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# INSTITUTE FOR TRANSURANIUM ELEMENTS



## ACTIVITY REPORT 2 0 0 1

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JOINT RESEARCH CENTRE  
Report EUR 20252 EN

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.



### European Commission

Joint Research Centre

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# Institute for Transuranium Elements

## Activity Report 2001



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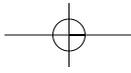
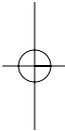
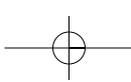
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## Foreword

In the following pages, an overview of the work carried out at the Institute in 2001 is presented.

The Institute's main aim continues to be research of the highest quality, covering both institutional and competitive activities. One clear measure of this is the quality and number of publications in refereed journals. Another is the high level of competitive and support activities to our different customers.

Our basic research achievements, summarised in the scientific "Highlights" and described in detail in the second part of the report, clearly demonstrate the attractiveness and challenges of nuclear science and the potential for new discoveries and innovative developments. Following the initiative of Commissioner Philippe Busquin for a European Research Area, ITU is moving at "full steam ahead" to define with partners European networks of excellence in basic nuclear science.

Interest in nuclear science was underlined by the summer school on "Actinide Science and Applications" held at ITU. The meeting was attended by over 70 young scientists and hopefully will become a regular event in the Institute's calendar. In addition, ITU launched an "Actinide Multi-User Laboratory" to provide the infrastructure necessary for the training and education in the handling of actinides and their compounds.

Consistent with previous years, a review article – this time on the TRANSURANUS code development – on a particularly timely or topical issue, is included. The present article describes the strong collaboration with research institutions, licensing authorities and industry in this multi-disciplinary field of modelling of fuel pin behaviour in nuclear reactors.

The issue of nuclear waste continues to dominate public opinion regarding the acceptability of nuclear energy. In this regard, the visit of Commissioner Loyola de Palacio to the Institute for discussions on this subject underlined the Commission's increased interest in Partitioning and Transmutation activities.

ITU continues to investigate and develop spin-off activities outside the nuclear fuel cycle. Identification and production of alpha-emitting radionuclides for cancer therapy is one such activity. Through international collaboration, clinical phase trials on patients have been initiated with this innovative cancer therapy.

Another activity – environmental sampling and nuclear forensics – continues to gain importance. Due to an increased interest in combating nuclear terrorism, international organisations such as the IAEA and Europol have shown interest in using the Institute's experience to develop new analytical techniques for the identification of nuclear material.

Finally, I would like to thank the Institute staff for another successful year at ITU!



**Roland Schenkel**  
Director

## Scientific Objectives

### Scientific Objectives

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 2001 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 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. Separating long-lived

nuclides from the waste, recycling them with appropriate fuels in reactors for transmuting or "burning" them is therefore considered an important waste management option.

Under its partitioning and transmutation programme, and in close co-operation with its European partners, ITU tests and evaluates processes that permit an efficient separation (partitioning) of radiotoxic elements from spent fuel with a minimum of losses. Advanced aqueous and dry reprocessing techniques are both investigated. Pyrometallurgy offers some important advantages in a transmutation cycle and ITU is developing a laboratory pilot facility with international collaboration. ITU aims also at optimising fuel fabrication technology for novel, minor-actinide containing fuels for the transmutation or "incineration" of long-lived actinides and fission products. The Institute is, therefore, testing existing and new fabrication techniques for fuels and targets used in irradiation experiments.

#### Safety of nuclear fuel

The extended use of nuclear fuel in existing reactors is a major objective of plant operators. It contributes to a better use of energy resources, and an overall reduction of nuclear waste and transport requirements.

With respect to the safety of the nuclear fuel, at very high burn-up, under normal and under transient conditions, ITU concentrates on mechanical and chemical interactions at the fuel / cladding interface and on enhanced fission gas release and related modifications of the microstructure of the fuel. Modelling is an integral part of safety studies. The TRANSURANUS fuel performance code is extended with

new data and training of users will continue, including 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 the behaviour 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. Together with European partners, ITU is developing advanced fuel fabrication techniques based on the sol-gel process and carbo-thermal reduction.

#### 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 worldwide.

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, perfecting them to perform forensic analysis and identify seized, illicit material. 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.

## Scientific Objectives

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 to the European Union. The ITU nuclear materials data-bank 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), in soils and in sludges to provide the scientific community, dealing with radioactivity in the environment with the necessary assessed analytical protocols. This research is carried out in collaboration with institutional research centres and universities from Member 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. A good knowledge of fundamental physical, chemical and materials science data on actinides and actinide-containing compounds, i.e. nuclear fuels and nuclear waste, is the basis for addressing nuclear issues at ITU.

ITU scientists aim at developing an understanding of these properties, including the electronic structure of actinides and actinide compounds. Activities range from preparing and purifying the elements to studying single crystals and thin films by sophisticated physical techniques, some of which involve the use of intense synchrotron beams, neutron or muon beams. Theoretical research on the electronic properties of the actinides backs up experiments and suggests new avenues for investigation. With new fuel materials for advanced waste management options under discussion, materials science data are urgently required. The supply of data such as phase diagrams, thermal properties, pressure behaviour and irradiation behaviour is a genuine task for basic actinide research. Findings of investigations can also help to answer questions arising in connection with the management of highly active waste.

In the frame of these activities ITU hosts scientists for well-defined experiments. With the creation of the Actinide User Laboratory, its attractiveness has grown. Particular attention is given to training the next generation of scientists, especially those from Member States, which lack

of nuclear installations suitable for training.

### Health and nuclear medicine

As a spin-off 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 radioelements. 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 under alpha-immunotherapy).

## Highlights 2001

### The strange magnetism of NpP

When the  $5f$  electrons of the actinides are strongly interacting, and the temperature is lowered, the  $5f$  electrons often form an ordered *magnetic* ground state. The study of such configurations allows us to understand the interactions between various electron states in the solid, as well as interactions with the lattice. For example, the magnetic anisotropy of actinide compounds is frequently exceedingly high compared to other materials and the reason for this is still controversial.

The actinide monopnictides exhibit a rich variety of magnetic structures in the ordered phase with relatively high magnetic ordering temperatures and large magnetic moments, increasing with the lattice parameters as the ligand changes from N to Bi. The systematic study of these compounds gives insight into the behaviour of the  $5f$  electrons and their interactions. NpP is one of the most puzzling of these materials. It orders initially at  $\sim 115$  K with a magnetic unit cell incommensurate with the lattice. However, at  $\sim 74$  K it adopts a relatively simple magnetic arrangement consisting of 3 planes of moments pointing „up“ followed by 3 planes of moments pointing „down“ [1]. It has been suggested that the 3 planes are not in fact identical, and doubts remain about what occurs in a magnetic field [2]. In this work we have revisited the magnetic phase diagram with our new SQUID apparatus (Fig. 1). This allows us to use one small single crystal (0.9 mg) and rotate the sample at low temperature in a magnetic field to establish the magnetic phase diagram.

These experiments have allowed to complete the magnetic phase diagram and show a new metamagnetic transition that can be interpreted as the missing intermediate step when the system evolves from the low-field phase (3+3-) to the high-field phase inferred as (6+). This work was performed in collaboration with the CEA-Grenoble and the ILL. Further neutron-diffraction experiments are planned.

Resonant x-ray magnetic scattering experiments have also been performed on a small (0.74 mg) single crystal of NpP. The feature we focus on in this article is the observation of a *resonant* peak at the momentum position  $(0\ 0\ 2+2k)$ , where  $k$  is the quantity specifying the inverse magnetic periodicity,

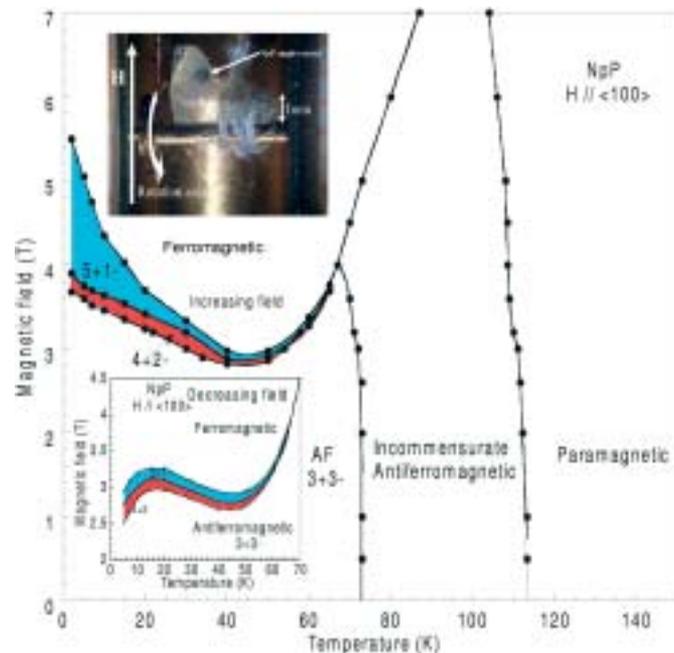


Fig. 1: Magnetic phase diagram of Np along  $\langle 100 \rangle$ , as inferred from measurements with our SQUID magnetometer. The lower insert shows the diagram for a decreasing magnetic field. The upper insert shows the experimental set-up of the NpP single crystal glued (epoxy) on a plexiglass plate mounted on the rotator, allowing measurements along the three main crystallographic axis  $[110]$ ,  $[111]$  and  $[001]$  while rotating the sample from  $0^\circ$  to  $90^\circ$ . The rotation axis and the field direction ( $H$ ) are indicated.

in this case at low temperature  $k = 1/3$ , so the magnetic configuration repeats itself in 3 chemical unit cells. The signal is seen only in the non-rotated photon channel, which implies that it is coming from a *charge modulation* induced in the unit cell by the magnetic periodicity. A possible model for the displacements is shown in Fig. 2 (right). This modulation gives rise to scattering at a  $(0\ 0\ 2+2k)$  reflection, but normally it would not have a strong dependence on energy. This expectation is in contradiction to the observations (see Fig. 2 left part). The full-width of this peak (in energy space) is even narrower than the *magnetic* resonance peak arising from the magnetic periodicity at  $(0\ 0\ 2+k)$ . The explanation for this exceptionally narrow peak is that the signal comes from the *difference* in charge distribution of the outer  $5f$  electrons between the sites A and B.

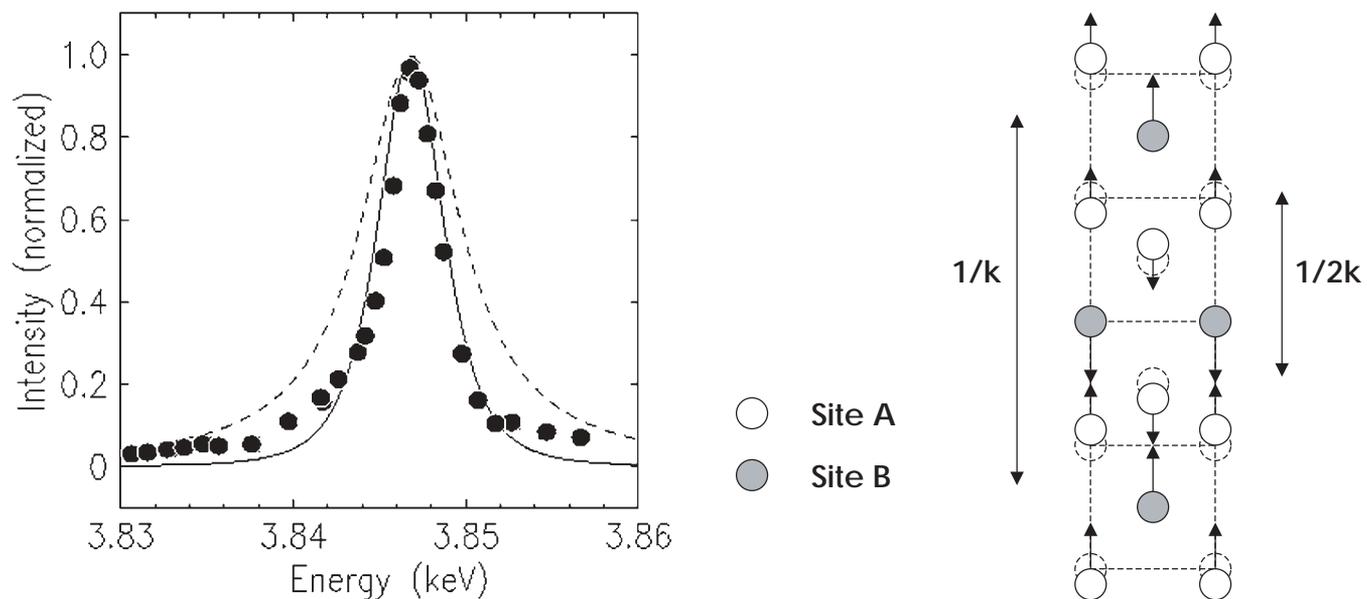


Fig. 2: Right: Model of the charge displacement with a periodicity of  $1/2k$ , whereas the magnetic periodicity is  $1/k$ , with  $k=1/3$  at low temperature. The atoms A have moved off their special positions (indicated by dashed circles). The atoms B do not move. Left: Intensity as a function of photon energy of the  $(0\ 0\ 2+2k)$  charge satellite measured at the ESRF, Grenoble on the ID20 beamline. The solid line is a fit assuming a difference in the charge distribution around atoms A and B. The dashed line gives the shape of the 1<sup>st</sup>-order magnetic satellite arising from the resonance process. The charge peak observed in NpP is clearly much narrower in energy than the magnetic peak.

Interestingly, the original Mössbauer spectra of NpP at low temperature were fit with a model [1] that required a *different* quadrupole charge distribution at the two sites A and B. But this idea was rather speculative, and no direct evidence was available. The interpretation of our results is completely consistent with this assumption. The magnetic ordering leads to the formation of inequivalent Np sites, despite the (initially) simple rocksalt structure above the ordering temperature. Furthermore, the interaction of these

aspherical charge distributions with the lattice leads to a strong distortion of the lattice so that it changes from cubic to tetragonal at low temperature.

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## Highlights 2001

# Innovative Acoustic Measurements of Elastic Modulus on Irradiated LWR-Fuels

As a complement of the ITU-EdF programme aimed at determining the mechanical properties of LWR-fuels via microindentation [1], a new co-operation programme with EdF (Électricité de France) and the University of Montpellier, France, has been initiated to assess alternatively the elastic properties of the fuels by microacoustic methods [2].

In this frame, an ultrasonic microprobe developed at the LAIN-Montpellier [3] has been installed and successfully operated in the ITU Hot-cells. For the first time this method has been applied on genuine commercial nuclear fuels for local acoustic determinations of porosity, grain size and elastic modulus (E) in fuel areas  $\geq 100 \times 100 \mu\text{m}^2$ . First results of E-modulus determinations with this apparatus for simulated and irradiated fuels in the burn-up range 0-200 GWd/tM are summarised in Fig. 1.

In the upper part of the figure, the variation of the assessed E-modulus with burn-up is shown, after correction for the effect of porosity [2]. The bottom part of the figure shows the micro-acoustic image of a non-irradiated  $\text{UO}_2$  sample [4], as obtained with the device in the microscope mode. The particularity of this image is that it was taken on purpose focusing the microacoustic lens at a plane some  $\mu\text{m}$  below the sample surface. In this form, the image is free of surface defects, e.g. free of the typical grain pullout effect that otherwise enlarges the sample porosity in optical micrographs. The method is therefore useful not only for E-modulus determinations but also for subsurface microstructure observations.

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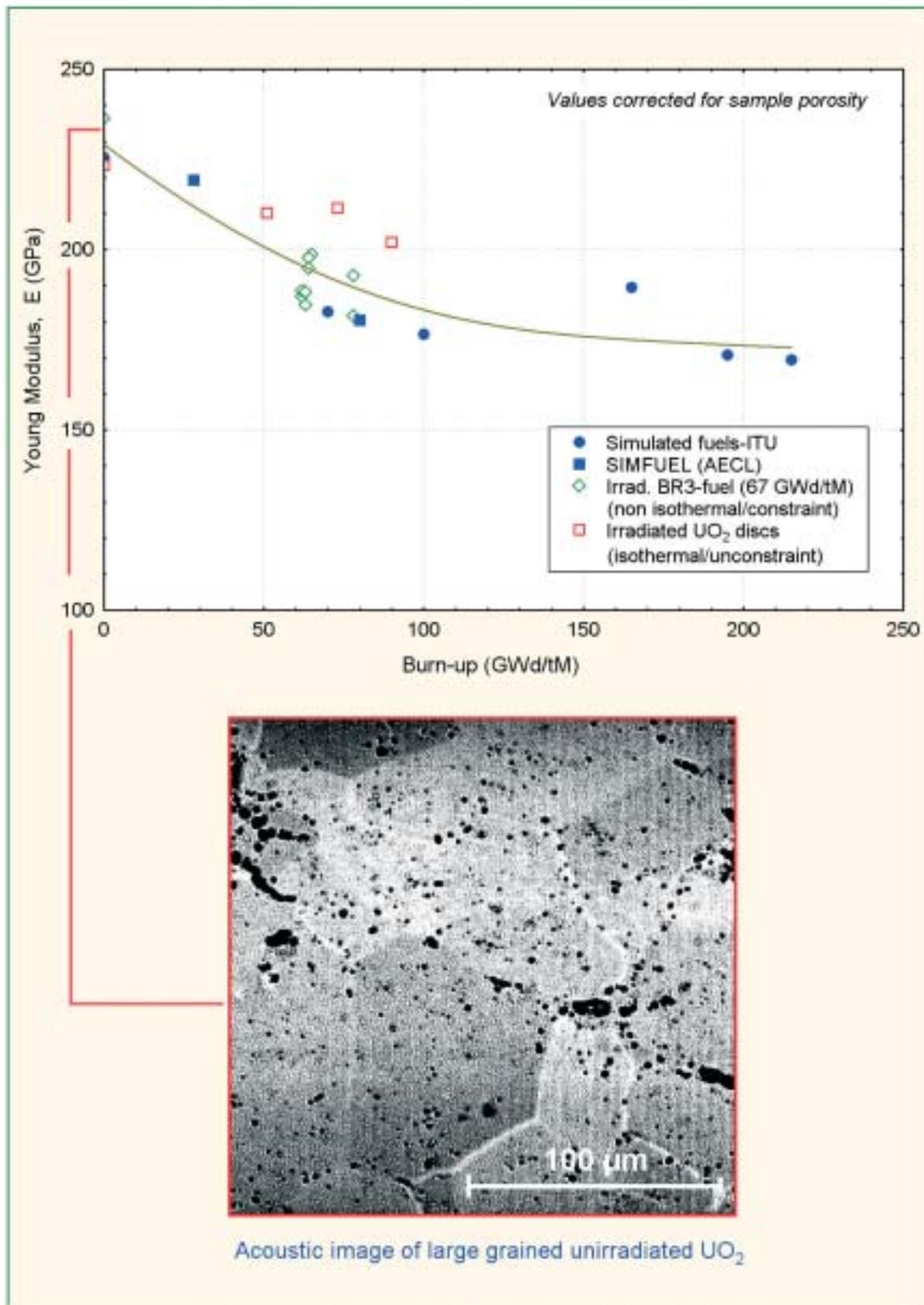


Fig. 1 Young modulus vs. burn-up and microstructure of UO<sub>2</sub>-fuels as determined by acoustic microscopy.

## Highlights 2001

# Fast Transport of Fission Energy through Shock Waves

In nuclear reactor, the main mechanism of conversion of fission energy into heat consists in the passage and stopping of fission fragments (FF) in the fuel matrix. After a fission event, two particles of energy of approximately 100 MeV and mass around 100 amu are ejected in nearly opposite directions.

Usable quantum-mechanical models can only approximately describe the various forms of energy losses that the fragment undergoes along its path. From the macroscopic viewpoint, however, the passage of the fission fragment is only considered as a source of intense local heating, mechanical pulses and atomic displacements. These phenomena are generally referred to as „spikes“ (e.g. thermal spikes, pressure spikes, displacement spikes, etc.).

The nature of the thermal spike, evolving from highly energetic interactions of the fission fragments with the target atoms, is generally considered irrelevant for the fuel in-pile behaviour. In practice, in heat-insensitive materials, this spike is essentially treated as a conventional, instantaneous thermal source, which rapidly comes to an end in the macroscopic thermostat of the medium. In this view, except for an infinitesimal contribution to the system enthalpy, no other traces are left back by the spike. This is, however, only part of the experimental evidence. In fact, in an irradiated material the most effective damage occurs at its physical boundaries, where swelling or densification of the body is realised by creation of surface defects (from Schottky point defects to macroscopic extended defects). Actually, if the original free surface of an irradiated fuel sample is observed, pits appear at the points of emergence of fission fragments. These defects, called surface tracks, are certainly *not* caused by nuclear collisions; neither can simple thermal spike models explain them.

The production of surface tracks affects the geometrical stability of nuclear fuel. For instance, the fabricated porosity of sintered UO<sub>2</sub> pellets is gradually destroyed by fission tracks (see Fig. 1), which essentially contribute in a fuel densification process known in reactor technology as „in-pile sintering“. This effect, inexplicable in terms of simple matter diffusion, is strictly related to long-range perturbations brought about by fission fragments.

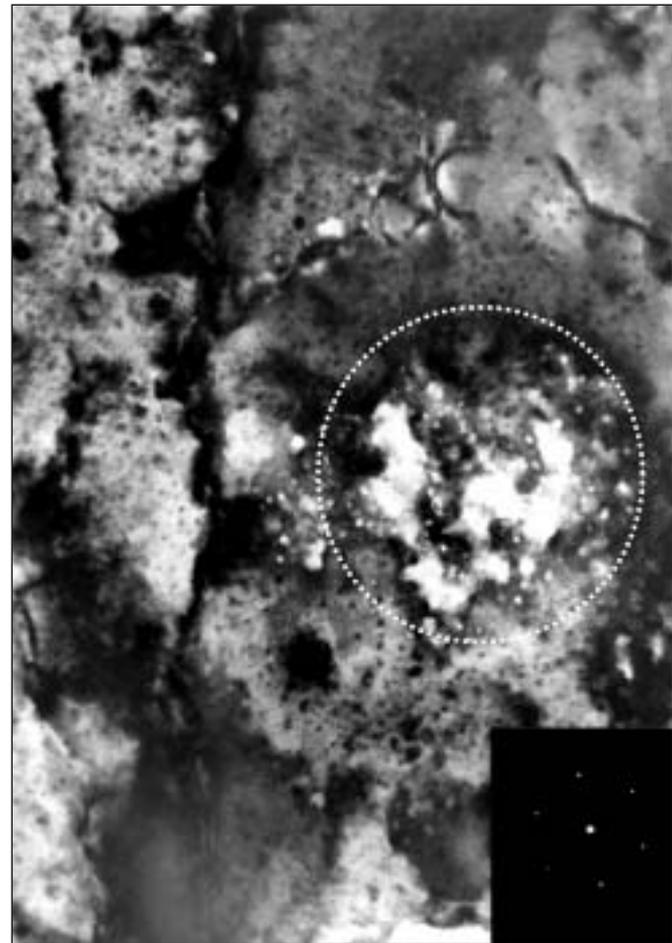


Fig. 1 TEM micrograph of a LWR UO<sub>2</sub> fuel irradiated to 35000 MWd/t. The dotted white circle indicates the location of an initial sintering pore where radiation enhanced re-densification (in-pile sintering) occurred through the passage of fission fragments.

These phenomena were studied by transmission electron microscopy (TEM) of irradiated thin foils of UO<sub>2</sub> single crystals. The TEM images provide evidence on the nature of the fission fragment interactions with the medium.

We have examined the size and shape of surface tracks created by energetic fission fragments (Fig. 2), as well as the effect of the associated thermal spikes on the oxygen superstructure of U<sub>4</sub>O<sub>9</sub>.

Whilst the extent of the deformations produced around the tracks indicates a release of energy, which is much larger than that possibly attributed to classical thermoelastic perturbations developed around the fragment trajectory, electron diffraction reveals in the bulk a substantial stability of

the long-range order in the interstitial-oxygen lattice of  $U_4O_9$  (Fig. 3).

Non-linear heat transport models were examined to explain the conversion of the FF energy losses into thermal and mechanical energy in times of less than a few picoseconds. The

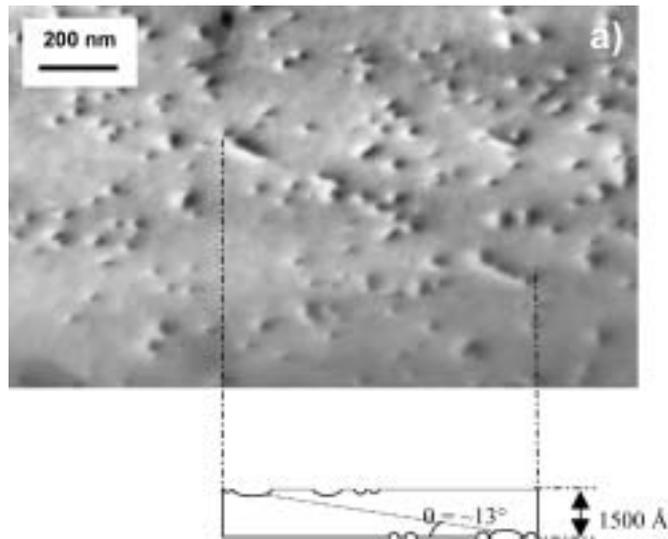


Fig. 2 Discontinuous fission tracks for different angles of FF emission. The scheme evidences the exit points of the FF, as well as the intermediate areas sputtered off by the shock wave of the spike reaching the surface

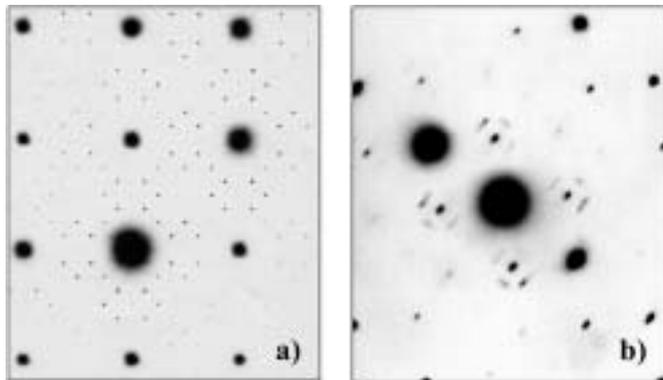


Fig. 3 Electron diffraction patterns of  $U_4O_9$ : a) before and b) after irradiation. The faint reflection spots from the extra oxygen sub-lattice surrounding the intense spots from the  $UO_2$  lattice have evolved in streaks after irradiation (see arrows). This transformation is known to occur at approximately 800 K, whilst the streaks completely disappear at 1500 K.

generation of a shock wave around the FF trajectory (Fig. 4) was shown to be the consequence of a very rapid deposit of thermalised electronic heat losses into the lattice. Whilst the high energy density of this wave is sufficient to create spallation effects on the free surface of  $UO_2$  having the magnitude of the observed large tracks, the speed of its front is too high to create atomic displacements in the bulk. This model adequately explains all the observed features.

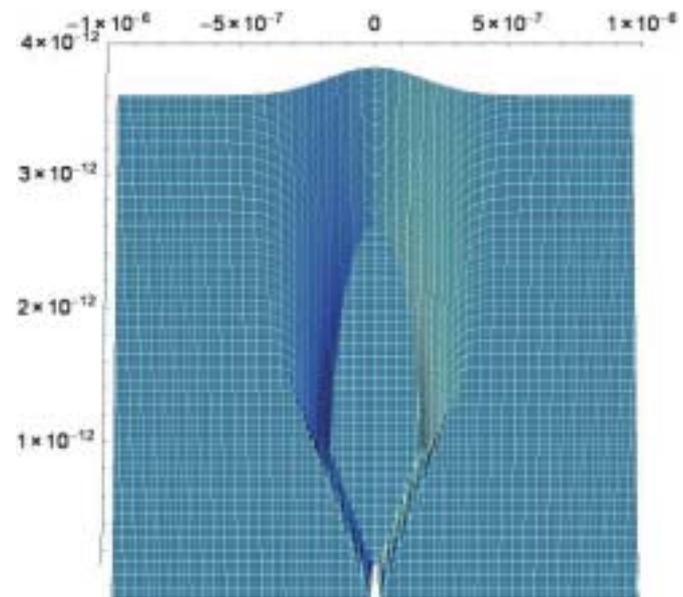


Fig. 4 Temperature spike around a fission fragment (FF) as calculated from the non-linear heat transport equation. The FF is supposed to have passed across the page at time zero (white mark at the bottom). The vertical axis is the time elapsed from the FF passage, in seconds, and the horizontal axis is the distance, in centimetres, from the FF trajectory. The graph shows the development of the temperature profile with time. At  $t < 1$  ps a large temperature discontinuity is calculated on a the wave front which propagates at a supersonic velocity and decreases in intensity with elapsing of time. The energy associated to this wave corresponds to a large fraction of the FF electronic losses. For  $t < 2.6$  ps. the centreline temperature peaks are clipped.

One can finally conclude that more than 70% of the fission energy dissipated as electronic stopping power is not dispersed through conventional slow diffusion processes, but carried out by energetic shock waves travelling at velocities higher than the speed of sound in the fuel.

## Highlights 2001

### Helium formation during transmutation of americium

Following transmutation of minor actinides in nuclear reactors, helium is produced from newly formed  $\alpha$ -decaying actinides. The impact on the fuel mechanical and structural properties is of great relevance for material selection and design purposes.

A reactor irradiation test (EFTTRA T4 experiment) demonstrated the feasibility of transmutation of Am in an inert matrix,  $\text{MgAl}_2\text{O}_4$ . However, higher short living alpha-emitting actinides (e.g.,  $^{242}\text{Cm}$  which decays to  $^{238}\text{Pu}$ ) were also formed from americium by neutron capture. This resulted in a high helium production (about 2.9 mg/g of fuel at end of irradiation), which eventually caused a large swelling (~ 18%) of the matrix.

Knudsen-Cell vaporization measurements were performed in conjunction with electron microscopy investigations with the aim of determining the location of helium in the matrix and its behaviour under thermal annealing conditions. From the release/vaporisation rates (see Fig.) of a number of components (matrix atoms, volatile-, metallic- and ceramic fission product compounds, actinides, fission gas and helium) present in the irradiated material, one can see that the onset of helium release occurs at approximately 900 K, but a large part is retained up to 1650 K and above.

From the microstructure observations (see the inset scanning electron micrograph revealing a porosity of about 15%) and from the profile of the release curves, one can infer that helium was trapped mainly in  $\mu\text{m}$ -sized pores, whose formation is likely controlled by combined precipitation and ripening processes.

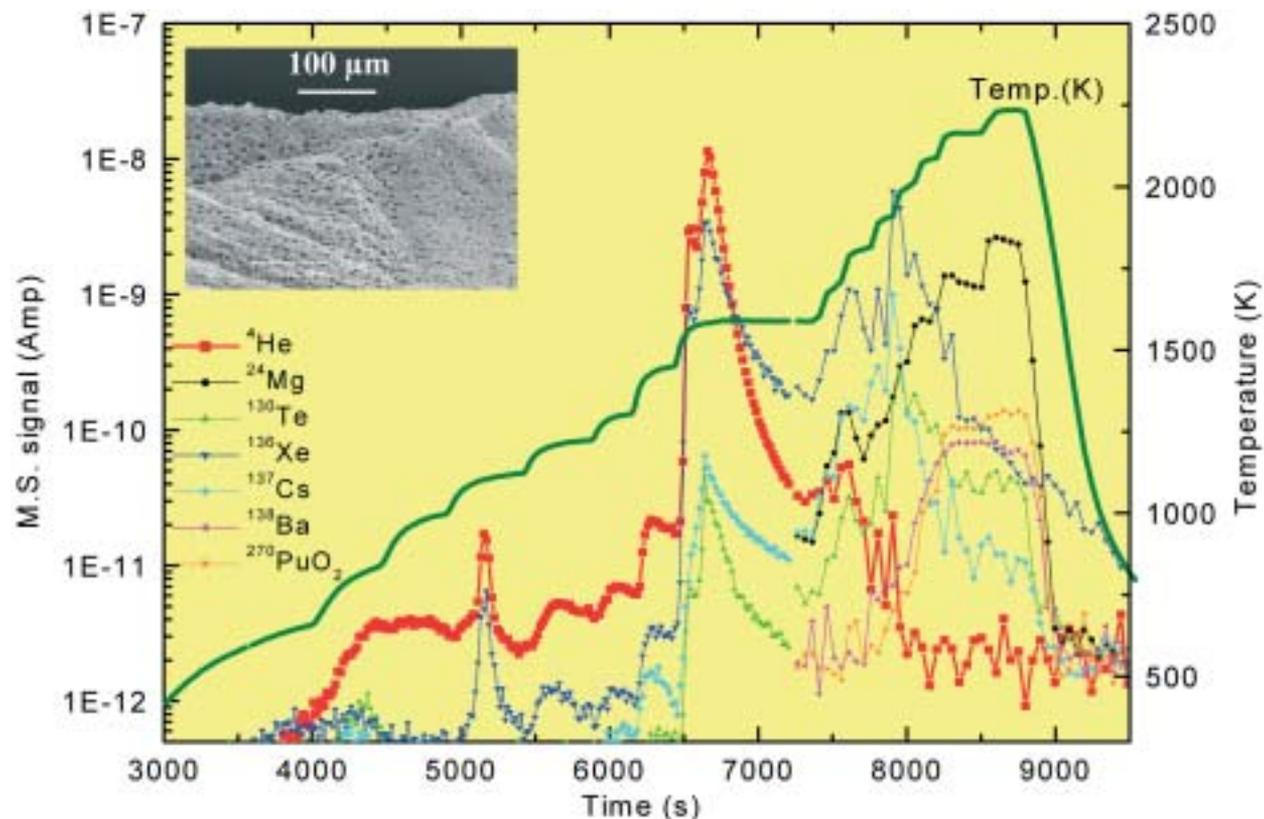


Fig.: Release profile of helium and of selected isotopes representative for fission gases, volatile FPs, actinides and for the EFTTRA T4 matrix. The inset shows a SEM micrograph of the specimen after annealing at 1650 K

## Analysis Carried Out in the Context of a Case of Theft of Radioactive Material

The support of the Institute was requested by the German authorities in the context of a case of theft of radioactive waste material from a nuclear installation which is being decommissioned. A number of samples had to be analyzed and expertise was provided on the origin of the samples and their respective interrelation. Nuclear forensic investigations were carried out involving a number of analytical techniques and comparison with measurement data from known sources.

Reportedly, two contaminated items had been taken out of the installation and were seized by the police some time later. One of the samples is shown in Fig. 1, it consists of a broken plastic vial which contains a radioactive residue. The dissolution behavior of the residue was studied in order to be able to explain the observed variations in certain element ratios as compared with some of the other samples.



Fig. 1 Broken sample vial containing dried residue of radioactive waste material.

Further samples were taken by the police in the living-environment of the suspect. These were investigated in order to answer the question whether their contamination originated from the two contaminated items mentioned above. Samples consisted, for example, of pieces of cloth, gloves, clothes and vacuum-cleaner bags. An example is shown in Fig. 2.

All samples were first measured by gamma-ray spectrometry in order to determine the total amount of radioactive material. Significant amounts of fission products  $^{125}\text{Sb}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$  could be detected in addition to uranium, plutonium and  $^{241}\text{Am}$ . The isotopic composition of Pu was also measured using gamma-ray spectrometry. By Inductively

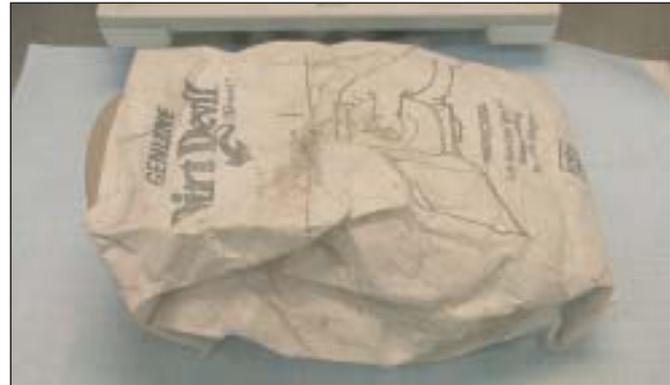


Fig. 2 Vacuum-cleaner bag from one of the contaminated apartments. The dust was analysed for radioactive contamination and isotopic composition of uranium and plutonium.

Coupled Plasma Mass Spectrometry the isotopic composition of uranium and plutonium was measured as well as the concentration of the non-radioactive impurities. Electron microscopic investigations on the nature of the support material (cloth) provided additional information on the potential origin of some of the samples and their interrelation. Fig. 3 shows a piece of tissue carrying high levels of activity arising from fission products.

The investigations were carried out within a very short time and the final report was provided for the responsible authorities only five weeks after receipt of the first sample.

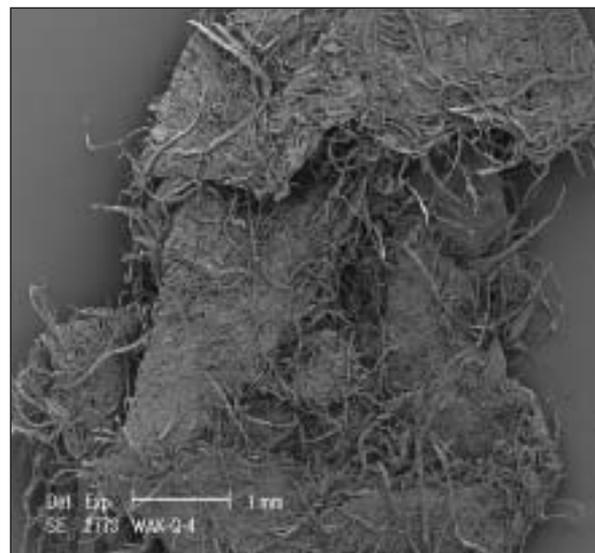


Fig. 3 Contaminated piece of cloth as found in one of the apartments of the suspect.

## Highlights 2001

# Radiometric Analytical Methods for Pyroprocessing

The ongoing development of the Pyrochemical Partitioning Process at ITU requires continuous and timely analytical support. In this process the actinides are separated from the fission products by electrotransport using metal electrodes and a molten salt electrolyte. This process is then followed by liquid metal/molten salt extraction (see diagram below) of the minor actinides (Np, Am, Cm). Analytical methods for the accurate assay of the actinide elements in these matrices needed to be developed. Quantitative assay is required in order to establish a material balance for process development and -at a later stage- for accountancy and control purposes.

The respective samples (Fig. 1) were available in small quantities ( $\cong 100$  mg) either in the form of eutectic salt or in metallic form with Cd, Zr or Bi as major metallic matrix con-

stituents. Substantial development work for measurement and for data analysis was needed to correctly interpret the measurement responses obtained with the different radiometric techniques.

Curium is measured by neutron coincidence counting (NCC). Detailed neutron transport calculations, using MCNP, were performed to relate the detector response of the sample to the response of a  $^{240}\text{Pu}$  (multiplicity) neutron calibration source. Typical amount measured is about 100 to 400 ng  $^{244}\text{Cm}$ .

New analytical procedures had to be developed. For example, for the absolute determination of  $^{241}\text{Am}$  using High Resolution  $\gamma$  Spectrometry (HRGS), 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. Fig. 2 shows the quantitative  $^{241}\text{Am}$  and  $^{243}\text{Am}$  determination by  $\gamma$ -spectrometry against the 63.29 keV  $\gamma$  ray from  $^{234}\text{Th}$  (a decay product of  $^{238}\text{U}$ ). The typical amount measured is about 1 to 50 ng of  $^{241}\text{Am}$  and of  $^{243}\text{Am}$ .

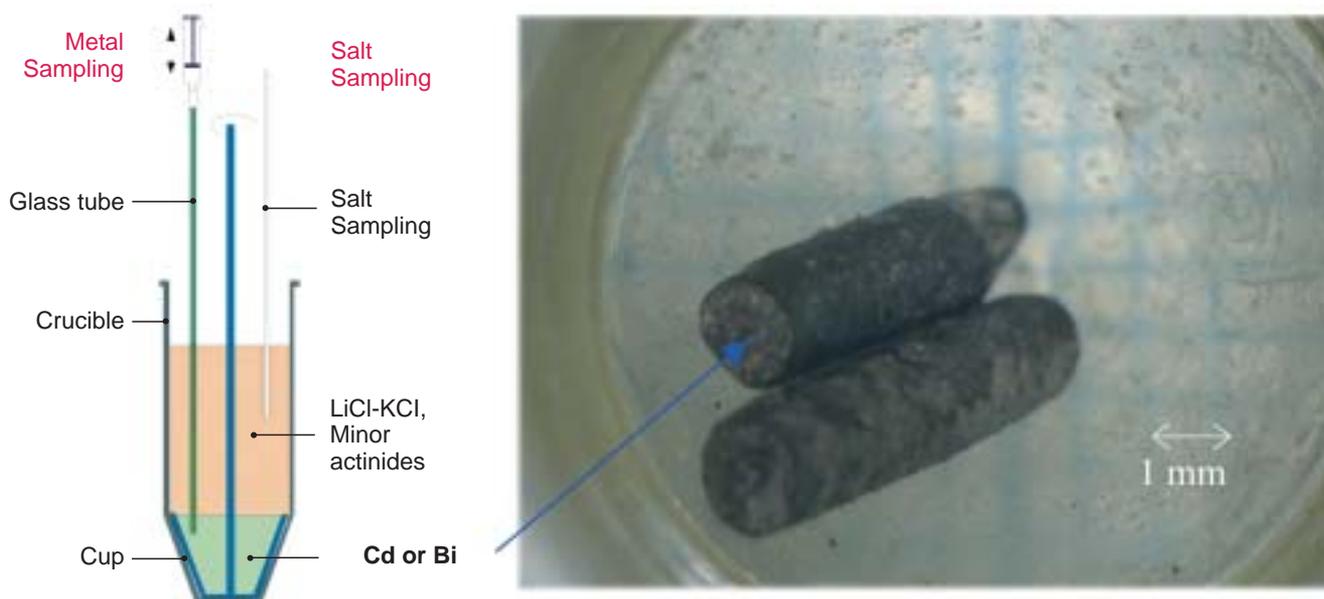


Fig. 1 Extraction of the minor actinides from molten salt into liquid metal. The adjacent photograph shows samples taken from the metal phase.

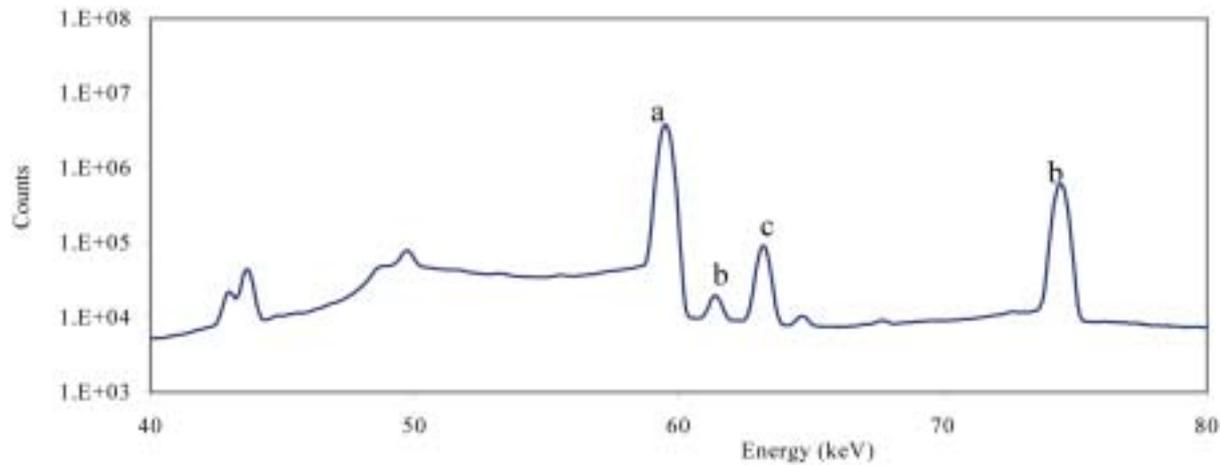


Fig. 2:  $\gamma$ -spectrum for  $^{241}\text{Am}$  (a) and  $^{243}\text{Am}$  (b) spiked with  $^{238}\text{U}$  (c)

Furthermore, analysis software and measurement procedures for the energy-dispersive X-ray fluorescence (XRF) analysis needed to be adapted, optimized and developed (Fig. 3). 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 ab-

solute quantity of the others. The typical amount measured is about 0.4 to 1 mg for each actinide.

An important step in establishing analytical methods for the assay of small quantities of actinides has been made. Further developments along these lines are in progress.

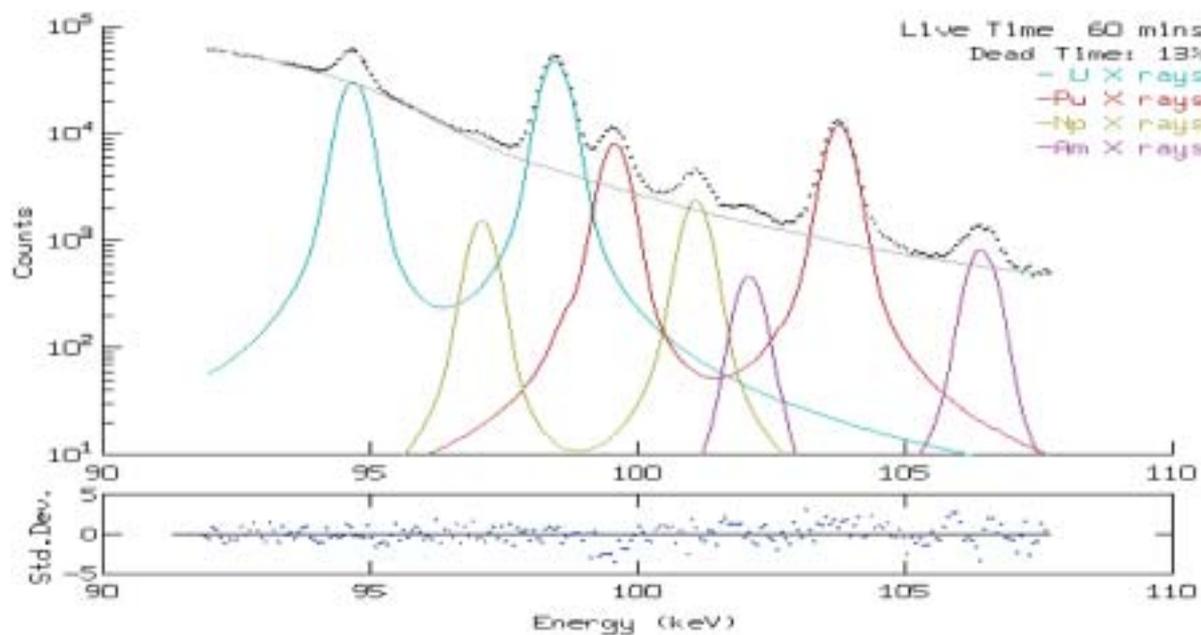


Fig. 3: X-ray fluorescence spectra of U, Pu, Np and Am

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## The TRANSURANUS Code - Past, Present and Future

K. Lassmann

### Introduction

At first sight, a nuclear reactor fuel rod appears to be a rather simple device, consisting of a stack of ceramic pellets sealed in a long metal tube. During irradiation, however, the fission process causes considerable disruption to the physical and thermodynamic properties of fuel and cladding. Furthermore, a complex thermo-mechanical system arises from the steep radial temperature gradient existing within the fuel and from the requirement for an effective heat transfer between pellets, cladding and coolant. Altogether, a fuel rod is far from being a simple system:

1. It is one of today's most complex technological structures known.
2. It is safety related since the fuel matrix and the cladding act as the first barrier for the release of radioactive fission products. It must therefore undergo a licensing process.
3. It is operated under varying conditions and its behaviour must not only be known for a wide range of normal, off-normal and accidental conditions, eventually also in case of interim or long-time dry storage.
4. It is of high economical relevance. If one roughly estimates that for the world-wide existing reactors 25% of all fuel rods are replaced annually, the costs amount to the order of  $10^{10}$  Euro per year. Despite the high total costs, one kWh of electricity can be produced at fuel costs of approximately 0.005 Euro.
5. There are inevitable uncertainties: almost none of the many quantities of interest can be measured directly; design-, fabrication- and irradiation parameters have errors, which are sometimes unknown.

If these items are considered in more detail the following conclusions can be drawn:

1. The modelling of the fuel rod behaviour is an interdisciplinary field covering neutron physics, fabrication tech-

nology, materials science, fluid dynamics, thermal and mechanical analysis, computer science etc. Unfortunately, this field is nowhere taught at university and the community of modellers of fuel rod behaviour must organise the acquisition and dissemination of knowledge themselves.

2. Only carefully validated theoretical models allow for the detailed understanding of the many complex and interacting processes. Since almost all of these processes are highly non-linear only numerical solutions are possible. Numerical methods must be carefully constructed to obtain stable but also practicable solutions.

### The strategy and goals of the TRANSURANUS project

The strategy and goals of the TRANSURANUS project may be expressed as follows:

1. To develop a tool, the TRANSURANUS code, which describes and combines the many interacting phenomena.
2. To transfer the detailed basic knowledge to the level of applied technology.
3. To transfer the knowledge and the results to research institutions, to industry and licensing authorities. The strong feedback from these institutions forces a customer-driven and customer-oriented research.

Thus, the TRANSURANUS project contributes to societal objectives such as acquirement and transfer of knowledge, contribution of science and technology to industrial competitiveness and regulatory and normative functions.

### The development of the TRANSURANUS code

Most of the important concepts of the TRANSURANUS code were developed in the years 1973-1984 at the Technical University Darmstadt [1,2] and in parallel from 1978-1982 at the Karlsruhe Research Centre (URANUS code):

1. A clearly defined mechanical-mathematical framework into which physical models can easily be incorporated; "build-in mathematics" supports the modification and extension of the code and guarantees numerical stability.
2. A consistent modelling of very different situations, as given for instance in an experiment, under normal, off-normal and accident conditions.

3. A high flexibility: different fuel rod designs, time scales of irradiation conditions may range from milliseconds to years, a comprehensive material data base for oxide, mixed oxide, carbide and nitride fuels, Zircaloy and steel claddings and different coolants.
4. Incorporation of a Monte Carlo technique for probabilistic analyses. A simpler probabilistic technique, the Numerical Noise technique, augments the Monte Carlo technique for specific analyses.

Since 1982 the main development was done at ITU [3,4]. It concentrated in the years 1982 to 1992 to Fast Breeder Reactors (FBRs), a development, which was abandoned in

1992. Besides oxide, also carbide and nitride fuels were modelled and the TRANSURANUS code has been coupled with the European Accident Code EAC [5], which aimed at analysing a hypothetical FBR core disruptive accident. Various further improvements were made and the name was changed from URANUS to TRANSURANUS. Since 1992 mainly high burn-up models for Light Water Reactors and a version for Russian VVER reactors were developed. During the whole development great effort was spent on obtaining an extremely flexible tool with modular structure, which is easy to understand and to handle, and which exhibits fast running times. The TRANSURANUS code is in use in several organizations, both research, private industry and licensing

Tab. 1 Organizations in research, licensing and industry, to which the TRANSURANUS code has been released.

Organization	Remarks
Commissariat à l'Energie Atomique (CEA) CEN Cadarache <sup>1</sup>	General usage in a research organization; the original TRANSURANUS version has been modified and renamed (METEOR-TRANSURANUS code)
Electricité de France <sup>1</sup> (EdF) France	General usage in industry; the original TRANSURANUS version has been modified and renamed (TRANSURANUS-EDF or CYRANO or OBERON code)
FRAMATOME S.A. <sup>1</sup> , FRAMATOME ANP SAS, FRAMATOME ANP GmbH, FRAMATOME ANP Inc., Duke Power, France, Germany, USA	General usage in industry; the original TRANSURANUS version has been modified and renamed (COPERNIC/TRANSURANUS)
Ente per le Nuove tecnologie, l'Energia e l'Ambiente, ENEA, Italy <sup>1</sup>	General usage in industry; at present analysis of fuel rods for ADS designs
TÜV - Süddeutschland <sup>1</sup> , München, Germany	Usage in fuel licensing
TÜV – Energie und Systemtechnik GmbH <sup>1</sup> , Mannheim, Germany	Usage in fuel licensing
TÜV Nord e.V., Hamburg <sup>1</sup> , Germany	Usage in fuel licensing
TÜV Hannover/Sachsen-Anhalt e.V. <sup>1</sup> (TÜV Nord), Hannover, Germany	Usage in fuel licensing
Paul Scherrer Institut <sup>1</sup> (PSI) Villigen, Switzerland	General usage in a research organization; support for safety analyses
Centro de Investigaciones Energeticas, Medioambientales y Tecnológicas <sup>1</sup> (CIEMAT) Madrid, Spain	
Armenian Nuclear Power Plant, ANPP <sup>2</sup> , Armenia	Support for safety analyses
Bulgarian Academy of Sciences, Institute for Nuclear Research and Nuclear Energy <sup>3</sup> (INRNE) Sofia, Bulgaria	General usage in a research organization; support for safety analyses
Committee on the Use of Atomic Energy for Peaceful Purposes <sup>2</sup> (CUAEP) Sofia, Bulgaria	Support for safety analyses; these analyses are not yet included in the formal fuel licensing procedures
State Office for Nuclear Safety <sup>2</sup> (SONS) Prague, Czech Republic	Support for safety analyses
Nuclear Research Institute Řež plc <sup>4</sup> (NRI) Řež, Czech Republic	General usage; support for safety analyses
Atomic Energy Research Institute <sup>2</sup> (AEKI) Hungary	General usage in a research organization; support for safety analyses
National Atomic Energy Agency <sup>2</sup> , Institute of Atomic Energy (IAE), Warsaw, Poland	General usage in research
Institute for Nuclear Research <sup>2</sup> (INR) Pitesti, Romania	General usage in research
VUJE Trnava – engineering, design and research organization <sup>2</sup> , Trnava, Slovak Republic	General usage in research, usage in fuel licensing
State Scientific and Technical Centre for Nuclear and Radiation Safety <sup>2</sup> (SSTC NRS) Kiev, Ukraine	Support for safety analyses

<sup>1</sup>TRANSURANUS code obtained through bilateral agreement

<sup>2</sup>TRANSURANUS code obtained through IAEA RER 4/12 and 4/19 Technical Co-operation Projects

<sup>3</sup>TRANSURANUS code obtained through Phare Project FERONIA-Bulgaria

<sup>4</sup>TRANSURANUS code obtained through Phare Project FERONIA-Czech Republic

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Fig. 1 Usage of the TRANSURANUS Code inside Europe

authorities (see Tab. 1 and Fig. 1). The total development effort amounts to approximately 20-30 man-years. Much more time has been used for running the TRANSURANUS code. Different groups including our own probably spent already more than 60-100 man-years in performing fuel rod analyses.

The TRANSURANUS code is an "open" code, where the user obtains the source code and all related knowledge. Due to the complexity of this field a user should be familiar with the basic concepts, limitations and models. We offer therefore the code together with several training courses and subsequent and continuous user service. Typically, TRANSURANUS user meetings are held once per year (see below).

The following numbers indicate the "size" of the TRANSURANUS code project:

1. The TRANSURANUS code project consists of a large amount of data:

	Number of files
TRANSURANUS code	350
Test programs, pre- and post processors	11,000
Databases	10,000
Documentation, quality assurance	8,500

- For a deterministic analysis of a "typical" irradiation history each model or correlation is called at least 100,000 times. If such a model is embedded in the innermost iteration loop it may be called 3-4 times more. For a probabilistic Monte Carlo analysis of the same irradiation typical 500-1000 runs are required. Consequently, modern numerical techniques as well as many aspects of computer science have played and are still playing a large role in the development of the TRANSURANUS code.

## Verification of the TRANSURANUS code

The verification has been done in three steps: comparison with analytic solutions, code-to-code comparisons and most importantly comparisons with irradiation experiments.

The first step has been done extensively since many analytic solutions are available for the thermal and mechanical analysis and – for specific conditions - for practically all physical models. Every model or correlation has been tested in a specific test environment before it has been incorporat-

ed into the TRANSURANUS code. In almost all cases different numerical methods were compared, sometimes Monte Carlo methods were employed where millions of comparisons were made. This "test environment" consists of the approximately 11,000 files mentioned above.

Code-to-code comparisons were continuously made over the past 20 years. One important result from the IAEA-FUMEX blind exercise (see below) should be mentioned: since we prefer models of "adequate complexity" and avoid overcomplicated, highly mechanistic models with too many fitting parameters, the code predictions were never on either extreme side of all predictions.

In 1993, one member of the ITU TRANSURANUS development team (KL) proposed to the OECD/NEA Nuclear Science Committee to develop a database, which includes well-characterised and instrumented fuel rod irradiations [6]. The IAEA and the OECD followed this recommendation. The "International Fuel Performance Experiments" (IFPE) Database with approximately 400 irradiations is existing now [7] and we use it extensively for the verification of the TRANSURANUS code. This verification work is shared between several TRANSURANUS groups and forms the basic work within the TRANSURANUS Research Network (see

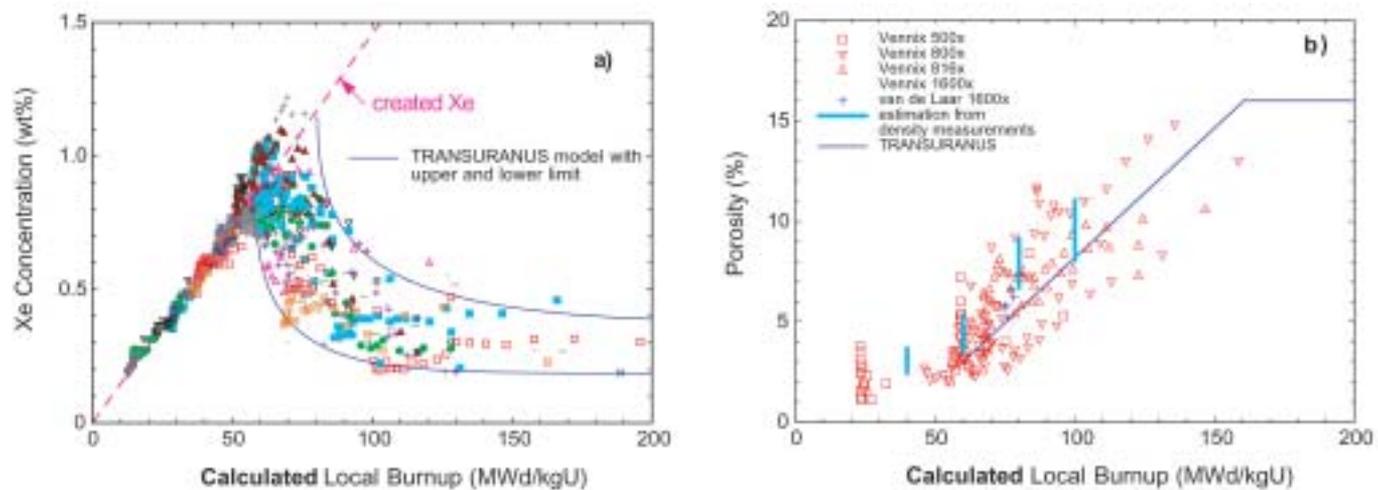


Fig. 2 Example of data interpretation: the TRANSURANUS code has been used to calculate the local burn-up, which was used here as the independent variable. Measurements of the Xe concentration (C.T. Walker) and the porosity in the outer regions of different fuel rods were analyzed [8]. Clearly, from both figures it can be concluded that around a local burn-up of 60-80 MWd/kgU something happens: The Xe concentration in the fuel matrix decreases whereas the porosity increases. This has been identified as consequence of the formation of a new microstructural fuel zone, the so-called "High Burn-up Structure" (HBS).

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below). Up to now approximately 70 irradiations from the IFPE Database have been analyzed. Further irradiation experiments for the verification of the TRANSURANUS code come from the Halden Project, where ITU became a member in 2001. From this project up to now six major irradiations have been analyzed covering  $\text{UO}_2$  fuel at high burn-up as well as gadolinium and MOX fuels.

The result of the whole verification is documented in the TRANSURANUS Verification Database. Two examples of the data interpretation and the verification work are given in Figures 2 and 3.

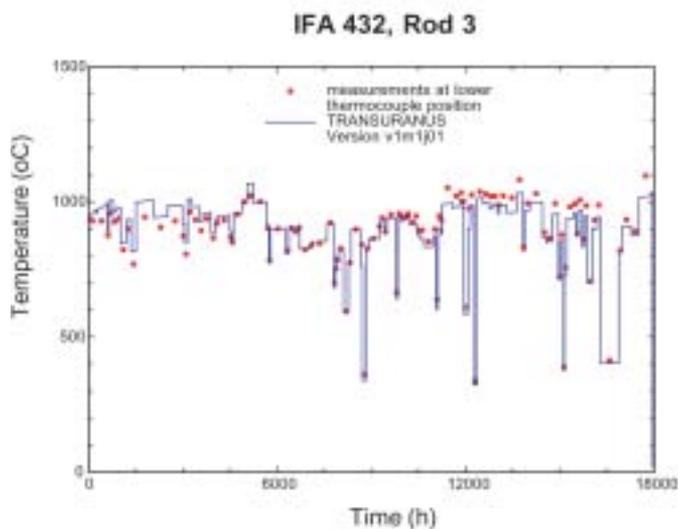


Fig. 3 Example of the extensive TRANSURANUS verification work: comparison between measured and calculated temperatures.

### Training courses and user support

It has been mentioned before that the important subject of the fuel rod behaviour is not taught at universities. Newcomers might find it even difficult to extract from the many reports and papers available (approximately 40,000-50,000!) the few overview articles. In order to bridge this gap, the ITU Modelling Group has continuously offered training courses, meetings on specific topics, as well as consulting. In other words, the users are not been left alone and are continuously informed about the latest developments, which are made available on request.

Our future planning foresees to use also the Internet for such training purposes. It is planned to put not only the

latest developments to the Internet, but also the whole verification database including data cases and all results. The user will find well-documented test data cases and a specific form of the TRANSURANUS User's Handbook.

### Application of the TRANSURANUS Code

As mentioned before, the TRANSURANUS code is used by research organizations, industry and licensing authorities (c.f. Tab. 1). The main development done at research organizations is in the areas burn-up extension, transients, new fuels and new cladding materials. All users in industry have adopted the TRANSURANUS code to their specific fuel design and know-how including specific details of materials and fabrication. In general, the industry uses the code in the fuel rod design process and for fuel rod safety reports, where it must be proven that given design criteria defining maximum temperatures, inner pressure, cladding deformation, cladding oxidation etc. are fulfilled for a wide range of conditions. These safety reports are independently checked within the licensing procedure (fuel licensing) by licensing authorities. It seems that the licensing of fuel differs significantly between Western and Eastern countries. In some Eastern countries fuel licensing is not even done and it will be one goal of our future PECO (Pays d'Europe Centrale et Orientale) programme (see below) to harmonise fuel licensing.

### The TRANSURANUS research network

The different groups, which use and further develop the TRANSURANUS code, have different goals, which may range from basic research to licensing needs. Nevertheless, there is a huge overlap of joint interests. Especially the verification work is an ideal task for co-operation since the time needed to fully understand a complex irradiation is almost everywhere underestimated. Consequently, the TRANSURANUS research network concentrates on

1. The release of the latest TRANSURANUS versions including the revision of the handbook and the transfer of all related knowledge
2. Exchange of results from verification and the incorporation of the results to the TRANSURANUS Verification Database
3. Discussion of open problems and future priorities.

Up to now, the TRANSURANUS research network is more or less based on the good will amongst colleagues from very different organizations. However, it should be considered to re-organise this network in a more formal structure.

## Co-operation with Eastern European countries

In the period 1990-92, following the political changes in Eastern Europe, nuclear safety in Eastern-European countries looked somewhat precarious. Independent nuclear regulatory authorities were almost non-existent and nuclear fuel was loaded in reactors without normal licensing procedures. In addition, quality assurance systems (QA) were essentially unknown [9]. Nevertheless, help from many national and international organizations, especially the IAEA and the EU was organized.

Within the FUMEX (Fuel Modelling at Extended Burn-ups) Co-ordinated Research Programme and two other related IAEA programmes (RER 4/12 and RER 4/19) the TRANSURANUS code was released to 8 organizations in 6 different Eastern European countries. Together with the release, several training programmes were organized. Two EU Phare programmes, FERONIA-Bg and FERONIA-CZ, helped to transfer the TRANSURANUS code to two further organizations in the Czech Republic (Řež) and Bulgaria (INRNE) and to develop a specific VVER version of the TRANSURANUS code. Several other projects were executed from which the two running projects, the PECO and the EXTRA projects should be mentioned:

PECO is a joint project between the INRNE (Bulgaria), AEKI (Hungary), VUJE (Slovak Republic) and ITU, which will end by the middle of 2002. The different activities may be characterised as follows:

- ❑ Further verification of the TRANSURANUS-VVER version, general verification of selected irradiations from the IFPE Database, development of a modern graphical user interface; final goals: better physical understanding, verification for VVER licensing, improvement of the usage (**INRNE**)
- ❑ Analysis of recent VVER irradiations and other irradiations in the Halden reactor; extension of the VVER Database for TRANSURANUS verification; final goal: better usage for licensing (**AEKI**)

- ❑ Usage of the TRANSURANUS code within RELAP safety analyses (LOCAs and RIAs); final goals: to better determine safety margins by using the more detailed TRANSURANUS code instead of the RELAP built-in model (**VUJE**).
- ❑ Co-ordination and specific developments (**ITU**)

EXTRA is a shared cost action between AEKI (Hungary), VUJE (Slovak Republic) and ITU that started December 2001 and will be finished in 2003. This project concentrates on loss of coolant accidents (LOCA) as well as reactivity initiated accidents (RIA) for VVER rods. The behaviour of the VVER specific cladding alloy (Zirconium with 1% Nb) at elevated temperatures has to be modelled (oxidation, hydrogen pick-up, deformation).

Since 1992 sixty colleagues from 8 different countries in Eastern Europe visited the ITU Modelling Group for short and long-term visits. For 2002 we expect the visit of approximately 15 colleagues.

## Future projects and outlook

Modern reactor fuel in operation today has proven extremely reliable with a very small failure rate. Although the discharge burn-up increased in the past 30 years by approximately 30 MWd/kgU, the rod failure rate decreased by nearly three orders of magnitude to approximately 1 defect rod per  $10^6$  rods and approaches a zero failure rate. Nevertheless, the OECD/NEA Nuclear Science Committee (NSC) stated in 1993 that scientific issues in modelling fuel behaviour are an important topic for future investigation [6]. The most important argument was that higher discharge burn-up and the whole range of design basis accidents place stricter demands on the performance of a fuel rod.

We have organized our research in view of the OECD/NEA's recommendation. The present development concentrates on the behaviour of different fuels ( $UO_2$ , Gadolinium and MOX fuels) at high burn-up. In the years 2002-2004 the TRANSURANUS code will be used within three shared cost actions: the projects OMICO and MICROMOX will help to further validate the TRANSURANUS MOX version, whereas the EXTRA project is directed towards the analysis of loss of coolant and reactivity initiated accidents for VVER reactors. A fourth project is under consideration, the continuation of the present PECO project. The ideas go mainly into the di-

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rection to establish in the area of modelling the fuel behaviour closer links (maybe even on a more formal basis) between the four Eastern European countries running VVER reactors, *i.e.* the Czech and the Slovak Republic, Hungary and Bulgaria. Possibly licensing related aspects could also be harmonised.

Further work needs not only to be done in scientific but also in practical areas, for instance in improving the usability of codes in general. Two areas should be mentioned:

1. "Intelligent", knowledge-based support should be given to a user.
2. The models developed by different groups all over the world should be constructed, much more than at the moment, as exchangeable, object-oriented modules, which allow fast and easy linkage to any code.

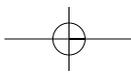
More generally, the time is ripe to re-consider more detailed models for processes like fission gas release and swelling, a development that has been more or less abandoned at the end of the seventies. With the knowledge of today, *i.e.*

- the many well-documented, highly instrumented irradiations,
- the tremendously improved computer power and
- well developed codes such as TRANSURANUS

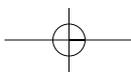
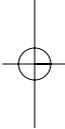
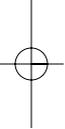
it should be possible to go deeper into microstructural details of the behaviour of fuel and cladding under the various reactor conditions.

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## Highlights 2000



## Basics

# The Year at a Glance

## January

The year started with a discussion on the status of nuclear waste management in Europe with Rudolf Linkohr (MEP) and Axel Fischer (Member of the German Bundestag). ■ ITU hosted a group of representatives from the German mining industry led by Prof. Friedrich Wellmer, director of the Bundesanstalt für Geowissenschaften.

## February

At the University of Ghent, the first Belgian alpha-immunotherapy laboratory was inaugurated. ITU assisted in the construction phase with the installation of a glove box and related technology. ■ A delegation from the German "Europa-Union" had a first insight into research activities in ITU.

## March

ITU's quality management system was certified to the new ISO 9001:2000 standard. ■ Phase I clinical trials (B-cell malignancies) with Bismuth-213 labelled anti-CD-20 antibody started in Heidelberg (Germany). Over the year, nine patients were treated.

## April

Prof. Yoichi Fujii-e, chairman of the Japan Atomic Energy Commission, visited ITU to discuss future co-operation. ■



Jörg Tauss, Member of the German Bundestag and responsible for tech-

nology, technological risk assessment and new media, came to ITU for the first time. ■ The European Roadmap for Developing Accelerator Driven Systems for Nuclear Waste Incineration was published with major input from ITU.

## May

The results of the collaboration with Bulgaria, Hungary and the Slovak Republic were reviewed during a fuel modelling group meeting (TRANS-URANUS code). ■ The contacts with the JRC-Board of Governors (BoG) were strengthened by the visit of Philippe Garderet, Commissariat à l'Energie Atomique (CEA) and Member of the BoG. ■ At the recommendation of Prof. Fujii-e, Dr. Keiji Hirai from the Japan Atomic Power Company discussed at ITU the organisation of a high level workshop in 2002 between Japan and the European Commission on innovative reactors and fuel cycles. ■ Barry Mc Sweeney visited ITU for the first time after being appointed JRC Director General.

## June

Gérard Caudron, MEP and rapporteur for the 6th Framework Programme, visited ITU to become familiar with the Institute's research activities. ■



More than 70 students and young researchers, from the European Union and candidate countries, and from



China, India, Japan, Russia, Ukraine and the US took part in the first ITU Summer School. Experts gave the group an insight in basic actinide physics and chemistry and applications. ■

ITU signed an agreement with the Institute of Nuclear Energy Technology, Tsinghua University, China on separation processes for radionuclides.

## July

Patrick Ledermann, Director of "Simulation and Experimental Tools", CEA visited ITU to discuss future collaboration between the two organisations and the establishment of a network of excellence.



In this context, Frank Carré, CEA, held a seminar on "Future Nuclear Energy System Studies at CEA:"



## August

In the affair around the theft of nuclear material from the reprocessing plant "WAK" (Germany), ITU upon request of the German authorities, analysed the found material in order to establish its origin, age, type and composition.

## September

Loyola de Palacio, Vice-President of the Commission and responsible for Transport and Energy, was very enthusiastic about research on waste management, partitioning and transmutation and alpha-immunotherapy during her visit to ITU. ■



Within the collaboration between the Korean Atomic Energy Research Institute (KAERI) and ITU, the first workshop took place in Karlsruhe. Vice-President Dr. Park was very pleased with the decision to establish collaborative projects on topics of common interest such as high burn-

up fuel, partitioning and waste management. ■ ITU signed a framework co-operation agreement with the German Ministry for Environment and Nuclear Safety in the field of illicit trafficking and the analyses of nuclear material for conditioning and final disposal.

## October

Competence management, customer relationship, communication and knowledge sharing were selected for benchmarking during a meeting with representatives from JRC institutes (IE, ISPC, ITU) and the Technical Research Centre Finland (VTT). ■ Heide Rühle, MEP (Greens/European Free Alliance), accompanied by a local Green party delegation made a tour of ITU and acknowledged the role of the Institute as a reference laboratory. ■



At the request of the Landeskriminalamt Kiel, Germany, ITU analysed soil samples in order to clarify a longstanding debate about possible plutonium contamination in Schleswig-Holstein.

## November

Christian Waeterloos, Director of the Euratom Safeguards Office, and representatives from Directorate General Transport & Energy (DG TREN), reviewed at ITU the co-operation between DG-TREN and the JRC in the field of nuclear safeguards and nuclear forensics. ■ Opportunities for collaboration in view of the European Research Area (ERA) and the 6th Framework Pro-

gramme (FP6) were defined with Pascal Colombani, General Administrator and President of the Supervisory Board of AREVA (the new association of nuclear industries in France). ■



The yearly assessment of all scientific and supporting projects of ITU once again involved many of the staff members during a two week period. ■ On the last day in November a new five-year contract was signed with Framatome ANP to increase the quality and safety of nuclear fuel in the future.

## December

Helen Garnett, Executive Director of the Australian Nuclear Science and Technology Organisation signed a Memorandum of Understanding at ITU. This was the result of a fruitful collaboration in the field of particle and trace element analysis in environmental samples. ■

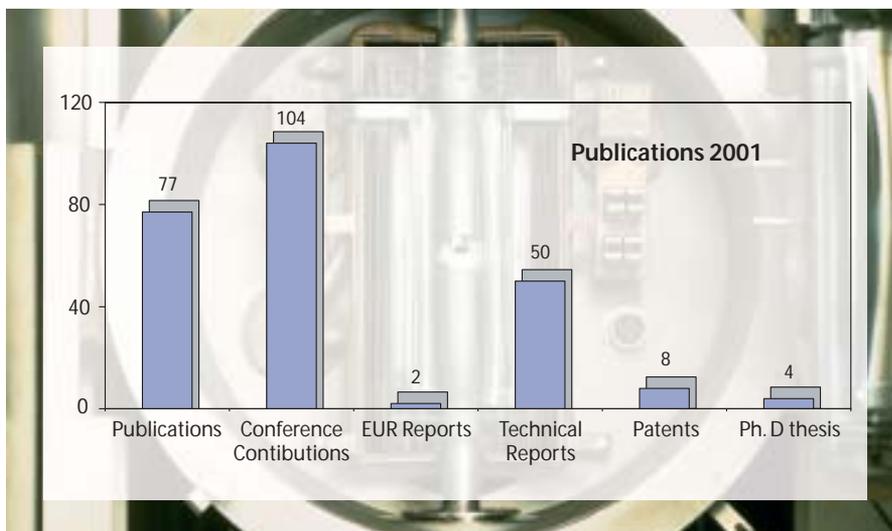


During the annual Christmas Seminar, Roland Schenkel awarded on behalf of Barry Mc Sweeney the JRC Young Scientists Prize 2001 to Andreas Lindbaum. ■ ITU created the "Technik Preis ITU" for outstanding technical achievements realised at the Institute.

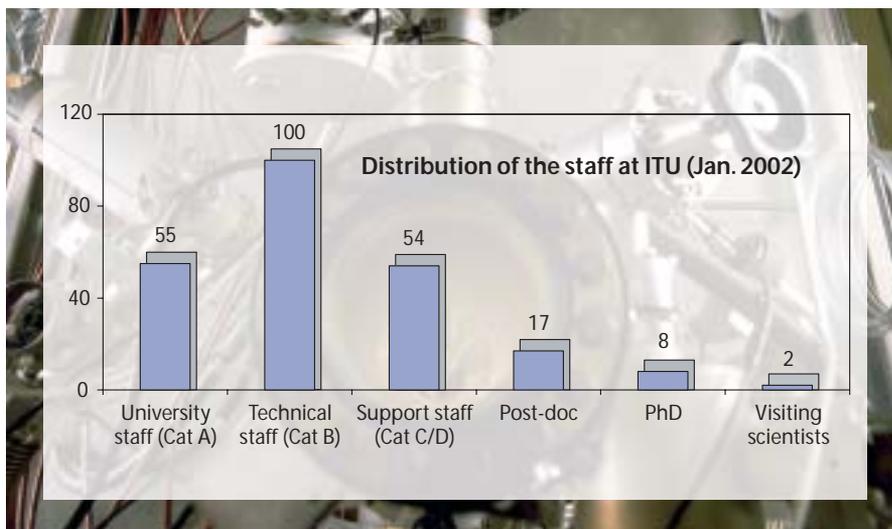
Basics

# Facts & Figures

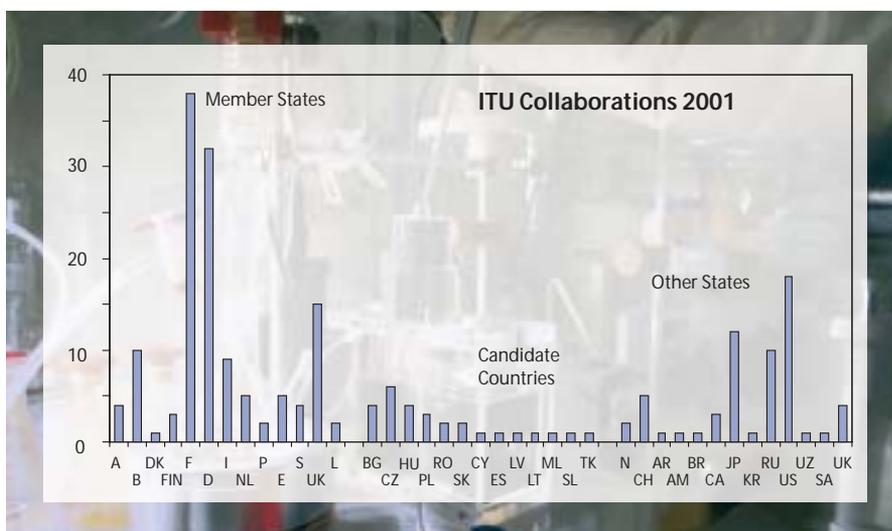
Scientific productivity of the Institute in 2001 was reflected in the number of publications. There were 77 publications in peer-reviewed journals and 104 in conference proceedings. ITU issued 2 EUR reports. Technical reports (50) have been issued mostly to our different customers under various competitive activities. In 2001, 1 patent was applied for, and 8 were granted. Four Ph.D. theses were finalised. More detailed information on publications can be found in annex I.



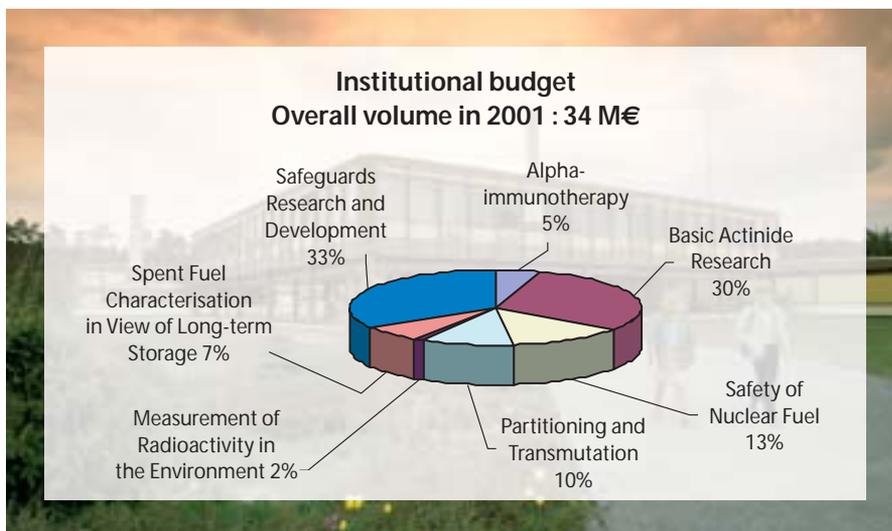
In addition to a statutory staff of 209, a total of 27 grant holders and visiting scientists were present at ITU in 2001. This category of staff is of vital importance to transfer knowledge to a new generation of European scientists. Additionally, ITU makes its facilities, materials and experience available to universities, research centres and other organisations throughout Europe to implement further its educational and training role.



The Institute collaborates at various levels with many institutions in Europe and other countries. In Basic Actinides Research, for example, collaborations with 36 universities / laboratories within the European Union and about 10 outside the EU were running during the year 2001. Details are given in annex II.

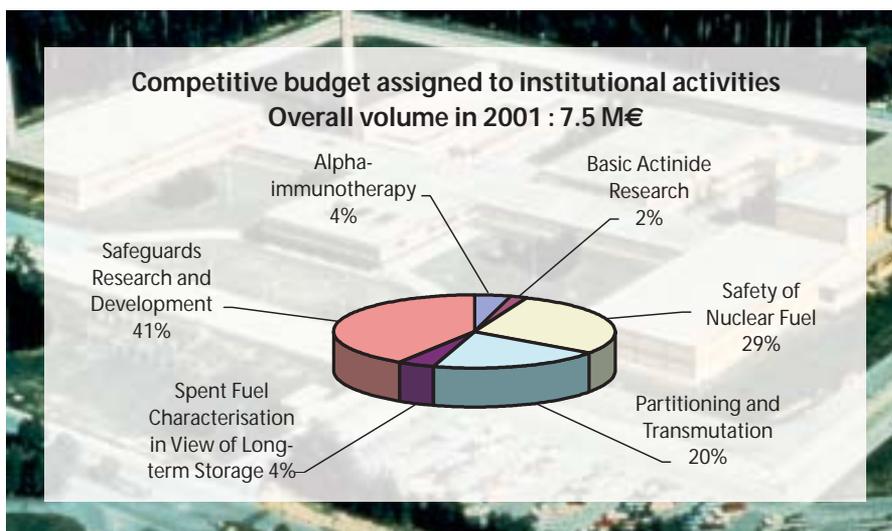


Two major categories of activities are performed in the Institute. The first category is the so-called institutional projects, which covers activities carried out on behalf of the European Commission. With the exception of Alpha-Immunotherapy financed by the EC programme "Serving the Citizen" all other activities are supported by the Euratom budget.

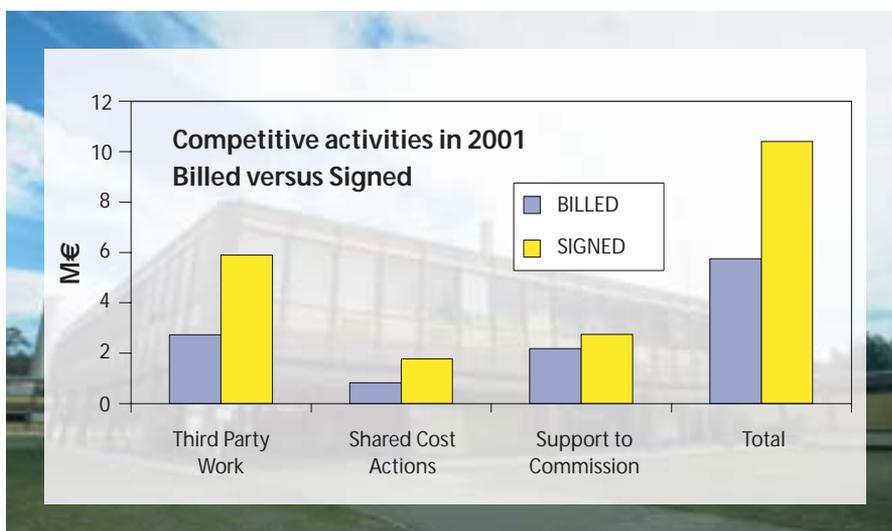


The second category is the so-called competitive activities: Third Party Work, Shared Cost Actions and Support to other Directorates of the Commission.

The repartition of this income to the various institutional projects is indicated. More than 50% is related to the Safety of the Nuclear Fuel Cycle (including waste management). About 40 % is related to Safeguards relevant activities (incl. OSL/LSS as service for DG TREN / ESO).



Income generated from competitive activities continued at a high level in 2001. The large difference between billed and signed for the Third Party Work is determined by the signature of some longer-term contracts in 2001 with major industrial partners.



## Basics

# Benchmarking and Total Quality Management

In agreement with the general quality approach of the Joint Research Centre, the Total Quality Management (TQM) process was further developed in the Institute. A major achievement in 2001 was the certification of ITU according to the new norm ISO 9001:2000, in March.

The evaluation of the results of the self-assessment 2000, and of the staff satisfaction surveys led to the decision to increase the information distributed to the staff through the intranet. Also, management training sessions were organized for the ITU leaders at all levels, to foster the development of an internal leadership culture, based on good communication and team building techniques. An internal customer satisfaction survey and a grantholder satisfaction survey were launched.

The self-assessment 2001 showed an increase of the score from 300 (score of 2000) to 391 points, which reflects an overall improvement on the implementation of the TQM concepts in ITU. This applies particularly to the prepa-

ration of the 6th Framework Programme. It should be remembered that a consequent increase for the „Results“ criteria requires at least 3 years of recorded standing improvement, i.e. can only be expected with the same delay after the installation of a set of indicators.

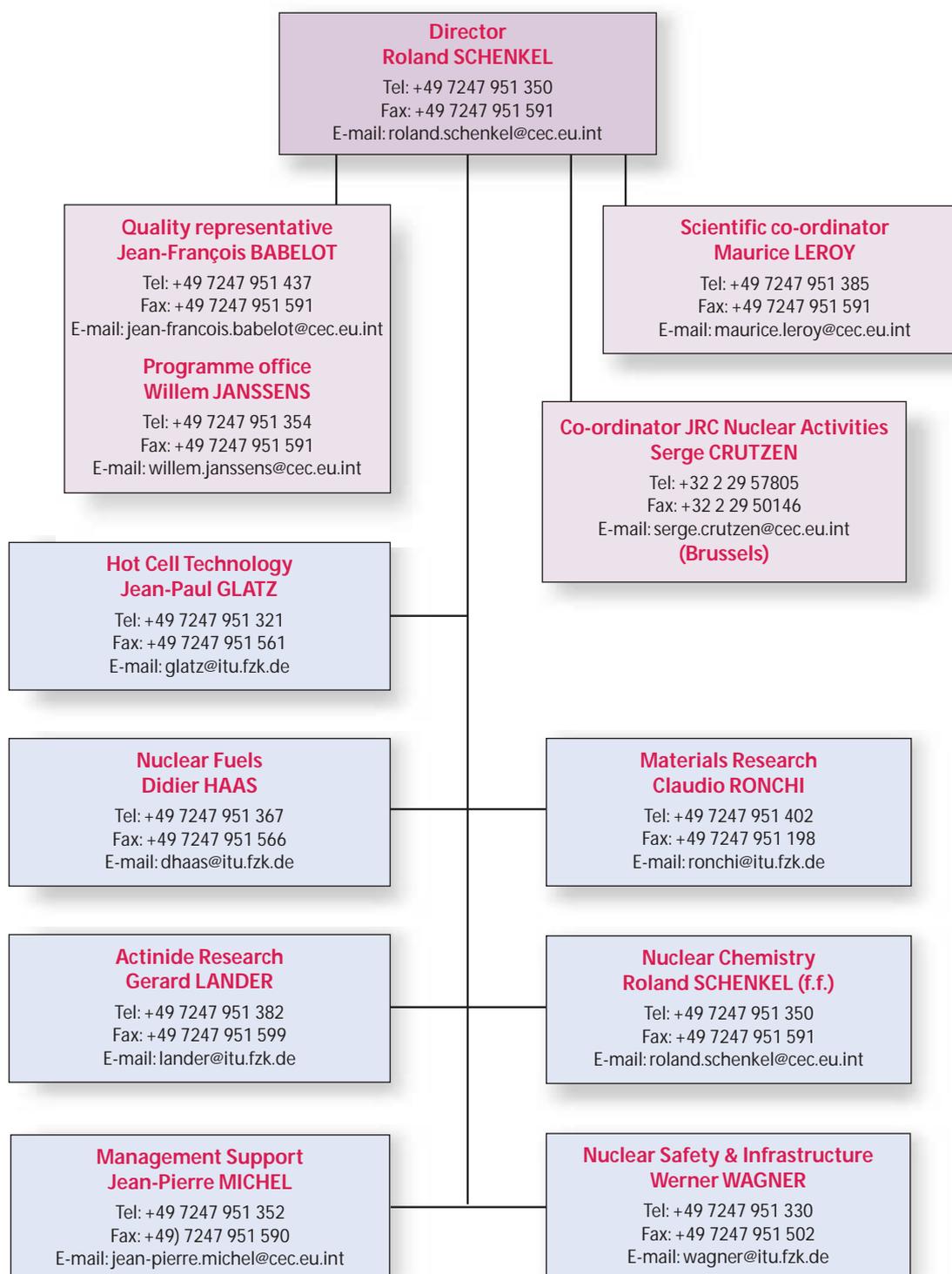
The introduction of the new norm gave also the opportunity to train the internal audit team, and to strengthen it with new auditors. The team now comprises 12 auditors. This should reduce the workload on each auditor and contribute to the deployment of the quality culture of ITU within the units. The internal audit method was also changed: it was adapted to the new norm, and made more efficient in terms of definition of the corrective actions.

The benchmarking with two VTT Institutes and the two JRC Institutes IE and IPSC concentrates precisely on the processes, with the aim of an exchange of best practices. The ongoing exercise concerns three processes, namely Competence Management, Customer Relationship, and Communi-

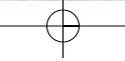
cation and Knowledge Sharing. The Institute participates also in the JRC benchmarking group, involving more external partners, and concerning the key performance indicators, i.e. more the JRC output than the processes themselves. Both benchmarking activities are complementary to each other.

The review of the ITU processes continued. Working sessions were organized with the process owners, actors and customers to clarify the individual steps of the different processes, and the responsibilities at all levels. It was the opportunity to discuss the proposed process performance indicators, and to include the collection of data in the procedures. As a follow-up of the benchmarking on processes with VTT, special attention was given to the process Competence Management, an important element of the ITU strategy. The detailed information produced during these process review meetings is incorporated into a QM software installed on the ITU internal network, which will be accessible to all staff in the first half of 2002.

## Organisation Chart of the Institute



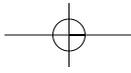
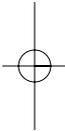
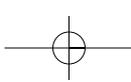
January 2002



# PROJECTS



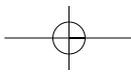
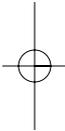
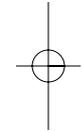
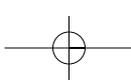
*itu*  
Institute for  
Transuranium  
Elements



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# 1. Alpha-Immunotherapy

## Introduction

To selectively kill cancer cells, alpha-immunotherapy uses alpha-emitters such as  $^{213}\text{Bi}$  and  $^{225}\text{Ac}$  that are linked, through a bifunctional chelator, to specific carriers. ITU scientists have developed several methods to produce  $^{225}\text{Ac}$  (and  $^{213}\text{Bi}$ ) for preclinical and clinical use (TUAR-2000, p. 55-61). Today our challenge is extended to harness also other  $\alpha$ -emitters, which might be beneficial for the treatment of cancer and to learn more about behavior and biological effects of these radionuclides.

## 1.1 Preclinical and Clinical Collaboration

Under financing from the European Commission, a Phase I clinical study for Non-Hodgkin's lymphoma (NHL) and other B-cell-malignancies was started in March 2001, in the German Cancer Research Centre (DKFZ) in Heidelberg, in collaboration with ITU and the University Hospitals of Heidelberg and Düsseldorf (both Germany), Ghent (Belgium) and Hasselt (Belgium). The preclinical work was carried out in the different institutes and ITU contributed to the development and testing of the chelates for coupling Bi to the antibodies and proving the efficacy of the  $^{213}\text{Bi}$  labelled construct on relevant cell lines. In the DKFZ the *in vivo* stability of the  $^{213}\text{Bi}$  -CHX-A"-CD19 and -CD20 radioimmunoconjugate was proven and the toxicity in mice was evaluated. The data indicated that the radioimmunoconjugates are expected to be both safe and very effective, due to the high cytostatic (cell killing) potency of the alpha-emitter. Since April 2001 nine B-cell-malignancies patients from three different German hospitals have been treated at three

dose-levels (15, 30 mCi and 45 mCi of  $^{213}\text{Bi}$ ). The higher dose level will be applied in the near future and an extension of the application to other centers, such as the University Hospital in Düsseldorf, is planned. Tab. 1.1 presents the summary of the clinical trials with bismuth-213, to which ITU has contributed.

## 1.2 Effects of the Lysine for Kidney Protection

Only few chelates with bismuth proved to be stable *in vivo*: CHXA-DTPA and DOTA. The use of DOTA is limited for peptides, due the slow binding kinetic at room temperature. When  $^{213}\text{Bi}$  is coupled to mAbs using benzyl-DTPA chelates the Bi accumulation in the kidneys is very high. Lysine (an amino acid) protection is used with radiolabelled peptides and Fab-fragments to prevent the accumulation of radiolabelled immunoconjugates in the kidneys. In collaboration with the department of Nuclear Medicine from Technische Universität, München we studied lysine protection against bismuth accumulation in the kidneys when benzyl-DTPA chelate was used for conjugating  $^{213}\text{Bi}$  on the antibodies.

The mice were injected intraperitoneal several times during the study with different concentrations of lysine solution to protect the kidneys from bismuth accumulation. The  $^{213}\text{Bi}$  labelled benzyl-DTPA-6H8 antibody was injected into mice and mice were sacrificed at different time points and the amount of  $^{213}\text{Bi}$  was determined from selected tissues by a gamma counter. When  $^{213}\text{Bi}$  labelled benzyl-DTPA antibody was administrated without lysine protection, already in 15 minutes there was a clear  $^{213}\text{Bi}$  accumulation in the kidneys. In one hour the kidney activity reached 55% of the injected dose per gram of tissue. Simultaneously the activity in the blood was decreased from 30% to 10%. When lysine protection is used, the bismuth accumulation in the kidneys was decreased from 55% down to 20% of injected dose per

	Memorial Sloan-Kettering Cancer Center (USA)	Deutsches Krebsforschungszentrum (Germany)	Kantonsspital Basel (Switzerland)
Year	1996 - 1999	2001	2001
Disease	Myeloid leukemia	B-cell malignancies	glioblastoma
Carrier molecule	CD-33	CD-20	Substance-P, Octreotide (somatostatin analogue)
Number of patients	18	9	2
Dose levels	16 - 95 mCi	10 - 45 mCi	12 - 30 mCi
Future	Phase I/IIa (ongoing)	Dose increase (2002)	Pilot trial (2002)

Tab. 1.1  
Clinical trials  
with bismuth-213

## Projects

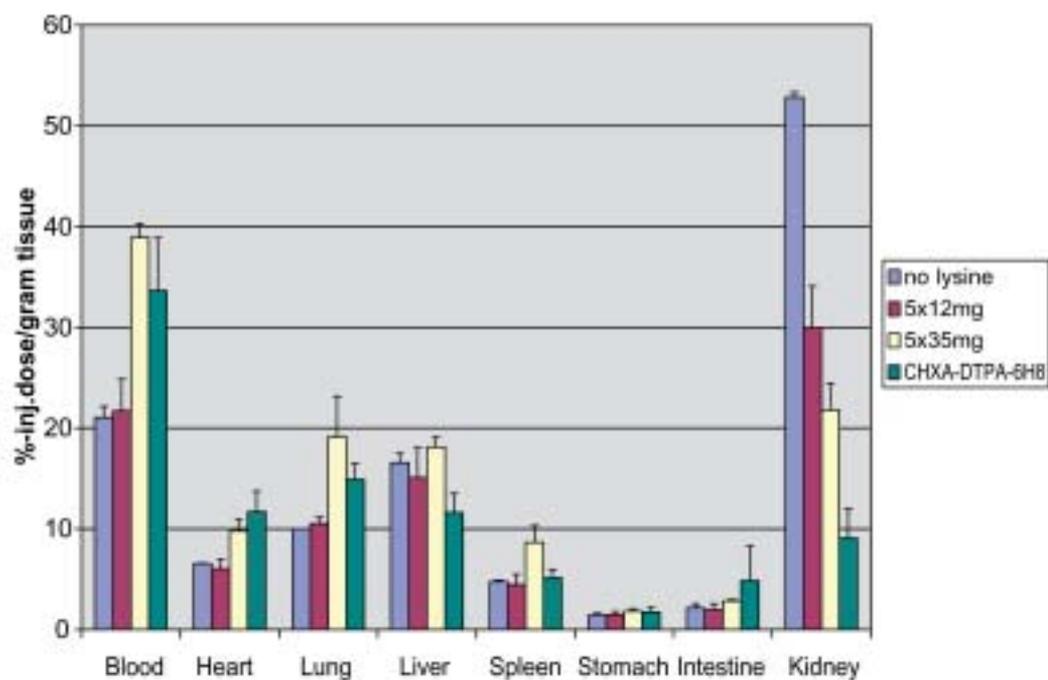


Fig. 1.1  
Biodistribution of  $^{213}\text{Bi}$ -Benzyl-DTPA-6H8+lysine 5x0, 12, 35 mg  
1h after injection

gram tissue after one hour (Fig. 1.1) and simultaneously the activity in the blood circulation is increased twofold. In comparison  $^{213}\text{Bi}$ -CHXA-DTPA-6H8 activity in the kidneys is still clearly lower. It shows that lysine does not fully protect bismuth accumulation in the kidneys. There was no significant difference between  $^{213}\text{Bi}$  acetate with or without lysine protection.

When the blood samples were analyzed in more detail using protein-G beads, the radioactivity bound on the antibody was increased from 66% to 81% of the total radioactivity in the serum.

The data suggest that lysine prevents either competition of the other metals with bismuth *in vivo* or prevents metallothionein-like proteins to accumulate in the kidneys. Because of the short half-life of  $^{213}\text{Bi}$  (45 min),  $^{213}\text{Bi}$  labelled peptides and Fab-fragments are required for fast localisation on the tumour. Already, small changes on the structure of the chelated peptides might destroy their capability to bind to the target receptors. The observation that lysine also protects Bi accumulation in the kidneys supports the use of the existing peptides carrying DTPA chelate for alpha-radioimmunotherapy.

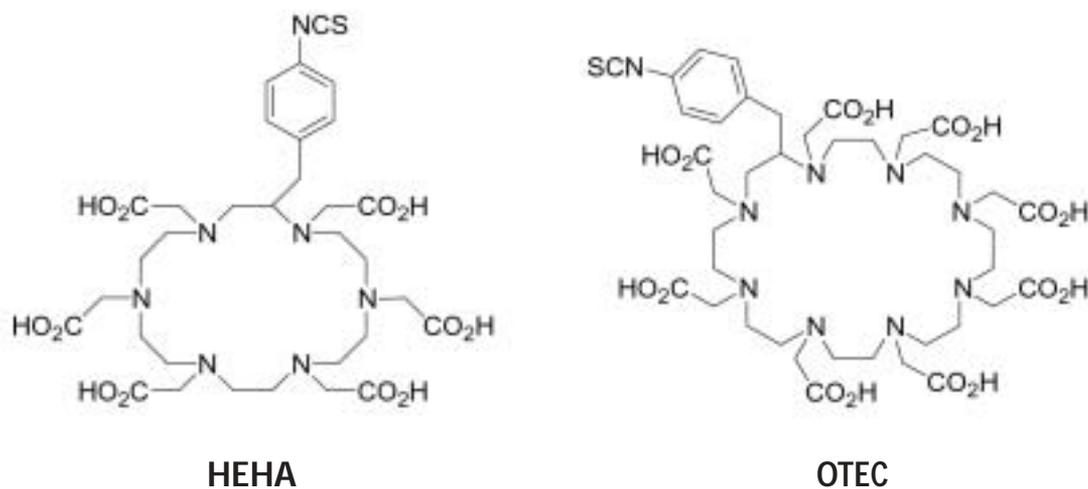


Fig. 1.2  
The structure formula of HEHA and OTEC

### 1.3 Chelators

In order to bind a radionuclide to a vector it is necessary to use bifunctional chelating agents (BCA) that have two specific sites. One site is to be coupled to the vector and the other has to form very stable complexes with the radionuclide to be used.

To achieve that for the coupling of  $^{225}\text{Ac}$ , we prepared the HEHA (Fig. 1.2) compound which is functionalised on the cycle by either an isothiocyanate termination for future covalent bonding to biomolecules or any activated linker ready for coupling reaction. It was also found that OTEC (Fig. 1.2) appeared to be a good chelating agent of  $^{225}\text{Ac}$ , and the synthesis of the compound is in progress. HEHA was patented and a patent application on OTEC has been filed.

### 1.4 Separation of $^{223}\text{Ra}$

Based on its decay characteristics,  $^{223}\text{Ra}$  may be the most suitable radium isotope for targeted therapy of cancer.

$^{223}\text{Ra}$  ( $t_{1/2}=11.4$  days) is generated from the decay of  $^{227}\text{Th}$  ( $t_{1/2}=18.7$  days) which again is a product of the decay of  $^{227}\text{Ac}$  ( $t_{1/2}=21.77$  years).  $^{227}\text{Ac}$  can be produced through thermal neutron irradiation of  $^{226}\text{Ra}$  in a nuclear reactor [1]. For the chemical separation of radium and thorium from actinium in the kBq range, several methods have been reported [2].

In our case, however, approx.  $600\ \mu\text{g}$  ( $=43.7\ \text{mCi} = 1.61 \times 10^5\ \text{kBq}$ ) of  $^{227}\text{Ac}$  were used as source for the isolation of  $^{223}\text{Ra}$

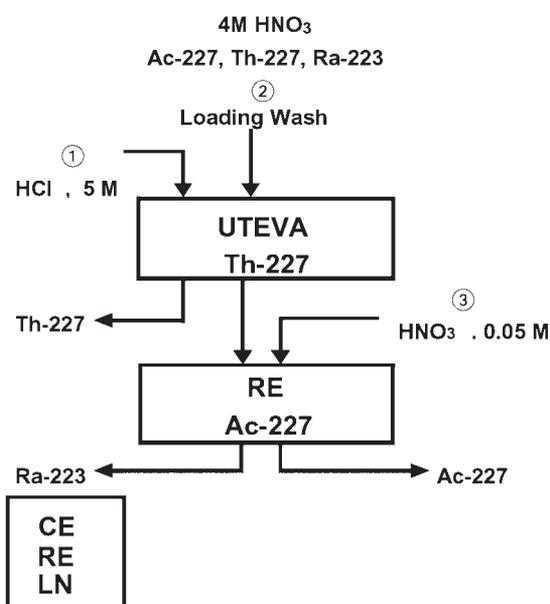


Fig. 1.3 Separation of  $^{223}\text{Ra}$  from  $^{227}\text{Ac}$  and  $^{227}\text{Th}$

and  $^{227}\text{Th}$ . Due to strong radiolysis effects the construction of a generator column for  $^{223}\text{Ra}$  as in [2] is not possible. It is necessary to strip actinium and thorium of the column after the separation procedure for subsequent reuse if required. Fig. 1.3 shows the newly developed separation method for actinium, thorium and radium.

A column filled with UTEVA is linked to another column with RE-resin. Thorium is retained on the first column from 4 M  $\text{HNO}_3$  solution; actinium is extracted on the second column, while radium is eluted. Subsequently thorium is recovered from UTEVA using 5 M  $\text{HCl}$  and can be reused after 3 weeks to extract newly generated  $^{223}\text{Ra}$ .  $^{227}\text{Ac}$  can be stripped from the RE-resin using diluted acid. After evaporation  $^{223}\text{Ra}$  is further purified using cation exchange (CE), RE-resin (RE) or Ln.spec (LN).

Fig. 1.4 shows the alpha-spectrum of  $^{227}\text{Ac}$  in radioactive equilibrium with its daughter nuclides and the spectra of separated fractions.

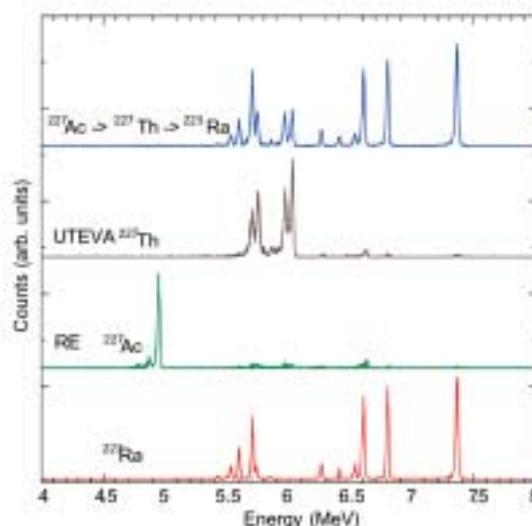


Fig. 1.4 Alpha-spectrum of  $^{227}\text{Ac}$  (equilibrium) and separate fractions ( $^{227}\text{Th}$ ,  $^{227}\text{Ac}$ ,  $^{223}\text{Ra}$ )

#### References

- [1] Gmelin Handbuch der Anorganischen Chemie. Actinium. Suppl. Vol. 1, Springer Verlag (1981) 83
- [2] G. Henriksen, P. Hoff, J. Alstad, R. H. Larsen. Radiochimica Acta 89 (2001) 661-666

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## 2. Basic Actinide Research

### Introduction

Actinide research has as its main goal the understanding of the physics and chemistry of such systems. 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 will now be funded from Brussels for visitors from May 2002 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 Preparation and Characterization

Our central objective is the elucidation of the electronic structures of the actinide metals and compounds, in partic-

ular the behaviour of the 5f-electrons. This goal is experimentally approached by either selective investigations of single compounds or a systematic approach to a whole class of compounds. The activity includes the preparation, characterization, and encapsulation of specific samples directly requested by „customers“, either internal or external.

The progress achieved is divided into two parts. The first one gives an overview of the systems investigated and samples prepared, characterised, and encapsulated for collaborative studies. In the second part we have chosen to highlight one main result achieved in 2001.

#### 2.1.1 Compounds and alloys synthesis: Overview 2001

To give here an exhaustive listing of the 59 new samples prepared and 126 samples characterised would be a tedious exercise. Indeed, the preparation and characterization processes often only finds fulfilment when either a full system is completed (e.g. see next part 2.1.2) or when the physical properties of the compounds show new phenomena. We limit the present part to a summary of the main systems investigated and the underlying motivations.

Complementing the work presented in 1999 and 2000 [1], we continued our efforts on the single crystal growth of NaCl type compounds, and the chemical transport reaction crystal growth of mixed oxides. New pseudo-binary PuSb single crystals respectively doped with  $Y^{3+}$  or  $Th^{4+}$  were obtained. Single crystals of  $(U_{1-x}Pu_x)O_2$  and  $(Th_{1-x}U_x)O_2$  mixed dioxides were grown. Attempts to apply this growth technique to other oxides, i.e.  $U_3O_8$ , were also successfully conducted.

In the frame of our investigation of large isostructural ternary intermetallic families,  $(U_{1-x}Np_x)_2Rh_2Sn$  solid solutions were synthesised and characterised. The 2.2.1 ternary intermetallic compounds  $(An_2T_2X)$  with An = actinide, T = d-transition metal and X = In, Sn) display a wide range of magnetic properties, thus offering the possibility to follow the evolution of key characteristics along the series. An extended discussion of their electronic properties is proposed in section 2.2.2 and their crystallographic characterization summarised in Tab. 2.1.

Beside these main investigations, exploratory research started on the synthesis of new ternary intermetallic compounds ( $NpFe_4Al_8$ ,  $UNiGe_3$ ,  $(U,Np)Rh_yGe_{2-x}$ ,  $Np_3MoGe_5$ ).

To conclude this overview, we should emphasise that our capability to obtain pure and well-characterised new phas-

Compound	Structure type (Space Group)	Lattice parameters (Å)		An-An distance (Å)
		a	c	
U <sub>2</sub> Rh <sub>2</sub> Sn	U <sub>3</sub> Si <sub>2</sub> (P4/mbm)	7.529(1)	3.630(1)	3.630
(U <sub>0.75</sub> Np <sub>0.25</sub> ) <sub>2</sub> Rh <sub>2</sub> Sn		7.521(1)	3.641(1)	3.641
(U <sub>0.5</sub> Np <sub>0.5</sub> ) <sub>2</sub> Rh <sub>2</sub> Sn		7.514(1)	3.651(1)	3.651
(U <sub>0.25</sub> Np <sub>0.75</sub> ) <sub>2</sub> Rh <sub>2</sub> Sn		7.507(1)	3.662(1)	3.662
(U <sub>0.1</sub> Np <sub>0.9</sub> ) <sub>2</sub> Rh <sub>2</sub> Sn		7.499(1)	3.665(1)	3.665
(U <sub>0.05</sub> Np <sub>0.95</sub> ) <sub>2</sub> Rh <sub>2</sub> Sn		7.494(1)	3.667(1)	3.667
Np <sub>2</sub> Rh <sub>2</sub> Sn		7.500(1)	3.673(1)	3.673

Tab. 2.1  
Crystallographic parameters  
of the (U<sub>1-x</sub>Np<sub>x</sub>)<sub>2</sub>Rh<sub>2</sub>Sn series of  
compounds

es is essential to sustain ITU's worldwide reputation in actinide research and a key factor to maintain and generate scientific collaborations. This is illustrated through the 94

samples prepared and encapsulated for various physical properties measurements performed in house or in external institutions in collaborative studies as listed in Tab. 2.2.

Tab. 2.2 Samples prepared, characterised and encapsulated in 2001 for the indicated measurements

Measurements	Laboratories	Compounds	Form
Mössbauer Spectroscopy	ITU-Karlsruhe	Np <sub>5</sub> Ge <sub>4</sub> , Np <sub>3</sub> Ge <sub>5</sub> , Np <sub>5</sub> Ge <sub>3</sub> , NpGe, Np <sub>3</sub> Si <sub>2</sub> , Np <sub>2</sub> Mo <sub>3</sub> Ge <sub>4</sub> , Np <sub>2</sub> Nb <sub>3</sub> Ge <sub>4</sub> , Np <sub>2</sub> Nb <sub>3</sub> Si <sub>4</sub> , (U <sub>0.1</sub> Np <sub>0.9</sub> ) <sub>2</sub> Rh <sub>2</sub> Sn	P
		(U <sub>0.05</sub> Np <sub>0.95</sub> )O <sub>2</sub> , (U <sub>0.95</sub> Np <sub>0.05</sub> )O <sub>2</sub>	G-SC
Neutron Scattering	ILL-Grenoble Brookhaven Nat. Lab.	NpP UO <sub>2</sub>	SC
Magnetism	ITU-Karlsruhe	Np <sub>2</sub> Rh <sub>2</sub> (Sn <sub>0.5</sub> In <sub>0.5</sub> ), (U <sub>1-x</sub> Np <sub>x</sub> )Rh <sub>2</sub> Sn (x=0.9, 0.75, 0.5), Np <sub>2</sub> Mo <sub>3</sub> Ge <sub>4</sub> , Np <sub>2</sub> Nb <sub>3</sub> Si <sub>4</sub>	AcM
		Pu <sub>1-x</sub> Am <sub>x</sub> (in collaboration with CEA-Valduc)	AcM
		(U <sub>1-x</sub> Np <sub>x</sub> )O <sub>2</sub> (x= 0.95, 0.55, 0.25, 0.05), (U <sub>1-x</sub> Pu <sub>x</sub> )O <sub>2</sub> (x=0.05, 0.30, 0.40, 0.80, 0.95, 0.985, 1), (U <sub>0.54</sub> Pu <sub>0.41</sub> Np <sub>0.05</sub> )O <sub>2</sub> , NpSi, USb, UGe <sub>2</sub> , UGe <sub>2-x</sub>	SC
		NpP (in collaboration with CEA-Grenoble)	SC
		USb, (Pu <sub>0.9</sub> Y <sub>0.1</sub> )Sb, (Pu <sub>0.8</sub> Y <sub>0.2</sub> )Sb (for high-temperature measurements)	SC
		UN UPdSiH <sub>x</sub> , UCoAlH <sub>x</sub> , (U <sub>0.5</sub> Th <sub>0.5</sub> )RhAl (In collaboration with Charles Univ.-Prague)	TF P
Optical spectroscopy Dissolution mechanism	CEA-Saclay Univ. Paris-Sud	ThO <sub>2</sub> , UO <sub>2</sub> , CeO <sub>2</sub>	SC
Thermophysical properties	ITU-Karlsruhe	<sup>242</sup> PuO <sub>2</sub>	P
NMR-spectroscopy	Univ. Liège	CmO <sub>x</sub>	P
Pyrometallurgy	ITU-Karlsruhe	Am, Pu metals, UPuZrREAm <sub>2</sub>	P
Surface Science Photoelectron spectroscopy	ITU-Karlsruhe Los Alamos Nat. Lab.	Pu, Th metals	P
		PuSb, PuS, PuTe	SC
Magnetic X-ray Scattering	ESRF-Grenoble	NpO <sub>2</sub> , UO <sub>2</sub> , (U <sub>1-x</sub> Pu <sub>x</sub> )O <sub>2</sub>	SC
High-Pressure X-ray Diffraction	ITU-Karlsruhe	ThO <sub>2</sub> , UO <sub>2</sub>	SC
		GdSi, ThSi, UN, Pa-metal, UGe <sub>2</sub>	P
			P
High-Pressure Resistivity	ITU-Karlsruhe	NpTe, NpSe	SC
		U <sub>5</sub> Ge <sub>4</sub> , UGe <sub>2-x</sub>	AcM
Reference Materials (Mass spectrometry)	JRC-IRMM-Geel	UPt <sub>3</sub> , UPt <sub>5</sub> , URu <sub>3</sub> , UIr <sub>3</sub> , UIr <sub>5</sub>	AcM

AcM = arc melting, SC = single crystal, P = powders, polycrystalline sample, G-SC = grinding single crystals, TF = thin films

## Projects

### 2.1.2 Structural Chemistry of the Neptunium-Silicon binary system

It is known that the electronic properties of intermetallic compounds are very sensitive to structural disorder and homogeneity. For a proper understanding of these effects, a detailed knowledge of the phase relations is required. However, few systems have been studied in the conditions of high purity as required to compare with theory and even, as recently shown for widely studied U-systems, the binary systems themselves are not correctly known. For the transuranium system almost nothing is known. In this frame we have recently reinvestigated the complete Np-Ge binary system [1 and TUAR-2000], establishing 5 new binary phases. Following this work, and taking into account the considerable attention paid to the metal-rich silicides of uranium, we have extended our interest to the binary neptunium-silicon system.

The Np-Si binary phase diagram was reinvestigated and X-ray diffraction measurements performed over the whole composition range of this system. The phase diagram is characterised by 6 different phases, whereas only 3 were previously reported in the literature. The existence and the crystal structure of  $\text{NpSi}_3$  (AuCu<sub>3</sub> type) and of the binary

richest in neptunium  $\text{Np}_3\text{Si}_2$  ( $\text{U}_3\text{Si}_2$  type) were confirmed. The  $\text{ThSi}_2$  type compound was also confirmed but a slight defect found on the silicon site, as often observed in the rare-earth or actinide systems with silicon and germanium. For the first time, a hexagonal  $\text{AlB}_2$  type compound was isolated, showing a larger silicon defect than the  $\text{ThSi}_2$ -type previously determined. A new phase forming a 1:1 (NpSi) composition and showing a polymorphic transformation was also observed and isolated. In this last phase, a primitive orthorhombic FeB type structure (as commonly observed in the rare-earth systems), and an original C-centred orthorhombic type structure were obtained depending on the annealing process. Tab. 2.3 displays the results obtained from a Rietveld-type profile refinement method of the X-ray diffraction patterns of the sample prepared.

One may notice that the lattice parameters seem to vary depending on the sample. The characterization of the phases was performed on as-cast samples. The variations can be understood as resulting from structural disorder (defects) rather than due to the presence of a finite homogeneity domain, as for each identical phase its volume remains constant. The various crystallographic structures are shown in Fig 2.1.

Tab. 2.3 Samples prepared in the Np-Si binary system and their crystallographic parameters

Sample Composition (in at.%)	Phase(s) obtained	Structure Type	Space Group	Unit Cell Parameters (Å)			
				a	b	c	Volume (Å <sup>3</sup> )
$\text{Np}_{25}\text{Si}_{75}$	$\text{NpSi}_3$	AuCu <sub>3</sub>	Pm3m	4.0248(2)			65.20
	$\text{NpSi}_{2-x}$	$\text{ThSi}_2$	$I4_1/\text{amd}$	3.9558(4)		13.761 (1)	215.33
$\text{Np}_{33.3}\text{Si}_{66.7}$	$\text{NpSi}_3$	AuCu <sub>3</sub>	Pm3m	4.0318(9)			65.54
	$\text{NpSi}_{2-x}$	$\text{ThSi}_2$	$I4_1/\text{amd}$	3.9589(2)		13.7386(8)	215.32
$\text{Np}_{36.7}\text{Si}_{63.3}$	$\text{NpSi}_{2-x}$	$\text{AlB}_2$	P6/mmm	3.8476(3)		4.0947(4)	52.49
$\text{Np}_{37.5}\text{Si}_{62.5}$	$\text{NpSi}_{2-x}$	$\text{AlB}_2$	P6/mmm	3.8557(2)		4.0836(3)	52.57
$\text{Np}_{40}\text{Si}_{60}$	$\text{NpSi}_{2-x}$	$\text{AlB}_2$	P6/mmm	3.8486(3)		4.0871(4)	52.42
	NpSi	FeB	Pnma	7.7868(4)	3.8356(4)	5.6585(6)	169.00
$\text{Np}_{50}\text{Si}_{50}$	NpSi	FeB	Pnma	7.7935(5)	3.8386(2)	5.6625(4)	169.40
		NpSi	Cmcm	4.2207(5)	12.625 (2)	6.3123(9)	336.35
$\text{Np}_{55.6}\text{Si}_{44.4}$	NpSi	FeB	Pnma	7.7943(5)	3.8400(2)	5.6646(4)	169.54
	$\text{Np}_3\text{Si}_2$	$\text{U}_3\text{Si}_2$	P4/mbm	7.404 (2)		3.970 (2)	217.63
$\text{Np}_{60}\text{Si}_{40}$	$\text{Np}_3\text{Si}_2$	$\text{U}_3\text{Si}_2$	P4/mbm	7.4236(1)		3.9379(1)	217.01

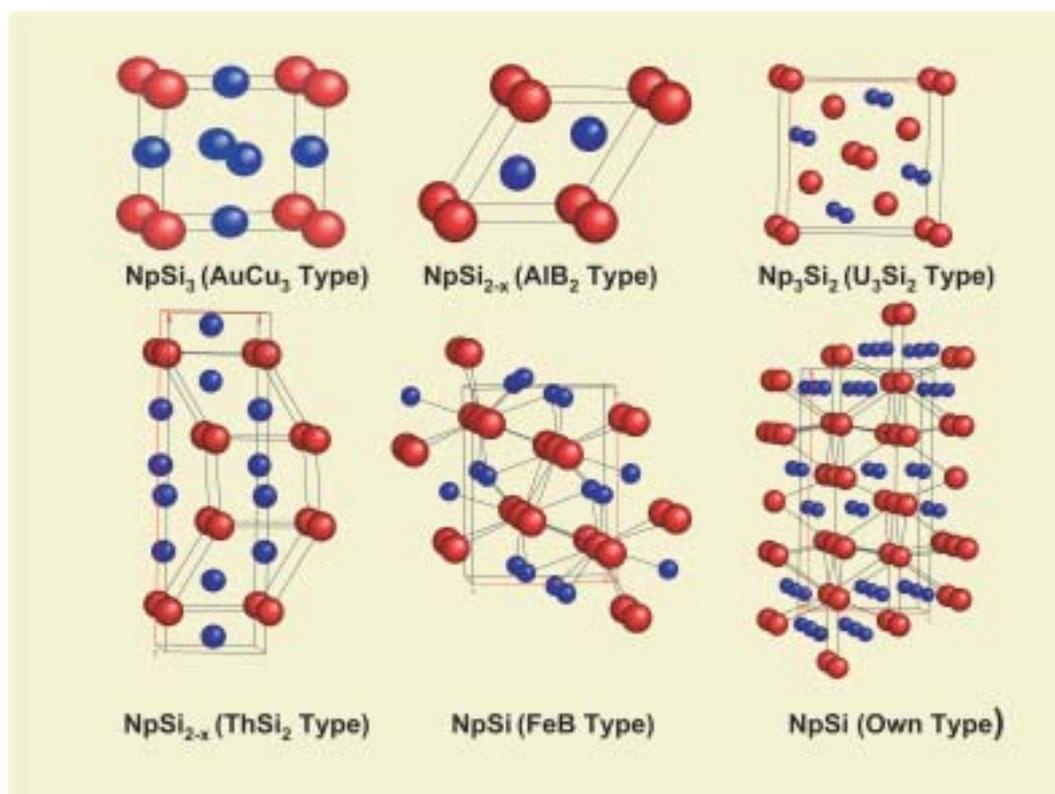


Fig. 2.1 Crystallographic structure of the various phases identified in the Np-Si system (Np atoms in red, Si atoms in blue)

Tab. 2.4 Comparison of the crystallochemistry of the uranium, neptunium and plutonium silicon systems

Stoichiometry	Structure Type (Space Group)	Uranium	Neptunium	Plutonium
1:3	AuCu <sub>3</sub> (Pm3m)	USi <sub>3</sub>	NpSi <sub>3</sub>	Not observed
1:2	ThSi <sub>2</sub> (I4 <sub>1</sub> /amd)	USi <sub>2-x</sub>	NpSi <sub>2-x</sub>	PuSi <sub>2-x</sub>
	AlB <sub>2</sub> (P6/mmm)	USi <sub>2-x</sub>	NpSi <sub>2-x</sub>	PuSi <sub>2-x</sub>
1:1	FeB (Pnma)	Not observed	NpSi	PuSi
	USi (I4/mmm)	USi	Not observed	Not observed
	NpSi (Cmcm)	-	NpSi	-
5:4	U <sub>5</sub> Si <sub>4</sub> (P6/mmm)	U <sub>5</sub> Si <sub>4</sub>	Not observed	Not observed
3:2	U <sub>3</sub> Si <sub>2</sub> (P4/mbm)	U <sub>3</sub> Si <sub>2</sub>	Np <sub>3</sub> Si <sub>2</sub>	Pu <sub>3</sub> Si <sub>2</sub>
5:3	W <sub>5</sub> Si <sub>3</sub> observed	Not observed	Not	Pu <sub>5</sub> Si <sub>3</sub>
3:1	AuCu <sub>3</sub> (anti) (Pm3m)	U <sub>3</sub> Si	Not observed	Not observed

To complete our An-Si binary system investigation, the Pu-Si system was also reinvestigated. In this system, all previously reported phases could be obtained and no new phases were identified. To conclude this part, a comparison of the crystallochemistry of the U-, Np-, Pu-Si is summarised in the Tab. 2.4.

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### 2.2 Solid State Physics Studies

The investigation of the basic physical properties is the first step to elucidate the electronic structure of actinide metals and compounds. Our main goal is to use the in-house facilities developed in the last decade to provide a first characterization of the physical properties of new systems obtained, and then to select the most interesting for further studies involving different research efforts, for example synchrotron and neutron scattering.

Some of the results obtained in 2001 are highlighted in the following sections.

#### 2.2.1 "The Actinide User Laboratory"

Since many laboratories are now unable to work with transuranium elements (and sometimes not even with uranium), we have undertaken to develop in-house facilities for solid-state studies on transuranium compounds. These facilities are open to external users in the frame of a "User's laboratory" and complement the preparation and characterization part of our effort. The principal methods involve Mössbauer spectroscopy, transport (resistivity), magnetic measurements at cryogenic or elevated temperatures (from 2 K to 800 K) and photoelectron spectroscopy. In 2001, an average of 20% of our experimental machine time was devoted to external users both within the frame of internal programmes involving external collaborations, or specific requests from external users (see also previous section).

It should be highlighted that in 2001, our laboratory was selected as a user facility to participate in the: European Community-Access to Research Infrastructures action of the Improving Human Potential Programme (IHP) which supports access to our actinide facility for the selected users teams, travel and subsistence fees of visiting scientists. The duration of the contract is 28 months (to start early 2002). The programme is open to EC users and to scientists of the associated states (details may be found on ITU's website, Actinide User Laboratory).

#### 2.2.2 $^{237}\text{Np}$ Mössbauer investigations of $(\text{U}_{1-x}\text{Np}_x)_2\text{Rh}_2\text{Sn}$

The study of magnetic and electronic properties of large isostructural compounds families offers the possibility to follow the evolution of key characteristics along the series, as well as to identify general trends and better understand the underlying physics. Among the ternary intermetallic family  $\text{An}_2\text{T}_2\text{X}$ ,  $\text{U}_2\text{Rh}_2\text{Sn}$  and  $\text{Np}_2\text{Rh}_2\text{Sn}$  exhibit a peculiar and unexpected behaviour: whereas  $\text{U}_2\text{Rh}_2\text{Sn}$  orders at  $T_N \gg 24$  K [1],  $\text{Np}_2\text{Rh}_2\text{Sn}$  does not order magnetically [2]. This contradicts the usual stronger tendency for

5f-moment formation of neptunium compounds compared to their uranium counterparts. In order to shed more light on this surprising result, we investigated the electronic and magnetic properties of  $x = 0.25, 0.50$  and  $0.75$  in  $(\text{U}_{1-x}\text{Np}_x)_2\text{Rh}_2\text{Sn}$  by  $^{237}\text{Np}$  Mössbauer spectroscopy. The spectra recorded at different temperatures, show that both uranium-rich ( $x = 0.25$  and  $x = 0.5$ ) compounds order magnetically around 11 K. Interestingly, the compound with high neptunium content ( $x = 0.75$ ) is also found to order: The lines of the spectrum begin to broaden around 6 K, suggesting the occurrence of magnetic order, confirmed by the spectra recorded at 4.2 K and 1.5 K, where the Np ions carry an average moment estimated as  $m_{\text{Np}} \gg 0.38 m_B$ .

The paramagnetic spectra consist of pure quadrupolar splitting with a non-zero asymmetry parameter arising from the  $m_{2m}$  symmetry of the Np site. The spectra recorded at 4.2 K are more complex to analyse. They display clear hyperfine field splittings – corresponding to magnetic moments up to  $m_{\text{Np}} \gg 1.3 m_B$  – but consist of complex patterns that cannot be fitted assuming only one Np site. The gaussian distribution of hyperfine fields used in the pure  $\text{Np}_2\text{T}_2\text{X}$  compounds [2,3] failed to reproduce the spectra here and we used a free distribution.

As observed in all investigated  $\text{Np}_2\text{T}_2\text{X}$  compounds, the absolute value of the quadrupole interaction parameter  $e^2qQ$  in the  $x = 0.75$  compound is strongly reduced in the magnetic state. This suggests that the Np moments are not parallel to the main principal axis of the electric field gradient (EFG) [2,3]. However, in both the  $x = 0.50$  and  $0.25$  samples the reductions are less, suggesting a rotation of the magnetic moment as  $x$  increases, *i.e.* from the uranium to the neptunium system. The moments of uranium in  $\text{U}_2\text{Rh}_2\text{Sn}$  are parallel to the  $c$ -axis, which constitutes an exception to the rule that  $f$  moments should point perpendicularly to the shortest  $f$ - $f$  bond distance [1]. If we assume that U moments in  $\text{U}_2\text{Rh}_2\text{Sn}$  point in the same direction as Np moments in  $x = 0.25$ , we infer the direction of the EFG main principal axis – not known from symmetry considerations in  $\text{An}_2\text{T}_2\text{X}$  compounds – to be parallel to  $c$ . This information is thus an indication that Np moments in magnetically ordered  $\text{Np}_2\text{T}_2\text{X}$  compounds tend to be oriented within the basal plane of the tetragonal structure, in one of the configurations allowed by symmetry. On the other hand, the isomer shift – affected by the delocalisation of 5f-electrons – decreases with  $x$ , as magnetic order weakens and finally disappears in the  $(\text{U}_{1-x}\text{Np}_x)_2\text{Rh}_2\text{Sn}$  compounds, pointing out the key role of hybridisation in the magnetic properties of this system. Indeed, the isomer shift versus Np-Np spacing varies widely over the  $\text{Np}_2\text{T}_2\text{Sn}$  series (see Fig. 2.2).

The three compounds which exhibit magnetic order at low temperature ( $T = \text{Pd, Pt and Ni}$ ) are situated on a straight line

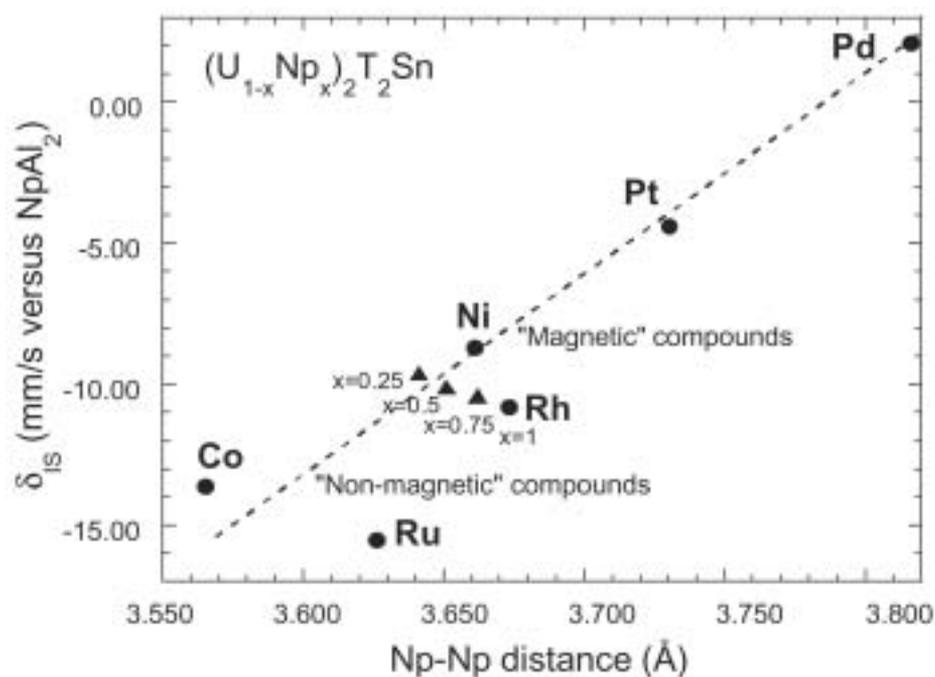


Fig. 2.2  
Isomer shift versus the Np-Np distance in  $Np_2T_2Sn$  (circles) and  $(U_{1-x}Np_x)_2Rh_2Sn$  (triangles) compounds. The bold letters represent the T element.

whereas the non-ordering compounds ( $T = Rh, Ru$  and  $Co$ ) deviate. The linear variation of the isomer shift may be explained by volume effects; the decreasing lattice parameter compressing the 6s shell, and thus increasing the electronic density at the nucleus and lowering the isomer shift. The deviation of non-ordered compounds from the straight line would then arise from varying degrees of hybridisation, as the delocalisation of 5f-electrons lowers the screening of s-electrons, and thus changing the isomer shift.

Our conclusions suggest a non-parallel alignment of U magnetic moments in the small x compositions, arising from the different hybridisation of U and Np 5f-electrons. Such a configuration could be verified by element specific magnetic X-ray scattering.

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## 2.3 Surface Science Studies

### 2.3.1 Photoemission study of actinide nitrides

Among the actinide compounds, nitrides have received special interest recently because of their role as advanced fuels and targets for fast reactors [1] and for the transmutation of Pu and minor actinide elements (Np, Am, Cm) [2]. For example, UN has been considered as nuclear fuel in advanced reactors due to its high melting point ( $\sim 2850^\circ\text{C}$ ), density ( $14.32 \text{ g cm}^{-3}$ ) and thermal conductivity. Knowledge of the thermodynamic properties of actinide nitrides, but also their surface and interface reactivity (corrosion and interdiffusion) is therefore important. All of this is ultimately related to the electronic structure, which can be directly probed by photoemission.

We studied Th [3], U [4] and Pu nitrides, prepared as thin films by reactive sputtering in an  $\text{Ar}/\text{N}_2$  plasma. We investigated the synthesis of the various nitrides, and in particular the question whether higher nitrides ( $\text{AnN}_x$ ,  $x > 1$ ) may be formed by this technique. On a fundamental level, we are interested in the electronic structure of the nitrides, which is part of their characterization. In particular, we concentrate on the issue of localisation of the 5f-electrons as a function of stoichiometry. Photoemission measurements were complemented by XRD characterization of the phases. Fig. 2.3 shows valence band spectra of  $\text{ThN}_x$  films. The nitrogen content was controlled by the  $\text{N}_2$  partial pressure during deposition.

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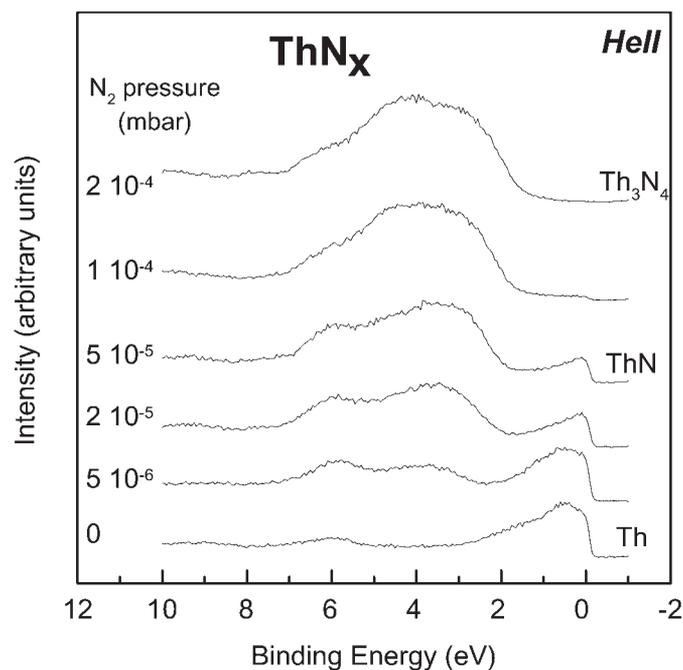


Fig. 2.3 UPS spectra using the Hell line of  $\text{ThN}_x$  as a function of  $\text{N}_2$  partial pressure.

Metallic Th ( $p_{\text{N}_2} = 0$  mbar) shows a broad peak between 0 and 2 eV binding energy (BE), which is attributed to 6d7s conduction band [5]. Th is the only actinide without f-electrons, and can serve as reference material showing the influence of the 6d7s-electrons. With increasing nitrogen pressure, the N-2p valence band grows between 2 and 6 eV BE. Simultaneously the conduction band signal decreases in intensity, due to the transfer of the 6d7s-electrons into Th-N bonds (appearing in the spectra as N-2p band). At ( $p_{\text{N}_2} = 5 \times 10^{-5}$  mbar) ThN is formed, as confirmed by XRD. The density of states (DOS) at the Fermi-level ( $E_F$ ) is reduced, when compared to Th metal. ThN has the golden colour of many transition metal nitrides (e.g. TiN), since the plasma oscillation of the free electrons is screened by the valence band electrons, which shifts the electron plasma frequency to lower energy. At higher nitrogen pressures all 6d7s states are transferred into the N-2p band. The DOS at the Fermi-level drops to zero, and the resulting compound ( $\text{Th}_3\text{N}_4$ ) is an insulator.

Uranium, in contrast to thorium, has 5f-electrons participating in bonding. In metallic uranium, which has a  $5f^3(6d7s)^3$  configuration, the 5f-electrons form a band pinned at  $E_F$  (Fig. 2.4) [5]. With increasing nitrogen concentration, the N-2p valence appears between 2 and 6 eV, but in contrast to Th, the 5f dominated conduction band stays virtually un-

changed. In UN ( $p_{\text{N}_2} = 1 \times 10^{-5}$  mbar) the shape of the 5f band is still similar to U metal. The 5f-electrons stay itinerant, but they are not transferred into the N-2p band. Only at higher nitrogen pressure, when  $\text{U}_2\text{N}_3$  is formed, does the 5f-band change, developing intensity at higher BE. The 5f-states undergo a Mott-Hubbard transition and become partially localised. However  $\text{U}_2\text{N}_3$  still has a DOS at the Fermi-level and thus is a metal.

Plutonium sits at the 5f-localisation threshold, where the 5f-electrons barely participate in bonding. In the metal, the 5f DOS has a maximum right at the Fermi-level, but localisation effects lead to the presence a satellite structure at higher binding energy [6]. In Pu metal, with its  $5f^6(6d7s)^3$  configuration, the 5f signal dominates the photoemission spectrum. Addition of nitrogen immediately affects the 5f band. The maximum at the Fermi-level is suppressed, and the satellite at 1 eV BE becomes a broad maximum. The N-2p peak is less visible than in U (and even less than in Th), because of the large number of f-states, which have a high cross-section in UPS-Hell (Fig. 2.5). Analysis of the surface composition by XPS-core level spectroscopy (N1s/Pu4f intensity ratio) shows that PuN is formed at ( $p_{\text{N}_2} = 1 \times 10^{-5}$  mbar). No higher nitrides could be produced so far by reactive sputtering. Pu seems to show a lower tendency for formation of higher oxidation states than U. This difference in reactivity is already reminiscent of the higher actinide (or rare-earth) behaviour, and can be related to the sensitivity of

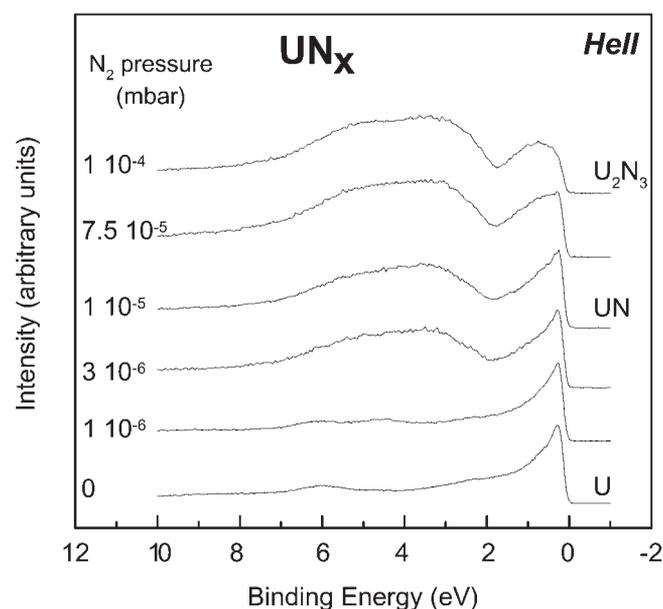


Fig. 2.4 UPS-Hell spectra of  $\text{UN}_x$

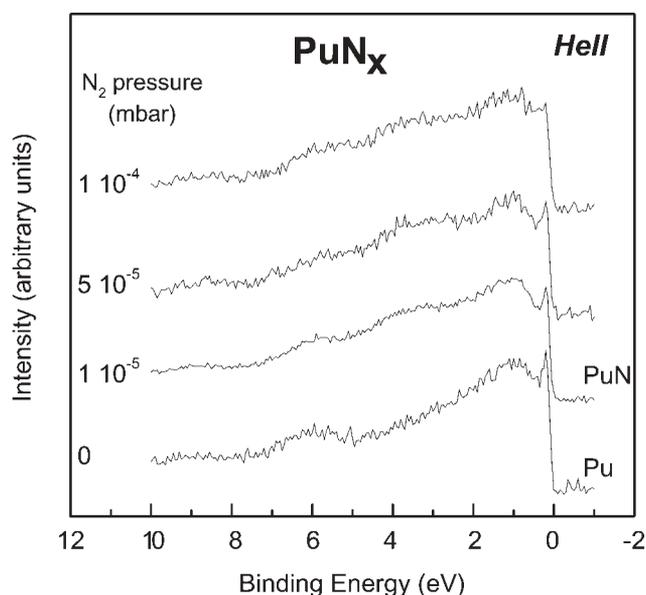


Fig. 2.5 UPS-Hell spectra of  $\text{PuN}_x$

the 5f states to increases in the core potential upon oxidation. The 5f states becomes more localised and further ionisation (necessary for formation of higher oxidation states), becomes more difficult.

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## 2.4 High-Pressure Studies

### 2.4.1 High-pressure resistivity study

This year, two main objectives have been achieved. The first one was to recover resistivity measurement capabilities under pressure on active materials at low temperature (1.5 K). This has been achieved, and a complete phase diagram till 21 GPa on NpTe has been established. The second one was to be able to determine resistance of active materials until very low temperature (0.3 K): this is required to follow the superconductive transition  $T_c$  of Am metal under pressure. This has been also achieved in looking for possible superconductivity of  $\text{UGe}_{2-x}$  under 1 K and also on NpTe.

The main result of NpTe study is that we could correlate the resistivity behaviour with pressure to the expected phase transition around 10 GPa [1]. Moreover, we have been able to follow the antiferromagnetic temperature  $T_N$  when applying pressure: this is another proof of existence of magnetism in this material [2].  $T_N$  decreases rapidly and almost linearly with pressure. Above 7 GPa we were unable to follow the signal. This material exhibits a large hysteresis when increasing and decreasing pressure (see inset). One interesting thing is that in the CsCl phase, NpTe exhibits linear dependence of the resistance with T. A Kondo-like shape of resistance evolves at the transition and we obtain a positive linear contribution (Fig. 2.6). Moreover, under 5 K, a large de-

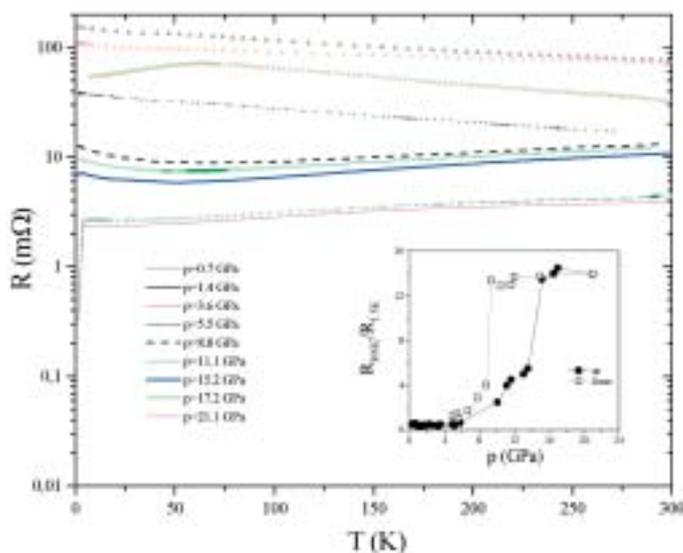


Fig. 2.6 Evolution of resistance of NpTe with pressure. The low-pressure behaviour resembles a semi metal with high resistance, and at high-pressure the resistance is small. The inset shows variation of ratio  $R_{300K}/R_{1.5K}$  with pressure corresponding to NaCl-CsCl phase transition.

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crease of the resistance occurs but it does not go to zero. The shape is close to that observed in UTe under pressure [3], but the T-scale where this phenomenon develops is much smaller (5 K compared to 200 K).

The development of our  $^3\text{He}$  refrigerator device has been used to check the appearance of possible superconductivity in  $\text{UGe}_{2-x}$  under pressure [4]. We have scanned this material from 0.5 to 1.7 GPa down to 0.3 K. We have not observed any indication of superconductivity on this material till 271 mK, nor the  $\text{AT}^2$  Fermi liquid contribution.  $T_C$ , the ferromagnetic transition temperature, evolves rapidly under pressure and, as in  $\text{UGe}_2$  [5], is suppressed above 1.6 GPa.

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### 2.4.2 Structural studies under pressure

The structural behaviour of an  $\text{Am}_{0.5}\text{Cm}_{0.5}$  alloy has been recently investigated at the High-Pressure-ID30 beamline of the ESRF Grenoble. The use of synchrotron radiation, diamond anvil cell and 2D detector has allowed us to collect very high quality diffraction patterns up to pressures of 65 GPa. As for pure Am metal [1,2], we find that the pressure-induced delocalisation of the 5f-electrons in  $\text{Am}_{0.5}\text{Cm}_{0.5}$  occurs in two distinct stages rather than a single step. The initial structure of the alloy was the normal double hexagonal close packed (*dhcp*) form (space group:  $P6_3/mmc$ ) that has been reported as the stable ambient temperature/pressure phase for pure Am and Cm metals. This *dhcp* form started to convert to a face cubic centred (*fcc*) structure (space group:  $Fm\bar{3}m$ ) at about 8 GPa, and the transition was completed by 13 GPa. With additional pressure, we observed that the *fcc* phase transformed around 21 GPa to a face centred orthorhombic (*fco*) structure (space group  $Fddd$ ). This structure, which is the same as the one found for pure Am metal, was observed up to 42 GPa. This third phase exhibits the  $\gamma$ -Pu structure. In Pu, this structure is accepted as reflecting the presence of itinerant 5f-electrons. A fourth phase appeared around 45 GPa and was retained up to 65 GPa, the highest pressure reached during our experiments. This structure is primitive orthorhombic (space

group:  $Pnma$ ,  $Am$  or  $Cm$  on 4c sites  $x, \frac{1}{4}, z$ ). We made Rietveld refinements (Fig. 2.7) using *Fullprof* software, and were able to determine the lattice parameters and the precise position of the atom on the 4c site.

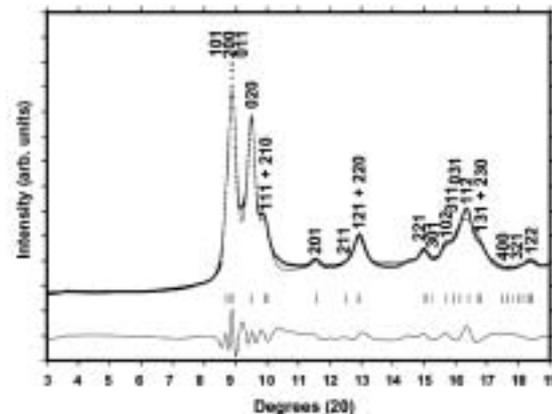


Fig. 2.7 Rietveld fit of the orthorhombic (space group:  $Pnma$ ) fourth phase at 64 GPa ( $\lambda=0.3738 \text{ \AA}$ ) showing the observed (crosses) and calculated (line) diffraction patterns, reflection tick marks, Miller indices, and difference profile.

The Bragg R value for this refinement was 5.16 and  $R_F$  factor 3.44. This was the only structure of the four where the atomic position parameters were not fixed by space group symmetry. As with pure americium, the atomic position parameter  $z$  is stable with pressure, taking values of about 0.11 to 0.13, and not equal to zero, which would lead to the  $\alpha$ -uranium structure.

In (Fig. 2.8) the relative volume ( $V/V_0$  where  $V_0$  is the volume of the *dhcp* phase at normal pressure) is plotted versus pressure.

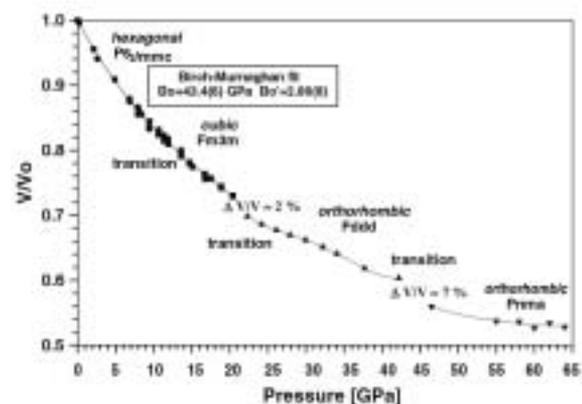


Fig. 2.8 Relative volume of  $\text{Am}_{0.5}\text{Cm}_{0.5}$  alloy as a function of pressure up to 65 GPa

From the figure one can observe the structural changes as described previously. The behaviour of the  $\text{Am}_{0.5}\text{Cm}_{0.5}$  alloy with pressure is very similar to that of pure Am metal. One observes the sequence  $dhcp \rightarrow fcc \rightarrow fco$  ( $\gamma$ -Pu structure)  $\rightarrow$  primitive orthorhombic (distorted  $\alpha$ -U structure). The structural transitions occur, as expected with the addition of curium, at higher pressures than for pure americium metal. Curium metal is expected to require higher pressure for comparable transitions, due to effects from increased  $Z$  and from the stability of having a half-filled 5f-electron orbital. As found with Am metal, two changes in relative volume with pressure are observed with the alloy. The first has a magnitude of  $\sim 2\%$  for the cubic (phase II) to the orthorhombic phase (phase III). The second sharp change, of  $\sim 7\%$ , is found between the orthorhombic-orthorhombic transition (phase III to phase IV). These volume collapses are assigned to the progressive onset of f-electron contribution to the metallic bonding present in the alloy, assumed to represent hybridisation of 5f-electrons with the spd conduction electrons.

The isothermal bulk modulus and its pressure derivative were obtained by fitting the Birch-Murnaghan equation of state to the compression curve of the two first phases (localised 5f-electrons). We found  $B_0=43.4(6)$  GPa and  $B_0'=2.80(8)$ . These values are slightly higher but in line with comparable values calculated for americium metal (29.7 and 3.7) [1,2]. This increase is in accord with expectations that for a series of elements with comparable bonding and structures, the bulk modulus would increase with atomic weight. In the alloy, 50% of the atoms are now curium. We conclude that the delocalisation phenomena involving the 5f-electrons for Am metal and the alloy studied are very similar.

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### 2.4.3 UPtAl and URuGa

Two compounds with the ZrNiAl structure type, URuGa and UPtAl, were also investigated to prove the relation of the assumed 5f bonding directions with the „soft“, *i.e.* more compressible crystal directions. UPtAl with long c-axis (413 pm) has a much shorter U-U spacing in the basal plane. As shown in (Fig. 2.9), we found that the compressibility along the a-axis,  $K_a = 1.50 \times 10^{-3}/\text{GPa}^{-1}$ , exceeds  $K_c = 0.04 \times 10^{-3}/\text{GPa}^{-1}$ , which is a similar type of anisotropy as found in previous

studies for all U (and Th) compounds with this structure type [1]. URuGa represents a rare opposite case - the lattice parameter  $c$  is very short (379 pm), which makes the U-U spacing along  $c$  the shortest, *i.e.* the preferred 5f bonding, direction. Indeed, the compressibility  $K_c = 1.19 \times 10^{-3}/\text{GPa}$  reaches about the same value as  $K_a = 1.55 \times 10^{-3}/\text{GPa}$ , which corroborates the conjecture of the bonding situation distinctly different than in other U compounds with this structure type.

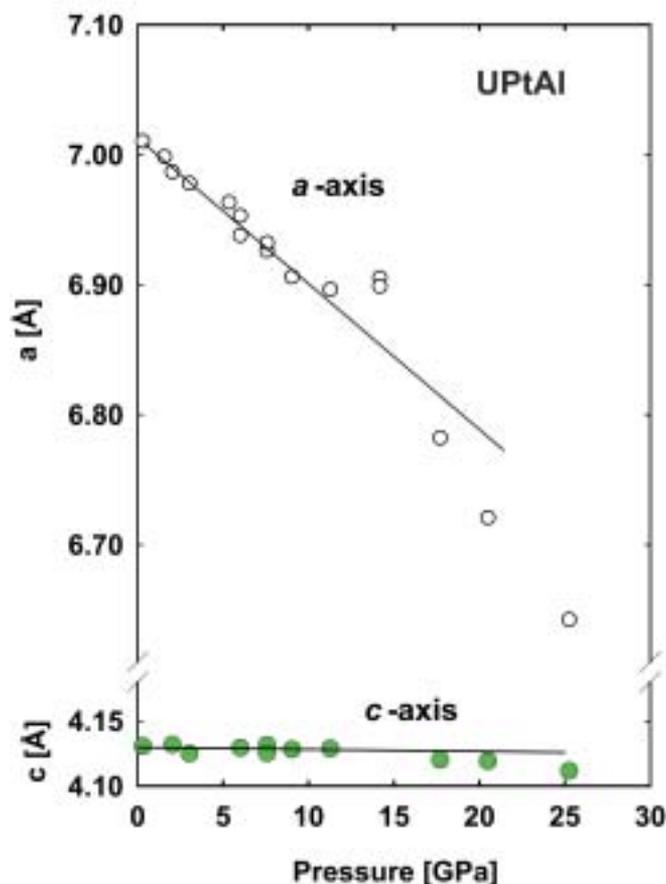


Fig. 2.9 Compressibilities of  $a$  and  $c$  lattice parameters for UPtAl.

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## Projects

### 2.5 Scattering Studies

#### 2.5.1 Neutron scattering investigations

We have this year concentrated on using polarised neutrons, and, in particular performed experiments with the "spherical neutron polarimeter". This instrument analyses the polarisation of the scattered neutrons in experiments and is capable of giving detailed information about the magnetic interactions in solids. An example of using this technique in elastic scattering was our work on the heavy-

fermion superconductor  $\text{UNi}_2\text{Al}_3$ , published in Physical Review B 64, (2001) 134413, where we were able to determine the exact magnetic ground-state configuration, and showed that it remains unchanged when the material becomes superconducting.

We have also used this technique for *inelastic* scattering, which looks at the excitations in solids, to examine the character of the magnetic excitations in  $\text{UO}_2$ . Although the excitations in  $\text{UO}_2$  were first measured in 1968 [1], and there have been many studies subsequently, there remains considerable interest in the problem as the exact nature of the

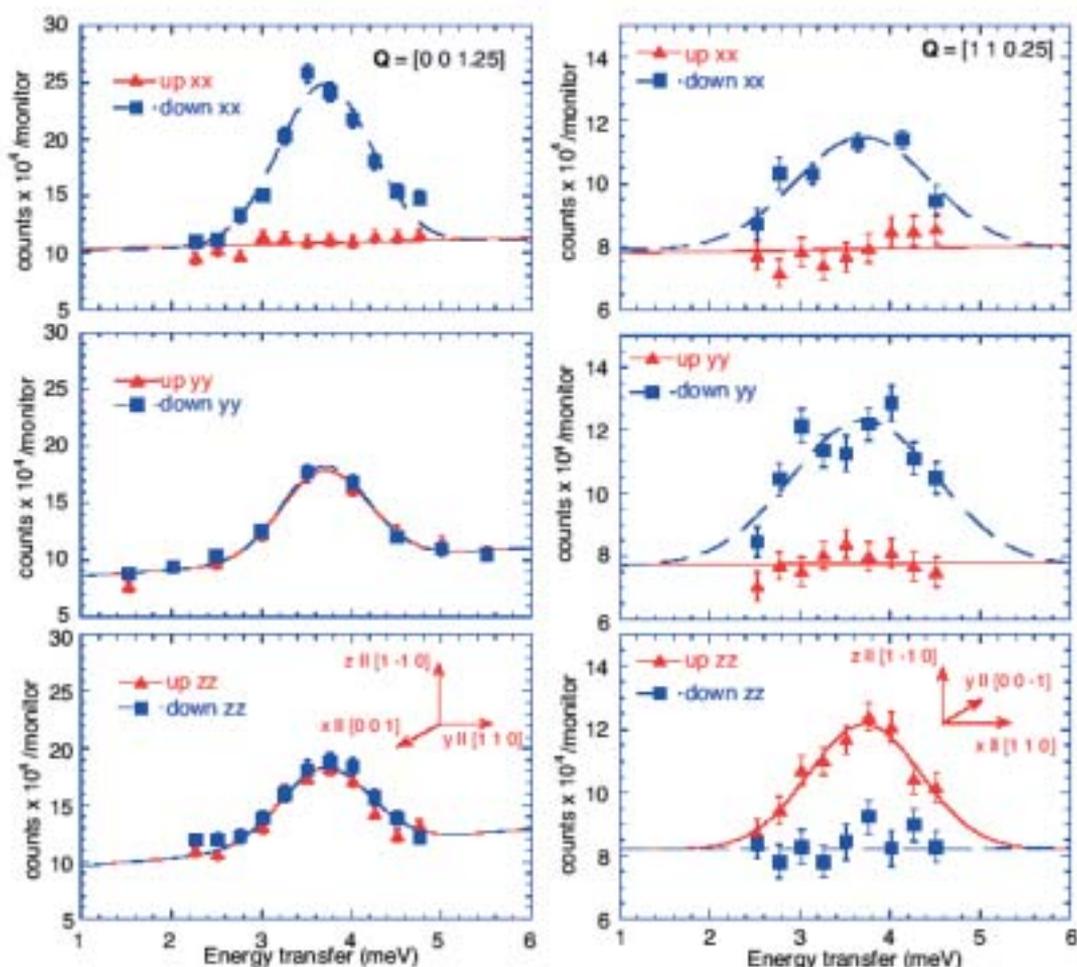


Fig. 2.10 Constant-Q scans for different polarisation channels. Data are collected at 5 K and correspond to a magnon excitation belonging to the lowest energy spin wave branch propagating along the [001] axis. For the neutron polarisation the x-axis is parallel to the momentum transfer  $Q$ ; it is then along the [001] direction for the left side of the figure, but along almost the [110] direction for the right side. The z-axis is vertical, and always parallel to the [1 -1 0] direction. Labels such as xy, refer to a situation in which the initial polarisation vector is parallel to y and the x component of the final polarisation is analyzed. The only terms are those of the diagonal of the polarisation matrix, i.e. xx, yy and zz. Off-diagonal terms showed no polarisation behaviour.

spin-lattice interactions have never been elucidated. A more recent effort by ourselves [2], using incident polarised neutrons but no polarisation analysis, also failed to establish any direct evidence for strong spin-lattice interactions, despite the use of such ideas to explain many of the phenomenon found in  $\text{UO}_2$ .

Examples of the results obtained for the excitations belonging to the lowest energy magnon branch propagating along the  $[0\ 0\ 1]$  direction are shown in Fig. 2.10. The three panels on the left show neutron groups measured in a constant- $\mathbf{Q}$ , longitudinal scan at  $\mathbf{Q} = [0\ 0\ 1.25]$ , the three panels on the right show results at the same point of the dispersion curve but measured in a transverse scan at  $\mathbf{Q} = [1\ 1\ 0.25]$ . The red and blue symbols correspond, respectively, to intensities of neutrons scattered with spin up and down with respect to the chosen analysis direction. A difference between these two counts implies a component of polarisation of the scattered beam in this direction.

Starting with the  $[001]$  direction we examine the three components ( $xx$ ), ( $yy$ ), and ( $zz$ ). The co-ordinate system is given in the lower panel. Since the  $x$ -axis is along the scattering vector, the transverse components of the excitation, which will be in the direction  $y$  and  $z$ , will change the polarisation of the scattered neutrons. Thus incident neutrons "up" will all be scattered to the "down" channel. The top two frames are thus exactly as expected for a transverse magnetic excitation. For neutrons incident along  $y$ , the excitation propagating along  $[001]$  will have components parallel and perpendicular to  $y$ . A strong polarisation is expected, and observed in the left centre panel. An identical situation is observed with the neutrons parallel to  $z$  in the lower left-hand panel.

The unusual situation is in the lower two panels on the right-hand side, when the excitation propagates along the  $[001]$  direction but we move away from the magnetic zone centre  $[110]$ . In these two panels, as in the ones on the left-hand side, we would expect depolarisation; instead the neutron beam is polarised. The only way that this can happen is if the component in the  $y$  direction is absent. For ( $yy$ ) scattering the beam polarisation is reversed, up  $\rightarrow$  down, whereas the ( $zz$ ) component is left unchanged up  $\rightarrow$  up. The result is that for this lowest energy magnetic excitation the transverse components are *only* in the plane perpendicular to the propagation direction  $[001]$  of the magnetic structure. The same behaviour is observed all along the lowest-energy magnon branch, which is one that has been assumed to be strongly hybridised with a transverse acoustic phonon.

A different behaviour is observed for the two highest-energy branches. The results obtained indicate isotropic fluctuations, not only at the magnetic and nuclear zone centres, but also within the whole Brillouin zone.

Despite the fact that we anticipated observing «mixed» magnon-phonon excitations in  $\text{UO}_2$ , and, as a result, cross terms of the form  $xy$ ,  $xz$ , etc in the polarisation dependence, no such off-diagonal terms were observed in the polarisation matrix. However, the observation of an unexpected anisotropy in the lowest-energy magnon is a theoretical challenge. Is this a consequence of the magnon-phonon interaction, the  $3\text{-k}$  magnetic configuration of  $\text{UO}_2$ , or of an anisotropy induced by the large orbital moment of the 5f-electrons? More experiments and theory are needed, but our unexpected results show what a new instrumental technique can bring to an old and apparently well understood system.

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#### 2.5.2 Ab Initio calculation of crystal field levels and magnetic susceptibility in $\text{PuO}_2$

$\text{PuO}_2$  is a singlet  $\Gamma_1$  ground state magnet. The  $\Gamma_1 \rightarrow \Gamma_4$  transition is measured to be 123 meV by neutron scattering [1]. However analysis of magnetic susceptibility suggests that the transition energy is 284 meV [2].

We have calculated the ground state electronic structure and crystal field levels of  $\text{PuO}_2$  by means of a *symmetry constrained* local density approximation to density functional theory [3]. The crystal field excitation energies are obtained from total energy differences between states for which the symmetry of the 5f charge density is constrained to be  $\Gamma_1, \Gamma_3, \Gamma_4$  and  $\Gamma_5$ , respectively. The calculated  $\Gamma_1 \rightarrow \Gamma_4$  excitation energy of 99 meV is in reasonable agreement with the value obtained from neutron scattering. We have also calculated the  $\Gamma_3$  and  $\Gamma_5$  crystal field levels to be 162 and 208 meV above the ground state, respectively.

The measured magnetic susceptibility therefore appears to be anomalous. However, we have calculated the electronic structures of all of the actinide dioxides [4] and noticed that, apart from the number of 5f-electrons, they are very similar. We would therefore argue that the antiferromagnetic exchange interactions between the 5f states are about constant across the series. We have evaluated the molecular

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field in  $\text{UO}_2$ , which is an anti-ferromagnet, from its measured susceptibility [5]. The Heisenberg exchange model of antiferromagnetic exchange then enables us to evaluate the molecular field,  $\lambda$ , in  $\text{PuO}_2$  by changing the spin from that of the  $f^2$  ( $\text{UO}_2$ ) to that of the  $f^4$  ( $\text{PuO}_2$ ) configuration. When the magnetic susceptibility is re-analyzed from the calculated crystal field levels and molecular fields the measured low temperature susceptibility is obtained and the apparent discrepancy between the two experiments removed (Fig. 2.11).

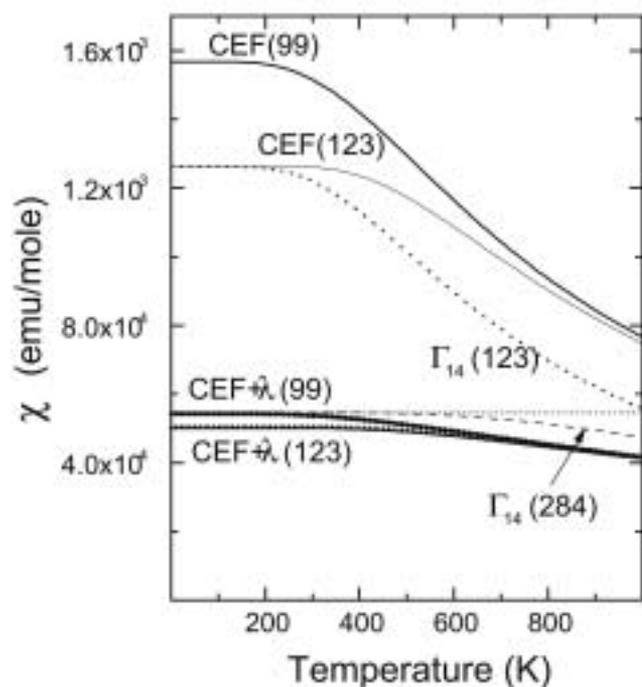


Fig. 2.11 The magnetic susceptibility,  $\chi$ , of  $\text{PuO}_2$ .

The temperature independent straight dotted line represents the measurements. The calculated bare susceptibility with a sole  $\Gamma_1 \rightarrow \Gamma_4$  excitation energy of 284meV (which fits the data at  $T=0$ ) is the dashed line labelled  $\Gamma_{14}(284)$ . The corresponding calculated bare susceptibility with a sole  $\Gamma_1 \rightarrow \Gamma_4$  excitation energy of 123meV, which fits the neutron scattering data, is the dotted line labelled  $\Gamma_{14}(123)$ . Adding calculated additional crystal field transitions to the 123meV transition produces the improvement shown by the solid line labelled CEF(123) whereas replacing the measured  $\Gamma_1 \rightarrow \Gamma_4$  excitation energy by the calculated 99meV transition produces the solid line labelled CEF(99). The effect of using the antiferromagnetic molecular field deduced from that of  $\text{UO}_2$  to enhance the latter two bare susceptibilities results in the full curves labelled CEF+ $\lambda$ .

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## 2.6 Thermophysical Properties

### 2.6.1 Measurement of the thermal diffusivity and conductivity of new fuels

Thermal diffusivity measurements of different types of new fuels continued. The apparatus (laser flash LAF.1) has been substantially upgraded in performance: firstly, conditional heating is now provided both by furnace and laser heating based on an additional 60W CW-YAG laser; secondly, the temperature operation range is extended up to 1800 K. Furthermore, a spectral reflectivity system was installed in the glove box, which improves the heat capacity measurements.

The thermal diffusivity of  $\text{ZrO}_2$ - and  $\text{ThO}_2$ -based inert matrices and MOX was measured. As some of these materials are semi-transparent, a special coating was used to obtain reproducible laser-probe absorption. The heat conductivity data are plotted in Fig. 2.12. Heat conductivity of Pu-doped zirconia (rather opaque) decreases vs. T, as in most ceramics. The thermal conductivity of the Ce-doped  $\text{ZrO}_2$  (more transparent) increases with T. This behaviour is attributed to heat transport via radiation.

Melting experiments started in 2000 on chemically non-invariant nuclear materials are continuing. The high-T diagram of  $\text{ZrO}_2$ - $\text{UO}_2$  (relevant for the analysis of LOCA accidents) as well as MOX and some recently developed  $\text{ZrO}_2$ -based inert matrices are investigated. A common feature of these materials is the melting-solidification transition occurring across a solidus/liquidus gap. The available literature data are in this respect scanty and unprecise.

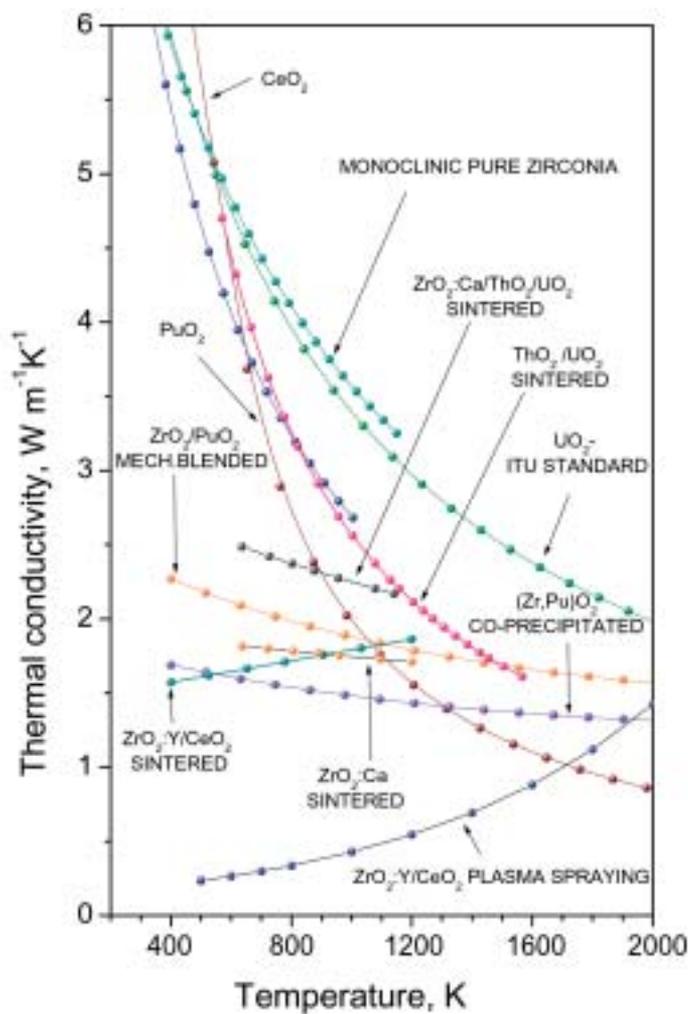


Fig. 2.12 Thermal conductivity of several advanced fuels and nuclear targets measured at ITU.

Laser heating followed by cooling of liquid under controlled conditions was applied. As solidification of these substances under non-isothermal conditions requires a complex analysis, a model was developed for calculating axial temperature profile and composition, dynamics of the inter-phase boundary, size of the molten region, and degree of non-homogeneity after solidification.

A further improvement was obtained in the performance of the multichannel pyrometer developed in our laboratory: the recording time was extended (200 ms) and the speed of measurement reduced (0.8 ms); furthermore, the stability of the spectrometer against calibration was increased by inserting an optical fibre between the field stop and the input slit.

Experiments on melting of hyper-stoichiometric  $\text{UO}_{2+x}$  were carried out in 1000 bar helium. The samples were prepared by treating  $\text{UO}_2$  pellets in  $\text{CO}/\text{CO}_2$ ; the final composition was determined by thermogravimetry. Raman spectrometry was also applied in view of further use for post-melting characterisation. A sufficient sensitivity of the Raman spectra to the value of  $x$  was found.

The measured liquidus/solidus temperatures of  $\text{UO}_{2+x}$  show a dramatic decrease with  $x$  and a marked deviation from the currently assumed estimates.

### 2.6.2 Experimental determination of the $\text{UO}_2$ melting line

Though of limited application, the lowering of the melting point of a substance with increasing pressure may be used for determination of the heat of fusion or to verify if melting occurs without molecular change. The latter is of particular relevance for the study of the equation of state of  $\text{UO}_{2\pm x}$ . Experimental data on high-pressure melting of non-stoichiometric  $\text{UO}_2$  were obtained in our high-temperatures laboratory. A high-pressure autoclave (4000 bar of inert gas) was used to allow minimising surface vaporisation effects and measuring the slope of the melting line in the P-T diagram [1]. A new method was developed where two superimposed pulsed Nd:YAG laser beams were mixed within the same optical fibre and then focused on the sample surface (see Fig. 2.13).

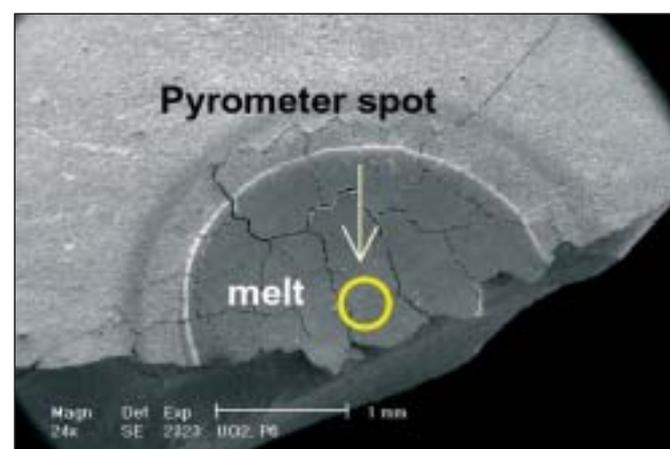


Fig. 2.13 SEM micrograph showing a  $\text{UO}_2$  pellet after laser surface melting.

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The melting point  $T_m = T_m(p)$  of uranium dioxide was measured at pressures up to 2500 bar with a precision better than  $\pm 5$  K. The slope of the melting line is not constant within the resulting accuracy, since low pressure data are scarce (probably due to vaporisation effects). However, above 500 bar the measured slope (Fig. 2.14) is

$$dT_m/dP = 10.5 \pm 1.55 \text{ K/kbar.}$$

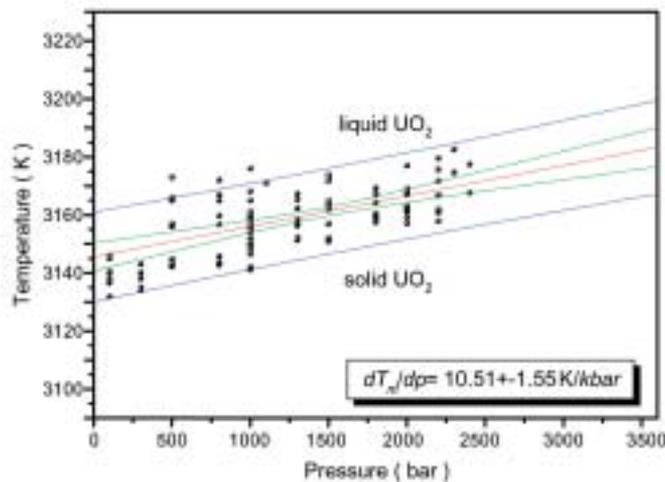


Fig. 2.14  $UO_2$  melting line. The plotted curves represent the linear fitting with confidence and prediction band.

This slope can be compared with that predicted by the Clausius-Clapeyron equation:

$$\left(\frac{dT_m}{dP}\right) = \frac{T_m \Delta v_m}{\Delta H_m}$$

where  $\Delta v_m$  is the specific volume variation upon melting,  $T_m$  is the melting temperature, and  $\Delta H_m$  is the latent heat of fusion. Substituting for these thermodynamic quantities the recommended literature values along with the respective uncertainties in [2], one obtains

$$dT_m/dP = 9.33 \pm 3.84 \text{ K/kbar.}$$

Though the measurements are still slightly affected by cracking of the sample, and possible changes in the O/U ratio at pressures below 500 bar, the agreement with thermodynamic predictions is good, and the uncertainty is even better than that allowed by the established data on melting properties of  $UO_2$ .

Measurements on non-stoichiometric samples are in course in order to determine the  $UO_{2\pm x}$  solidus-liquidus diagram, which is still uncertain.

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## 2.7 Nuclides.net: An Integrated Environment for Computations on Radionuclides and their Radiation

Nuclides.net will be available by summer 2002. The Nuclides.net book, together with CD and registration form for online access, will be published by Springer Verlag, Heidelberg.

### What's new in Nuclides.net (compared with Nuclides 2000)

- A new user interface to view the nuclide charts (with zoom features). Additional nuclide charts are based on spin, parity, binding energy etc.
- There are four new applications: (applications now run over the internet rather than from the CD-ROM. This allows for easier maintenance and updates).

(1) "Dosimetry and Shielding" module allows the calculation of dose rates from both unshielded and shielded point sources. A choice of 10 shield materials is available.

(2) "Virtual Nuclides" allows the user to do decay and dosimetry and shielding calculations on mixtures of nuclides (see example in Fig. 2.15).

(3) "Fission Yield" module gives the user access to fission products and yields for 36 fissioning nuclides (data for spontaneous fission and neutron induced fission with thermal, fast and 14 MeV neutrons) from the main international datafiles.

(4) The "Universal Nuclide Chart" runs locally on the user computer and displays the most important basic data. It can also be used to simulate decay processes and reaction paths in nuclear reactors.

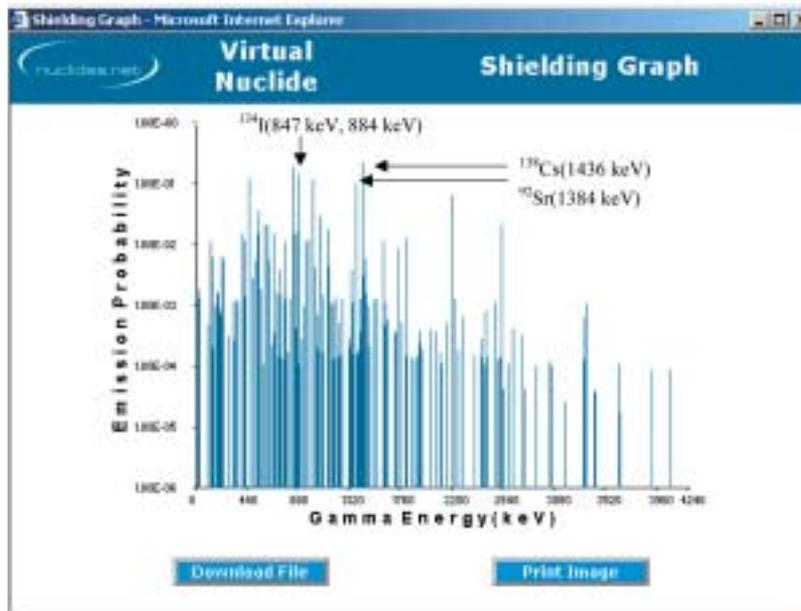


Fig 2.15 Simulation of laser induced fission experiments on uranium using the virtual nuclides module in Nuclides.net. Gamma spectrum of the main fission products of uranium.

In addition:

- Data on 3650 ground states and isomers (increased from 2656 in Nuclides 2000). Data is from internationally recognised sources.
- "FactSheets" gives important properties derived from the basic data. In addition to heat, neutron, and gamma emission rates, information on radiotoxicity and nuclide transportation given.
- "Cross Sections" gives averaged neutron cross sections from the main international datafiles. Data includes the

cross sections for room temperature, Maxwell averaged, resonance integral, fission averaged, and 14 MeV neutrons.

- "News" gives latest information on Nuclides.net.
- "Forum" where users can exchange information on the features and applications.

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## 3. Safety of Nuclear Fuels

### 3.1 High Burn-up Performance

#### 3.1.1 Second rim-like restructuring at intermediate radii in a UO<sub>2</sub> LWR-fuel at 100 GWd/tM.

In the frame of the ITU/LWR-fuel characterization programme aimed at determining the structure, microstructure and physical-chemical changes affecting the behaviour of the fuel at high burn-ups [1,2], examinations of a commercial UO<sub>2</sub> LWR-fuel with average burn-up 100 GWd/tM have

been completed, using OM, SEM, micro-indentation and micro-XRD. The results of these investigations are summarized in Fig. 3.1. Of special interest is the measured two-fold decrease of the fuel lattice-constant towards the pellet periphery (Fig. 3.1, bottom left). This suggests the appearance of two-restructuring processes across the pellet radius, namely the usual rim structure at  $r/r_o = 1 - 0.8$  and a second rim-like process that would extend from  $r/r_o \sim 0.7$  to about to  $r/r_o = 0.4$ . As shown in previous works [1,3], the decrease of the fuel lattice constant towards the pellet periphery evidences the formation of the rim structure, as it indicates the release of the in-service accumulated lattice strains during recrystallisation. In the present case, therefore, two restructuring processes appear to be superimposed.

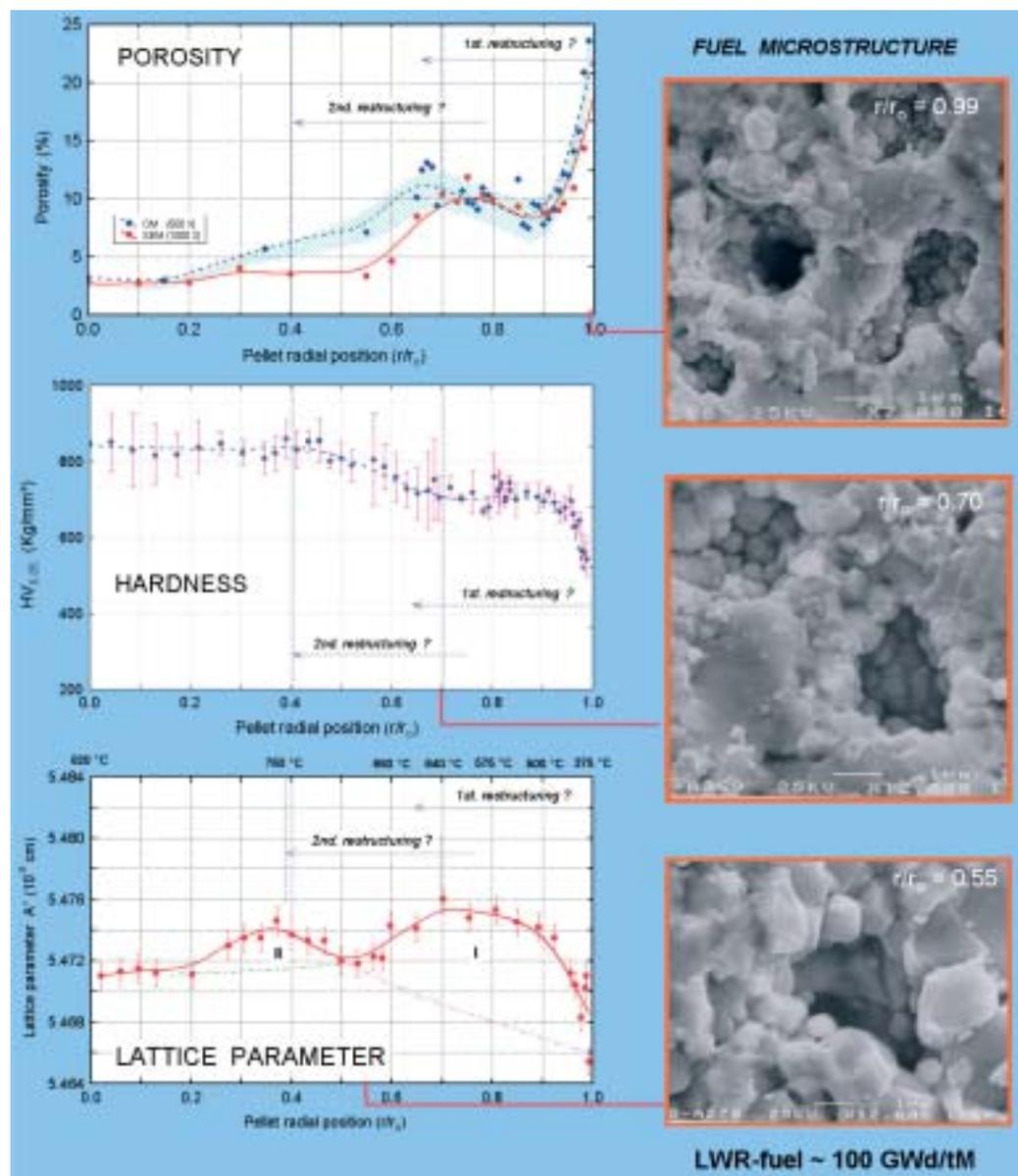


Fig. 3.1  
Structure properties variation in a LWR-fuel at ~100 GWd/tM, with evidence of a second rim-like restructuring process at middle pellet radius.

The onset of the second restructuring process at intermediate radii is also evidenced in the porosity and hardness profiles. As shown in Fig. 3.1 (top and middle, left) these curves exhibit respectively a local maximum and a minimum (or inflection point) at about  $r/r_o \sim 0.7$ , congruently with the outer maximum of the lattice parameter profile. The described features, in addition to the grain subdivision observed up to at least the pellet middle (Fig. 3.1, right), lead us to assume an extension of the second rim-like structure from approximately  $r/r_o \sim 0.7$  to  $r/r_o \sim 0.4$ . Opposite to this, the decrease of the lattice constant from  $r/r_o \sim 4$  to  $r/r_o \sim 0$ , occurring at estimated local temperatures  $> 760^\circ\text{C}$  (Fig. 3.1, bottom left), indicates the thermal healing of irradiation defects and therefore the disappearance of the causes that lead to the high burn-up restructuring [3]. Due to the possible impact in the fuel performance especially on gas release, correlation of the here presented structure features with the corresponding Xe-behaviour is being done at present.

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

In the framework of the contract with FRAMATOME ANP 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 12 fuel rods from two boiling water reactors and 7 fuel rods from a pressurised water reactor were transferred to the hot cells in ITU. In addition, 6 segments re-fabricated and shipped to HFR, Petten, for ramping were transported back for post-irradiation examination. A list of the types and number of examinations carried out on the different fuel rods and segments are given in Tab. 3.1.

The installation of a new device for testing the mechanical properties of cladding under intermediate storage conditions was completed. Three non-active samples and one plenum sample were successfully tested.

Focal points of examinations for this period have been: creep behaviour of cladding materials (long-term, interme-

Tab. 3.1 Type and number of examinations performed on PWR and BWR fuel and cladding during 2001.

Type of Examination	Performed
Visual examination	5
Fuel rod length	2
Fuel rod profilometry	2
Eddy current testing (cladding defects)	2
Eddy current testing (oxide layer thickness)	4
Gamma scanning	6
Fission gas analysis	9
Free volume determination	9
Metallography	1
Ceramography	1
SEM (cladding)	1
Re-fabrication	6
Glow discharge	1
Creep (long term)	4
Halden transport (container)	1
<b>Total:</b>	<b>54</b>

mediate 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  $\text{UO}_2$ -fuels and the re-fabrication of segments for ramp testing.

#### References

- [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. 97, EUR 19812 (TUAR-2000), p. 86.

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## 3.2 Fission Products

### 3.2.1 Analysis of fission gas release from high burn-up fuel

The operating conditions of the mass spectrometer were optimized so that results were as accurate and consistent as possible given its limits of performance. It was also programmed to switch from the principal  $^{86}\text{Kr}$  and  $^{136}\text{Xe}$  isotope analysis during initial monitoring to complete Kr and Xe isotopic analyses when release occurred.

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Segments of a high burn-up  $\text{UO}_2$  commercial fuel 3 mm thick were tested in small transients to 750°C - 900°C from a normal operating temperature of 500°C as a simulation of a loss of coolant accident (LOCA). A result is seen in Fig. 3.2a for a low power segment of the fuel (estimated at 50 GWd/tU burn-up) for the temperature profile and the cumulative  $^{85}\text{Kr}$  release as measured by  $\gamma$ -spectroscopy. In Fig. 3.2b the on-line krypton and xenon releases during the transient are given for the same segment.

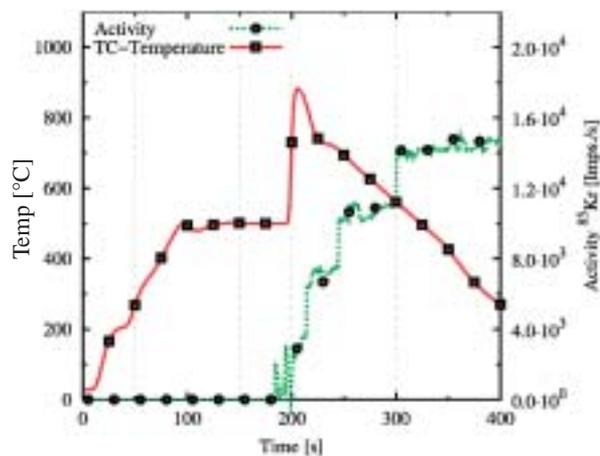


Fig. 3.2a) The fission gas release from a high burn-up fuel (low power position: burn-up 50 GWd/tU) under a simulated loss of coolant accident (LOCA) temperature transient from 500 to 900°C.

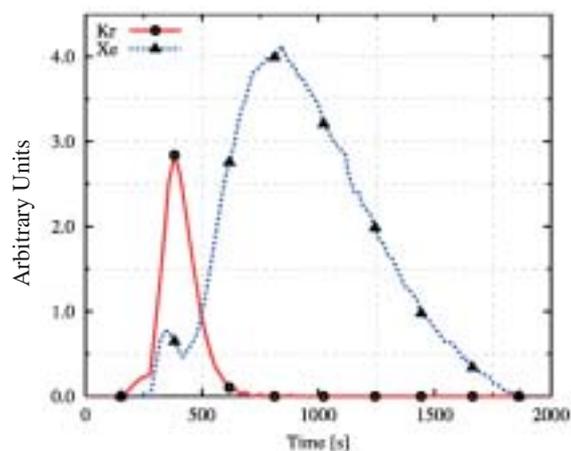
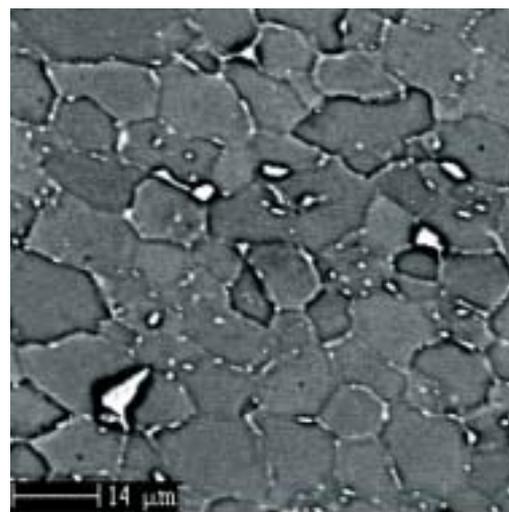


Fig. 3.2b) The fission gas release measured by mass spectroscopy during the temperature transient simulating the LOCA.

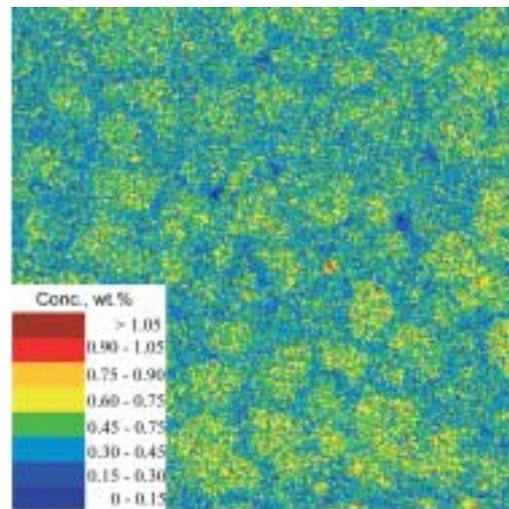
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### 3.2.2 Microstructural studies of irradiated SBR MOX fuel

Post irradiation examination of BNFL's first commercially irradiated SBR MOX fuel continued in 2001 with emphasis on the investigation of the microstructure and microchemistry of the material. During the period additional SEM and EPMA investigations provided further evidence that SBR MOX fuel behaves very similarly to  $\text{UO}_2$  fuel during irradiation. In particular, it was seen that fission gas release of around 1% in the 3-cycle SBR MOX rods was accompanied by the development of gas bubble networks on the grain boundaries (Fig. 3.3).



Absorbed Electron



Xe X-ray Map

Fig. 3.3 Absorbed electron image and false colour X-ray map of the MOX matrix in the centre of SBR MOX fuel. The grain boundaries are decorated with gas bubbles and depleted in xenon even at locations where gas bubbles are absent.

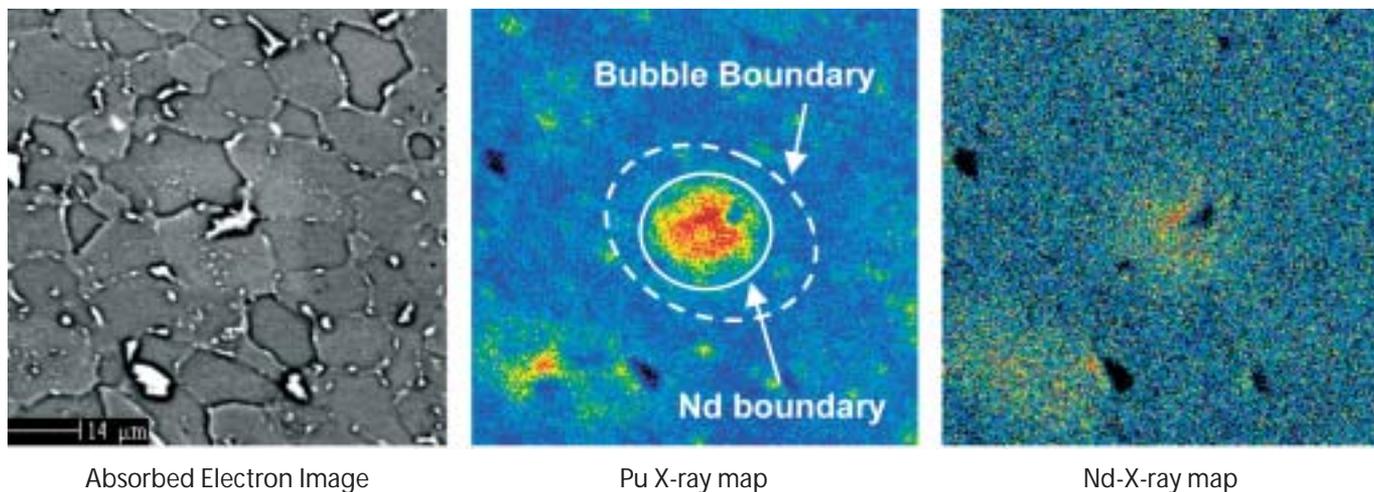


Fig. 3.4 Absorbed electron image and false colour X-ray maps of a Pu-rich spot in the centre of SBR MOX fuel. Comparison of the maps with the microstructure reveal that gas bubbles form outside the Pu-rich spot in the MOX matrix due to a combination of diffusion and recoil.

Such networks are apparently not observed in irradiated MOX fuels fabricated by other routes. Their presence in SBR MOX fuel is attributed to the small volume fraction and small size of the Pu-rich spots (1 vol% and average 10  $\mu\text{m}$ , respectively). Because the volume fraction of Pu-rich spots is small, less than 5% of the total fission gas generated in the fuel is produced in the spots. The rest is formed in the mixed oxide matrix. Moreover, owing to their small size most of the gas generated in the Pu-rich spots is eventually deposited in the mixed oxide matrix by a combination of recoil and diffusion (Fig. 3.4).

Taken together with the finding that the threshold temperature for gas release from SBR MOX fuel is about the same as that for  $\text{UO}_2$  fuel [1], the similarity between the microstructure of irradiated SBR MOX fuel and  $\text{UO}_2$  fuel implies that fission gas release is controlled by the same processes. These processes are namely, diffusion of single gas atoms to grain boundaries, nucleation and growth of gas bubbles on grain boundaries and bubble interconnection to form escape paths to the rod free volume. Minor differences in release behaviour are attributable to the higher irradiation temperature of MOX fuel, which is a consequence of its lower thermal conductivity, and to a generally higher third cycle rating imposed by operational constraints.

#### References

- [1] R.J. White, S.B. Fisher, P.M.A. Cook, R. Stratton, C.T. Walker and I.D. Palmer, J. Nucl. Mater. 288 (2001) 43

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### 3.3 The Phébus PF Project

#### FPT4

This year has seen the initiation of new phases of this international project. The FPT4 test focussed on the behaviour of medium and low volatile fission products in a solid debris bed of oxidized zircaloy cladding and  $\text{UO}_2$  fuel, to ascertain what releases occur at high temperatures. The vapours and aerosols generated during the degradation were captured for a succession of temperature plateaux up to 2700°C on six 1 m long filters that were opened in turn on a carousel directly above the bundle. The fuel particle and fission product deposits on the 30 cm long filter cartridges were dissolved in 7M nitric acid. Diluted aliquots were then taken for analysis by ICP-MS at ITU. Aliquots were also sent for analysis to PSI Würenlingen and Chalmers University, Göteborg for data intercomparison.

A section of the plenum tubing directly above the FPT4 test section will be characterized by electro-optical analysis and revaporisation testing on samples will be carried out.

### 3.4 COLOSS Project

The COLOSS project is a shared cost action in the Nuclear Fission Operational Safety section of the Fifth Framework Programme of the Commission, with 17 partners and sub-contractors from both Western and Central Europe. ITU's task in the project is the study of the dissolution of high burn-up irradiated  $\text{UO}_2$  and MOX fuel by liquid zircaloy un-

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der severe accident conditions. For this purpose, a new resistance furnace designed for temperatures up to 2500 °C was installed in the ITU hot cells. Before the installation in the cell, the oven was tested to prove its thermal performance and to test the equipment for its ease of handling under active conditions. First tests are expected to be performed in early 2002.

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### 3.5 Advanced Fuels

#### 3.5.1 Fabrication of ThO<sub>2</sub> pellets

The fabrication of ThO<sub>2</sub> pellets from particles produced by the sol gel liquid to particle conversion process has been investigated. Thorium nitrate was dissolved and, following addition of polymers necessary for the sol gel process, the Th concentration was adjusted as required in the 80-120 g/l range. This solution was dispersed and the droplets produced were collected in an ammonia bath where gelation occurred. Following washing and azeotropic drying, the beads were calcined at 400°C in air.

Independent batches of beads were calcined further in the 700 – 1000°C range, and were subsequently compacted at three different pressures into pellets, which were then sintered at 1700°C in a humidified Ar/H<sub>2</sub> atmosphere for 6 hrs. The results shown in Fig. 3.5 indicate that the optimum calcination temperature is about 850°C. The effect of the metal

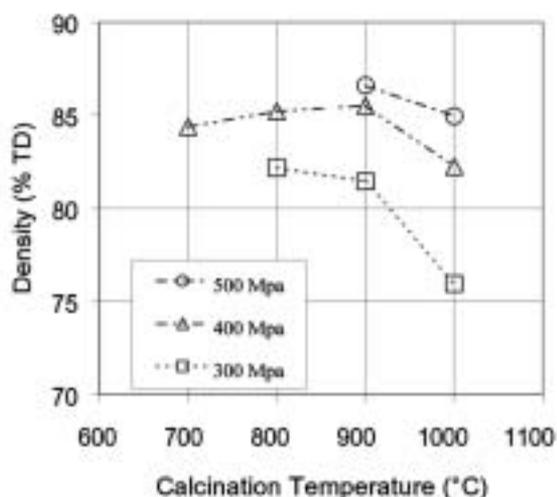


Fig. 3.5 ThO<sub>2</sub> pellet density as a function of bead calcination temperature and compaction pressure.

concentration in the feed solution on the final pellet density was also investigated. The results shown in Fig. 3.6 indicate that the metal concentration should not be lower than 120 g/l.

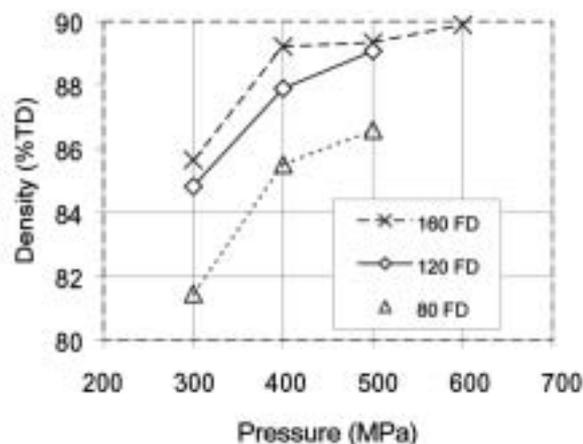


Fig. 3.6 ThO<sub>2</sub> pellet density as a function of compaction pressure and metal concentration in the initial feed solution.

Pellet densities of only 90% TD could be reached. In other investigations, the water content of the sinter gas atmosphere had a large influence on the final density suggesting that oxidising sintering atmospheres are more favourable for sintering this material. This will be investigated in the future.

#### 3.5.2 Fabrication of (U,Th)O<sub>2</sub> fuels (Thorium Cycle SCA)

##### HFR irradiation

The sol gel liquid to particle conversion process was used to fabricate uranium and thorium MOX fuels for irradiation in the HFR, Petten. The compositional specifications of the fuels are given in Tab. 3.2. The fuels were in pellet form ( $\phi = 5.48$  mm) and were transported to Petten, where they were inserted into instrumented (thermocouple and pressure transducer) stainless steel fuel rods. Their irradiation along with two further pins (UO<sub>2</sub> and ThO<sub>2</sub>) produced by NRG began in November 2001, and will continue until November 2003, so that a burn-up of 55 GWd/tM will be reached. The two MOX pins will be then returned to ITU for PIE.

Tab. 3.2 HFR Irradiation: Specified fuel molar composition.

Fuel No.	M/ (M+Pu+Am)	(Pu+Am)/ (M+Pu+Am)	O/M
3 (M = U)	0.904	0.096	2.00
4 (M = Th)	0.894	0.106	2.00

### KWO Irradiation

As a part of the same shared cost action, a  $(Th,Pu)O_2$  fuel (3 wt.%  $Pu_{fiss}$ ) was fabricated and encapsulated in a zircaloy fuel pin. The production of this fuel by the sol gel route proved intricate. Pellet pressing difficulties were overcome by granulation of the sol gel particles using compaction and sieving steps. For the welding, a new pressurisation chamber was installed and commissioned. Eventually the exacting specifications, set by FRAMATOME ANP and Kraftwerk Obrigheim (KWO), for the fuel and welding were achieved, so that, based on the report of the independent assessor (TÜV-EN-BW), a permit for the irradiation experiment was received. The pin was loaded in the KWO pressurised water reactor in July 2001 and has been running at maximum power since. The irradiation will continue until July 2005, and a burn-up of 40 GWd/tM will be reached. A ceramograph of a fuel pellet and a picture of the fuel pin are shown in Figs. 3.7 and 3.8, respectively.



Fig. 3.7 Ceramograph of a pellet ( $\phi = 8.054$  mm) of the  $(Th,Pu)O_2$  fuel being irradiated in KWO.

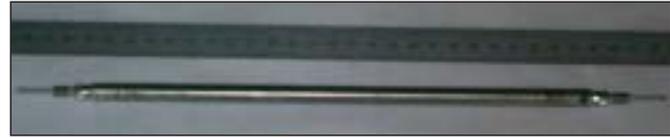


Fig. 3.8 The  $(Th,Pu)O_2$  fuel pin being irradiated in KWO.

### 3.5.3 HTR fuel fabrication and testing

The HTR-F shared cost action encompasses the retrieval of high temperature reactor (HTR) fuel technology knowledge in Europe, the performance of irradiation experiments on existing spherical fuel elements, and the re-establishment of key fuel fabrication safety and fabrication testing facilities.

#### Kernel production

A review of relevant literature has been made, but detailed information needed to construct and operate a kernel production facility is not available. Nevertheless, a design for the construction of a production unit has been made and its construction has begun. In parallel, tests, based on existing know-how, have been initiated on the production of  $HfO_2$  kernels. While near spherical particles can be produced by gelation, several problems remain to be overcome, in particular the control of the particle size, the surface smoothness, and the large shrinkage in the drying steps, which causes excessive cracking of the particles.

#### Installation of the KÜFA device

The re-installation of the Kühlfinger apparatus (KÜFA) device for cold testing started at the beginning of 2001. The process control electronics, the detectors for the  $^{85}Kr$ -measurement and the lifting system were ordered. The delivery of these components is expected at the beginning of the next year. The decontamination of the  $\alpha$ -containment for the housing of the new device was also completed. The first cold test is foreseen for March 2002.

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## 4. Partitioning and Transmutation

### Project Objective

The final goal of Partitioning and Transmutation (P&T) is to achieve large radiotoxicity reduction factors from nuclear waste. Therefore, new and efficient spent fuel-reprocessing techniques and fuel fabrication processes have to be tested. The out- and in-pile properties of these new materials have to be determined. ITU's programme in 2001 mainly consisted in the experimental research on these new processes and materials, and in the progress of the construction of related new facilities.

ITU's programme is consistent with the conclusions of the „Roadmap“ on Accelerator Driven Systems for Nuclear Waste Transmutation issued by the European Technical Working Group (TWG), under the chairmanship of Prof. Carlo Rubbia.

### 4.1 Advanced Partitioning Studies

#### 4.1.1 Advanced techniques for aqueous processing

The principal aim of the programme is to define sustainable and environmentally friendly solvent extraction processes capable of selective separation of minor actinides (MA), especially Am(III) and Cm(III) contained in the high active raffinate (HAR) from PUREX reprocessing of spent nuclear fuels. Up to now processes have been successfully designed for the co-separation of MA and Ln from HAR, i.e. the DIAMEX process, and for the subsequent separation of MA from Ln, i.e. the SANEX process. These processes will, in the PARTNEW programme, be demonstrated also for genuine high active

concentrate (HAC) which is about 10 to 20 times as concentrated as HAR. The advantage of using the concentrate lies in the volume reduction of the feed to be reprocessed and the corresponding minimisation of plant size and costs. The resulting higher metal concentration, however, has the possible drawback of causing precipitation or third phase formation. In order to produce HAR, a total of 1.5 kg of spent MOX fuel has been dissolved yielding some 7 liters of spent fuel solution. This solution has now been reprocessed by an optimised PUREX process, see Fig. 4.1, resulting in some 10 liters of representative genuine HAR. A part of this solution will be concentrated into HAC and used for the upcoming tests of the DIAMEX and SANEX processes.

A small part of the HAR has been used to test a direct separation of MA from HAR using nPr-BTP as extraction reagent. This reagent is normally used, at medium acidity, for the separation of MA from lanthanides, but might have the ability of a selective separation of MA directly from high acidity (3-5 M HNO<sub>3</sub>) HAR. The results, see Tab. 4.1, indicate a sufficient separation of MA from lanthanides (represented by Am and Eu) but a low MA extraction efficiency.

Tab. 4.1 Distribution coefficients (D-value) and separation factors (SF) for Am and Eu obtained from batch extraction experiments using HAR and nPr-BTP.

	D-value Am	D-value Eu	SF
HAR (acidity 3.4 M) HEDTA 0.025M	0.56	0.08	7
HAR (adjusted to 2 M acidity) HEDTA 0.025 M	1.94	0.04	49
HAR (adjusted to 2 M acidity)	1.39	0.03	50

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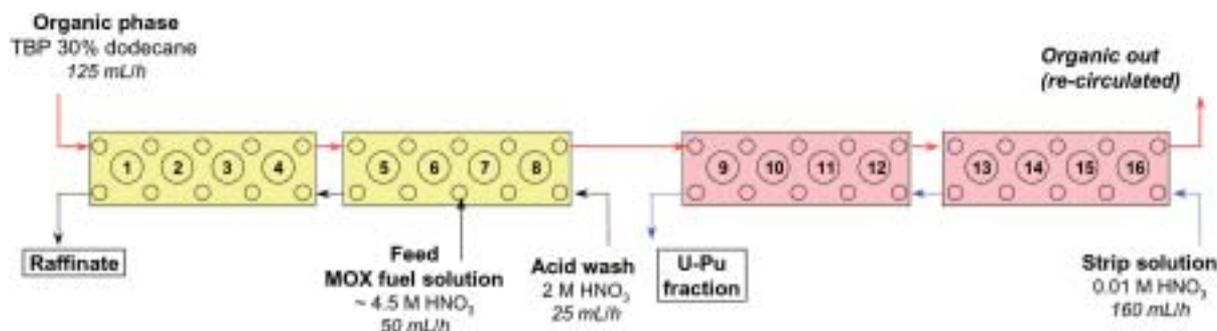


Fig. 4.1 Optimised PUREX process for production of HAR. U and Pu feed decontamination factors are in the order of 10<sup>3</sup> with recoveries higher than 99% for both elements in the U-Pu fraction. The organic phase has been re-circulated (in order to minimise waste) after conditioning with 1 M NaOH followed by acidification.

#### 4.1.2 Pyrochemical reprocessing

##### Pyrometallurgical processing research programme

The overall intention of this programme is to yield sufficient basic data to assess pyrometallurgical processing of irradiated fuels and targets. The work carried out is mainly devoted to investigating the separation of minor actinides from lanthanides by electrorefining. The investigations concentrated so far on the electrochemical behaviour and electrolysis of inactive lanthanum and neodymium in molten chloride salt but is now extended to include also actinides. An Am containing salt has been produced by dissolution (oxidation) of 200 mg Am metal in a molten LiCl-KCl eutectic and the electrochemical behaviour studied by different electrochemical techniques, such as cyclic voltammetry, chronopotentiometry and square wave voltammetry. Fig. 4.2 shows the comparison of typical cyclic voltammograms obtained for Am and Nd.

The two steps involved in the electrochemical reduction reveal the multivalent nature of these two elements in chloride salts. One electron has been shown to be transferred in the first step and the second step is thus assumed to be a two-electron process.

Fig. 4.2 also shows that metallic deposits of Nd is formed at a more negative potential than Am - a difference that indicates the possibility of separation of these two elements by electrodeposition.

Electrodepositions of La and Nd have been carried out onto solid Ni and liquid Cd cathodes. Much higher deposition efficiency is obtained for La compared to Nd on a solid cathode. This is an effect of the multivalent nature of Nd in the chloride melts.

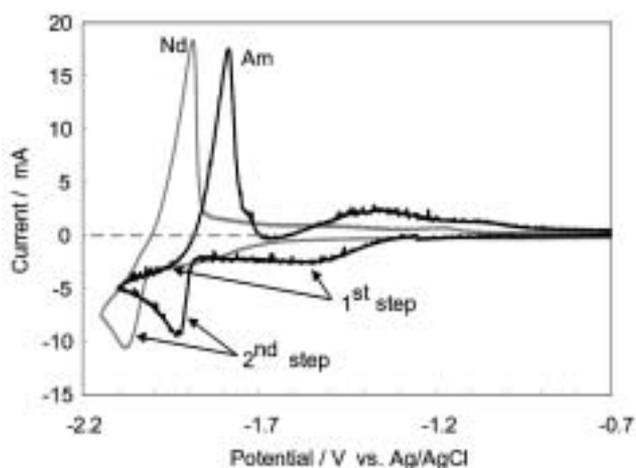


Fig. 4.2 Cyclic voltammograms of Nd and Am in LiCl-KCl melt;  $\text{NdCl}_3$  0.59 wt.%;  $\text{AmCl}_3$  0.5 wt.%;  $T = 733 \text{ K}$ ;  $v = 200 \text{ mV/s}$ ;  $SW = 0.19 \text{ cm}^2$ .

##### Pyro-processing demonstration facility

In the joint study between CRIEPI and ITU an installation to demonstrate pyrometallurgical reprocessing of metallic fuels and high-level-liquid-waste (HLLW) has been constructed (see TUAR-99, p. 41) and is in operation. After successful demonstration of pure U and Pu metal reprocessing (see TUAR-2000, p. 106) the experiments have now progressed to electrorefining of fresh metal alloy fuel.

In the experiments the alloy, U-Pu(20)-Zr(10), was anodically dissolved and, in several successful electrorefining runs, U collected onto a solid cathode and Pu into a liquid Cd cathode. The deposition of U onto the solid cathode progressed with high efficiency. The deposit, see Fig. 4.3, proved to be of different morphology compared to the typical dendritic deposits obtained from electrorefining of pure U or U-Zr alloy.



Fig. 4.3 Solid cathode after passing 16,000 Coulomb. The deposit consists of U and entrained salt. The amount of U indicated an efficiency of around 85%.

This is an effect of Pu being present in the salt. Electrorefining using a liquid Cd cathode was carried out with a constant current of 0.4 A. Chemical analysis of the Cd ingot showed that Pu, U and small amounts of Am (from the decaying of  $^{241}\text{Pu}$ ) had efficiently been deposited, demonstrating the feasibility of TRU recovery from U-Pu-Zr alloy for the

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first time. The anodic dissolution behaviour of the metallic alloy was found to progress from outside to inside, leaving a dense Zr containing salt layer around the fuel, see Fig. 4.4.



Fig. 4.4 A piece of metallic alloy fuels after anodic dissolution in the electrorefining experiment. U and Pu have oxidised and dissolved in the salt phase, leaving a peripheral Zr rich black salt layer. The metallic shining centre part of the alloy fuel is unaffected.

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## 4.2 Transmutation Studies

### 4.2.1 Fuels and targets fabrication

#### Fabrication and Characterization of $(Zr,Y,An)O_{2-x}$ and $MgO+(Zr,Y,An)O_{2-x}$

The ceramograph (see Fig. 4.5) indicates it is devoid of cracks or other defects. Nevertheless, the contours of original spheres in the pellets can be discriminated, as the porosity is mainly located in the peripheral regions surrounding the original spheres. Almost no pores are observed in the spheres themselves.

Pellets of  $(Zr,Y,Pu)O_{2-x}$  were fabricated by the infiltration of small spherical beads, a method that was described in detail

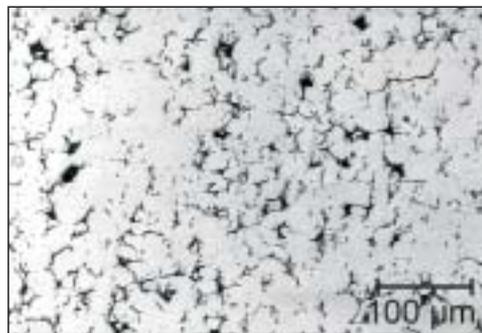


Fig. 4.5 Optical micrographs of a  $(Zr_{0.792}Y_{0.163}Pu_{0.045})O_{2-x}$  pellet

in the ITU Annual Report 2000. The pellets were characterised by ceramographic analysis and X-ray diffraction. Fig. 4.6 shows the  $\alpha$ -autoradiograph of a polished axial section of a  $(Zr_{0.792}Y_{0.163}Pu_{0.045})O_{2-x}$  pellet. The uniform nature of the  $\alpha$ -autoradiograph of these pellets indicates that the plutonium is evenly distributed through the pellets.

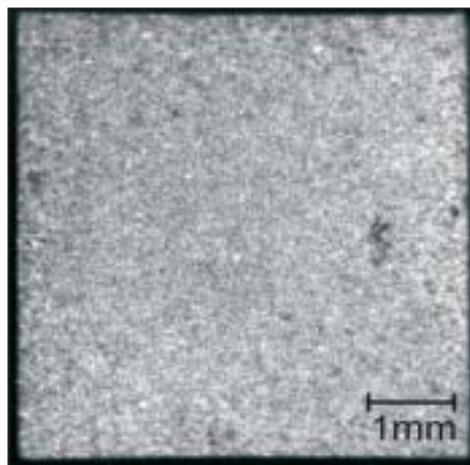


Fig. 4.6  $\alpha$ -autoradiograph of a  $(Zr_{0.792}Y_{0.163}Pu_{0.045})O_{2-x}$  pellet sectioned in the axial direction

During 2001 the fabrication process for composite pellets of  $MgO+(Zr,Y,An)O_{2-x}$  has been improved to obtain pellets with a crack-free matrix and a homogeneous distribution of the actinide phase. To avoid the cracking due to the differences in dilatation of the two materials (see TUAR-2000, p. 109) a systematic study has been carried out to optimise the size and thermal treatment of the MgO granulates in function of the  $(Zr,Y,An)O_{2-x}$  inclusions size. Composite pellets with macro- (80-100 $\mu$ m) and microdispersion (40-60 $\mu$ m) of the actinide phase have been successfully fabricated using ceri-

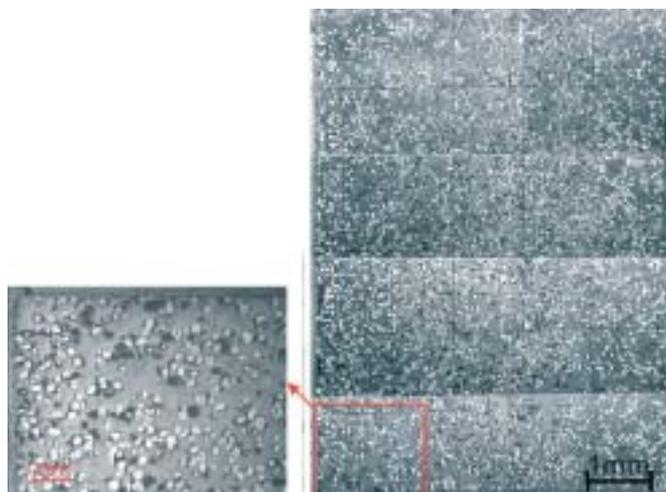


Fig. 4.7 Optical micrograph of an axial section  $MgO+(Zr_{0.602}Y_{0.123}Ce_{0.275})O_{2-x}$  pellet (70:30 volume ratio)

um as a simulant. Fig. 4.7 shows an optical macrograph of a test pellet sintered under air with  $(Zr_{0.602}Y_{0.123}Ce_{0.275})O_{2-x}$  macrospheres, revealing the absence of cracks.

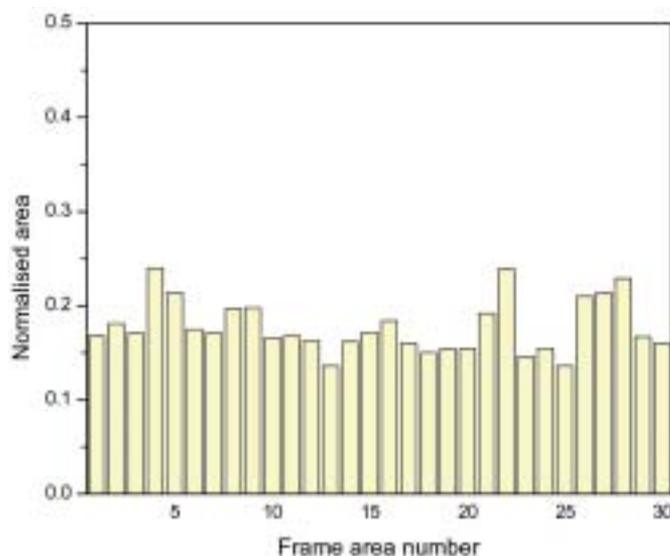


Fig. 4.8 Sphere distribution in an axial section of a  $MgO+(Zr_{0.602}Y_{0.123}Ce_{0.275})O_{2-x}$  pellet divided in 30 area frames

The distribution of the spheres is shown in Fig. 4.8 as the area fraction of the  $(Zr,Y,Ce)O_{2-x}$  phase in an axial section that was divided in 30 area frames.

The composite pellets were sintered under different atmospheres, e.g. air, Ar and Ar/H<sub>2</sub>. Sintering in air and Ar gave good results with respect to pellet integrity, but in Ar/H<sub>2</sub> the beads on the surface are pulled out. X-ray diffractometry (XRD) measurements of sintered pellets indicated two structures in the ZrO<sub>2</sub> phase: pyrochlore ( $a=1.066\text{nm}$ ) and fluorite ( $a=0.519\text{nm}$ ) for those sintered under Ar and Ar/H<sub>2</sub>, for pellets sintered under air only the fluorite phase was identified ( $a=0.521\text{nm}$ ).

These processes have now been tested with cerium or plutonium, but they are intended for americium. The previous experience with these techniques obtained in the SUPERFACT and EFTTRA experiments gives confidence that they can be extended to americium without difficulties. Tests with americium are foreseen as soon as the Minor Actinide laboratory is ready. A detailed layout of this facility was presented in TUAR-2000, p. 115-116. The construction and installation work for the MA-lab has progressed considerably in 2001. The installation of the glove boxes 4-10 is nearing completion. Also the infrastructure (lead, water and polyethylene protection walls) is almost completed. Operation with actinides is foreseen for second half of 2002 when the qualification for the fabrication of fuels for the CAMIX-COCHIX and the EFTTRA-T5 irradiation experiments is planned.

#### Fabrication and Characterization of (Am,Zr)N

The synthesis of americium mononitride (AmN) in microgram scale by the reaction of the hydride or metal with either ammonia or nitrogen [1,2] or by carbothermic reduction of the oxides [3] has been reported. For the fabrication of (Am,Zr)N the carbothermic reduction route has been chosen, because it has been extensively used in ITU laboratories in the past for the fabrication of UN and (U,Pu)N. The carbothermic reduction into (Am,Zr)N will be performed at a temperature as low as possible ( $T < 1570\text{K}$ ) to avoid the vaporisation loss of americium. Preliminary investigations in order to determine the optimised conditions for nitride fabrication are performed by using neodymium as a simulant of the actinide (americium).

Two fabrication routes have been proposed and tested for the fabrication of the oxide precursors. In the first method the (Zr,Nd) oxide precursor was synthesised by a sol-gel method [4] and calcined at 800°C. In the second case, ZrO<sub>2</sub> beads were synthesised by the same sol gel route. Once calcined at 800°C the beads were infiltrated with a neodymium nitrate solution. The beads were dried at 100°C and subsequently calcined at 800°C for 2 hours to convert the nitrates into oxides and give a mixed (Zr,Nd) oxide used as a precursor for carbothermal reduction. ZrO<sub>2</sub> beads were also used

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as a precursor of ZrN. The effect of the carbon-to-oxide mole ratio was varied between 2 and 2.50 to investigate its effect on residual carbon and oxygen in the final nitride product for each oxide precursor (from route 1 or 2). Sintering was carried out at 1650°C for 8 hours in an Ar/H<sub>2</sub> stream in order to prevent the formation of higher nitrides.

In an attempt to simplify the multistage powder carbothermic reduction pellets route for nitrides, a direct pressing (DP) method for pellet fabrication, developed at ITU [5], has also been tested. The DP method follows the usual carbothermic reduction route. But, unlike the conventional comminution method, these nitride compacts are repressed and the pellets are sintered to the final required density (see Fig. 4.9).

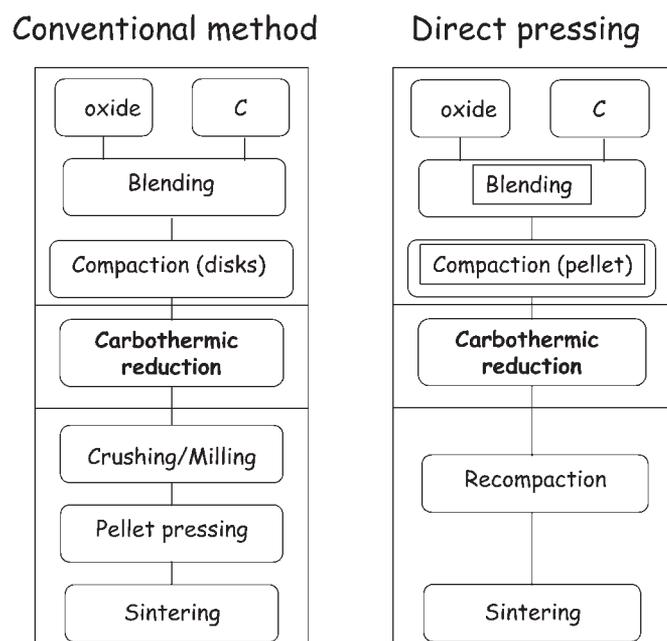


Fig. 4.9 Pellet fabrication methods investigated.  
(a) Conventional method,  
(b) Direct pressing

X-ray powder diffractometry was used to identify the phases and to determine the lattice parameters. In all cases three phases have been detected, the correspondent nitride ZrN or (Zr,Nd)N, ZrO<sub>2</sub> monoclinic and a third phase not yet identified (most likely is a intermediate carbonitride).

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### Fabrication of metallic fuels by powder metallurgy

Following preliminary actions described in [1], testing of different powder metallurgy routes for the fabrication of metallic fuels (Zr-TRU alloys) has been continued, as low-temperature alternatives to the melting-casting technique. Regarding the traditional powder metallurgy route, one of the major difficulties remains still the production of sinterable powders, particularly of Zr due to the relatively high ductility of this metal. For this reason, also different methods are being tested to efficiently powderize metal bars emulating the electrodes arising from pyrometallurgical reprocessing. Fig. 4.10 shows that even non-optimised Zr-powders obtained by filing can reach high densification at relatively low temperatures (1000°C) compared to the melting point, implying less risks of Am-volatilisation if preparing the alloy by diffusion/sintering. The last is of great importance since to ensure the success of any P&T strategy, total TRU-losses must be kept strictly below 0.1% at any step of the selected processes [2]. Further remaining works concern therefore the preparation of homogeneous sintered-alloys, as well as the optimisation of the powder production methods.

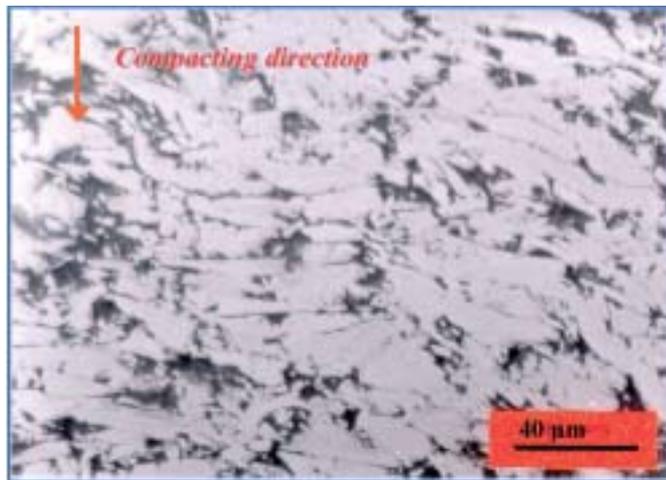
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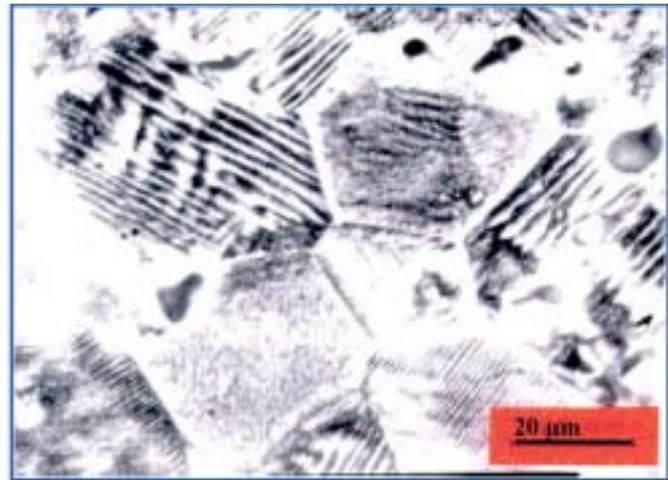
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**Pressed Zr-filed powder**  
**Compaction pressure: 800 MPa**  
**Density: 65% of theoretical**



**Sintered Zr-filed powder**  
**Conditions: 1000°C/2h, 0.3 bar (He)**  
**Density: 93% of theoretical**

Fig. 4.10 Microstructure of compacted and sintered Zr-filed powders

## 4.2.2 Materials properties

### He-release behaviour from fully stabilised zirconia

Previous studies which focused on the resistance of zirconia against fission damage (fission product and recoil atoms effects) [1,2] have shown a good behaviour of zirconia, *i.e.* no amorphization, after irradiation with 72 MeV iodine-ions to fluences up to  $10^{16}$  ions/cm<sup>2</sup>. Another important aspect that must be investigated to assess the suitability of a material to incorporate minor actinides is the resistance against  $\alpha$ -decay damage ( $\alpha$ -particle and recoil atom) and the corresponding accumulation of a large quantity of helium in the matrix (TUAR-2000, p. 110-113, and p. 126-128) [3,4]. Fully Stabilised Zirconia (FSZ) samples have been implanted with helium-ions of different energies (200 keV and 1 MeV) and with different fluences ( $1.4 \cdot 10^{14}$  to  $1.4 \cdot 10^{16}$  He<sup>+</sup>/cm<sup>2</sup>). The samples were implanted at room temperature with the Van der Graaf generator of the Forschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik (collaboration with R. Fromknecht). Effusion experiments have been performed on these samples using the Knudsen cell apparatus at ITU. The samples were annealed up to ~2000 K with a heating rate of 30 K/min and analyzed by electron microscopy during the various annealing stages. Fig. 4.11 shows the typical release profiles of He as a function of temperature for low- and high-fluence/energy samples.

For the low-fluence samples, a very narrow temperature interval for release was observed, probably associated to a vacancy/defect-assisted diffusion mechanism. An activation energy of 1.6 eV was calculated for this vacancy-assisted interstitial diffusion of He. For the higher implanted fluence, the helium-release begins earlier and continues up to high-

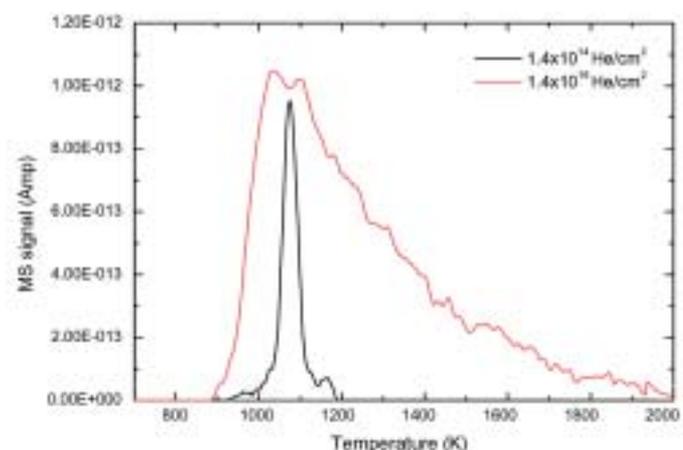


Fig. 4.11 Helium release as a function of temperature for low- and high-fluence/energy helium-implanted samples of fully stabilised ZrO<sub>2</sub>

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er temperatures. Probably the He release mechanism in the higher fluence case is connected to the formation of high-pressure bubbles during thermal annealing, as reported by other authors [5]. These investigations will continue to achieve a better-defined picture of the mechanisms acting and a comprehensive modelling of the release.

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### Final Results of the EFTTRA-T4 Irradiation Experiment

The first irradiation of an americium-containing inert matrix target, the so-called EFTTRA-T4 experiment in the HFR Petten, demonstrated the feasibility of transmutation of minor actinides in a once-through scenario in an epithermal neutron flux. However the selected target, composed of americium oxide and  $MgAl_2O_4$ , showed a rather poor behaviour under the irradiation conditions which was attributed to the large helium production due to formation of  $^{242}Cm$  by neutron capture of the  $^{241}Am$  [1]. Therefore complementary post-irradiation examinations were performed aiming at better understanding the behaviour of the irradiated EFTTRA-T4 material and also addressing the behaviour in case of a (simulated) temperature transient.

The electron probe microanalysis (EPMA) results showed a homogeneous distribution of most elements except Pu (Fig. 4.12). The plutonium profile showed an increase of Pu content from the rim of the pellet to the centre. A zone with high Am and/or Pu concentration, which was found in the fabricated samples, was not observed probably indicating that the radial cut was made at a position where the fabrication inhomogeneity was absent. The EPMA also revealed

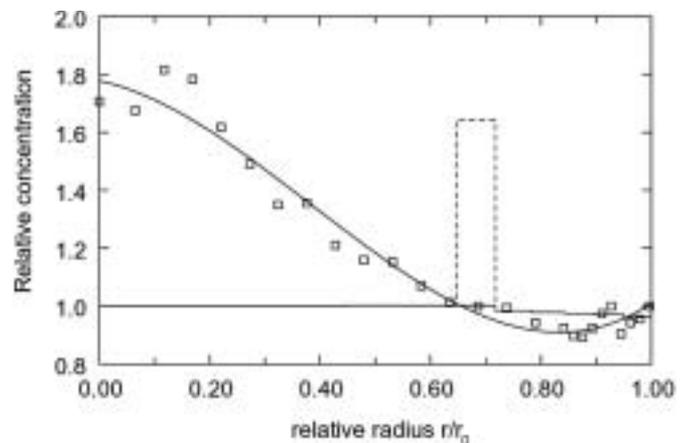


Fig. 4.12 Plutonium distribution in the EFTTRA-T4 target; □ EPMA results; curve MCNP/FISPACT calculations; the broken line shows the distribution assuming a zone of high Am content as was observed in the unirradiated sample.

that at least two different Pu-containing phases are present in the target whose Pu content and whose relative concentration vary radially. No identification of these phases could be made, but the formation of a hybonite-type phase ( $MgPuAl_{11}O_{19}$ ) cannot be excluded.

The microstructure analysis by TEM revealed some interesting aspects. Fig. 4.13 represents a TEM micrograph showing a Pu-Al rich area (hybonite?) as identified by EDX measurements that was formed from the originally 2-3  $\mu m$  Am-inclusions, after the transmutation process and the large pores formed by the high He-production which are all located within these inclusions.

Gas bubbles ranging between 5 and 20 nm were observed mainly in the Pu-Al inclusions but could anyway be found in the matrix. The surrounding matrix has been restructured *i.e.* the original 10  $\mu m$  sized grains of  $MgAl_2O_4$  have recrystallized in 200 – 500 nm grains, probably after forming an amorphous state. Previous experiments on ion-irradiated  $MgAl_2O_4$  have shown that this material can be turned amorphous easily by fission product irradiation and that it recrystallizes when exposed to ionising radiation (electrons) [2]. This fact supports well the observation made on the EFTTRA-T4 material where fissions occurred and  $\beta$ - and  $\alpha$ -decays accumulated during storage (the material was stored nearly 4 years after irradiation).

The helium release from the sample was studied with the Knudsen Cell and stepwise as well as ramp rate (30 K/min) annealings were performed. Apart from the helium, the release of fission gases (FGs), fission products (FPs), matrix atoms and actinides were recorded. Subsequently SEM analyses were performed.

The release of helium started at 900 K but the main He-release occurred at 1650 K. The behaviour of the fission gases is rather different in the sense that although a fraction was released together with the helium, a large part of e.g. Xe has been released with the effusion of the matrix. The release curve supports the assumption that the helium has precipitated mainly in the big pores whereas the FGs were probably less mobile and accumulated preferentially in the smaller bubbles like those observed by TEM in the matrix (see Fig. 4.13). Indeed the release of the FGs occurred to a large extent with the release of the matrix at temperatures above 1800 K.

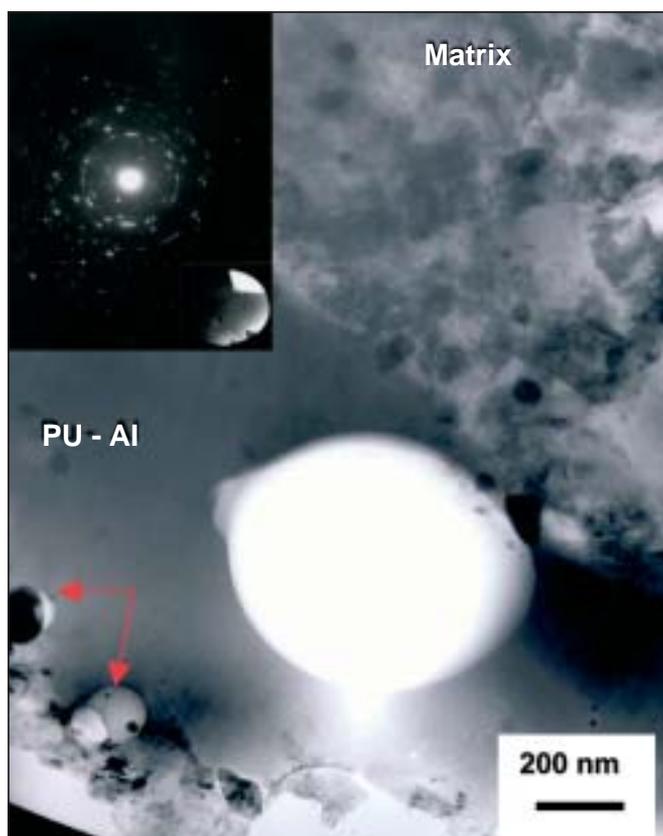


Fig. 4.13 TEM micrograph showing part of the nano-recrystallized matrix and a Pu-Al rich area containing a pore. The arrows indicate gas bubbles associated with insoluble FPs (Tc, Ru, Pd, Mo) precipitates (black dots inside the bubbles). The inset shows the diffraction pattern recorded in this area indicating its polycrystalline nature.

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#### 4.2.3 Special studies

In addition to the core activities in this project, special studies on particular scenarios were undertaken. These studies covered:

##### Fast Islands instead of fast Reactors?

ITU has patented the idea of using fast zones in thermal reactors (in which the neutron spectrum is hard) for transmutation purposes. This could provide a more economic alternative to the use of fast neutron reactors for such purposes [1].

##### „Mini“ ADS

Based on the use of thin layers of fissile material, a sub-critical booster unit has been designed for neutron multiplication. With this unit, coupled with a commercially available cyclotron, neutron fluxes similar to those produced in full-scale accelerator driven systems can be produced [2].

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### 4.3 Conditioning of Actinides in Pyrochlores

Pyrochlore compounds of the general formula  $A_2B_2O_7$  are studied as ceramic host phases for selective immobilisation of radionuclides in partitioning and conditioning strategies. In the above general formula A is usually a trivalent cation (e.g. a lanthanide) and B a tetravalent ion such as Zr or Ti. At ITU zirconium-based pyrochlores are under investigation for the selective immobilisation of transuranium elements such as Pu, Am and Cm, which can be incorporated in the A-site of the pyrochlore.

The reference material at ITU is neodymium-zirconium pyrochlore,  $(Nd_{2-x}An_x)Zr_2O_7$ , where An represents the actinide element. The pure  $Nd_2Zr_2O_7$  end member of this series has been prepared using a sol-gel process. After a compaction/milling step, dense pellets of the material have been produced for further characterization. Subsequently, investigations on the preparation of (porous) substoichiometric  $(Nd_{2-x}V_x)Zr_2O_7$  has been started (V representing a Nd vacancy) into which an actinide solution can be infiltrated to obtain the  $(Nd_{2-x}An_x)Zr_2O_7$  phase. The region of substoichiometry maintaining the pyrochlore structure extends up to  $x = 0.5$ . Infiltration experiments to produce  $(Nd_{1.9}Pu_{0.1})Zr_2O_7$  are underway. Neodymium-gadolinium-zirconium pyrochlore,  $(Nd_{2-x}Gd_x)Zr_2O_7$ , is also under investigation, as the addition of Gd as a neutron absorber is an interesting option. The pure gadolinium end member could not be stabilised in the pyrochlore structure, but this structure was easily obtained for the composition range  $0 < x < 1.5$ .

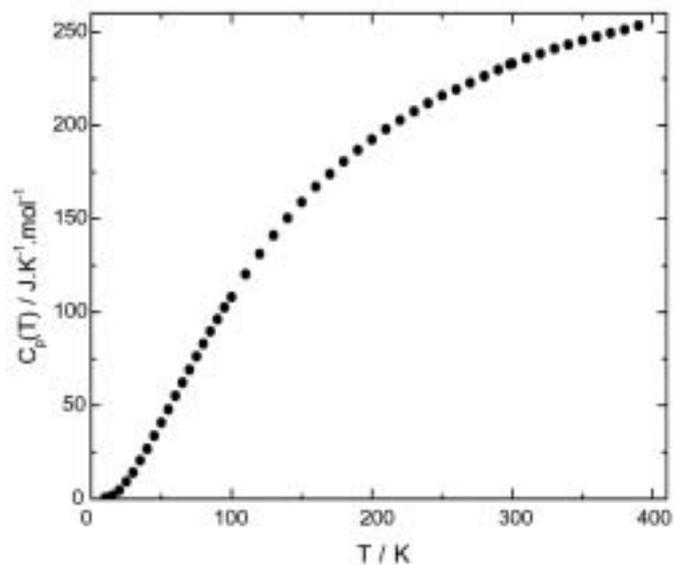


Fig. 4.14 The low temperature heat capacity of  $Nd_2Zr_2O_7$  as measured in collaboration with the University of Utrecht.

A programme on the characterization of the  $Nd_2Zr_2O_7$  material has been started. This includes thermodynamic and thermophysical characterization of the product. Fig. 4.14 shows the results of the low-temperature heat capacity measurements performed in collaboration with the University of Utrecht (The Netherlands), which yielded the standard entropy.

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## 5. Spent Fuel Characterization in View of Long-Term Storage

### Introduction

The goals of this project are to study: *a)* the behaviour of spent nuclear fuel during extended interim storage, *b)* the corrosion of fuel in repository water after failure of the container, and *c)* the effects of  $\alpha$ -damage and helium accumulation on the physical properties of spent fuel.

The investigation lines during the reporting year converged to a consolidation of the cumulative results obtained in the past, and to a definition of distinct questions concerning modelling of the spent fuel behaviour in nuclear waste repositories.

One topic is the effect of  $\alpha$ -radiolysis on fuel corrosion processes. This phenomenon is investigated in our laboratories by *doping*  $\text{UO}_2$  samples with highly  $\alpha$ -active  $^{238}\text{Pu}$ . Objections, concerning possible chemical effects of the dopants, were definitively answered this year by experiments that demonstrate the comparatively negligible role of plutonium chemistry in the uranium dissolution process. The crucial question regards the radiolysis conditions after relevant storage times, as well as the definition of the threshold above which radiolysis becomes dominant among other dissolution reactions in the repository groundwater. Our recent experiments on electrochemical noise analysis (ENA) proved to be sufficiently sensitive to detect this threshold.

The fuel corrosion behaviour is analyzed both under *oxic*

and *anoxic* conditions. Though the presence of oxidising species in water produces an increase in the corrosion rate, we observed that re-precipitation of hydrated uranium peroxide creates conditions that are extremely sensitive to variation of the surface morphology and to convection in water. Therefore, a study is in progress, aimed at characterising the microscopic features of the attacked surfaces. On the other hand, new leaching experiments have been started in anoxic water, to study the *dissolution-inhibiting* conditions, which are expected in a repository, where  $\text{H}_2$  is present at geological pressures of up to 100 atm.

Measurements of the corrosion potential were performed using electrodes made of spent fuel of low to medium burn-up. In addition, leaching experiments under water flow conditions have been started with pure  $\text{UO}_2$  and SIMFUEL.

The problem of characterising the state of the fuel after long storage times still represents an important issue.

Studies of  $\alpha$ -radiation damage were continued on ion-implanted and Pu-doped samples. Release and precipitation of helium was extensively investigated through thermal annealing and *Knudsen vaporisation* measurements, in conjunction with *scanning and transmission electron microscopy*. Yet, the prominent effects seem to occur at a macro-structural level as a consequence of relaxation of internal stress fields created by damage. A dramatic example is shown in Fig. 5.1. It is conceivable that the  $\alpha$ -damage density alone was the cause

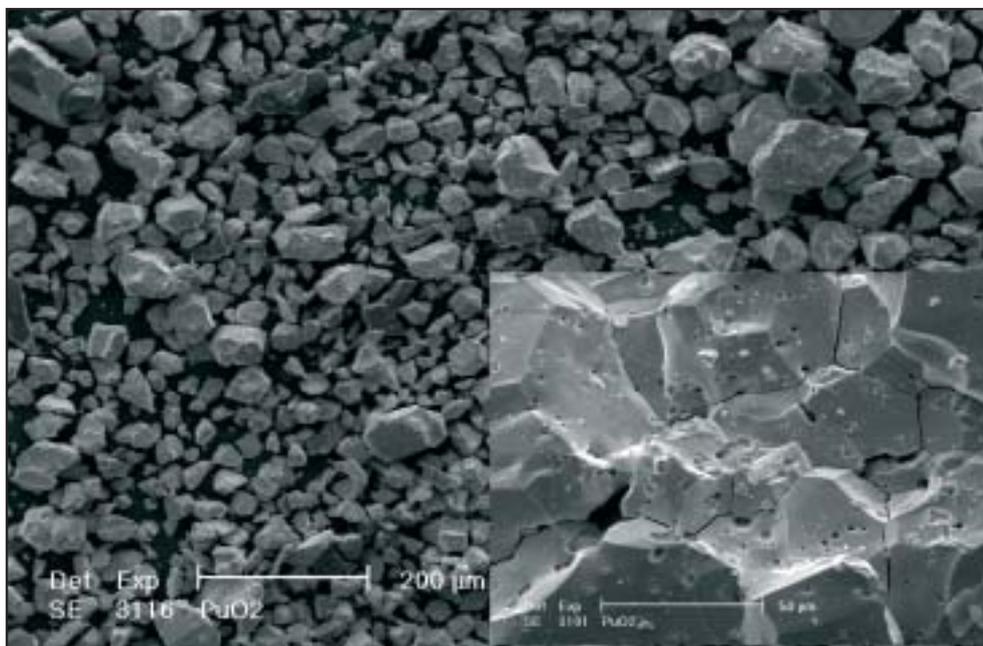


Fig. 5.1  
A  $\text{PuO}_2$  pellet fabricated in the ITU ceramics laboratory in 1966 exhibits after 45 years storage in inert atmosphere complete disaggregation of the sintered grains.

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of extensive micro-cracking. It is this morphology that must be subject to some interpretation, and may force an alternative approach to the prediction of spent fuel damage.

### 5.1 Corrosion and Dissolution Studies of $\text{UO}_2$ Containing $\alpha$ -Emitters

Experiments were performed on  $\text{UO}_2$  leaching containing  $^{238}\text{Pu}$  (simulating the  $\alpha$ -activity of spent fuel) in water under un-aerated conditions and showed enhanced U dissolution in the presence of  $\alpha$ -radiolysis [1,2,3,4]. These experiments were carried out in combination with surface analysis by X-ray photoelectron spectroscopy (XPS), to investigate oxidation/dissolution/re-precipitation. Three materials were used: pure  $\text{UO}_2$  ( $\text{UO}_2\text{-0}$ ), and  $\text{UO}_2$  containing  $\sim 0.1$  and  $\sim 10$  wt.%  $^{238}\text{Pu}$  ( $\text{UO}_2\text{-01}$  and  $\text{UO}_2\text{-10}$ , respectively). The  $\alpha$ -activity of  $\text{UO}_2\text{-10}$  represents irradiated MOX at discharge, that of  $\text{UO}_2\text{-01}$  corresponds to irradiated PWR fuel at  $\sim 35$  GWd/tM at  $< 10$  years after discharge and MOX after 1000 years.

#### Leaching

Static sequential leaching experiments were performed at room temperature under  $\text{N}_2$  atmosphere ( $< 0.4\%$   $\text{O}_2$ ) from 1 to 6800 hours. The concentration of  $^{238}\text{Pu}$  in the leachates was measured using low-level liquid scintillation counting (LSC) in combination with  $\alpha$ -spectrometry [5,6].

Fig. 5.2 shows the cumulative fractions of inventory in the aqueous phase (FIAP) of U and Pu in the leachates as a function of leaching time.

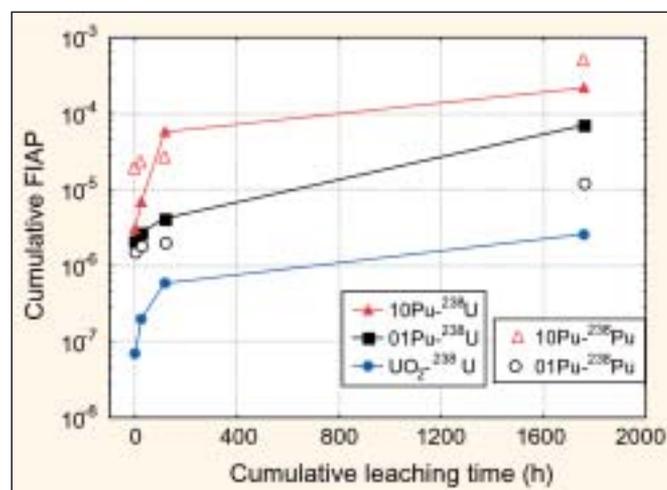


Fig. 5.2 Cumulative fraction of inventory in the aqueous phase of  $^{238}\text{U}$  and  $^{238}\text{Pu}$  for  $\text{UO}_2\text{-10}$ ,  $\text{UO}_2\text{-01}$  and  $\text{UO}_2\text{-0}$ .

The amount of U in the leachates for the  $\alpha$ -doped samples was higher than that for  $\text{UO}_2\text{-0}$ . The amount of U released in solution from  $\text{UO}_2\text{-10}$  increased during the initial time, while for longer contact times a small additional release was measured. The values for  $\text{UO}_2\text{-10}$  were higher than those of  $\text{UO}_2\text{-01}$  and  $\text{UO}_2\text{-0}$ . In  $\text{UO}_2\text{-01}$ , the FIAP was initially increasing less rapidly (but steadily) than in  $\text{UO}_2\text{-10}$ . At long times, the amount of U released from  $\text{UO}_2\text{-01}$  approached that of the high  $\alpha$ -activity material (the concentration of U in the leachates for  $\text{UO}_2\text{-10}$  reached a saturation limit). The fraction of  $^{238}\text{Pu}$  in the leachates for  $\text{UO}_2\text{-10}$  was always higher than the corresponding value of U, suggesting that more U than Pu had reprecipitated. This is in line with the presence of a relatively weaker Pu-peak in the XPS spectra after leaching times of 10 h or more. Work is ongoing to quantify the composition of the re-precipitated layers. Also, it is not clear why, for  $\text{UO}_2\text{-01}$ , release of Pu was lower than that of U.

The pH remained constant during the tests, as previously observed [3,4]. Amounts of U were found in the rinse solutions, in quantities higher than in the leachates – likely due to re-precipitation on the walls. The deposit was observable, as yellowish crystals. Fig. 5.3 shows the cumulative release in the leachates and in the rinse solutions.

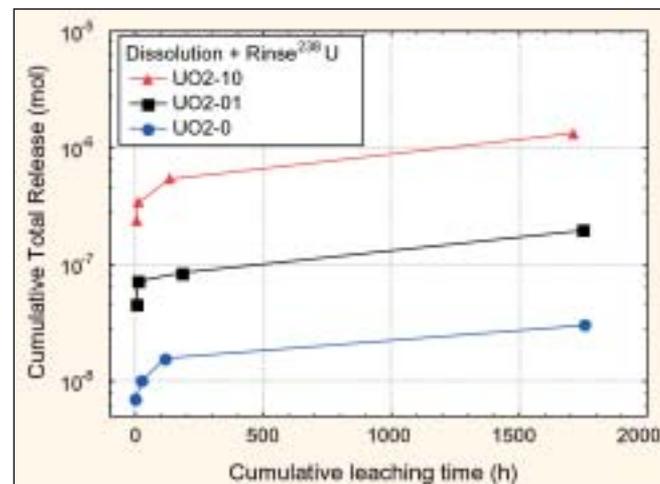


Fig. 5.3 Total release of  $^{238}\text{U}$  as a function of leaching time for  $\text{UO}_2\text{-10}$ ,  $\text{UO}_2\text{-01}$  and  $\text{UO}_2\text{-0}$ . The data represent the cumulative amount of U in the leachates and in the acid rinse solutions.

Adding the uranium concentration from the rinse solutions modifies the trends to become linear over the test time span. The convergence of the fractions in solution after long leaching times (see Figs. 5.4 and 5.2) disappears. The data in Fig. 5.3 underestimate the amount dissolved from  $\alpha$ -doped

samples, in particular from UO<sub>2</sub>-10, because they do not include the fractions re-precipitated on the surface of the samples.

The small initial amount of U(VI) indicates that surface oxidation occurred between the annealing and the XPS analysis preceding the leaching tests. After dissolution of this surface layer, UO<sub>2</sub>-10 showed a rapid increase in U(VI)/U(IV), and for leaching times > 10 h mostly U(VI) was detected on the sample surface. The ratio of U(VI)/U(IV) for UO<sub>2</sub>-0 and UO<sub>2</sub>-01 decreased during the first ~10 hours, whilst at longer times it began to increase. However, for UO<sub>2</sub>-0 after >100 h leaching, the ratio essentially levelled off around values corresponding to ~UO<sub>2.33</sub> [5,6], whilst in UO<sub>2</sub>-01, the increasing trend continued. XPS and solution analysis data are compared in Fig. 5.4.

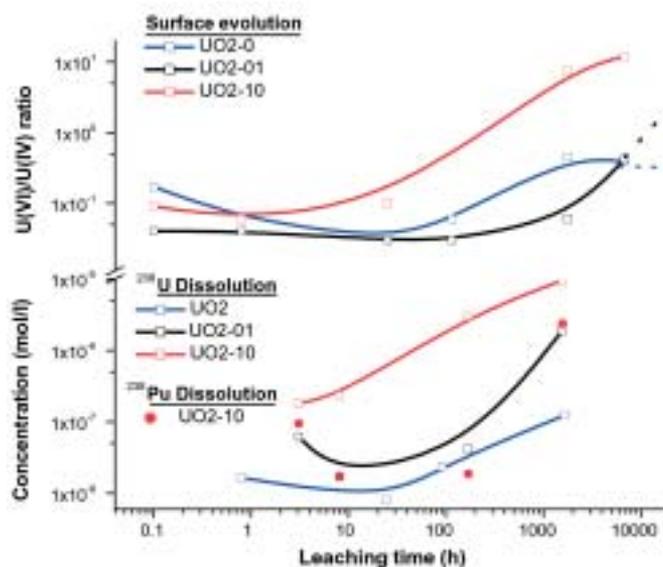


Fig. 5.4 Comparison of U(VI)/U(IV) measured on the sample surface with the concentration in solution vs. leaching time.

### X-ray photoelectron spectroscopy

XPS analysis of surface oxidation was performed. The spectral features of the U-4f core-level lines are sensitive to the chemical state of uranium. Each line consists of U(IV) and U(VI) components. The binding energy of the U(VI) is 1.5 eV higher than that of U(IV). Thus, the partition fraction of U in the two valences can be determined [7,8,9].

The U(VI)/U(IV) ratios and the corresponding uranium oxide compositions as a function of leaching time are summarised in Tab. 5.1.

Similar trends are observed in the two sets of data. After an initial decrease, both surface oxidation and U release increase: very rapidly for UO<sub>2</sub>-10, slowly, but continuously, for UO<sub>2</sub>-01, and with a tendency to stabilise at a level corresponding to ~UO<sub>2.33</sub> for UO<sub>2</sub>-0. Also plotted in Fig. 5.4 are the non-cumulative concentrations of Pu in the leachates for UO<sub>2</sub>-10.

After longer leaching times, the surface oxidation for undoped UO<sub>2</sub> levels off at ~UO<sub>2.33</sub> [5,6,7]. In the case of  $\alpha$ -doped UO<sub>2</sub>, radiolytic species augment surface oxidation and release of U, depending on the  $\alpha$ -activities. In UO<sub>2</sub>-10, the surface is covered by U(VI) after 100 hours. In UO<sub>2</sub>-01, oxidation reaches a level corresponding to ~UO<sub>2.41</sub>. Uranium saturation in solution is quickly reached in UO<sub>2</sub>-10, and, slowly, in UO<sub>2</sub>-01 (see Fig. 5.2). In spite of initial anoxic conditions, radiolysis produces oxidation and causes enhanced release of U. The dependence of U release on the  $\alpha$ -activity can be partially masked by saturation and re-precipitation [4]. This can be realised by considering the data in Fig. 5.3, which include the amounts of U re-precipitated on

Tab. 5.1 U(VI)/U(IV) measured by XPS before and after the leaching experiments on the sample surface. The O/U value was deduced from the U(VI)/U(IV) ratio.

Leaching time (hours)	U(VI)/U(IV) ratio	O/U ratio
UO <sub>2</sub> -0		
0	0.169	2.14
2	0.065	2.06
10	0.032	2.03
140	0.065	2.06
1700	0.502	2.33
6800	0.393	2.29
UO <sub>2</sub> -01		
0	0.040	2.04
2	0.037	2.04
10	(0.002)	(2.00)
140	0.067	2.06
1700	0.063	2.06
6800	0.600	2.41
UO <sub>2</sub> -10		
0	0.094	2.09
2	0.058	2.06
10	0.095	2.09
140	—	—
1700	7.479	2.88
6800	10.000	3.00

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the walls. In fact, higher amounts of U are dissolved from the  $\alpha$ -doped samples. This mobilisation process continues also after re-precipitation of U(VI).

The concentration of Pu in the leachates for  $\text{UO}_2$ -10 was higher than that of U, probably due to saturation and re-precipitation of uranium. XPS analyses detected Pu on the surface of  $\text{UO}_2$ -10 also after long leaching times, when the surface is covered with U(VI) phases.

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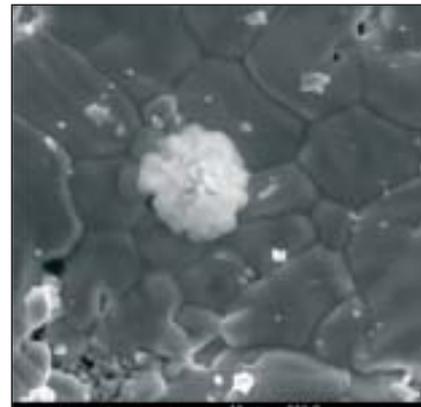


Fig. 5.5 SEM image of an alteration phase found on the  $\text{UO}_2$  sample leached at  $180^\circ\text{C}$  in groundwater containing a Si concentration of  $10^{-2}$  mol/l.

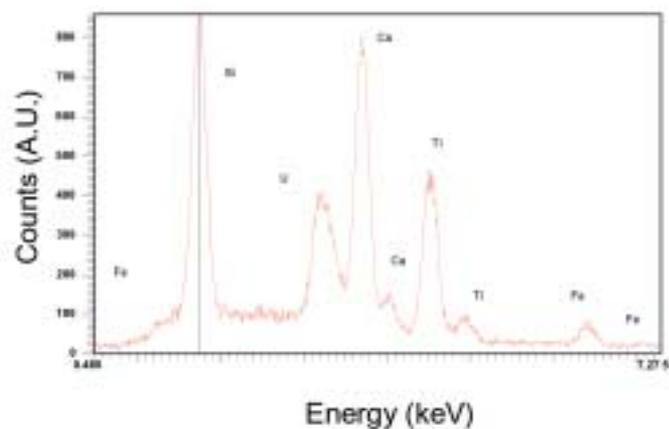


Fig. 5.6 EDX spectrum of the phase shown in Fig. 5.5, showing the elements U, Si, Ca, Ti and Fe present.

## 5.2 Phase Formation During Anoxic Fuel Leaching Processes

Mobilisation of uranium from solid  $\text{UO}_2$  takes place by oxidative dissolution (positive Eh values in oxidising redox conditions) by changing the valence of U from +IV to +VI. In final storage in deep geological formations, anoxic or reducing geo-chemical conditions are expected for spent fuel. Efforts were therefore made to investigate the alteration mechanisms of  $\text{UO}_2$  in contact with repository water ions - namely co-precipitation with calcium, dissolution with carbonate ligands under anoxic conditions, and solid phase alterations (coffinitization) in contact with Si (see Figs. 5.5 and 5.6).  $\text{UO}_2$  pellets were exposed to groundwater with altered ionic compositions under ambient ( $25^\circ\text{C}$ ) and hydrothermal ( $180^\circ\text{C}$ ) conditions. In this study bulk analysis was used, in conjunction with optical microscopy and SEM-EDX to examine the contacting liquid/solid surfaces after the tests.

The results suggest secondary mineral formation in Si-enriched solutions as possible alteration mechanisms. Co-precipitation with Ca or solid phase formation with carbonate was *not* detected. Formation of U(IV)-Si-phases could alter the crystal lattice of  $\text{UO}_2$  by conversion from the Fluorite- to the Zircon-type structure. Silicates with a U:Si-ratio of 1:2 were found by EDX analysis. A remarkable observation was the formation of secondary products containing U, Si, Fe, Ca and Ti, which were compositionally quantified and compared with their geo-chemical counterparts.

One can conclude that U(IV)-Si-phases, as well as mixed U(IV) minerals (possibly Brannerite or Ekanite) were formed in Si-enriched solutions under hydrothermal conditions (see Tab. 5.2). This will be further diversified when fission products or actinides are present, which can form own phases or incorporate into the secondary products.

Tab. 5.2 Element contents (wt.%) of the observed U-Si-Ca-Fe-Ti phase and values found for naturally occurring similar minerals [1].

Element this work	observed in	Ekanite	Brannerite
U	25,68	20,07	92,97
Si	21,39	27,66	-
Ca	28,43	7,08	6,25
Fe	2,90	9,78	22,63
Ti	21,61	-	18,73

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### 5.3 Phase Formation During Radiolysis Simulation Experiments

The influence of water chemistry and oxidant concentration on radiolysis-enhanced fuel dissolution was investigated in experiments simulating chemical radiolysis effects. Leaching tests under ambient air with solutions of de-ionized water and natural groundwater (GW) containing the water radiolysis product  $H_2O_2$  in various concentrations were performed. After 72 h of leaching, the U concentration was measured and the solid surfaces examined with scanning electron microscopy and electron-dispersive X-ray analysis (SEM-EDX).

At lower  $H_2O_2$  concentrations, dissolved uranium concentration was found to be higher. Furthermore, the uranium concentration in groundwater was always lower than in pure water (Fig. 5.7).

Different alteration phases on the sample surface were found (Figs. 5.8 and 5.9). If this was treated in pure water, a yellow discoloration was observed, whereby the surface was covered with amorphous products (at low  $H_2O_2$  concentrations) and with numerous acicular crystals forming a thick layer (at high  $H_2O_2$  concentrations).

In the case of the treatment in GW, the samples remained black, and no layer was formed. Instead, crystals of octahedral shape were found on the almost intact surface. All alteration phases contain only U with, possibly, O, H, and C. Different polymorphs of uranium(IV)oxihydroxides (para-, meta-Schoepite, hemihydrate) and of uranium(VI)peroxide (Studtite, meta-Studtite), were likely formed, and, in the case

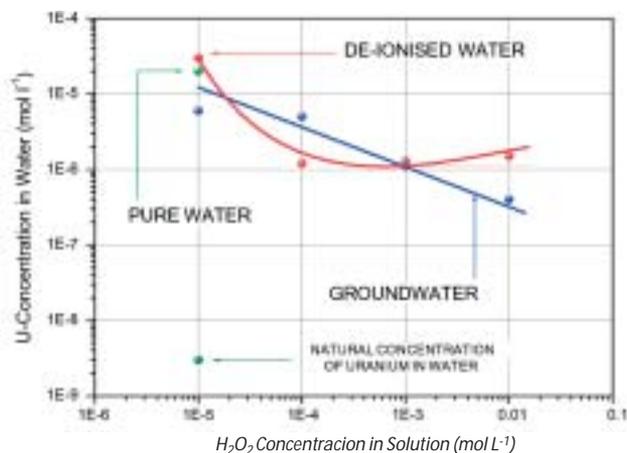


Fig. 5.7 The dissolution of  $UO_2$  under the influence of the water radiolysis product  $H_2O_2$  was measured generally higher in pure water (red points) than in groundwater (blue points).



Fig. 5.8 After  $H_2O_2$  treatment in pure water, acicular crystals of a U(VI) compound (most obviously U peroxide) form on the  $UO_2$  surface.



Fig. 5.9  $H_2O_2$  treatment in groundwater results in formation of a U compound of octahedral shape. The black colour and crystal shape analysis suggest a higher oxide, like  $U_3O_8$ .

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of GW, some scavenging mechanism leads to deactivation of  $\text{H}_2\text{O}_2$ . Octahedral crystals are also observed for higher oxides ( $\text{U}_3\text{O}_8$ ). Comparison with natural analogues as well as with results of previous work on geo-chemical solubility limits supports this theory.

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## 5.4 The Kinetic of Dissolution of Irradiated $\text{UO}_2$ Fuel

To predict the evolution of the solid/aqueous systems representing spent fuel in contact with water data on both thermodynamics and kinetics are necessary. A way to obtain this information is to produce a *continuous flow-through reactor* [1-3] for solid dissolution reactions. Aim of this work is to determine the dissolution rates in the absence of secondary phases. The experimental set up used in this investigation prevents precipitation of dissolved reaction products since these are swept out of the vessel before the solution becomes saturated [4].

The continuous flow was designed for hot-cell use, allowing us to determine dissolution rates with the method of mixed flow reactors (continuously stirred tank reactors). Dissolution tests were performed under oxidic conditions, in granite groundwater (GW) on LWR  $\text{UO}_2$  spent fuel at room temperature. The investigation was focused on the released amounts of fuel and on the dissolution rates calculated from these data. The samples were two fuel rod slices of, respectively, 29 and 53 MWd/Kg burn-up (2.070 g and 2.574 g, including cladding of 4.6 mm radius).

Oxidic conditions were obtained by equilibrating the leachant (from GW with 1 mM carbonate concentration) with air at room temperature. The circulation rate was maintained in the range of 0.025 to 0.15 ml/min, ensuring that reactor steady state conditions are achieved. These were determined in a previous work [5].

The leachant was finally filtered through a 450 nm membrane, and afterwards acidified with 5%  $\text{HNO}_3$ . Uranium analyses were carried out with a mass spectrometer modified to handle radioactive samples.

The measured pH did *not* show significant alterations during leaching. The dissolution rates, determined under a continuous flow-through, are based on the uranium concentra-

tion of the effluent under steady state (it must be made sure that this corresponds to the steady state and *not* to the equilibrium solubility). The dissolution rates were calculated from a kinetic equation [6] containing the measured spent-fuel dissolved concentrations. The results indicate that with the used flow rates *no precipitation of secondary phases occurs*. Preliminary results indicate that the spent fuel dissolution rate depends on burn-up as shown in Tab. 5.3.

Tab. 5.3 Dissolution rates of spent fuel

Sample	Groundwater [ $\text{CO}_3\text{H}^-$ ]	Dissolution rate ( $\text{mol m}^{-2} \text{s}^{-1}$ )
$\text{UO}_2$ LWR fuel 29 MWd/Kg U	[1mM]	6.77E-11
$\text{UO}_2$ LWR fuel 53 MWd/Kg U	[1mM]	2.66E-10

The ongoing work is focused on the dissolution rates of different radionuclides contained in spent fuel. Furthermore, higher burn-up fuels, including MOX, will be investigated.

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## 5.5 Electrochemical Studies on Spent Nuclear Fuel

Extensive electrochemical measurements have been previously performed on fresh  $\text{UO}_2$  as well as on doped fuel simulating different burn-ups, in order to identify the dissolution mechanisms, and to quantify the rate-controlling steps [1,2,3,4,5]. Our findings were confirmed by the work of Shoosmith *et al.* [6,7,8], who carried out examinations of electrodes of unirradiated  $\text{UO}_2$  fuel in water, and measured

the effects of  $\alpha$ - and  $\gamma$ -sources on fuel electrodes of CANDU spent fuel [9].

These results are now compared with the effects of groundwater on irradiated fuel under final storage conditions. Irradiated PWR spent fuel samples of different burn-ups were examined (both  $\text{UO}_2$  and MOX, with high radioactivity levels). The observed corrosion behaviour is in agreement with the previous results. Yet, under extreme conditions, the lack of an appropriate electrode design still entails limitations in the accuracy of the experiments, so that, e.g., the determination of the corrosion behaviour of fuel rated at high burn-ups and/or submitted to water exposure for long times still requires improvements in the experimental techniques.

### Testing of $\text{UO}_2$ and MOX-fuel

In synthetic granitic-bentonitic groundwater, the free corrosion potential (proportional to the logarithm of the corrosion rate [10]) is higher in spent fuel than in  $\text{UO}_2$ , and increases with burn-up. Its development is 2-3 times faster in spent fuel than in fresh  $\text{UO}_2$ , indicating a readier initial oxidation (Fig. 5.10).

The corrosion potential of the fuel at 45.2 GWd/t is higher than that produced in pure  $\text{UO}_2$  by oxygen ingress of 2 ppm. This is explained by formation of oxidative radiolysis products that lead to a faster surface oxidation and build-up of

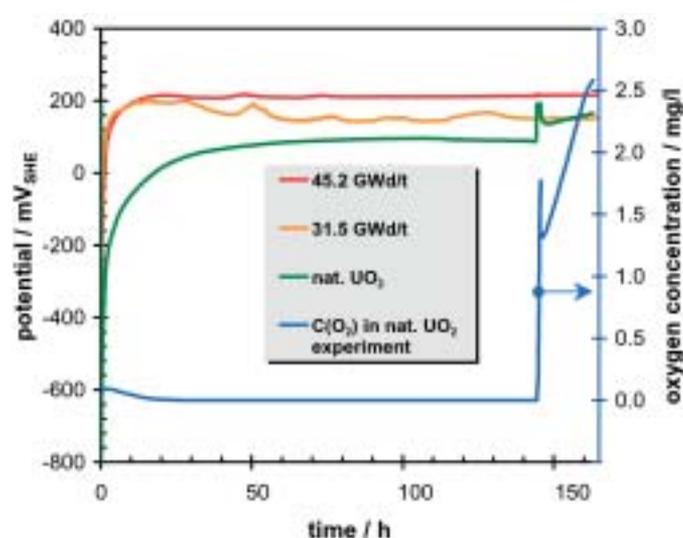


Fig. 5.10 Corrosion potential of spent fuel in GW as a function of immersion time compared to that of fresh uranium dioxide. The latter is plotted for variable oxic conditions (blue curve).

corrosion products. In addition, reacting fission products will also influence the oxidation process. The corrosion rates calculated from the corrosion potentials are, respectively,  $0.06 \text{ mg m}^{-2} \text{ d}^{-1}$  at a burn-up of 31.5 GWd/t, and  $0.3 \text{ mg m}^{-2} \text{ d}^{-1}$  at 45.2 GWd/t, whilst in fresh  $\text{UO}_2$  a corrosion rate of  $0.01 \text{ mg m}^{-2} \text{ d}^{-1}$  (increasing to  $0.06 \text{ mg m}^{-2} \text{ d}^{-1}$  after ingress of 2 ppm oxygen) was measured.

Experiments on spent MOX fuel (7.5% Pu in average, and 25%  $\text{PuO}_2$  in the Pu-rich phase) and fresh  $\text{UO}_2$  in 0.1 M NaCl were carried out. Under strictly similar conditions the MOX samples showed different behaviour. Fresh  $\text{UO}_2$  exhibits in the first 100 h a lower corrosion potential than spent MOX (of 21 GWd/t burn-up). Furthermore, the corrosion potential of  $\text{UO}_2$  increases, while at this stage that of MOX remains 100 mV lower. This means that the dissolution rate of the  $\text{UO}_2$  phase in MOX is one order of magnitude slower than in fresh  $\text{UO}_2$ . On the other hand, the measured corrosion potential of  $\text{UO}_2$  was 150 mV higher than that previously measured in synthetic granitic-bentonitic GW in a laboratory environment. This effect can be attributed on the radioactivity background in the hot cell, which causes radiolysis and  $\gamma$ -induced photo corrosion.

## Testing of $\alpha$ -doped $\text{UO}_2$

### Electrochemical Noise

The investigation of current and potential fluctuations in electrochemical systems by means of Fast Fourier Analysis provides detailed information on the ongoing corrosion processes [11,12]. This method is very sensitive to the state of the solid/liquid-interface. As result of electrochemical noise analysis (ENA), the frequency-dependent noise resistance and the noise power are obtained. These quantities are related to slow electrochemical processes, like those observed in corrosion activated by applied alternating potentials of low frequency. On the other side, physical properties of the electrode and solid surface processes (e.g. evolution of gas bubbles) manifest at higher frequencies. Noise power and noise resistance measurements have been carried out for the first time at ITU with  $\text{UO}_2$  and  $\alpha$ -doped ( $^{238}\text{Pu,U}$ ) $\text{O}_2$  in de-aerated GW (Fig. 5.11).

The results are in good agreement with those obtained with alternative techniques. For instance,  $10 \text{ w/o } ^{238}\text{Pu}$ -doped  $\text{UO}_2$  has the highest noise power and lowest noise resistance - that is the highest chemical reactivity in de-aerated GW. This is followed by the  $0.1 \text{ w/o } ^{238}\text{Pu}$ -doped material and, finally, by pure  $\text{UO}_2$ , which exhibits the lowest reactivity.

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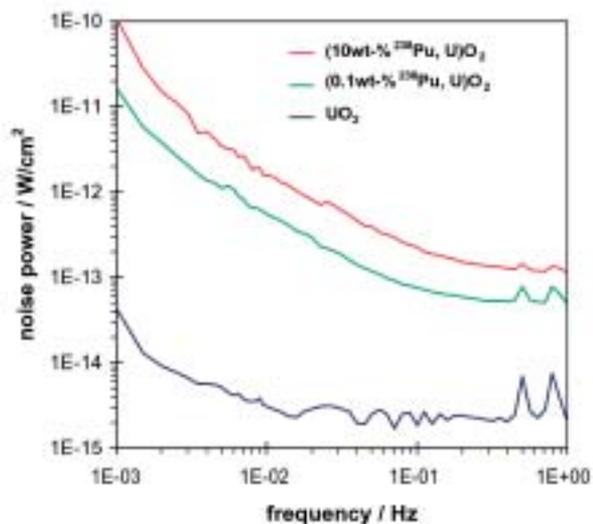


Fig. 5.11 Electrochemical noise power spectra obtained from  $\text{UO}_2$  and  $\text{UO}_2$  doped with  $^{238}\text{Pu}$  show a large difference in noise power between a-doped and pure  $\text{UO}_2$ . This can be used to identify possible thresholds for the  $\alpha$ -radiolysis effect.

Compared to pure  $\text{UO}_2$ , in 10 w/o  $^{238}\text{Pu}$  doped samples the noise power decreases with time for *all* frequencies, and noise resistance increases only for the *low* frequencies. This is apparently linked to the decrease in corrosion rate with elapsing immersion time. The low frequency noise is thought to be mainly associated to interfacial processes, e.g. to the presence of certain radiolysis products or to extended defects (see e.g. 10 w/o  $^{238}\text{Pu}$  doped  $\text{UO}_2$ ) where radiolytic reactions are more intense.

### Influence of $\text{H}_2\text{O}_2$

Radiolysis of water produces both molecular ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ ) and radical products ( $\text{OH}^\cdot$ ,  $\text{HO}_2^\cdot$ ,  $\text{H}^\cdot$ ,  $e_{\text{aq}}^-$ ), whereby  $\text{H}_2\text{O}_2$  plays the most important role [13]. In the first few hundred years after disposal, the initially strong  $\gamma$  and  $\beta$  activity of spent fuel decreases by three orders of magnitude. On the other hand, an activity persists, and, after a few hundred years of storage, produces the entire fuel radiation field

A conspicuous local production of compounds like  $\text{H}_2\text{O}_2$  is expected at the spent-fuel/water interface, establishing pronounced local oxidising conditions. These leaching mechanisms were analyzed as further components of the electrochemical process [14] governing  $\text{UO}_2$  corrosion.

Free corrosion potential, oxygen content and redox potential measurements are carried out in 0.1 M NaCl solution un-

der anoxic conditions. After addition of 2.5 ml of 3 mM  $\text{H}_2\text{O}_2$ , the corrosion potential of  $\text{UO}_2$  increases (200 mV). This is coupled to an increase in oxygen content and in the redox potential (120 mV). As a result, the corrosion rate first increases from  $0.1 \text{ mg m}^{-2} \text{ d}^{-1}$ , before addition of peroxide, up to  $100 \text{ mg m}^{-2} \text{ d}^{-1}$ , and then, after 500 h, decreases down to  $1 \text{ mg m}^{-2} \text{ d}^{-1}$ . Solution analysis of samples taken at different immersion times shows no increase of U concentration. In fact, the U concentration remains constant after addition of peroxide in the range of  $2 - 6 \cdot 10^{-10} \text{ g/l}$ . This behaviour confirms results reported above, according to which precipitation of U in the form of hydrated uranium peroxide (metastudtite:  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ ) takes place.

Techniques like cathodic sweep experiments and impedance measurements have been performed to analyse changes in the surface state of the electrode. The former shows larger reduction peaks after peroxide addition. This indicates that thicker oxidised layers of some uranium compound are present. Also impedance measurements confirm this conclusion. Fitting of the impedance curves obtained before and after addition of  $\text{H}_2\text{O}_2$  shows an increase in thickness of the oxidised layer.

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## 6. Measurements of Radioactivity in the Environment

With the Fifth Framework Programme, a new project in support to DG Environment started at ITU. This project is concerned with the implementation of the OSPAR Convention, and with the protection of the marine environment in the northeast Atlantic Sea from discharges of radioactive substances [TUAR-99, p. 117].

ITU staff participated as part of the EU delegation in the meeting of the OSPAR group on „Radioactive substances“ held in January 2001 in Tromsø (Norway) and in the four working groups and in the steering committee for the updating the MARINA study on the radiological exposure of the European Community from radioactivity in North European marine waters [TUAR-2000, p. 119].

ITU shall provide DG Environment and member states with technical assistance in sampling and in measurements. In this context, analytical procedures were developed during 2001 and applied to real samples collected in radioactively contaminated environments. Entire cores of sediment sam-

ples collected in the Irish Sea have been screened by low level  $\gamma$ -spectrometry for actinides and for fission products. In Fig. 6.1 an example representing the profile of  $^{241}\text{Am}$  obtained by  $\gamma$ -spectrometry is reported. The layers presenting the highest activity, have been investigated for the presence of particles containing americium using the  $\alpha$ -tracks method. The  $\alpha$ -spots were selected and investigated by SEM and SIMS. In Fig. 6.1 the  $\alpha$ -tracks obtained for one hot spot as well as its image obtained at mass 241 by SIMS in the layer 26-28 cm depth are illustrated. Since in the SIMS spectrum the mass 239 and 240 were not detected, the signal obtained at mass 241 confirms that  $^{241}\text{Am}$  is the alpha emitter generating the  $\alpha$ -tracks in the hot spot investigated

The marine sediments were also analyzed directly by GDMS as for  $^{237}\text{Np}$  concentration. A calibration curve was obtained spiking a sediment reference material with a standard solution of  $^{237}\text{Np}$ . From the calibration curve the relative sensitivity factor for the determination of  $^{237}\text{Np}$  was obtained.

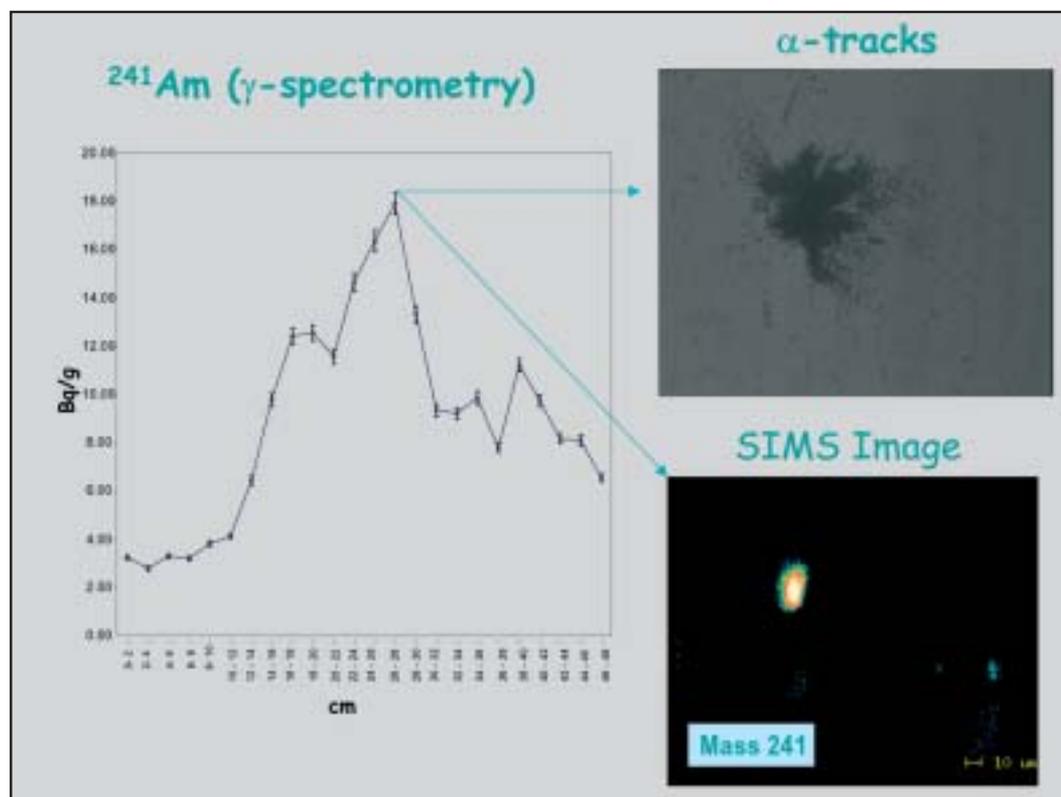


Fig. 6.1  $\gamma$ -spectrometry for an entire core from Irish sediment.  $\alpha$ -tracks and SIMS image from the layer 26-28 cm depth.

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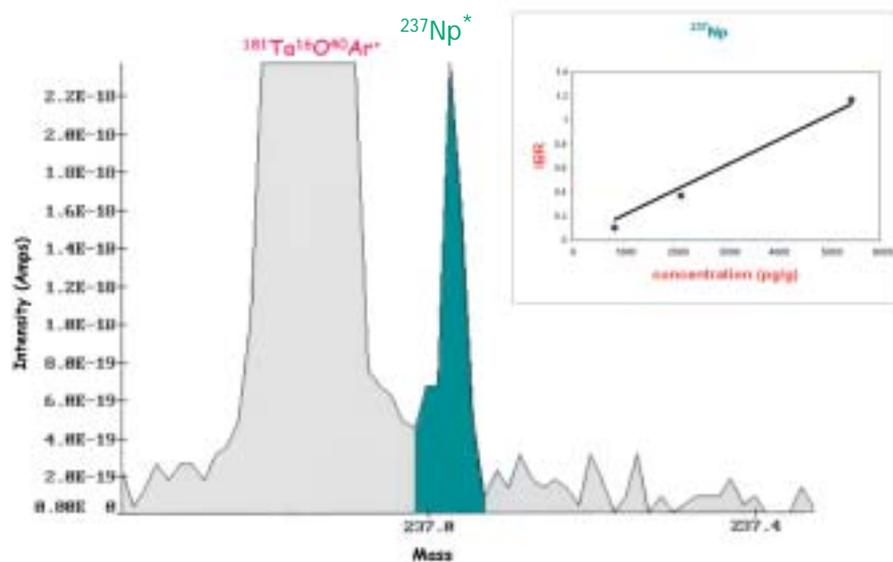


Fig. 6.2

$^{237}\text{Np}$  measurements by GDMS in marine sediments. (Mass Resolution 6000, Integration time 4.5 s, Detection limit is 6 pg./g).  $^{237}\text{Np}$  concentration corresponds to 2 ng/g (50 mBq/g).

In Fig. 6.2 the mass spectrum obtained for a sediment sample along with the calibration curve are illustrated. The detection limit of the procedure is 6 pg/g.

In Tab. 6.1 the results obtained for  $^{237}\text{Np}$  in three sediment layers by GDMS are compared with those from  $\gamma$ -spectrometry – based on the measurement of  $^{233}\text{Pa}$  – and they are in very good agreement.

In collaboration with the Bundesamt für Seeschifffahrt und Hydrographie in Hamburg, ITU staff participated in a sampling campaign in the Baltic Sea. Sediments and water samples were collected and will be analyzed in both institutions in the framework of an intercomparison exercise for validation of analytical procedures.

In the framework of the IAEA Coordinated Research Programme on “Radiochemical, Chemical and Physical Characterization of Radioactive Particles in the Environment”, particles containing depleted uranium stemming from soil samples collected in September by the UNEP depleted Uranium assessment team and IAEA in Kosovo were characterized by SEM and by SIMS. Studies of the oxidation

Tab. 6.1 Quantitative analysis of  $^{237}\text{Np}$  by glow discharge mass spectrometry and  $\gamma$ -spectrometry (based on  $^{233}\text{Pa}$ ) from different Irish sediment layers.

Sediment Layer	GDMS		$\gamma$ -spectrometry	
	Pg/g	mBq/g	Pg/g	mBq/g
18 - 20 cm	3420.9	89.2	3120.6	81
20 - 22 cm	1922.4	50.1	1958.5	51
22 - 24 cm	1739.3	45.5	1689.7	44

state of the depleted uranium particles were performed by micro-XANES at the HASYLAB at DESY (Hamburg) in collaboration with the AEKI Atomic Energy Research Institute (Budapest). The results obtained indicate that uranium is present in particles mostly in the U(IV) form, a maximum ratio of U(VI) to the total uranium content was obtained as 24% indicating that the particles contained mainly the less mobile form of uranium. In Fig. 6.3 micro-XANES spectra obtained for two particles are shown.

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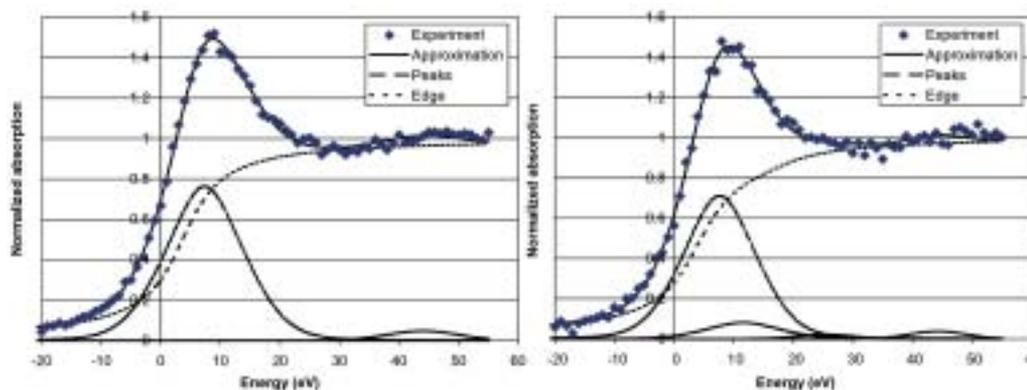


Fig. 6.3

Least square fitting of the spectra of single particles, (a) Kosovo 4a and (b) Kosovo 4b. The zero of the energy scale was close to the inflection point of the U(IV) standard.

## 7. Safeguards Research and Development

### Introduction

The Institute's safeguards programme was continued in the reporting period according to the needs of its major customers, *i.e.* the EURATOM Safeguards Office (ESO) and the International Atomic Energy Agency (IAEA). The development work aims at providing measurement tools that complement a suite of technical means for effectively safeguarding nuclear material, *i.e.* the verification of international treaties. The tasks involved can basically be categorized as being research and development activities or as measurement support activities. In the latter category the operation of the on-site laboratories at La Hague (LSS) and at Sellafield (OSL) represent a major effort which is covered by an administrative arrangement between ESO and ITU. Supporting activities to ESO for sample measurements, particle analysis, in-field analysis and technical support were continued. Development work focused on improvement of radiometric techniques, analysis of alternative nuclear materials and analytical methods related to dry reprocessing of spent fuel. In the area of nuclear forensics, methodologies for age determination of Pu particles and bulk amounts of highly enriched uranium were developed.

### 7.1 Improvement of Measurement Techniques and Methods

Radiometric measurement techniques are widely used for the assay of nuclear material. Development work focused both on the improvement of existing techniques as well as on the development of new methodologies for novel applications. Recent challenges, such as the analysis of Np and

Am in spent fuel solutions and in waste, the accurate assay of actinides in an advanced fuel cycle (pyro-processing) were addressed and solutions for particular scenarios were developed.

#### 7.1.1 Performance of isotope correlations for the estimate of $^{242}\text{Pu}$

High-resolution gamma spectrometry is a rapid and precise method for measurement of the isotopic composition of plutonium. It suffers from the absence of a useful gamma line from the isotope  $^{242}\text{Pu}$ . The isotope abundance of  $^{242}\text{Pu}$ , however, can be estimated through a so-called isotope correlation.

In the mid-nineties a new type of isotope correlation for estimating the  $^{242}\text{Pu}/^{239}\text{Pu}$  ratio in LWR plutonium has been introduced, based on the following relation [1,2] with recommended coefficients  $C_0$ ,  $C_1$  and  $C_2$  for PWR and BWR fuels, respectively:

$$\frac{^{242}\text{Pu}}{^{239}\text{Pu}} = C_0 \cdot \left[ \frac{^{238}\text{Pu}}{^{239}\text{Pu}} \right]^{C_1} \cdot \left[ \frac{^{240}\text{Pu}}{^{239}\text{Pu}} \right]^{C_2}$$

We have adopted this type of correlation for the routine analysis of Safeguards samples in the EURATOM On-Site Laboratories and in the Institute for Transuranium Elements. In order to cover the full range of plutonium materials received for analysis, the application of the above correlation has been also extended to AGR and Magnox-type plutonium. Tab. 7.1 summarizes our best numerical values for the coefficients  $C_0$ ,  $C_1$  and  $C_2$  derived from a larger set of measured isotopic data.

Since in many instances the origin and the type of the plutonium are not known a priori, criteria for categorization were established helping to select the appropriate isotope correlation. Parametric plots of the ratios  $^{238}\text{Pu}/^{239}\text{Pu}$  versus

Tab. 7.1 Average performance of the isotope correlations for  $^{242}\text{Pu}$

Type of Pu	Help Quantity $\epsilon$	Coefficient			[242, ICT]-[242, TIMS]	
		$C_0$	$C_1$	$C_2$	Mean (%)	St. Dev. (%)
Magnox	<0.028	0.210	0.075	2.020	1.25	7.16
AGR	<0.55	1.859	0.705	0.554	-1.00	7.95
BWR	<0.1	1.117	0.315	1.650	3.00	6.40
PWR	>0.1	1.313	0.330	1.700	-1.40	3.95

## Projects

$^{240}\text{Pu}/^{239}\text{Pu}$  generally allow to discern unambiguously Magnox, AGR and LWR plutonium, and to some extent also BWR and PWR plutonium, as shown in Fig. 7.1. With this kind of categorization by means of a help quantity  $\epsilon = [^{238}\text{Pu}/^{239}\text{Pu}]/[^{240}\text{Pu}/^{239}\text{Pu}]^{1.857}$  the performance of the  $^{242}\text{Pu}$  estimate is substantially improved in most cases. The right-hand column in Tab. 7.1 lists the observed mean differ-

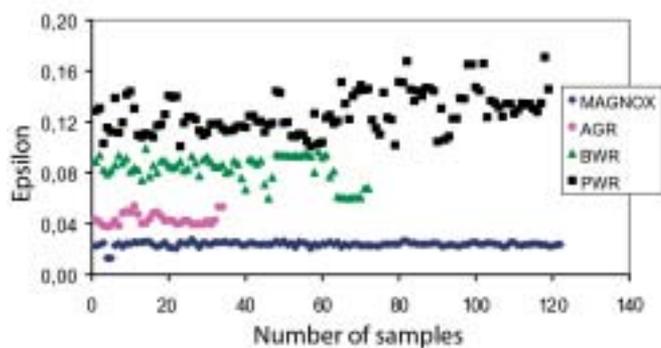


Fig. 7.1 Categorization of plutonium for selecting the appropriate isotope correlation

ences and standard deviations of  $^{242}\text{Pu}$  isotope abundances determined by isotope correlation (ICT) and thermal ionization mass spectrometry (TIMS).

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- [2] G. Bignan, W. Ruther, H. Ottmar, A. Schubert, C. Zimmerman, "Plutonium Isotopic Determination by Gamma Spectrometry: Recommendations for the  $^{242}\text{Pu}$  Content Evaluation Using a New Algorithm", ESARDA Bulletin 28 (1998) 1

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### 7.1.2 Upgrade of COMPUCEA

Significant modifications and improvements related to hardware/software and measurement methodology were made to COMPUCEA (Combined Product Uranium Concentration and Enrichment Assay), which for the time being represents the main in-field measurement technique utilized by EURATOM for physical inventory verification in low-

enriched uranium fuel fabrication plants. The previous software was transformed to a Windows NT platform with added features for improved automation and quality assurance. The methodological improvements made concern the K-edge densitometry part of COMPUCEA, which has been recently equipped with a new type of photon source in the form of a mixed  $^{57}\text{Co}$ - $^{153}\text{Gd}$  source.

The use of the new type of photon source has prompted a detailed experimental study to establish accurate correction factors and/or procedures for reliable bias correction. Two kinds of matrix effects of practical relevance were studied: the effect of nitric acid used as solvent for the dissolution solid uranium samples, and -more importantly- the impact of varying amounts of gadolinium occurring in some of the uranium materials to be analyzed. High-precision measurements were carried out on carefully characterized reference solutions offering reasonable ranges of matrix variation for the influencing parameters to be studied. The improved analysis procedures and bias corrections resulting from the study were implemented in the COMPUCEA software and successfully employed during the in-field measurement campaigns conducted for EURATOM in 2001.

### 7.1.3 Analytical methods for pyro-processing

The ongoing development of the pyro-reprocessing process at ITU requires a continuous and timely analytical support for the assessment of the separation processes conducted in the existing test facilities. To this end non-destructive assay (NDA) techniques such as energy-dispersive X-ray fluorescence (XRF) analysis, neutron coincidence counting (NCC) and high-resolution gamma spectrometry (HRGS) were extensively employed for the quantitative determination of actinides (U, Np, Pu, Am, Cm) in the process samples. The respective samples were available in small quantities ( $\cong 100$  mg) either in the form of eutectic salt or in metallic form with Cd, Zr or Bi as major metallic matrix constituents.

Substantial development work for measurement data analysis was needed to correctly interpret the measurement responses obtained with the different NDA techniques from the given samples for quantitative analysis. This included both calculational methods (e.g. Monte Carlo calculations) as well as intensified calibration efforts. Existing analysis software and measurement procedures for the NDA techniques, originally developed and routinely used for Safeguards measurements on uranium and plutonium-

bearing product samples, could be rarely directly applied because of the different nature of the measurement samples. In some instances also new analytical procedures had to be developed. For example, for the absolute determination of  $^{241}\text{Am}$  two HRGS techniques based on the technique of internal spiking, either with uranium or with plutonium, were established for routine use.

Typical threshold quantities needed by the various NDA techniques for quantitative analysis range from about 1 ng for the  $^{241}\text{Am}$  measurement by HRGS to 0.5 mg for the  $^{244}\text{Cm}$  determination by NCC, and about 0.1 mg for the determination of U, Np and Pu by means of energy-dispersive K-XRF analysis.

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#### 7.1.4 Techniques for flow sheet verification of $^{237}\text{Np}$

The IAEA envisages the application of Safeguards measures for the control of  $^{237}\text{Np}$  as an alternative fissile nuclear material for nuclear arms. The Safeguards measures currently discussed anticipate a more qualitative verification approach for this nuclide based on flow sheet verification (FSV) measures in reprocessing plants.

We performed reactor code calculations in order to estimate the amounts of  $^{237}\text{Np}$  produced in different types of reactor as a function of initial fuel composition and of burn-up. It could be shown, that light water reactors using  $\text{UO}_2$  fuel and operated at high burn-ups are the most important source of Np. We have investigated and experimentally tested straightforward measurement techniques applicable to the quantification of  $^{237}\text{Np}$  in a reprocessing plant at identified key measurement points normally carrying the major inventory of this isotope, namely the input solution and the high-level liquid waste (HLLW). Our measurement approach has been designed to add minimum costs and efforts to existing Safeguards measures for uranium and plutonium, and to use presently available non-destructive assay instrumentation to a maximum extent. To this end we have identified the hybrid K-edge densitometer (HKED) and high-resolution gamma spectrometry (HRGS), both being available in advanced on-site Safeguards analytical laboratories, as most suitable measurement vehicles.

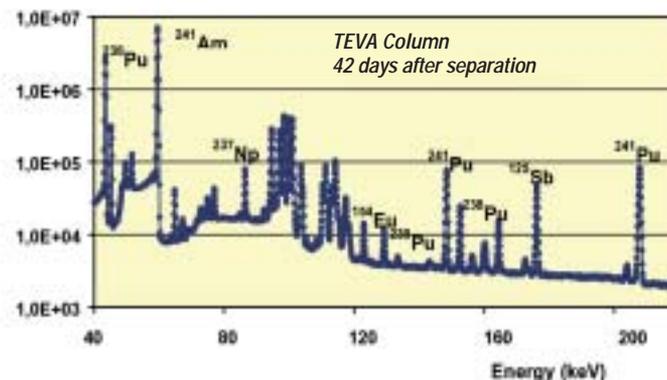


Fig. 7.2 Gamma spectrum from a TEVA column

The XRF part of the HKED instrument allows a direct determination of  $^{237}\text{Np}$  in the high-level liquid waste stream, given the expected typical concentration level of about 1 g  $^{237}\text{Np}/\text{l}$ . A somewhat more elaborate procedure had to be worked out for the  $^{237}\text{Np}$  determination in the input solution, which is not possible from a direct XRF measurement because of the more unfavorable measurement conditions (lower  $^{237}\text{Np}$  concentration, large U/Np ratio). The developed analysis method for  $^{237}\text{Np}$  in input solutions consists of a selective chromatographic extraction of Np and Pu using TEVA resin followed by a determination of the Np/Pu ratio on the column by HRGS. The knowledge of the Pu concentration in the input solution from the routinely performed HKED measurements then allows evaluating the  $^{237}\text{Np}$  concentration. The method has been tested on simulated solutions and validated on real spent fuel solutions with known Np/Pu ratio. Fig. 7.2 shows a typical gamma spectrum from a TEVA column holding the Np-Pu fraction together with some traces of fission products. The common multi-group-analysis (MGA) code can be used for the  $^{237}\text{Np}/\text{Pu}$  ratio determination from the gamma spectrum.

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## 7.2 Detection Methods and Measurements of Micro-Particles

In the framework of the projects "Environmental Sampling" and "High Performance Trace analysis" in support to IAEA and ESO, the research has been focused on the characterization of particles containing U/Pu. Since either TIMS and SIMS cannot resolve directly on particles between isobars

## Projects

$^{238}\text{U}/^{238}\text{Pu}$  and  $^{241}\text{Pu}/^{241}\text{Am}$ , a new project – awarded by the JRC General Directorate in the framework of the “Innovation Project Competition” launched by the “Co-operation Strategy and Technology Transfer” – was started at the end of 2001. The project consists in the exploitation of a laboratory (industrial) prototype based on resonance ionization mass spectrometry for the characterization of environmental radioactive microparticles (nm dimensions). The innovative characteristic of the system is its capability to resolve isobaric interferences without chemical separation to be overcome by the original sample. The system could also be equipped with a sample holder for bulk analysis.

An automated Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray (EDX) analyzer has been installed for the control of the chemical composition and of the size of particles, before measurement by secondary ion mass spectrometry (SIMS). The system also allows determining light elements like F, N and O in the particle.

A study on the relationship between enrichment in  $^{235}\text{U}$  in particles of uranium oxide and number of fission tracks produced during irradiation in a nuclear reactor has been completed [1]. The irradiation experiments were conducted in the Triga reactor at the University of Mainz on samples prepared using the control particles produced at ITU [2].

An interlaboratory exercise has been organized in collaboration with the IAEA (see chapter 7.7) for testing the performance of SIMS for microparticle characterization.

### References

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 [2] O. Stetzer, Final report PhD-thesis, JRC-ITU-TN-2001-11

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## 7.3 Analytical Support to EURATOM

On behalf of ESO, verification measurements were carried out on samples sent to ITU for analysis by EURATOM inspectors. On a routine basis, 150 product samples (*i.e.*  $\text{UO}_2$ ,  $\text{PuO}_2$  and MOX) were analyzed using the appropriately qualified radiometric and chemical measurement techniques. In order to ensure a maximum of confidence in the results communicated to ESO, each set of samples is accompanied throughout the entire analytical process by a “quality con-

trol sample”, *i.e.* a primary or secondary reference material that serves as a quantitative check on the procedure.

In the framework of the „High-Performance Trace Analysis“ project in support to IAEA and ESO, the determination of the isotopic composition of uranium particles was implemented for routine safeguards inspections. Samples were taken by EURATOM inspectors in three European enrichment plants. The uranium isotope ratios were measured on particles from 43 swipe samples using SIMS. Based on the implementation of the SIMS methodology of particle analysis in safeguards (Fig. 7.3) also contracts with ABACC and KAERI for particle analyses were concluded.

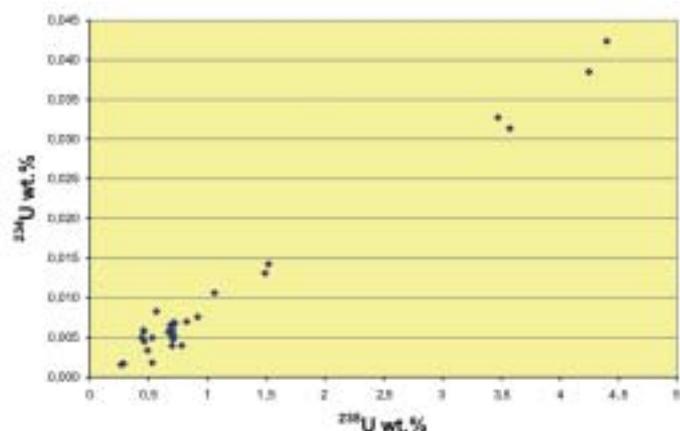


Fig. 7.3 Correlation of uranium isotope mass abundance ( $^{234}\text{U}$  vs.  $^{235}\text{U}$ ) as measured in particles sampled in enrichment plants

For the inventory verification in fuel fabrication plants using low enriched uranium (LEU) the COMPUCEA instrument is used in so-called in-field measurement campaigns. The major improvements in hard- and software are described in section 7.1.2. These upgrades, complemented by advanced staff training, significantly contributed to the timely provision of high quality results. During five inspection campaigns at locations in Spain, France, Sweden, Belgium and the UK, uranium enrichment and concentration measurements were carried out by ITU staff on 92 samples.

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## 7.4 Illicit Trafficking and Nuclear Forensic Science

### 7.4.1 International Technical Working Group (ITWG)

The Institute participated under the codename 'Galapagos' in the ITWG Uranium Round Robin exercise in February 2001, as one of a total of nine separate laboratories. This was a follow-on exercise to the ITWG Plutonium Round Robin test, which was described in TUAR-2000.

The aim of the exercise was to identify the 'illicit' material, its origin and the possible intended use, and was performed within the ITWG reporting system of a 24 hour, one week and two months report. A conventional forensic science analysis was also requested in the framework of an invented scenario. The exercise was performed in collaboration with officers from the Bundeskriminalamt (BKA, Wiesbaden) with the intention of investigating how the different requirements of conventional forensic science and nuclear forensic science can be optimized. The BKA carried out an initial test

for conventional explosive devices concealed within the container; an essential prerequisite on suspect illicit samples before they can be permitted entry into the Institute.

The sample consisted of 2.323 g of a fine grey-black powder, identified as  $U_3O_8$  with an enrichment of 89.9 wt. %  $^{235}U$ . The presence of 0.68 wt. %  $^{236}U$  indicated that the sample contained reprocessed material. No plutonium could be detected. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that the sample consisted of three morphologically different components, as illustrated in Fig. 7.4. These can be described as:

1. Agglomerates (up to about 300  $\mu m$  in diameter) of very small irregular  $U_3O_8$  particles, with an average size of about 1  $\mu m$ , forming the major component of the material.
2. Dendritic-type agglomerates of fibrous particles of  $U_3O_8$ .
3. Small thin platelets of  $U_3O_8$  with an average platelet size of 0.91  $\mu m$ .

An examination by SIMS showed, however, that all the components had the same isotopic composition. The material

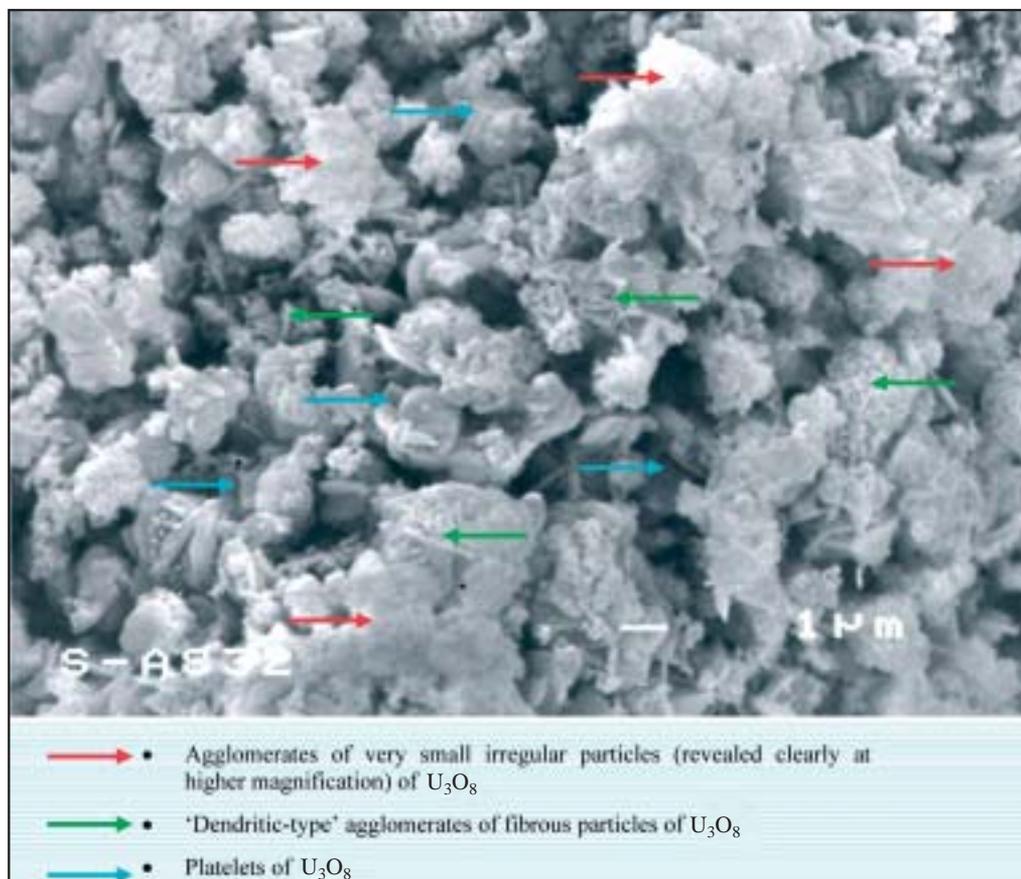


Fig. 7.4

Scanning electron micrograph of the surface of an agglomerate indicating that several distinct components are present. Some examples of these are indicated as follows:

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*Fig. 7.5 Fingerprint impression revealed on the alpha-contaminated SF1-type brass container number LH 384 in the ITWG Round Robin Uranium Test. The fingerprint was made visible by cyanoacrylate-ester vapour deposition (the so-called 'super glue' technique), followed by soot dusting in a fume hood in the Institute.*

was extremely pure, with only 125 µg / g UO<sub>2</sub> of trace impurities, as measured by inductively coupled plasma mass spectrometry (ICP-MS).

The age of the material since the last processing was determined to be 22.4 ± 1.2 years using the <sup>234</sup>U / <sup>230</sup>Th isotopic ratio, measured by TIMS.

An analysis using conventional forensic science techniques was made and various fibre and glass traces were identified inside the packing material. Of special interest was the identification and imaging of a fingerprint on a contaminated sample – the first time that this has ever been achieved. This was performed using cyanoacrylate deposition followed by dusting with soot under glovebox conditions, and the result is shown in Fig. 7.5. These techniques are being developed further and are of great importance in conventional forensic science.

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### 7.4.2 Age determination of Pu particles

A consistent multi-isotope approach had been developed for the precise and accurate determination of the age of Pu in bulk samples. In the reporting period the methodology was transferred to age determination in single, micrometer-sized particles. This is important because it allows age dating of mixtures and thus reveals the ages of individual components in powders. The method may be applied in nuclear forensics, in safeguards and in view of a fissile material cut-off treaty (FMCT) where Pu age determination can be used for treaty verification purposes.

The parent/daughter ratios <sup>238</sup>Pu/<sup>234</sup>U, <sup>239</sup>Pu/<sup>235</sup>U and <sup>240</sup>Pu/<sup>236</sup>U were measured in the individual particles directly by SIMS. First, Pu standards of known ages were analyzed in order to establish a relative sensitivity factor (RSF), which was applied to correct the difference in ionisation efficiency of Pu and U. This experimentally determined RSF was then used in the calculation of the ages of real samples. The ages obtained on particles by SIMS were proven by other methods on bulk samples, thus underlining the potential of this method in Pu particle age dating.

As the U/Pu separation in reprocessing can hardly be complete, the residual traces of U may cause a systematic error in the determined age of the Pu. The effect of residual uranium in reprocessed Pu for Pu age determination was investigated for the parent daughter ratios mentioned above. Isotopic compositions of residual U were calculated for reactor and weapons grade Pu by ORIGEN2 and SCALE computer codes. The amount of the individual U isotopes was compared to the amounts growing in from the decay of the plutonium parent isotopes. These calculations showed that generally weapons grade Pu is more sensitive to residual U than reactor grade material. In particular the age derived from the <sup>238</sup>Pu/<sup>234</sup>U ratio of weapons grade Pu may show high positive biases. The effect is somewhat less pronounced for the <sup>240</sup>Pu/<sup>236</sup>U ratio. It was noticed that U impurity levels below 500 ppm did not result in significant bias for reactor grade Pu.

### 7.4.3 Age determination of highly enriched uranium

Age determination of highly enriched uranium is important for nuclear safeguards, for the verification of the FMCT and in nuclear forensic investigations. A methodology was developed using the decay of <sup>234</sup>U to <sup>230</sup>Th with a half-life of 2.45·10<sup>5</sup> years and investigations started using the decay of <sup>235</sup>U to <sup>231</sup>Pa (half-life: 7.04·10<sup>8</sup> years). Three different measurement techniques were employed: thermal ionisation

mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS) and alpha spectrometry (AS). For TIMS and AS analysis U/Th separation was performed using TEVA ion chromatography resin. Prior the separation, samples were spiked with  $^{233}\text{U}$  and  $^{232}\text{Th}$  (TIMS) and  $^{228}\text{Th}$  (AS), respectively. The age was then calculated from the  $n(^{234}\text{U})/n(^{230}\text{Th})$  ratio. The new Multi-Collector ICP-MS (12 Faraday detectors and an ion counter) was used to determine the  $n(^{234}\text{U})/n(^{230}\text{Th})$  and  $n(^{235}\text{U})/n(^{231}\text{Pa})$  ratios directly without U/Th/Pa separation and spiking. Using NBL (New Brunswick Laboratory) reference materials of known ages, we could prove that the TIMS and AS techniques produced accurate and precise results, whereas ICP-MS still needs further development work to fully exploit the potential of this versatile instrument.

#### 7.4.4 Analysis of samples

In the context of a case of theft of radioactive material from a German nuclear installation, ITU was asked by the national authorities to provide technical assistance. A large number of samples were analysed by gamma spectrometry, mass spectrometry and alpha spectrometry in order to identify possible correlations between the individual samples and to explain the origin of the contaminations. The isotopic composition of U and Pu were determined in each sample as well as the age of the latter. Nuclide ratios of gamma emitters were determined in order to find out whether the samples had been subjected to some kind of treatment. Microstructural investigations on some of the samples provided additional information.

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#### 7.4.5 Supporting PECO countries in combating illicit trafficking of nuclear materials

In order to support the development of an effective and validated response to counteract illicit trafficking of nuclear materials in the EU, the candidate countries and some CIS countries, ITU is currently executing a series of projects with the Candidate Countries to the European Union, based upon the experience gained in previous Phare and Tacis projects. Following the recommendations of the International Technical Working Group, the objectives of the projects are:

- assessment of the national situation during a fact-finding mission in the country,
- technical upgrade and/or training related to the categorisation of nuclear material on the spot and assistance for the identification of seized nuclear material, through joint analysis at ITU,
- implementation of the recommended Model Action Plan in the form of a national handbook called RITNUM (Response to Illicit Trafficking of Nuclear Material),
- validation of the national Model Action Plan by the organization of a demonstration exercise in the country involving all the identified services in the field.

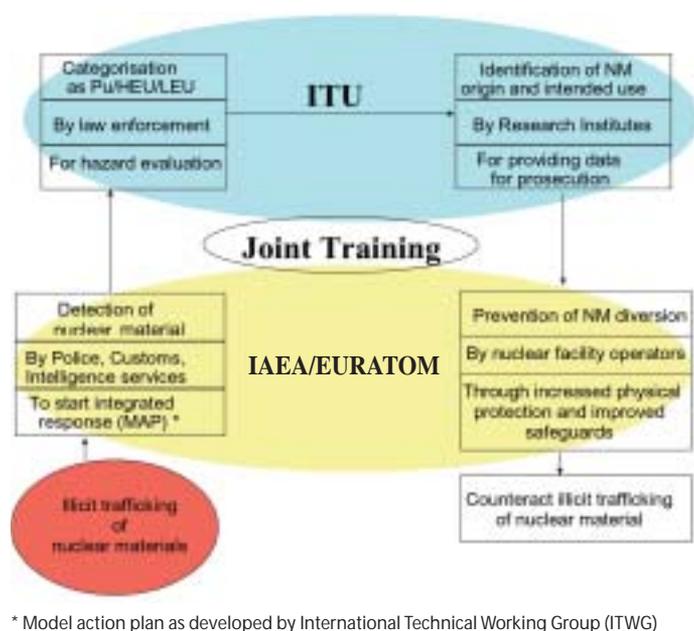
After a kick-off meeting held in Karlsruhe in November 2000 and attended by two participants of each country, 6 fact-finding missions have been already performed (Romania, Slovenia, Cyprus and the three Baltic States). A general meeting with all the involved parties (customs, police, intelligence services, health physics, nuclear reference laboratory...) was organized to describe the procedure of the integrated response and the national needs were assessed.

In the frame of the Technical Co-operation Project RER/9/060 of the International Atomic Energy Agency on Physical Protection and Security of Nuclear Materials a training Workshop for Law Enforcement Services and Radioanalytical Laboratory Experts on Combating Illicit Trafficking of Nuclear and/or Radioactive Materials will be organized at ITU (first group: 21-25 January 2002, second: March 2002) for states where assistance projects are underway. Technical experts from law enforcement services (customs, police or intelligence service) and representatives of a radioanalytical laboratory will follow a series of lectures to:

- train customs officer and criminal police or intelligence agent to categorize on-site radioactive and nuclear material by hand-held instruments
- familiarize a radioanalytical expert with nuclear forensic techniques to characterize nuclear material and be able to write expert reports according to ISO standards.

This joint action will be extended to other eastern countries (Belarus, Ukraine, Azerbaijan, Kazakhstan) on IAEA request. As EUROPOL showed interest during the kick-off meeting, a close co-operation is being organized including training for EUROPOL staff and a common follow-up of the above-cited projects. Participation to the demonstration exercises is foreseen.

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\* Model action plan as developed by International Technical Working Group (ITWG)

Fig. 7.6. Interaction between different initiatives and organizations involved in combating illicit trafficking of nuclear materials

As illustrated in Fig. 7.6, the subject projects are fully integrated in the interplay of the other international efforts in combating illicit trafficking of nuclear material. IAEA is strongly involved in the training sessions for the national expert, as explained above. Information exchange is also organized with DG Environment and DG Transport and Energy from EURATOM who are respectively organizing either local training sessions for custom officials (see: detection) or central training for nuclear facility operators (see: prevention).

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## 7.5 Laboratoire Sur Site (LSS), La Hague

The LSS was designed to perform analysis of input and product samples in the framework of EURATOM safeguards for nuclear material verification (TUAR-00, p. 24-25).

The LSS is equipped with a shielded suite for the remote handling of input samples, a suite of 4 boxes – 2 being equipped with telemanipulators – to perform measurements of PuO<sub>2</sub> samples, a glove-box to measure concentra-

tion and enrichment of uranium solutions and a suite of glove-boxes housing a robot dedicated to the chemical separations of U and Pu fractions prior to isotope dilution mass spectrometry measurements.

The destructive analysis technique is used for about 10 to 15% of the samples measured by non destructive techniques (hybrid K-edge densitometer, neutron and gamma counters) to assure their measurement controls and whenever a NDA measurement has to be corroborated.

### 7.5.1 Sample throughput and manpower

During this first full year of operation 193 mission weeks were carried out on site (*i.e.* a team of 4 analysts/week) to perform analytical, maintenance and administrative tasks. During the 48 weeks of presence 489 samples have been analyzed. A detailed list of the samples and the related measurements (including calibration and quality control ones) is given in Tab. 7.2 and 7.3.

Tab. 7.2 Number of samples analyzed

Sample type	Number of samples
Input	320
UCD	83
PuO <sub>2</sub>	27
UN	12
UN 1 <sup>st</sup> cycle	40
Occasional	7

Tab. 7.3 Number of measurements performed

Measurement type	Number
HKED	1400
Density	690
Neutron counter	200
Chemical separations	650
Mass spectrometer	1400

### 7.5.2 Problems encountered

Two main problems were encountered this year. The first one concerned the spiking of undiluted input samples using the so-called Large Size Dry Spikes (LSD). The presence of an organic compound added during their manufacturing was causing dissolution problems of the spiking material. The problem could be resolved in short time by elaboration of a new procedure. The experience gained in the LSS will also be at the benefit of the On Site Laboratory (OSL) installed

at Sellafield which just started to use this spiking method. The other major problem was caused by a chemical reaction between the PuO<sub>2</sub> powders and the polymer material of the containers in which they were sampled. As soon as this problem was noticed, the inspectors were asked to change the container type. However, significant efforts were made in order to analyze the PuO<sub>2</sub> samples, which were provided in the plastic containers.

### 7.5.3 Perspective

In December 2001, the contract between ESO and ITU for the operation of the laboratory was renewed. For 2002, the throughput is expected to exceed 1000 samples including a new type of sample coming from the reprocessing of „old“ plutonium batches.

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## 7.6 On Site Laboratory (OSL), Sellafield

The OSL was constructed to analyze samples at the site of the Sellafield reprocessing plant (UK) and has now been operated routinely for the second year. Input samples originating from the Magnox reprocessing plant have been analyzed as a new sample type since the beginning of the year. A comparative study using different spikes was done to double-check the method. The procedures for dissolution and dilution of uranium powders and pellets have been optimized. In October and November a substantial exercise was done to calibrate the Thorp hybrid K-edge for input material and the OSL hybrid K-edge for MOX. Simultaneously, a comparative study of the OSL and Thorp procedure for Large Size Dried spiking was done in the OSL.

### 7.6.1 Sample throughput

The OSL was manned on an average with three analysts per week except at the beginning of the year due to an extended outage of the Thorp and Magnox plants. A total of 202 samples were analyzed in the OSL (see Tab. 7.4). Tab. 7.5 gives an overview of the distribution according to the sample type. Analysis of MOX samples was started this year in view of the foreseen start up of the new MOX plant.

### 7.6.2 Analysis of Magnox input samples

Magnox input samples were sent to the OSL on a regular basis since January 2001. The U/Pu ratio was much higher and the <sup>239</sup>Pu-fraction lower than expected for input samples. Repeating the analysis using <sup>239</sup>Pu spikes instead of <sup>244</sup>Pu spike confirmed all results. The <sup>239</sup>Pu spike is now routinely used for Magnox input samples. <sup>239</sup>Pu is more available and can be prepared in the OSL while the <sup>244</sup>Pu spike is a very precious material that should be used in routine safeguards analysis only in well justified cases.

### 7.6.3 Dissolution procedure for uranium samples

Uranium samples can be measured in the OSL either by COMPUCEA technique or by a combination of K-edge and thermal ionisation mass spectrometry for concentration and enrichment determination. In both cases the isotopic dilution mass spectrometry (IDMS) is used as quality control method. The dissolution method was adapted so that the same solution can be used for both COMPUCEA and K-edge, hence streamlining the analytical procedure.

### 7.6.4 Extended calibration exercise

The hybrid K-edge at Thorp was re-calibrated after installation of a new workstation with the latest update of the HKED software. All standards used for this purpose were prepared in the OSL. In view of the commissioning of the

Tab. 7.4 Number of samples analyzed in the OSL in 2001

Plant	Samples
Magnox	65
Thorp	109
Springfields	24
MDF	4

Tab. 7.5 Type of samples analyzed in the OSL in 2001

Material	Samples
Pu Nitrate solution	71
PuO <sub>2</sub> powder	39
U Nitrate solution	18
U powder/pellet	40
U/Pu input solution	30
MOX pellet	4

## Projects

Sellafield MOX plant by the end of 2001, the XRF in the OSL was calibrated for MOX. Again, standards prepared in the OSL were used. Combining both calibration exercises into a single one allowed to simultaneously increase the quality of the calibrations (intercomparison, internal redundancy, common characterization) and cut costs.

The standards were prepared using certified uranium pellets, and excess Pu Nitrate. All standards were LSD spiked in the OSL and subsequently analyzed by mass spectrometry to confirm the uranium value, and to determine the plutonium concentration. LSD spiking on four of the standards was also performed by BNFL operators in their high active cells, giving the OSL the opportunity to compare both procedures. LSD spiking at Thorp is foreseen to start soon, allowing the OSL to routinely perform bias control measurements for the Thorp hybrid K-edge.

### 7.6.5 External quality control

The OSL participated in the EQRAIN external quality control programme. The two remaining plutonium nitrate solutions and one uranium nitrate solution were analyzed. The results are in good agreement with the certified values and provide us with confidence that the analyses are performed according to the highest standards.

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## 7.7 Analytical Support to IAEA

In the framework of the Member State Support Programme, the Joint Research Centre offers significant support to the IAEA. ITU's contribution focuses on its areas of expertise, namely particle analysis, sample analysis for U, Pu and minor actinide assay, automation, separation methods and on-site laboratories.

With respect to the latter, a major task was agreed with the IAEA in order to make ITU's large and unique experience in designing, setting-up and operating on-site laboratories available for the agency's own OSL project at the Rokkasho reprocessing plant (RRP) in Japan. This will gain increasing importance and require significant effort in the next years. Furthermore, software for data acquisition and reduction for hybrid K-edge instruments was comparatively evaluated by ITU experts. Sample changers for automation of the HKED to

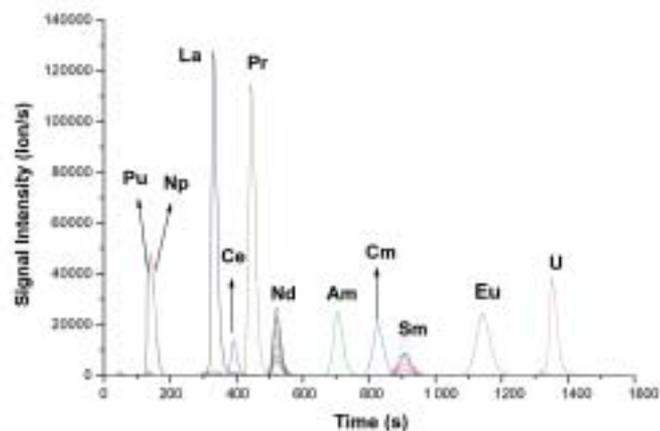


Fig. 7.7 Elution diagram showing the separation of lanthanides and actinides using the ion-chromatographic method developed.

be installed at RRP are being built by ITU under contract with the Japanese national safeguards authority, the Nuclear Material Control Center (NMCC).

With reference to particle analysis, test samples were prepared by controlled deposition of monodisperse micro particles of uranium oxide. These samples were distributed to 10 different laboratories around the world, in the framework of an interlaboratory exercise that was organized in collaboration with IAEA. The objective of this intercomparison is to test the performance of SIMS instruments. The preliminary results were discussed in the IAEA Consultants' meeting held on 4-7 December 2001 at IAEA Headquarters in Vienna. A workshop, dedicated to the full interpretation of the results will be organized in April 2002 at ITU.

ITU experts visited the IAEA Safeguards Analytical Laboratory (SAL) in April 2001 in order to assist in the validation of the procedure for on-line separation of actinides coupled to ICP-MS. This method has been developed at ITU and was transferred to SAL. An elution diagram is shown in Fig. 7.7. Furthermore, procedures for the on-line separation of fission products and lanthanides were developed at ITU. These methods shall also be transferred to SAL.

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*Gouder, T.; Havela, L.; Miserque, F.; Wastin, F.; Rebizant, J.*  
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*Solatie, D.; Betti, M.; Carbol, P.*  
Application of Liquid Scintillation Counting (LSC) to the Measurement of Plutonium, Uranium, Curium and Strontium in Environmental, Swipe and Spent Fuel Samples

**International Conference on Security of Material - Measures to Prevent, Intercept and Respond to the Illicit Uses of Nuclear Material and Radioactive Sources May 7-11, 2001 Stockholm (Sweden)**

*Janssens, W.; Daures, P.; Mayer, K.; Cromboom, O.; Schubert, A.; Koch, L.*  
Assisting Eastern European Countries in the Setting up of a National Response to Nuclear Smuggling  
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*Wallenius, M.; Pajo, L.; Mayer, K.*  
Development and Implementation of Methods for Determination of the Age and Origin of Nuclear Materials  
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*Daures, P.; Richir, P.; Cremer, B.; Ottmar, H.; Mayer, K.; Blohm-Hieber, U.; Decobert, G.; Rincel, X.*  
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*Mayer, K.; Peerani, P.*  
Neptunium Build up and Analytical Concepts for its Control

*Morgenstern, A.; Apostolidis, C.; Mayer, K.*  
Separation of U, Pu, Np and Fission Products by Extraction Chromatography

*Morgenstern, A.; Apostolidis, C.; Mayer, K.; Ottmar, H.*  
Determination of Traces of <sup>244</sup>Cm in PuO<sub>2</sub> Samples

*van Belle, P.; Ottmar, H.*  
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## Annex I

### Jahrestagung Kerntechnik 2001 - Annual Meeting on Nuclear Technology 2001 May 15-17, 2001 Dresden (Germany)

Haas, D.  
The European Minor Actinides Transmutation Programme

### TOPFUEL 2001 - Swedish Nuclear Society May 28-30, 2001 Stockholm (Sweden)

Haas, D.; Somers, J.  
Experimental Production Methods for Advanced MOX Fuels

Weston, R.; Palmer, B.J.; Wright, J.M.; Rossiter, G.D.; Corcoran, R.C.; Gilmour, T.C.; Walker, C.T. Bremier, S.  
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Apostolidis, C.; Betti, M.; Carlos-Márquez, R.; Janssens, W.; Molinet, R.; Nikula, T.; Ouadi, A.  
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### Expert Meeting on „Depleted Uranium in Kosovo: Radiation Protection, Public Health and Environmental Aspect“ June 19-22, 2001 Bad Honnef (Germany)

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### 48. Annual Meeting of the Society of Nuclear Medicine June 23-27, 2001 Toronto, Ontario (Canada)

Miederer, M.; Beyer, G.; Seidl, C.; Vranjes, S.; Comor, J.; Huber, R.; Nikula, T.; Apostolidis, C.; Schumacher, C.; Becker, K.F.; Senekowitsch-Schmidtke  
<sup>149</sup>Tb and <sup>213</sup>Bi: Impact of Particle Energy for Alpha-Radioimmunotherapy  
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Nikula, T.K.; Apostolidis, C.; Molinet, R.; Carlos-Marquez, R.; Brandes, K.; Senekowitsch-Schmidtke, R.  
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### Symposium on Magnetic Multilayers June 24-29, 2001 Aachen (Germany)

Sürgers, C.; Gajdzik, M.; Kelemen, M.T.; Brooks, M.S.S.; Dormann, E.; v. Löhneysen, H.  
Structural and Magnetic Properties of Mn<sub>5</sub>Si<sub>3</sub>C<sub>x</sub> Films

### 16. International Conference on X-ray Optics and Microanalysis July 2-6, 2001 Vienna (Austria)

Bremier, S.; Walker, C.T.  
Large Area Quantitative X-ray Mapping of (U,Pu)O<sub>2</sub> Nuclear Fuel Pellets Using Wavelength Dispersive Electron Probe Microanalysis  
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### XXXII Colloquium Spectroscopicum Internationale July 9-14, 2001 Pretoria (South Africa)

Aldave de las Heras, L.; Hrncsek, E.; Bocci, F.; Perna, L.; Mendes, E.; Betti, M.  
Comparison of Radiometric and Mass Spectrometric Methods to Determine Traces of Radionuclides in Environmental Samples

Tamborini, G.; Aldave de las Heras, L.; Bildstein, O.; Bocci, F.; Huber, T.; Betti, M.  
Correlation Between Bulk and Particles Analysis in Environmental Samples by Different Mass Spectrometric Techniques: SIMS, GDMS and ICP-MS

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### SCES 2001 - International Conference on Strongly Correlated Electron Systems August 6-10, 2001 Ann Arbor, MI (USA)

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Lander, G.H.  
Magnetic Scattering with Synchrotrons: New Developments.  
Plenary Talk

**Radiation Effects in Insulators (REI 11)  
September 3-7, 2001 Lisbon (Portugal)**

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and Migration - Behaviour of Actinides and Fission Products  
in the Geosphere  
September 16-21, 2001 Bregenz (Austria)**

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Hrnecek, E.; Aldave de las Heras, L.; Betti, M.  
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September 23-27, 2001 Kingston, Ontario, (Canada)**

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September 30 – October 4, 2001 Bruges (Belgium)**

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 The Kinetic of Dissolution of Irradiated UO<sub>2</sub> Fuel under Oxidising  
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*Wegen, D.H.; Bottomley, P.D.W.; Glatz, J.P.*  
 The Electrochemical Modelling of Irradiated UO<sub>2</sub> Surface Reactions  
 in Groundwater Solutions

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 Modeling and Experimental Support  
 October 1-5, 2001 Albena (Bulgaria)**

*Schubert, A.; van de Laar, J.; Elenkov, D.*  
 The Statistics Version of TRANSURANUS – Recent Developments  
 and Applications to WWER Fuel –

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 des matériaux  
 October 10, 2001 Paris (France)**

*Rabaglino, E.; Baruchel, J.; Boller, E.; Elmoutaouakkil, A.; Ferrero, C.;  
 Ronchi, C.*  
 Microtomography of Irradiated Beryllium Pebbles

**5. International Workshop on Beryllium Technology for Fusion  
 October 10-12, 2001 Moscow (Russia)**

*Rabaglino, E.; Ronchi, C.; Scaffidi-Argentina, F.; Wiss, T.*  
 Helium and Tritium Release and Sub-Microscopic Restructuring in  
 Irradiated Beryllium Pebbles

**XIV Tage der Seltenen Erden, Technische Universität München  
 October 11-13, 2001 München (Germany)**

*Apostolidis, C.; Rebizant, J.; Walter, O.; Kanellakopoulos, B.*  
 Synthese, Struktur und Eigenschaften der Tetrakis (1-pyrazolyl)bo-  
 rate der dreiwertigen Lanthanoide: Ln(Bpz<sub>4</sub>)<sub>3</sub>

**10. International Conference on Fusion Reactor Materials  
 (ICFRM-10)  
 October 14-19, 2001 Baden-Baden (Germany)**

*Rabaglino, E.; Ronchi, C.; Scaffidi-Argentina, F.*  
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 Proceedings Journal of Nuclear Materials

*Rabaglino, E.; Ronchi, C.; Thiele, H.*  
 Optical and Transmission Electron Microscopy Examination of the  
 Microstructure of Irradiated Beryllium Pebbles  
 Proceedings Journal of Nuclear Materials

**Energiebronnen: Uitdaging voor Fysici Koninklijke  
 Nederlandse Academie van Wetenschappen  
 October 18, 2001 Amsterdam (Netherlands)**

*Konings, R.J.M.*  
 Transmutatie van Kernafval

**Magnetism of Intermetallic Workshop, University of Coimbra  
 October 18-19, 2001 Coimbra (Portugal)**

*Boulet, P.; Colineau, E.; Wastin, F.; Rebizant, J.; Bouexière, D.; Kinnart, F.*  
 Magnetism of Neptunium Binary Compounds with Silicon and  
 Germanium

**International Workshop on Advanced Reactors and  
 Innovative Fuels  
 October 22-24, 2001 Chester (United Kingdom)**

*Somers, J.; Fernandez, A.; Konings, R.J.M.; Ledergerber, G.*  
 Some Views on the Design and Fabrication of Targets or Fuels  
 Containing Curium

**European Working Group Hot Laboratories and Remote  
 Handling  
 October 22-24, 2001 Madrid (Spain)**

*Cobos, J.; Glatz, J.P.; Serrano, J.A.; de Pablo, J.*  
 New Flow through Reactor Installed in the ITU Hot Cell Laboratory  
 to Investigate the Dissolution Rates of the Irradiated Fuels

**7. Inert Matrix Workshop (IMF-7)  
 October 25-26, 2001 Petten (Netherlands)**

*Fernandez, A.; Konings, R.J.M.; Somers, J.; Haas, D.*  
 Fabrication of Zirconia-Plutonium Targets by the Infiltration  
 Method

*Konings, R.J.M.*  
 The Estimation of Thermochemical and Thermophysical Properties  
 of Minor Actinide Compounds for Predicting the Behaviour of  
 Transmutation Fuels

**IAEA Symposium on International Safeguards - Verification  
 and Nuclear Material Security  
 October 29 - November 1, 2001 Vienna (Austria)**

*Abousahl, S.; Ottmar, H.; Matussek, P.*  
 Matrix Effect Corrections for the Uranium Assay with a  
<sup>57</sup>Co-<sup>153</sup>Gd Isotopic Source-Based K-Edge Densitometer

*Abousahl, S.; van Belle, P.; Eberle, H.; Ottmar, H.*  
Performance of Isotope Correlations for the Estimate of  $^{242}\text{Pu}$

*Bragin, V.; Carlson, J.; Leslie, R.; Schenkel, R.; Magill, J.; Mayer, K.*  
Proliferation-Resistance and Safeguardability of Innovative Nuclear Fuel Cycles

*Duinslaeger, L.; Zuleger, E.; Mayer, K.; Castelyn, K.*  
Evaluation of Uncertainties for Pu and U Measurements Achieved in the On-Site Laboratory by Thermal Ionisation Mass Spectrometry during Two Years of Operation

*Janssens, W.; Daures, P.; Cromboom, O.; Mayer, K.; Koch, L.*  
Supporting PECO Countries in Combating Illicit Trafficking of Nuclear Materials. Status of the Ongoing Projects

*Mayer, K.; Duinslaeger, L.; Cromboom, O.; Ottmar, H.; Wojnowski, D.; van der Vegt, H.*  
Analytical Quality Control Concept in the EURATOM On-Site Laboratories

*Ottmar, H.; Mayer, K.; Morgenstern, A.; Abousahl, S.*  
Demonstration of Measurement Technologies for Neptunium and Americium Verification in Reprocessing

*Schenkel, R.; Magill, J.; Glatz, J.P.; Mayer, K.*  
Partitioning and Transmutation – Technical Feasibility, Proliferation Resistance and Safeguardability  
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*Wallenius, M.; Apostolidis, C.; Morgenstern, A.; Mayer, K.*  
Age Determination of Highly Enriched Uranium

**International Conference: Actinides 2001  
November 4-9, 2001 Hayama (Japan)**  
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Self-irradiation Effects in Plutonium Alloys Stabilized in the Delta-phase

*Dancausse, J.P.; Haire, R.G.; Heathman, S.; Benedict, U.*  
High-Pressure X-ray Diffraction Studies of Americium and Curium Dioxides

*Gouder, T.; Havela, L.; Miserque, F.; Wastin, F.; Rebizant, J.*  
Forced Oxidation of Th, U, and Pu

*Gouder, T.; Havela, L.; Wastin, F.; Rebizant, J.*  
5f-Localization in Ultrathin Pu Layers (invited paper)

*Havela, L.; Gouder, T.; Black, L.; Miserque, F.; Wastin, F.; Rebizant, J.*  
XPS and UPS Study of U- and Th-Nitrides

*Konings, R.J.M.*  
Predicting and Understand the Behaviour of Transuranium Targets for Transmutation

*Lander, G.H.*  
Resonant X-ray Magnetic Scattering from Actinides

*Le Bihan, T.; Haire, R.G.; Heathman, S.; Idiri, M.; Lindbaum, A.*  
Investigating the Structural Behavior of Transplutonium Elements to one Megabar via Synchrotron Radiation (invited paper)

*Malmbeck, R.; Konings, R.J.M.*  
Critical Evaluation of Fundamental Data for Pyrochemical Partitioning Process

*Wastin, F.; Colineau, E.; Rebizant, J.; Lander, G.H.*  
Magnetic Studies of Transuranium Compounds

**Winter Meeting of the American Nuclear Society - Nuclear Applications in the New Millennium  
November 11-15, 2001 Reno, NV (USA)**

*Galy, J.; Magill, J.; Van Dam, H.; Valko, J.*  
A Neutron Booster for Spallation Sources – Application to Accelerator Driven Systems

## Theses

Four doctoral grantees from the Institute have obtained their PhD

**A. Bombardi**  
Localisation électronique et magnétisme dans les monochalcogénures et les monopictures de l'uranium et du neptunium, étude des systèmes:  $\text{U}_x\text{La}_{1-x}(\text{S,Se})$ ,  $\text{U}_{0,2}(\text{La}_{0,15}\text{Y}_{0,85})_{0,8}\text{Te}$  et  $\text{NpAs}_{1-x}\text{Se}_x$   
Université Joseph Fourier – Grenoble 1 (France) 21.03.2001

**F. Miserque**  
Photoelectron Spectroscopy and Electrochemical Studies of Uranium Oxides and Nitrides Thin Films  
Facultés Universitaires Notre-Dame de la Paix – Namur (Belgium) 27.07.2001

**O. Stetzer**  
Spaltspuranalyse von Uranoxidpartikeln  
Johannes Gutenberg-Universität Mainz (Germany) 14.05.2001

**M. Wallenius**  
Origin determination of reactor produced plutonium by mass spectrometric techniques: application to nuclear forensic science and safeguards  
University of Helsinki – Faculty of Science (Finland) 17.02.2001

## Annex I

### EUR Reports

*Richter J.; Magill J.*

Annual Report 2000 – Institute for Transuranium Elements  
EUR 19812 EN (2001), ISBN 92-894-1044-2

*Konings, R.J.M.*

Advanced Fuel Cycles for Accelerator-Driven Systems: Fuel  
Fabrication and Reprocessing  
EUR 19928 EN (2001)

### Technical Notes

Technical Notes (TN) are printed in limited numbers. Please contact the authors for further information.

*Amme, M.*

Element solubilities and secondary phase formation during anoxic  
leaching processes of nuclear fuels in groundwaters with altered  
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*Boulet, P.*

Binary actinide systems with silicon, germanium and tin (crystallo-  
chemistry and magnetic properties)  
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*Damen, P.M.G.*

Investigations on the helium behaviour in inert matrix fuels by  
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*Daures, P.; Duinslaeger, L.; Richir, P.*

Exploitation du Laboratoire sur Site, La Hague et du On-Site  
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*Fiedler, R.*

Performance tests of the new multi-collector ICP-MS on U and Pu  
high accuracy isotopic measurements; Comparative evaluation  
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*Galla, Y.*

Benutzerhandbuch WissIntra Version 1 – Mai 2001  
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*Galy, J.; Magill, J.*

Gamma-Dose: A Dosimetry and Shielding Module for Nuclides  
2000  
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*Galy, J.; Valkó, J.; van Dam H.*

Neutron Booster Feasibility and Property Investigations  
JRC-ITU-TN-2001/03

*Griveau, J.-C.*

High-pressure research at low temperature on actinide com-  
pounds  
JRC-ITU-TN-2001/21

*Györi Csaba; van de Laar J.*

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*Haas, D.; Glatz, J.-P.*

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gramme description  
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*Hrnecek, E.*

Development of analytical techniques for the identification and  
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JRC-ITU-TN-2001/20

*Idiri, M.*

X-ray high-pressure experiments on actinide and lanthanide com-  
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*Knoche, D.*

Progress report on the installation and testing of a gas analysis sys-  
tem for use with irradiated fuel annealing for application in the  
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JRC-ITU-TN-2001/19

*Lutique, S.*

Fabrication and characterisation of pyrochlore-type zirconate, a  
matrix for the immobilisation of plutonium and high level waste  
JRC-ITU-TN-2001/05

*Magill, J.; Galy, J.*

Virtual nuclides: A formalism for the application of the Bateman so-  
lution of mixtures  
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*Magill, J.; Y. Galla; J. Galy*

The Universal Nuclide Chart. An interactive JAVA-based Chart  
JRC-ITU-TN-2001/29

*Manara, Dario*

A new laser method for  $UO_{(2\pm x)}$  freezing temperatures measure-  
ments.  
JRC-ITU-TN-2001/04

*Morgenstern, Alfred*

Rapid methods for the separation of actinides  
JRC-ITU-TN-2001/14

*Ouadi, A.*

Synthèse d'un agent chélatant de l'actinium 225 pour des applica-  
tions en radioimmunothérapie.  
JRC-ITU-TN-2001/04

*Perna, L.*

Pre-concentration methods for ultra-trace determination of fission products and actinides in environmental samples

JRC-ITU-TN-2001/09

*Stetzer Olav*

Spaltspurenanalyse von Uranoxidpartikeln

JRC-ITU-TN-2001/11

*Tamborini, G.*

Status of the progress on HPTA (Project 1751/6)

JRC-ITU-TN-2001/13

*Tamborini, G.*

Progress on Particle Analysis

JRC-ITU-TN-2001/06

*Wallenius, Maria*

Origin determination of reactor produced plutonium by mass spectrometric techniques: application to nuclear forensic science and safeguards

JRC-ITU-TN-2001/25

*Windbühl, T.*

Entwicklung einer Strategie zur Gestaltung und effizienten Erstellung des 'Annual Report'

JRC-ITU-TN-2001/17

## Patents

During 2001, the Institute has submitted 1 patent proposal; 1 patent has been deposited (first application) and 9 patents have been granted.

## First Application

(with priority data)

*Apostolidis, C.; Gestin, J.-F.; Ouadi, A.*

Bifunctional chelating agent for actinium

17/09/2001 90 834 LU

## Patents granted

*Fuger, J.; Koch, L.; van Geel, J.*

A method for producing actinium-225 and bismuth-213

23/02/1990 90-87684 LU (Priority)

16/01/2001 2 075 297 CA

*Caperan, P.; Richter, K.; Somers, J.*

Method and device for the agglomeration of particles in a gaseous flow

29/04/1996 96-88751 LU (Priority)

01/05/2001 6 224 652 US

*Caperan, P.; Richter, K.; Somers, J.*

Method and device for the agglomeration of particles in a gaseous flow

29/04/1996 96-88751 LU (Priority)

13/06/2001 0 923 410 EP

*Fourcaudot, S.; Fuchs, C.; Richter, K.; Somers, J.*

Method for preparing highly radioactive materials for transmutation and/or burn-up

19/03/1996 96-88727 LU (Priority)

13/06/2001 0 888 623 EP

*Babelot, J.-F.; Hiddemann, L.; Koch, L.; Niemax, K.*

Telemetering of uranium or plutonium in glass

30/08/1995 19531988.5 DE (Priority)

10/07/2001 6 259 757 US

*Ronchi, C.; Cheindline, M.*

Multipurpose laser-flash setup for measurement of the thermal diffusivity under remote manipulation

23/12/1996 96120836.0 EP (Priority)

14/08/2001 6 273 603 US

*Apostolidis, C.; Gestin, J.-F.; Ouadi, A.*

Bifunctional chelating agent

14/03/2000 90 544 LU (Priority)

17/09/2001 90 544 LU

*Apostolidis, C.; Janssens, W.; Koch, L.; Mc Ginley, J.; Moellenbeck, J.;*

*Molinet, R.; Ougier, M.; Schweickart, H.; van Geel, J.*

Method for producing AC-225 by irradiation of Ra-226 with protons

02/06/1998 98109983.1 EP (Priority)

09/10/2001 6 299 666 US

*Magill, J.; Peerani, P.*

Method of incineration of minor actinides in nuclear reactors

26/04/2000 90 570 LU (Priority)

29/10/2001 90 570 LU

## 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:** TRANSURANUS fuel pin code development (A. Martirosian)

### 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:** Resistivity of alloys and high-pressure effects (E. Gratz, A. Lindbaum)

### BELGIUM

**Belgonucléaire:** Ariane project: Inventory of high burn-up UO<sub>2</sub> 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)

**SCK-CEN, Mol:** Fabrication of alpha-doped UO<sub>2</sub> (K. Lemmens); MOX programme (P. D'Hondt, M. Verwerft)

**University Hospital Ghent, Clinic for Radiotherapy and Nuclear Medicine:** a-immunotherapy (F. Offner)

**University of Leuven:** Xe-implantation (H. Pattyn)

**University of Liège:** Single crystal growth, X-ray diffraction, and analyses (J.F. Desreux, L. Martinot, M.R. Spirlet)

**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 (P. Ardenska); 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)

### CANADA

**AECL Chalk River:** Gas release, SIMFUEL production and property studies, oxygen potential of UO<sub>2</sub> fuel (R. Verrall); Behaviour of Rb and Cs in SIMFUEL (W. Hocking),

**University of Kingston:** Inert matrices (P.G. Lucuta)

### CYPRUS

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

### CZECH REPUBLIC

**Charles University, Prague:** Magnetic and electrical measurements (V. Sechovsky, L. Havela, P. Javorsky)

**Nuclear Research Institute Replc, Re :** 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)

### DENMARK

**Risø National Laboratory:** Neutron scattering (B. Lebech)

### ESTONIA

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

### FINLAND

**MAP Medical Technologies Oy:** Alpha-immunotherapy (J. Hiltonen)

**STUK - Finnish Centre for Radiation and Nuclear Safety:** Illicit trafficking, (E. Kainulainen)

**VTT Energy Aerosol Technology:** Revaporisation of aerosol deposits (J. Iokiniemi, A. Auvinen)

### FRANCE

#### Commissariat à l'Énergie Atomique (CEA)

**CEA, Cadarache:** Transmutation of actinides - irradiation experiments: DEC (Ch. Bonnet, P. Martin, S. Pillon, D. Warin); Inert matrices (M. Beauvy and N. Chauvin); shared cost action 'Core loss during a severe accident (COLOSS)' (B. Adroguer, M. Barrachin); Thermophysical measurements on ECRIX material 'M<sub>9</sub>O-AmO<sub>2</sub>' (T. Albiol, Y. Croixmarie)

**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. Bousier)

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

**CEA, Saclay:** Neutron diffraction (J.M. Mignot, B. Hennion); Post-irradiation examinations (J.I. Blanc, F. Couvreur); Radiation damage (A. Dunlop); PIXE analyses (S. Lequien)

**CEA, Valduc:** Electronic properties of Pu<sub>x</sub>Am<sub>1-x</sub> solid solutions (P. Rofidal, N. Richard, M. Dormeal)

**CEA, Bruyères le Châtel:** Microparticles in safeguards and radioactivity on environment (R. Chiappini, S. Baude); Radioactive particles - toxicity (P. Fritsch)

#### CNRS, Lab. de Cristallographie, Grenoble:

Crystallography of phase transitions (J.C. Marmeggi);

**Orsay:** Basic studies on spent UO<sub>2</sub> fuel (J.C. Dran); ARAMIS accelerator, radiation damage, ion implantation (L. Thomé)

**COGEMA-La Hague:** Laboratoire sur Site (G. Decobert) Marcoule (Division des combustibles): 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 UO<sub>2</sub> (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 Laue et Langerin (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)

**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)

### GERMANY

**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 (G. Heusener)

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

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

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

**Hahn-Meitner-Institut (HMI), Berlin:** High-energy ion implantation (S. Klaumünzer)

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

**Kraftwerk Obrigheim:** Irradiation of Thorium-Plutonium fuel (D. Somer)

**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)

**Technische Hochschule Darmstadt:** Theory of actinides (L. Sandratskii)

**Technischer Überwachungsverein Hannover/Sachsen-Anhalt e.V.:** TRANSURANUS fuel pin code development (H. Märten, 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 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 fission (R. Sauerbrey, H. Schwoerer)

**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 (S. Elo)

**Hungarian Academy of Sciences, Institute of Isotopes, Budapest:** Forensic nuclear analyses for safeguards (J. Safar)

**Hungarian Atomic Energy Authority, Budapest:** TRANSURANUS fuel pin code development (M. Gado), Illicit trafficking (I. Czoch)

### ITALY

**ENEA; Bologna:** Partitioning and Transmutation, Accelerator Driven Systems (G. Gherardi); Thermal conductivity of Inert Matrix Fuels (F. Vettrano); TRANSURANUS fuel pin code development (F. Vettrano)

## Annex II

**Technical Working Group on Accelerator Driven Systems:** Roadmap on ADS (C. Rubbia)

**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)

### 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. Kinoshita)

**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)

**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)

### 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)

### THE NETHERLANDS

**EUROPOL, The Hague:** Nuclear forensic science (F. Zablót)

**Interfaculty Reactor Institute, Delft:** He release from inert matrices (A. van Veen); Neutronics of thin fissile layers (H. van Dam)

**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)

### POLAND

**Institute of Atomic Energy, Otwock/Swierk:** TRANSURANUS fuel pin code development (M. Szuta)

**Institute for Low Temperature and Structure Research, Warsaw:** Bulk properties and neutron scattering (R. Troc, W. Suski, D. Kaczorowski)

**National Atomic Energy Agency, Warsaw:** Illicit trafficking (J. Niewodniczanski)

### PORTUGAL

**Instituto Tecnológico e Nuclear (ITN), Sacavem:** Physical chemistry of actinides (A. Pires de Matos, M. Almeida, J.C. Warenborgh)

**University of Coimbra:** Neutron and X-ray studies (J.A. Paixão)

### 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); Studies on high-melting materials (V. Fortov)

**All Russia Research Institute of Inorganic Materials (A.A. Bochvar Institute), Moscow:** Setting up of three laboratories for safeguards, metrology, nuclear forensics (A. Petrov)

**ENIL, Moscow:** Thermophysical properties of high temperatures (E. Volkov)

**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:** Equation of State of UO<sub>2</sub> and Nuclear Fuels (V. Fortov)

**Institute of Chemical Physics, Chernogolowka:** code calculations of Equation of State of UO<sub>2</sub> (V. Gryaznov)

**MINATOM, Moscow:** Nuclear Safeguards (V. Limonaev)

### 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)  
**Ministerio de Industria y Energía; de Ciencia y Tecnología, Madrid:**

*Instituto de Tecnológica Nuclear:* TRANSURANUS fuel pin code development (J. Lopez Jimenez)

**Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT):** Waste management, leaching tests (J.L. Diaz)

**UPC, University Polytechnic of Catalunya:** Waste management, leaching tests (Prof. J. de Pablo)

**QUANTISCI:** Waste management, leaching tests (J. Bruno)

**SWEDEN**

**Chalmers University, Göteborg:** Minor actinides partitioning (J.P. Liljenzin)

**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)

**Kantonsspital Basel, Institut für Nuklearmedizin:**

a-immunotherapy (H.R. Mäcke)

**Paul Scherrer Institut, Villigen und Würenlingen:** Thermal conductivity of inert matrices (C. Deguelde); TRANSURANUS fuel pin code development (C. Hellwig); Post-irradiation structural investigations by electron microscopy, Phébus PF FPT1 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. Yermenko)

**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 (J. Edwards, C. Brown)

**NNC, Winfrith:** Neutron sources for waste assay systems (S. Daish)

**Rutherford Appleton Laboratory, Chilton:** Neutron Synchrotron studies (N. Bull, S. Langridge); Laser induced fission (R. Norreys)

University of Bristol, Interface Analysis Centre: Surface corrosion (G. Allen)

**University of Glasgow, Dept. of Physics and Astronomy/Rutherford Appleton Laboratory:** Laser induced fission (K.W.D. Ledingham)

**University of Liverpool:** X-ray and neutron scattering (W.G. Stirling)

**University of London:** Magnetic & transport studies (K. McEwen, S. Zochowski)

**University of Oxford:** Preparation of multilayers (M. Wells, R. Ward); UO<sub>2</sub> surface properties (A. Castell, C. Muggelberg)

**University of Warwick:** Compton scattering (M.J. Cooper); Theory of liquid state (G. Hyland)

**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. Chichester)

**Memorial Sloan Kettering Cancer Center, New York, NY:** Alpha-immunotherapy (D.A. Scheinberg)

**National Institute of Health, Bethesda, MD:** Alpha-immunotherapy (M.W. Brechbiel)

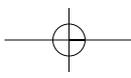
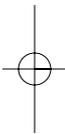
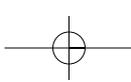
**Oak Ridge National Laboratory, TN:** Material preparation, high-pressure X-ray and optical studies (R.G. Haire, J.R. Peterson); Radiation damage in ceramics (S.J. Zinkle)

**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)

**UZBEKISTAN**

**Physical Technical Institute, Tashkent:** Radiative properties of UO<sub>2</sub> at high temperatures (T. Salikhov)



## 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  
**ADS:** accelerator driven systems  
**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  
**AS:** alpha spectrometry

**BCA:** bifunctional chelating agents  
**BE:** binding energies  
**BKA:** Bundeskriminalamt, Wiesbaden (Germany)  
**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  
**CEA:** Commissariat à l'Énergie Atomique (France)  
**CEF:** crystal electric field  
**CIEMAT:** Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, Madrid (Spain)  
**CIS (countries):** Commonwealth of Independent States  
**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)  
**CUAAPP:** Committee on the Use of Atomic Energy for Peaceful Purposes, Sofia (Bulgaria)

**DESY:** Deutsches Elektronen-Synchrotron, Hamburg (Germany)  
**DG:** Directorate General  
**dhcp:** double hexagonal close packed  
**DIAMEX:** diamide extraction process  
**DKFZ:** Deutsches Krebsforschungszentrum, Heidelberg (Germany)  
**DOS:** density of states  
**DOTA:** 1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid  
**DP:** direct pressing  
**DTPA:** diethylenetriaminepentaacetic acid

**EAC:** European Accident Code  
**EdF:** Électricité de France  
**EDX:** energy-dispersive X-ray spectroscopy  
**EFG:** electric field gradient  
**EFTRA:** Experimental Feasibility for Targets and Transmutation  
**EMPA:** electron micro-probe analysis (also EPMA)  
**ENA:** electrochemical noise analysis  
**ENEA:** Ente per le Nuove Tecnologie, L'Energia e l'Ambiente, Rome (Italy)  
**EPMA:** electron probe microanalysis (also EMPA)  
**EQRAIN:** évaluation de la qualité du résultat d'analyse dans l'industrie nucléaire  
**ESO:** Euratom Safeguards Office  
**ESRF:** European Synchrotron Radiation Facility, Grenoble (France)  
**EURATOM:** European Atomic Energy Community  
**EUROPOL:** European Police Office  
**EXTRA:** extension of TRANSURANUS code applicability with Nb containing cladding models

**FBR:** Fast Breeder Reactor  
**fco:** face centred orthorhombic  
**FD:** final density  
**FERONIA:** fuel rod modelling and performance project  
**FF:** fission fragment  
**FG:** fission gas  
**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  
**FSZ:** Fully Stabilised Zirconia  
**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
- HAC:** high active concentrated raffinate  
**HAR:** high active raffinate  
**HASYLAB:** Hamburger Synchrotronstrahlungslabor (Germany)  
**HBS:** high burn-up structure  
**HEDTA:** hydroxyethyl ethylenediamine 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  
**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)  
**IAE:** National Atomic Energy Agency, Institute of Atomic Energy, Warsaw (Poland)  
**IC-ICP-MS:** ion chromatography inductively coupled plasma mass spectrometry  
**ICT:** isotope correlation  
**IDMS:** isotope dilution mass spectrometry  
**IFPE:** International Fuel Performance Experiment  
**IHP:** Improving Human Potential Programme  
**ILL:** Institut Laue Langerin, Grenoble (France)  
**INR:** Institut für Neutronenphysik und Reaktortechnik, FZK (Germany)  
**INRNE:** Institute for Nuclear Research and Nuclear Energy, Sofia, Bulgaria  
**IRMM:** Institute for Reference Materials and Measurements, Geel (Belgium)  
**ISO:** International Organisation 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
- KAERI:** Korea Atomic Energy Research Institute, (Republic of Korea)  
**KFKI:** Atomic Energy Research Institute, Budapest (Hungary)  
**KÜFA:** Kühlfinger apparatus  
**KWO:** Kraftwerk Obrigheim (Germany)
- LAIN:** Laboratoire d'Analyse des Interfaces et de Nanophysique, Montpellier (France)  
**LEU:** low enrichment uranium  
**LN:** Lanthanides  
**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)  
**MAB:** Münchener Apparatebau für Elektronische Geräte GmbH (Germany)  
**MAGNOX:** Magnesium non-oxidizing (fuel sheath)  
**MARINA:** The Radiological Exposure of the European Community from Radioactivity in the North European Waters  
**MAP:** Model Action Plan  
**MCNP:** Monte Carlo N-particle transport code system  
**MGA:** multi-group-analysis  
**MICROMOX:** the influence of microstructure of MOX fuel on Hs irradiation behaviour under transient conditions  
**MOX:** mixed oxide fuel of uranium and plutonium  
**MWd/kgU:** Megawatt day per kg of uranium
- 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  
**NM:** nuclear material  
**NMCC:** Nuclear Material Control Center  
**NRG:** Nuclear Research and consultancy Group  
**NRI:** Nuclear Regulatory Institute Rez plc, near Prague (Czech Republic)  
**NSC:** Nuclear Science Committee
- OECD:** Organization for Economic Co-operation and Development, Paris (France)  
**OM:** optical microscopy  
**OMICO:** oxide fuels – microstructure and composition variations  
**ORIGEN:** The Oak Ridge National Library-Isotope generation and depletion code

## Annex IV

**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-octazacyclotetracosane-1,4,7,10,13,16,19,22-octaacetic acid

**PARTNEW:** Partitioning: New solvent extraction processes for minor actinides (5<sup>th</sup> Framework programme)

**PCI:** pellet clad interaction

**PECO:** Pays d'Europe Centrale et Orientale (Pays de l'Europe centrale et de l'Est)

**PIE:** post-irradiation examination

**P&T:** partitioning and transmutation

**PSI:** Paul Scherrer Institut, Villigen (Switzerland)

**PUREX:** plutonium and uranium recovery by extraction

**PWR:** pressurized water reactor

**QA:** quality assurance

**QM:** quality management

**RELAP:** code name

**RER:** IAEA Regional Technical Co-operation Project

**RIA:** reactivity initiated accident

**RITNUM:** Response to Illicit Trafficking of Nuclear Material

**RRP:** Rokkasho reprocessing plant (Japan)

**RSF:** relative sensitivity factor

**SAL:** Safeguards Analytical Laboratory

**SANEX:** selective actinides(III) extraction

**SBR:** short binderless route

**SCA:** Shared Cost Action

**SEM:** scanning electron microscopy

**SF:** spontaneous fission

**SF:** separation factor

**SIMFUEL:** simulated high burn-up fuel (with major non-volatile fission products)

**SIMS:** secondary ion mass spectrometry

**SMART:** study of mixed actinides recycling and transmutation

**SONS:** State Office for Nuclear Safety, Prague (Czech Republic)

**SQUID:** superconducting quantum interference device

**SSTC NRS:** State Scientific and Technical Centre for Nuclear and Radiation Safety, Kiev (Ukraine)

**SUPERFACT:** Minor Actinide Irradiation in Phénix (France)

**TD:** theoretical density

**TEM:** transmission electron microscopy

**TEVA:** tetravalent actinide resin

**TIMS:** thermal ionization mass spectrometry

**TRANSURANUS:** fuel behaviour code (ITU), Karlsruhe (Germany)

**TRU:** transuranic waste

**TUAR:** Institute for Transuranium Elements annual report, Karlsruhe (Germany)

**TÜV:** Technischer Überwachungsverein

**TWG:** European Technical Working Group

**UNEP:** United Nations Environment Programme

**UPS:** ultraviolet photoelectron spectroscopy

**UTEVA:** uranium tetravalent actinide resin

**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

## Previous Activity 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	-				
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.



European Commission

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**Abstract**

The annual report 2001 of the Institute for Transuranium Elements (ITU) of the Joint Research Centre (JRC) describes the progress made during the third year of the 5th European Community Framework Programme (FP5).

In the first part of the report a summary of the main achievements is given. A chronology of events follows in the 'year at a glance', followed by a summary of staff and budget resources. In addition to a review article on The TRANSURANUS Code, Past, Present and Future, a series of highlight articles on important progress made during 2001 are presented on:

- The Strange Magnetism of NpP;
- Innovative Acoustic Measurements of Elastic Modulus on Irradiated LWR-Fuels;
- Fast Transport of Fission Energy through Shock Waves;
- Helium Formation during Transmutation of Americium;
- Analysis Carried Out in the Context of a Case of Theft of Radioactive Material;
- Radiometric Analytical Methods for Pyroprocessing;

In the second part of the report, a more in-depth technical description of progress made is given. Topics covered focus on: Alpha-Immunotherapy Studies, 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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