.77 μ_B and 1.40 μ_B. Within this model, which is still provisional, the magnetisation of the first site would represent 72% of the total magnetisation, in good agreement with the values inferred from the SQUID (74 ± 10 %).

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Contact (2.3): Jean Rebizant • tel.: +49 7247 951 228 fax: +49 7247 951 599 • rebizant@itu.fzk.de

2.4 Surface Science

The electronic structure of actinide alloy films has been the focus of interest this year. Thin film techniques have been used to prepare alloys with continuously varying composi-tion – even off-stoichiometric systems. The incoming atoms – from atomic sources – are instantaneously frozen in the surface films thus ensuring homogeneity on an atomic level, even if the compound is thermodynamically unstable. Using thin film techniques we could thus follow the evolu-tion of the electronic structure of actinides, as they are dilut-ed in a matrix. Two opposing effects influence the bonding properties of the *5f*-electrons and thus the electronic struc-ture of actinides in such systems. On the one hand, dilution suppresses direct *f-f* overlap and thus pure *f*-band forma-tion: this favours *5f*-localisation. On the other hand, actinide-ligand interactions favour *f*-hybrid band formation, thus pushing *f*-states towards itinerancy.

We present here the results for two binary actinide alloys, $Pu_{1-x}Si_x$ and $U_{1-x}Pd_x$. The electronic structure of $Pu_{1-x}Si_x$ alloys, prepared as thin films (1 μg, 50 atomic layers) by sputter deposition, has been studied by photoelectron spectroscopy (Fig. 2.7).

We investigated how the bonding properties of the Pu-*5f*-electrons evolve as Pu becomes diluted in the Si matrix. In pure Pu the *5f*-states participate in the chemical bonding, forming a narrow conduction band, which produces the intense peak with the maximum at the Fermi-level (E_F) in α- and δ-Pu (Fig. 2.7). Adding small amounts of Si disrupts this band, and the Pu *5f*-electrons become localised

(*i.e.* non-bonding). The intensity of the emission at E_F decreases dramatically and the *5f*-spectral intensity is shifted towards higher binding energy (BE), around 1-3 eV. For a one-to-one (PuSi) composition the *5f*-electrons are almost completely localised (there is only a small peak left at the Fermi-level), and this may be attributed to the large Pu-Pu spacing preventing direct *5f-5f* orbital overlap and thus *f*-band formation. The localised character of the *5f*-state is also shown by the presence of a strong local magnetic moment in PuSi (see chapt. 2.3). Interestingly, at higher Pu dilution, the *5f*-electrons regain some of their bonding properties: photoemission spectra show an increased signal at the Fermi-level with clear *f*-character. This *5f*-peak must be due to the chemical interaction between the Pu and the Si ligand atoms, as it becomes more pronounced with increasing Si concentration. It is part of the so-called three-peak structure reported in previous years for other Pu systems [1] and may be due to multiplet transitions from a weakly localised $5f^6$ configuration. Indeed, theoretical calculations of the multiplet intensities predict a three-peak structure for the $5f^6$ configuration [2], and both energy position and relative intensities of the different terms match well with the experiment. In addition, the $5f^6$ configuration would account for the strongly decreased local magnetic
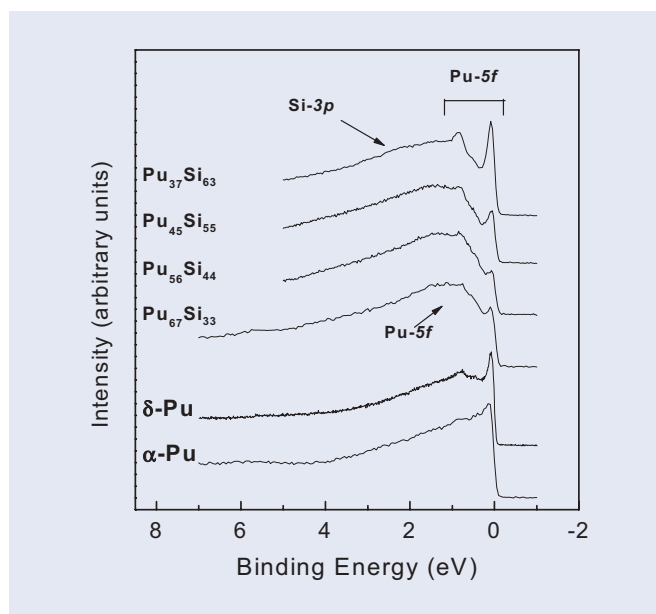

Fig. 2.7   *Hell spectra of Pu metal (α and δ) and $Pu_{1-x}Si_x$ (x in atomic percent) compounds. The Pu-5f intensity at the Fermi-level is directly related to the itinerant character of the 5f-states.*

moment in PuSi$_2$, as spin and orbital moments cancel each other in this configuration. The spectrum of PuSi would be typical for a $5f^5$ configuration, which has a local magnetic moment. Indeed the PuSi spectrum is very similar to the spectra of PuSb and Pu$_2$O$_3$, which both are $5f^5$ systems. This study also shows the complementarity of experimental tools in our laboratory, and helps to describe how bonding between the 5f-electrons and ligand atoms occurs.

Localisation phenomena have also been observed in the U$_{1-x}$Pd$_x$ system. The effect of dilution / hybridisation can be followed for both U and Pd, as their valence levels (U-$5f$ and Pd-$4d$) have strong photoemission signals. Pd was chosen as ligand element, because UPd$_3$ is one of the few U inter-metallics with localised $5f$-electrons. $5f$-localisation is explained as well by the specific binding energy of the Pd-$4d$ band (not favourable to hybridisation with the U-$5f$) and the specific crystal structure of UPd$_3$ (suppressing direct f-f overlap of neighbouring U atoms) [3]. When doping UPd$_3$ with U atoms, eventually delocalisation must occur as U-U bonding becomes more important. The question is how the transition from localised to itinerant behaviour occurs. Either there is formation of a narrow band, which widens as the U concentration increases (homogeneous

response) or there is a superposition of a wide $5f$-band (in U rich regions) and localised $5f$-levels (in U poor regions), with the weight of the wide band increasing (inhomogeneous response). Valence band spectra allow us to distinguish between these two situations. Fig. 2.8 shows spectra of pure Pd, pure U and a series of mostly Pd rich intermetallics.

In pure U the $5f$-electrons form a narrow band of itinerant states, appearing as a sharp peak cut by the Fermi-level (pinning at the Fermi-level is an indication for $5f$ itinerancy). Pure Pd has a broad peak, attributed to the Pd-$4d$ band containing 9.7 electrons, which is cut by the Fermi-level. Doping Pd with about 9% of U (U$_9$Pd$_{91}$) results in a dramatic decrease of the signal at the Fermi-level and a shift of the Pd-$4d$ to higher binding energy. There is no sharp U-$5f$-peak at E$_F$, thus proving $5f$-localisation [4]. But also the Pd-$4d$ peak is removed from the Fermi-level and shifted to higher binding energy. This shift is due to the filling of the $4d$ band – which needs only 0.3 electron state. Once full it is no longer pinned at the Fermi-level and moves to higher BE. The shift continues with increasing U concentration, up to the UPd$_3$ (U$_{23}$Pd$_{77}$) intermetallic. This intermetallic has the highest possible U concentration, and further uranium cannot bond directly with Pd. Photoemission data indeed show that there is no further high BE shift, but rather a narrowing of the Pd-$4d$ emission. This is attributed to the dilution of Pd atoms in a U matrix, which leads to their isolation and thus more atomic-like behaviour. The supplementary U does not form a separate phase, but both elements are atomically dispersed. Therefore a homogeneous response should also be expected for the U-$5f$-states, instead of an inhomogeneous one. Evolution of the valence band spectra of U$_{1-x}$Pd$_x$ is thus consistent with the scenario that for U concentrations lower than in UPd$_3$ the $5f$-electrons are localised, but then gradually become itinerant, first forming a narrow band, which then broadens to become similar to that of U metal.
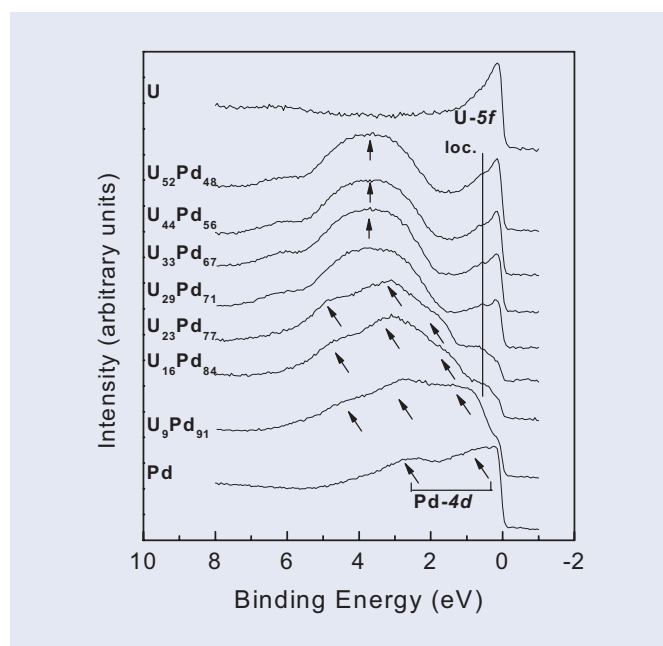
Fig. 2.8   Hell spectra of U, Pd and U-Pd intermetallics. At low U concentrations, the U-5f-states are displaced from the Fermi-level, thus pointing to their localised behaviour.

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Contact (2.4): Thomas Gouder • tel.: +49 7247 951 243 fax: +49 7247 951 599 • gouder@itu.fzk.de

2.5 High-Pressure Studies

High-Pressure Resistivity Study

Considerable progress has been made this year in getting the high-pressure resistivity equipment working, and now two instruments are operational.

Americium metal

Studies started with a ^{241}Am batch [1] and were the first reported on this isotope under 4 K. The critical current behaviour has been determined up to 16 GPa and values around 10^7A/m^2 were found; increasing with pressure. An important self-damage effect of this isotope occurs at low temperature (T<1K) and the large self-heating effect (~110 mW/g) [2] is so important that the minimum temperature was limited to T~550 mK.

The second study was performed on foils of ^{243}Am, as used previously at ITU [3]. Our results (Fig. 2.9) are consistent with those reported before [3] with the currently accepted Am phase diagram [4]; but, in addition, we measured the critical field as function of pressure.

Earlier work [5] at ambient pressure found H_{c1} ~ 50 mT, which suggests type-I superconductivity. When applying

pressure, a large enhancement of H_c(T) is observed (Fig. 2.10). The critical field reaches over 1 T at the maximum of T_c (6 GPa) and the slope at T_c, is close to the orbital limit. This raises the question of whether the type of superconductivity changes in Am when the 5f-states become delocalised at higher pressure. Further experiments to higher pressure are in progress.
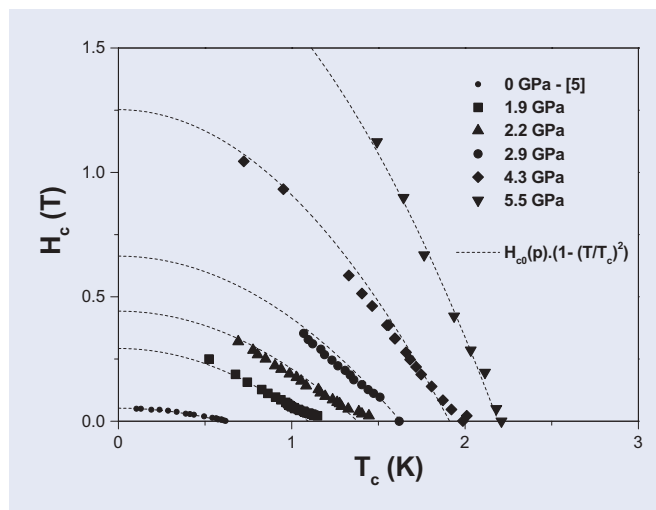
Fig. 2.10 Evolution of critical field of Americium metal under pressure in structure I (p<6GPa). We observe a large enhancement of all values with p: T_c, H_{c0} and slope -dH_{c2}/dT.

PuCoGa$_5$

Both PuCoGa$_5$ (T_c=18.2) [6] and PuRhGa$_5$ (T_c~8.8(2) K) [7] are type-II superconductors and H_{c2}(0) is close to the orbital limit with values around 53 and 21 T, respectively. However, by considering bulk properties (specific heat, resistivity and magnetisation) no information about the nature of the coupling mechanism is available. A survey of transport properties on PuCoGa$_5$ plates with current application j//ab planes was started. T_c increases with pressure up to 9 GPa (Fig. 2.11), then stabilises. The behaviour of the resistivity indicates that the material is metallic. The resistivity decreases with pressure and then increases again when T_c stabilises. We did not observe any Fermi Liquid regime previously reported at ambient pressure.

The superconductivity in PuCoGa$_5$ is remarkably insensitive to pressure. At 16 GPa T_c is 22 K and the material is far from the classical behaviour of BCS elements or heavy-Fermions superconductors. The behaviour is closer to A15 or Chevrel

Fig. 2.9 T_c(p) diagram of 2 isotopes of Americium metal ^{241}Am and ^{243}Am. The different phases, indicated by the vertical lines, have been established by x-ray diffraction [4].
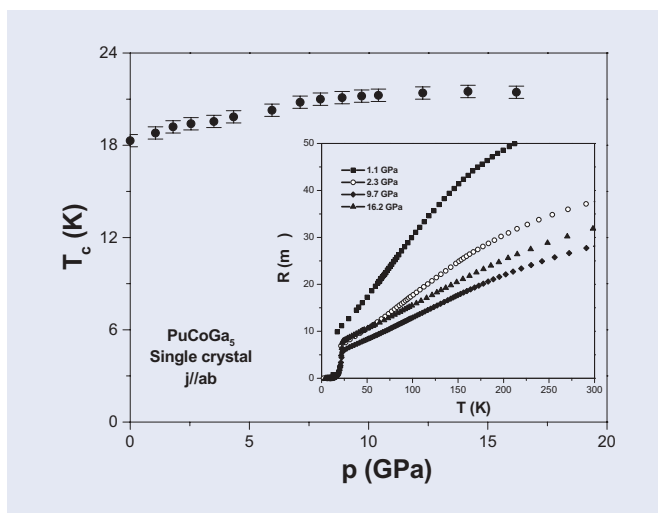
Fig. 2.11 $T_c(p)$ *variations for PuCoGa$_5$ single crystal. The insert presents the evolution of R(T) with pressure. The width of 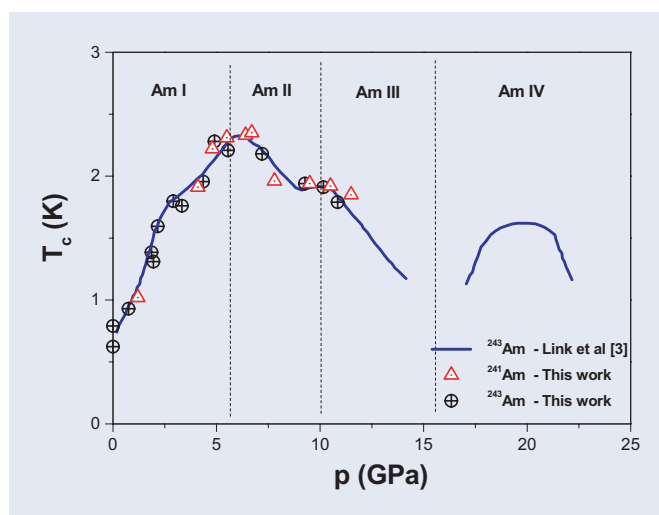the superconducting transition (~ 4 K) is considerable and could come from non-hydrostatic effect on the anisotropy of the material.*

phases (pressure behaviour and H$_{c2}$(0) values). Plutonium based superconductors present a new challenge in understanding unconventional superconductivity.

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Structural studies under pressure

Because of their itinerant *5f*-electrons the lighter actinides have more complicated structures at ambient pressure and tend to show fewer phase transitions under pressure as well as being less compressible. In contrast, the heavier transplutonium metals such as americium [1-2] do not have *5f*-electrons contributing to their cohesive energies at atmospheric pressure. They are more compressible, and show multiple phase transitions before their *5f*-electrons become itinerant. After delocalisation of these electrons, where pressure drives them into a bonding state, they acquire structures displayed by the light actinides.

Continuing our studies into the structural behaviour of the actinide metals with pressure using diamond-anvil cells and the high brilliance available at the ID30 beamline of the European Synchrotron Radiation Facility, we have completed experiments on alpha uranium and protactinium.

High-pressure studies of these metals were performed at room temperature using many different DAC designs. The experiments were performed in an angular dispersive mode using monochromatic synchrotron radiation.

Fig. 2.12 shows a summary of the results up to 100 GPa on samples prepared at both ITU and Oak Ridge National Laboratory [3-6]. The pressure behaviour is shown, where the relative volumes (V/Vo, where V and Vo are the atomic volumes under pressure and at atmospheric pressure, respectively) are plotted against pressure.
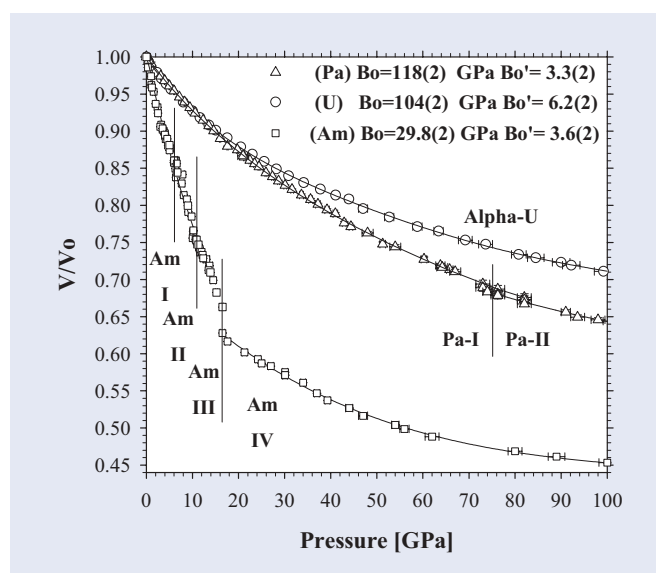
Fig. 2.12 Relative volumes as a function of pressure for U [3], Pa [4], Am [1-2]. The different phases and the bulk moduli are shown.

As a function of pressure the tetragonal structure of protactinium Pa-I (space group, *I4/mmm*) converts to an orthorhombic, alpha-uranium structure Pa-II (space group, *Cmcm*) at 77(5) GPa, where the atomic volume has been reduced by approximately 30%. Therefore, the *5f*-electron contribution to the bonding increases under pressure towards that present in alpha uranium at ambient pressure. The phase transition is accompanied by a very small 0.8% volume collapse which is due to a small additional influx of *5f*-electron character into protactinium's bonding under pressure.

Values for the isothermal bulk modulus and its pressure derivative for the Pa-I phase of the metal were obtained by fitting the experimental data to the Birch-Murnaghan equation of state. The values obtained in this work were 118(2) GPa for the modulus (Bo) and 3.3(2) for the derivative (Bo').

The variation and progression with pressure of each of the lattice parameters for the Pa-I and Pa-II phases are shown in Figure 2.13. A smooth decrease with pressure is observed in the "a" and "c" parameters of the tetragonal Pa-I structure up to the transformation point, where the "c" parameter then becomes the "a" parameter of Pa-II, and the "a" parameter converts to the "b" and "c" parameters of the orthorhombic structure. These changes result in the formation of the lower-symmetry Pa-II phase.
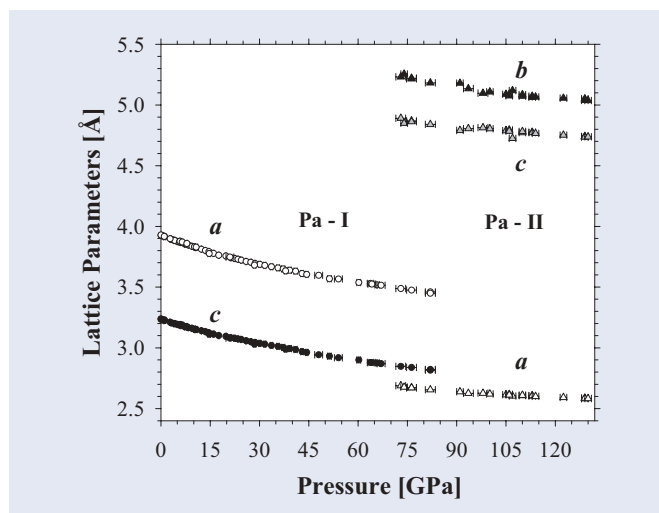
Fig. 2.13 Variation of lattice parameters with pressure for the Pa-I and Pa-II structures. The transition zone is assigned as being 72-82 GPa.

The structural behaviour under pressure of α-uranium at ambient temperature was also studied up to 100 GPa [3]. This study showed that (a) the α-U structure (space group, *Cmcm)* is stable to 100 GPa and (b) that the bulk modulus is lower than all previous determinations with x-rays. α-U is exceptional in the sense that it is the only actinide that does not exhibit any phase transition below 100 GPa. The y-parameter in the *Cmcm* structure has been determined as a function of pressure and remains virtually unchanged. Fig. 2.14 shows the variation of the atomic y position plotted against pressure for both α-U and the Pa-II phase of protactinium, which has the same *Cmcm* crystallographic orthorhombic structure.
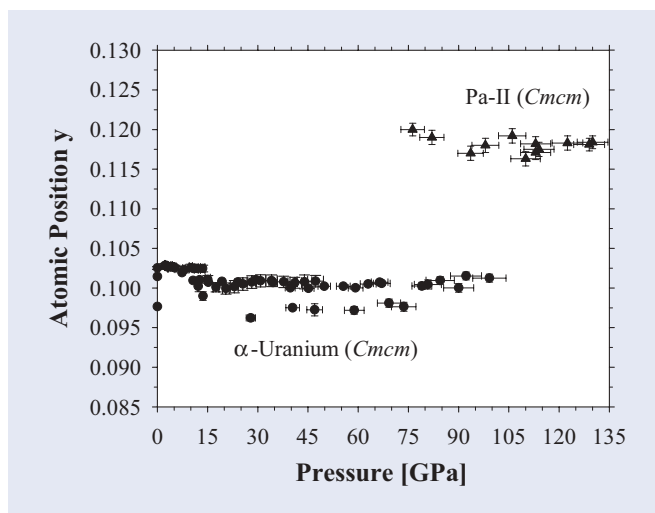
Fig. 2.14 Atomic positional parameter y of the α-U and Pa Phase II (Cmcm) structures as a function of pressure.

In summary these results illustrate the difference between the earlier metals (Pa, U) and those further across the actinide series (Am, Cm, and Cf). Protactinium is the first actinide to have itinerant *5f*-electrons and americium the first with fully localised *5f*-electrons. From the pressure versus volume curves for Pa, U and Am shown in Figure 2.12, it is possible to see clearly this difference. For Pa and U the bulk moduli are comparable [118(2) GPa for Pa, 104(2) GPa for U], and their pressure-volume curves are therefore similar. In the case of americium we observe high compressibility [29.8(2) GPa] and 3 phase transformations occurring at less than 20 GPa.

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Contact (2.5): Steve Heathman • tel.: +49 7247 951 277 fax: +49 7247 951 599 • heathman@itu.fzk.de

2.6 Scattering investigations

Neutron scattering

The following experiments were performed:

(1)   Reflectometer studies with polarised neutrons were made on a number of U/Fe multilayers (prepared at Oxford University as part of a joint project) at both ILL D17 and the reflectometer at ISIS. These experiments give important information about the magnetism of the Fe layers, which dominates the total behaviour and thus may be correlated with the bulk magnetisation measurements. At the same time, resonant magnetic x-ray scattering is being used to examine principally what occurs in the U layers and at the U/Fe interface. The neutron results do show that the moment on the Fe atom is reduced from the elemental value of 2.2 μ_B to ~ 1.5 μ_B, presumably because of hybridisation between the U *5f* and Fe 3*d* electrons.

(2)   At the Los Alamos spallation source a neutron inelastic scattering experiments on UO_2 and $(U_{0.4}Th_{0.6})O_2$ was performed. The large samples were fabricated at ITU. UO_2 orders magnetically at 30 K, whereas the Th doped sample does not order magnetically. This implies that the exchange interactions are much reduced in the doped compound compared to the pure one. On the other hand, the Jahn-Teller (JT) interactions between the U *5f*-electrons and the lattice are the same in both compounds. The experiment, on a polycrystalline sample, measured the excitations between the Γ_5 ground state and the higher crystal-field levels. The data are shown in Fig. 2.15. The centroids of the energy levels are the same in both materials, but the lower-energy excitation is much sharper in the pure compound. This can be understood as due to a splitting of the Γ_5 ground state by the exchange interaction in UO_2. However, the breadth of the first peak in the doped compound is a measure of the JT interaction in both the pure and doped materials. A detailed analysis should allow a separation of these effects for the first time.

Synchrotron X-ray scattering

Papers were published on the work on multi-**k** configurations, which presents a new method for examining multi-**k** configurations [1]; and also a synchrotron study of NpP [2]. (This latter was highlighted in TUAR 2001). Other studies include:
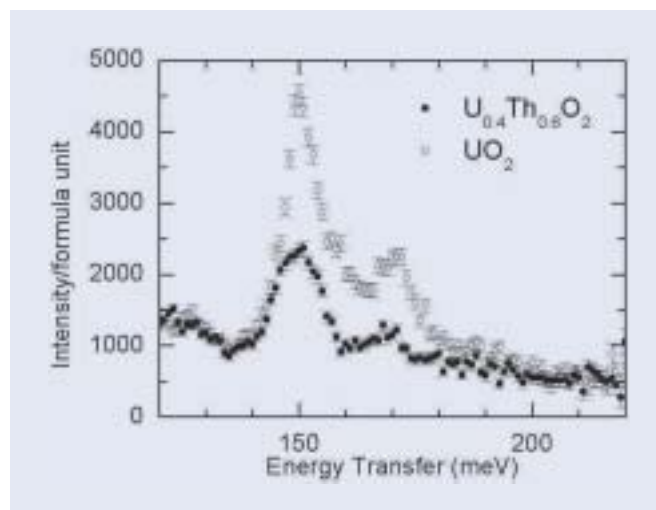
Fig. 2.15 Crystal field spectra taken at the Pharos chopper inelastic neutron scattering spectrometer at the LANL spallation neutron source on pure and Th-doped UO_2. Note the substantial difference between the spectra, even though the energy positions are the same. The incident neutron energy was 250 meV, and both spectra are taken at 20 K.

(1) Observation of quadrupolar ordering in NpO_2 below 25 K

The low-temperature properties of NpO_2 have remained a mystery for experimentalists and theorists alike for half a century. Resonant x-ray scattering at the ID20 beamline at the ESRF this year on a small single crystal made a major advance [3]. Using photons tuned to the Np M_4 edge the scattering is sensitive to asphericity in the *5f-charge* distribution. The experiments showed the development of a *quadrupolar* ordering below the famous T_o (25 K) transition, where so much effort has been extended in the past. Many techniques, including neutron scattering and conventional x-ray scattering, are not sensitive to such ordering, so the resonant x-rays bring a new dimension to studies of this sort. The resulting crystal structure is shown in Fig. 2.16. Two unusual aspects of the configuration are that no structural distortion is observed below T_o, thus implying the 3**k** configuration for the quadrupoles, and there is no dipole ordering in NpO_2 down to at least 1.5 K. However, there are still some unsolved puzzles in NpO_2 and specific-heat experiments are scheduled.

This experiment on NpO_2 required the application of so-called azimuthal scattering together with polarisation analysis. Azimuthal scans, in which we can monitor the scattered intensity as the crystal is rotated about the scattering vector, has never been done previously for a transuranium sample and required a special apparatus. However, it is now clear that most of our experiments should be performed with these capabilities [3].

The phonons were measured for only one polarisation, as this was a test experiment, and are compared to the curves established by neutron inelastic scattering [5] in Fig. 2.17. There is some discrepancy in the high-energy optic modes that is not understood. The success of this technique opens the way to extend the measurements to high temperature on α-U, to consider measuring phonons under pressure in actinides, and to attempt the plutonium experiment.

Fig. 2.16 Crystal structure of NpO_2 in the antiferro-quadrupo-lar state below 25 K. The ellipsoids represent the orientation of the local symmetry axis at the Np position, not the actual charge distributions. The oxygen atoms are shown as spheres. Taken from Ref. [3].
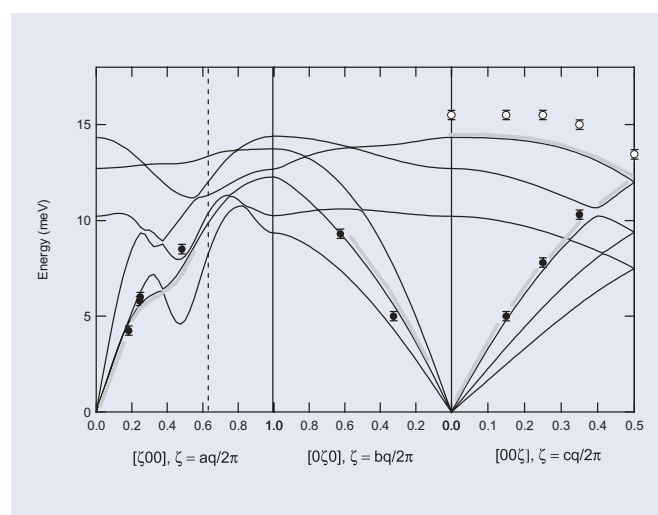
Fig. 2.17 Phonon dispersion curves as determined from the force constant model [5]. The data points are from the present experiment. The grey lines indicate the phonon branches selected by the scattering geometries in our experiment. For the longitudinal optic [00ζ] modes the neutron data fall on the line of the model. Taken from Ref. [4].

(2) Phonons in alpha-uranium by inelastic x-ray scattering

Although neutron scattering remains the probe of choice to measure phonon dispersion curves, the technique requires large single crystals of the order of 100 mm^3 and cannot be performed on many actinide isotopes, *e.g.* ^{239}Pu, because of the large absorption of neutrons. Accordingly, in collaboration with Los Alamos National Laboratory scientists, an experiment was performed on α-U (for which the phonons are known) with the new technique of inelastic x-ray scattering at the Advanced Photon Source at Argonne National Laboratory [4]. The large absorption of photons in heavy elements (the penetration depth is calculated as 6 μm) implied a scattering mass corresponding to only ~ 40 μg.

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Contact (2.6): Gerard Lander • tel.: +49 7247 951 351 fax: +49 7247 951 591 • lander@itu.fzk.de

2.7 Theory of Spin and Orbital Magnetic Moments in Actinide Compounds

Many actinide compounds are observed to have large spin and orbital magnetic moments at the actinide site. A representative example is uranium sulphide for which accurate neutron diffraction results are available [1]. Conventional theory [2] has been unable to reproduce the magnitudes of the spin and orbital magnetic moments from self-consistent calculations. A theory of exchange polarization has been developed in order to address this problem and incorporated into computer codes for self-consistent electronic structure calculations for crystals. The magnetic part of the local spin density approximation [2] to the electronic potential is replaced by a potential due to screened exchange interactions where the screening is based upon the Thomas-Fermi approximation [3]. The resulting magnetic scattering amplitude, for the uranium site in uranium sulphide is compared with neutron diffraction measurements [1] in Fig. 2.18.
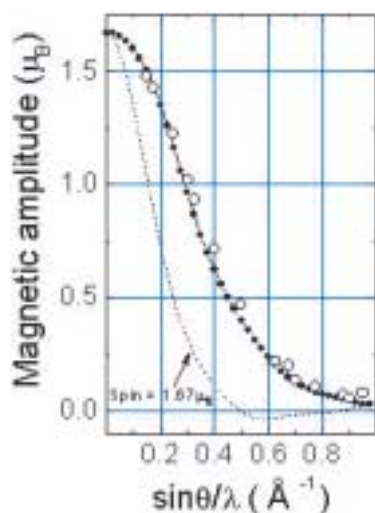
Fig. 2.18 The measured (open circles) from Ref. [1] and calculated (filled circles) magnetic scattering amplitude of uranium sulphide. The dotted line is the result if the moment had only a spin component.

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Contact (2.5.2): Michael S.S. Brooks • tel.: +49 7247 951 476 fax: +49 7247 951 599 • brooks@itu.fzk.de

2.8 Thermodynamic Studies

2.8.1 High-temperature thermodynamic model for non-stoichiometric solid actinide oxides

Melting of uranium-plutonium oxide is an essential issue in the description of severe reactor accidents, where the phase diagrams of the actinide-oxygen systems at very high temperatures play an important role. Even in the simplest case of uranium dioxide, our knowledge of the high-temperatures properties of solid as well as of the solidus-liquidus (S–L) curves is still highly uncertain. The parameters of these curves in the temperature-stoichiometry (T-x) plane date from scanty experimental data published over thirty years ago. Experimental investigations of the S-L – in progress in ITU - are providing a more consistent database, but they will be not sufficient to completely define the thermodynamic properties of the system. The only practical way to solve this problem is to combine new measurements with theoretical calculations based on realistic models.

A reliable equation of state (EOS) for the solid, which is able to describe the whole set of thermodynamic properties in a wide range of temperatures, pressures and compositions, is so far missing. Rigorous theoretical approaches have been successfully applied only to the simplest one-component solids with short-range atomic interactions. In these studies, it was found that near the melting temperature anharmonicity of lattice vibrations plays the most important role. For the examined oxides, there is an additional problem, which makes the construction of such an EOS more complicated. This is the presence of a phase transition (λ-transition) at about 0.85 of the melting temperature. This transition is of order-disorder type and is due to the increasing instability of the oxygen sub-lattice with increasing temperature. A first attempt to solve this problem was proposed within the study Project "Construction of Equation of State of Uranium Dioxide in Solid, Liquid and Vapour Phases" (ITU Report No 7644-2001-03 FISC KAR RU). The method proposed - based on statistical mechanics - proved to be adequate for simple anharmonic solids. An equation for the Helmholtz free energy was now written, describing all thermodynamic properties (including those, which are specific for non-stoichiometric systems, *e.g.,* oxygen potential). The model contains two additional contributions: a) a Coulomb contribution to free energy, and b) a contribution of short-range interactions between Frenkel defects. We proposed a new simplified form for the first contribution

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as a sum of Coulomb energy in an ideal ionic crystal and an additional (defect-related) Coulomb term based on results of the integral equation theory. This part of free energy appears to govern the density-temperature relation and is able to explain the unusual property of non-stoichiometric uranium oxide – *i.e.,* raise of density with increasing O/U ratio. The second addition to the free energy equation is responsible for the oxygen sub-lattice stability and is crucial for predictions of order-disorder transitions. We proposed a model treating defects as specific kind of dipoles whose interactions are of short-range rather than Coulombic. At high concentrations, when all suitable positions in the lattice become occupied, the additional repulsive three-dipole interaction leads to a decrease of lattice stability and, finally, to the λ-transition. Using limited experimental data, we calibrated the model to reproduce the λ-transition in stoichiometric UO_2 as well as to predict the transition line in the non-stoichiometric region.

The new EOS reproduces the experimental density of UO_2 as well as entropy and oxygen vapour pressure over the nearly stoichiometric solid at high temperatures. It is able to extrapolate the thermodynamic properties of the non-stoichiometric solid and, in combination with the EOS for liquid uranium dioxide (This EOS was developed earlier within INTAS 93-66 Project.), predicts the location of the *S-L* curves both in the hypo- and hyper-stoichiometric regions.

First results for solid $UO_{2\pm x}$ presented in our report "*Equation of state of non-stoichiometric $UO_{2\pm x}$: validation of the ITU-INTAS model in the vicinity of the liquidus/solidus with emphasis on the interval {- 0.10 < x < + 0.25}*" are encouraging. We were able to evaluate self-consistently and correctly the density, enthalpy, entropy, heat capacities (C_p and C_v), isothermal compressibility, thermal expansion and oxygen potential for the non- stoichiometric UO_2.

These results require further justification and, very likely, additional model development. Important features of the phase diagram (*e.g.,* triple points) are outside the scope of current EOS's and cannot be used for calibration and/or validation of the model. Extensions of the EOS range will also allow a more reliable reconstruction of the solidus-liquidus phase boundaries based on the two EOS's for liquid and solid. Generalisation of the model for plutonium oxides as well as for mixed uranium-plutonium oxides is also a topic that will be considered in the future.

2.8.2 Experimental determination of the melting behaviour of UO_{2+x}

The salient feature of the high-temperature state diagram of the O_v-UO_2-O_i solid solution is a solubility gap, which is defined by the dependence of the *solidus* and *liquidus* temperatures on the concentration of oxygen defects. However, at these temperatures (2500-3200 *K*), chemical interactions with the containment as well as fast and incongruent material evaporation make conventional experimental methods inadequate for accurate melting investigations. A self-crucible technique in conjunction with fast laser heating in a high-pressure autoclave was, therefore, applied eliminating unwanted chemical interactions and sufficiently suppressing evaporation.

The sample heating was performed with two pulsed Nd-YAG lasers operating simultaneously, and delivering different powers and pulse lengths. The beams of both lasers were merged and channelled through a single optical fibre [1].

The specimen was heated during several tens of milliseconds under gas pressures up to 2.5 *kbar*. The sample temperature was measured by a high-speed pyrometer along with an *ad-hoc* developed multichannel (500-900 *nm*) pyro-spectrometer (Fig. 2.19). The real temperature of the sample was deduced from the measured set of spectral intensities.
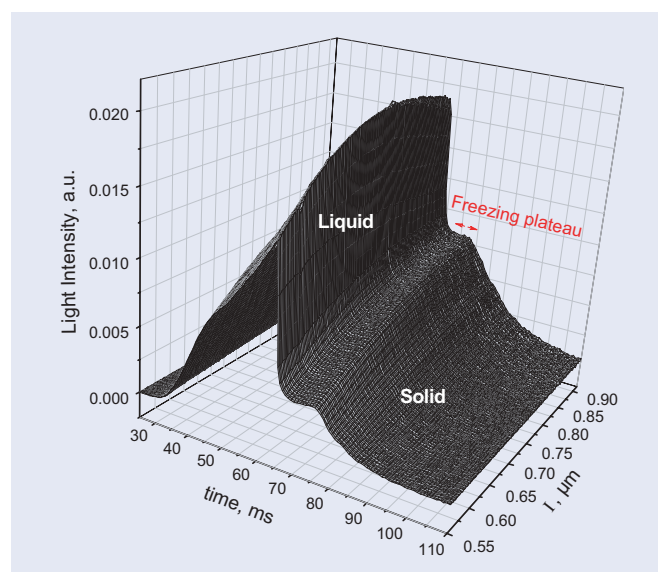
Fig. 2.19 256-spectra buffer recorded with the multichannel spectrometer during a melting-freezing process.

Thermal arrest plateaux and/or points of inflection were observed on the pulse thermograms due to release of the latent heat of phase transformations. Since the thermo-analysis of a freezing material consisting of two, non-miscible components involves a complex sequence of processes, we performed a numerical simulation based on an ideal model. These results were used for an accurate interpretation of the experimental thermograms. Experimental results on the high-temperature UO_{2+x} phase diagram were obtained in the range $0 \leq x \leq 0.20$ (Fig. 2.20).

The obtained *solidus* and *liquidus* lines are markedly different from the only available data published by Latta and Fryxell [2], whose measurements were likely affected by a relevant change in the samples composition during the experiments.

These results are particularly useful since, besides direct consequences (*e.g.*, in $UO_{2.2}$ melting must be expected 400 K below the previously assumed temperature), they are now being used for a validation and a thorough review of our equation of state of liquid urania [4], and for a self-consistent coupling of this equation with a new model for the solid, based on consolidated high temperature thermodynamics properties.

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Contact (2.8.1-2.8.2): Claudio Ronchi · tel.: +49 7247 951 402 fax: +49 7247 951 198 · ronchi@itu.fzk.de

2.8.3 Fission product release in vacuum and in the presence of oxygen

The fission product (FP) release from hyper-stoichiometric irradiated fuel of 70 GWd/t was measured by using a modified Knudsen cell allowing gas inlet up to some mbar oxygen. After a heat treatment of irradiated UO_2 during 4 hour at 500 K in 1 mbar O_2 the O/U ratio was determined to be 2.66, close to that of U_3O_8. A small release of fission gas, volatile fission products, and helium was detected during the oxidation process, corresponding to less than 1% of the inventory.
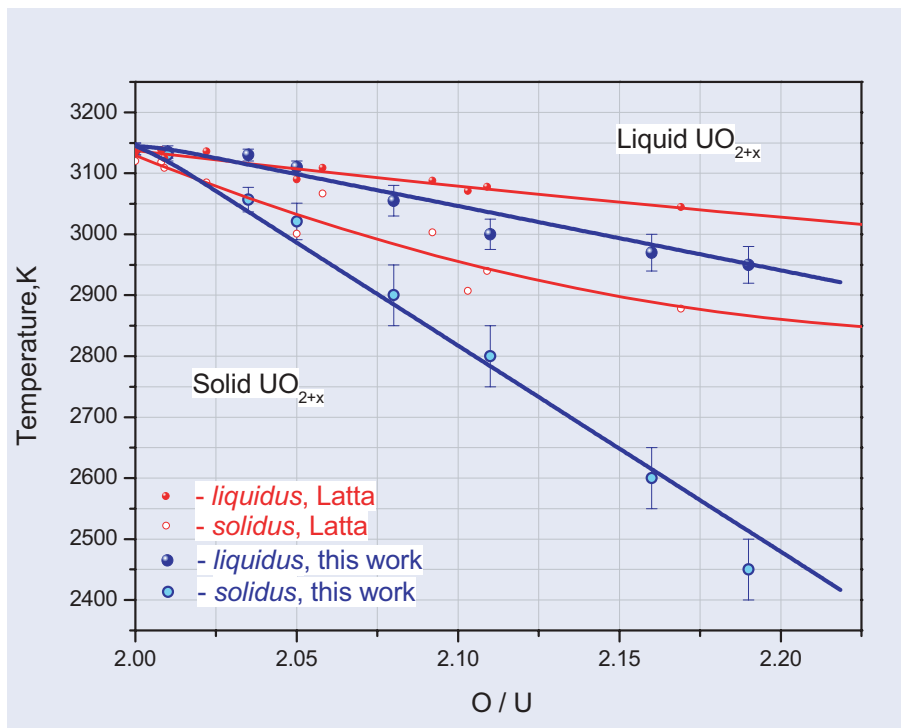
Fig. 2.20
Solidus and liquidus lines for UO_{2-x} deduced from the measurements performed in this work. The experimental points are compared with measurements of Latta and Fryxell [2], and with the curves calculated by Babelot et al. [3].

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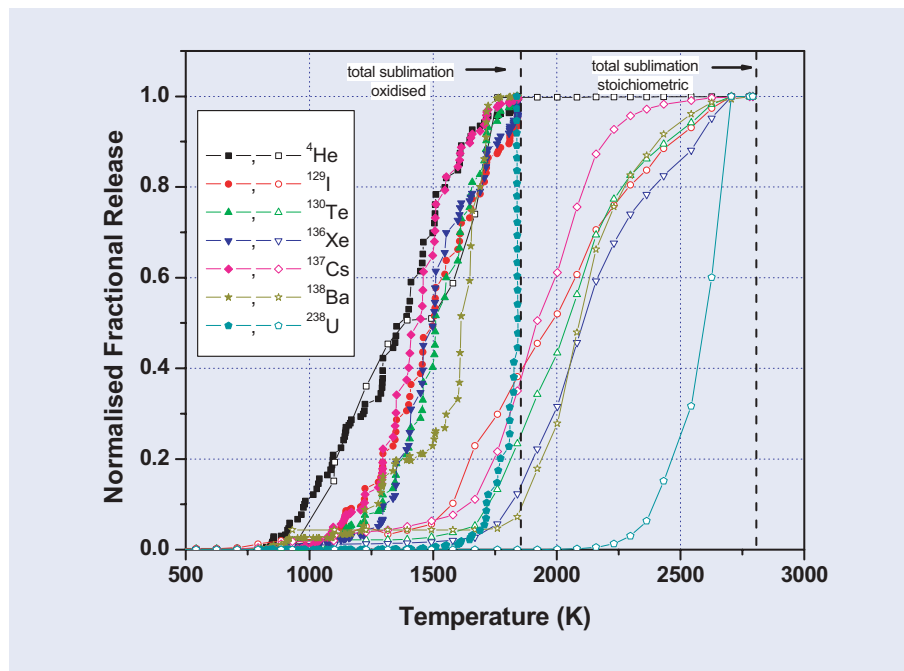
Fig. 2.21
Fission products release from two irra-
diated UO_2 samples heated in vacuo
(open symbols) and in the presence of
1 mbar O_2 (full symbols) plotted as a
function of the annealing temperature.
The arrows show the upper tempera-
ture limit for total sample vaporisation.

The fractional release rates obtained during subsequent sample treatments at higher temperatures in the same oxygen atmosphere are shown in Fig. 2.21, and compared with those obtained with the same specimen in vacuo.

The fractional release curves for fission gas and volatile fission products present a mean shift of approximately 500 K from hyper to near-stoichiometric UO_2, indicating a drastic change of the diffusion parameter and a completely different behaviour of the fission products in the matrix. The release of He, on the contrary, seems to be completely independent of the oxidation level of the uranium oxide.
At 1800 K the oxidised sample totally vaporises, the vapour pressure of uranium $UO_{2.66}$, mainly defined by the UO_3 (g) component being almost four orders of magnitude higher

than that in stoichiometric UO_2. It can be seen that the release sequence of the volatile fission products changes from normal to oxidised conditions, barium and tellurium becoming less mobile in comparison with fission gas. Furthermore, the high oxygen activity entailed a large release of Mo and Ru, mainly in the form of MoO_3 (g) and RuO_2 (g). In effusion experiments with fuel samples at end-of-life after irradiation under normal conditions, these elements have been never observed in the equilibrium vapour phase up to 2800 K. Finally, no lanthanides were detected, in oxygen and in vacuo below 2000 K.

Contact (2.8.3): Jean-Pol Hiernaut • tel.: +49 7247 951 385 fax: +49 7247 951 198 • hiernaut@itu.fzk.de

3. Safety of Nuclear Fuels

3.1 High Burn-up Performance

Reactor safety remains a priority in the EU, especially in view of enlargement. In particular, there is a need to monitor ageing of nuclear installations and also to evaluate new advanced nuclear systems. At present one of the major goals is to make the most efficient use of existing facilities by increasing the burn-up of nuclear fuel under safe operating conditions. There is a need to study the behaviour of nuclear fuels under these high burn-up conditions and to establish databases on the properties for UO_2 (at burn-up >100 GWd/t) and MOX (at burn-up > 50 GWd/t). An extremely valuable tool in this context is the Fuel Performance Modelling code TRANSURANUS, where a detailed description of the fuel rod behaviour at very high burn-up including transient conditions is achieved. Furthermore the fabrication of advanced fuels for existing and new reactor generations requires a consistent R&D work in this field.

3.1.1. Porosity dependence of the mechanical and thermal properties of LWR-fuel

A compilation of microhardness measurements in the porous rim region of high burn-up LWR-fuels has been performed, with the aim to determine the role of the pore type in the property vs. porosity variation. Fig. 3.1 shows the results of the relative fuel hardness (Hv/Hv_o) as a function of the porosity fraction (P) for both rim material [1] and unirradiated UO_2 [2], indicating clearly a lower property decay in the first case.

The difference of behaviour is attributed to the variation of the minimum-solid-area (m.s.a.) fraction in each case, representing the portion of material sustaining load [1, 3]. Thus, while the fresh fuel behaviour appears well fitted by the m.s.a. curve of a system of intersecting solid particles (e^{-bP}, with b ~ 5 [3]), the rim zone behaviour is more properly fitted by the m.s.a. curve of a system of spherical pores immersed in a continuous matrix (e^{-bP}, with b ≤ 3 [3]) (Fig. 3.1) [1].
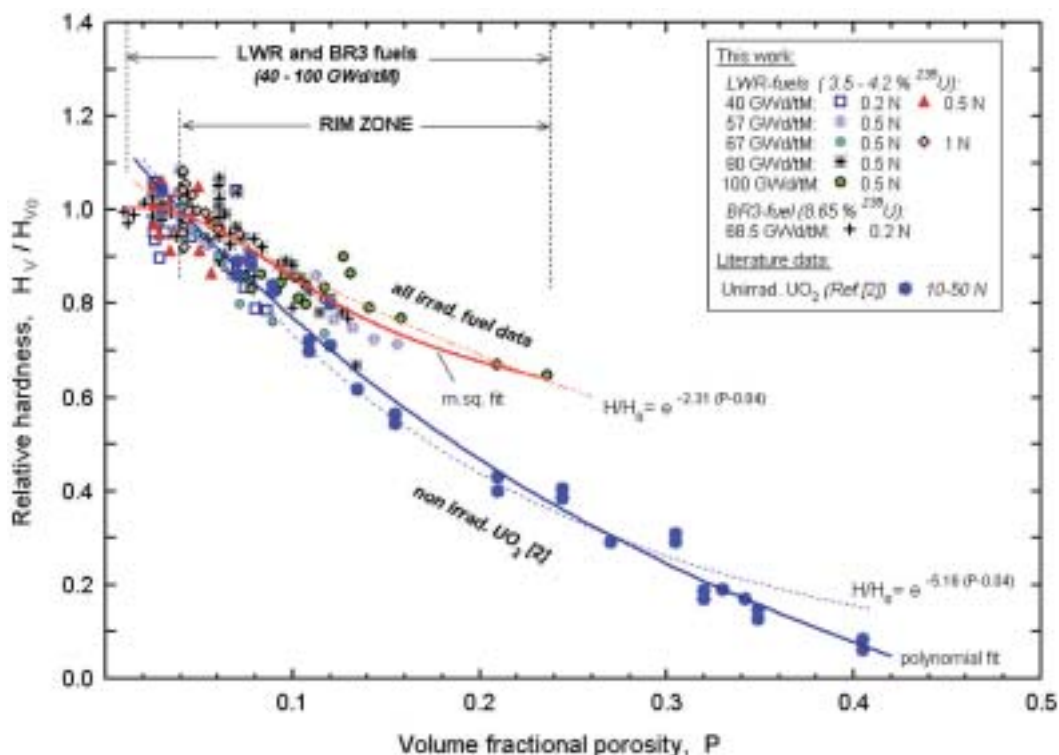
Fig. 3.1 Relative Vickers hardness vs. fractional porosity data of irradiated LWR-fuels (present work) compared to non-irradiated UO_2 (literature data).

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Due to the associated pore configuration, the rim material appears thus not only stiffer, but to exhibit higher percolation and pore connectivity limits, and hence lower trend to gas-release, than the fresh (or low exposed) fuel [1]. Extending the analysis to other properties depending on the minimum solid area (pore ligament) fraction, essentially mechanical and thermal properties [3], less porosity deterioration is in general anticipated for the rim material compared to the as-sintered fuel [1]. Fig. 3.2 shows these trends concerning the E, H, k values.

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3.1.2 Fractal studies of the high burn-up induced fuel restructuring

As a complement of previous characterization studies of the high burn-up restructuring of LWR-fuels [1-2], a novel fractal study approach has been initiated, to reveal possible topological critical aspects of the transformation. The work has been performed in collaboration with the Solvay Institute, Brussels, Belgium and the Joint Institute of Nuclear Research, Dubna, Russia. In the first step, a series of "as-polished" and "as-etched" micrographs of commercial LWR-fuels with burn-ups between 16 and 65 GWd/tM have been treated, in order to compute their fractal dimension by application of the codes PLATO [3] and BIP [4].

As summarised in Tab. 3.1, the results show that the micrographs fractal dimension gradually decreases with increasing burn-up [5], with the sharpest decrease occurring at burn-ups associated with the onset of the rim structure formation, *i.e.* typically ≥ 40 GWd/tM (pellet average) [6] (see Tab. 3.1, as-etched micrographs).

Also, agreeing with the fact that the rim zone penetrates deeper into the fuel as the average burn-up increases, the fractal non-rim/rim transition is shown to move to higher burn-ups as the investigated zone is shifted towards the pellet interior (Tab. 3.1, D2-values) [4]. Further studies are envisaged to individualise the critical processes underlying the observed trends.
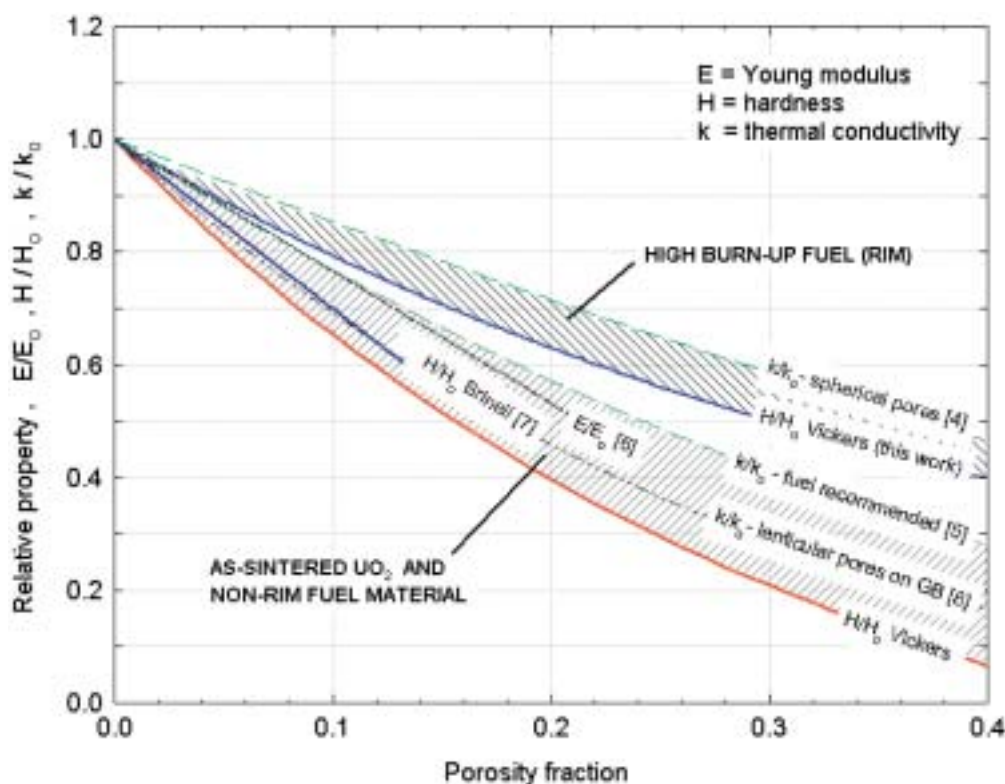
Fig. 3.2
Various measured and estimated „relative property vs. porosity" relations for non-irradiated and irradiated UO_2 [4-8].

Tab. 3.1 Fractal dimensions of LWR-fuel micrographs in the as-polished and as-etched conditions. (Rim transformation apparently associated with D ≤ 1.17)

Fractal dimension	Fuel average burn-up :			
	16.2 GWd/tM	43.9 GWd/tM	54.8 GWd/tM	65 GWd/tM
As-polished micrographs:				
D1 (at pellet edge)	1.21	1.35	0.98	1.05
D2 (at 150-200 µm from pellet edge)	1.51	1.32	1.49	1.14
As-etched micrographs:				
D1 (at pellet edge)	1.34	1.14	1.06	1.17
D2 (at 150-200 µm from pellet edge)	1.40	1.24	1.24	1.08

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3.1.3 Bulk modulus of simulated high burn-up fuels via Synchrotron-compressibility tests

In collaboration with the Actinides unit of ITU an activity has been started to determine the bulk modulus of simulated high burn-up fuels by application of high-pressure XRD techniques. Aim of the study was to determine the effect of dissolved fission products in the elastic response of the fuel lattice. For the present experiments a configuration of synchrotron radiation, diamond anvil cell and energy dispersive detector was selected, with application in the low-pressure range (0-25 GPa). The synchrotron facilities at HASYLAB, DESY, Hamburg, Germany, were used. The materials checked were UO_2 and simulated fuels with 3, 8 and 20 % burn-up, pre-treated under reducing atmosphere. The samples were loaded in the anvil cell in powdered form. The effect of the fabrication porosity in the measurements was hence minimized.

Fig. 3.3 shows the obtained relative volume V/V_o *vs.* pressure curves, where V and V_o are respectively the pressurized and non-pressurized unit-cell volumes.

The bulk moduli (K), obtained by fitting the data with the Birch-Murnaghan equation of state [2], indicate an increase with burn-up (Fig. 3.3). In Fig. 3.4 two types of elastic moduli for the simulated fuels are plotted, *i.e.* those derived from
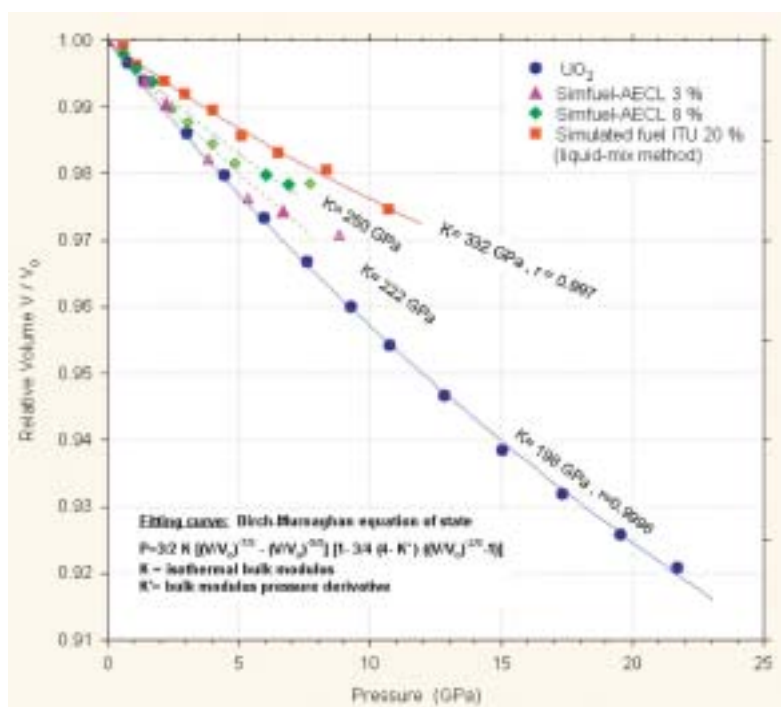
Fig. 3.3
Synchrotron compressibility curves of UO_2 and simulated fuels with 3, 8 and 20% burn-ups and corresponding bulk moduli through Birch-Murnaghan equation of state.

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the compressibility tests as $E^{comp} = 3\,K\,(1\text{-}2\upsilon)$, with υ = Poisson's ratio ~ 0.3, and those derived from the hardness measurements as $E^{hard} = H_V/c$, with H_V = Vickers hardness and c = 0.026 [3]. The agreement between the values up to 80 GWd/tM is remarkable. The departure above this burn-up is attributed to solubility saturation in samples prepared by solid state reaction [4]. However, these results disagree with recent micro-acoustic measurements in irradiated and simulated fuels [5], indicating a completely opposite E-moduli trend (Fig. 3.4). Here the effect of the microstructure, *e.g.* grain boundaries and precipitates, appears crucial. Hence, alternative experiments and theoretical estimations of the elastic constants seem worthy to elucidate the discrepancy.

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Contact (3.1.1-3.1.3): José Spino • tel: +49 7247 951 233
fax: +49 7247 951 561 • jose.spino@itu.fzk.de

3.1.4 Post-irradiation examination of pressurised and boiling water reactor fuel rods

In the framework of the contract with FRAMATOME Advanced Nuclear Power GmbH, non-destructive and destructive examinations of power reactor fuel rods were carried out. The work performed and described in the previous annual reports [1] has continued.

This year 16 fuel rods from two boiling water reactors (BWR) and 8 re-fabricated segments were shipped back from the Petten reactor for post-irradiation examination after the ramp testing. Six-conditioned BWR fuel rods were sent back to the reactor pool.

The installation of the new creep device (testing of the mechanical properties of cladding under intermediate storage conditions) was tested with fully active samples.

Focal points of examinations for this period have been: creep behaviour of cladding materials (long-term, intermediate storage conditions), hydrogen pickup and local corrosion phenomena in advanced zirconium alloys (blisters, shadow corrosion, etc.), dimensional behaviour and high burn-up gas release phenomena of innovative UO_2-fuels and the behaviour of re-fabricated segments after ramp testing.
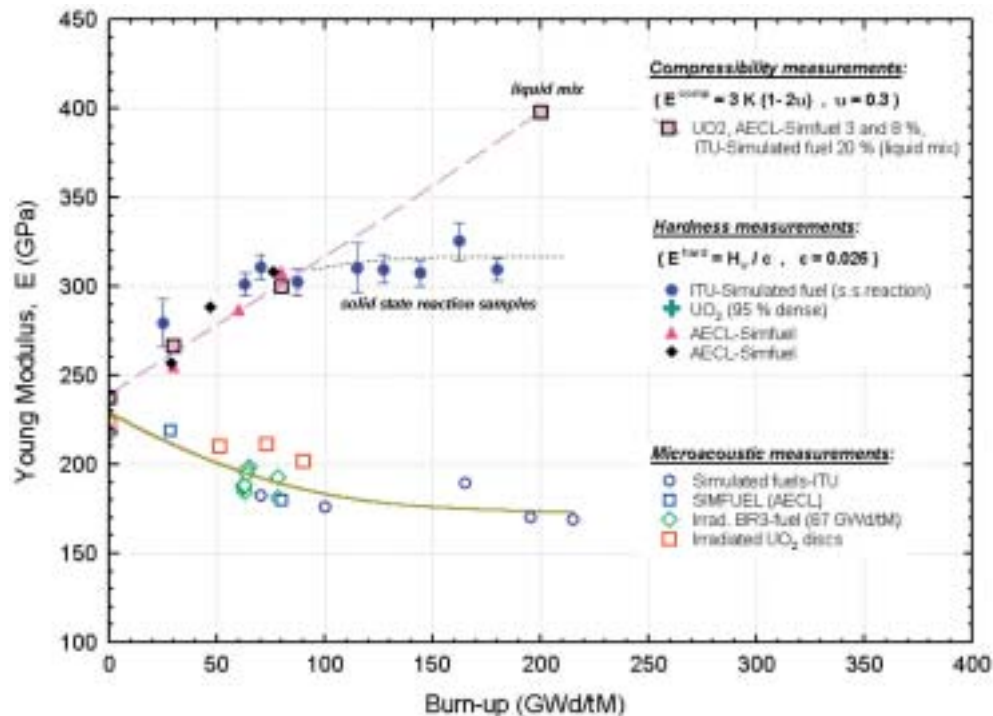
Fig. 3.4
Comparison of E-moduli values for irradiated and simulated LWR-fuels according to hardness, synchrotron-compressibility and micro-acoustic measurements

In addition, a new contract was signed with WESTINGHOUSE Atom AB. In the framework of the contract two fuel rods were transferred to our hot cell installation.

Reference
[1]   EUR 14493 (TUAR-91), p. 199; EUR 15154 (TUAR-92), p. 199; EUR 15741 (TUAR-93), p. 227; EUR 16152 (TUAR-94), p. 205; EUR 16368 (TUAR-95), p. 199;   EUR 17296 (TUAR-96), p. 127; EUR 17746 (TUAR-97), p. 74; EUR 18715 (TUAR-98), p. 74; EUR 19054 (TUAR-99), p. 74; EUR 19812 (TUAR-2000), p. 86; EUR 20252 (TUAR-2001), p. 55.

Contact (3.1.4): Enrico Toscano • tel.: +49 7247 951 409 fax: +49 7247 951 561 • toscano@itu.fzk.de

3.1.5 Oxygen potential and thermal diffusivity of high burn-up UO_2 fuel

In the framework of the joint research programme on the performance of PWR fuel at high burn-up pursued by Framatome-ANP and the Institute, the oxygen potential and thermal diffusivity of UO_2 fuel with an average burn-up of about 100 MWd/kgHM have been measured. The oxygen-potential, $\Delta\bar{G}(O_2)$ was measured using a miniature solid-state galvanic cell [1, 2]. Measurements were made on samples taken from the pellet rim, from the outer region of the fuel, from the middle of the pellet radius, and from the central region of the pellet. The measured $\Delta\bar{G}(O_2)$ values are in agreement with those previously measured on high burn-up UO_2 fuel and continually increased with distance from the fuel centre. The results are currently being evaluated.

The thermal diffusivity of the fuel was measured at temperatures in the range 350 to 830°C using the laser flash technique [3]. It was not possible to make measurements at higher temperatures, because the restructuring stresses generated during the measurement at 830°C caused the specimen to disintegrate. The measurements were carried out on an area of the sample 1mm in diameter located between the mid-radial position and the pellet centre. The thermal diffusivity values obtained are in good agreement with those previously measured on high burn-up fuel samples for the HBRP. The results are also currently being evaluated.

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3.1.6 Ramp testing of irradiated SBR MOX fuel

In-pile performance studies of BNFL's SBR MOX fuel continued in 2002 with ramp testing of eight fuel segments in the High Flux Reactor at Petten and their post-irradiation examination. The segments with a fuel stack of approximately 30 cm were refabricated from two, 3-cycle rods with average burn-ups of 31.2 and 33.6 MWd/kgHM, which had been irradiated in the Beznau-1 PWR. The power schedules of the eight ramp tests were similar, except that different conditioning powers of 20, 25 and 30 kWm^{-1} were used and the terminal power varied from 39 to 50 kWm^{-1} (Tab. 3.2). In seven of the eight tests the segments were held at the terminal power for 12 hrs, in the remaining test the hold time was shortened to 20 minutes with the aim of gathering data on the initial stages of fission gas release and swelling.

Tab. 3.2   Test Matrix for Ramp Testing of the SBR MOX Segments in the Petten High Flux Reactor

Segment Number	Conditioning Power (kWm^{-1})	Terminal Power (kWm^{-1})	Hold Time (hrs)
HR-1	25	40	12
HR-2	30	39	12
HR-3	20	50	12
HR-4	25	50	12
MR-1	20	40	12
MR-2	25	45	12
MR-3	30	44	12
MR-4	20	45	1/3

Since none of the eight segments failed in the ramp-testing program, it can be concluded that the threshold for the PCI failure of SBR MOX fuel rods is higher than that of conventional UO_2 rods. Axial gamma scanning revealed that axial migration of Cs had occurred during the ramp tests at powers above approximately 38 kWm^{-1}. Fig. 3.5 shows the pre- and post-ramp gamma scans for segment HR-4 that had been ramped to 50 kWm^{-1}. It can be seen that prior to ramp testing, if the burn-up gradient is ignored, the gamma scan is flat, and pellet interfaces are clearly visible. After ramp-testing minima between the pellets remain only at the bottom of the fuel stack, where lower temperatures prevailed. In the middle of the rod over a distance of 140 mm, Cs has accumulated at the pellet-interfaces resulting in intensity peaks.

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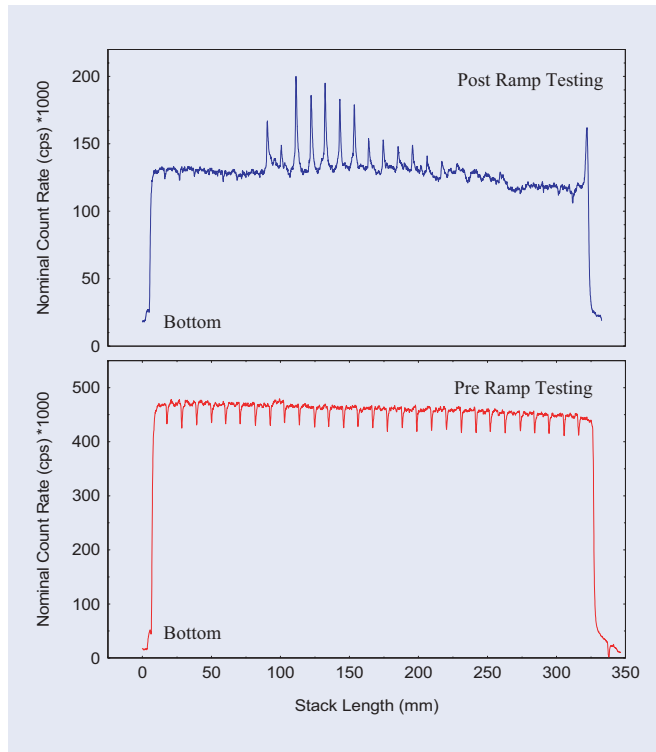
Fig. 3.5   Pre- and post-ramp axial gamma scans for segment HR-4. The gamma scans represent the axial distribution of Cs in the fuel stack. Significant axial redistribution of Cs has occurred during the ramp test. Cs released from the pellets at the top of the fuel stack has condensed in the middle of the stack.

Contact (3.1.5-3.1.6): Clive Walker • tel.: +49 7247 951 477 fax: +49 7247 951 590 • clive.walker@itu.fzk.de

3.2 Severe Accident Research

3.2.1 COLOSS

This is a multi-partner shared cost action (SCA) project with financial support from the European Commission in which severe accidents with a core loss of geometry (COre LOSS) were investigated. The various work packages range from single effect tests of fuel element interactions and small scale tests with single fuel rods or segments through to bundle tests. ITU's contribution was to examine the dissolution of irradiated UO_2 or MOX fuel by molten Zircaloy at temperatures of 2000°C; particularly the influence at higher burn-ups. Burn-up effects had been seen previously in the project CIT (see TUAR 1999 - EUR 19054 EN, p.101).
This first stage required ITU to complete the new furnace installation with filters and gas-lines before installation in an already active hot cell. This required the cell to be cleaned of radioactive samples and construction of a tent around the rear of the cell before opening the inner caisson by removing the near plexiglas panel. The installation of the furnace needed great care to avoid breaking the tungsten heating elements, despite all personnel wearing thick, fully protective gear. The oven was tested at 2000°C for 45 mins to check operation (see Fig. 3.6).

Fig. 3.6 View of the new high temperature oven facility after installation in the hot cell 106.

The gas lines were also checked and were able to maintain a good vacuum overnight and push oxygen levels down to < 1 ppm O_2 to avoid oxidation of the tungsten filament. The first tests were carried out with segments of natural UO_2; by contrast the irradiated MOX showed clearly an increased rate of attack compared to the natural UO_2. The metallographic examination showed two factors:
1. The cracking in the irradiated MOX resulted in a more rapid break-up and dissolution of the fuel.
2. The fission gas evolving from the fuel results in mixing of the melt.

The second factor can also reduce the reaction by preventing the melt from making contact with the fuel. Further testing will be needed to establish the reaction kinetics with times up to 1 hour, as well as examining the variation with temperature from 1800 - 2200°C. In a second stage, high burn-up UO_2 fuel (~ 65 GWd/tU) will be examined to see if the effect of burn-up can be quantified.

3.2.2 PHEBUS FP project

Phebus FP (Fission Product) is an international project investigating severe accident behaviour of fuel & fission products, and is led by the IRSN, Cadarache (Institut de Radioprotection et Sûreté Nucléaire). It is co-financed by the European Commission. The programme involves monitoring the behaviour of a severely overheated and degrading 20x1m-rod fuel bundle and the fission products released from it.
ITU has been actively involved in the project since the beginning (see TUAR 2000 - EUR 19812, p. 93) and it is continuing its involvement with FPT4.
The FPT4 test examined the end-phase of the severe accident by heating up in steps up to 2700°C a debris bed of irradiated fuel (~ 35 GWd/tU burn-up) and oxidised cladding. This drove off the volatile, then semi-volatile and finally the non-volatile fission products or irradiation products/structural materials from the degrading fuel. The fission products were captured on 6 successive filters, situated above the debris bed. The deposits of the filter cartridges were dissolved in nitric acid. The solution was then analysed by ICP-MS (Inductive-coupled plasma mass spectroscopy). Most of the fission products were volatilising from the bundle in the lower to mid-temperature range, with the maximum releases (in weight of deposits) in the range from 2200°C to 2500°C (1st and 2nd filters). The deposits were dominated by the volatiles such as Cs, Mo, Sn and Te. A sample of the deposits on the plenum insulation that was positioned directly above the debris bed was also examined at ITU by ICP-MS. Here the deposit although still containing volatiles (*i.e.* Cs, Mo, Te), showed considerably more of the semi- or non-volatile fission products/structural materials such as Ba, Sr as well as fuel (U and Pu). The higher actinides appear to disperse together with the U matrix. This is believed to be due to the fuel breaking up on heating and that particles of fuel impact onto the plenum in turbulent flow.

Contact (3.2): David Bottomley • tel: +49 7247 951 364 fax: +49 7247 951 561 • bottomley@itu.fzk.de

3.3 The Fuel Performance Code TRANSURANUS

TRANSURANUS is a computer program for the thermal and mechanical analysis of fuel rods in nuclear reactors, which has been developed at ITU [1]. It is fully described in the literature and has been outlined in previous Activity Reports. The TRANSURANUS code is in use in several European organizations, both research and private industry and is under continuous development.

The ITU modeling group participates in several projects: The OECD Halden Reactor Project and the OECD/NEA-IAEA International Fuel Performance Experiments Database (IFPE) [2] significantly contribute to the development and verification of the code. The projects PECO-1 and EXTRA focus on specific issues for Russian-type VVER fuel. Together with FUMEX-II (co-ordinated research project of IAEA) they further strengthen the TRANSURANUS research network. The shared-cost actions MICROMOX and OMICO cover simplified pre-irradiation calculations for prototype fuels manufactured at ITU.

Code development and verification

In the course of the participation of ITU in the OECD Halden Reactor Project a comprehensive verification of fuel centre temperatures calculated with TRANSURANUS standard options was performed. For making use of the full experimental information obtained at the Halden reactor, a new data condensation method was developed [3] and applied to detailed irradiation histories.

The TRANSURANUS-MOX version was refined and a specific correlation for the fuel thermal conductivity was developed. The correlation was implemented as dependence on local temperature and local burn-up. It is based on data (so far unpublished) measured with the laser-flash apparatus at ITU (cf. TUAR-2001 – EUR 20252, p. 50-51).

In combination with the PECO-1 project, a total of 33 fuel rods irradiated at the OECD Halden reactor were analysed. This large database covers UO_2, MOX and Gd-doped LWR fuel of Western suppliers as well as UO_2 fuel for Russian-type VVER reactors. The analysis contains more than 46.500 points of measured and calculated fuel centre temperatures. Details can be found in [4].

Projects

For VVER fuel, additional data compiled in the IFPE allow to compare the behaviour of measured and calculated fuel centre temperatures for irradiations in different test reactors. Fig. 3.7 shows the corresponding scatter plot for VVER fuel irradiated in the Sofit programme and such irradiated at the OECD Halden reactor. The behaviour of the two data sources is consistent.
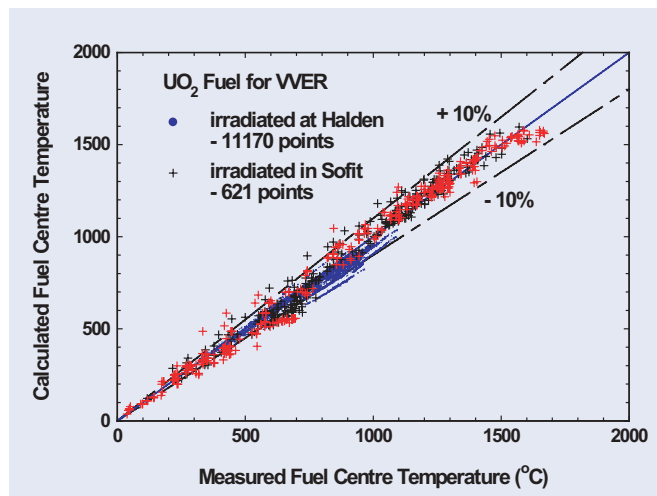
Fig. 3.7   Scatter plot of calculated fuel centre temperature versus in-pile data for VVER fuels – measured at the OECD Halden reactor (circles) – and in the Sofit programme (black and red crosses).

PECO-1

The PECO-1 project was successfully completed. The tasks were organized as follows:

– Co-operation with INRNE Sofia, Bulgaria:
In total more than 40 cases from the OECD/NEA-IAEA International Fuel Performance Experiments Database (IFPE) [2], covering both fuel for Russian-type VVER reactors and Western type fuel, were analysed. The TRANSURANUS-VVER version was further verified and a modern graphical user interface for the postprocessor UrPlot was developed.

– Co-operation with AEKI Budapest, Hungary:
A methodology for preparation of irradiation data (received within the OECD Halden Reactor Project) was developed. The VVER Database for TRANSURANUS verification was extended by 9 fuel rods irradiated in the OECD Halden Reactor. Together with Western-type reference fuel, a total of 23 fuel rods were analysed.

– Co-operation with VUJE Trnava, Slovakia:
For the first time the TRANSURANUS code was used together with the thermohydraulic system code RELAP in safety analyses (loss-of-coolant and reactivity-initiated accidents). The application of TRANSURANUS could considerably improve the description of the fuel thermal conductivity and of the fuel-cladding gap conductance in RELAP.

EXTRA

EXTRA is a shared cost action between AEKI Budapest, VUJE Trnava and ITU. The project concentrates on the properties of VVER-specific cladding alloy at elevated temperatures. New correlations will be implemented in the TRANSURANUS code and applied to modeling of loss-of-coolant accidents. Progress was made in the compilation of the experimental data from cladding ballooning tests done at AEKI and in the mathematical description of large strains. In order to apply the project results to the M5 cladding material, the TÜV Hannover (consultant organization for German licensing procedures) is involved as observer since 2002.

FUMEX-II

The ITU modeling group is involved in the new co-ordinated research project FUMEX-II (fuel modeling and extended burn-up) organized by the IAEA. For this exercise a comprehensive set of irradiations from the IFPE database [2] has been selected. Post-irradiation computations will be performed by different fuel performance codes.

MICROMOX and OMICO

These two projects are shared-cost actions for investigation of innovative fuel containing U, Pu and Th. The fuel is manufactured at ITU and covers different compositions and microstructures. Instrumented irradiations are planned at BR2 Mol and HFR Petten. Pre-irradiation calculations with the TRANSURANUS code have been performed for all designed UO_2 and $(U, Pu)O_2$ fuels. They confirmed that the targets of controlled fission-gas release should be reached within the planned irradiation conditions and the safety criteria (in terms of maximum fuel temperature and inner pin pressure) are well respected in all fuel segments.

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Contact (3.3): Klaus Lassmann • tel: +49 7247 951 297
fax: +49 7247 951 379 • k.lassmann@itu.fzk.de

3.4 Advanced Fuels

Improvement of pellet microstructure

Fuel microstructure (porosity, grain size…) has an important
influence on fission gas release and in pile performance.
Several activities have been pursued to improve the
microstructure of pellets prepared by both powder metal-
lurgy and sol gel processes. For MOX pellets produced by

the MIMAS process, grain growth, and homogenization of
the Pu from the primary blend throughout the pellet has
been achieved by two means: the use of additives, and
the use of an advanced UO_2 powder in the dilution step to
prepare the secondary blend. Both of these fuel types will be
irradiated in the BR2 reactor in Mol starting in 2003.

Powders produced by the sol gel process are dust free and
give a completely atomically homogeneous product in the
form of a solid solution of the components. In non-optimal
conditions, however, pellets produced from these particles
exhibit pores surrounding the precursor particles – an effect
known as the "blackberry structure" (see Fig. 3.8 (a)). The
addition of carbon black to the sol gel feed solution before
its dispersion gives porous particles and improves their
compaction. Simultaneously, the pores created within each
precursor particle can be retained to some extent during
sintering to give the desired microstructure. In particular,
the sintering between individual precursor particles is
enhanced in comparison to their own internal sintering,
so that the "blackberry" structure is diminished. The results
obtained using this process are shown in Fig. 3.8 (b).

Fuel developments in the frame of shared cost actions

The ITU is involved in several projects supported by shared
cost actions in the 5th Framework Programme.

(a)   (b)
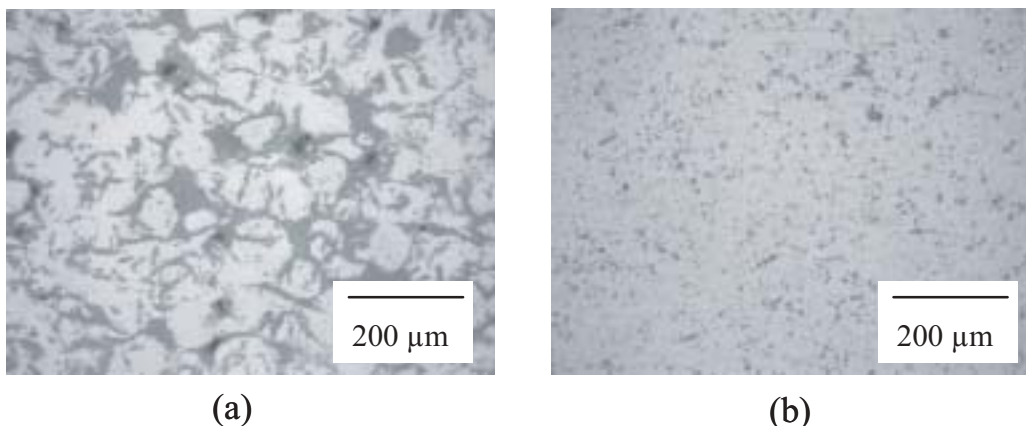
*Fig. 3.8   (a) Yttria stabilized zirconia prepared by the sol gel method exhibiting the "blackberry"
             microstructure and (b) the same material prepared with 20 g/l C in the feed solution.*

Projects

Thorium Cycle

Two fuel pins fabricated by ITU have been irradiated for over one year in the HFR Petten. The irradiation will continue until December 2003, after which the pins will be unloaded and returned to ITU for PIE. A further pin in the KWO Obrigheim pressurized water reactor has been irradiated for 18 months and has reached a burn-up of about 18 MWd/kg. Visual inspection and dimensional measurement at the end of the first irradiation year showed no anomalies.

MICROMOX

Within this programme four fuels were produced at ITU: two homogeneous (sol gel) MOX fuels with different grain size, a heterogeneous MOX fuel and a UO_2 reference fuel. The fabrication is now completed and the shipment of the materials to Petten will be finalized in January 2003. The pins will be irradiated in the HFR Petten. The target burn-up is 50 MWd/kg. The goal of the experiment is to study the effects of the microstructure on the irradiation behaviour. After a base-irradiation, a power transient will be simulated at the end of the irradiation.

OMICO

The OMICO project investigates the onset of fission gas release in fuels with various composition and microstructure. The specifications and enrichments are now agreed with SCK/CEN. The fabrication of the sol gel powders required for four of these fuels is now completed. The pellets for the sol gel UO_2 reference and MIMAS U-MOX reference have now been fabricated. In 2003 the pellets for the remaining four fuels will be fabricated, encapsulated in twelve pins and shipped to Mol for irradiation.

HTR-F

Two activities concerning High Temperature Reactor (HTR) fuel are in progress at ITU. UO_2 particles have been produced, but further development is still required to produce kernels, meeting HTR fuel specifications. The installation of the KÜFA device to test irradiated HTR compacts under accident conditions is nearing completion in the hot cells. First hot tests are foreseen in 2003.

Contact (3.4): Joe Somers · tel: +49 7247-951 359 · fax: +49 7247-951 599 · somers@itu.fzk.de

4. Partitioning and Transmutation

4.1 Advanced Techniques for Aqueous Processing

New solvent extraction processes have been defined and tested with the aim to accomplish an effective and selective recovery of minor actinides (MA) from highly active raffinate (HAR) and concentrate (HAC).

A 16 stage DMDOHEMA extraction process, see Fig. 4.1, using a centrifugal extractor battery has been used to demonstrate the separation of minor actinides from genuine HAR.

Recoveries for Am and Cm in the Ln/An effluent of 99.98% and >99.95%, respectively were achieved (Tab. 4.1), *i.e.* the losses of these elements in the process are very low. Oxalic acid and HEDTA showed to be very efficient in preventing co-extraction of Mo, Zr and Pd.

The next step aims at the demonstration of the DIAMEX process using HAC as feed, in view of an industrial application. The volume reduction (up to 16 times) would reduce the size of the installation and thereby the costs of the process.

An apparatus for concentration and denitration of HAR has, therefore, been designed, assembled and successfully tested using simulate HAR solutions, in which lanthanides are expected to behave as MA. Parametric studies have shown that concentration-denitration of HAR, without lanthanide precipitation, is possible up to a concentration factor (CF) of 11, ending at a final acidity of 3.5 to 4 M, see Tab. 4.2. Based on the present results a final CF of 10 has been decided as a goal for the „hot" concentration-denitration experiments.

Tab. 4.1   Recovery and decontamination factor (DF) for key elements in the different outlet fractions of the performed DIAMEX test.

Element	Recovery (%)			Decontamination factor	
	DIAMEX Raffinate	An/Ln Fraction	Organic - out	Extraction	Back - Extraction
Zr	99.91	< 0.05	< 0.05	1	2
Mo	99.88	0.1	< 0.02	1	6.6
Pd	99.95	0.04	< 0.01	1	4.5
La	0.057	99.942	< 0.001	1750	163600
Nd	0.11	99.888	< 0.001	906	77790
Np	1.788	97.01	< 1.207	56	81
Am	0.021	99.98	< 0.001	4821	100500
Cm	< 0.028	99.95	< 0.019	3587	5311

Tab. 4.2   Results obtained for concentration-denitration experiments.

Experiment	CF	% precipitation of lanthanides	Acidity of final HAC (M)
1	9	< 0.02	4.1
2	9	< 0.01	4.4
3	11	< 0.01	4.1
4	14	0.3	3.7
5	39	2	4.0

In parallel, parametric studies to find the optimum conditions to run a DIAMEX-HAC extraction process have been initialised, pointing at a maximum concentration of 0.2 M oxalic acid in the HAC (without precipitation and no third phase formation) for Diamide concentrations of 0.65 and 1 M.

Contact (4.1): Birgit Christiansen • tel: +49 7247 951 328 fax: +49 7247 951 99 328 • christiansen@itu.fzk.de

Organic phase
0.65 M DMDOHEMA
in TPH
76 mL/h

Organic out

1 2 3 4   5 6 7 8   9 10 11 12   13 14 15 16

Raffinate   **Feed - HLLW**
3.9 M HNO$_3$
0.1 M oxalic acid
0.01 M HEDTA
51 mL/h

Scrub
3.0 M HNO$_3$
0.2 M oxalic acid
0.015 M HEDTA
25 mL/h

Acid scrub
1 M HNO$_3$
23 mL/h

An/Ln fraction

Strip solution
0.1 M HNO$_3$
69 mL/h

Fig. 4.1   A schematic diagram of the 16 stage DIAMEX process

Projects

4.2 Pyro-processing Demonstration Facility

In the framework of the joint CRIEPI-ITU study on pyrometallurgical processing, an installation has been constructed and put into operation to demonstrate the feasibility of reprocessing of metallic fuels and high-level-liquid-waste (HLLW). Electrorefining of fresh U-Pu-Zr alloy fuel was successfully performed in 2001. During the reporting period the following tasks have been performed:

1. Detailed measurements of anode residue and solvent chloride after electrorefining step
2. Multi-step reductive extraction by using LiCl-KCl/Cd or LiCl-KCl/Bi systems for the evaluation of the distribution coefficient of different minor actinides
3. Preparation of the equipment for denitration and chlorination of simulated HLW

1. During electrorefining experiments on UPuZr, a thin metallic layer appears on the surface of the liquid cadmium cathode (LCC) container consisting of Al_2O_3. Interactions between Zr and the crucible material could be responsible of this anomalous plating. Additional experiments have been carried out using other LCC containers such as BeO and AIN to check the compatibility of these materials with Zr under different temperatures (480°C, 500°C). On each

Oxidized part of UPuZr fuel with remaining Zr

Unoxidized part of UPuZr fuel
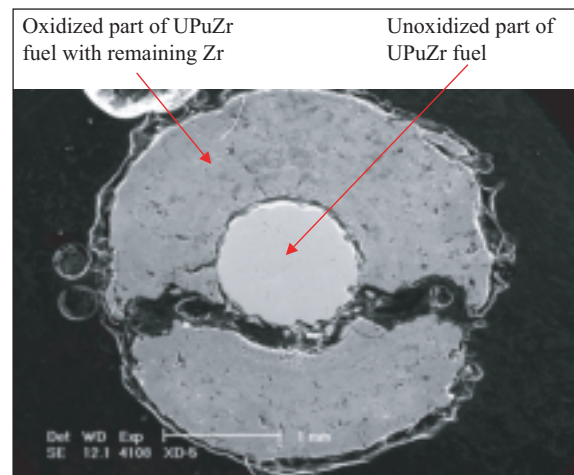
Fig. 4.2 SEM image of cross section of anode residue after anodic dissolution of U-Pu-Zr fuel

type of material, Cd plating was found on the surface of the crucible. Further experiments have to be performed to optimise the electrorefining of fuel containing Zr.

The residue remaining in the anode basket after anodic dissolution of U-Pu-Zr alloy has been investigated. It presents a concentric circle structure. Fig. 4.2 shows a SEM picture of the cross section of the residue and the Fig. 4.3 the corresponding mapping for U, Zr, and Cl elements.
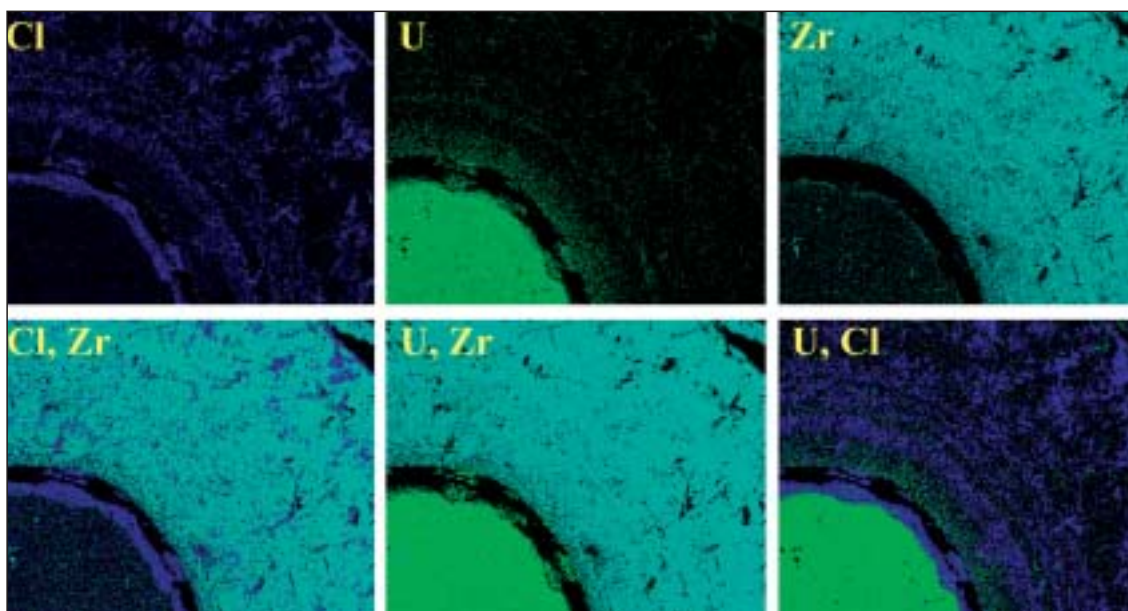
Fig. 4.3 X-ray mapping of anodic residue (part of specimen)
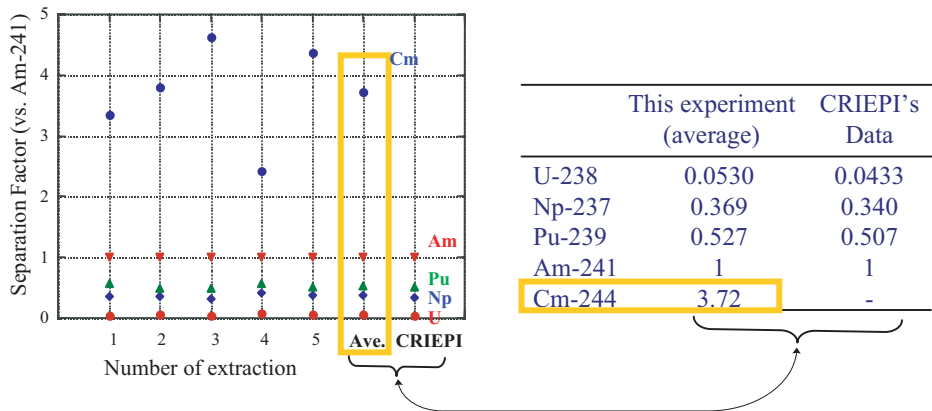
Fig. 4.4
Separation Factor (vs Am-241) in LiCl-KCl/Bi system obtained for five extractions.
Separation factor (of metal M) = [X(M)/Y(M)] / [X(Am)/Y(Am)] with X(M): Concentration of M in salt and Y(M):Concentration of M in Bi)

	This experiment (average)	CRIEPI's Data
U-238	0.0530	0.0433
Np-237	0.369	0.340
Pu-239	0.527	0.507
Am-241	1	1
Cm-244	3.72	-

The centre and outer regions correspond to the remaining U-Pu-Zr alloy and undissolved Zr, respectively. A gap observed at the interface between these two regions has a higher concentration of Cl. As the undissolved Zr region is very porous, a significant amount of salt was also detected in the outer part having a different composition compared to the one in the bulk. The concentration of LiCl is far higher and the concentration of actinide chlorides lower than in the bulk. This may result in solidification of the salt phase at the interface and may prevent further anodic dissolution. Optimised anodic dissolution condition will be studied in 2003.

2. Typical result on single-step reductive extraction on U61Pu19Zr10MA5RE5 (wt.%) fuel using Bi or Cd as solvent is shown in Fig. 4.4.

The distribution coefficient is defined as the ratio of mole-fraction of each actinide in salt and in metal. The distribution coefficient of actinides is summarised with respect to that of Am. The data for Cm is newly obtained in the present study and they indicate that the separation of Cm from rare earth is more difficult than Am. Based on these results, a demonstration test for a multi-step reductive extraction was successfully performed.

3. One objective of the pyrometallurgical project is to demonstrate the feasibility of the recovery of actinides contained in HAW with a ratio TRUs/REs of about one in the final product. Fig. 4.5 shows the chlorination apparatus developed for this purpose.
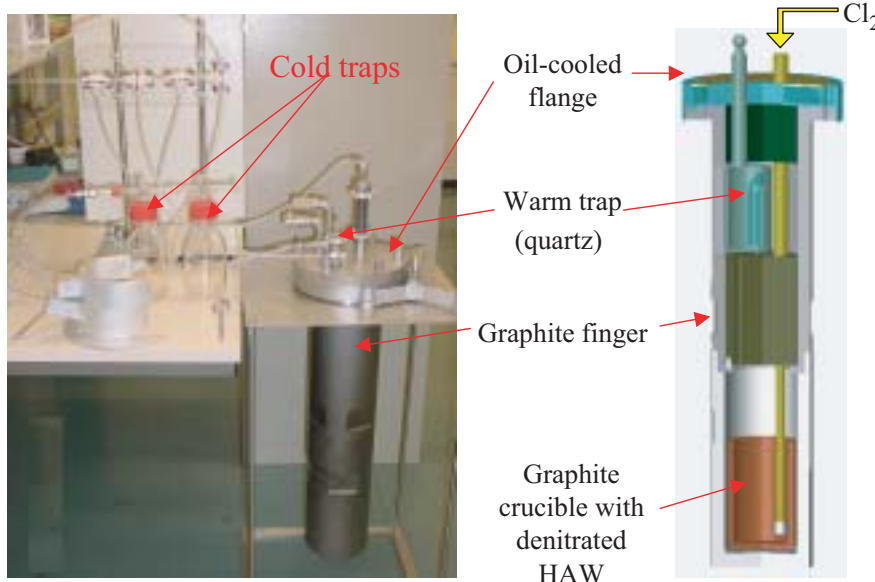
Fig. 4.5 Chlorination test apparatus

This device is made with pyro-coating graphite to prevent the corrosion by chlorine gas. Since the chlorination temperature is estimated to be around 700°C, a top oil-cooled flange will maintain the graphite device inside the experimental well installed in the caisson. A graphite crucible loaded with the simulated denitrated HLLW powder and LiCl-KCl salt will be inserted at the bottom part of the graphite assembly. The chlorination test is planed for the beginning of 2003.

Contact (4.2): Michel Ougier • tel: +49 7247 951 281 fax: +49 7247 951 561 • ougier@itu.fzk.de

4.3 SMART

The goal of the SMART (Study of Mixed Actinides Recycling and Transmutation) experiment is to study the irradiation behaviour of cermic metal fuels for transmutation. Three fuel pins manufactured at ITU are presently irradiated at the HFR-Petten. Thereafter they will be examined at ITU. Two pins contain MOX fuels pellets with high Pu content (up to 45% in weight) and were originally prepared for the TRABANT 2 experiment. Their irradiation started in September 2001. The other pin contains uranium-free fuels, in which the Pu (density 0.9 g·cm^{-3}) is incorporated in an yttrium stabilised zirconia (YSZ) matrix. One segment of the pin is made of homogeneous $(Pu,Y,Zr)O_{2-x}$ fuel, for which the fabrication process has been already described in detail
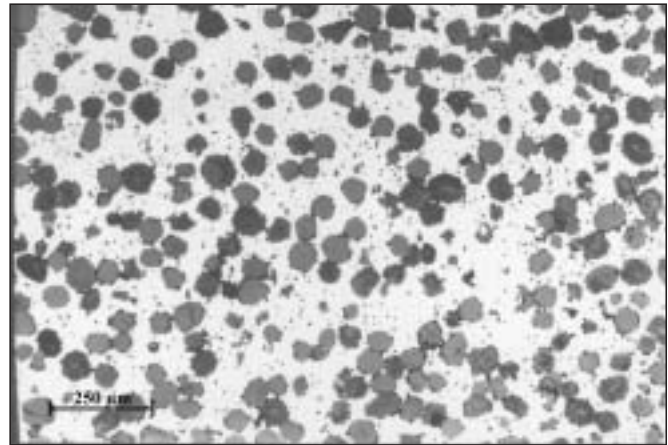
Fig. 4.6 Ceramograph of SMART fuel

in the TUAR 2001, p. 62. The second segment is made of a composite fuel in which the $(Pu,Y,Zr)O_{2-x}$ phase is mixed with stainless steel powder that acts as the fuel matrix, a so-called cermet fuel.

The fabrication process for the cermet fuel partially overlaps with the homogeneous one. YSZ spheres were sieved and a selected size fraction, 63-80 μm, was infiltrated to obtain $(Pu_{0.241}Y_{0.128}Zr_{0.631})O_{2-x}$. After a thermal treatment at 1150°C the spheres were mixed with the required amount of stainless steel powder and pressed into pellets. The pellets were sintered at 1275°C for 3 hours. The final pellets have a densi-
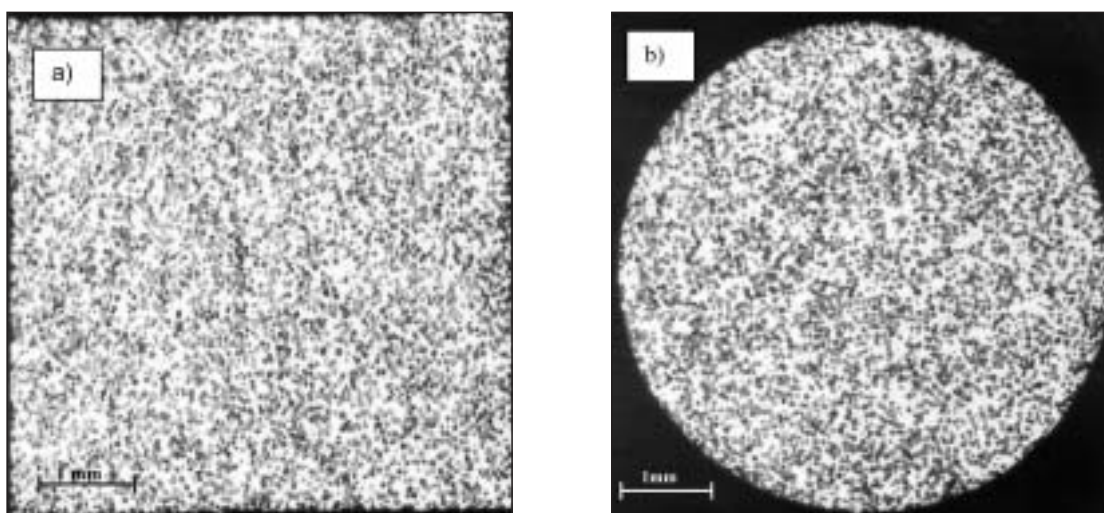
Fig. 4.7 Optical microscopy of an axial (a) and a radial (b) section of a Pu0.241Y0.128 Zr0.631O2 – stainless steel pellet.

ty of 87.2 ± 0.2% TD, the porosity principally occurring in the ceramic phase (see Fig. 4.6), which thus can accommodate the accumulation of fission gases and therefore mitigate swelling during the irradiation.

The optical micrographs shown in Fig. 4.7 indicate that all particles are uniformly distributed in the matrix.

Contact (4.3): Rudy Konings · tel:+49 7247 951 391 fax:+49 7247 951 599 · konings@itu.fzk.de

4.4 Studies on Fission Damage in Neodymium Zirconate

During the reporting period the basic studies on the properties of candidate matrices for actinide transmutation have been focused on zirconia-based compounds, and in particular on zirconate pyrochlores [1, 2, 3].
Inert matrices would be subjected to radiation damage from fission during reactor operation. This process is known to strongly affect the physical and chemical properties of some materials [4, 5, 6, 7, 8] and is a key parameter to assess the suitability of an inert matrix candidate (see also TUAR 98, p. 85-88; TUAR 99, p. 113-115; TUAR 00, p. 110-115; TUAR 01, p. 65-67).

In order to evaluate the resistance against fission fragment damage of neodymium zirconate (where Nd is intended to be partly replaced by the actinides in real targets fabrication), ion implantation with iodine ions of 120 MeV were performed at the VIVITRON accelerator (TANDEM type) of the IReS Institute in Strasbourg. Pellets with 97% of the theoretical density (TD = 6325 kg·m^{-3}) and with pyrochlore structure (lattice parameter a = 1.07 nm) were used to prepare bulk slices and thin foils for Transmission Electron Microscopy (TEM) investigations.
Two slices were irradiated at fluences of 10^{14} and 3×10^{14} ions.cm^{-2} and two pre-thinned TEM specimens at a fluence of 5.6×10^{10} ions.cm^{-2}. After irradiation the specimens were analysed by Scanning Electron Microscopy (SEM), TEM (after final thinning) and by X-ray diffraction. The range and the energy losses were calculated using the code SRIM2000. The maximal dE/dx value of 22 keV.nm^{-1} corresponds to the maximal energy loss of a heavy fission product.
SEM observation of samples irradiated to 10^{14} and 3.0×10^{14} ions.cm^{-2} revealed a smoothening of the surface. No major differences could be observed as a function of the total
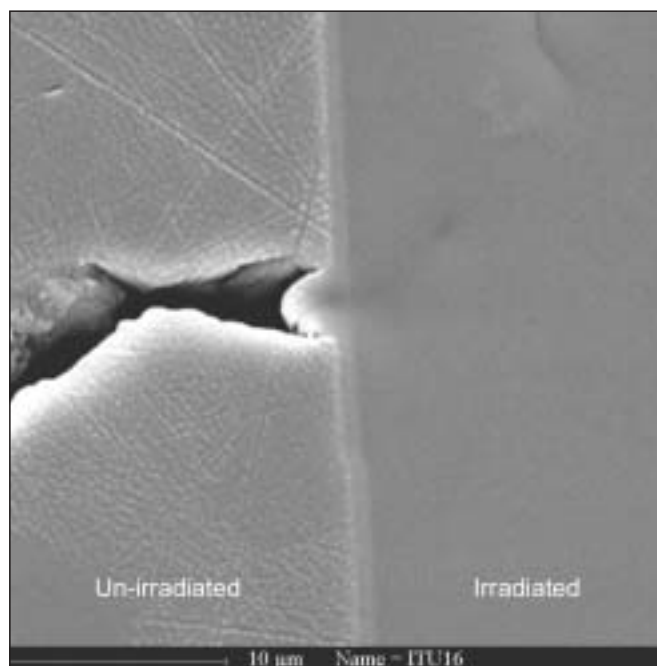
Fig. 4.8   SEM micrograph of a sample partly irradiated at a fluence of 3 10^{14} ions.cm^{-2}.

fluence. Pores and polishing tracks appeared filled with material, thus evidencing the occurrence of material transport in the specimens during irradiation. Fig. 4.8 shows a SEM micrograph of a specimen irradiated to the highest fluence. The boundary region between irradiated and unirradiated zone is shown. The disappearance of the polishing tracks on the irradiated area can be clearly seen in the SEM micrograph. Additionally, the picture shows a pore located across the boundary: the irradiated part of the pore is filled. Profilometry measurements did not indicate a significant swelling of the irradiated part (no step was detected between the irradiated/unirradiated areas). The observed behaviour seems to indicate that melting occurred on the surface of the samples.
TEM observations on samples irradiated at low fluence (5.6×10^{10} ions.cm^{-2}) clearly showed that tracks were formed in the pyrochlore. Fig. 4.9 shows two TEM micrographs exhibiting a) tracks under normal incident beam condition and b) with the sample tilted in the electron beam. The diameter of the tracks sized about 5 nm. Electron diffraction indicates that a new crystalline phase was formed. Concentric rings were observed in the diffraction pattern, but the corresponding calculated lattice spacing could not be unequivocally assigned to any Zr- and/or Nd-containing phase.

Projects
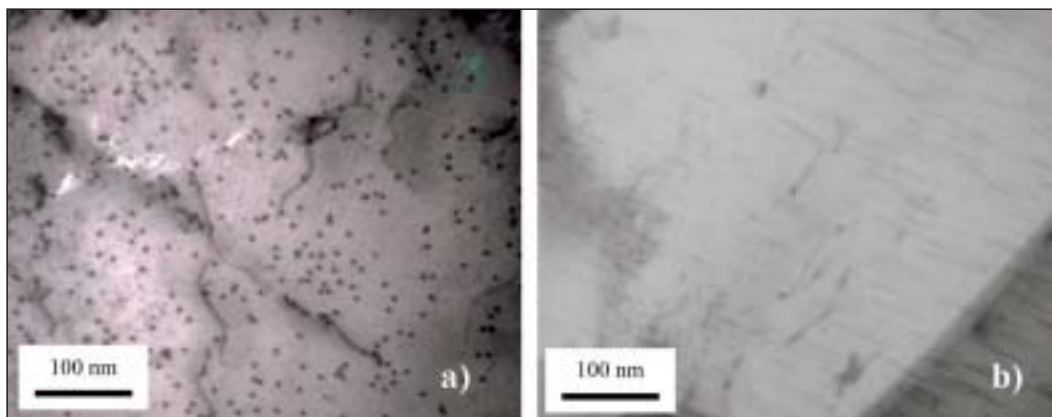
Fig. 4.9   TEM micrograph of a sample irradiated at a fluence of 5.6x10^{10} ions.cm^{-2}. a) normal incident beam condition b) sample tilted in the electron beam.

XRD analysis of the sample irradiated at a higher fluence revealed the formation of a second crystalline phase, in addition to pyrochlore. This new phase could not be identified as being either ZrO_2(c) ZrO_2(m) ZrO_2(t) Nd_2O_3, $Nd_2Zr_2O_7$ (pyrochlore or fluorite). The characterization of these new phases is continuing. These results, at least within the experimental conditions considered (room temperature fission damage simulation), provide a clear indication of poor resistance against fission damage of neodymium zirconate and cast some doubts on the effectiveness of this material for reactor applications. The ongoing work will improve the insight on the processes determining the observed behaviour.

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Contact (4.4):
Vincenzo V. Rondinella • tel.: +49 7247 951 279
fax: +49 7247 951 199 • rondinella@itu.fzk.de

4.5 Conditioning of Actinides in Ceramics

Mineral-like ceramics are being studied as host materials for specific conditioning *i.e.* tailor-made waste forms for separated elements. The work is focussed on two groups of materials: pyrochlores (general formula $A_2Zr_2O_7$ where A is an actinide or lanthanide) and monazite/brabantite type phosphates (general formula $Ln_{2-x}(CaAn)_{x/2}(PO_4)_2$).

Lanthanide zirconate pyrochlores have been synthesised and characterized. Three different compounds were prepared: $Nd_2Zr_2O_7$, $Eu_2Zr_2O_7$ and $Gd_2Zr_2O_7$. The latter is the last lanthanide zirconate that can exist in the pyrochlore structure and its fabrication was finally achieved by adjusting the temperature of the procedure. The low-temperature heat capacity measurements of all three compounds has been completed using ITU equipment in the 0.4–20 K range and equipment of the Utrecht University (Netherlands) in the 5-400 K range (see Fig 4.10).

Combining the results with data for $La_2Zr_2O_7$ the excess heat capacity due to the 4f-electron excitations could be deduced (Fig 4.11) and compared to the excess heat capacity calculated from the crystal field energies, measured in a collaboration with the Institut de Physique Nucléaire of Orsay (Paris).

Fabrication of mixed lanthanide-actinide zirconate pyrochlores was performed. Substoichiometric neodymium zirconate was infiltrated with plutonium and uranium solutions. Thus the compounds $(Nd_{1.57}Pu_{0.43})Zr_2O_{7+x}$ and
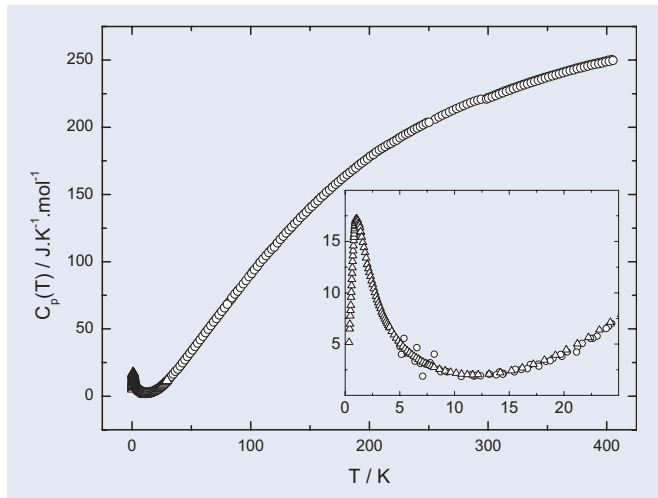
Fig. 4.10 Low temperature heat capacity of $Gd_2Zr_2O_7$ measured at ITU (triangle) and in collaboration with the University of Utrecht (circle). The inset shows these data in the 0-25 K temperature range.
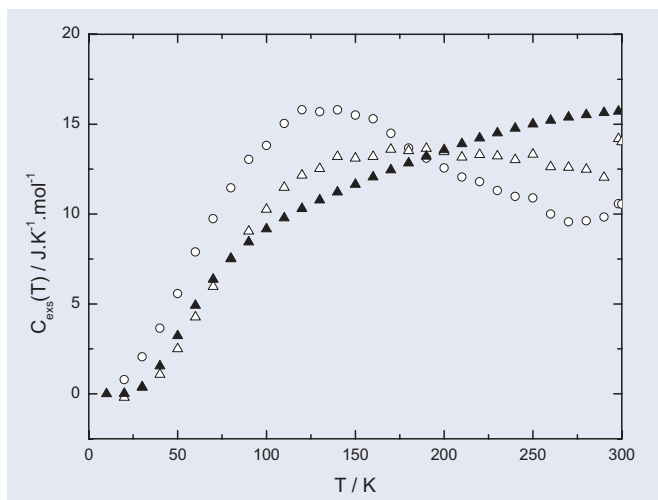
Fig. 4.11 Excess heat capacity due to the 4f-electron excitations of $Nd_2Zr_2O_7$ (circle) and $Eu_2Zr_2O_7$ (open triangle) compared to the calculation from the crystal field energies (closed triangle).

$(Nd_{1.57}U_{0.43})Zr_2O_{7+x}$ were obtained and X-ray analysis confirmed their pyrochlore structure. The value of x, due to the presence of 4+ ions, is not yet known.

For the phosphate system, the phase relations between monazite $(LnPO_4)$, brabantite $(CaTh(PO_4)_2)$ and huttonite $(ThSiO_4)$ are under investigation in order to establish the composition range in which complete solid solution exists.

Such a solid-solution host material could accommodate both trivalent and tetravalent actinides on the Ln and Zr positions. Fabrication of some of the solid-solution end-members has been realised.

4.6 Minor Actinide Laboratory

The fabrication of fuels and targets containing americium and curium will be done in the new Minor Actinide Laboratory (MA-lab). It consists of seven cells shielded by walls containing water (50 cm) and lead (5 cm) to protect the operators from gamma and neutron radiation (Fig. 4.12). Telemanipulators are used for normal operation. In addition, extensive automation using remote control and robots has been included in the design. The construction of this laboratory has reached its final stage and the first tests with inactive materials have been started. On 25 September 2002 the laboratory has been inaugurated in the presence of many international guests. The first active operations are foreseen for 2003.

Fig. 4.12 The front of the MA-lab cells 6-10

ERMT-II

On September 26 and 27, 2002 ITU hosted the Second Seminar on European Research for Transmutation. During this seminar international experts presented and discussed the current state of the development of fuels and targets for transmutation of actinides and long-lived fission products. The proceedings of the Seminar will be published in the Journal of Nuclear Materials.

Contact (4.5-4.6): Rudy Konings · tel:+49 7247 951 391 fax:+49 7247 951 599 · konings@itu.fzk.de

5. Spent Fuel Characterization in View of Long Term Storage

Introduction

In the reporting year, the „Spent Fuel" Project was partly reassessed by bridging the goals reached in the terminating FP5 with the new objectives of FP6, which have been established in the context of the recent development of the work on nuclear waste and spent fuel management.

From the one side, the situation is presently characterized by a tightening of the research projects, in which the JRC has confirmed an active participation. In particular, the shared-costs action "Spent-Fuel Stability" has practically led to a convergence of objectives of all major national European projects on nuclear waste disposal. In this context, ITU has assumed the specific task of investigating near-field aspects of irradiated fuel leaching, with emphasis on burn-up and radiolysis effects. Furthermore, a tight co-operation and co-ordination of the basic research work on actinide chemistry (both aqueous and in solid) was agreed with CEA, SCK/CEN and FZK-INE in the recent formal proposal of the ACTINET-6 „Network of Excellence". These commitments will effectively engage all the manpower made available for our Spent-Fuel project in the FP6.

From the other side, though European public and private sector research efforts concerning nuclear waste treatment and storage technologies are converging, the state of the implementation of individual technical solutions is presently somewhat diverging. For instance, Swedish SKB had established in the past a common research programme with ITU on near-field effects of spent-fuel leaching in granitic water under strong reducing conditions. Now the results of these studies are considered as sufficiently qualifying, and the future research is focussed on more conclusive questions, like, *e.g.*, statistical aspects of canister corrosion.

However, ITU action will continue to cover near-field problems of spent-fuel leaching. It will address processes occurring during long term storage in deep geological strata, with networking of the activities carried out on various sites in the three main types of geological formations envisaged in Europe.

The effect of α-radiolysis of ground water remains an important topic. The experiments carried out at ITU in the last months, where samples with relatively low α-rate have been submitted to leaching tests, still exhibit a substantial effect of radiolysis. The relation between radiolysis and leaching rate is, however, complex, as it implies a sequence of intermediate, possibly cycling, chemical reactions which are presently under investigation.

Furthermore, the fuel corrosion process is strongly influenced by solid radiation damage. Our observations have shown that α-damage itself may produce vast damage and structural changes (one of the highlights of this TUAR presents an extreme case). This aspect is now considered from the sub-microscopic point of view, with the intent of defining the role of lattice defects in the development of the fuel corrosion layer.

Micro-gravimetric techniques with sensitivity of the order of nanograms have also been developed to study the surface reactions. These phenomena are being systematically investigated with the aim of obtaining a detailed insight into the chemical process and, finally, proposing a parametric formulation of the corrosion rate.

The work on leaching of irradiated fuel is continuing, with the analysis of UO_2 and MOX rodlets immersed in water for more than four years. The corrosion patterns along the free surfaces of fuel and claddings were identified. However, the problem of interpreting and predicting the mobilization of radioactive fission products is strictly bound to that of the morphology of their host phases. The distinction elements contained in „open" phases (as, *e.g.*, caesium), and those contained in closed „phases" (as, *e.g.*, strontium) are in this respect essential.

The question of a detailed characterization of spent fuel as a function of irradiation parameters is, therefore, to be answered before entering the analysis of the corrosion processes.

5.1 Effects of α-Radiolysis on Fuel Corrosion

Leaching of α-doped UO_2 in natural granite ground water and XPS characterization

During previous reporting periods, corrosion studies involving leaching in demineralized water (DM) and solid phase characterization experiments have been performed on UO_2 pellets containing [238]Pu (α-doped UO_2) to investigate the

effects of α-radiolysis on the corrosion behaviour of spent fuel [1-6; TUAR 1998 p. 98-100; TUAR 1999 p. 120-123; TUAR 2000 p.126-128; TUAR 2001 p. 70-72]. The α-doped UO_2 is used to simulate the α-radiation field of different types of commercial LWR spent fuel after different storage times. During the present reporting period, this analysis was extended to leaching experiments in natural granite groundwater (GW). The leached surfaces were examined by X-ray Photoemission Spectroscopy (XPS), and Scanning Electron Microscopy (SEM).

The materials used for this investigation were standard UO_2 (labelled UO_2-0), and UO_2 containing 0.1 wt. % and 10 wt. % of an oxide constituted mainly of ^{238}Pu (labelled UO_2-01 and UO_2-10, respectively). The composition of the additive oxide, the fabrication procedure of the pellets, the evolution with time of the lattice parameter and of other properties of the α-doped materials under the effects of accumulating α-decay damage have been reported previously (TUAR 2000, p. 126-128) [1-5].

Static sequential leaching experiments were performed in groundwater at room temperature under oxic conditions. An extensive description of the experimental procedure and of the techniques used is available elsewhere [5, 6]. Fig. 5.1 shows the uranium concentrations measured in the leachates as a function of leaching time. The values are normalised to the geometric surface area.

Similarly to all previous experiments, the amount of uranium in the leachates for the α-doped materials was higher than that for UO_2. Significant precipitation of U on the walls of the leaching vessel occurred. As previously observed, the trend for the low-activity α-doped material showed an initially less rapid, but overall steadier increase than for the high activity sample. After longer leaching times, the amount of uranium found in solution from the two α-doped materials was converging. The pH remained ~6.0 in DM and ~7.5 in GW during all the leaching tests. The values of concentration in solution were generally slightly higher in groundwater (which contains ~10^{-3} M bicarbonate) than in demineralized water.

The leaching experiments in natural granite ground water at room temperature confirmed the α-radiolysis enhancing effect on the fuel dissolution. The presence of carbonate had no major effects on the trends observed.

XPS analysis of the oxidation state of the surface after leaching in GW was performed similarly to previous investigations [TUAR 2001, p. 70-72; 5-6]. The O/M ratios – derived from the U(VI)/U(IV) ratios obtained by XPS - as a function of leaching time are shown in Fig. 5.2.

A decrease of the O/M after the shortest leaching times was observed for UO_2-0, corresponding to the dissolution of
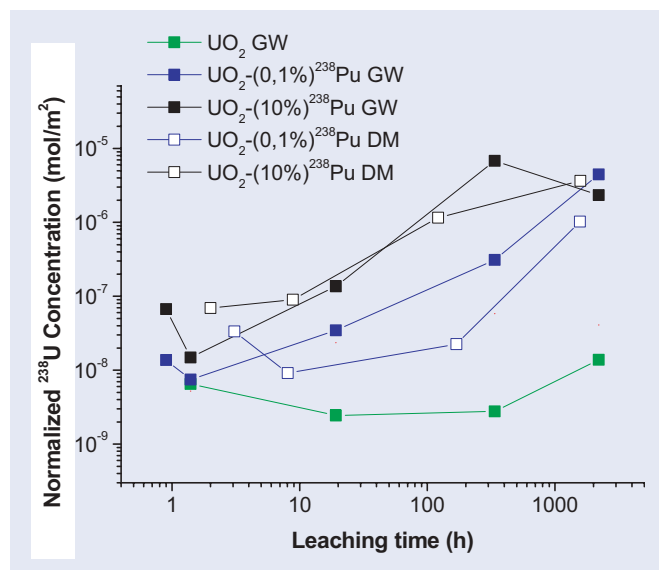

Fig. 5.1 ^{238}U concentration in solution released during the leaching experiments in natural granite groundwater (GW) and demineralized water (DM).
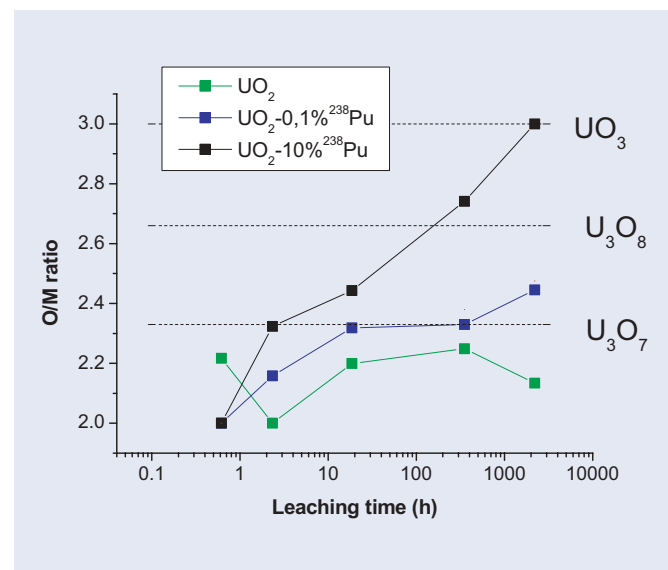
Fig. 5.2   O/M ratio measured on the surface of the samples as a function of leaching time in groundwater.

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an oxidized surface layer formed during the time interval between the annealing and the XPS analysis preceding the leaching tests (at least 24 h). No evidence for this initial decrease was found for the α-doped samples, differently from the case in demineralized water. The O/M trend for UO_2-10 showed a relatively rapid increase. After leaching times longer than 10 h mostly U(VI) (and a very small peak for Pu) was detected on the surface of the UO_2-10 disk. The trends of the U(VI)/U(IV) ratio for UO_2-01 were characterized by a slower increase of the U(VI) component. As expected, the ratio for UO_2-0 essentially levelled off slightly below the value corresponding to $\sim UO_{2.33}$ [6-8]. In the case of UO_2-01, however, the increasing trend continued beyond this level, consistently with the consideration that in the case of α-doped materials a constant source of radiolytically produced oxidising species is present in the system.

SEM characterization of surfaces leached in demineralized water

SEM characterization of α-doped UO_2 surfaces leached in demineralized water [5-6, TUAR 2001 p. 70-72] was completed. The corrosion process during leaching caused the precipitation of UO_{2+x} crystals, resulting in enhanced formation of studtite under stronger radiation field and schoepite under lower radiation fields on the surface of the pellet. No re-precipitation of Pu-rich phases was directly observed. A pale yellow crust covered the specimen with the strongest alpha-activity (UO_2-10) after the longest leaching time as shown by optical microscopy examination

(cf. Highlight in this report). A sharp etching of the initial surface occurred, with extensive grain boundary corrosion. SEM analysis revealed a remarkable structure of the precipitated phases as shown in Fig. 5.3.

The yellow crust formed on this specimen appeared to consist of numerous inter-grown acicular crystallites sizing about 5 µm in length. The thickness of this crust sized a few micrometers covering the whole specimen, which exhibits many cracks. The oxidation to U(VI) in such conditions is known to produce studtite $[UO_2|O|(OH)_2] - 3H_2O$ or metastudtite $[UO_2|O|(OH)_2] - 2H_2O$, which is probably just a de-hydrolysed alteration product of studtite. Leaching experiments simulating radiolysis using He-ion beams showed the formation on the surface of metastudtite [9], while experiments simulating α-radiolysis production with a high concentration of H_2O_2 led to the formation of the hydrated uranium peroxide UO_4-$2H_2O$, characterized by XRD and RBS in previous work [TUAR 2001, p. 73-74].

The sample with lower alpha-activity did not show such extensive modifications. Optical microscopy showed only a partial yellowish coloration of the sample surface. SEM examination revealed the presence of re-precipitated phases of various shape and distribution, with radial aggregates sizing up to ~10 µm of length, some of them being assembled in stellar shapes (Fig. 5.4 (1)). Acicular crystallite (see Fig. 5.4 (3)) could also be observed on the surface of this specimen as well as dense hedgehog-shaped aggregates of ~1 µm grains (see Fig. 5.4 (2)).
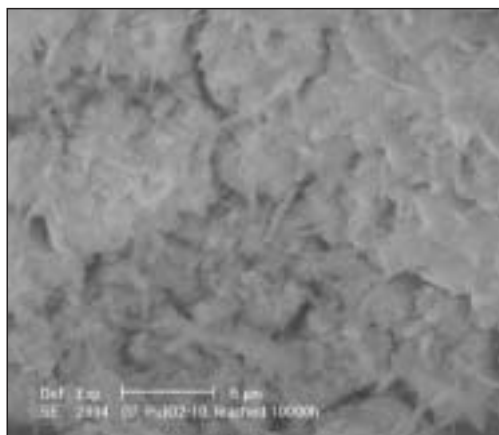
Fig. 5.3 SEM micrographs of the UO_2-10 surface after the longest leaching time showing precipitated radial aggregates constituting a crust.

Fig 5.4 SEM micrographs of UO_2-01 after the longest leaching time showing stellar- (1), hedgehog- (2) shaped aggregates and acicular crystallites (3) on the surface.

The main constituents of these precipitates are dehydrated schoepite crystallites ((UO_3-n(H_2O), n < 2). The formation of the aggregates (stellar- and hedgehog-shaped) occurred preferentially at the grain boundaries while acicular crystallites were found distributed all over the surface. This behaviour could be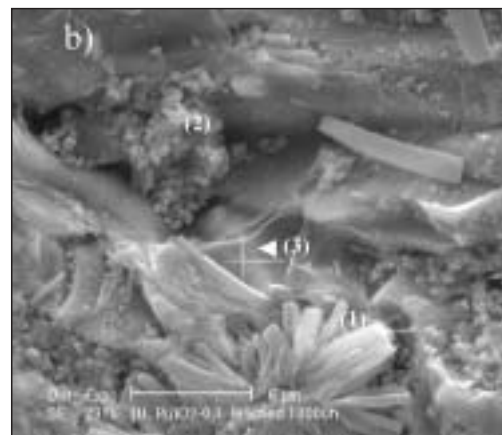 a combination of several factors. The penetration of water in grain boundaries coupled with probably longer residence time than on the regular surface could lead to local saturation of uranyl ions in the water. Precipitation would therefore be expected to be locally higher.

The surface of the reference UO_2-0 pellet leached under the same conditions presented only rare precipitation of schoepite crystallites, showing for the most part an essentially pristine surface.

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Contact (5.1):
Vincenzo V. Rondinella • tel.: +49 7247 951 279
fax: +49 7247 951 199 • rondinella@itu.fzk.de

5.2 Investigations on UO_2 Corrosion Products: Natural Analogues to Alpha Radiolysis

Natural analogue studies are of great use when the behaviour of materials over long timescales has to be assessed. In this study it was found that substances, which are formed by water radiolysis at the surface of uranium compounds in natural environments, could be stable for long periods of time. The investigations showed that these by-products of alpha radiolysis are generated in natural systems when alpha emitters of specific activity higher than that of ^{238}U are accumulated in the surrounding host matrices.

Spent nuclear fuel, foreseen to be disposed in deep geological formations, contains in the $^{238}UO_2$ matrix material a variety of fission and activation products and long-lived actinides. In the case of a container failure and subsequent water intrusion, water radiolysis phenomena are expected to take place at the solid-liquid interface.

Apart from the solution chemistry, which is influenced by the radiolytic oxidant production, radiolysis turns also the secondary phase chemistry (formation of new phases) at the immersed fuel surface into different directions, compared to the normal oxidative dissolution mechanism. Former investigations have made clear that uranium peroxides ($UO_4 \cdot$ n H_2O, known as studtite minerals) play a key role in the reaction mechanisms. These phases were observed in simulated radiolysis experiments [1]; they are generated by the attachment of a peroxide (O-O) group to the uranyl (O-U-O) unit during the reaction of uranyl ions with hydrogen peroxide. But how could studtite and meta-studtite – nature´s only U-peroxide minerals – be formed under geological conditions, considering that the metastable hydrogen peroxide will not be present for long timescales? The alpha activity of $^{238}UO_2$ alone does not produce peroxide in amounts sufficient for the formation of studtite minerals. This question is of importance for repository safety assessment considerations and was therefore investigated in detail.

Samples of natural $UO_4 \cdot$ n H_2O were collected from the Menzenschwand former U mine (Schwarzwald, Germany). An optical investigation showed that all these mineral samples were associated with phases containing either Ca (*e.g.*, uranophane, Ca(UO_2)SiO_3(OH)$_2 \cdot$ 5 H_2O), or Ba (*e.g.*, baryte). In order to investigate the molecular structure of the uranium compounds in these samples, Raman spectroscopy was used for measuring their characteristic vibrations. The method allows differentiating similar compounds, which are of nearly the same atomic composition but of different structure (common for uranium minerals), by "fingerprint" signals in their Raman spectrum. Raman spectra of the natural studtite samples were recorded and compared with the phase generated during simulated radiolysis experiments.

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$UO_4 \cdot n\ H_2O$ was identified by its "fingerprint" Raman active peroxide vibration at 870 cm^{-1}, thus proving that uranium peroxide was formed on the surface of the treated UO_2 pellet (Fig. 5.5).

<table>
<tr><td>Raman spectrum: neoformed studtite on UO_2</td><td>Raman spectrum: natural studtite, UO_4 n H_2O</td></tr>
<tr><td>SEM micrograph: neoformed studtite on UO_2</td><td>SEM micrograph: natural $UO_4 \cdot$ n H_2O</td></tr>
</table>
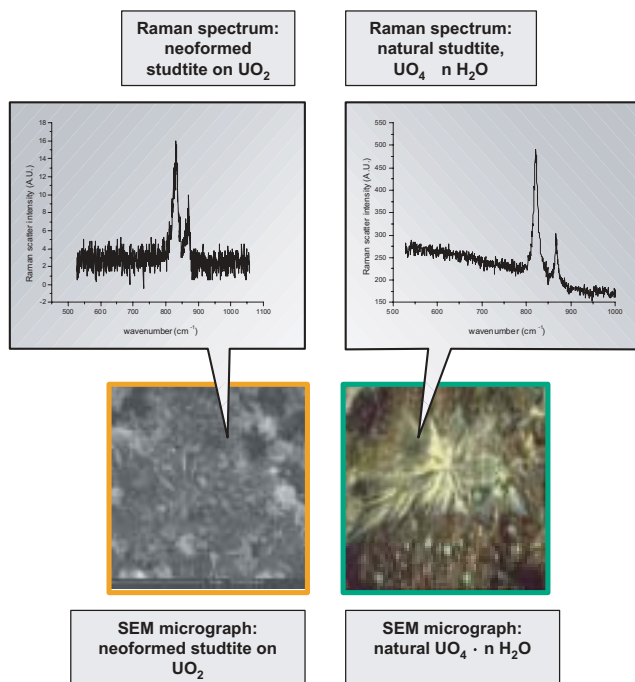
Fig. 5.5   Comparison of natural uranium (VI) phases with those produced during laboratory leaching experiments.

Microscopical investigations found baryte (BaSO$_4$) associated with the studtite samples from Menzenschwand, whereas UO_2 (pitchblende) was not present. According to the suggestions mentioned in [2] this is due to the enrichment of Ra in BaSO$_4$ (the compound is able to host Ra for Ba by substitution in the crystal lattice), resulting in an alpha activity four times higher than that of pitchblende (see Tab. 5.1).

Tab. 5.1   Accumulation of alpha emitters in natural materials (after [2]).

Phase	Pitchblende (UO_2)	Radiobaryte (Ba[Ra]SO$_4$)
alpha activity (relative)	1	4.02
Ra content (pmm)	0.29	1.0
associated with $UO_4 \cdot$ n H_2O	no	yes

In the case of uranophane, higher concentrations are expected (not yet investigated).

The secondary U(VI) phases found in the mine Menzenschwand have an age in the range of 240,000 – 340,000 years. Even if the formation period of radiobaryte and radiouranophane is considered in that timespan, the stability of natural uranium peroxide phases can be considered as high. This fact gives evidence that these substances could play an important role in the long-term dissolution behaviour of spent nuclear fuel.

In conclusion, we can state that the conditions, which lead to the formation of uranium peroxides in natural environments, are obviously linked to the accumulation of alpha emitters with a higher activity than ^{238}U. In the case observed here, a substitution of Ra for Ba in the lattice of surrounding mineral phases is supposed to cause natural water alpha radiolysis, which leads to the formation of hydrogen peroxide and the subsequent precipitation of uranium peroxide. Once formed, the peroxide phases seem to be stable for long times. The question whether or not *e.g.* Pu (as strong alpha emitter) will have the same effect on immersed spent fuel, as Ra had on the systems observed here, will be investigated. Taking into account the chemical similarity to uranium, formation of transuranic peroxide phases seems probable.

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Contact (5.2):
Vincenzo V. Rondinella • tel.: +49 7247 951 279
fax: +49 7247 951 199 • rondinella@itu.fzk.de

5.3 Microgravimetric Corrosion Studies on UO_2

Hydrogen peroxide is an important radiolysis product. Therefore, studies were conducted to measure the influence of H_2O_2 on the dissolution behaviour of UO_2. In the presence of hydrogen peroxide, the formation of a corrosion surface layer was observed. This layer was investigated by impedance spectroscopy and by cathodic sweep voltammetry. Both techniques show an increase of the layer thickness with time, while the derived thickness values differ by one

order of magnitude. To clarify this discrepancy additional information about the corrosion process like, for instance, the mass change is needed. A suitable instrument to study very small mass changes is the quartz crystal micro balance (QCM). The QCM (Fig. 5.6) is an excellent tool to determine *in situ* corrosion rates and inhibition effects.
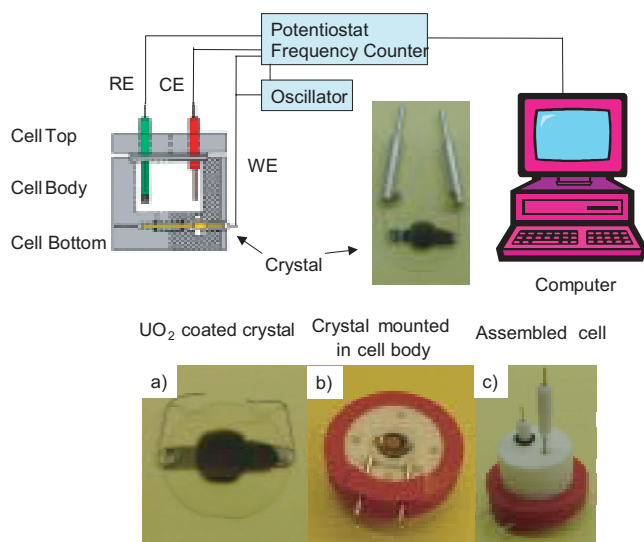
Fig. 5.6   Experimental set-up of the electrochemical quartz crystal micro-balance. The mass change of the oscillating quartz crystal is proportional to the measured frequency shift of the crystal. a) Quartz crystal coated with UO_2 by sputter deposition. b) Quartz crystal mounted in bottom of cell. c) Cell mounted completely with electrodes.

The method being highly sensitive, mass changes in the sub nanogram range can be detected. On the other side, the total mass that can be used with the QCM is restricted to some 100 µg and, therefore, only thin films of UO_2 can be investigated. These were prepared by sputter deposition of UO_2 [TUAR 1999, p. 76-77] on a gold-coated surface of an 8 MHz AT cut quartz crystal. The stoichiometry of UO_2 is adjustable via the oxygen partial pressure in the vacuum chamber during the sputter process and can be followed by XPS measurements.
On non-polished crystals scaly coatings with a bad surface coverage are formed, which are not suitable for electrochemical experiments. Uniform, adhesive UO_2 films were finally obtained on polished crystals. These enabled us to carry out electrochemical tests on UO_2 by neglecting side reaction, which might occur on non-covered gold.

By combining a thin film technique with QCM measurements, a direct *in situ* detection of the mass change of UO_2 under potentio-dynamic control could be carried out for the first time (Fig. 5.7).

In 0.01 M NaCl solution and with addition of H_2O_2 the mass change was reproducible after a full potential sweep cycle from -800 $mV_{Ag/AgCl}$ up to $+500$ $mV_{Ag/AgCl}$, and back to -800 $mV_{Ag/AgCl}$. Starting the sweep with a fresh and clean UO_2 surface one could observe in the anodic direction only a very small mass loss, increasing at 400 $mV_{Ag/AgCl}$ - whereby also the anodic current rises indicate anodic dissolution of UO_2. During the cathodic sweep, the mass loss decreases, and then the mass remains constant from $+400$ $mV_{Ag/AgCl}$ to -200 $mV_{Ag/AgCl}$.

At higher cathodic potentials, the mass increases but does not recover the starting value. This may be interpreted as a precipitation of corrosion products of UO_2 on the electrode
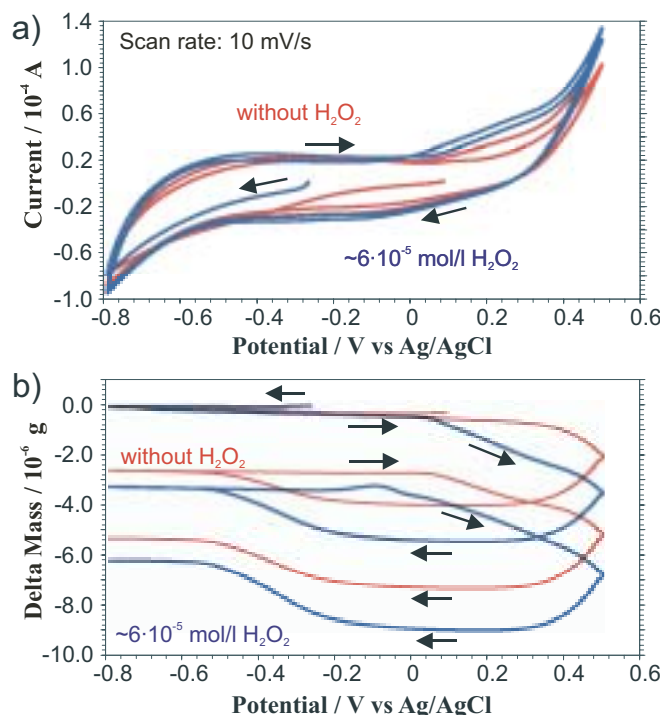
Fig. 5.7   Results obtained from electrochemical quartz crystal micro balance experiments performed on UO_2 in 0.01 M NaCl solution with and without addition of hydrogen peroxide (20°C). a) Cyclovoltammogramme. b) Mass change during potential sweep.

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surface. This layer dissolves during the following anodic potential sweep between +50 mV$_{Ag/AgCl}$ and +350 mV$_{Ag/AgCl}$ before the anodic dissolution at +400 mV$_{Ag/AgCl}$ starts. This behaviour can be seen from the higher anodic current and a small shoulder at +350 mV$_{Ag/AgCl}$ on the mass loss curve.

Addition of ~6 10^{-5} mol/l H$_2$O$_2$ leads to a higher mass loss, particularly at anodic potentials. In this case, the mass change curve shows an additional peak at –100 mV$_{Ag/AgCl}$, which indicates a further oxidation before dissolution of the layer at +50 mV$_{Ag/AgCl}$ starts. An increased H$_2$O$_2$ concentration of 3 10^{-4} mol/l has only a small effect on the mass loss. The mass changes in anodic and cathodic direction rise with H$_2$O$_2$ concentration.

5.4 Post Leaching Studies of Defect Rodlets

The dissolution behaviour of spent nuclear fuel is affected by parameters concerning the structure and composition of the material, the properties of the leaching solution (oxygen contents, redox conditions, *etc*.) and the interaction with the surrounding cladding material. To get an insight into such a complicated system an integrated experiment was launched in '97 simulating ground water intrusion into a fuel pin in the case of a small cladding failure (TUAR 1997, p. 101). In practice, UO$_2$ and MOX fuel rodlets with pre-set defects (small holes drilled in the cladding tube) have been immersed in water and the actinide and fission product dissolution was measured at subsequent intervals during a time of four years.

The main findings obtained from the solution analysis were as follows (see also TUAR 1998, p. 101):

During the initial fast dissolution, the release of all products, except for uranium, is in the MOX higher than in UO$_2$. The dissolution was one order of magnitude higher for fission products and almost two orders of magnitude higher for plutonium - though the burn-up of MOX (12 GWd/t) was only half that of UO$_2$. This behaviour was likely due to the two-phase structure of the MOX fuel, where the fission product inventory is concentrated in the Pu-rich agglomerates and at their grain boundaries. To confirm this, post leaching examinations of the MOX and UO$_2$ fuels (30 GWd/t) were performed after four years leaching time under oxic conditions.

After removing the samples from the water, a thin film of a yellow-brownish substance was visible on the cladding surface near the defects (Fig. 5.8). These coloured zones indi-
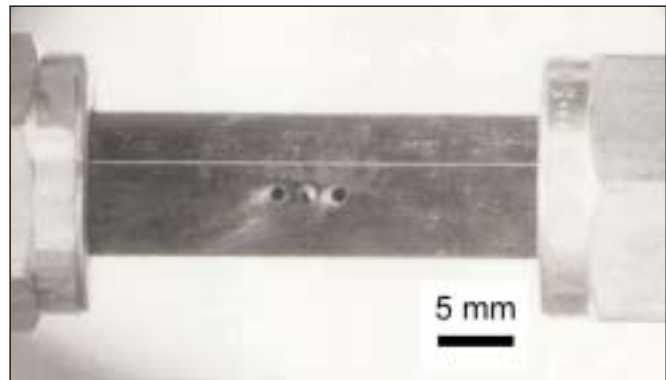
Fig. 5.8   A defective rodlet (3 drilled holes, 1mm diameter) of UO$_2$ fuel (burn-up 30 GWd/t) after ~4 years leaching shows yellow-brownish layers on cladding and in holes.

cate that during leaching a material flow was taking place from the defect along the outer surface of the cladding.

Measurements of the width of the fuel/cladding gap show for both samples a very irregular radial variation in the range from ~1 µm to ~100 µm, with an equal mean value of ~ 40 ± 20 mm. Only in the case of the UO$_2$ fuel a slight increase of the gap width from the initial 26 ± 12 µm might be significantly attributed to water exposure. However, micrographs show a damaged oxide layer on the cladding surface, while the UO$_2$ fuel is only slightly attacked at the grain boundaries on the pellet free surface (Fig. 5.9).

In contrast, the MOX fuel exhibits a much deeper corrosion attack. In the region of the cladding defect, the fuel has a rounded contour without any sharp edges, and appears to be leached. The fuel is cracked, and intergranular attack is found not only at the pellet surface but also at the inner parts. If one assumes that water has penetrated through larger cracks into the fuel pellet, then the onset of corrosion will have continued along inner grain boundaries. This finding would also explain the high „release" of fission products in the case of MOX fuel.

From these results one must conclude that identification of the structural distribution of fission products in spent fuel is necessary in order to express a prognosis on the course of the leaching processes.

Fig. 5.10 shows the fractional vaporisation of various fission products and of the UO$_2$ matrix of an irradiated fuel in a comparative plot.
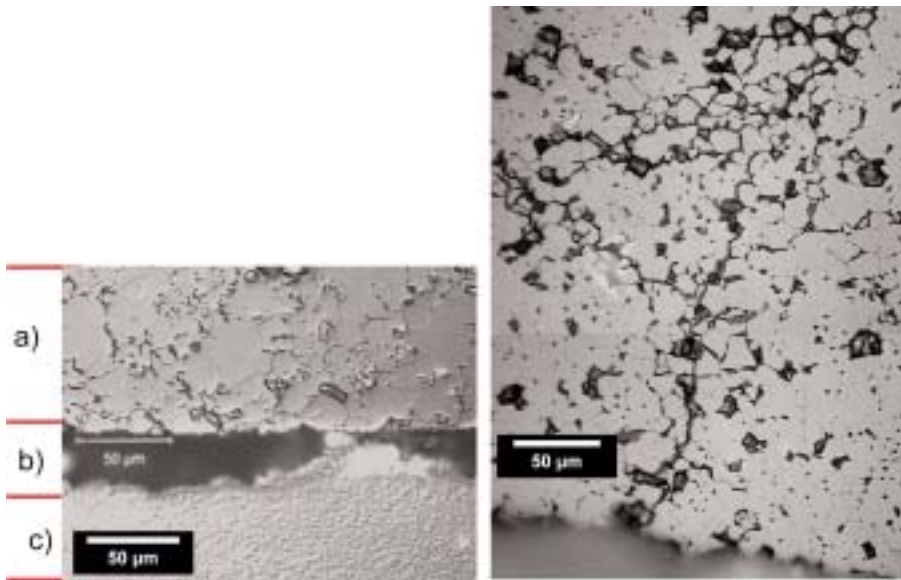
Fig. 5.9
Left side shows UO$_2$ fuel (ion etched) after ~4 years leaching under oxic conditions in water: a) slightly attacked UO$_2$ fuel; b) gap and damaged oxide layer; c) zircaloy cladding. MOX fuel shows intergranular attack (right side).
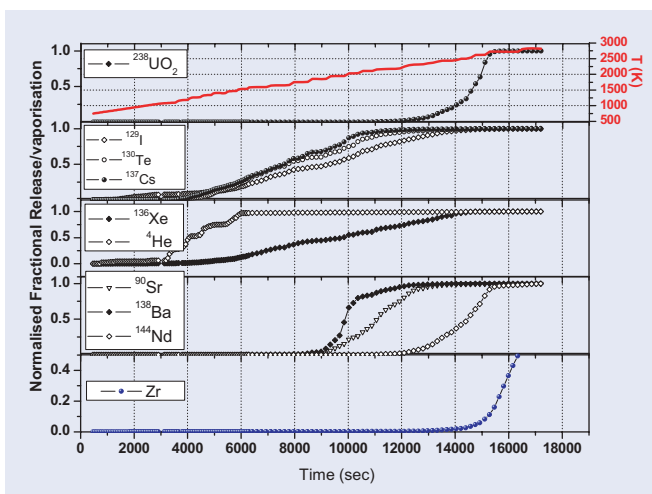
Fig. 5.10 Fractional release of caesium and strontium during fuel total vaporisation in a Knudsen-cell at the temperature indicated at the top. For the sake of comparison, the graph shows also the release curves of other fission products.

It can be seen that, whilst caesium vaporises at relatively low temperatures - indicating that it was present in a morphologically open phase, strontium is only released at much higher temperatures, at which a deep restructuring of the UO$_2$ matrix takes place. This obviously entails that the latter was present in an embedded phase and its vaporisation was prevented until the re-crystallisation process removed it from the bulk.

Characterization work based, *e.g.,* on the investigation of the vaporization behaviour of different fission products from spent fuels with different compositions and irradiation history can provide useful information concerning their distribution and their suitability for prompt release in case of fuel exposure to groundwater.

Contact (5.3 and 5.4):
Detlef Wegen • tel.: +49 7247 951 364
fax: +49 7247 561 • wegen@itu.fzk.de

6. Measurement of Radioactivity in the Environment

During the 5th Framework Programme (FP5) of the European Commission, a reference laboratory for the measurement of radioactivity in the environment (MaRE lab) has been set up at ITU to support the policy of the Directorate General Transport and Energy H.4 of the European Commission for the implementation of Art. 35 and 36 of the Euratom Treaty as well as in the framework of the OSPAR Convention for the protection of marine environment of the North-East Atlantic.

ITU staff participated as part of the EU delegation in the meeting of the OSPAR group on "Radioactive substances", in the four working groups, and in the steering committee for the updating the MARINA study on the radiological exposure in North European marine waters. The MARINA II study was completed in 2002 and its results presented at the International Conference on Radioactivity in the Environment held in Monaco in September 2002 [1].

ITU actively collaborated with DG TREN H.4 for the scientific organization of the Stakeholders' Conference on "Approaches to the Management of Environmental Radioactivity" held in Luxembourg on 2-3 Dec. 2002.

Considering the role of ITU in providing DG TREN H.4 and Member States with technical assistance in sampling and measurements, a quality assurance and quality control policy was applied to several analytical methods for the determination of radionuclides at ultra-low levels of concentrations [2].
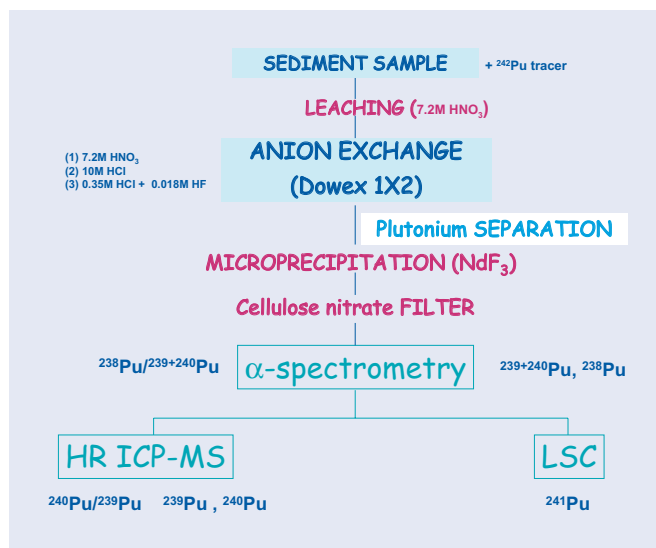
Fig. 6.1   Separation and detection scheme of Pu isotopes based on microprecipitation on membrane filters coupled to α-spectrometry, liquid scintillation counting and mass spectrometric.

Microprecipitation on membrane filters was applied for α-spectrometry and after re-dissolution liquid scintillation counting and mass spectrometric determination of plutonium isotopes [3]. The developed procedure is schematised in Fig. 6.1 and the results obtained by its application to a sediment core from the Irish Sea as well as to a reference sample with the same matrix, are given in Tab. 6.1.

Tab. 6.1   Comparison of ^{239}Pu and ^{240}Pu results as obtained by the procedure of Fig. 6.1 by α-spectrometry and ICP-MS. ^{241}Pu was measured by LSC. Errors are ± 1 sigma.

	ICP-MS		α-spectrometry		LSC
Sample	^{240}Pu/^{239}Pu atom ratio	^{239}Pu + ^{240}Pu Bq/kg	^{239}Pu + ^{240}Pu Bq/kg	^{238}Pu Bq/kg	^{241}Pu[a] Bq/g
IAEA 135	0.230 ± 0.005	196 ± 13	206 ± 12	40.3 ± 3.8	1.9 ± 0.2
0 - 2 cm	0.233 ± 0.005	2146 ± 67	2243 ± 63	517 ± 20	25.2 ± 1.0
2 - 4 cm	0.229 ± 0.005	1724 ± 105	1778 ± 29	392 ± 10	20.9 ± 0.7
4 - 6 cm	0.231 ± 0.005	1851 ± 105	1848 ± 31	421 ± 11	24.6 ± 0.8
6 - 8 cm	0.225 ± 0.005	1982 ± 48	1906 ± 32	418 ± 9	20.0 ± 1.2
8 - 10 cm	0.234 ± 0.005	2469 ± 66	2467 ± 79	542 ± 23	26.3 ± 1.1
10 - 12 cm	0.238 ± 0.005	2997 ± 60	3110 ± 87	713 ± 25	33.2 ± 1.3
a : Reference date is 7th Sept 2001 for ^{241}Pu.					

During 2002 MaRE lab has been invited to participate in certification campaigns for radionuclides concentrations in seaweed and marine sediments organized by NIST and IAEA-MEL. The campaigns will be completed in 2003.

Capillary electrophoresis (CE) has been exploited for speciation studies. The first results have been obtained for the separation of lanthanides. As seen in Fig. 6.2, CE allows carrying out the analysis much faster and with a smaller amount of sample than with IC. It takes only 8 min. and injecting a sample of 2-5 µl instead of 250 µl. The methodology is very promising and development will be continued in 2003 when CE will be coupled with an Electrospray mass spectrometer.
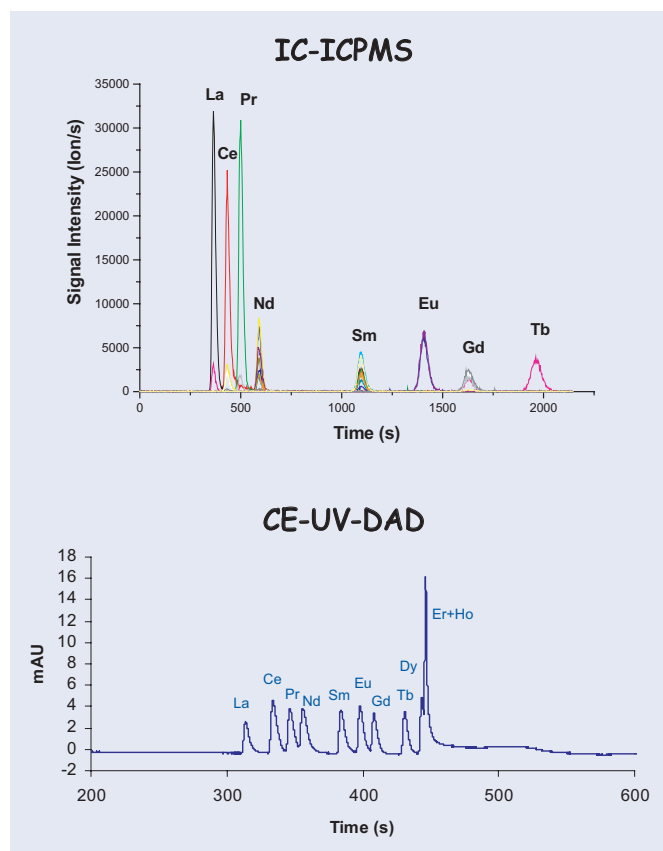
Fig. 6.2 *Lanthanides separation: comparison between capillary electrophoresis and ion chromatographic separation.*

The measurement of ^{241}Am in environmental samples is of importance in monitoring its release (both controlled and accidental) and in assessing the environmental impact and radioecology of this nuclide. The principal source terms are from nuclear weapon testing, nuclear accident and spent fuel reprocessing. Moreover ^{241}Am is a decay product of

^{241}Pu and the level of ^{241}Am in the environment will increase due to its ingrowth from ^{241}Pu. A procedure to clean up the sample from the matrix for the Am determination in environmental samples by alpha spectrometry is described. The method is based on the use of three analytical chromatographic columns. TEVA-Spec. from Eichrom has been packed in analytical chromatographic column to carry out the lanthanides/actinides separation. A CS5A mixed bed column from Dionex was used to separate Am from lanthanides impurities and other actinides. A TCC-II column from Dionex was used to connect the TEVA to the CS5A and act as pre-concentrator column for the trivalent ions. The behaviour of the columns was studied coupling the chromatograph to an ICP-MS. A chromatographic fraction has been used for sample preparation for alpha spectrometric determination of ^{241}Am. The analytical procedure has been validated with certified reference materials (sediment and soil) and was applied to sediment core samples from Irish Sea as reported in Tab. 6.2. The total recovery of the new procedure is about 90 %.

Tab. 6.2 *Results of Americium determination in environmental samples by the new analytical procedure developed. Errors are ± 1 sigma.*

Sample	Sample Size (g)	^{241}Am (Bq/kg) (Experimental Value)	^{241}Am (Bq/kg)	Chemical yield (%)
IAEA 135 (Sediment)	5.950	337 ± 18	318[a] ± 6.4	90.6
NIST 4353A (Soil)	10.776	1.40 ± 0.08	1.25[a] ± 0.09	86.3
K (Sediment)	1.572	13897 ± 269	14629[b] ± 383	86.1
P (Sediment)	1.160	8986 ± 169	9111[b] ± 227	87.0
T (Sediment)	2.243	9674 ± 214	9523[b] ± 258	85.1
[a] Information value, [b] measured by γ-spectroscopy				

References
[1] A. Janssens, M. Betti, G. Hunter, "The MARINA study II: An introduction from the perspective of the European Commission and OSPAR policies with regard to the radioactivity in the Marine Environment", Monaco, 2-5 Sept. 2002
[2] M. Betti, L. Aldave de las Heras, Quality assurance for the measurements and monitoring of radioactivity in the environment" J. of Environmental Radioactivity, accepted.
[3] E. Hrnecek, L. Aldave de las Heras, M. Betti, Radiochimica Acta, 90 (2002) 721-725

Contact (6.): Maria Betti • tel.: +49 7247 951 363
fax: +49 7247 951 186 • betti@itu.fzk.de

7. Safeguards Research and Development

Introduction

For many years ITU has been providing scientific and technical support to the safeguards authorities of Euratom (DG TREN) and IAEA. The customers' needs refer to the areas of measurement support and to development work. In the latter area the tasks aim at providing solutions to specific technical problems or to developing new approaches or to improving existing techniques. Routine measurement support comprises the operation of the on-site laboratories at Sellafield and La Hague (on behalf of DG TREN) and the analysis of uranium particles (for DG TREN and for IAEA) represents a major effort, the cost of which are covered by administrative arrangements or contracts. Furthermore, emphasis was given to co-operation with EU candidate countries in combating illicit trafficking of nuclear and radioactive material. An overview of ITU's activities in this area in recent years is provided in the Review Article in Part A of this report.

7.1 Improvement of Measurement Techniques and Methods

Plutonium assay by calorimetry

The measurement of the heat produced by the natural (alpha) decay of plutonium isotopes offers the possibility for a purely non-destructive assay of plutonium. An important advantage of this technique arises from fact that the amount of heat measured in a calorimeter is completely independent of the chemical and physical constitution of the measured plutonium sample. On the other hand, for the conversion of the measured heat into the corresponding amount of plutonium the isotopic composition of the measured plutonium (and the abundance of other heat producing isotopes like ^{241}Am, if present) must be accurately known. This means in particular that for the assay of reactor-grade plutonium materials, where ^{238}Pu may contribute up to 60-70 % to the produced heat, the accuracy limits of calorimetry will be likely determined by the uncertainty associated with the abundance of this isotope. Pertinent performance data are still needed to be established.

In order to study and to evaluate the performance of the calorimetric assay for reactor-grade plutonium materials, an experimental programme has been started addressing both the performance of the heat and ^{238}Pu isotope abundance measurements. Two advanced small sample calorimeters, equipped with thermopile technology for the heat flow measurements, were available on loan for initial test measurements: a laboratory prototype system from the Los Alamos National Laboratory, and a commercial system (Antech 601) provided by JRC Ispra. Extensive thermal power measurements on a variety of Pu-bearing samples performed in both calorimeters proved that the typical heat generated by about 1 g of reactor-grade plutonium ($\approx$10 mW) can be safely determined with a precision and accuracy of about 0.1%. Three different techniques were used for the determination of the ^{238}Pu isotope abundance: gamma spectrometry, alpha spectrometry and – after a careful U-Pu separation – mass spectrometry. A detailed performance assessment of the ^{238}Pu analysis by the three techniques is still under way.

Radiometric methods for pyrochemical-reprocessing

The ongoing development of the Pyrochemical Process at ITU requires continuous and timely analytical support. Quantitative assay is required in order to establish a material balance for process development. To this end dedicated radiometric measurement techniques, which may become also of interest for the safeguarding of advanced partitioning and transmutation fuel cycles, were studied, tested and applied for routine analysis. Specifically, the radiometric techniques of X-ray fluorescence analysis, passive neutron coincidence counting and high-resolution gamma spectrometry were extensively employed for the determination of major and minor actinides [1, 2].

The study of the efficiency of the pyrometallurgical actinide extraction required, amongst others, the absolute assay of submicrogram quantities of Am and Cm in small samples provided either as metallic (Bi or Cd) or salt samples. This particular analysis has been achieved with a combined neutron-gamma counting. The high efficiency of the neutron counter offered a detection limit of 25 ng of Cm, with the Cm assay being practically insensitive to the matrix of the sample. To address the issue of potentially strong gamma self absorption in the metallic samples for the simultaneous Am assay, a dedicated Monte-Carlo based simulator has been developed to model the gamma transport for the given counting configuration. Tests on synthetically prepared

matrices with a known Am content have shown that corrections up to 60% or more are correctly estimated (Fig. 7.1). The absolute counting geometry in combination with the gamma transport calculations ensures a measurement accuracy of approximately 1% or better, with a detection limit at 10 ng of ^{241}Am.
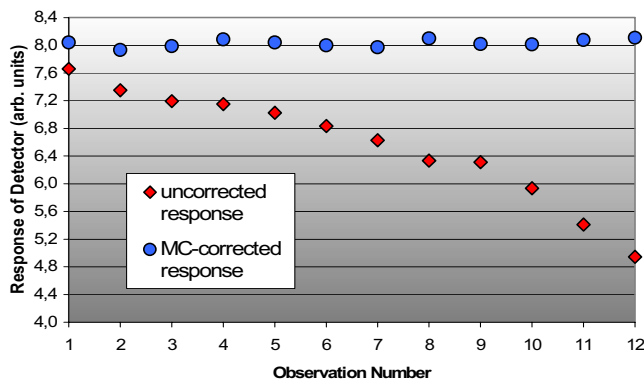
Fig. 7.1   *Observed and Monte-Carlo corrected response of gamma detector for ^{241}Am mixed with varying amounts of Bi.*

References
[1]   S. Abousahl, P. van Belle, H. Ottmar, K. Mayer; Radiometric assay techniques for the control of minor actinides applied to advanced fuel cycles; 24th ESARDA Annual Meeting, Luxembourg, 28-30 May 2002
[2]   S. Abousahl, P. van Belle, H. Eberle, H. Ottmar, P. Vallet, K. Mayer; Radiometric analytical methods for the pyrochemical partitioning process; 43rd INMM Annual meeting, Orlando, FL, 23-27 June 2002

Determination of minor isotopes in alpha-doped UO_2 pellets

In the framework of a contract between ITU and SCK/CEN, Mol (Belgium), seven batches of UO_2 pellets containing the α-emitters ^{233}U and ^{238}Pu have been prepared and shipped to SCK/CEN for investigation of the long-term behaviour of spent nuclear fuel in geological repositories. The ratios ^{233}U/^{238}U and ^{238}Pu/^{238}U were in the range between 10^{-4} and 10^{-7}. The concentration of the two minor actinides had to be determined at each stage of the production process, from the characterization of the start solutions up to the analysis of the finished pellets. For this purpose new methods of analysis had to be developed, particularly for the ^{238}Pu determination, because of the problem of isobaric interference between ^{238}U and ^{238}Pu in conventional TIMS and ICP-MS analysis.

The technique of intrinsically calibrated high-resolution gamma spectrometry was applied for the determination of the isotope ratios ^{238}Pu/^{235}U, ^{238}Pu/^{233}U and ^{233}U/^{235}U (Fig. 7.2), while from the TIMS analysis the relative isotope abundances of ^{233}U and ^{235}U in uranium were obtained. The combination of the results from both techniques allowed the calculation of the ratios ^{238}Pu/U and ^{233}U/U. From this data, and from the U/UO_2 ratio determined by IDMS or KEDG, the final ratios ^{238}Pu/UO_2 and ^{233}U/UO_2 were obtained.
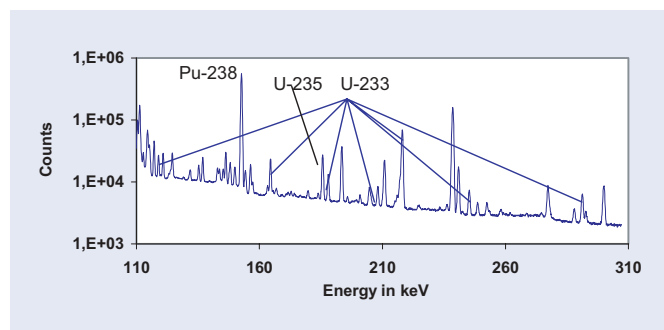
Fig. 7.2   *Example of a gamma spectrum recorded from a dissolved UO_2 pellet doped with ^{233}U and ^{238}Pu.*

Further efforts were undertaken to determine the total plutonium content, the ratio ^{238}Pu/UO_2, and the relative Pu isotope abundances in the finished UO_2 pellets also by means of an IDMS analysis. Since the Pu/U ratio in the pellets was very small, as mentioned above, a special chemical separation was necessary for the separation of ppm amounts of plutonium from bulk uranium with a Pu recovery of 100%.

Tab. 7.1   *Comparison of Gamma and IDMS results for the ratios ^{233}U/^{235}U and ^{238}Pu/UO_2. Samples marked with * were only doped with ^{233}U, therefore no Gamma/IDMS comparison.*

Batch	^{233}U/^{235}U Gamma/TIMS	Ratio^{238}Pu/UO_2 Gamma/IDMS
1	1.0067	1.020
2	1.0015	0.994
3	1.0386	0.998
4	1.0164	1.004
6	1.0044*	-
7	1.0015*	-
Mean: St.dev:	1.0115 0.0144	1.004 0.011

Projects

Plutonium and zirconium assay for advanced fuels

In support of the Minor Actinides containing fuel produc-
tion pursued at ITU, master solutions of Pu and Zr, and the
master blend of both elements, had to be carefully charac-
terized for the two element concentrations. To this end sev-
eral independent methods were used in parallel: XRF for Zr
and Zr/Pu ratio, ICP-MS and IDMS for Zr, K-edge densitome-
try for Zr and Pu, and titrimetry for Pu. The radiometric K-XRF
and K-edge densitometry measurements made for the
Zr determination (Figs. 7.3 and 7.4) represented a first exam-
ple of the planned extension of the Hybrid K-Edge
Densitometer (HKED) to element analysis of typical matrix
elements foreseen for MA fuels (*e.g.*, Sr, Zr, rare earth
elements).
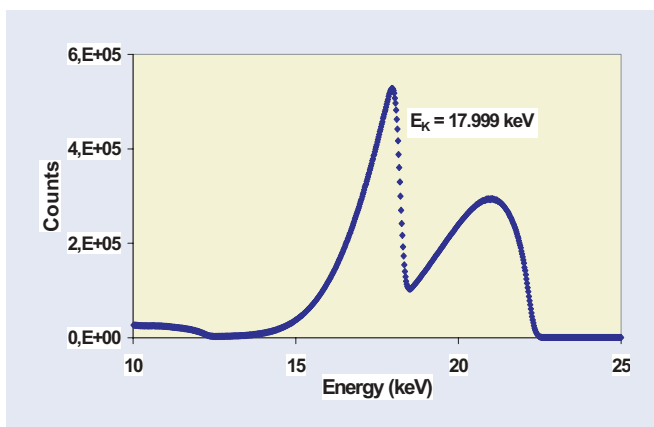
Fig. 7.3   K-edge spectrum from a Zr master solution.
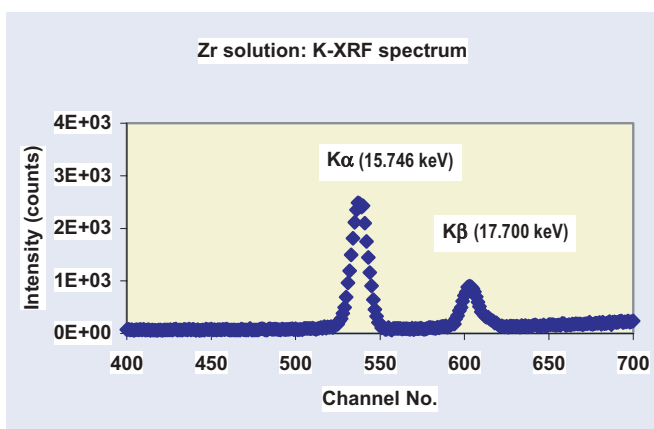
Fig. 7.4   K-XRF analysis for the Zr/Pu-ratio determination.

In order to verify the results obtained by radiometric meth-
ods, the Zr concentration in the solutions was also measured
by mass spectrometric methods. A spike solution was pre-
pared on gravimetrical basis from isotopically enriched ^{94}Zr
metal of high chemical purity. The concentration of the
spike was verified by reverse isotope dilution mass spec-
trometry using Zr of natural isotopic composition.

Pu reference samples for testing the measurement capa-
bility of waste assay systems

Assaying the amounts of Pu in waste drums is of relevance
prior to final disposal of the waste, it may also be useful for
closing the material balance in a nuclear facility. The respec-
tive measurement systems are generally based on passive
neutron measurements. In the framework of a contract, two
series of Pu containing sources have been manufactured.
The first series consisted of six discrete sources, containing
plutonium amounts between 0.2 and 0.8 mg. They were
manufactured by drop deposition of a Pu solution on a
dished stainless steel planchet. Certification of the solution
for concentration and Pu isotopic composition had been
achieved by isotope dilution mass spectrometry.
Subsequently, the solution was dried and the steel planchet
was heated to 600 °C for calcination of the Pu. These
planchets were then encapsulated in stainless steel discs
(see Fig. 7.5), welded and leak tested.

*Fig. 7.5   Plutonium containing neutron sources for testing
waste assay systems at their lower limit of detection*

Verification measurements were performed by a combina-
tion of gamma spectrometry and neutron coincidence coun-
ting to verify the gravimetrical make-up value. The second
series consisted of three sources, containing between 150
and 600 mg of Pu. This series is intended for calibration of
the measurement device in the typical range of operation.

*Contact (7.1): Klaus Mayer · tel.: +49 7247 951 545
fax: +49 7247 951 99545 · mayer@itu.fzk.de*

7.2 Detection Methods and Measurements of Microparticles

In the framework of the projects „Environmental Sampling" and „High Performance Trace analysis" in support to IAEA and DG TREN (Euratom Safeguards), the research has been focused on the relocation of particles of interest containing uranium.

Multiple analyses, elemental and isotopic, of single radioactive particles in the µm-size range are keytools in for verification of compliance with international treaties and in nuclear forensics. They require the ability to locate and identify particles of interest (POIs) via scanning electron microscopy (SEM) and to precisely re-locate them for mass spectrometric measurement (SIMS). The triangulation re-location method, based on microscopic reference marks imprinted on the sample holder, has been developed and successfully implemented at the IAEA (Seibersdorf) clean laboratory [1]. A joint Round-Robin-type test was performed by IAEA and ITU. A sample loaded with uranium oxide monodisperse particles was prepared at ITU and sent to the IAEA where 25 POIs have been selected after being identified in an automated particle search SEM. The sample was then returned to the ITU, where the same particles were re-located and analysed in both the SEM and the SIMS. The re-location precision was better than 10µm in the SEM and 20 µm in the SIMS over the whole sample area of 2 cm in diameter. In fact, as can be seen in Fig. 7.6 the deviation of the actual from the predicted locations in SIMS for the majority of the particles re-located was better than10 µm.

The experiment proved that the method facilitates repeated analyses of single µm-size particles in different instruments, even though developments are still needed in order to further improve the re-location accuracy.

To exploit oxygen isotopic measurements by SIMS on microparticles, the magnitude and reproducibility of O-isotope instrumental mass discrimination for O-isotope standards has been evaluated [2]. Tests for matrix-dependent discrimination effects on three different O-isotope standards with substantially different matrix compositions have been performed. The results were checked by an interlaboratory comparison of O-isotope discrimination with those obtained in the SIMS laboratory at the Lawrence Livermore National Laboratory on two standards. The results from the two laboratories were in good agreement, indicating statistically indistinguishable instrumental mass discrimination factors for $^{18}O/^{16}O$ ratios on the Cameca 6f and 4f instruments.

References
[1] U. Admon, F. Rudenauer, D. Donohue, E. Chinea-Cano, H. Aigner, "Precise re-location of radioactive particles in SEM/SIMS analysis of environmental samples", Proc. INMM-43 Annual Meeting, Orlando, June 23-27, 2002.
[2] G. Tamborini, D. Phinney, O. Bildstein, M. Betti, Anal. Chem. 74 (2002) 6098-6101

Contact (7.2): Maria Betti · tel.: +49 7247 951 363
fax: +49 7247 951 186 · betti@itu.fzk.de
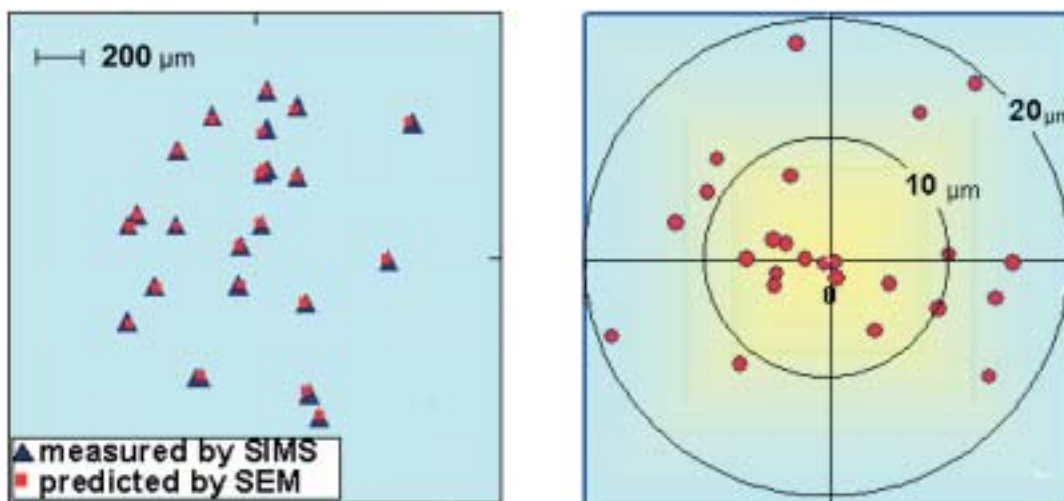
Fig. 7.6   Difference between reference locations and locations predicted by SIMS.

Projects

7.3 Analytical Support to Euratom Safeguards

Samples of nuclear material are taken by Euratom inspectors in order to perform verification measurements. These measurements are carried out in specialised, independent laboratories. Most samples are analysed at ITU. Using qualified radiometric and chemical measurements techniques, 53 product samples (*i.e.* UO_2, PuO_2 and MOX) originating from different fuel fabrication facilities were analysed on request of DG TREN (Euratom Safeguards).

The efforts that had been undertaken to further improve the accuracy and reliability of the in-field COMPUCEA measurement [TUAR 2001, p. 80] have resulted in simplified handling of the software, in improved robustness and in increased confidence in the results. The approach for in-field calibration prior to each measurement campaign has been completely changed. Adequate reference solutions for calibration are now freshly produced on site from well-characterized reference materials (in the form of sintered pellets), which are kept on site under the custody of the Euratom inspectors. The training of the ITU analysts performing the in-field measurements has been intensified. As a result of these efforts, the performance of the COMPUCEA measurements has further improved [1]. The results obtained for 98 samples analysed during the campaigns conducted in 2002 show very good agreement with the declared values, both for the U-element content and for the ^{235}U isotope abundance. The measurement uncertainty is well within the IAEA Target Values.

The isotopic composition of uranium particles from swipe samples collected inside enrichment plants is measured using Secondary Ion Mass Spectrometry (SIMS) (see also section 7.2). These isotopic signatures reflect the range of production (feed material, tails and products) of a particular facility and thus enable the detection of undeclared activities. ITU is carrying out such particle analysis of uranium on swipes under contracts with the IAEA, with DG TREN, with ABACC and with KAERI. In the reporting period the isotopic composition of uranium particles was routinely determined in 63 swipe samples.

References
[1] S. Abousahl, H. Ottmar, G. Marissens, N. Albert, P. Matussek; Matrix effect correction for the uranium assay with a 57Co-153Gd isotopic source based K-edge densitometer; 24th ESARDA Annual Meeting, Luxembourg, 28-30 May 2002
[2] S. Abousahl, G. Marissens, N. Albert, H. Ottmar, L. Pierssens; Compucea principles-design-performance; Report, JRC-ITU-TN-2002/41

Contact (7.3): Omer Cromboom · tel.: +49 7247 951 360 fax: +49 7247 951 99360 · cromboom@itu.fzk.de

7.4 Illicit Trafficking and Nuclear Forensic Science
(see also Highlight p. 16 in this report)

Characteristic pattern for origin determination

Chemical impurities in nuclear material are expected to provide useful information on the origin of the material. Impurities may enter the material at different stages of the process; their presence might be due to:

a) incomplete separation from the base material (uranium ore or reprocessing of spent fuel)
b) intentionally added compounds to obtain certain characteristics (*e.g.* Gd as burnable neutron poison, Zn-stearate to improve powder fluidity)
c) trace elements contained in chemical reagents or scour from tools and container walls

We started a systematic study of the content of chemical impurities in uranium ores from different mines and the respective intermediate (yellow cake) and final products (natural uranium oxide).

A "horizontal" comparison was performed in order to compare the same type of material for different mines. Fig. 7.7 shows that comparing the concentration of chemical impurities in the same material (yellow cake) varies for some elements by more than an order of magnitude from mine to mine.

Moreover, a "vertical" comparison was performed in order to understand how impurities contained in the ore propagate through the process. As can be seen from Fig. 7.8 a drastic reduction of $\sim 10^3$ in the impurity concentration was seen after the ore processing.
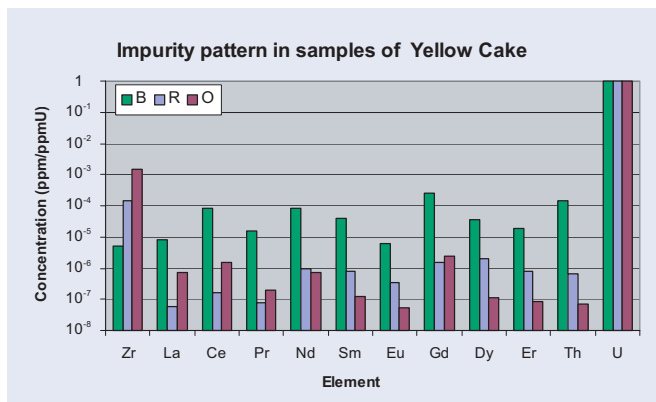
Fig. 7.7   *Comparison of concentration of chemical impurities of yellow cake (YC) from different mines ("Horizontal comparison")*
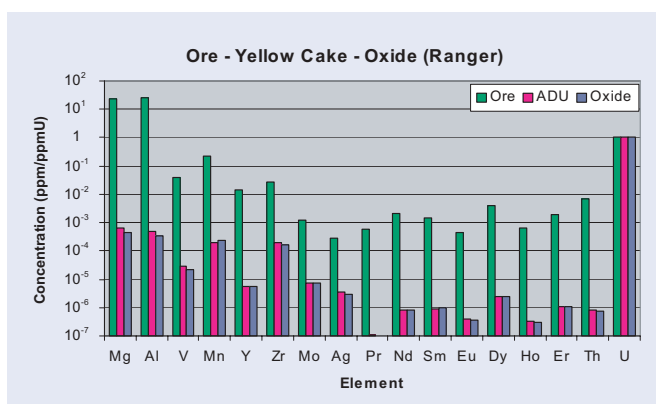
Fig. 7.8   *Comparison of concentration of chemical impurities at different stages of processing uranium: ore, yellow cake, uranium oxide ("Vertical comparison")*

The impurity pattern, however, was not much affected (except in the case of Pr), it still followed the same trend, especially for the rare earth elements. A closer analysis of the data shows that the ratio of concentration of some elements does not change significantly throughout the process. The observed ratios *e.g.* for Zr/Th – both being tetravalent elements - do not change significantly from yellow cake (Ammonia diuranate, $(NH_4)_2U_2O_7$) to the corresponding U_3O_8. Yet, in the two other mines this ratio is orders of magnitude different. This is illustrated in Tab. 7.2, where we selected two elemental pairs. It can be seen that the Zr/Th and Ce/Dy ratios differ several orders of magnitude between the mines and thus only determining these two ratios, the mine of origin could be revealed. There are also additional signatures or elements that can be used to underpin the results [1].

Tab. 7.2   Elemental ratios showing significant difference between the mines, thus they are useful for identifying the origin of natural uranium ("Horizontal comparison").

Mine	Elemental ratios				Additional characteristic impurities
	Zr/Th		Ce/Dy		
	YC	Oxide	YC	Oxide	
Ranger	217	11.7	0.09	0.14	Mg, Al, V, Mn, Y, Mo, Ag, Ho
Olympic	21000	12200	12.4	17.9	Cu, Mo, Ag
Beverley	0.036	-	2.36	-	Al, Sc, V, Sr, Y, Ho

References
[1]   M. Wallenius, K. Mayer, G. Tamborini, A. Nicholl; Investigation of correlations in some chemical impurities and isotope rations for nuclear forensie purposes; International Conference on Advances in Destructive an Non-Destructive Analysis for Environemental Monitoring and Nucklear Forensics, Karlsruhe, Germany, 21-23-October 2002

Contact: Maria Wallenius, tel: +49 (0)7247 951-579
fax: +49 (0)7247 951-99579, e-mail: wallenius@itu.fzk.de

Age determination of low enriched uranium

Methods for the determination of the age of Pu and of highly enriched uranium have been developed and validated in the past. This is significantly more difficult for low enriched uranium as the amount of daughter nuclides ([230]Th and [231]Pa) built up from decay of the long-lived isotopes [234]U and [235]U is extremely small. Consequently, chemical separations of high recovery and high decontamination factors were developed, working with picograms of daughter nuclides. Highly sensitive measurement techniques such as low-level alpha spectrometry, thermal ionization mass spectrometry or inductively coupled plasma mass spectrometry were applied for the actual measurement. For ICP-MS no separation was performed, hence the parent/daughter ratios were measured directly. Great care was taken to accurately quantify the results and the related uncertainty. The methodology was validated using NBL reference materials of known age. Figure 7.9 shows the results obtained in direct comparison to the "true" age; as can be seen the calculated difference is not significant, demonstrating that the experimentally determined age of the different materials is in good agreement with the expected value. Also, the different methods that were applied deliver results, which are not significantly different.

Projects
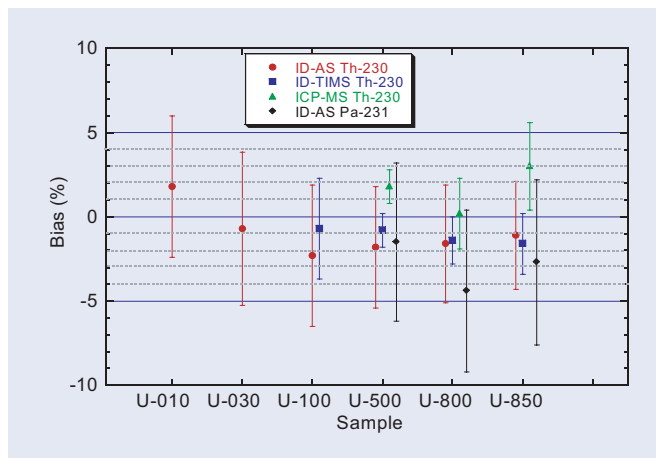
Fig. 7.9   Difference between experimentally determined age of certified uranium reference materials and the "true" age.

Contact: Alfred Morgenstern, tel: +49 (0)7247 951-248, fax: +49 (0)7247 951-99248, e-mail: morgenstern@itu.fzk.de

Supporting PECO countries in combating illicit trafficking of nuclear materials

The aim of the on-going PECO projects is to:

● improve the protection of the EU citizens against the risks arising from the illicit trafficking of nuclear material,
● improve the capacities for analysis of nuclear material in the country by the means of training and transfer of know-how,
● implement the recommended ITWG Model Action Plan on a national basis,
● extend the nuclear materials database at ITU for identification and determination of the intended use,
● upgrade the capabilities for categorisation on the spot of seized nuclear materials,
● establish the basis for joint analysis of seized nuclear material at ITU.

In close co-operation with the International Atomic Energy Agency (IAEA), ITU developed a training module on combating illicit trafficking of nuclear materials. Three training workshops, dedicated to Law Enforcement Services and Radioanalytical Laboratory Experts, were held in 2002 at ITU with participants from the Candidate Countries as well as Russia and the NIS Countries. The goal of the training is twofold in providing

● basic information on nuclear material, share experience on previous cases and provide practical training in using hand-held measurement devices for on-site categorisation (dedicated to customs officers, criminal police or intelligence agents),
● specific technical training covering all methods used in nuclear forensic investigations at ITU: Non Destructive Analysis techniques (NDA) such as gamma spectrometry and neutron coincidence counting, elemental and isotopic analysis (titration or mass spectrometry), impurity analysis (inductively coupled plasma mass spectrometry, ICP-MS) and microstructural investigations (scanning and transmission electron microscopy, SEM, TEM) (dedicated to radioanalytical experts).

Four demonstration exercises in Lithuania, Romania, Hungary and at the Kapikule border crossing between Bulgaria and Turkey have been organised with the support of ITU. These exercises allowed assessing the national Model Action Plan created within the project and enhancing the international collaboration in the field. An integrated and harmonised response to illicit trafficking is now being implemented in the Candidate Countries to the European Union.

Delivery of appropriate equipment has been made for the categorisation on the spot of seized materials in the form of hand-held detectors and appropriate software (MGA, MGA-U, Nuclides 2000) for isotopes identification.

The future activities of ITU in this area will focus on the extension of the projects to current Member States, to Russia and to eastern countries in order to establish a common and integrated international response to illicit trafficking of nuclear materials, continuation of a close collaboration with international organizations in particular the IAEA through the participation to its regional training programme and specific Co-ordinated Research Programme (CRP). The co-operation will continue in order to build a network of national expert laboratories in the field. ITU will continue to support and co-ordinate the efforts of individual countries and act as a focal point and leader in the identification of nuclear materials.

Contact: Pascal Daures, tel: +49 (0)7247 951-289, fax: +49 (0)7247 951-99289, e-mail: daures@itu.fzk.de or Saïd Abousahl, +49 (0)7247 951-256, fax: +49 (0)7247 951-99256, e-mail: abousahl@itu.fzk.de

Co-operation with Russia

The existing database system for support of analyses of nuclear material of unknown origin (TUAR-96, p. 135 and TUAR-98, p. 33-35, 104) was maintained and extended. Further data for UO_2 and MOX fuel produced in the EU have been included:

● two datasets with coupled information on enrichment and macroscopic fuel geometry
● one dataset with information on characteristic impurities covering
   – specifications of maximum concentrations of Al, B, Cd, Fe, Mo, Na, Ni, Si, and V
   – real values of impurities C, Cl, F, and N

For allowing full use of this new data, the relational table system was extended and the graphical user interface was refined.

The co-operation with the All-Russia Institute for Inorganic Materials (VNIINM) Moscow was continued by:

● Maintaining and updating the installation of the common database sector at VNIINM, symmetric to that at ITU
● Completing a bilateral contract on a dedicated literature database. In this pilot project VNIINM experts compiled an electronic archive with more than 350 reports and corresponding English keywords on special nuclear materials used in the former USSR. All these documents belong to special publication categories (VNIINM institute preprints, Russian conference reports) that were so far impossible to access from EU institutions.

In the framework of a TACIS project, support for upgrading the laboratory capabilities was given to VNIINM. Factory acceptance tests for a thermal ionisation mass spectrometer were carried out with participation of VNIINM experts. Further equipment was tendered and technical and financial evaluation of the tenders was performed. A follow-up project was started, the respective Term of Reference was agreed upon and the administrative agreement was signed by DG AIDCO.

Contact: Arndt Schubert, tel: +49 (0)7247 951-406,
fax: +49 (0)7247 951-99406, e-mail: schubert@itu.fzk.de
or Klaus Mayer, tel : +49 (0)7247 951-545,
fax: +49 (0)7247 951-99545, e-mail: mayer@itu.fzk.de

7.5 Laboratoire sur Site (LSS), La Hague

The laboratory which is located on the site of the French reprocessing plant at Cap de La Hague was designed to perform analysis of input and product samples in the framework of EURATOM safeguards for nuclear material verification.

The LSS is equipped with a suite of hot-cells for the remote handling of input samples, a suite of 4 boxes - 2 being equipped with telemanipulators - to perform measurements of PuO_2 samples, a glove-box to measure concentration and enrichment of uranium solutions and a suite of glove-boxes housing a robot dedicated to the chemical separation of U and Pu prior to Isotope Dilution Mass Spectrometry (IDMS) measurements. The latter, being a destructive analysis technique (and relatively time and resource consuming), is applied as a quality control measurement to 10 – 15% of the samples analysed by Non Destructive Analytical (NDA) techniques (Hybrid K-Edge Densitometry, neutron coincidence counting and gamma spectrometry) and whenever a NDA measurement has to be corroborated.

Sample throughput and manpower

During this second full year of operation, the laboratory was operated by highly skilled ITU staff members who carried out 200 mission weeks on site (*i.e.* a team of 4 analysts/week) to perform analytical, maintenance, administrative tasks and to follow mandatory site specific (re-) training courses. 49 weeks of laboratory operation were assured by ITU analysts, 503 samples were analysed, a detailed list of samples is given in Tab. 7.3

Tab. 7.3 Number of samples analysed, sorted per sample type (UCD = unité de conditionnement des déchets, i.e. facility for recovery of residual plutonium from waste prior to conditioning for final disposal; URP = unité de retraitement du procédé, i.e. facility for reprocessing old plutonium in order to remove the americium)

Sample type	Number
Input	360
UCD	67
URP (" old Pu ")	54
Inventory + occasional	38

Projects

and the total number of measurements including calibration and quality control can be found in the Tab. 7.4.

Tab. 7.4   Number of measurements performed, sorted per measurement technique

Measurement type	Number
Hybrid K-Edge	1700
Density	680
Neutron Coincidence Counting	100
Chemical Separations	700
Mass Spectrometry	1700

Some milestones

This year, for the first time samples from reprocessed "old" plutonium (thus already containing a large amount of ^{241}Am) have been transferred to the LSS for analysis. The initial set of samples was first measured by IDMS in order to perform the calibration of the NDA instrumentation. The latter was then used to perform routine measurements of 5 of these samples per week.

Due to the very high activity of the input solutions, they can be handled in a glove-box only after having been previously diluted inside the hot-cell. Depending on the activity of the input solution, the dilution factor could even reach 40 000. As a consequence, the sample contains only nano-gram amounts of Pu and micro-grams of uranium. This poses a challenge to the separation chemistry and to the mass spectrometric measurements. A simple and rapid method has been developed by the LSS team to perform a separation of U and Pu from the other actinides and from the fission products inside the hot-cells. This operation drastically reduces the dose rate and thus allows the transfer of the U-Pu fraction into a glove-box, yet without the need of a high dilution factor. This method which is now being implemented in the LSS will also lead to a reduction of the solid waste volume produced in the hot-cells.

Perspective

Next year, the throughput is expected to exceed 750 samples including a new type of sample coming from the reprocessing of spent MOX fuel.

Contact (7.5): Patrice Richir, tel: +49 (0)7247 951-211, fax: +49 (0)7247 951-99211, e-mail: richir@itu.fzk.de

7.6 On Site Laboratory (OSL), Sellafield

The OSL was installed in order to perform sample verification measurements at the Sellafield reprocessing plant (UK) in the framework of EURATOM safeguards. The laboratory has been operated routinely for three years.

The calibration of the analytical instruments for the measurement of Mixed Oxide (MOX) samples was finalised as well as validation of the techniques concerned. The OSL now analyses MOX samples originating from the new Sellafield MOX Plant (SMP) on a regular basis.

In the framework of ITU's in-field support to DG TREN, OSL analysts have also dedicated part of their time to support the Euratom THORP inspectors to assure proper operation of their Hybrid K-edge instrument.

Sample throughput and manpower

The OSL staff performed 124 mission weeks during the year 2002. 113 of these mission weeks were used to perform analysis on samples received from THORP, Magnox, SMP and Springfields. A total of 292 samples were analysed (see Tab. 7.5). Tab. 7.6 gives an overview of the distribution according to sample type.

Further 11 weeks were necessary maintenance of the laboratories and the analytical instruments and to keep the personnel trained to the highest standards.

Validation of analytical methods for MOX samples

At the beginning of 2002, the X-ray fluorescence instrument in the OSL was calibrated for MOX, using standards specifically prepared for this purpose in the OSL. The dissolution behaviour of MOX pellets was first studied and subsequently the procedures for dissolution, dilution and analysis were optimised.

Meanwhile, BNFL had started the commissioning of the new Sellafield MOX plant (SMP). All MOX samples received were analysed with all available techniques for method intercomparison: High Level Neutron Coincidence Counting (HLNCC), K-Edge (for U assay), X-ray fluorescence (for Pu assay) and Isotope Dilution Mass Spectrometry (IDMS). As the results were very satisfactory, in routine application only a subset of 10 - 15 % of all samples will be subject to IDMS measurements, for quality control purposes.

Tab. 7.5 Samples analysed in the OSL in 2002 sorted according to their origin (Magnox= reprocessing plant at Sellafield for fuel from Magnox reactors, THORP= reprocessing plant at Sellafield for fuel from Light Water Reactors, Springfields= uranium oxide fuel fabrication plant, SMP/MDF= Sellafield MOX Plant and MOX Demonstration Facility)

Plant	Samples
Magnox	78
Thorp	145
Springfields	57
SMP/MDF	12

Tab. 7.6 Samples analysed in the OSL sorted according to material type

Material	Samples
Pu nitrate solution	97
PuO_2 powder	40
Oxalate Mother Liquor	9
U Nitrate solution	8
U powder/pellet	81
U/Pu input solution	39
MOX pellet	12
Other	6

Support to Euratom THORP K-edge

The Euratom inspectors at the THORP plant operate their own hybrid K-edge densitometer for the analysis of reprocessing input samples. The re-calibration of the instrument was performed by OSL staff, starting end of 2001, and fully achieved in January 2002. Training was given to the inspectors in the use of the new software. The OSL analysts visit the THORP K-edge on a regular basis to check the instrument and to offer scientific-technical support in case problems occur.

External quality control

The OSL participates in the EQRAIN external quality control programmes. The first uranium nitrate solution of a batch of four was analysed.

Contact (7.6): Lily Duinslaeger · tel.: +49 7247 951 299 fax: +49 7247 951 99 299 · duinslaeger@itu.fzk.de

7.7 Analytical Support to IAEA

ITU is providing support to the IAEA in the framework of the European Commission's co-operative support programme to the IAEA. The corresponding scientific and technical activities are carried out in the areas of particle analysis, actinide analysis, automation and on-site laboratories.

With regard to the on-site laboratory currently under construction at the Rokkasho Reprocessing Plant (RRP) in Japan, the IAEA has a considerable need for support. For measuring Cm in spent fuel solutions and in highly active waste, ITU elaborated a design for extension of the existing hybrid K-edge by a Neutron Coincidence Counter. Monte Carlo calculations were performed to evaluate the counting efficiency and to optimise the design. The construction of a prototype instrument has been started. With respect to the routinely applied analytical methods for U and Pu assay, reference documents were exchanged in order to share the experience gained by ITU with the IAEA. Furthermore, the huge expertise built up through the development and continuous update of a tailored Laboratory Information Management System has been made available for the RRP-OSL project. Provisions are being made for implementation of the analytical methodology developed at ITU for Flow Sheet Verification (FSV) of Neptunium (TUAR 2001, p. 81) with extensive consulting through ITU. A training programme for IAEA analysts, comprising K-edge, mass spectrometry and tele-manipulators has been set up and will start in early 2003.

The OSL-RRP will be operated jointly between IAEA and the Nuclear Material Control Center (NMCC – the national Japanese Safeguards Authority). Under contract with NMCC two more sample changers for the hybrid K-edge instruments were constructed and delivered in 2002, after having passed the factory acceptance tests. ITU provided assistance for their provisional installation at Tokai-mura and site acceptance. They are scheduled to be transferred to Rokkasho-mura in spring 2003, again with the assistance of ITU.

The implementation of FSV at ITU, based on a voluntary offer by the Commission, was started by the IAEA. In an initial report the respective technical information was compiled. A training course on FSV application to research installations is foreseen in 2003 with ITU participation.

Projects

The results from the interlaboratory exercise conducted during the year 2001 [TUAR 2001, p. 88] to test the performance of the SIMS instruments used by the network of analytical laboratories (NWAL) of the IAEA for the characterization of micro particles have been discussed in a workshop held at ITU in April 2002. The results have been compiled and will be presented in IAEA technical reports as well as a scientific publication.

The samples investigated are reported in Tab. 7.7 while the laboratories participating are listed in Tab. 7.8.

An important parameter that characterises a SIMS instrument and its detection capability is the so-called useful yield. The useful yield determines the ultimate detection sensitivity for a small particle in the case when analysis time is not of prime importance and the particle can be sputtered to complete consumption. In this case the useful yield is given by the ratio between the number of detected ions of an element X and the number of atoms of that element sputtered during the same measurement time. The useful yields obtained by the different laboratories for two different series of particles with two different image fields are shown in Fig. 7.10. As can be seen, they are quite consistent for each laboratory but differ among them.

In Fig. 7.11 the ratio of the useful yield obtained from the results on the two series of particles with the two different image fields are reported and the internal consistency in each laboratory is evident. Except for the value related to VTT, which is operating a completely different SIMS instrument compared to other NWAL, the agreement between the participating laboratories is good. That is demonstrating a good quality control of the instrumental performance of the SIMS in each network analytical laboratory of IAEA.

Tab. 7.7 Samples investigated in the SIMS round robin exercise.

Sample ID	Sample	Description	Supplier	Parameter investigated
U	NU metal foil	25 µm thick, ~ 4x4 mm;	GOOD-FELLOW	Pract. Sensitivity
U500-X	UO_2 Particle standard	NBS500 - based, 0.8 mm diameter graphite planchet	ITU	Useful yield
SRR_CX	UO_2 Particle standard	LEUS5 (3.7 wt%), 3.6 mm diameter graphite planchet	AEA / SAL	Useful yield

Tab. 7.8   List of participant laboratories in the SIMS round robin exercise.

| Institution	Country	Acronym	Instrument
CEA/DAM/DRIF	France	CEA	Cameca 6f
International Atomic Energy Agency	IAEA	SAL - IAEA	Cameca 4f
MINATOM	Russia	LMA	Cameca 4f
Australian Nuclear Science & Technology Organisation	Australia	ANSTO	Cameca 5f
National Institute of Standards and Technology	USA	NIST	Cameca 4f
Tokai Research EstablishmentJapan Atomic Energy Research Institute	Japan	JAERI	Cameca 6f
VTT Chemical Technology	Finland	VTT	VG IX70S
Institute for Transuranium Elements	EU	ITU - AC	Cameca 6f
Institute for Transuranium Elements	EU	ITU - AS	Cameca 4f
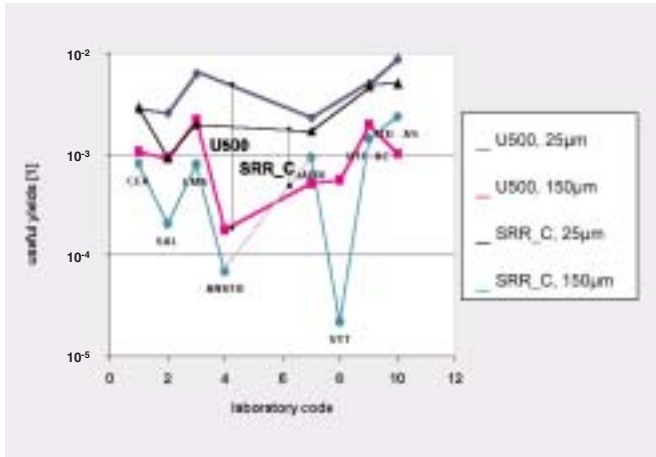
Fig. 7.10 Useful yields from two series of particles at two differ-
ent image fields (25 μm and 150 μm).
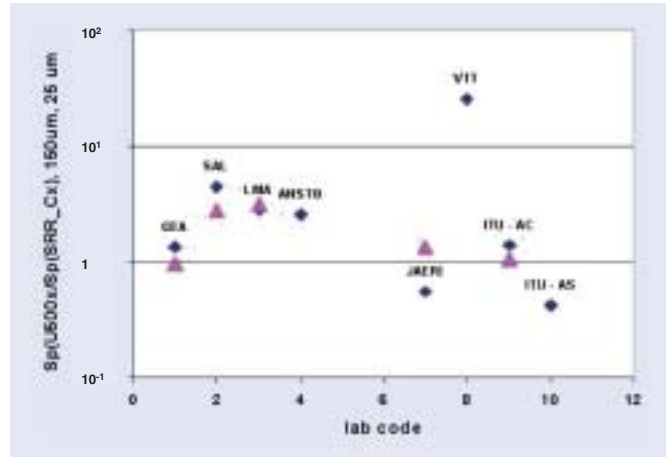
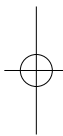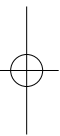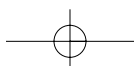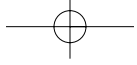Fig. 7.11 Ratio of useful yields at both image fields for the two
series of particles.

**Contact (7.7): Maria Betti · tel.: +49 7247 951 363 · fax: +49 7247 951 186 · betti@itu.fzk.de or
Klaus Mayer · tel.: +49 7247 951 545 · fax: +49 7247 951 99 545 · mayer@itu.fzk.de**

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Journal of Nuclear Science and Technology Suppl. 3 (2002) 118-121

Annex I

Conferences

26. Annual International Conference on Advanced Ceramics & Composites:
Ceramics in the New Millennium
January 13-18, 2002 Cocoa Beach, FL (USA)

Boccaccini, A.R.; Spino, J.L.; Cannillo, V.
Hermetic Glass Bodies with Controlled Porosity: Processing and Properties

Fuel Safety Research Specialists Meeting, JAERI
March 4-5, 2002 Tokai-mura (Japan)

Hellwig, Ch.; Wallin, H.; Lassmann, K.
RIA Modelling - A Comparison between TRANSURANUS and FREY

32. Journées des Actinides
March 20-22, 2002 Ein-Gedi (Ireland)

Boulet, P.; Colineau, E.; Wastin, F.; Rebizant, J.
The Binary System Np-Si and Magnetic Properties of Np_3Si_2

Christianson, A.; Lander, G.H.; Kern, S.; Harrison, N.; Vogt, O.
High Field Magnet Experiments on US Single Crystals

Ghosh, D.B.; De, S.K.; Oppeneer, P.M.; Brooks, M.S.S.
Electronic Structure Investigation of the Americium Monopnictides

Javorsky, P.; Givord, F.; Boucherle, J.X.; Berna-Lelièvre, E.; Andreev, A.V.; Sechovsky, V.; Bourdarot, F.
Magnetization Densities in UPtAl Studied by Polarized Neutron Diffraction

Longfield, M.J.; Paixao, J.A.; Bernhoeft, N.; Lander, G.H.
Resonant X-ray Scattering from Multi-k Magnetic Structures
Physical Review B Condensed Matter 66 (2002) 544171-7

Wastin, F.; Boulet, P.; Colineau, E.; Rebizant, J.
Empirical Comparison between Superconducting Uranium Compounds and their Np/Pu Homologues

19. Meeting Condensed Matter Division/European Physic Society
April 7-11, 2002 Brighton (United Kingdom)

Brooks, M.S.S.; Colarieti-Tosti, M.; Eriksson, O.
Density Functional Theory for Crystal Field Excitations

Colarieti-Tosti, M.; Eriksson, O.; Nordström, L.; Wills, J.M.; Brooks, M.S.S.
Ab Initio Calculation of Crystal Field Levels and Magnetic Susceptibility in PuO_2

Litfin, K.; Gouder, T.; Havela, L.; Brooks, M.S.S.; Schoenes, J.
Electronic Structure, Chemical Bonding and Optical Properties of Uranium Carbide, Nitride and Oxide

Meeting of the American Chemical Society
April 7-11, 2002 Orlando, FL (USA)

Morgenstern, A.; Apostolidis, C.; Ottmar, H.; Mayer, K.
Safeguarding Alternative Nuclear Materials: Analysis of ^{237}Np in Spent Fuel Solutions

6. International Symposium on Fusion Nuclear Technology (ISFNT-6)
April 7-12, 2002 San Diego, FL (USA)

Rabaglino, E.; Ferrero, C.; Reimann, J.; Ronchi, C.; Schulenberg, T.
Study of the Microstructure of Irradiated Beryllium for the Validation of the ANFIBE Code
Fusion Engineering and Design 61-62 (2002) 769-773

Jahrestagung Kerntechnik 2002
May 14-16, 2002 Stuttgart (Germany)

Schenkel, R.
Nuklearforschung im Europäischen Institut für Transurane

ESARDA 24. Annual Meeting
Workshop on „R&D Response to the New Safeguards Environment"
May 28-30, 2002 Luxembourg (Luxembourg)

Abousahl, S.; van Belle, P.; Ottmar, H.; Mayer, K.
Radiometric Assay Techniques for the Control of Minor Actinides applied to Advanced Fuel Cycles
Proceedings EUR 20385/EN (2002)

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May 28-30, 2002 Luxembourg (Luxembourg)

Schenkel, R.; Mayer, K.; Poucet, A.; Wellum, R.
Focused Research Contributing to More Effective and Efficient Safeguards
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Wallenius, M.; Abousahl, S.; Ottmar, H.; Mayer, K.
Detection of illicit trafficking of nuclear material and nuclear forensic analysis

Modelling the Behaviour of Spent Fuel under Repository Conditions Workshop
June 6-7, 2002 Avila (Spain)

Quinones, J.; Cobos, J.; Rondinella, V.V.
First Modelling Approach to $(U_{1-y}{}^{238}Pu_y)O_{2(+x)}$ Leaching Behaviour in Water

2002 Annual Meeting of the American Nuclear Society
June 9-13, 2002 Hollywood, FL (USA)

Ronchi, C.; Halton, D.; Sheindlin, M.; Staicu, D.; Kinoshita, C.
The Thermal Diffusivity of Uranium Dioxide and MOX up to 100.000 MWd/t
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49. Annual Meeting, Society of Nuclear Medicine
June 15-19, 2002 Los Angeles, CA (USA)

Heeger, S.; Moldenhauer, G.; Egerer, G.; Wesch, H.; Eisenmenger, A.; Nikula, T.; Apostolidis, C.; Janssens, W. Brechbiel, M.W.; Haberkorn, U.; Ho, A.D.; Haas, R.
Treatment of B-Lineage Non-Hodgkin's Lymphoma using a [213]Bi-Labeled Anti-CD20-CHX-A"-DTPA Antibody Conjugate

E-MRS Spring Meeting 2002
June 18-21, 2002 Strasbourg (France)

Rabaglino, E.; Baruchel, J.; Boller, E.; Elmoutaouakkil, A.; Ferrero, C.; Ronchi, C.; Wiss, T.
Study by Microtomography of 3D Porosity Networks in Irradiated Beryllium
Nuclear Instruments and Methods B

Gedeon-Practis Workshop "The Molten Salt Reactors"
June 19-29, 2002 Cadarache (France)

Konings, R.J.M.
Chemical Aspects of Fuels for Molten-Salt Reactors

43. INMM Annual Meeting, Institute for Nuclear Material Management
June 23-27, 2002 Orlando, FL (USA)

Wallenius, M.; Mayer, K.; Abousahl, S.; Schubert, A.; Ray, I.; Koch, L.
Experience and Development in Analysing Illicit Nuclear Material
Proceedings of the Conference

Abousahl, S.; van Belle, P.; Vallet, P.; Eberle, H.; Ottmar, H.; Mayer, K.
Radiometric Analytical Methods for the Pyrochemical Partitioning Process

6. Prague Colloquium on f-Electron Systems
July 6-9, 2002 Prague (Czech Republic)

Colineau, E.; Boulet, P.; Wastin, F.; Rebizant, J.
Magnetic Ordering in the $(U_{1-x}Np_x)_2Rh_2Sn$ System

Gouder, T.; Havela, L.; Wastin, F.; Rebizant, J.
5f Localization in Ultrathin Pu Layers

Idiri, M.; Le Bihan, T.; Heathman, S.; Rebizant, J.
Structural Behaviour of UO_2 and ThO_2 under High Pressure

Javorsky, P.; Givord, F.; Boucherle, J.X.; Lelievre-Berna, E.; Andreev, A.V.; Sechovsky, V.
Magnetization Densities in UPtAl Studied by Polarized Neutron Diffraction

Wastin, F.; Lander, G.H.; Colineau, E.
The Actinide User Laboratory at ITU-Karlsruhe

International Conference on Strongly Correlated Electron Systems
July 10-13, 2002 Krakow (Poland)

Bernhoeft, N.; Lander, G.H.; Longfield, M.; Langridge, S.; Mannix, D.; Lidström, E.; Colineau, E.; Hiess, A. Vettier, C.; Wastin, F.; Rebizant, J.; Lejay, P.
Introducing the Concept of a Dynamical Phase in Magnetic Order: Possible Implications for URu_2Si_2

Boulet, P.; Colineau, E.; Wastin, F.; Rebizant, J.
Magnetic Properties of the New NpX_{2-x} (X = Si, Ge) with the AlB_2 Type Structure
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Griveau, J.C.; Wastin, F.; Rebizant, J.
High Pressure Behaviour of NpTe
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Photoelectron Spectroscopy Study of Pu and Pu-based Systems
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Javorsky, P.; M.; Schweizer, J.; Givord, F.; Boucherle, J.X.; Sechovsky, V.; Andreev, A.V.; Lelievre-Berna, E.; Boudarot, F.
Uranium Form Factors in Selected UTX Compounds
Acta Physica Polonica

Metoki, N.; Koike, Y.; Bernhoeft, N.; Lander, G.H.; Tokiwa, Y.; Haga, Y.; Onuki, Y.
Magnetic Excitations in UPt_2Si_2

CIMTEC 2002
July 14-18, 2002 Florence (Italy)

Lutique, S.; Konings, R.J.M.; Rondinella, V.V.; Somers, J.; Wiss, T.
High Temperatures Thermal Properties of $Nd_2Zr_2O_7$ Pyrochlore

16. European Conference on Thermophysical Properties
September 3-5, 2002 London (United Kingdom)

Manara, A.; Ronchi, C.; Sheindlin, M.
High-Pressure Melting Behaviour of Non-Stoichiometric Uranium Dioxide
Proceedings High Temperatures High Pressures

International Congress of the European Nuclear Society (ENC 2002)
September 6-9, 2002 Lille (France)

Languille, A.; Phelip, M.; Obry, P.; Perrais, C.; Perez, M.; Conrad, R.; Bakker, K.; Den Exter, M.J.; Hittner, D.; Guillermier, P.; von Lensa, W.; Nabielek, H.; Werner, H.; Fachinger, J.; Somers, J.; Toscano, E.H.; Abram, T.
The European Programme on High Temperature Reactor Fuel Technology

von Lensa, W.; Ohlig, U.; Ruetten, H.-J.; Raepsaet, C.; Damian, F.; Dolci, F.; Bernnat, W.; Kuijper, J.C. De Haas, J.B.M.; Kloosterman, J.L.; Cerullo, N.; Lomonaco, G.; Negrini, A.; Brinkmann, G.; Feltes, W.; Magill, J.; Bonin, B.; Greneche, D.; Abram, T.
The European Programme on High Temperature Reactor Nuclear Physics, Waste and Fuel Cycle Studies

22. Symposium on Fusion Technology (SOFT)
September 9-13, 2002 Helsinki (Finland)

Rabaglino, E.; Ronchi, C.; Cardella, A.
Recent Improvements in the Modelling of Irradiated Beryllium:
The ANFIBE Code Version 1

Rabaglino, E.; Elmoutaouakkil, A.; Ferrero, C.; Ronchi, C.; Cardella, A.
Gas Release from irradiated Beryllium: A Study of Percolation
Mechanisms by Microtomography

Uranium Mining and Hydrogeology (UMH) III International
Conference
September 15-20, 2002 Freiberg (Germany)

Amme, M.
Raman Microspectrometric Investigations of UO_2 Alteration
Products: Natural Analogues to Alpha Radiolysis Effects

5. International Symposium on Contribution of Materials
Investigation to the Resolution of Problems Encountered in
Pressurised Water Reactors
September 23-27, 2002 Fontevraud (France)

Ronchi, C.; Sheindlin, M.; Staicu, D.
The Thermal Diffusivity of Uranium Dioxide, Uranium-Gadolinium
Oxyde and MOX up to 100.000 MWd/t

2. Seminar on European Research on Materials for
Transmutation (ERMT II)
September 26-27, 2002 Karlsruhe (Germany) ITU Karlsruhe

Berthou, V.; Degueldre, C.; Magill, J.
Transmutation Characteristics in Thermal and Fast Neutron
Spectra: Application to Americium
Proceedings Journal of Nuclear Materials

Croixmarie, Y.; Abonneau, E.; Fernandez, A.; Konings, R.J.M.;
Desmoulière, F.; Donnet, L.
Fabrication of Transmutation Fuels and Targets: The ECRIX and
CAMIX-COCHIX Experience
Proceedings Journal of Nuclear Materials

Neeft, E.; Bakker, K.; Schram, R.P.C.; Conrad, R.; Konings, R.J.M.
The EFTTRA T3 Irradiation Experiment on Inert Matrix Fuels
Proceedings Journal of Nuclear Materials

Pillon, S.; Somers, J.; Grandjean, S.; Lacquement, J.
Aspects of Fabrication of Curium-based Fuels and Targets
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Thermophysical Properties of Inert Matrix Fuels for Actinide
Transmutation
Proceedings Journal of Nuclear Materials

Wiss, T.; Konings, R.J.M.; Walker, C.T.; Thiele, H.
Microstructure Characterization of Irradiated Am-containing
$MgAl_2O_4$
Proceedings Journal of Nuclear Materials

van Veen, A.; Konings, R.J.M.; Fedorov, A.V.
Helium in Inert-Matrix Dispersion Fuels
Proceedings Journal of Nuclear Materials

11. International Conference on Emerging Nuclear Energy
Systems
September 29 – October 4, 2002 Albuquerque (USA)

McKenna, P.; Ledingham, K.W.D.; Spencer, I.; McCanny, T.; Singhal, R.P.;
Galy, J.; Magill, J.; Rondinella, V.V.; Rebizant, J.; Schenkel, R.; Beg, F.N.;
Krushelnick, K.; Wei, M.S.; Norreys, P.A.; Lancaster, K.L.; Clarke, R.J.;
Clark, E.L.
Experiments in Laser Induced Nuclear Physics
Proceedings ICENES (2002) 338-346

Galy, J.; Magill, J.; Rondinella, V.; Rebizant, J.; Schenkel, R.; Ewald, F.;
Schwoerer, H.; Sauerbrey, R. Ledingham, K.W.D.; McKenna, P.;
Spencer, I.; Krushelnick, K.; Norreys, P.A.
Fission of Actinides Using High Intensity Laser Plasma Interactions:
A Comparison of Tabletop and Giant Laser Pulse Systems
Proceedings ICENES (2002) 347-353

International Congress of the European Nuclear Society
(ENC 2002)
October 6-9, 2002 Lille (France)

Haas, D.; Konings, R.J.M.; Magill, J.; Berthou, V.
Partitioning and Transmutation: Challenges and Perspectives
Proceedings of the Conference

2. International Workshop on Spin and Orbital Magnetism in
Actinides
October 13-15, 2002 Berkeley, CA (USA)

Biasini, M.; Ferro, G.; Sterne, P.A.; Lander, G.H.
Fermi Surface Studies of Actinides Compounds via Positron
Annihilation Experiments

Brooks, M.S.S.
Theory of Ground State Spin and Orbital Moments with Screened
Exchange Interactions

Durakiewicz, T.; Butterfield, M.; Guziewicz, E.; Arko, A.; Morales, L.;
Moore, D.; Sarrao, J.; Wills, J.; Lander, G.H.
Electronic Structure of Pu and Pu Compounds from Photoelectron
Spectroscopy

Durakiewicz, T.; Butterfield, M.; Guziewicz, E.; Joyce, J.; Lander, G.H.;
Arko, A.; Wastin, F.; Rebizant, J.
Photoemission Studies of AnSb and AnTe Single Crystals (An = Np,
and Pu)

Fournier, J. M.; Baclet, N.; Dormeval, M.; Wastin, F.; Colineau, E.;
Rebizant, J.; Lander, G.H.
Magnetic Properties of PuAm Solid Solutions: Evidence for a
Curie-Weiss Behaviour and Aging Effects

Gouder, T.; Havela, L.; Wastin, F.; Rebizant, J.
5f Localization in Ultrathin Pu Layers

Jolly, L.; Baclet, N.; Fournier, J. M.; Dormeval, M.; Wastin, F.; Colineau, E.; Rebizant, J.; Lander, G.H.
Magnetic Properties of Pure and Alloyed Plutonium Metal

Lander, G.H.
NpO2, Resonant X-ray Scattering Casts New Light on an old Problem

7. Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation
October 14-16, 2002 Jeju (Korea)

Klaassen, F.C.; Schram, R.P.C.; Bakker, K.; Neeft, E.; Conrad, R.; Konings, R.J.M.
Spinel Inert Matrix Fuel Testing at the HFR Petten
Proceedings of the Conference

Serp, J.; Konings, R.J.M.; Malmbeck, R.; Rebizant, J.; Scheppler, C.; Glatz, J.P.
Electrochemical Behaviour of Plutonium Ion in LiCl-KCl Eutectic Melts
Proceedings OECD-NEA

Serrano-Purroy, D.; Birck, S.; Christiansen, B.; Glatz, J.P.; Hollas, S.; Malmbeck, R.; Römer, K.; Scheppler, C. Teixeira, E.; De Weerd, W.; Van Winckel, S.
Towards a DIAMEX Process Flow Sheet using High Active Concentrate (HAC)

8. Inert Matrix Fuel Workshop (IMF-8)
October 16-18, 2002 Tokai, Ibaraki (Japan)

Damen, P.M.G.; Wiss, T.; van Veen, A.; Fromknecht, R.
TEM Investigations and Helium Release Experiments at Fully Stabilized Zirconia
Proceedings Journal of Nuclear Materials

Damen, P.M.G.; van Veen, A.; Labohm, F.; Schut, H.
Thermal Annealing Behaviour and Defect Evolution of Helium in Fully Stabilzed Zirconia
Proceedings Journal of Nuclear Materials

Fernandez. A.; Konings, R.J.M.; Somers, J.
Design and Fabrication of CERamic-METallic (CERMET) Composite Dispersion-type Fuels and Targets
Proceedings Journal of Nuclear Materials

Klaassen, F.C.; Bakker, K.; Schram, R.P.C.; Conrad, R.; Somers, J.; Konings, R.J.M.
Post Irradiation Examination of the EFTTRA T4bis/ter Irradiation on AmOx and UO_2 in $MgAl_2O_4$ Spinel
Proceedings Journal of Nuclear Materials

Lutique, S.; Konings, R.J.M.; Rondinella, V.V.; Somers, J.; Staicu, D.; Wiss, T.
Thermal Properties and Radiation Resistance of Nd-Zirconate Pyrochlore
Proceedings Journal of Nuclear Materials

International Conference on Advances in Destructive and Non-Destructive Analysis for Environment Monitoring and Nuclear Forensics
October 21-23, 2002 Karlsruhe (Germany)

Dolgov, Y.; Bibilashvili, Y..; Schubert, A.
Development of an Electronic Archive on Non-Conventional Fuels as Integral Part of a Nuclear Forensic Laboratory
Proceedings IAEA-CN-98/1/07

Galy, J.; Magill, J.
Nuclides.net: An Integrated Environment for Computations on Radionuclides and their Radiations

Meeting of the German and Austrian Society of Hematology and Oncology (DGHO)
October 27-30, 2002 München (Germany)

Martin, S.; Kronenwett, R.; Offner, F.; Vandenbulcke, K.; Steidl. U.; Kliszewski, S.; Nikula, T.; Apostolidis, C.; Janssens, W.; Haas, R.
Alpha-Particles Gamma-Rays, Fludarabine and Prednisolone Induce Cytotoxic Effects by Different Mechanisms in B-CLL

IXth Workshop on Magnetism and Intermetallics
November 21-22, 2003 Porto (Portugal)

Conçalves, A.P.; Almeida, M.; Wastin, F.; Boulet, P.; Colieau, E.
Crystallographic and magnetic properties of $NpFe_4Al_8$

Enlarged Halden Programme Group Meeting, High Burn-up Fuel Performance,
Safety and Reliability
November 8-13, 2002 Gol (Norway)

Lassmann, K.; Györi, C.; Schubert, A.; van de Laar, J.
Interpretation of Halden Irradiations Employing the TRANS-URANUS Code

Lassmann, K.; van de Laar, J.
A New Data-Condensation Method Based on Multidimensional Minimisation

International Symposium on Advances in the Physics of f-electron Systems
November 12-14, 2002 Tokai, Ibaraki (Japan)

Boulet, P.; Colineau, E.; Wastin, F.; Griveau, J.C.; Rebizant, J.
The Binary System Pu-Si: Crystallochemistry and Magnetic Properties

Caciuffo, R.; Paixao, J.A.; Detlefs, C.; Longfield, M.J.; Santini, P.; Bernhoeft, N.; Rebizant, J.; Lander, G.H.
Multipolar Ordering in NpO_2 below 25 K
Proceedings Journal of Physics Condensed Matter

Lindbaum, A.; Heathman, S.; Le Bihan, T.; Haire, R.G.; Idiri, M.; Lander, G.H.
High-pressure Crystal Structures of Actinide Elements to 100 Gpa
Proceedings Journal of Physics Condensed Matter

Annex I

Nakamura, M.; Matskuda, T.D.; Kakurai, K.; Takeda, M.; Lander, G.H.; Kawarazaki, S.; Onuki, Y.
Magnetic Order of UGa3 Investigated by Neutron Scattering under Uniaxial Pressure
Proceedings Journal of Physics Condensed Matter

Sarrao, J.L.; Thompson, J.D.; Moreno, N.O.; Morales, L.; Wastin, F.; Rebizant, J.; Boulet, P.; Colineau, E.; Lander, G.H.
Discovery of Plutonium-Based Superconductivity
Proceedings Journal of Physics Condensed Matter

Wastin, F.; Boulet, P.; Rebizant, J.; Colineau, E.; Lander, G.H.
Advances in the Preparation and Characterization of Transuranium Elements
Proceedings Journal of Physics Condensed Matter

**Fall Meeting 2002 for the Materials Research Society
December 2-6, 2002 Boston (USA)**

Damen, P.M.G.; Lutique, S.; Fromknecht, R.; Hiernaut, J.-P.; Wiss, T.
Helium Behaviour in Pyrochlores during Thermal Annealing

**MRS 2002: Scientific Basis for Radioactive Waste Management
December 2-6, 2002 Boston (USA)**

Cobos, J.; Wiss, T.; Gouder, T.; Rondinella, V.V.
XPS and SEM Study of Unirradiated MOX Fuel Corrosion in Demineralized and in Carbonated Granitic Water

**Conference „Physics on Non-Ideal Plasmas"
December 3-4, 2002 Moscow (Russia)**

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JRC-ITU-TN-2002/14
Final report for Post-Doctoral fellowship

Berthou, V.; Magill, J.
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Final report, Visiting scientist

Galy, J.
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Final report, Visiting scientist

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Extension of the validation matrix of the TRANSURANUS code
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Final report, Visiting scientist

Heikinheimo, E.
Research activities during a stay at ITU as visiting scientist
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Hrnecek, E.
Development of analytical techniques for the identification and verification if radioactive traces from emissions, discharges and wastes during nuclear activities
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Final report Post-Doctoral fellowship

Idiri, M.
X-ray high pressure experiments on actinide dioxides and AmCm alloy
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Intermediate report for PhD fellowship

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Annex I

Longfield, M.J.
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JRC-ITU-TN-2002/49
Final report for Post-Doctoral fellowship

Lutique, Stéphanie
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A matrix for the transmutation or the disposal of actinides
JRC-ITU-TN-2002/18
Intermediate report for PhD fellowship

Luzzi, L.
Validation of the TRANSURANUS code on the basis of the Stusvik Super-Ramp PWR database files
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Intermediate report for PhD fellowship

Morgenstern, Alfred
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Final report for Post-Doctoral fellowship

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Schalge, V.
Innovative nuclear fuel concepts
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Serrano-Purroy, D.
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van Belle, P.; Daures, P.; Duinslaeger, L.; Mayer, K.; Richir, P.
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van Belle, P.; De Weerd, W.; Nicholl, A.
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Intermediate report for Post-Doctoral fellowship

Wasselin-Trupin, Virginie
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Wastin, F.
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Patents

First Application

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Patents granted

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Method and apparatus for preparing Bi-213 for human therapeutic use
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Babelot, J.F.; Hiddemann, L.; Koch, L.; Niemax K.
Telemetering of uranium and plutonium in glass
30/08/1995   19531988.5   DE (Priority)
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Dezeure, F.; Janssens, W.; Koch, L.; Van Geel, J.; Vanstraelen, D.
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Kinoshita, M. ; Matzke, Hj.
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06/02/2002   0855083 EP

Annex II

Collaborations with External Organizations

ARGENTINA
Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC), Rio de Janeiro: Safeguards (E. Palacio, C. Feu Alvim, O. Mafra Guidicini)

ARMENIA
Armenian Nuclear Regulatory Authority, Yerevan: TRANS-URANUS fuel pin code development (A. Martirossian)

AUSTRALIA
Australian Nuclear Science and Technology Organization (ANSTO): Impact of nuclear activities on environment, health and safety (H. Garnett)

AUSTRIA
International Atomic Energy Agency (IAEA), Vienna: Evaluation and automation of techniques for safeguards analyses (K. Lessmon); *Division of Safeguards Directorate:* Environmental analyses (D. Fisher); *Seibersdorf Analytical Laboratory (SAL):* Co-operative support programme (Y. Kuno)
Technical University of Vienna: High-pressure crystal structures of actinides and actinide compounds (A. Lindbaum)

BELGIUM
Belgonucléaire: Ariane project: Inventory of high burn-up UO_2 and MOX fuel (M. Lippens); Post irradiation examinations (S. Pilate, Y. Vanderborck, M. Lippens, J. Basselier); Measurements of thermal conductivity of high burn-up MOX fuel (GERONIMO) (M. Lippens); MOX identification data base of Belgonucléaire MOX production 1986-2002
SCK-CEN, Mol: Fabrication of alpha-doped UO_2 (K. Lemmens); MOX programme (P. D'Hondt, M. Verwerft)
University Hospital Ghent, Clinic for Radiotherapy and Nuclear Medicine: Alpha-immunotherapy (F. Offner)
University of Leuven: Xe-implantation (H. Pattyn)
University of Liège: NMR of Cm-compounds (J.F. Desreux)
University of Namur: *Laboratoire Interdisciplinaire de Spectroscopie Electronique:* Surface spectroscopy and electrochemistry (R. Caudano, J. Riga)
Virga Jesse Clinik, Hasselt: Alpha-immunotherapy (D. Vanstraelen)

BRASIL
Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC), Rio de Janeiro: Safeguards (E. Palacio, C. Feu Alvim, O. Mafra Guidicini)

BULGARIA
Committee on the Use of Atomic Energy for Peaceful Purposes, Sofia: TRANSURANUS fuel pin code development (D. Elenkov); Illicit trafficking, (A. Gotsev)
Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, Sofia: Fuel rod modelling and performance (D. Elenkov); Illicit trafficking, (A. Strezov); Radioactivity in the environment (A. Strezov)

CANADA
AECL *Chalk River:* Gas release, SIMFUEL production and property studies, oxygen potential of UO_2 fuel (R. Verrall); Behaviour of Rb and Cs in SIMFUEL (W. Hocking),
University of Kingston: Inert matrices (P.G. Lucuta)

CHINA
China Institute of Atomic Energy, Department of radiochemistry: Methodologies for the characterization of radiactive microparticles, with emphasis to SIMS technique (Prof. A. Li)
INET University Tsinghua, Beijing: Research tasks on nuclear chemistry (Prof. J. Xu)

CYPRUS
Ministry of Health, Nicosia: Illicit trafficking (S. Christofides)

CZECH REPUBLIC
Charles University, Prague: Actinide user laboratory; Electronic structure of AnX thin layers, high-pressure magnetic and electrical resistivity studies of intermetallics (V. Sechovsky, L. Havela)
Nuclear Research Institute Rez plc, Rez: TRANSURANUS fuel pin code development (F. Pazdera); *Central Analytical Laboratory:* Illicit trafficking (F. Sus); Pyro-processing (I. Uhlir)
State Office for Nuclear Safety, Prague: TRANSURANUS fuel pin code development (P. Krs); Illicit trafficking, (L. Bartak)

ESTONIA
Estonia Radiation Protection Centre, Tallinn: Illicit trafficking (I. Maalmann)

FINLAND
MAP Medical Technologies Oy: Alpha-immunotherapy (J. Hiltonen)
STUK - Radiation and Nuclear Safety Authority: Illicit trafficking (E. Kainulainen); Radioactive particles and environmental radioactivity (S. Salomea, R. Pollonen)
VTT Energy Aerosol Technology: Revaporisation of aerosol deposits (J. Iokiniemi, A. Auvinen)
VTT Processes: Process benchmarking (M. Auer)
VTT Industrial Systems: Process benchmarking (H. Kleemola)

FRANCE
Commissariat à l'Énergie Atomique (CEA)
CEA, Bruyères le châtel: Microparticles in safeguards and radioactivity on environment (R. Chiappini, S. Baude); Radioactive particles – toxicity (P. Fritsch)
CEA, Cadarache: Transmutation of actinides - irradiation experiments: DEC (J. Rouault, L. Brunel, F. Sudreau, S. Pillon); Inert matrices (M. Beauvy); Shared cost action 'Core loss during a severe accident (COLOSS)' (B. Adroguer, M. Barrachin); Thermophysical measurements on ECRIX material 'MgO-AmO$_2$' (T. Albiol, Y. Croixmarie); High temperature X-ray diffraction studies on actinide materials (R. Belin)

CEA, Grenoble: Neutron diffraction, magnetic studies; Transport properties and Mössbauer studies; Actinide User Laboratory (P. Burlet, N. Bernhoeft, J.P. Sanchez, D. Braithwaite and F. Bourdarot)

CEA, Marcoule: Partitioning of actinides, DIAMEX process (C. Madic); Characterization of transuranium cyano-complexes (D. Meyer); Behaviour of He in waste glasses (D. Ghaleb); Radiation damage in glasses (E. Vernaz); Partitioning of actinides (H. Boussier); Np environnement in a borosilicate glass (S. Peuget, X. Deschanels); Characterization of transuranium complexes (D. Meyer)

CEA, Saclay: Project management (P. Lederman, D. Warin, F. Carré); Post-irradiation examinations (J.I. Blanc, F. Couvreur); Radiation damage (A. Dunlop); PIXE analyses (S. Lequien)

CEA, Valduc: Electronic properties and structural investigations (EXAFS) of $Pu_{1-x}Amx$ solid solutions (N. Baclet, P. Rofidal, L.Jolly)

CNRS, Lab. de Cristallographie, Grenoble: Crystallography of phase transitions (J.C. Marmeggi)

COGEMA-La Hague: Laboratoire sur site (G. Decobert)

COGEMA-MELOX, Marcoule: Development of MOX fuels (M. Chiarelli)

Électricité de France (EdF)

Septen, Villeurbanne: Transmutation of actinides (G. Vambenepe);

Div. Recherche, Paris: RIM effect (D. Baron); Chemical and mechanical interactions fuel/cladding (thermal reactor) and determination of mechanical properties of irradiated UO2 (D. Baron)

ESRF, Grenoble: Synchrotron studies on actinides (C. Vettier, G. Grübel, P. Carra, W.G. Stirling)

FRAMATOME ANP SAS: Post-irradiation examinations (P. Blanpain, E. Van Schel, O. Gentil)

Grand Accélérateur National d'Ions Lourds, GANIL, Caen: Radiation damage in inert matrices (M. Toulemonde)

Institut de Physique Nucléaire of Orsay (Paris): Basic studies on spent UO_2 fuel (J.C. Dran); ARAMIS accelerator, radiation damage, ion implantation (L. Thomé); Physical and structural characterization of actinide phosphates (M. Genet, N. Dacheux); Studies of self-irradiation damages on the electronic properties of actinide materials (E. Simoni)

Institut Laue Langevin (ILL), Grenoble: Polarized neutron diffraction and neutron inelastic scattering (P.J. Brown, A. Hiess)

Institut de Radioprotection et de Sureté Nucléaire (IRSN), PHEBUS PF programme: Bundle post irradiation examinations and sample post-test analyses (M. Schwartz, R. Zeyen); Melting point of corium (M. Schwartz); Examination of FP deposits by mass spectrometry (M. Schwartz)

Institut National de la Santé et de la Recherche Médicale (INSERM), Nantes: Alpha-immunotherapy by Bi-213 (J. F. Chatal)

Institut National Polytechnique de Lorraine: Thermal wave properties (A. Degiovanni)

LAIN, Université de Montpellier II: Acoustic porosity measurement (J.M. Gamel, D. Laux)

OECD Nuclear Energy Agency, AEN-NEA, Paris: Database on fuel performance (E. Sartori)

SICN, Veurey-Voroize: Automated bismuth-213 generator (Mr. Huguet)

Subatech, Ecole des Mines, Nantes: Production of Ac-225 (H. Gutbrod)

Université Louis Pasteur, Strasbourg: Radiochemistry (J. Billard); Analytical chemistry (A. Hagége); Organic chemistry (J. Vicens, Z. Asfari); Material Science (M. Drillon)

Bundesamt für Seeschifffahrt und Hydrographie, Hamburg: Environmental sampling (H.Nies)

Bundeskriminalamt, Wiesbaden: Nuclear forensic science (S. Babl; S. Limmer; P. Setzer)

Bundesministerium für Umwelt, Naturschutz, und Reaktorsicherheit, Berlin: Vagabonding nuclear material (J. B. Fechner); Treatment of nuclear fuels (H. Dumpich)

Bundesministerium für Bildung und Forschung: Environmental sampling (H. Remagen)

Deutsches Krebsforschungszentrum, Biophysik und Medizinische Strahlenphysik, Heidelberg: Alpha-immunotherapy (G. Moldenhauer, S. Heeger)

Forschungszentrum Karlsruhe (FZK) *Hauptabteilung Zyklotron (HZ):* Production of Ac-225 (H-J. Gils)

Zyklotron AG Karlsruhe: Production of Ac-225 (H. Schweikert)

Institut für Nukleare Entsorgung (INE): Shared cost action: Spent fuel stability under repository conditions (T. Fanghaenel)

Institut für Kern- und Energietechnik (IKET): Be under neutron flux irradiation (Th. Schulenberg, L.V. Boccaccini, E. Rabaglino

Institut für Festkörperphysik (IFP): Radiation damage studies, RBS analyses, channeling, ion implantation (R. Fromknecht, G. Linker)

Programm Nukleare Sicherheitsforschung (NUKLEAR): Irradiation experiment CAPRA-TRABANT (J. Knebel)

Stabsabteilung Technologietransfer und Marketing: KEIM initiative (J. Wüst)

FRAMATOME ANP GmbH, Erlangen: Post-irradiation fuel rod examination (R. Manzel)

GEOMAR Institut, Abteilung für marine Umweltgeologie: Age determination of uranium and geolocation (A. Eisenhauer)

Hahn-Meitner-Institut (HMI), Berlin: High-energy ion implantation (S. Klaumünzer); Magnetic and electrical properties of actinide materials under high pressure (K. Prokes)

Heinrich Heine Universität Düsseldorf: Klinik für Hämatologie, Onkologie und klinische Immunologie: Alpha-immunotherapy (R. Haas)

Kraftwerk Obrigheim: Irradiation of thorium-plutonium fuel (D. Somer)

Leibniz-Institute of Solid State & Materials Research, Dresden: Theory of actinide systems and electronic structure of americium pnictides (P. Oppeneer)

Max-Planck Research Group 'Theory of Complex and Correlated Systems', Dresden: Theory of the Kerr-effect (P.M. Oppeneer)

Ministerium für Umwelt und Verkehr Baden Württemberg, Stuttgart: Nuclear forensic science (A. Bertzem-Berg)

Technischer Überwachungsverein Hannover/Sachsen-Anhalt e.V.: TRANSURANUS fuel pin code development (H. Märtens, D. Bour)

Technischer Überwachungsverein Norddeutschland e.V., Hamburg: TRANSURANUS fuel pin code development (J.F. Schriek)

Technischer Überwachungsverein Süddeutschland e.V., München: TRANSURANUS fuel pin code development (G. Sauer)

Technischer Überwachungsverein Südwest e .V., Mannheim: TRANSURANUS fuel pin code development (I. Brestrich)

Technische Universität Bergakademie Freiberg: Institur für Metallkunde: X-ray diffraction of thin layers and nanocrystalline materials (D. Rafaja)

Annex II

Technische Universität Braunschweig: *Institut für Halbleiterphysik und Optik:* Magnetic and optical properties of actinide-compounds (J. Schoenes, D. Kolberg)

Technische Universität München, Nuklearmedizinische Klinik und Poliklinik: Alpha-immunotherapy (R. Senekowitsch-Schmidtke)

Universität Heidelberg, Medizinische Klinik und Poliklinik V, Heidelberg: Alpha-immunotherapy (G. Egerer)

Universität Jena: Institut für Optik und Quantenelektronik: Laser induced nuclear reactions (R. Sauerbrey, H. Schwoerer)

Universität Karlsruhe: Physikalisches Institut: Single crystal growth, High Pressure resistivity of Pu superconductors (H. v. Löhneysen, C. Pfleiderer)

Universität Mainz, Institut für Kernchemie: Analytical techniques for particle characterization (J.V. Kratz, N. Trautmann)

Universität Marburg: Alpha-immunotherapy (T.M. Behr)

Universität München-Garching: High-energy ion implantation (W. Assmann)

HUNGARY

Atomic Energy Research Institute (AEKI), Budapest: TRANSURANUS fuel pin code development (C. Györi); Environmental radioactive microparticles (S. Török)

Hungarian Academy of Sciences, Institute of Isotopes, Budapest: Forensic nuclear analyses for safeguards (L. Lakosy)

Hungarian Atomic Energy Authority, Budapest: TRANSURANUS fuel pin code development (J. Zsoldos); Illicit trafficking (I. Czoch, J. Safar)

ITALY

ENEA; Bologna: Partitioning and transmutation, accelerator driven systems (G. Gherardi); Thermal conductivity of inert matrix fuels (F. Vettraino); TRANSURANUS fuel pin code development (F. Vettraino)

Istituto Superiore di Sanità (Rome): Radionuclides in foodstuff and water (S. Canoli; S. Risica; M. Gandolfo)

Istituto Fisiologia Clinica (Pisa): SIMS and GDMS for BNCT (P. Salvadori)

University of Ancona: Neutron and bulk magnetization studies (R. Caciuffo)

University of Aquila, Physics Department: Theory of optical properties (P. Monachesi)

University of Bologna, Ravenna, Environmental Science: Measurements of environmental radioactivity (Prof. Bruzzi)

University of Pisa, Chemistry Department: Instrumental analytical techniques for trace analyses (R. Fuoco)

University of Parma, Physics Department: Theory of oxides (G. Amoretti); Physical and structural characterization of actinide phosphates (A. Blaise, G. Amoretti)

JAPAN

Central Research Institute of Electricity Producing Industries (CRIEPI), Tokyo: Pyro-reprocessing studies (T. Inoue, M. Kinoshita); Spent fuel characterization for interim dry storage (T. Matsumura); Rim effect studies (K. Kinoshita); Measurements of thermal conductivity of irradiated fuel up to high burn-up (M. Kurata)

JAERI, Tokai Mura: Radiation damage in oxide fuels (K. Fukuda, T. Ogawa); Thermodynamic studies on actinide compounds (Y. Arai); Neutrons, NMR and theory (K. Kakurai, R. Waldstedt, N. Metoki); Safeguards (T. Adachi)

Mitsubishi Materials Corporation, Nuclear Fuel Cycle Technology Center: Liquid-liquid extraction (H. Yano)

Nuclear Material Control Center (NMCC), Tokai: Safeguards (T. Tsujino)

Tohoku University, Sendai, Japan: Reduction of Np metal, solid states physics (Y. Shiokawa); Studies of heavy fermion uranium compounds (N. Sato, T. Komatsubara, Y. Endoh); Preparation of actinide metals, Solid state physics and chemistry of actinide materials (Y. Shiokawa, D. Aoki, Y. Homma)

KAZAKHSTAN

Institute of Nuclear Physics Kazakhstan: Methodologies for characterization of environmental particles (S. Lukashenko)

KOREA

Korean Atomic Energy Research Institute (KAERI): PIE of high burn-up fuels; Thermal conductivity of MOX fuels (H.S. Park, W.-H. Kim)

LATVIA

Ministry of Environmental Protection and Regional Department, Riga: Illicit trafficking (A. Salmins)

LITHUANIA

Lithuanian Nuclear Power Safety Inspectorate (VATESI), Vilnius: Illicit trafficking (S. Kurselis)

LUXEMBOURG

EURATOM Safeguards Office (ESO), Luxembourg: Nuclear forensic science (G. Herbillon; F. Maclean)

International Technical Working Group (ITWG): Nuclear forensic science (G. Herbillon, G. Dudder)

MALTA

Customs, Valetta: Illicit trafficking (C. Magri)

MONACO

International Atomic Energy Agency (IAEA), Monaco: Principality of Monaco: Radioactivity in Marine Environment (P. Povinec)

THE NETHERLANDS

EUROPOL, The Hague: Nuclear forensic science (F. Zablot)

Interfaculty Reactor Institute, Delft: He release from inert matrices (A. van Veen)

NRG, Petten: Transmutation of fission products (H.U. Staal, R. Schram)

University of Utrecht: Low temperature heat capacity measurements (C. van Miltenburg, A. van Genderen)

NORWAY

OECD Halden Reactor Project: High burn-up RIM effect irradiation (E. Kolstad); TRANSURANUS fuel pin code development (W. Wieseneck)

University of Oslo: Co-ordinated research project of IAEA on particles (B. Salbu)

POLAND

Institute for Low Temperature and Structure Research, PAS-Wroclaw, Warsaw: Bulk properties and neutron scattering (R. Troc, W. Suski, D. Kaczorowski); High pressure resistivity (VH Tran)
National Atomic Energy Agency, Warsaw: Illicit trafficking (J. Niewodniczanski)

PORTUGAL

Departemento de Fisica, Universidade de Coimbra, Coimbra: Neutron and X-ray studies, Bulk properties (J.A. Paixão)
Instituto Tecnológico e Nuclear (ITN), Sacavem: Physical chemistry of actinides (A. Pires de Matos, M. Almeida, J.C. Warenborgh); Single crystal growth and physical bulk properties, Actinide user laboratory (M. Almeida, A. Gonçalves)

ROMANIA

Institute for Nuclear Research, Nuclear Fuel Performance Analysis, Pitetsi: TRANSURANUS fuel pin code development (G. Horhoianu)
National Commission for Nuclear Activities Control, Bucharest: Illicit trafficking (V. Grama)

RUSSIA

Academy of Sciences, IVTAN, Moscow: Equation of uranium dioxide (I. Iosiliewski)
Academy of Science, Vernadsky Institute, Moscow: Methodologies for characterization of environmental radioactive samples and actinide speciation (B.F. Myasoedov)
All Russia Research Institute of Inorganic Materials (A.A. Bochvar Institute), Moscow: Setting up of three laboratories for safeguards, metrology, nuclear forensics (A. Petrov)
Flerov Laboratory, Dubna: Radiation damage in ceramics (V.A. Skuratov)
GOSATOMNADZOR, Moscow: Nuclear Safeguards (A. Dmitriev)
Heat & Power, JSI, Moscow: Calculations of thermophysical high temperature processes (K. Davidov)
High Energy Density Institute, Moscow: shock-wave theory (V. Fortov)
Institute of Chemical Physics, Chernogolowka: Code calculations of equation of state of UO2 (V. Gryaznov)
MINATOM, Moscow: Nuclear safeguards (V. Limonaev)
RIAR, Dimitrovgrad: Partitioning and transmutation of minor actinides (M. Mayoshin)

SLOVAK REPUBLIC

Nuclear Power Plant Research Institute, Trnava: TRANSURANUS fuel pin code development (M. Cvan)
Nuclear Regulatory Authority of the Slovak Republic, Bratislava: Illicit trafficking (J. Vaclav)

SLOVENIA

Slovenian Nuclear Safety Administration: Illicit trafficking (M. Pecnik)

SOUTH AFRICA

University of Witwatersrand, Johannesburg: Transport measurements (P. du Plessis)

SPAIN

ENRESA: Waste management, leaching tests (J.L. Gonzalez, A. Martinez-Esparza)
Centro de Investigaciones Energéticas, Medioambientales y Tecnologías (CIEMAT): Waste management, leaching tests (J.L. Diaz)
QUANTISCI: Waste management, leaching tests (J. Bruno)
UPC, University Polytechnic of Catalunya: Waste management, leaching tests (Prof. J. de Pablo)

SWEDEN

Chalmers University, Göteborg: Partitioning of minor actinides (J.O. Liljenzin, J. Albinsson)
Royal Institute of Technology, Stockholm: Solid state theory of actinides (B. Johansson)
SKB: Spent fuel disposal (K. Spahiu)
University of Uppsala: Solid state theory of actinides (B. Johansson, O. Eriksson)

SWITZERLAND

ETH, Zürich: Single crystal growth, magnetic, optical and transport properties, preparation of U and Th compounds (O. Vogt, P. Wachter, K. Mattenberger)
Katonsspital Basel, Institut für Nuklearmedizin: Alpha-immunotherapy (H.R. Mäcke)
Paul Scherrer Institut, Villigen und Würenlingen: Thermal conductivity of inert matrices; Radiotoxicity Calculations (C. Degueldre); TRANSURANUS fuel pin code development (C. Hellwig); Post-irradiation structural investigations by electron microscopy, Phébus PF FPT bundle post irradiation examination (D. Gavillet)

TURKEY

Turkish Atomic Energy Authority, Ankara: Institute for Nuclear Research, Kiev: Illicit trafficking (F. A. Yücel)

UKRAINE

Institute for Nuclear Research, Kiev: Illicit trafficking (V. Tryshyn)
Ministry for environmental protection and nuclear safety of Ukraine: Illicit trafficking, (A. Smyshliaiev)
State Scientific and Technical Centre for Nuclear and Radiation Safety, Kiev: TRANSURANUS fuel pin code development (M. Yeremenko)
University of Odessa: Liquid state models, Pyrometallurgy of actinides (E. Yakub)

UNITED KINGDOM

BNFL, Sellafield: On-site laboratory (R. Strong, J. Reed); PIE examination of MOX spent fuel (S. Fisher); Melting point of irradiated MOX (S. Fisher); Fuel fabrication (C. Brown)
NNC, Winfrith: Neutron sources for waste assay systems (S. Daish)
Rutherford Appleton Laboratory, Chilton: Neutron and synchrotron studies (N. Bull, S. Langridge); Laser induced nuclear reactions (P. Norreys)
University of Bristol, Interface Analysis Centre: Surface corrosion (G. Allen)
University of Glasgow, Dept. of Physics and Astronomy / Rutherford Appleton Laboratory: Laser induced nuclear reactions (P. McKenna)

Annex II

University of Liverpool: X-ray and neutron scattering (W.G. Stirling)
University of London: Magnetic and transport studies, Actinide user laboratory (K. McEwen, S. Zochowski)
University of Oxford: Preparation of multilayers (M. Wells, R. Ward); UO_2 surface properties (A. Castell, C. Muggelberg)
University of Strathclyde: Laser induced nuclear reactions (K.W.D. Ledingham)
University of Warwick: Theory of liquid /solid transitions (M. Lewis)

UNITED STATES OF AMERICA

Argonne National Laboratory, IL: Neutron scattering and X-ray absorption spectroscopy (L. Soderholm), Transmutation experiments (S. Hayes); Pyro-processing of nuclear fuels (J. Laidler)
Battelle Pacific Northwest Laboratories, Richland, WA: Irradiation damage studies (W. Weber)
Brookhaven National Laboratory, NY: High-resolution and magnetic X-ray scattering (D. Gibbs)
Colorado State University, Fort Collins, CO: Studies of oxides (S. Kern)
Electric Power Institute (EPRI): MOX fuel studies (S. Yagnik)

Lawrence Berkeley National Laboratory, CA: Synchrotron studies of actinide surfaces and thin films (D. Shuh)
Lawrence Livermore National Laboratory (LLNL), CA: Forensic nuclear analyses (G. Dudder, S. Niemeyer)
Los Alamos National Laboratory, NM: Materials preparation, photoemission and theory (A.J. Arko, J. Joyce, A. Lawson, J. Wills); Radiation damage in ceramics (K. Sickafus); Transmuter fuel fabrication (K. Chidester); Magnetic and electronic properties (JL Sarrao, J.D. Thompson); EXAFS on actinide compounds and alloys (S. Conradson)
Memorial Sloan Kettering Cancer Center, New York, NY: Alpha-immunotherapy (D.A. Scheinberg)
National Institute of Health, Bethesda, MD: Alpha-immunotherapy (M.W. Brechbiel)
Oak Ridge National Laboratory, TN: Material preparation, high-pressure X-ray and optical studies (R.G. Haire, J.R. Peterson); Radiation damage in ceramics (S.J. Zinkle)
Stanford (SSRL): EXAFS on actinide compounds and alloys (S. Conradson)
University of Florida: Low temperature specific heat measurements of actinide compounds and bulk properties (G. Stewart)
University of Michigan, Ann Arbor, MI: High resolution TEM, radiation damage (R. Ewing, L.M. Wang)
University of West-Virginia, Morgantown, WV: Actinide theory (B.R. Cooper)

List of Contributors to the various Chapters

Scientific Objectives

M. Leroy

Scientific Highlights

(H1) P. Boulet, E. Colineau, G.H. Lander, J. Rebizant, F. Wastin (H2) J. Galy, J. Magill; (H3) J.-P Glatz, R. Malmbeck, J. Serp; (H4) J. Cobos Sabate**, V.V. Rondinella; (H5) C. Ronchi; T. Wiss (H6) P. Daures; K. Mayer

Review Article

K. Mayer; H. Ottmar; P. van Belle, S. Abousahl, M. Betti, G. Tamborini, M. Wallenius, A. Morgenstern

Basics

J.-F. Babelot, J. Richter, M. Rödder

Projects

1. Alpha-Immunotherapy (K. Lützenkirchen)
P. Jehenson, C. Apostolidis, S. Martin**; T. Nikula, A. Ouadi

2. Basic Actinide Research (G.H. Lander)
M.S.S. Brooks, P. Boulet, M. Colarieti Tosti*, E. Colineau, M. Eckle*, R. Eloirdi*, T. Gouder, J.C. Griveau*, S. Heathman, J.-P. Hiernaut, M. Idiri*, P. Javorsky*, D. Manara*, J. Rebizant, C. Ronchi, M. Sheindlin, G. Stewart**, F. Wastin; E. Yakub**

3. Safety of Nuclear Fuels (J.-P. Glatz)
D. Bottomley, Bremier, S.*, S. Heathman, D. Knoche*, K. Lassmann , M.C. Pujol*, A. Schubert, J. Somers , J. Spino, E.H. Toscano, C.T. Walker

4. Partitioning and Transmutation (D. Haas)
V. Berthou, B. Christiansen , P. Damen*, A. Fernandez, R.J.M. Konings, S. Lutique*, R. Malmbeck, M. Ougier, V.V. Rondinella, J. Serp*, J. Somers, C. Thiriet, T.A.G. Wiss

5. Spent Fuel Characterization in View of Long-Term Storage (C. Ronchi)
M. Amme, P. Carbol, J. Cobos Sabate**, J.-P. Hiernaut, T. Gouder, V.V. Rondinella, D. Solatie*, D. Wegen, T. Wiss

6. Measurement of Radioactivity in the Environment (K. Lützenkirchen)
L. Aldave de las Heras, M. Betti, E. Hrnecek*, J. Jernström*; L. Perna*,

7. Safeguards Research and Development (K. Lützenkirchen)
S. Abousahl, M. Betti, O. Cromboom, P. Daures, L. Duinslaeger, K. Mayer, A. Morgenstern, H. Ottmar, P. Richir, A. Schubert, G. Tamborini, M. Wallenius

*Research Fellows; **Visiting Scientist

Annex IV

Glossary, Acronyms and Abbreviations

ABACC: Agência Brasileiro-Argentina de Contabilização e Controlo dos Materiais Nucleares
Argentinian-Brazilian Agency for Accounting and Control of Nuclear Material
ADC: Analogue-to-Digital Converter
AEA: Atomic Energy Authority (United Kingdom)
AECL: Atomic Energy of Canada Ltd., Chalk River, ON (Canada)
AEKI-KFKI: Hungarian Atomic Energy Research Institute, Budapest (Hungary)
AF: antiferromagnetic
AGR: advanced gas-cooled reactor
AML: Acute myeloid leukaemia
ANM: alternative nuclear materials
ANSTO: Australian Nuclear Science & Technology Organization
AWE: Atomic Weapons Establishment, Aldermaston (United Kingdom)

BCS: Bardeen, Cooper and Schrieffer theory
BNFL: British Nuclear Fuel plc, Springfield (United Kingdom)
BWR: boiling water reactor

CADRA: consommation accrue des déchets dans les réacteurs rapides
CAMIX: composé d'américium dans Phénix
CANDU : Canadian Deuterium-Uranium reactor, using heavy water as the coolant and moderator
CAPRA: consommation accrue de plutonium dans les (réacteurs) rapides
CE: cation exchange
CE: capillary electrophoresis
CEA: Commissariat à l'Énergie Atomique (France)
CEF: crystal electric field
CERMET: ceramic metal
CF: concentration factor
CIEMAT: Centro de Investigaciones Energéticas, Medioambientales y Technológicas, Madrid (Spain)
CIS (countries): Commonwealth of Independent States
CIT: Corium interaction thermochemistry
COCHIX: conception optimisée vis-à-vis des microstructures dans Phénix
COGEMA: Compagnie générale des matières nucléaires, Vélizy (France)
COLOSS: Core loss during a severe accident
COMPUCEA: combined product-uranium concentration and enrichment assay

CRIEPI: Central Research Institute of the Electric Power Industry, Tokyo (Japan)
CRP: Co-ordinated Research Programme

DAC: Diamond anvil cell
DESY: Deutsches Elektronen-Synchrotron, Hamburg (Germany)
DF: decontamination factor
DG: Directorate General
DG AIDCO: Directorate General "Europe Aid Co-operation Office" of the Commission of the European Communities, Brussels (Belgium)
DG ENV: Directorate General "Environment" of the Commission of the European Communities, Brussels (Belgium)
DG RTD: Directorate General "Research" of the Commission of the European Communities (Research and Technological Development –RTD), Brussels (Belgium)
DG TREN: Directorate General "Energy and Transport" of the Commission of the European Communities, Brussels (Belgium)
DIAMEX: diamide extraction process
DKFZ: Deutsches Krebsforschungszentrum, Heidelberg (Germany)
DM: demineralized

EC: European Commission
EdF: Électricité de France
EDX: energy-dispersive X-ray spectroscopy
EFQM: European Foundation for Quality Management
EFTTRA: Experimental Feasibility for Targets and Transmutation
EMPA: electron micro-probe analysis (also EPMA)
EPMA: electron probe microanalysis (also EMPA)
EOS: Equation of state
EQRAIN: évaluation de la qualité du résultat d'analyse dans l'industrie nucléaire
ESARDA: European safeguard research and development association
ESO: Euratom Safeguards Office, Luxembourg
ESRF: European Synchrotron Radiation Facility, Grenoble (France)
EU: European Union
EURATOM: European Atomic Energy Community
EXTRA: extension of TRANSURANUS code applicability with Nb containing cladding models

FBR: Fast Breeder Reactor
fco: face centred orthorhombic
FERONIA: fuel rod modelling and performance project
FIAP: fraction of inventory in the aqueous phase
FISPACT: computer code for burn-up calculations by AEA-technology
FMCT: fissile material cut-off treaty
FP: fission product
FP: Framework Programme
FPT: fission product test
FRAMATOME ANP GmbH: FRAMATOME Advanced Nuclear Power GmbH
FSV: flow sheet verification
FUMEX: fuel modelling at extended burn-ups

GANIL: Grand Accélérateur National d'Ions Lourds, Caen (France)
GDMS: glow discharge mass spectrometry (spectrometer)
GW: natural ground water
GWd/tM: Gigawatt-day per (metric) ton metal

HAC: high active concentrated raffinate
HAR: high active raffinate
HASYLAB: Hamburger Synchrotronstrahlungslabor (Germany)
HAW: highly active waste
HBRP: high burn-up RIM project
HEDTA: hydroxyethyl ethylenc diamine triacetic acid
HEHA: 1,4,7,10,13,16-hexa-(2-carboxymethyl)-1,4,7,10,13,16-hexaazacyclododecane
HEU: highly enriched uranium
HFR: High flux reactor, Petten (Netherlands)
HKED: hybrid K-edge densitometer
HLLW: high-level liquid waste
HLNCC: High Level Neutron Coincidence Counting
HPTA: high-performance trace analysis
HRGS: high-resolution gamma spectrometry
HR-ICP-MS: high-resolution inductively coupled plasma mass spectrometry
HTR: high temperature reactor

IABAT: Impact of Accelerator-Based Technologies on Nuclear Fission Safety
IAEA: International Atomic Energy Agency, Vienna (Austria)
IC-ICP-MS: ion chromatography inductively coupled plasma mass spectrometry
IDMS: isotope dilution mass spectrometry
IFPE: International Fuel Performance Experiment
IHP: Improving Human Potential Programme
ILL: Institut Laue Langerin, Grenoble (France)
INE: Institut für Nukleare Entsorgungstechnik, FZK (Germany)

INRNE: Institute for Nuclear Research and Nuclear Energy, Sofia, Bulgaria
INRTAS: International Association for the promotion of Co-operation with Scientists form the Independent States of the former Soviet Union
IRMM: Institute for Reference Materials and Measurements, Geel (Belgium)
IRSN: Institut de Radioprotection et Sûreté Nucléaire, Cadarache (France)
ISIS RAL: spallation source, Rutherford-Appleton Lab., Rutherford (UK)
ISO: International Organization for Standardisation
ITU: Institute for Transuranium Elements, Karlsruhe (Germany)
ITWG: International Technical Working Group on nuclear smuggling

JAERI: Japan Atomic Energy Research Institute (Japan)
JRC: Joint Research Centre, European Commission
JT: Jahn-Teller

KAERI: Korea Atomic Energy Research Institute, (Republic of Korea)
KCMS: Knudsen Cell Mass Spectrometer
KEDG: K-edge densitometer
KÜFA: Kühlfinger apparatus
KWO: Kraftwerk Obrigheim (Germany)

LANL: Los Alamos National Laboratory, Los Alamos (NM), (USA)
LCC: liquid Cd cathode
LET: linear energy transfer
LEU: low enrichment uranium
LMA: MINATOM, Moscow (Russia)
LOCA: loss of coolant accident
LSC: liquid scintillation counting
LSD: large size dry spikes
LSS: Laboratoire Sur Site, La Hague (France)
LWR: light water reactor

MA: minor actinides (Am, Cm, Np)
MAGNOX: Magnesium non-oxidizing (fuel sheath)
MARINA: The Radiological Exposure of the European Community from Radioactivity
         in the North European Waters
MCNP: Monte Carlo N-particle transport code system
MDF: MOX Demonstration Facility
MGA: multi-group-analysis
MICROMOX: the influence of microstructure of MOX fuel on Hs irradiation behaviour under transient conditions
MIMAS: Micronized master blend
MOX: mixed oxide fuel of uranium and plutonium
m.s.a.: minimum-solid-area
MWd/kgU: Megawatt day per kg of uranium

Annex IV

NBL: New Brunswick Laboratory
NCC: neutron coincidence counting
NDA: non-destructive assay (analysis)
NEA: Nuclear Energy Agency, OECD, Paris (France)
NHL: Non-Hodgkin's lymphoma
NIS: new independent states
NIST: National Institute of Standards and Technology, Gaithersburg (USA)
NMCC: Nuclear Material Control Center
NMR: nuclear magnetic resonance
NWAL: network of analytical laboratories

OECD: Organization for Economic Co-operation and Development, Paris (France)
OM: optical microscopy
OMICO: oxide fuels – microstructure and composition variations
ORNL: Oak Ridge National Laboratory, Oak Ridge, TN (USA)
OSL: On-Site Laboratory, Sellafield (United Kingdom)
OSPAR: joint meeting of the Oslo and Paris Commissions
OSPAR Convention: convention for the protection of the marine environment of the North-East Atlantic
OTEC: 1,4,7,10,13,16,19,22-octaazacyclotetracosane-1,4,7,10,13,16,19,22-octaacetic acid

PARTNEW: Partitioning: New solvent extraction processes for minor actinides (5th Framework programme)
PCI: pellet clad interaction
PECO: Pays d'Europe Centrale et Orientale (Pays de l'Europe centrale et de l'Est)
PHARE: Pologne-Hongrie: Aide à la Reconstruction Économique
PIE: post-irradiation examination
PIXE: proton-induced X-ray emission
PNCC: Passive neutron-coincidence counting
POI: particle of interest
PSI: Paul Scherrer Institut, Villigen (Switzerland)
P&T: partitioning and transmutation
PUREX: plutonium and uranium recovery by extraction
PWR: pressurized water reactor

QA: quality assurance
QCM: quartz crystal micro-balance
QM: quality management

RAL: Rutherford Appleton Laboratory
RBS: Rutherford Backscattering Spectroscopy
R&D: research and development
RELAP: code name
RER: IAEA Regional Technical Co-operation Project
RIA: reactivity initiated accident
RRP: Rokkasho Reprocessing Plant (Japan)

SAL: Safeguards Analytical Laboratory
SBR: short binderless route
SCA: shared cost action
SCK/CEN: Studiecentrum voor Kernenergie - Centre d'Étude de l'Énergie Nucléaire, Mol (Belgium)
SEM: scanning electron microscopy
SIMS: secondary ion mass spectrometry
SMART: study of mixed actinides recycling and transmutation
SME: small and medium-sized enterprises
SMP: Sellafield MOX Plant
SQUID: superconducting quantum interference device

TACIS: Technical Assistance to the Commonwealth of Independent States
TD: theoretical density
TEM: transmission electron microscopy
TEVA: tetravalent actinide resin
THORP: Thermal oxide reprocessing plant, Sellafield (U.K.)
TIMS: thermal ionization mass spectrometry
TIP: Temperature Independent Paramagnet
TOF: Time-of-flight
TRANSURANUS: fuel behaviour code (ITU), Karlsruhe (Germany)
TUAR: Institute for Transuranium Elements annual report, Karlsruhe (Germany)
TÜV: Technischer Überwachungsverein
TWG: European Technical Working Group

UCD: unité de conditionnement des déchets
URP: unité de retraitement du procédé
USSR: Union of Soviet Socialist Republics
UTEVA: uranium tetravalent actinide resin

VNIINM: All-Russia Institute for Inorganic Materials, Moscow
VTT: Technical Research Centre of Finland VTT Energy (Finland)
VUJE: Nuclear Power Research Institute, Trnava (Slovakia)
VVER: (also WWER) Voda-Vodyanoi Energetichesky Reaktor pressurized water reactor (PWR) built by Russia

**WWER**: (also VVER) pressurized water reactor (PWR) built by Russia

XANES: X-ray absorption near-edge structure
XPS: X-ray induced photoelectron emission spectroscopy
XRD: X-ray diffraction
XRF: X-ray fluorescence analysis

YAG: yttrium aluminium garnet
YC: yellow cake
YSZ: yttrium stabilised zirconia

Annex V

Previous Progress Reports of the Institute for Transuranium Elements

TUSR	Period	COM Nr.	EUR-Nr.	TUSR	Period	COM Nr.	EUR-Nr.
1	Jan - Jun 1966	1580	-	**86**	Jan - Dec 1986	4302	12233 EN
2	Jul - Dec 1966	1522	-	**87**	Jan - Dec 1987		11783 EN
3	Jan - Jun 1967	1745	-	**88**	Jan - Dec 1988		12385 EN
4	Jul - Dec 1967	2007	-	**89**	Jan - Dec 1989		12849 EN
5	Jan - Jun 1968	2172	-	**90**	Jan - Dec 1990		13815 EN
6	Jul - Dec 1968	2300	-	**91**	Jan - Dec 1991		14493 EN
7	Jan - Jun 1969	2434	-	**92**	Jan - Dec 1992		15154 EN
8	Jul - Dec 1969	2576	-	**93**	Jan - Dec 1993		15741 EN
9	Jan - Jun 1970	2664	-	**94**	Jan - Dec 1994		16152 EN
10	Jul - Dec 1970	2750	-	**95**	Jan - Dec 1995		16368 EN
11	Jan - Jun 1971	2833	-	**96**	Jan - Dec 1996		17269 EN
12	Jul - Dec 1971	2874	-	**97**	Jan - Dec 1997		17746 EN
13	Jan - Jun 1972	2939	-	**98**	Jan - Dec 1998		18715 EN
14	Jul - Dec 1972	3014	-	**99**	Jan - Dec 1999		19054 EN
15	Jan - Jun 1973	3050	-	**00**	Jan - Dec 2000		19812 EN
16	Jul - Dec 1973	3115	-	**01**	Jan - Dec 2001		20252 EN
17	Jan - Jun 1974	3161	-	**02**	Jan - Dec 2002		20658 EN
18	Jul - Dec 1974	3204	-				
19	Jan - Jun 1975	3241	-				
20	Jul - Dec 1975	3289	-				
21	Jan - Jun 1976	3358	-				
22	Jul - Dec 1976	3384	-				
23	Jan - Jun 1977	3438	6475 EN				
24	Jul - Dec 1977	3484	7209 EN				
25	Jan - Jun 1978	3526	7459 EN				
26	Jul - Dec 1978	3582	7227 EN				
27	Jan - Jun 1979	3657	7483 EN				
28	Jul - Dec 1979	3714	7509 EN				
29	Jan - Jun 1980	3822	7857 EN				
30	Jul - Dec 1980	3846	8230 EN				
31	Jan - Jun 1981	3898	8447 EN				
32	Jul - Dec 1981	3927	8777 EN				
33	Jan - Jun 1982	3990	9581 EN				
34	Jul - Dec 1982	4048	10251 EN				
35	Jan - Jun 1983	4094	10266 EN				
36	Jul - Dec 1983	4117	10454 EN				
37	Jan - Jun 1984	4150	10470 EN				
38	Jul - Dec 1984	4165	11013 EN				
39	Jan - Jun 1985	4201	11835 EN				
40	Jul - Dec 1985	4263	11836 EN				

Previous Programme Progress Reports were confidential for a period of two years. Between 1977 and 1987 they had been made freely accessible after that period as EUR-Reports (on microfiches) and since 1988 they have been issued as regular EUR-Reports.
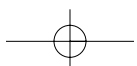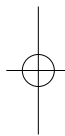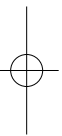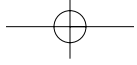
Abstract

The activity report 2002 of the Institute for Transuranium Elements (ITU) of the Joint Research Centre (JRC) describes the progress made during the fourth and last year of the 5th European Community Framework Programme (FP5).
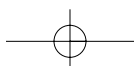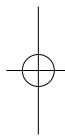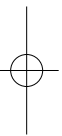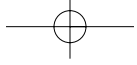
In the first part of the report a summary of the scientific objectives is given. Highlight articles on important progress made during 2002 are presented on:

● Discovery of Superconductivity in Plutonium-Based Compounds;
● Laser Induced Nuclear Reactions in Actinides;
● First Pyrochemical Separation of Minor Actinides from Lanthanide Fission Products by Electrolysis;
● Radiolysis Effects at Low Alpha-Radiation Rates;
● Effects of Extreme Self-Damage in Curium Oxide;
● Combating Illicit Trafficking of Nuclear and Radioactive Materials;

followed by a review article on 'Recent Developments in Analytical Methods of Safeguarding Nuclear Material'.

In the second part of the report, a more in-depth technical description of progress made is given. Topics covered focus on: Targeted Alpha-Radionuclide Therapy, Basic Actinide Research, Safety of Nuclear Fuel, Partitioning and Transmutation, Spent Fuel Characterization in View of Long-Term Storage, Measurement of Radioactivity in the Environment and on the work of the Safeguards Research and Development.

A detailed list of publications, patents and collaborations is given in the annex.
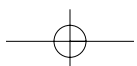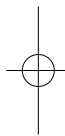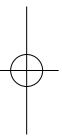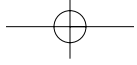
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