ECN

energy innovation

HIGHLIGHTS OF NUCLEAR CHEMISTRY
1994

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ECN's research results are published in a number of report series, each series serving a different public, from contractors to the international scientific world.

The I-series is for internal reports that contain results mainly of interest for (fellow) colleagues, principally within ECN but also for those employed elsewhere. Although these reports may not be in their final form, they may be referred to.

Het Energieonderzoek Centrum Nederland (ECN) is het centrale instituut voor onderzoek op energie- gebied in Nederland. ECN verricht fundamenteel en toegepast onderzoek op het gebied van kernenergie. fossiele-energiedragers, duurzame energie, beleids- studies, milieuaspecten van de energievoorziening en de ontwikkeling en toepassing van nieuwe materialen.

Bij ECN zijn ruim 900 medewerkers werkzaam. De opdrachten worden verkregen van de overheid en van organisaties en industrieën uit binnen- en buitenland.

De resultaten van het ECN-onderzoek worden neer- gelegd in diverse rapportenseries, bestemd voor ver- schillende doelgroepen, van opdrachtgevers tot de internationale wetenschappelijke wereld.

De I-serie is de serie interne rapporten die resultaten bevat bestemd voor de ECN-collega's, maar ook voor vakcollega's die elders werkzaam zijn. Deze rapporten hebben een minder definitief karakter, maar zijn wel refereerbaar.

HIGHLIGHTS OF NUCLEAR CHEMISTRY 1994

INHOUD

Ten Geleide / Introduction

Dit rapport bevat "highlights" van het chemisch onderzoek in de unit Nucleaire Energie over 1994. Ze zijn gekozen uit elk van de drie aandachtsgebieden van de unit: risico en veiligheid, en geavanceerde reactoren. De 8 "highlights" geven niet alleen een indruk van het veelzijdige karakter van dit onderzoek, maar ook van het directe nut voor de betreffende programma-onderdelen. Als zodanig vormen ze een essentieel onderdeel van de unit Nucleaire Energie.

This report contains highlights of the chemical investigations in the business unit Nuclear Energy carried out in 1994. They intend to give an impression of the diversity of the chemical research which is an essential part of the unit's work.

E.H.P. Cordfunke

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ECN-I-94-061

1. Fission product release: benchmark calculations for severe nuclear accidents.

Within the frame work of the European Union (EU) an experimental program on Molten Core-Concrete Interactions (MCCI) has started in 1993. As part of this program ECN-Nuclear Chemistry has performed calculations on fission product release in cooperation with Siemens/KWU and GRS (Gesellschaft für Anlagen- und Reaktorsicherheit).

Chemical equilibrium models are generally used to asses the importance of reactions occurring during severe nuclear accidents. In the present study a thermodynamic database for the calculation of MCCI and related problems was compiled at ECN. The use of such a database is required for the prediction and judgement of consequences as a result of severe nuclear accidents. It can also be applied in the development of Core Catchers, and the calculation of aerosol distribution in the containment building after an accident has occurred.

To obtain a thermodynamic database suitable for these purposes three databases for nuclear substances have been used: the ECN database (TBase), the GRS database and the SGTE database. The latter is a large European database with thermodynamic data obtained by, for instance, CEA/IPSN, and AEA-Technology. Nevertheless, large discrepancies were found in the SGTE database compared to the ECN- and the GRS database. After a careful evaluation of essential thermodynamic data, a new database has finally been obtained with emphasis on the ECN and the GRS database.

With the new database thus obtained, the fission product release of two ACE experiments (Advanced Containment Experiments), L6 and L8, have been recalculated using the ChemSage computer program. The ACE experiments, which have been conducted in the USA by order of EPRI (Electric Power Research Institute), are large experiments in which MCCI has been simulated. The results of the calculations are presented in the figures 1 and 2 for the L6 and the L8 experiments, respectively.

As a benchmark exercise similar, calculations have been performed on the ACE-L8 experiment by other institutes using other computer codes and other databases. As an example of this exercise the results of barium and uranium are presented in figure 3 as the logarithmic fractional release.

It can be concluded that with the new ECN database the release of most of the fission products can be predicted, within the usual uncertainty limits. Due to the uncertainty in the thermodynamic properties at the typical accident temperatures (> 2000 K) this limit is relatively large. Also, the present calculations were performed under the assumption that no chemical interference between the substances occurred (ideal behaviour). Knowing this, the results are very encouraging.

Nevertheless, two fission products are still overestimated: cerium and lanthanum. It was found in previous calculations that silicates and zirconates in particular have a destinct influence on the release behaviour of Ba, Ce, La

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Fig. 1 The calculated and the experimental release of the ACE-L6 experiment derived with Chemsage before (+) and after (●) the compilation of the new database.
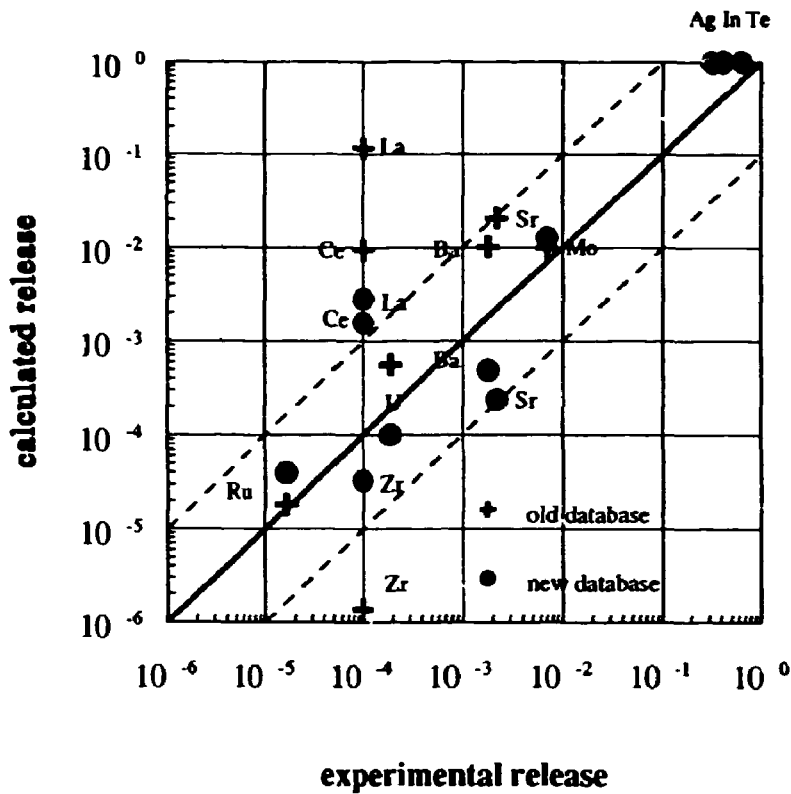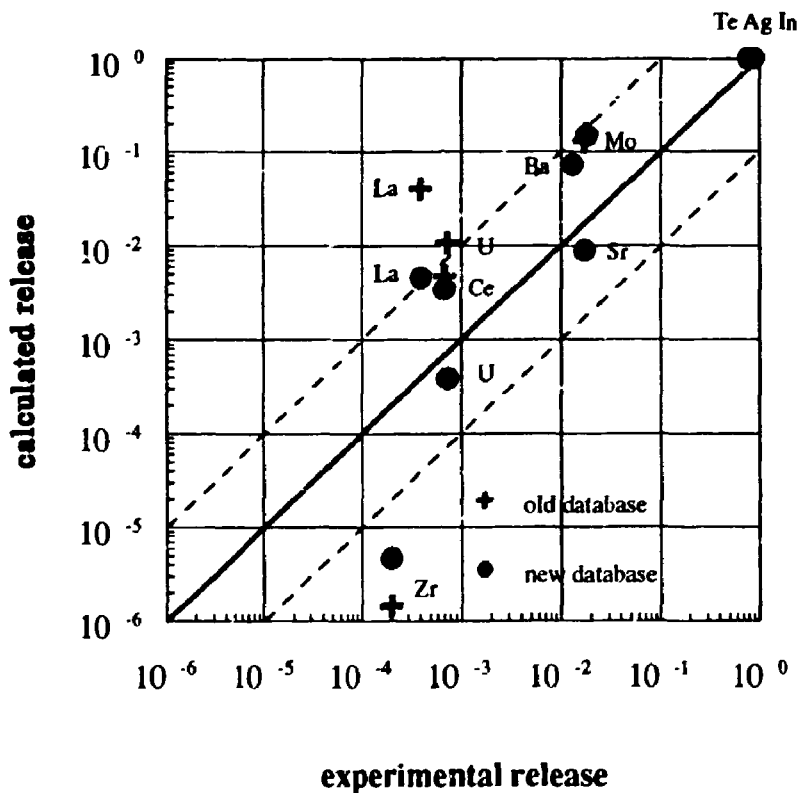

Fig. 2 The calculated and the experimental release of the ACE-L8 experiment derived with Chemsage before (+) and after (●) the compilation of the new database.

and Sr. The thermodynamic properties of the silicates and zirconates of Ba
and Sr have been the subject of a detailed investigation performed in the
recent years, whereas the thermodynamic properties of the silicates and
zirconates of Ce and La bearing species are poorly known. As a mater of
fact, in the present database they have been estimated. Recently, however,
new thermodynamic investigations have started in the Nuclear Chemistry
group to investigate the lacking properties.

M.E. Huntelaar

Fig. 3   Results of the ACE-L8 benchmark calculations for barium and
uranium derived by various organisations.

2. Thermochemical data for reactor materials and fission products

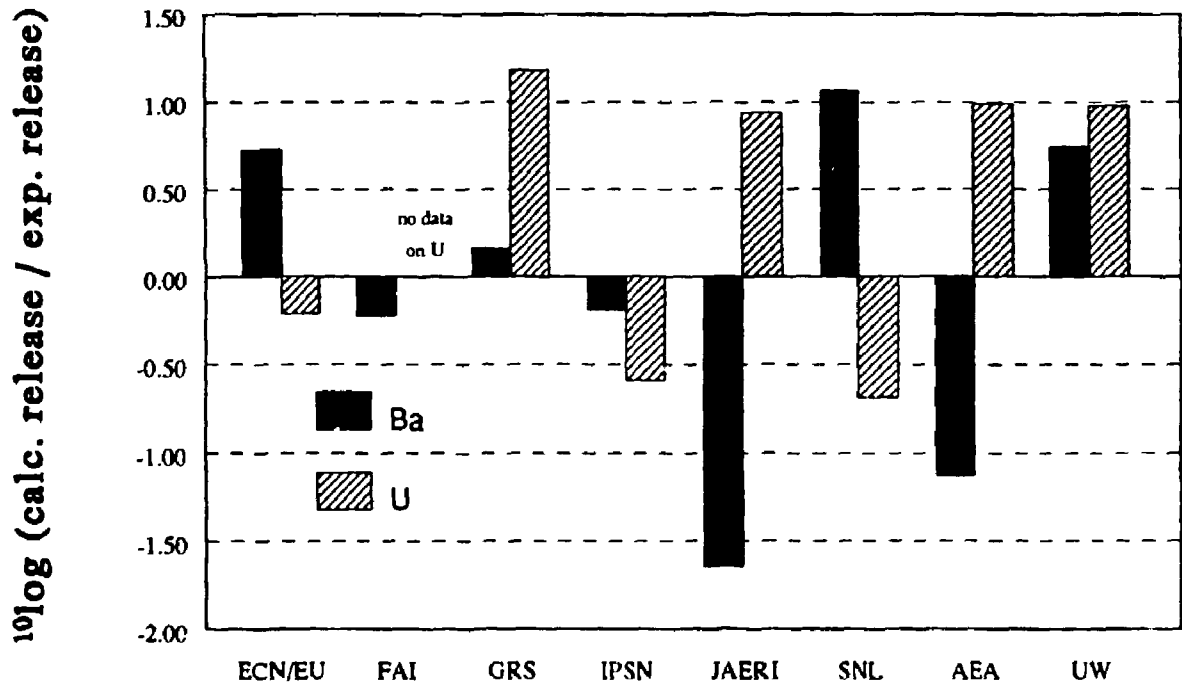Thermochemical models are an important tool in the assessment of the chemical behaviour of materials under extreme conditions of temperature and pressure. Since the Manhattan Project, nuclear technology has been a field where such models have been applied with much success. Typical examples are the release of fission products from the fuel and core-concrete interactions. But also in non-nuclear fields the role of thermochemical calculations is highly valued, for example for the development of halide lamps or chemical vapour deposition (CVD) processes.

With the introduction of (fast) computers, the potentiality of multi-element/multi-component calculations has become extremely large. Commercial packages like MTDATA, SolGasMix, ChemSage or GEMINI can be used for complex chemical systems containing compounds of up to 30 elements. Nowadays the algorithms for these codes are advanced and highly reliable and as a result the output of such calculations mainly depends on the thermochemical input data used: bad data give bad results (rubbish in, rubbish out).

In the Nuclear Chemistry group, the compilation of a reliable database for reactor materials and fission products has been undertaken since 1985 [1,2]. Presently, about 500 compounds of more than 35 elements have been evaluated by experts (see figure 4). This has been done by critical assessment of all available information in literature. To this purpose, a set of home-made computer programmes is used to obtain a uniform approach and to ascertain consistency of the data (see figure 5). Also, a computer programme for data consultancy, the so-called TBASE code, is available. All these programmes are operated on a VAXstation.

In order to facilitate the database management and to ascertain an easy exchange between the ECN database and commercial packages, the TBASE code has been re-designed in recent years by the Information Engineering group of ECN-Energy Engineering. It was decided to transfer the software from a VAX-VMS to a MS-DOS/Windows environment as most commercial programmes operate under the latter. For database management a code was developed on the basis of the MS-Access system. Both thermochemical and crystallographic data of pure compounds are being stored. For consultancy of the database, a new code was developed, TBASE-consult. This code has the following functions:

- visualising the data of pure compounds and reactions in the form of standard thermochemical tables and graphs,
- visualising the thermodynamic and crystallographic input data,
- export of data in ChemSage and MTDATA format,
- calculation and visualisation of predominance area diagrams.

Periodic table (Fig. 4)

H																	He
Li												B	C		O	F	Ne
Na	Mg											Al	Si	P		Cl	Ar
	Ca		Ti		Cr	Mn	Fe		Ni		Zn					Br	Kr
	Sr	Y	Zr		Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf		W	Re							Pb				

La	Ce		Nd			Eu									
Ac	Th		U	Np	Pu	Am	Cm	Bk	Cf						

Fig. 4   The elements treated in the ECN database

Flow diagram (Fig. 5)

LITERATURE

MOTHER   ENTHAL

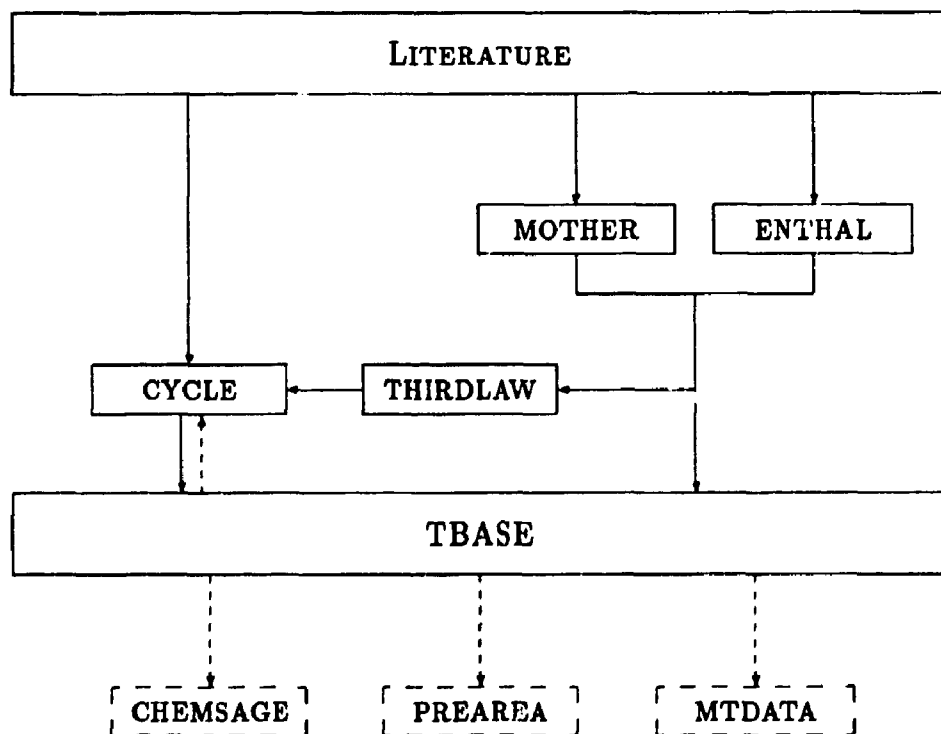CYCLE ← THIRDLAW

TBASE

CHEMSAGE   PREAREA   MTDATA

Fig. 5   Flow diagram of the ECN computer programmes used in the assessment of thermochemical properties

The TBASE consul software has been constructed in such a way that it can be easily offered to clients together with selected subsets from the ECN thermochemical database. In this way a commercialisation of the database has become possible.

R.J.M. Konings

References

[1] E.H.P. Cordfunke, R.J.M. Konings (Eds), Thermochemical data for reactor materials and fission products. North-Holland, Amsterdam, 1990.

[2] E.H.P. Cordfunke, R.J.M. Konings, Thermochemical data for reactor materials and fission products: the ECN database. J. Phase Equilibria 14 (1993) 457.

3. Thermochemical calculations on fuel of the High-Temperature Gas-cooled Reactor.

Thermochemical calculations were performed with the computer program ChemSage. The purpose of these calculations was to compare the chemical behaviour of both types of nuclear fuel. Two concepts of the High-Temperature Gas-cooled Reactor (HTGR) are of interest nowadays, namely the German and the U.S. concept. The German fuel concept consists of a TRISO [TRi-structural ISO(tropic)]-coated UO_2 kernel and the U.S. fuel concept consists of a TRISO-coated kernel with a mixture of UO_2 and UC_2. The characteristic differences between the U.S. fuel and the German are given in Table 1. The U.S. fuel is fabricated by carbothermic reduction of UO_2 and C at 1823 K. The TRISO-coating consists of thin carbon layers and a SiC layer for storage and retention of fission products. The most important layer for retention of the fission products is the SiC coating. The interaction of the SiC coating by the fission products can be simulated by ChemSage calculations. It is well known from literature that Pd causes the most severe damage to the SiC coating. Pd reacts with SiC to give Pd_2Si, dependent on the concentration of SiC or Pd; other low melting Pd-Si alloys can be formed as well. Also other fission products can cause damage to the coating. Ba, for instance, can react with SiC at a certain oxygen potential forming $BaSiO_3$.

Table 1. Differences between U.S. and German HTGR fuel.

	U.S.A.	German
composition	UCO	UO_2
Temperature (K)	973-1523	1523
Burn-up (%)	≤26	8-10
Enrichment (%)	19.6	10.6

The main difference between the U.S. fuel and the German fuel is that the U.S. fuel seems to be not thermodynamically stable at HTGR operating temperatures with respect to UO_2 and C. This is demonstrated in figure 6. In this figure the CO pressure of the U-C-O system is plotted as a function of the temperature showing the phase field where UO_2 and UC_2 are in equilibrium. At temperatures less than 1200 °C the phase field UO_2 and UC_2 does not exist.

The temperature and the oxygen potential are the most important parameters for the chemical behaviour of the fuel. Figure 7 shows the calculated total pressure in the kernel as a function of the oxygen potential. In case of high temperatures (2000 K) and high oxygen potentials (-350 kJ/mole) very high CO pressures were calculated for both the German and the U.S. fuel. The total pressures are minimal at the actual oxygen potentials of the German (between -450 and -550 kJ/mole) and the U.S. fuel (between -650 and -750 kJ/mole). The total pressures are higher in the U.S. fuel than in the German fuel. This is not surprising because the burn-up is much higher in the U.S. fuel concept. The Xe pressure is the highest of the fission products in the fuel. At low oxygen potentials Cs pressures are also high. In Figure 8 the Cs

pressure of both fuel concepts is given as a function of the temperature at an oxygen potential of -500 kJ/mole, resp. -650 kJ/mole.

Conclusions

1. The U.S. fuel seems thermodynamically to be unstable at the HTGR operating temperature.

2. The total pressure in the coated particles of the U.S. concept is much higher than in coated particles of the German concept, mainly due to the higher burnup.

3. At a high oxygen potential and a high temperature the CO pressure can be very high with both fuel concepts.

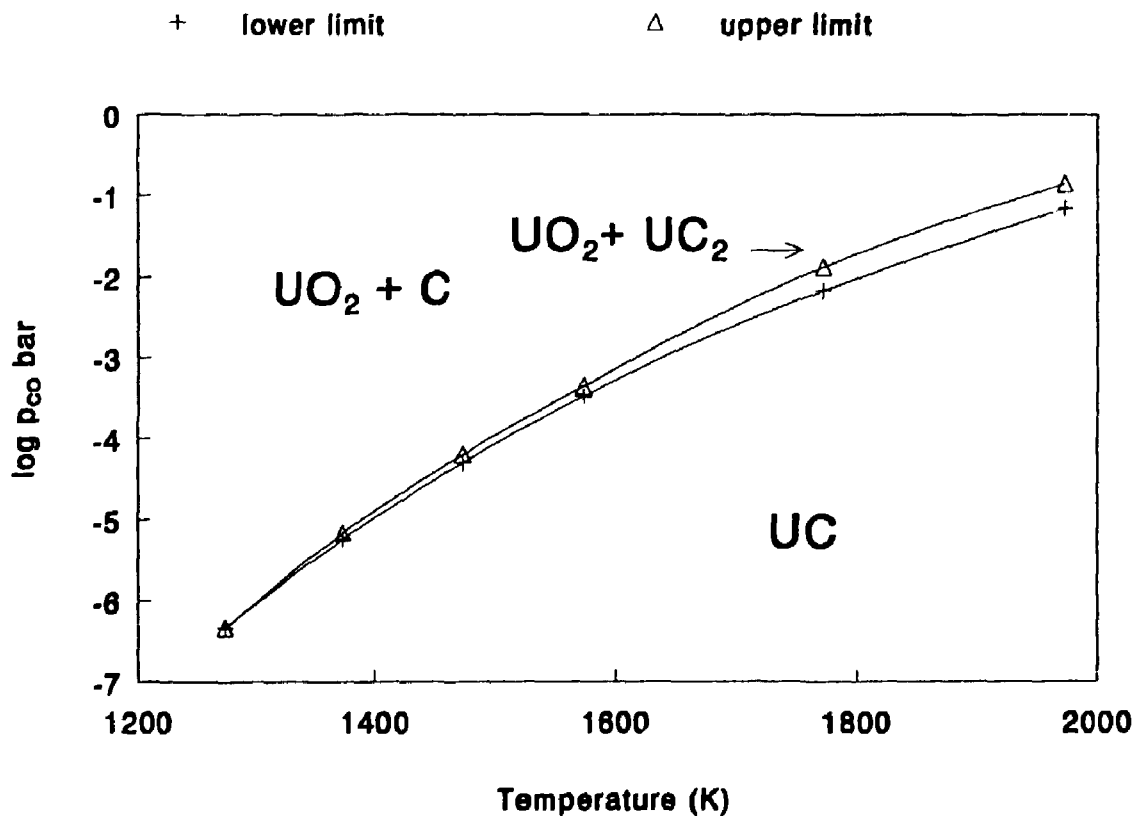4. At low oxygen potential the Cs pressure is high.

P. Groot

Fig. 6   Plot showing the phase field (CO pressure vs. temperature) where UO_2 and UC_2 are in equilibrium.
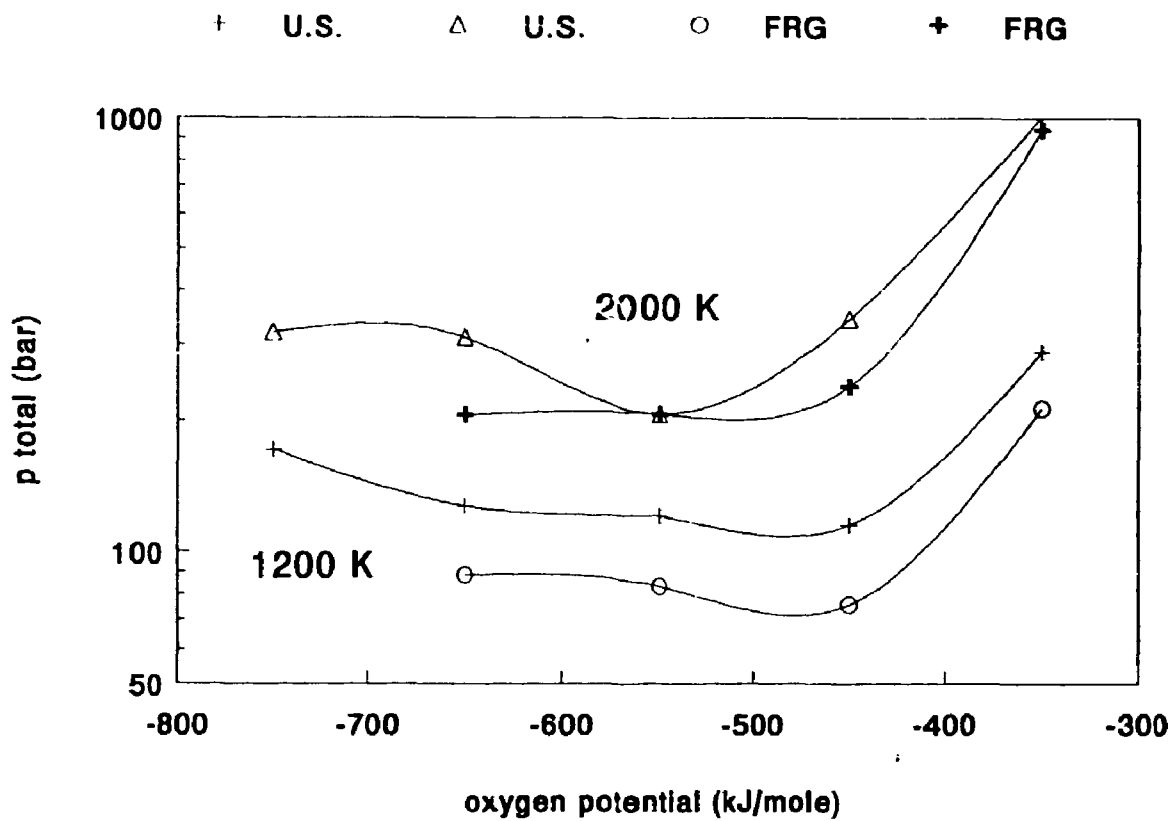
Fig. 7   Total pressure (bar) of the German and the U.S. coated particles as a function of the oxygen potential (kJ/mole).
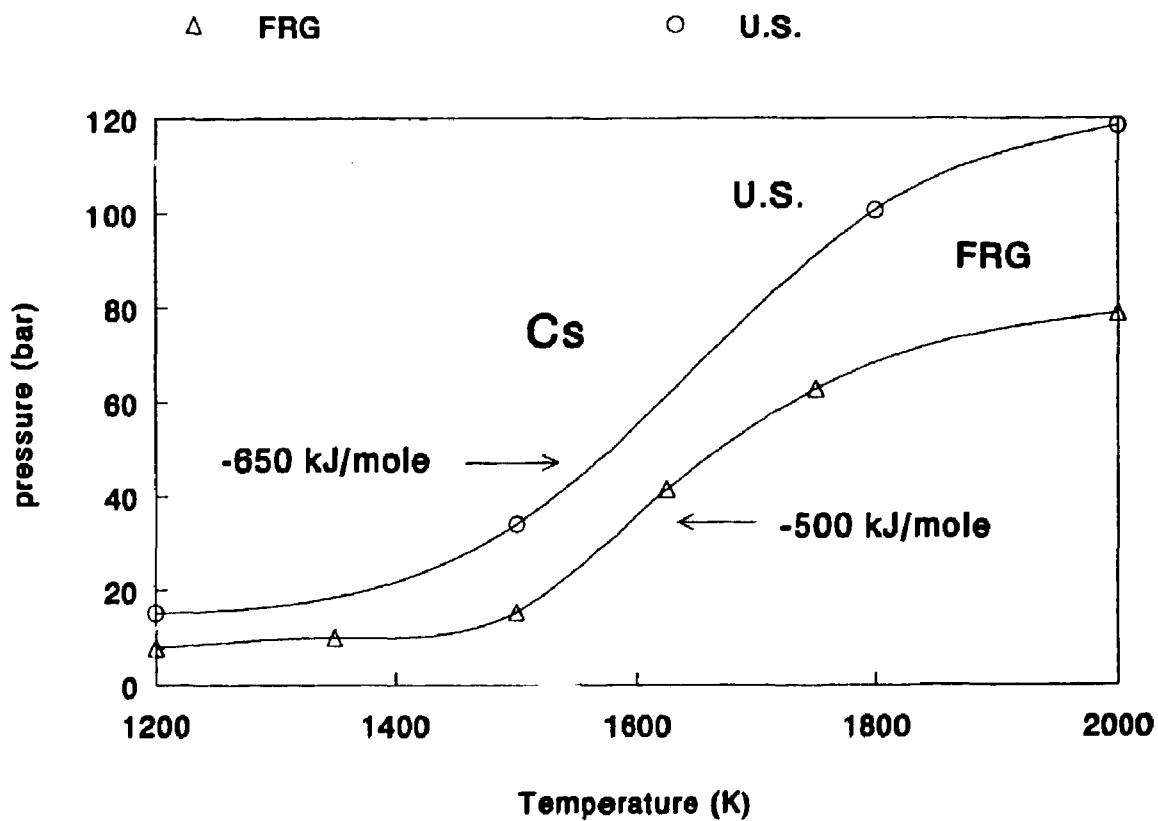

Fig. 8   Cs pressure (bar) of the German and U.S. coated particles with an oxygen potential of -550 kJ/mole as a function of the temperature (K).

4. Formation of organic tellurides during nuclear accidents?

Iodine is among the most radiotoxic products formed by fission of uranium in a nuclear reactor. In case of a nuclear accident iodine will be released and spread inside the containment or in the worst case also outside the reactor. Several reactions can occur that will slow down or accelerate the release of iodine. One of these reactions is the γ-irradiation induced reaction with organic compounds resulting in the formation of organic iodides. The lower alkyl iodides are very volatile and can easily contribute to the spread of radioactive iodine, which is a highly dangerous radioactive element for mankind, through the air. The sources for the organic compounds present in the containment are the natural background methane/ethane, and compounds released from paints and construction materials upon heating. Tellurium is closely related to iodine since the radioactive tellurium isotopes decay to iodine. It has been proposed several times that tellurium will also form organic tellurides upon γ-irradiation. Therefore, a better knowledge of the possible formation of organic tellurides is desirable, and the following program has been performed:

- determination of the thermodynamic properties of dimethyl telluride
- γ-irradiation induced formation of dimethyl telluride from tellurium/methane mixtures
- γ-irradiation induced decomposition of dimethyl telluride

The thermodynamic properties of gaseous dimethyl telluride, which are of interest for the use in models predicting the chemical equilibrium during a nuclear accident, can be calculated from statistical mechanics. The input parameters necessary for these calculations are: vibrational frequencies, electronic states, moment of inertia, symmetry of the molecule, and parameters concerning the rotation of the methyl groups. The vibrational frequencies have been obtained from Raman and infrared spectroscopy (Figure 9). Structural parameters have been derived from literature data. The final parameter, necessary for calculating the Gibbs energy of formation, is the enthalpy of formation of gaseous dimethyl telluride, which can be calculated from the enthalpy of formation of liquid dimethyl telluride and the enthalpy of vaporization. A membrane null manometer for measuring the vapour pressure of dimethyl telluride has been developed and a picture is shown in Figure 10. The enthalpy of vaporization can be obtained directly from the vapour pressure $(\log p = f(1/T)$.

The γ-irradiation experiments have been performed in the HFR at Petten. Glass capsules of 100 ml have been irradiated at 40°C. The contents of the capsules have been extracted with CS_2 and analyzed by gaschromatography.
Two sets of irradiation experiments have been performed. In the first set capsules with dimethyl telluride (55 mbar) have been irradiated with a total dose rate of 40 and 400 Mrad, respectively. The observed decomposition of 5% at 40 Mrad is comparable with the amount of decomposition of methyl iodide. At 400 Mrad 25% of the dimethyl telluride has been decomposed. In

the second set the capsules have been filled with methane (0.5 bar), after a tellurium mirror was deposited on the wall of the capsule. Analyses of the capsules after irradiation of 40 and 400 Mrad did, however, not show any dimethyl telluride.

Summary

- The thermodynamic properties of dimethyl telluride have been determined.
- Dimethyl telluride shows a normal decomposition behaviour upon γ-irradiation.
- The formation of dimethyl telluride will hardly contribute to the release of radioactivity.

M.G.M. van der Vis
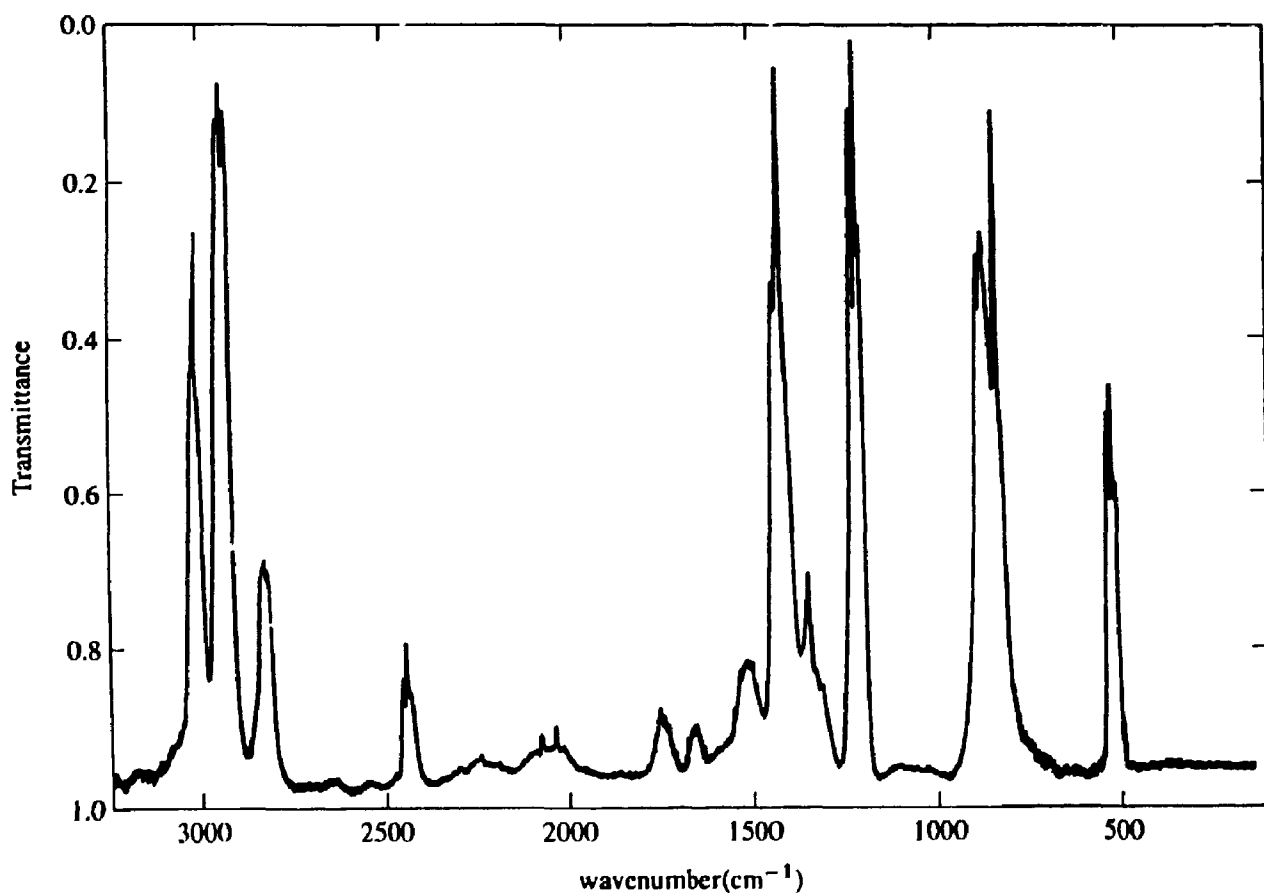
Fig. 9   Infrared spectrum of gaseous dimethyl teluride.

A: Sample chamber
B: Filling tube
C: Spoon
D: Construction to prevent breaking of
   the spoon
E: Pointer
F: Scale (0.2 mm division)
G: Connection to vacuum line
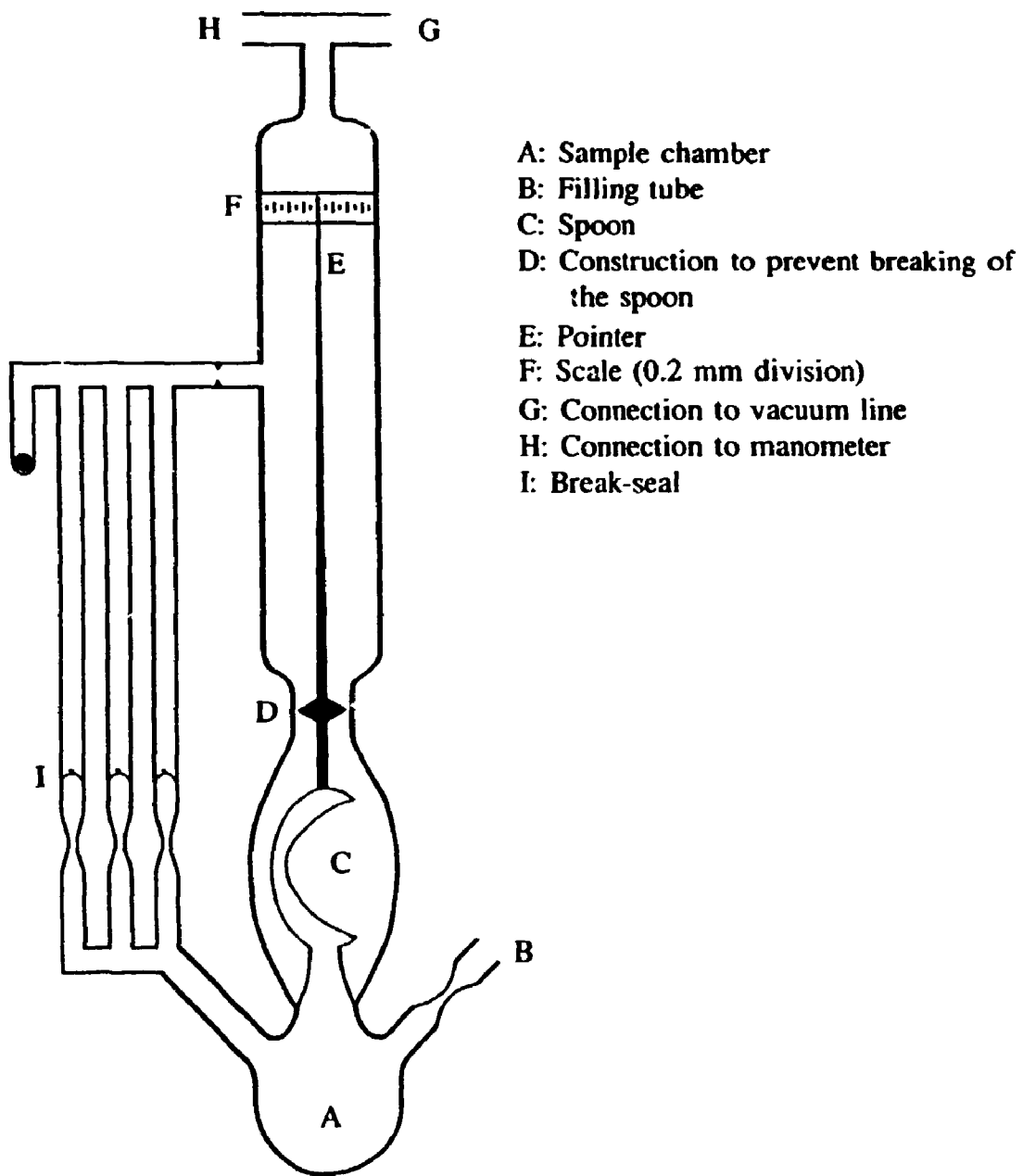H: Connection to manometer
I: Break-seal

Fig. 10   The Bourdon spoon gauge.

5. Reaction of tellurium with Zircaloy-4

Tellurium is an important fission product, since it is the precursor of the very hazardous iodine. Consequently, the release of tellurium partly determines the release of iodine in the case of a reactor accident.

During the initial stage of a reactor accident the fuel temperature rises and the volatile fission products are vaporized into the fuel-cladding gap. It has been observed that at this stage tellurium reacts with the Zircaloy cladding. Tellurium can dissolve in the Zircaloy or form a zirconium telluride compound. This process leads to a strong retention of tellurium in the reactor core, due to a strong decrease of the tellurium vapour pressure. For a reliable estimation of the release behaviour of tellurium this interaction needs to be taken into account in the computer codes (e.g. VICTORIA) which are used to calculate the fission product release behaviour. Therefore knowledge is required on the compounds, which are formed during this interaction and on their chemical stability.

To study the reaction behaviour of tellurium with Zircaloy and to establish which compounds are formed, reactions of tellurium with this cladding material have been conducted. One series of experiments consisted of heating Zircaloy-4 pellets or turnings in the presence of a weighed amount of tellurium to temperatures ranging from 400°C to 1000°C At the end of the experiment the reaction products were analyzed with X-ray powder diffraction and some pellets were after reaction embedded in resin and sawn through to examine their cross sections with SEM/EDX. At 400°C formation of the compounds $ZrTe_5$ and $ZrTe_3$ occurred. Above 800°C the compound $Zr_{1+x}Te_2$ was always found. Furthermore, it was clearly seen that reaction of tellurium vapour with the Zircaloy only occurs on the outer surface of the Zircaloy specimen, forming a layer of zirconium telluride. The bulk of the Zircaloy remains unattacked. This reaction behaviour is clearly seen in figure 11, where the growth of the telluride layer on the surface of a Zircaloy pellet at 450°C is shown after several time intervals. Figure 12 shows the cross section of this reacted pel¹
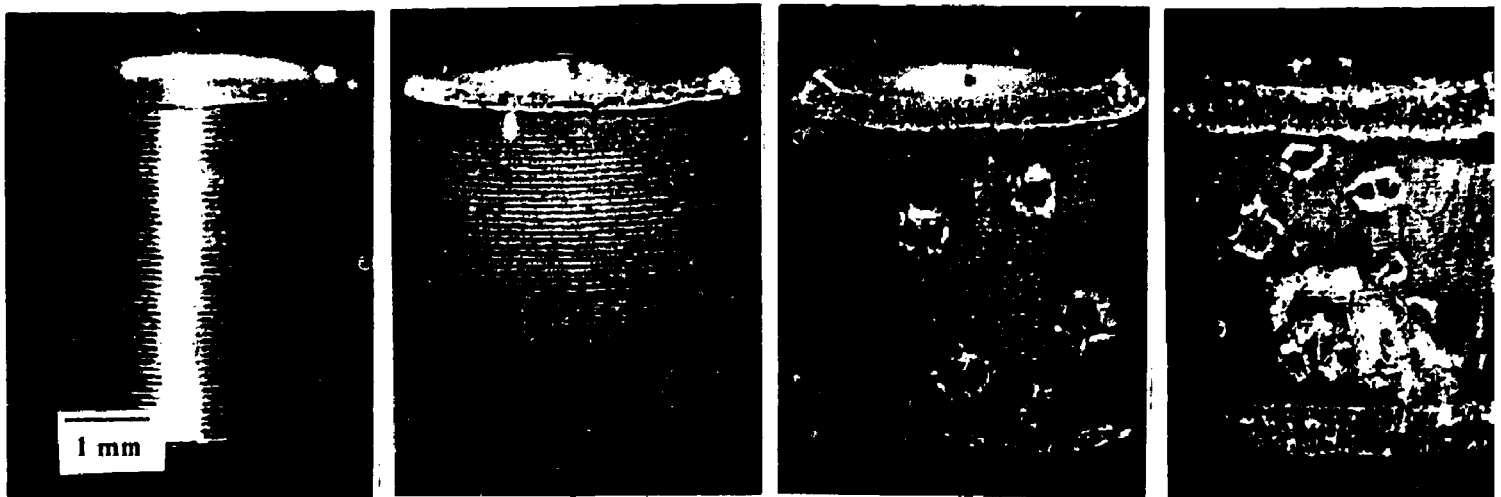

Fig. 11   Zirconium telluride formation on the surface of Zircaloy-4 at 450°C at several time intervals (before reaction, after 10 hours, after 30 hours, after 100 hours of reaction).
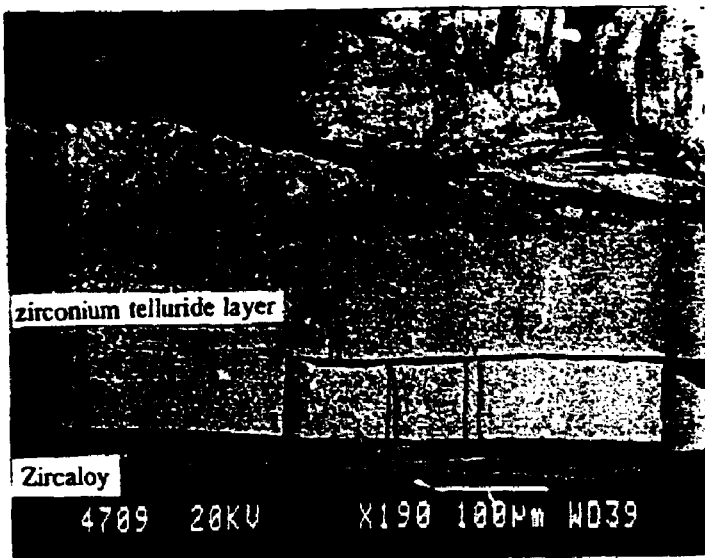
Fig. 12   SEM picture of the cross section of a reacted Zircaloy-4 pellet
after 100 hours at 450°C.

In another series of experiments the influence of the tellurium vapour
pressure on the reaction with Zircaloy is studied. An experimental setup was
used with which the tellurium vapour pressure and the reaction temperature
could be varied separately. It was again observed that the compound $Zr_{1+x}Te_2$
was formed in most cases of reaction temperature and tellurium pressures.
Only at reaction temperatures of 1000°C and at low tellurium pressures the
more zirconium-rich compound Zr_5Te_4 was formed. This compound was also
found when a Zircaloy specimen, which contained a layer of $Zr_{1+x}Te_2$ was
heated to a temperature close to its melting point. After the heat treatment the
$Zr_{1+x}Te_2$ was transformed into Zr_5Te_4.

This study has shown that for calculation of the release behaviour of
tellurium, formation of the compounds $Zr_{1+x}Te_2$ and Zr_5Te_4 during interaction
with the Zircaloy cladding needs to be taken into account. Although the
existence of the most zirconium rich compound, Zr_3Te, in the Zr-Te system
was established in separate experiments in our laboratory, this compound was
never observed in any of the experiments with Zircaloy-4 specimens.
Formation of Zr_3Te on the basis of thermodynamics would be most
favourable. Apparently, kinetic aspects, such as diffusional transport of
zirconium into the zirconium telluride layer and diffusion of tellurium into
the bulk of the Zircaloy, play a major role in the formation of   zirconium
tellurides on the surface of the Zircaloy cladding.

R. de Boer

6. Transmutation of fission products

Partitioning and transmutation (P&T) of fission products and actinides is considered to be a complementary option in the management of high-level nuclear waste. It involves the separation of specific elements (nuclides) from spent fuel, followed by re-irradiation in reactors or accelerators. The alpha-toxicity of the minor actinides is of course the major concern but from the point of view of the risk-during-storage, the beta-emitting fission products technetium-99 and iodine-129 cannot be neglected. This is mainly due to their mobility in the geological environment of an underground repository.

There is general agreement that the implementation of P&T in waste management is feasible but many technological issues still have to be solved. Especially with respect to the design of targets and fuels for transmutation and the testing of their irradiation behaviour much research is needed. To this purpose ECN has started a project on the irradiation of targets for transmutation within the framework of its RAS programme as well as the European EFFTRA collaboration. EFTTRA is the acronym for Experimental Feasibility of Targets for Transmutation. It is a collaboration of ITU and KfK in Germany, CEA and EdF in France and ECN and IAM in the Netherlands.

In the first phase of the project, the transmutation of the fission products technetium-99 and iodine-129 is being investigated. These radionuclides can be converted to stable ones by means of (thermal) neutron capture:

$$^{99}\text{Tc} + \text{n} \rightarrow {}^{100}\text{Ru}$$
$$^{129}\text{I} + \text{n} \rightarrow {}^{130}\text{Xe}$$
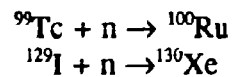
The aim is the study of the material and irradiation behaviour of selected samples. To this purpose nine samples have been prepared for in-core irradiation tests in the High Flux Reactor in Petten, three technetium and six iodine samples for which a special irradiation facility has been designed (figure 13). The characteristics of the different materials are summarized in Table 2.

The technetium samples were fabricated at the Institute for Transuranium Elements (ITU) in Karlsruhe. They consist of casted metallic rods which are encapsulated in 15-15 Ti stainless steel. For the iodine compounds, three different metal iodides have been selected on the basis of an analysis of their neutronic and physico-chemical properties: cerium triiodide (CeI_3), sodium iodide (NaI) and lead diiodide (PbI_2). The samples, fabricated at ECN, are also encapsulated in 15-15 Ti stainless steel. However, they do not contain the radioactive ^{129}I but the naturally occurring ^{127}I, as it was impossible to obtain and fabricate samples of the former. This substitution will not affect the outcome of the experiments as the transmutation process and chemical behaviour of the two iodine nuclides are similar. The thermal neutron fluence rate in the core position (C5) is about $2 \cdot 10^{18}$ m^{-2} s^{-1}, the irradiation temperature is about 710°K. At this temperature, PbI_2 is in a molten state. The irradiation started in April 1994 and will be stopped after 8 HFR cycles, in January 1995. The expected transmutation rates are about 4 % for the technetium samples and about 3 % for the iodine samples.

Table 2. Test matrix and experimental conditions for the RAS-1 experiment.

material	^{99}Tc	CeI$_3$	PbI$_2$	NaI
number of samples	3	2	2	2
sample mass [g]	10.4	1.3	1.7	1.6
capsule volume [cm^3]	1.45	1.6	1.6	1.6
irradiation time [cycles]	8	8	8	8
irradiation temperature [K]	~710	~710	~710	~710
melting point [K]	2430	1033	683	934
transmutation rate per cycle [%]	0.54	0.35	0.37	0.37

In 1995 the samples will be distributed among TUI, CEA and ECN for post irradiation examination (PIE). The examinations of the three technetium samples will focus on the material behaviour (swelling), the examination of the iodine samples on the interaction of the samples and the cladding. In addition, the transmutation efficiency will be determined by analysis of the produced ruthenium (radial distribution and absolute quantities) in case of technetium and of the produced xenon in the plenum of the iodine capsules.

References

R.J. Konings, K. Abrahams, W.M.P. Franken, H. Gruppelaar, J.L. Kloosterman, P.J.M. Thijssen, R. Conrad, Technological aspects of transmutation of technetium and iodine in : Proceedings Global-93, Seattle Washington (1993), p. 1260.
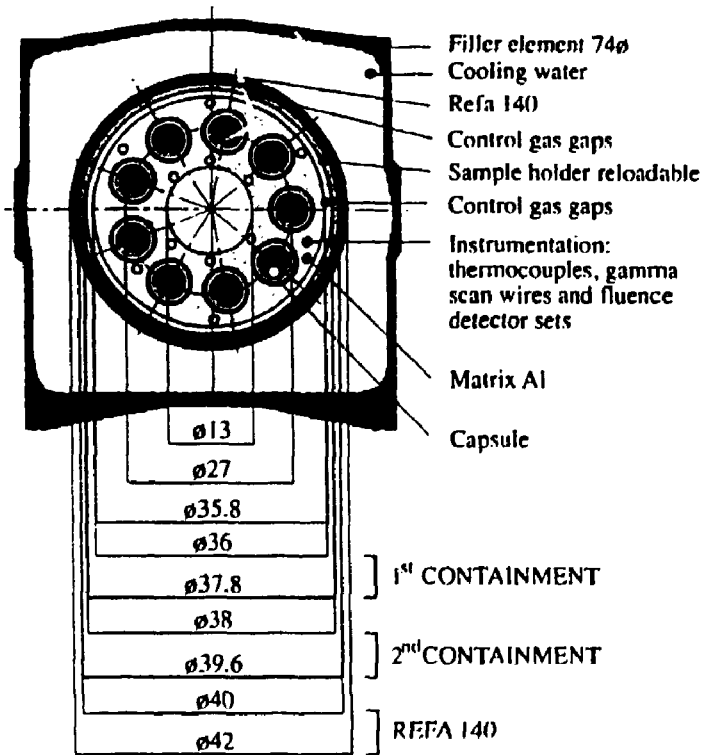
R.J.M. Konings

Fig. 13   Horizontal cross section of the irradiation facility for the RAS-1 experiment.

7. The thermal conductivity of high-burnup UO_2 fuel

The thermal conductivity of high-burnup UO_2 is an important property from a safety and economic point of view, since it plays a major role in determining the maximum power of a fuel element. The thermal conductivity of UO_2 is rather low and depends strongly on the temperature and the microstructure. The thermal conductivity of UO_2 decreases even further during irradiation, mainly as a result of:

1) The formation of fission products that dissolve as oxides in the fuel matrix.

2) The formation of fission gases that form additional pores.

Finite Element Method (FEM) calculations have been performed to determine the influence of thermal radiation across pores on the thermal conductivity of porous UO_2. It appeared that the radiative contribution to the overall thermal conductivity contributes significantly for large oblate ellipsoidal pores.

The irradiation induced porosity changes cause a considerable inaccuracy in the calculation of the influence of irradiation on the thermal conductivity. The thermal conductivity depends strongly on the shape, the orientation and the distribution of the pores. The influence of spherical, ellipsoidal and cylindrical porosity on the thermal conductivity has been computed with the FEM [1]. The thus obtained results have been used to verify various analytical thermal conductivity equations. The results of the formula that was derived by Schulz [2] are in good agreement with the results of the present FEM computations.

The complex pore shape in irradiated UO_2 can not be described accurately by the formula of Schulz, since this equation takes into account only ellipsoidal pores. In order to overcome this problem the FEM is used to compute the influence of a particular microstructure on the thermal conductivity. FEM computations were performed on the microstructure of a UO_2 pellet that has been irradiated to a burnup of approximately 25 MWd/kgHM. After the irradiation the pellet was cut in the radial direction and light-microscopy photographs were made. These photographs were used to digitize the microstructure of the UO_2 pellet and enter this microstructure in the FEM program. As a first approximation the FEM computations were performed in the two dimensional (2D) plane of the photograph (fig. 14a), since the three dimensional (3D) shape of the pores can not be determined from the photograph. The influence of this microstructure on the two dimensional (2D) temperature distribution and on the y-component of the 2D thermal flux (fig. 14b) was computed.
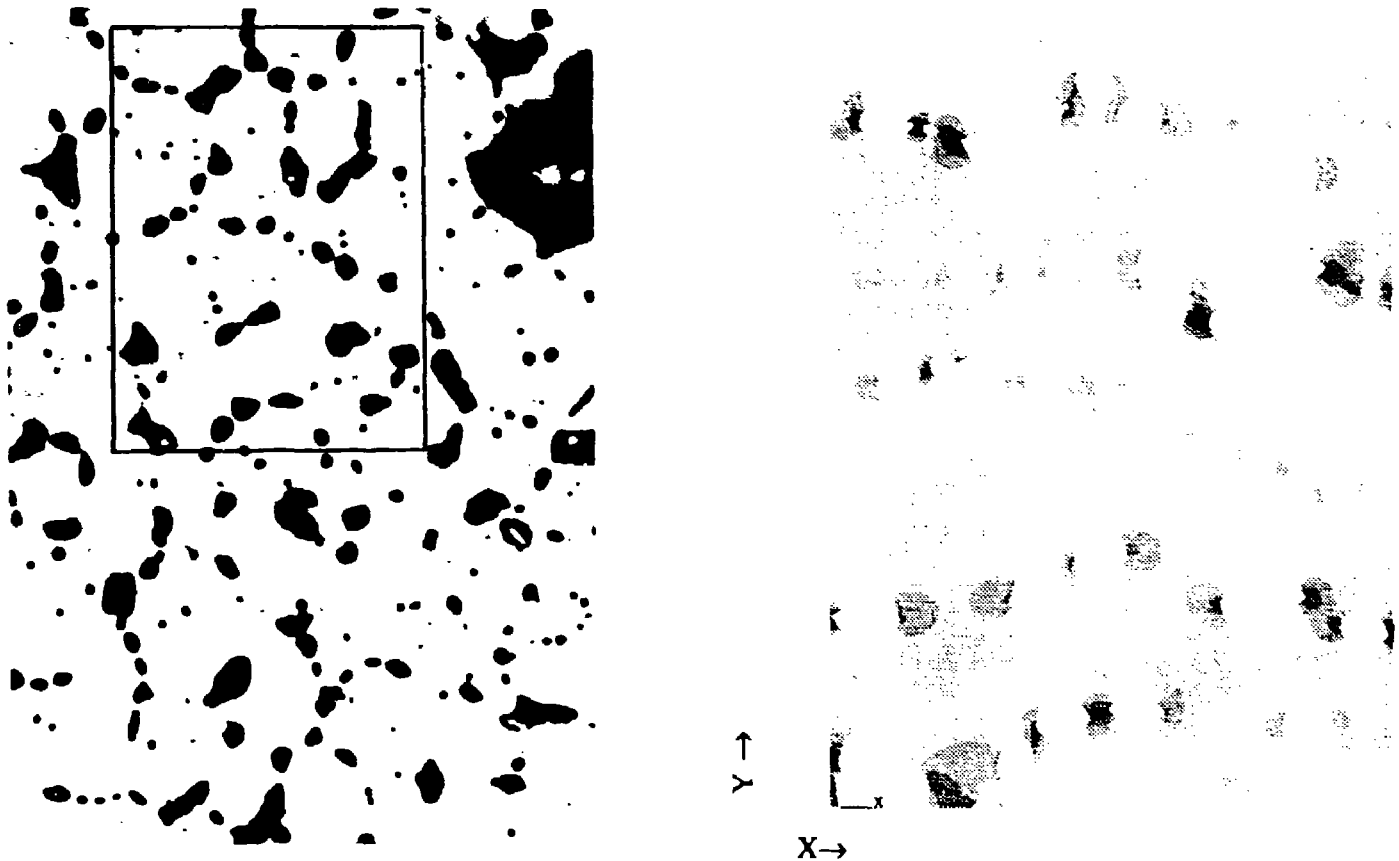
Fig. 14a A light microscopy photograph of a UO_2 pellet with a burnup of 25 MWd/kgHM.

Fig. 14b The distribution of the y-component of the thermal flux, as computed with the FEM, in the area marked in fig. la. The dark regions represent a larger flux than the light regions. The white regions represent the pores.

The FEM program determines for this microstructure both the porosity (p = 0.114) and the 2D thermal conductivity (f_{2D}) in the plane of the photograph (f_{2D} = 0.723). The extra degree of freedom of the thermal flux in the 3D case causes the 3D thermal conductivity (f_{3D}) to be larger than f_{2D}, thus f_{2D} is a lower limit of f_{3D}. This lower limit can be determined accurately with the FEM, which makes f_{2D} an important parameter. By comparing f_{2D} and f_{3D} for several well-defined pore shapes (circular/spherical, elliptical/ellipsoidal and rectangular/block shaped) a relation between f_{2D} and f_{3D} was found that is nearly independent of the 3D pore shape. This relation allows the conversion of f_{2D} into f_{3D}, without specific knowledge of the 3D pore shape:

$$\frac{1-p-f_{2D}}{1-p-f_{3D}} = 1.8 \pm 0.3 \tag{1}$$

Eq. 1 and the results of the FEM calculations (p = 0.114, f_{2D} = 0.723) were used to make an estimation of f_{3D} (f_{3D} = 0.795). These values for p and f_{3D} can be used in eq. 2 to calculate β that characterizes the influence of the pore shape and the pore orientation on the thermal conductivity.

$$f_{3D} = (1 \cdot p)^\beta \qquad\qquad (2)$$

For this particular microstructure a β value of 1.85 has been obtained. It should be kept in mind that the value of β depends strongly on the microstructure.

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8. Tritium retention in graphite.

Graphite and other carbon-based materials are considered as attractive materials for the protection of high heat flux components in existing and forthcoming tokamaks for example the International Thermonuclear Experimental Reactor (ITER). However, this reactor will produce intens neutron fluxes which could damage the microstructure and critical properties of the protective materials (e.g. thermal conductivity, swelling and tritium trapping). This could limit the utilization of these materials in fusion devices. One of the crucial problems which needs to be better understood is the behaviour of tritium in materials subjected to crystallographic and microstructural changes induced by neutrons. The anticipated enhancement of the tritium retention capacity could cause intolerably high tritium inventories in the graphite plasma-facing armours and as such represent a key safety problem.

At ECN the effect of the neutron dose and the irradiation temperature on the tritium inventory of various irradiated graphites has been investigated. Four materials have been tested: fine grained graphite S1611 and CL5890, carbon fiber reinforced carbon (CFC) A05 and Pfizer pyrolitic graphite. The neutron dose is represented by the number of displaced atomes (dpa) which ranged from 0.007 to 3.2 dpa. The irradiation temperatures were: 400 °C, 600 °C and 1500 °C. Irradiated samples were loaded with tritium by exposure to hydrogen containing 2 ppm tritium at a reference temperature of 850 °C. After loading the tritium was released by heating the specimens up to 1100 °C. The released amount of tritium was measured by an ionization chamber and by liquid scintillation counting (LSC) of the water inwhich the released tritium was trapped after being oxidized. A detailed description of the experimental procedure is given in [1]. Results of measurements on unirradiated specimens and of some preliminary data on irradiated specimens are presented in [2], together with some material characteristics.

Typical results are given in table 3 and in figure 15 for graphite CL 5890 and CFC A05 for a tritium loading temperature of 850 °C. Note that the line in figure 1 was drawn through data obtained at 400, 600, and 1500 °C. From these results it can be observed that the amount of tritium retained in the specimens after heating up to 1100 °C increases with neutron damage. Moreover, for equal dpa-values the amount of retained tritium was slightly higher for the specimens irradiated at 400 °C than those irradiated at 600 °C. A large increase in tritium retention occurred for specimens irradiated to 3.2 dpa at 1500°C compared to those of 1.2 dpa.

It was found that by oxydizing the specimens after heating up to 1100°C not all the tritium was released. The amount of tritium collected during oxydation varied from about 30% of that during release to about 100% for the specimens with a low dpa-value and irradiation temperatures of 400°C and 600°C. For specimens with high dpa-values (1.2 and 3.2 dpa) the amount of retained tritium after release at 1100°C was many times larger. However, it should be noted that much more tritum was released for the specimens

irradiated up to 3.2 dpa than for 1.2 dpa specimens. For A05 specimens with a damage of 3.2 dpa about 10 times as much tritium was measured during oxydation of the specimens than of those with 1.2 dpa. Apparently, during irradiation at a neutron damage >1 dpa a large number of tritium trapping sites are produced and that a temperature of 1100°C is not sufficient to release all the retained tritium. In addition, the rather high irradiation temperature of 1500°C does at least not completely anneal out the neutron damage. Causey [3] showed that the amount of tritium trapped in a sample of N3M graphite irradiated at 600°C to 10 dpa was reduced by approximately 50% when the sample was annealed at 1500°C in vacuum for 6 hours prior to the tritium exposure.

Table 3   Tritium retention of various graphites irradiated up to different neutron fluences and at various temperatures. Tritium loading: 10 hours at 850 °C using H_2+2ppm T_2 at 800 mbar. The tritium release temperature was 1100 °C.

| Material | Specimen ID | | Tritium retention, µCi/g, after release and oxidation and total | | |
	dpa-value	irr. temp.,°C	release	oxidation	total
CL 5890	-	-	0.6	0.3	0.9
	0.0072	400	1.6	1.1	2.7
	0.072	400	1.4	2.3	3.7
	0.0072	600	1.7	0.6	2.3
	0.072	600	1.8	1.9	3.7
	1.2	1500	2.6		
	3.2	1500	73	416	489
A05	-	-	0.6	0.2	0.8
	0.0072	400	1.7	0.9	2.6
	0.072	400	2.1	1.9	4.0
	0.0072	600	1.4	0.8	2.2
	0.072	600	2.2	1.2	3.4
	1.2	1500	2.5	47	49.5
	3.2	1500	69	478	547

Conclusions

-    From literature [3,4] it was suggested that for various types of graphite saturation of tritium retention occurs after a neutron damage of about 1 dpa. However, the present data of graphite CL5890 and CFC A05 irradiated at 1500°C show a rather steep increase in tritium retention at > 0.1 dpa.

- The amount of tritium retained in specimens of CL 5890 and A05 after release at 1100 °C was of the same order as that being released for specimens irradiated up to a low neutron damage (< 0.1 dpa). For specimens with a high neutron damage (> 1 dpa) a large fraction of the tritium retained in the specimens after release at 1100 °C.
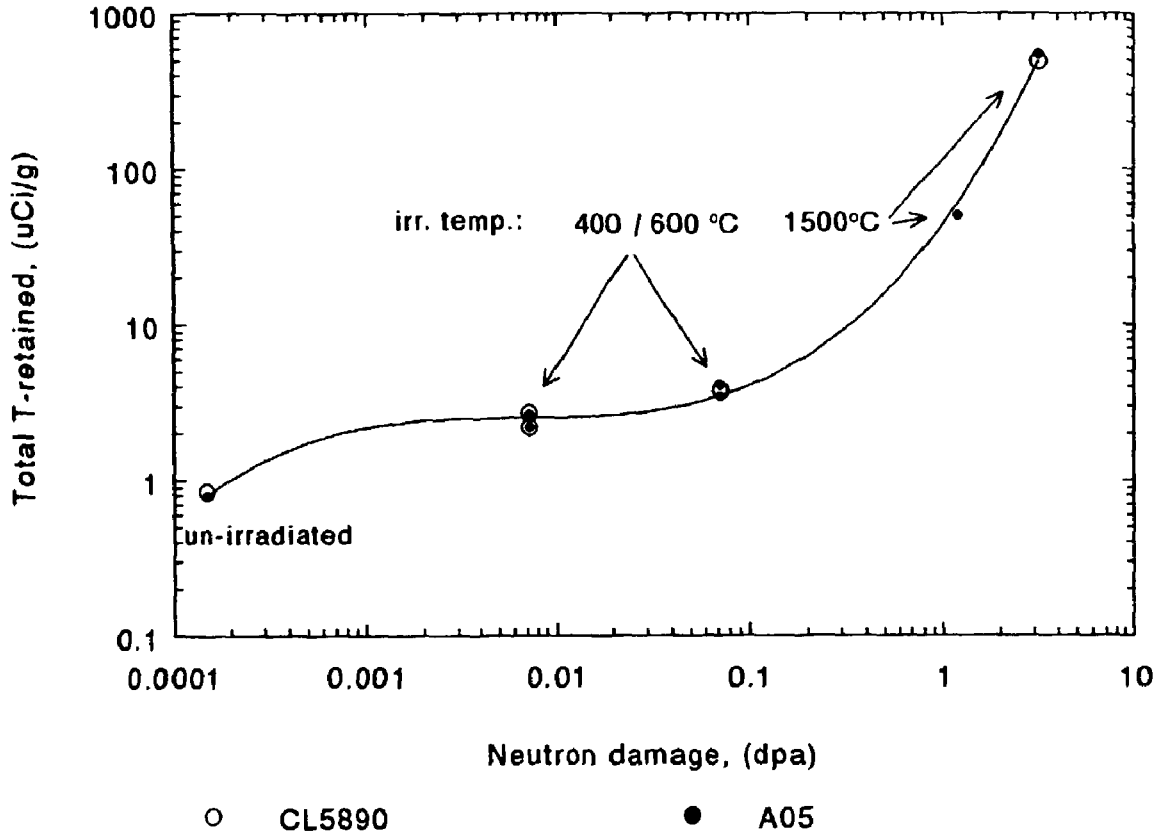

Fig. 15   Tritium retention of graphite CL5890 and CFC A05 as function of neutron damage. The loading occurred at 850 °C during 10 hours at 800 mbar, using H_2 + 2 ppm T_2.

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