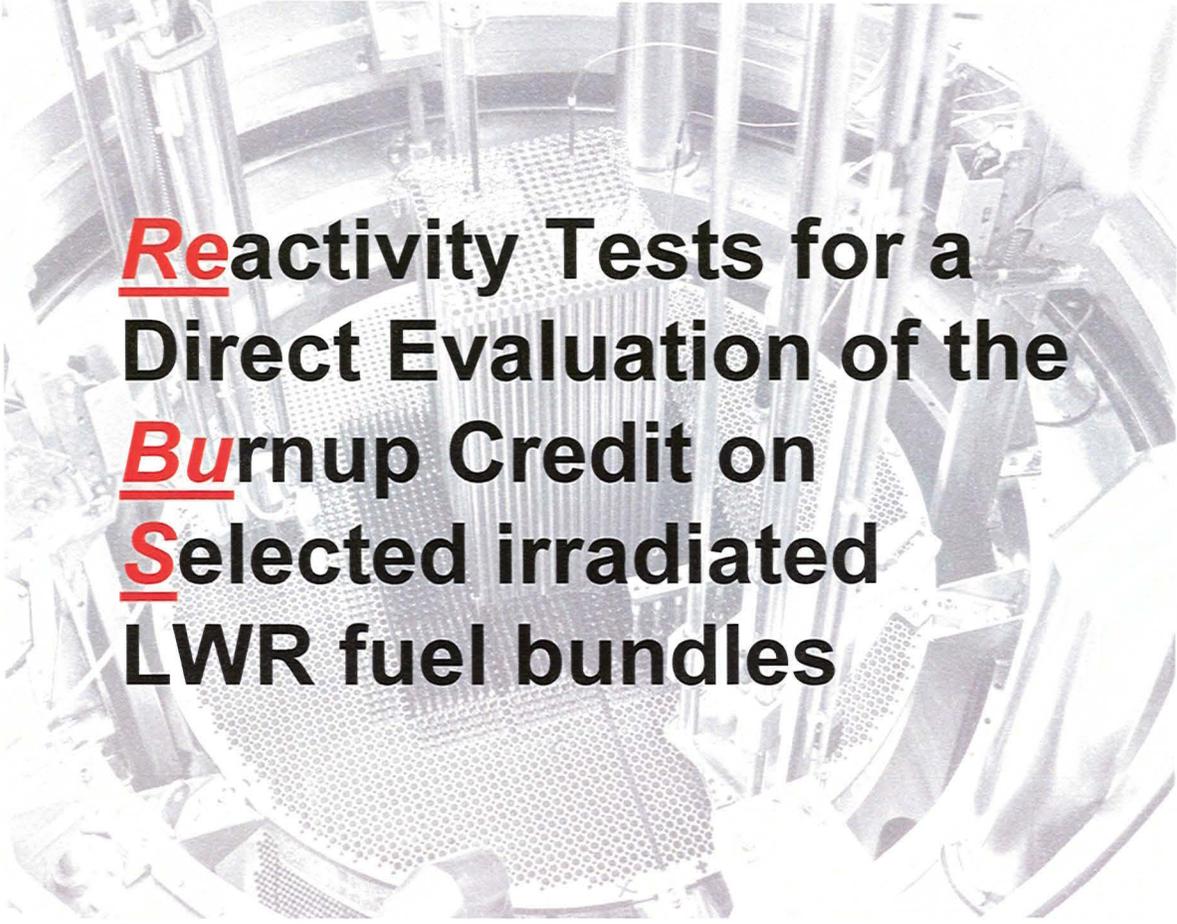


# " REBUS "

## International Programme

### PWR



**Reactivity Tests for a  
Direct Evaluation of the  
Burnup Credit on  
Selectd irradiated  
LWR fuel bundles**

Destructive Radiochemical Spent Fuel  
Characterization of a PWR UO<sub>2</sub> Fuel Sample

Issued May, 2006



Type of document :

Report

BN reference N°/ File - « Rev. » - Page

**0502640/221 - " A " 2**

Other reference :

RE 2005/35 Rev. A

## LIST OF MODIFICATIONS

DATE	REVISION	OBJECT
December 2005	" - "	Initial Edition
March 2006	" A "	<ul style="list-style-type: none"><li>- Nuclides concentration reported at the date of criticality in VENUS</li><li>- Axial location of the radiochemical sample recalled in the introduction</li></ul>



Type of document :

Report

BN reference N°/ File - « Rev. » - Page

**0502640/221 - " A " 3**

Other reference :

RE 2005/35 Rev. A

## **NOTICE**

## **LIABILITY**

\* \* \*

This document was prepared by SCK.CEN and reviewed by BELGONUCLEAIRE (BN). Neither BN or SCK.CEN, nor any person acting on behalf of BN:

- (a) gives any warranty, expressed or implied, with respect to the accuracy, completeness or usefulness of the information contained in this document, or that the use of any information, apparatus, method or process disclosed in this document may not infringe third party rights, or
- (b) assumes any liabilities with respect to the use of, or for damage resulting from the use of any information, apparatus, method or process disclosed in this document.

\* \* \*

FOR PUBLIC RELEASE



Type of document :

Report

BN reference N°/ File - « Rev. » - Page

**0502640/221 - " A " 4**

Other reference :

RE 2005/35 Rev. A

## TABLE OF CONTENT

\* \* \*

	<u>Pages</u>
Distribution List	5
Main Body : SCK.CEN Report	6



Type of document :

Report

BN reference N°/ File - « Rev. » - Page

**0502640/221 - " A " 6**

Other reference :

RE 2005/35 Rev. A

## **MAIN BODY**

### **SCK.CEN REPORT**

# **Destructive Radiochemical Spent Fuel Characterization of a PWR UO<sub>2</sub> Fuel Sample M11 – Final Report**

\* \* \*

Date: February, 2006

Chrono filling n° at SCK.CEN: R - 4311

Status: final

Number of pages: 25

\* \* \*

# **REBUS**

## **International Programme**

### **Destructive Radiochemical Spent Fuel Characterization of a PWR UO<sub>2</sub> Fuel Sample M11 – Final Report**

M. Gysemans  
P. Van Bree  
A. Dobney  
L. Vandeveld

**SCK•CEN Contract CO-90 98 1110**

Status: Confidential

Radiochemistry and Analysis  
SCK•CEN  
Boeretang 200  
2400 Mol  
Belgium

# Table of Contents

<b>ABSTRACT</b>	<b>2</b>
<b>1. INTRODUCTION</b>	<b>3</b>
<b>2. DESCRIPTION OF APPLIED CHEMICAL AND RADIOCHEMICAL METHODOLOGIES</b>	<b>4</b>
2.1 Sample preparation in the shielded cell	
2.1.1 Description of the acid dissolution of the spent fuel	
2.1.2 Description of the alkaline fusion of the residue	
2.1.3 Dissolution results for M11	
2.2 Chemical pretreatment and separations	
2.3 Chemical and radiochemical measurement techniques	
2.3.1 $\alpha$ -spectrometry	
2.3.2 $\gamma$ -spectrometry	
2.3.3 Thermal Ionization Mass Spectrometry	
2.3.4 Inductively Coupled Plasma Mass Spectrometry	
<b>3. SUMMARY OF ANALYSIS RESULTS</b>	<b>16</b>
3.1 Uranium	
3.2 Neptunium	
3.3 Plutonium	
3.4 Americium	
3.5 Curium	
3.6 Cerium	
3.7 Neodymium	
3.8 Samarium	
3.9 Europium	
3.10 Gadolinium	
3.11 Caesium	
3.12 Metallic fission products	
3.12.1 Spent fuel and residue solution	
3.12.2 Combined results	
<b>4. CALCULATION OF BURN-UP</b>	<b>21</b>
4.1 Burn-up determination in radiochemistry	
4.1.1 Calculation of $\sum N_E$	
4.1.2 Calculations of $\sum \Delta N$	
4.2 Mass Balance	
<b>5. REFERENCES</b>	<b>24</b>
<b>APPENDIX: NUCLEAR DATA</b>	<b>25</b>

## **Abstract**

The REBUS International Programme is dedicated to the validation of computer codes for criticality calculations that take into account the reduction in reactivity of the fuel as a result of burn-up. The use of such a code could contribute to a reduction of spent fuel storage dimensions and to an increase in the spent fuel capacity per shipment during transportation.

The REBUS validation program includes different types of measurement experiments, including reloading of the fuel in the VENUS facility of SCK•CEN to compare criticality measurements of the fresh and the spent fuel bundles, non-destructive examinations and also destructive radiochemical spent fuel characterisation.

This report describes the chemical and radiochemical analytical methodologies that were employed for the destructive characterization of a spent fuel sample of rod M11, a UO<sub>2</sub> PWR fuel. The concentrations of selected isotopes that play a major role in reactivity changes in the fuel are reported. The element inventory analyzed includes prominent actinides, a number of burn-up indicators and a selection of 19 absorbing fission products. Burn-up expressed as %FIMA in the analyzed sample was calculated using the experimental data from radiochemistry.

## **Keywords**

SPENT FUEL CHARACTERIZATION

DESTRUCTIVE RADIOCHEMICAL BURN-UP DETERMINATION

RADIOCHEMISTRY

GAMMA-SPECTROMETRY

ALPHA-SPECTROMETRY

THERMAL IONISATION MASS SPECTROMETRY

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

## 1. Introduction

The destructive spent fuel characterization is the last step in the comprehensive post-irradiation examination program of the International REBUS Program. For this purpose a sample corresponding to approximately 3 fuel pellets was cut from rod M11, a UO<sub>2</sub> fuel rod irradiated in the GKN PWR located in Neckarwestheim (Germany). The sample was cut from 1055 to 1085 mm from the top end of the original rod and then was transferred to a shielded cell in the Nuclear Chemistry department of SCK•CEN. This hot cell is dedicated to the chemical dissolution and treatment of high gamma-emitting samples for chemical and radiochemical analyses.

The isotope inventory selected for analysis consists of isotopes of prominent actinides and minor actinides, a number of burn-up indicators and a TOP 19 of absorbing fission products.

### REBUS – Isotope Inventory (RE 98/04 – Technical Proposal)

#### *ACTINIDES*

- <sup>234</sup>U, <sup>235</sup>U, <sup>236</sup>U, <sup>238</sup>U
- <sup>238</sup>Pu, <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu, <sup>242</sup>Pu
- <sup>241</sup>Am, <sup>242m</sup>Am, <sup>243</sup>Am
- <sup>242</sup>Cm, <sup>243</sup>Cm, <sup>244</sup>Cm, <sup>245</sup>Cm
- <sup>237</sup>Np

#### *BURN-UP INDICATORS*

- <sup>143</sup>Nd, <sup>144</sup>Nd, <sup>145</sup>Nd, <sup>146</sup>Nd, <sup>148</sup>Nd, <sup>150</sup>Nd
- <sup>137</sup>Cs, <sup>144</sup>Ce

#### *TOP 19 : ABSORBING FISSION PRODUCTS*

- <sup>95</sup>Mo, <sup>99</sup>Tc, <sup>101</sup>Ru, <sup>103</sup>Rh, <sup>105</sup>Pd, <sup>108</sup>Pd, <sup>109</sup>Ag
- <sup>133</sup>Cs, <sup>135</sup>Ce
- <sup>143</sup>Nd, <sup>145</sup>Nd
- <sup>147</sup>Sm, <sup>149</sup>Sm, <sup>150</sup>Sm, <sup>151</sup>Sm, <sup>152</sup>Sm
- <sup>153</sup>Eu, <sup>154</sup>Eu
- <sup>155</sup>Gd

## 2. Description of applied chemical and radiochemical methodologies

The analytical methodology used for spent fuel characterization can be divided into three major steps:

- i. Dissolution of the spent fuel sample in a shielded cell using a two step procedure. In a first step, the spent fuel is dissolved in a strong acidic medium. The remaining residue is dissolved in a second step using an alkaline fusion technique.
- ii. Sample preparation for analytical and radioanalytical determinations including dilutions, separations and preparation of suitable measurement sources
- iii. Analysis of selected isotopes in diluted and purified samples using chemical and radiochemical instrumental techniques, such as alpha- and gamma-spectrometry, thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS)

A short description of the methodologies applied in each of these steps is given.

### 2.1. Sample preparation in the shielded cell

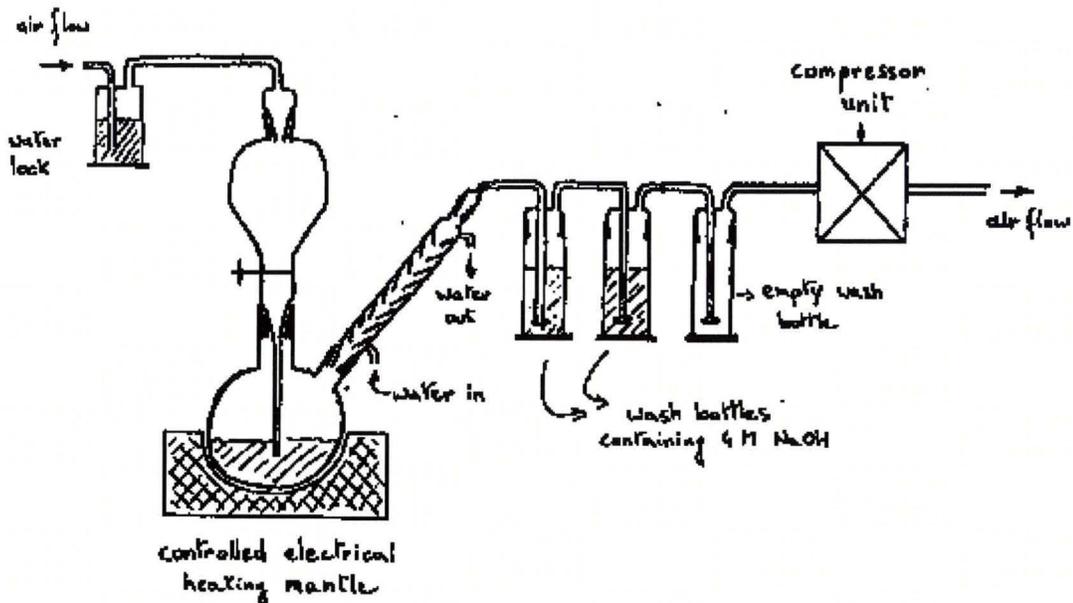
#### 2.1.1. Description of the acid dissolution of the spent fuel

The dissolution set-up used in the chemical hot cell for the dissolution of a nuclear fuel sample is shown in Figure 2-1. The sample, consisting of fuel + cladding, is introduced into the borosilicate reaction vessel. 90 ml of 8 M HNO<sub>3</sub> is placed in an introduction funnel and the system is closed at the funnel inlet using a water lock. At the outlet of the cooler, the off-gasses are led through a series of trapping bottles filled with sodium hydroxide solution using a vacuum pump. This is done to prevent release of corrosive NO<sub>x</sub> fumes into the stainless steel alpha-box of the hot cell. The 90 ml of 8 M HNO<sub>3</sub> is added through the funnel. The solution is slowly heated and brought to a gentle boil under reflux. Boiling is continued for another 5 to 6 hours. The solution is allowed to cool and subsequently is filtered using a paper filter. The cladding is washed with diluted nitric acid and removed. The cladding is dried in air and is weighed, allowing the determination of the fuel weight of the original sample.

The remaining filter may still contain some residual undissolved fuel particles. This residue + filter is treated again using 50 ml of 10 M nitric acid and 0.1 M hydrofluoric acid under reflux. The latter acid is added to ensure complete dissolution of the plutonium. This is done in the same glass set-up used for the initial dissolution step. Once again the solution is brought to a gentle boil for 5 to 6 hours. After cooling the solution is filtered off. After the second filtration,

there may still remain some residue which usually contains some undissolved metallic compounds. The filter is therefore dried in air and the mass of the residue is determined.

Figure 2-1 *Dissolution set-up for treatment of spent fuel samples*



The filtrates and wash solutions of acid dissolution steps 1 and 2 are combined and made up to 250 ml with 1 M nitric acid. The weight of the total solution  $V_0$  is determined. In the hot cell two consecutive dilutions  $V_1$  and  $V_2$  are prepared gravimetrically. One milliliter of the resulting  $V_2$  solution contains approximately 0,4 to 0,5 mg of fuel and represents an acceptable activity concentration and dose rate for treatment of analysis samples in laboratories within a controlled area.

Based on past experience and on measurements of the spent fuel and residue solution, the overall efficiency of dissolution of  $UO_2$  and MOX fuel samples during the acid dissolution step is almost quantitative for U, Pu, Np, Am, Cm, all lanthanides and Cs, i.e. > 99.9%. The efficiency of the acid dissolution for metallic fission products of Mo, Tc, Ru, Rh and Pd is less predictable. For some fuel samples up to 98% - 99% may be dissolved during the acid dissolution step, whilst for other fuels the dissolution efficiency may be noticeably lower.

A relative uncertainty of 0,32% is assigned to the different manipulations performed inside the shielded cell that are required for the preparation of a spent fuel solution suitable for analysis in the laboratory.

### 2.1.2. Description of the alkaline fusion of the residue

The filter + residue are brought into an open Ni crucible. The open crucible is placed in a cold muffle furnace and is slowly "dry-ashed" by gradually increasing the temperature to 250°C. After 30 minutes at 250°C, the crucible is heated further at 500°C for 2 hours. After cooling,  $\pm 4$  g of sodium peroxide is mixed with the residue remaining in the crucible. An additional amount of  $\pm 4$ g sodium peroxide is added to cover the residue/peroxide mixture. A Ni lid is placed on the crucible and the mixture is placed in the furnace. The temperature is slowly increased to 550°C over a time interval of 1 hour. During this time the crucible containing the molten salt is carefully shaken regularly to guarantee a good contact between residue and reagents. The molten salt is kept at 550°C for an additional 20 minutes. After cooling, the solidified melt is leached with 150 ml demineralized water in a 400 ml beaker. Once the melt is dissolved, the Ni crucible is taken out of the alkaline solution and carefully rinsed with demineralized water. This rinsing water is added to the solution. The alkaline solution is then acidified with 30 ml *aqua regia*. The resulting acidic solution is filtered and the beaker is rinsed with demineralized water. Both filtrate and washing solution are collected in a 250 ml flask. Demineralized water is added to obtain a final volume of  $\pm 250$  ml. A small aliquot of the residue solution is transferred to a laboratory in a controlled area for analysis.

The dissolution of the residue is performed inside a hot cell for chemical treatments located at the RMO department at SCK•CEN. The dissolution experiments on the REBUS filters were preceded and followed by treatments of a blank filter thereby allowing determination of possible cross-contaminations. These were found to be negligible and no corrections had to be made to the results obtained by ICP-MS and gamma-spectrometry.

Table 2-1 *Dissolution efficiency of metallics during fusion procedure*

<b>Element</b>	<b>Dissolution efficiency %</b>
<b>Mo</b>	95 $\pm$ 5
<b>Tc</b>	70 $\pm$ 15
<b>Ru</b>	70 $\pm$ 15
<b>Rh</b>	80 $\pm$ 20
<b>Ag</b>	60 $\pm$ 15
<b>Pd</b>	70 $\pm$ 15

The dissolution efficiencies for the different elements to be analyzed are determined partly using 'cold experiments' and partly derived from measurements performed in the framework of the Ariane project. For Rh no tests could be performed and the dissolution efficiency is taken as

80%. The dissolution efficiencies for the alkaline fusion technique and related uncertainties at a 95% confidence level are given in Table 2-1.

### 2.1.3. Dissolution results for M11

The shielded cell at NCS contains 2 weighing balances, i.e. one analytical balance and one top balance. These balances are used for determining the weights of the amount of fuel in the sample, the  $V_0$  spent fuel solution, the residue, all dilutions, etcetera.

Table 2-2 *Dissolution data of the M11 sample*

<b>Weight dissolved fuel</b>	15,5782 g
<b>Weight solution <math>V_0</math> (250 ml)</b>	294,3 g
<b>Dilution <math>V_1</math> (100 ml)</b>	6,7291 g $V_0$ → 101,7331 g $V_1$
<b>Dilution <math>V_2</math> (50 ml)</b>	5,7903 g $V_1$ → 51,5643 g $V_2$
<b>Weight residue (% initial fuel)</b>	0,014 g
<b>Weight residue solution</b>	260,21 g

## 2.2 Chemical pretreatment and separations

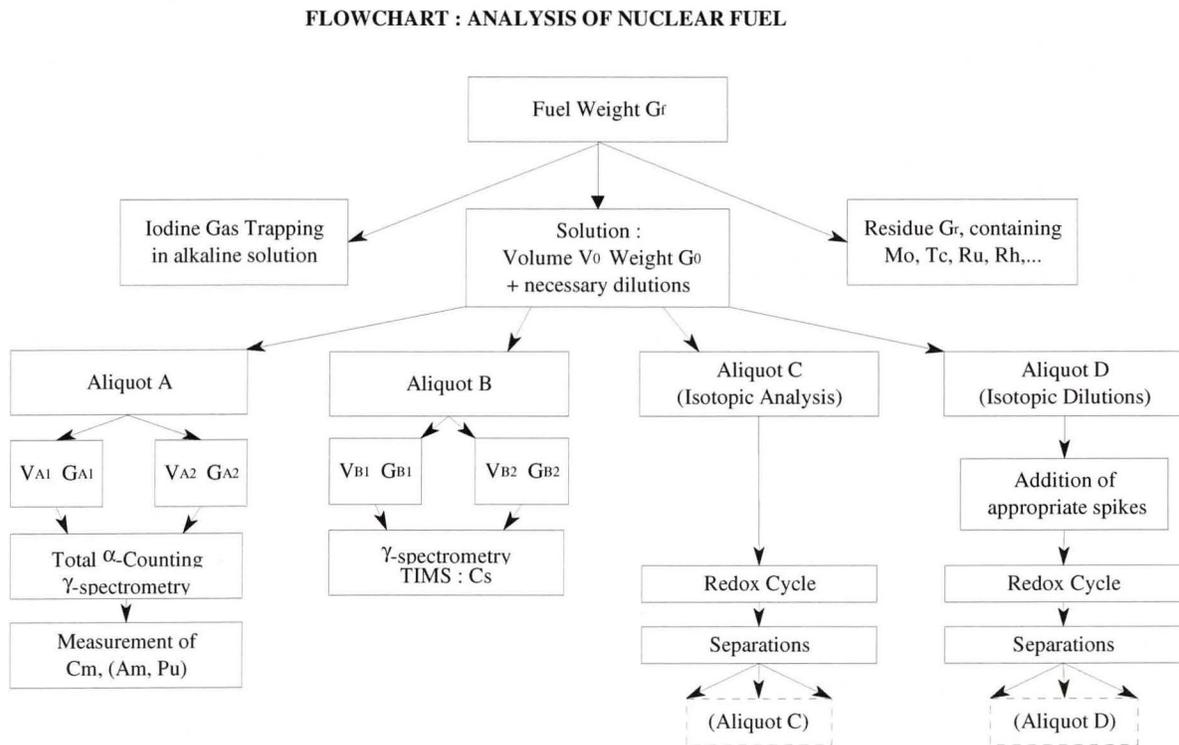
An aliquot of the  $V_2$  solution is transferred from the hot cell to the laboratory for sample pretreatment and/or separations. Suitable measurement sources and/or solutions for alpha- and gamma-spectrometry, ICP-MS and TIMS were prepared. A schematic overview of the complete sample preparation is given in Figure 2-2.

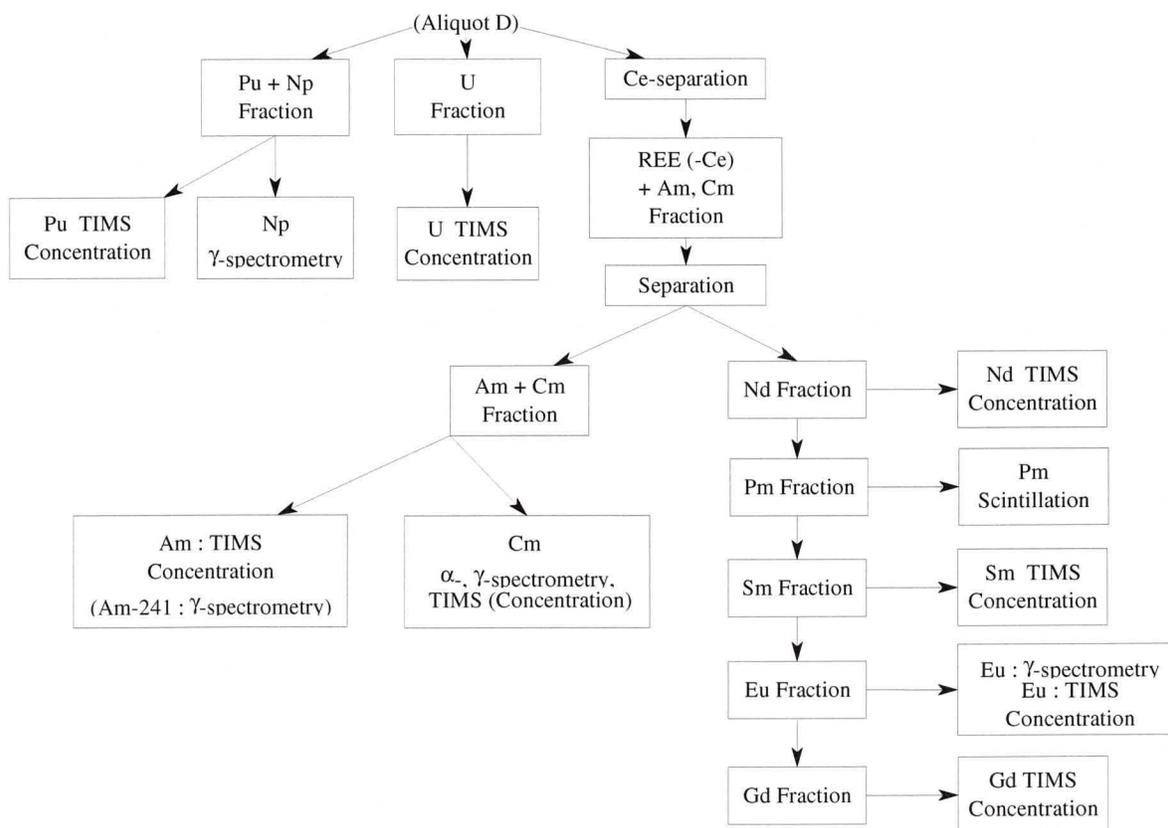
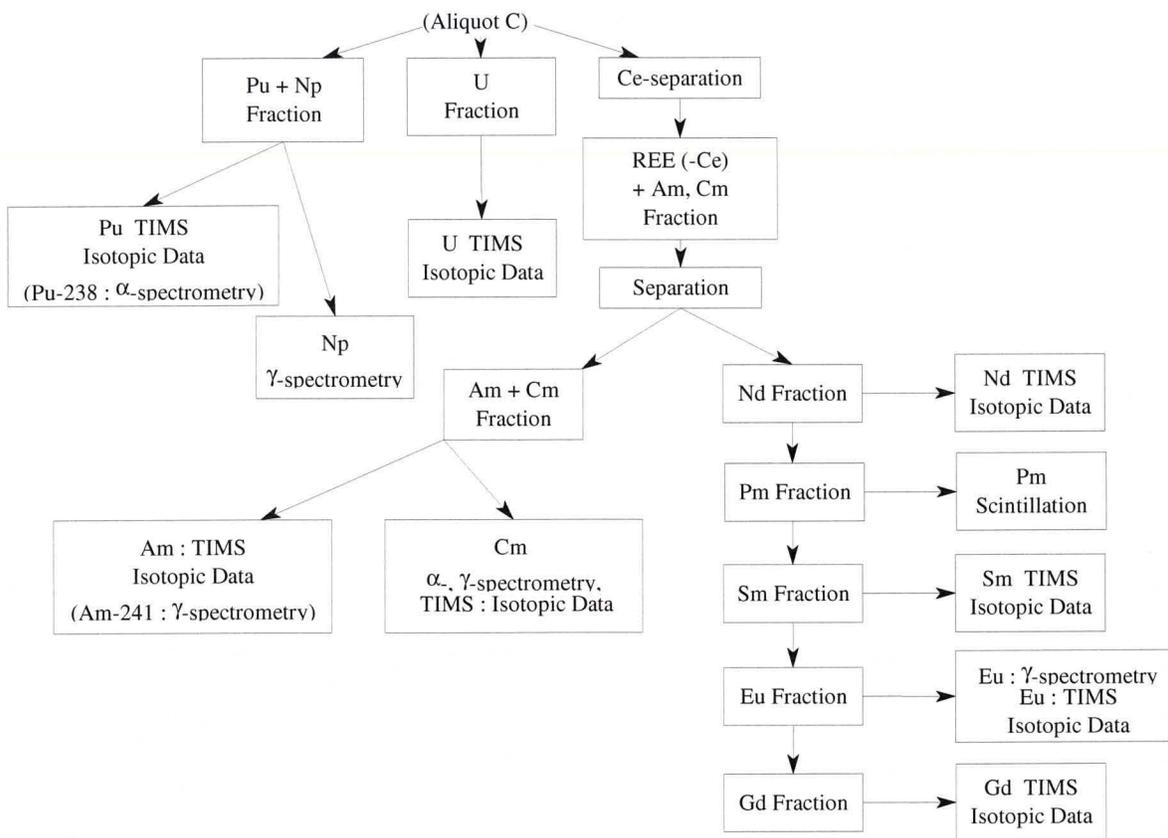
When performing Isotopic Analysis (IA) and Isotopic Dilution (ID) of specific elements by means of TIMS, in most cases separations have to be carried out to eliminate possible isobaric interferences from other nuclides and their derivatives. This is done for the elements uranium, plutonium, americium, curium, neodymium, samarium, europium, and gadolinium.

Isotopic Analysis (aliquot C) will result in the determination of the isotopic composition of an element. Isotopic Dilution (aliquot D) will result in the measurement of concentrations and for this purpose suitable spikes of the elements under investigation are added to aliquot D.

In a first separation step U and Pu are selectively separated from fission products and minor actinides on an anion exchange column. The efficiency of the separation of U and Pu is evaluated using alpha-spectrometry. The collected fission products and minor actinides are then taken through a second separation step where tetravalent Ce(IV), that can result in isobaric interferences on Nd due to the presence of the  $^{144}\text{Ce}$  isotope, is separated using a column with a mixture of lead oxide and anion exchange resin. Subsequently, the elements Am, Cm, Nd, Sm, Eu and Gd in the trivalent form are separated on a third column. For this purpose an extraction chromatography separation is performed on a kieselguhr column impregnated with bis(2-ethylhexyl)phosphate (HDEHP) and using a nitric acid gradient. In this step Am and Cm, which display very similar chemical properties, are not separated but are eluted together. The fraction with Am and Cm is not purified further and is used as such for the preparation of measurement sources for TIMS, gamma- and alpha-spectrometry. The separation efficiency of the trivalent elements is monitored using gamma-total measurements on a well-type NaI(Tl)-detector and gamma-spectrometry on a HPGe-detector.

Figure 2-2 Schematic overview of the sample preparation for measurement





## 2.3 Chemical and radiochemical measurement techniques

A brief description of the analytical and radioanalytical techniques applied is given. Emphasis is placed on the reference standards that are employed for calibration of the instruments and/or for spiking and on the uncertainties related to a given method for the measurement of specific elements, nuclides or radionuclides.

### 2.3.1. $\alpha$ -spectrometry

*Radionuclides to be analyzed by  $\alpha$ -spectrometry:*  $^{238}\text{Pu}$ ,  $^{244}\text{Cm}$ ,  $^{242}\text{Cm}$

Standard and sample sources are prepared by weighing and evaporation of a small aliquot on a tantalum disc according to an ISO17025 accredited analysis method used at NCS (IW.RA.010, internal SCK•CEN QA-document). From a suitable diluted spent fuel solution three separate discs A, B and C are prepared for measurement.

Alpha-total measurements are performed using solid scintillation ZnS-detectors that are efficiency calibrated against a standard source prepared from an  $^{241}\text{Am}$  standard solution with an uncertainty of 1,5 % at a 99% confidence level and traceable to a PTB standard (Physikalisch Technische Bundesanstalt). The activity ratio of the different alpha energy groups, i.e.  $^{239}\text{Pu}$  +  $^{240}\text{Pu}$ ,  $^{238}\text{Pu}$ + $^{241}\text{Am}$ ,  $^{243}\text{Cm}$ + $^{244}\text{Cm}$  and  $^{242}\text{Cm}$ , are determined by  $\alpha$ -spectrometry measurements using PIPS detectors. Although the alpha-energies attributed to  $^{243}\text{Cm}$  and  $^{244}\text{Cm}$  are almost identical, the measured  $^{243}\text{Cm}$ + $^{244}\text{Cm}$  peak can be assigned almost exclusively to  $^{244}\text{Cm}$  because the abundance of  $^{244}\text{Cm}$  in spent fuel is much higher than that of  $^{243}\text{Cm}$ . For the alpha-peak assigned to  $^{242}\text{Cm}$ , a small percentage of the counts can be attributed to  $^{243}\text{Cm}$  because about 10,4% of all alpha's emitted by  $^{243}\text{Cm}$  have an energy in the region of the  $^{242}\text{Cm}$  peak.

$^{242}\text{Cm}$  is relatively short lived ( $t_{1/2} = 162.94$  days) and due to the long cooling time of the M11 fuel sample one can assume that all  $^{242}\text{Cm}$  that was present at the end of irradiation has decayed by the time of analysis. However,  $^{242}\text{Cm}$  is also a decay product of  $^{242}\text{Am}$  and is therefore also constantly 'growing in' over time. Therefore small amounts of  $^{242}\text{Cm}$  can still be measured.

The overall uncertainty of the alpha-spectrometry measurement is derived from an internal validation document MT.RA.010 that was prepared for an alpha-spectrometry analysis procedure under ISO17025 accreditation for the 'determination of Pu-concentrations by alpha-spectrometry'. The derived relative uncertainty for the measurement of  $^{244}\text{Cm}$  and  $^{242}\text{Cm}$  is 2,5% and 32% respectively at a 95% confidence level.

### 2.3.2. $\gamma$ spectrometry

Radionuclides to be analyzed by  $\gamma$ spectrometry:  $^{137}\text{Cs}$ ,  $^{144}\text{Ce}$ ,  $^{154}\text{Eu}$ ,  $^{243}\text{Cm}$

For gamma-spectrometry measurements, three separate 5 ml ampoules A, B and C are prepared, i.e. one ampoule from a  $V_2$  and two ampoules from a  $V_3$  solution, each with a decreasing amount of spent fuel. The 5 ml ampoules are standard geometries and are prepared according to an ISO17025 accredited analyses method used at NCS (IW.RA.011, internal SCK•CEN QA-document). Each ampoule is measured on 2 independent HPGe-detectors CAN2 and ORT1, resulting in a total of 6 measurements. The activity concentrations of different gamma-emitting radionuclides present in the fuel, such as  $^{106}\text{Ru}$ ,  $^{125}\text{Sb}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{144}\text{Ce}$ ,  $^{154}\text{Eu}$ ,  $^{155}\text{Eu}$  and  $^{241}\text{Am}$ , can be determined.

$^{243}\text{Cm}$  can not be measured directly in the spent fuel solution, but only in the purified and more concentrated Am/Cm fractions. For the determination of  $^{243}\text{Cm}$ , calibrated 20 ml standard geometries are preferred.

Both HPGe-detectors are energy and efficiency calibrated over an energy range of 60 to 2000 keV using a gamma-ray reference solution with a mixture of 10 different radionuclides. The detector CAN2 is calibrated using a CAL3000 standard solution traceable to NIST (National Institute of Standards and Technology). The ORT1 detector is calibrated using a QCY58 standard solution traceable to NPL (National Physical Laboratory).

The overall uncertainty of the gamma-spectrometry measurement is derived using an internal validation document MT.RA.011 that was prepared for a gamma-spectrometry analysis procedure under ISO17025 accreditation for the determination of  $^{241}\text{Am}$ -concentrations in MOX solutions. The relative uncertainties at a 95% confidence level for the different gamma-emitters measured for REBUS, taking into account the uncertainty on the used standards, the efficiency calibration, the sample preparation and the actual measurement are given in Table 2-3. For the M11 samples with a long cooling time, the  $^{144}\text{Ce}$  content is low and therefore the counting statistics were less good resulting in a higher uncertainty for  $^{144}\text{Ce}$ .

Table 2-3 *Relative uncertainty at a 95% confidence level for  $\gamma$ spectrometry measurements*

Radionuclide	2s%
$^{137}\text{Cs}$	2,6%
$^{144}\text{Ce}$	10%
$^{154}\text{Eu}$	3,4%

$^{243}\text{Cm}$  is determined in a separated Am+Cm fraction that is also used for TIMS IA measurement. About one month after the separation of this fraction,  $^{243}\text{Am}$  that is also present in the solution is in equilibrium with its daughter  $^{239}\text{Np}$  which emits gamma's with the same  $\gamma$ -energies as  $^{243}\text{Cm}$ . From the  $^{243}\text{Am}$  concentration obtained from the TIMS measurement, the  $^{243}\text{Am}$  activity can be calculated and thus also the  $^{239}\text{Np}$  activity. The measured sum-activity of mutual ' $^{243}\text{Cm}+^{239}\text{Np}$ ' gamma-peaks minus the calculated  $^{239}\text{Np}$  activity results in a net  $^{243}\text{Cm}$  activity and concentration. The uncertainty of the derived  $^{243}\text{Cm}$  concentration for M11 is in the order of 20%.

### 2.3.3. Thermal Ionisation Mass Spectrometry (TIMS)

*Nuclides and radionuclides to be analyzed by TIMS:*  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ ,  $^{238}\text{U}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Am}$ ,  $^{243}\text{Am}$ ,  $^{241}\text{Am}$ ,  $^{245}\text{Cm}$ ,  $^{143}\text{Nd}$ ,  $^{144}\text{Nd}$ ,  $^{145}\text{Nd}$ ,  $^{146}\text{Nd}$ ,  $^{148}\text{Nd}$ ,  $^{150}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{149}\text{Sm}$ ,  $^{150}\text{Sm}$ ,  $^{151}\text{Sm}$ ,  $^{152}\text{Sm}$ ,  $^{153}\text{Eu}$ ,  $^{155}\text{Gd}$ ,  $^{133}\text{Cs}$ ,  $^{135}\text{Cs}$

The isotopic compositions (IA) and concentrations (ID) of different elements and/or selected isotopes are determined using TIMS according to an ISO17025 accredited procedures developed for the analysis of U and Pu using TIMS (IW.RA.921 and IW.RA.922, internal SCK•CEN QA-documents). These accredited procedures also form the basis for the measurement approaches for the lanthanides, minor actinides and cesium.

In case of the elements U, Pu, Am, Cm, Nd, Sm, Eu and Gd a separation is performed prior to the actual measurement to eliminate isobaric interferences. For ID experiments the samples are spiked with the appropriate isotopic or elemental standard solutions. The spikes and their uncertainties in their concentrations are given in Table 2-4.

Purified IA or ID fractions of the elements are selected, evaporated to dryness and are redissolved in a small volume of 1 M nitric acid to increase the element concentration in the solution. One  $\mu\text{l}$  of the resulting concentrate is evaporated on a rhenium filament that is the ionization source in TIMS.

During the TIMS measurements particular attention is paid to possible isobaric interferences resulting from specific isotopes or their oxides. For example, for Nd the efficiency of the Nd separation from other lanthanides having isotopes of similar atomic mass to the Nd isotopes is monitored. Interferences from the cerium isotope  $^{142}\text{Ce}$  on  $^{142}\text{Nd}$  and from samarium isotopes  $^{148}\text{Sm}$  or  $^{150}\text{Sm}$  on  $^{148}\text{Nd}$  and  $^{150}\text{Nd}$  are monitored by measurement of mass peak 140 for Ce and mass peaks 149 or 151 for Sm. Contamination of the separated neodymium fraction with natural neodymium is monitored using the  $^{142}\text{Nd}$  peak.  $^{142}\text{Nd}$  is not formed by fission in a spent fuel, although small amounts can be present as a result of (n, $\gamma$ ) reactions of  $^{141}\text{Pr}$ . When the isotopic

abundance of  $^{142}\text{Nd}$  in the spent fuel sample is very low, i.e. <1%, no corrections have to be made for a possible contamination by natural neodymium.

Table 2-4. *Spikes used for TIMS ID experiments*

Element	Spike
U	mixed U/Pu spike ( $^{233}\text{U}$ ) made up from a U-standard IRM-040-1 (IRMM) uncertainty on the certified concentration of 0,15% (2s)
Pu	mixed U/Pu spike ( $^{242}\text{Pu}$ ) made up from a Pu-standard IRM-049 (IRMM) uncertainty on the certified concentration of 0,15% (2s)
Am	$^{241}\text{Am}$ -spike, custom made and verified using a $^{241}\text{Am}$ standard solution (PTB) using an ISO-17025 accredited procedure (MT.RA.011) uncertainty on the concentration of 3,4% (2s)
Nd	Nd-spike custom made from 97,52% enriched $^{146}\text{Nd}$ -neodymium oxide from ORNL, standardized by TIMS by IA/ID with natural $\text{Nd}_2\text{O}_3$ (Specpure, Johnson Matthey Chemicals Limited) uncertainty on the concentration of 0,32% (2s)
Sm	Natural $\text{Sm}_2\text{O}_3$ (Specpure, Johnson Matthey Chemicals Limited) which was carefully calcinated, weighed and dissolved uncertainty on the concentration of 0,25% (2s)
Eu	natural $\text{Eu}_2\text{O}_3$ (Specpure, Johnson Matthey Chemicals Limited) which was carefully calcinated, weighed and dissolved uncertainty on the concentration of 0,25% (2s)
Gd	natural $\text{Gd}_2\text{O}_3$ (Specpure, Johnson Matthey Chemicals Limited) which was carefully calcinated, weighed and dissolved uncertainty on the concentration of 0,25% (2s)

Another example is the analysis of Pu, where in the case of an incomplete separation of U from Pu,  $^{238}\text{U}$  can interfere with the measurement of  $^{238}\text{Pu}$ . For this purpose the results of TIMS for  $^{238}\text{Pu}$  are verified by determining the ratio of  $^{238}\text{Pu}$  to  $^{239}\text{Pu}+^{240}\text{Pu}$  with an  $\alpha$ -spectrometric analysis of the purified Pu IA fractions. The latter procedure is a method under ISO17025

accreditation (IW.RA.915, internal QA-document). The uncertainty related to the  $^{238}\text{Pu}$  analysis is 3%.

At SCK•CEN the analysis procedures used for the determination of the isotopic compositions and concentrations of U and Pu in fresh MOX fuels by TIMS are methods under ISO17025 accreditation. Based on the results of the validation dossier MT.RA.BN/901 for this accredited analysis (internal SCK•CEN QA-document), and based on extensive TIMS experience, the uncertainty on a measurement of the isotopic composition of an element by TIMS in the absence of isobaric interferences is given in Table 2-5.

Table 2-5. *Relative uncertainties for isotopic compositions determined by TIMS*

<b>Abundance level of the isotope</b>	<b>Relative uncertainty (2s)</b>
> 10%	$\pm 0,1-0,2 \%$
3 - 10 %	$\pm 0,25\%$
0,5 - 3 %	$\pm 0,5\%$
0,05 – 0,5 %	$\pm 2\%$
0,01 – 0,05 %	$\pm 5\%$
0,003 – 0,01 %	$\pm 10\%$

For the determination of the concentration by Isotopic Dilution, the uncertainties on the characterization of the spike, on the weighing of both sample and spike, and on the isotopic ratio measurements have to be taken into account. This leads to an uncertainty at the 95% confidence level (2s) of 0,35% in case of U and Pu, 0,45% for Nd, 0,6% for Sm and Eu, 5% for  $^{155}\text{Gd}$  and 3,5% for Am. The uncertainty for the Gd is higher than for other elements because of its low abundance in the fuel. This is due to larger discrepancies for the Sm-concentration as derived from different Sm-isotopes. In total 3 measurements were performed on samples from 2 different separations, but the uncertainty remained the same. No explanation could be given for this phenomenon.

In case of Cs, IA measurements were performed directly on the V2 spent fuel solutions as they came out the hot cell. The mono-isotopic ID-spike of Cs that was available proved to be no longer suitable and it was decided to use only the results of the IA measurement with TIMS to determine the isotopic composition of the Cs in the fuel, i.e. the abundance of  $^{133}\text{Cs}$ ,  $^{134}\text{Cs}$ ,  $^{135}\text{Cs}$  and  $^{137}\text{Cs}$ . The concentration of  $^{137}\text{Cs}$  as derived from gamma-spectrometry measurements was used for the calculation of  $^{135}\text{Cs}$  and  $^{133}\text{Cs}$  concentrations. As a result the overall uncertainty of

both Cs-isotopes is higher than usual for TIMS measurements, but is still very acceptable i.e. 2,6% (2s).

As no Cm-spike is available, the same methodology applied for the  $^{135}\text{Cs}$  and  $^{133}\text{Cs}$  concentrations is used for the determination of  $^{245}\text{Cm}$  in the Cm-fraction analysed by TIMS. For the IA analysis of the purified Am/Cm fraction the measurements of  $^{244}\text{Cm}$  and  $^{245}\text{Cm}$  are not interfered. The concentration of  $^{244}\text{Cm}$  can be derived from alpha-spectrometry measurements and is used for the calculation of the  $^{245}\text{Cm}$  concentration. The combined overall uncertainty for the determination of the latter isotope is estimated to be 6% at a 95% confidence level.

#### **2.3.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)**

*Nuclides and radionuclides analyzed by ICP-MS:  $^{237}\text{Np}$ ,  $^{109}\text{Ag}$ ,  $^{108}\text{Pd}$ ,  $^{105}\text{Pd}$ ,  $^{103}\text{Rh}$ ,  $^{101}\text{Ru}$ ,  $^{99}\text{Tc}$ ,  $^{95}\text{Mo}$*

The concentration of metallic fission products  $^{95}\text{Mo}$ ,  $^{99}\text{Tc}$ ,  $^{101}\text{Ru}$ ,  $^{103}\text{Rh}$ ,  $^{105}\text{Pd}$ ,  $^{108}\text{Pd}$ ,  $^{109}\text{Ag}$  and of the actinide  $^{237}\text{Np}$  in the spent fuel and/or residue solution can be determined by ICP-MS analyses of the appropriate dilutions without having to perform any prior separations. The ICP-MS instrument is calibrated using external matrix matched standards. Special attention is paid to possible isobaric interferences and to matrix effects on the measurements.

The overall uncertainty that is attributable to ICP-MS measurements of complex matrices, such as spent fuel solutions, is estimated to be 10% at a 95% confidence level for the metallic isotopes and 20% for  $^{237}\text{Np}$ . For the residue solution with a high sodium salt content larger dilutions are needed and the uncertainty is estimated to be 20%.

### 3. Summary of analysis results

The analytical results are reported as mg of nuclide or radionuclide per g of fuel and mg of nuclide or radionuclide per g of  $^{238}\text{U}$  at reference date or analysis date. The overall uncertainty budgets for both reported units are comparable. However for the values reported as mg/g of  $^{238}\text{U}$ , uncertainties resulting from manipulations or spills during dissolution or dilutions performed in the hot cell are eliminated. On the other hand, for values reported as mg/g of  $^{238}\text{U}$ , the uncertainty in the  $^{238}\text{U}$ -concentration in the V2 solution has to be taken into account. For subsequent calculations, it is preferable to use the value expressed as 'mg/g  $^{238}\text{U}$ ' rather than the 'mg/g spent fuel' version. The results are reported at the date of analysis, as well as at the date of criticality inside VENUS (REBUS core 54/00, date 8 June 2004). Overall uncertainty budgets are reported as both absolute and relative uncertainties at a 95% confidence level (2s). Such relative uncertainty is always higher or equal at the date of criticality than the one reported at the date of analysis.

For the (radio)nuclides that are still formed in significant amounts due to decay of relatively shorter lived radionuclides present in the spent fuel solution, the date of separation is also reported. This is the case, for instance, for the  $^{241}\text{Am}$  daughter of  $^{241}\text{Pu}$ , the  $^{147}\text{Sm}$  daughter of  $^{147}\text{Pm}$ , the  $^{155}\text{Gd}$  daughter of  $^{155}\text{Eu}$  and  $^{144}\text{Ce}$  that decays to  $^{144}\text{Nd}$  through  $^{144}\text{Pr}$ .

#### 3.1. Uranium

	Ref. Date	mg/g fuel at Ref. date			mg/g $^{238}\text{U}$ at Ref. Date			mg/g $^{238}\text{U}$ at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
$^{234}\text{U}$	2004-12-09	0,129	0,006	5,0%	0,162	0,008	5,0%	0,161	5,0%
$^{235}\text{U}$	2004-12-09	4,43	0,03	0,69%	5,56	0,04	0,73%	5,56	0,73%
$^{236}\text{U}$	2004-12-09	4,63	0,03	0,69%	5,81	0,04	0,73%	5,81	0,73%
$^{238}\text{U}$	2004-12-09	797	4	0,51%	1000	6	0,57%	1000	0,57%
<b>Total</b>	<b>2004-12-09</b>	<b>806</b>	<b>4</b>	<b>0,47%</b>	<b>1012</b>	<b>5</b>	<b>0,53%</b>		

#### 3.2. Neptunium

	Ref. Date	mg/g fuel at Ref. date			mg/g $^{238}\text{U}$ at Ref. Date			mg/g $^{238}\text{U}$ at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
$^{237}\text{Np}$	2005-04-29	0,52	0,10	20%	0,66	0,13	20%	0,66	20%

### 3.3. Plutonium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>238</sup> Pu	2004-11-02	<b>0,371</b>	0,011	3,0%	<b>0,465</b>	0,014	3,1%	<b>0,467</b>	3,1%
<sup>239</sup> Pu	2004-11-02	<b>4,988</b>	0,03	0,5%	<b>6,26</b>	0,04	0,59%	<b>6,26</b>	0,59%
<sup>240</sup> Pu	2004-11-02	<b>2,777</b>	0,014	0,5%	<b>3,49</b>	0,02	0,59%	<b>3,48</b>	0,59%
<sup>241</sup> Pu	2004-11-02	<b>1,121</b>	0,006	0,5%	<b>1,407</b>	0,008	0,59%	<b>1,434</b>	0,59%
<sup>242</sup> Pu	2004-11-02	<b>1,013</b>	0,005	0,5%	<b>1,271</b>	0,008	0,61%	<b>1,271</b>	0,61%
<b>Total</b>	2004-11-02	<b>10,27</b>	0,05	0,5%	<b>12,89</b>	0,07	0,55%	<b>12,89</b>	

### 3.4. Americium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>241</sup> Am	2005-03-07	<b>0,457</b>	0.016	3.5%	<b>0,57</b>	0.02	3.5%	<b>0,55</b>	3.7%
<sup>242</sup> Am	2005-03-07	<b>0,00135</b>	0.00014	11%	<b>0,00170</b>	0.00018	11%	<b>0,00170</b>	11%
<sup>243</sup> Am	2005-03-07	<b>0,215</b>	0.007	3.5%	<b>0,270</b>	0.009	3.5%	<b>0,270</b>	3.5%

*Date of separation Am/Pu: 2004-10-21*

### 3.5. Curium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>242</sup> Cm	2004-09-29	<b>3,7E-06</b>	1,2E-06	32%	<b>4,7E-06</b>	1,5E-06	32%	<b>4,2E-06</b>	36%
<sup>243</sup> Cm	2005-03-07	<b>6,7E-04</b>	0.00014	20%	<b>8,4E-04</b>	0.00017	20%	<b>8,5E-04</b>	20%
<sup>244</sup> Cm	2004-09-29	<b>0,115</b>	0,003	2,5%	<b>0,144</b>	0,004	2,5%	<b>0,146</b>	2,5%
<sup>245</sup> Cm	2005-06-01	<b>0,0115</b>	0,0006	5,6%	<b>0,0144</b>	0,0008	5,6%	<b>0,0144</b>	5,6%

### 3.6. Cerium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>144</sup> Ce	2004-09-28	<b>4,2E-04</b>	0,4E-04	10%	<b>5,3E-04</b>	0,5E-04	10%	<b>6,9E-04</b>	10%

### 3.7. Neodymium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>142</sup> Nd	2005-02-28	<b>0,0451</b>	0,0003	0,74%	<b>0,0566</b>	0,0004	0,78%	<b>0,0566</b>	0,78%
<sup>143</sup> Nd	2005-02-28	<b>0,926</b>	0,005	0,59%	<b>1,162</b>	0,007	0,64%	<b>1,162</b>	0,64%
<sup>144</sup> Nd	2005-02-28	<b>1,951</b>	0,011	0,59%	<b>2,449</b>	0,016	0,64%	<b>2,449</b>	0,64%
<sup>145</sup> Nd	2005-02-28	<b>0,861</b>	0,005	0,59%	<b>1,081</b>	0,007	0,64%	<b>1,081</b>	0,64%
<sup>146</sup> Nd	2005-02-28	<b>1,016</b>	0,006	0,59%	<b>1,276</b>	0,008	0,64%	<b>1,276</b>	0,64%
<sup>148</sup> Nd	2005-02-28	<b>0,515</b>	0,003	0,61%	<b>0,647</b>	0,004	0,65%	<b>0,647</b>	0,65%
<sup>150</sup> Nd	2005-02-28	<b>0,2551</b>	0,0015	0,61%	<b>0,320</b>	0,002	0,65%	<b>0,320</b>	0,65%
<b>Total</b>	<b>2005-02-28</b>	<b>5,57</b>	0,03	0,55%	<b>6,99</b>	0,04	0,60%		

*Date of separation Nd/Ce: 2004-10-21*

### 3.8. Samarium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>147</sup> Sm	2005-02-10	<b>0,2578</b>	0,0018	0,71%	<b>0,324</b>	0,002	0,75%	<b>0,324</b>	0,75%
<sup>148</sup> Sm	2005-02-10	<b>0,2492</b>	0,0018	0,71%	<b>0,313</b>	0,002	0,75%	<b>0,313</b>	0,75%
<sup>149</sup> Sm	2005-02-10	<b>0,00206</b>	0,00004	2,11%	<b>0,00259</b>	0,00006	2,13%	<b>0,00259</b>	2,13%
<sup>150</sup> Sm	2005-02-10	<b>0,413</b>	0,003	0,71%	<b>0,518</b>	0,004	0,75%	<b>0,518</b>	0,75%
<sup>151</sup> Sm	2005-02-10	<b>0,01236</b>	0,00010	0,84%	<b>0,01551</b>	0,00014	0,88%	<b>0,01559</b>	0,88%
<sup>152</sup> Sm	2005-02-10	<b>0,1273</b>	0,0009	0,71%	<b>0,1598</b>	0,0012	0,75%	<b>0,1598</b>	0,75%
<sup>154</sup> Sm	2005-02-10	<b>0,0579</b>	0,0004	0,72%	<b>0,0727</b>	0,0006	0,76%	<b>0,0727</b>	0,76%
<b>Total</b>	<b>2005-02-10</b>	<b>1,119</b>	0,008	0,68%	<b>1,405</b>	0,010	0,72%		

*Date of separation Sm/Pm: 2004-10-28*

### 3.9. Europium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>153</sup> Eu	2005-02-10	<b>0,1661</b>	0,0014	0,86%	<b>0,2086</b>	0,0019	0,90%	<b>0,2086</b>	0,90%
<sup>154</sup> Eu	2004-09-28	<b>0,0199</b>	0,0007	3,4%	<b>0,0250</b>	0,0009	3,4%	<b>0,0256</b>	3,4%
<sup>155</sup> Eu	2004-09-28	<b>0,0053</b>	0,0003	6,0%	<b>0,0067</b>	0,0004	6,0%	<b>0,0070</b>	6,0%

### 3.10. Gadolinium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>155</sup> Gd	2005-02-10	0,0088	0,0004	5,0%	0,0110	0,0006	5,0%	0,0107	5,1%

*Date of separation Gd/Eu: 2004-10-28*

### 3.11. Caesium

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>133</sup> Cs	2004-11-15	1,39	0,04	2,6%	1,74	0,05	2,6%	1,74	2,6%
<sup>135</sup> Cs	2004-11-15	0,498	0,013	2,6%	0,625	0,016	2,6%	0,625	2,6%
<sup>137</sup> Cs	2004-09-28	1,45	0,04	2,6%	1,82	0,05	2,6%	1,83	2,6%

### 3.12. Metallic fission products

#### 3.12.1. Spent fuel and residue solution

	Ref. Date	mg in spent fuel solution			mg in residue solution		
		result	2s	2s%	result	2s	2s%
<sup>95</sup> Mo	2005-04-29	13,9	1,4	10%	0,12	0,02	20%
<sup>99</sup> Tc	2005-04-29	16,8	1,7	10%	0,045	0,009	20%
<sup>101</sup> Ru	2005-04-29	12,9	1,3	10%	0,16	0,03	20%
<sup>103</sup> Rh	2005-04-29	7,9	0,8	10%	< 0,01		
<sup>105</sup> Pd	2005-04-29	5,9	0,6	10%	0,15	0,03	20%
<sup>108</sup> Pd	2005-04-29	2,3	0,2	10%	0,049	0,010	20%
<sup>109</sup> Ag	2005-04-29	1,43	0,14	10%	< 0,01		

#### 3.12.2. Combined results

	Ref. Date	mg/g fuel at Ref. date			mg/g <sup>238</sup> U at Ref. Date			mg/g <sup>238</sup> U at 2004-06-08	
		result	2s	2s%	result	2s	2s%	Result	2s%
<sup>95</sup> Mo	2005-04-29	0,90	0,09	9,9%	1,13	0,11	9,9%	1,13	9,9%
<sup>99</sup> Tc	2005-04-29	1,08	0,11	10%	1,36	0,14	10%	1,36	10%
<sup>101</sup> Ru	2005-04-29	0,84	0,08	9,9%	1,05	0,10	9,9%	1,05	9,9%
<sup>103</sup> Rh	2005-04-29	0,51	0,05	10%	0,63	0,06	10%	0,63	10%
<sup>105</sup> Pd	2005-04-29	0,39	0,04	9,8%	0,49	0,05	9,8%	0,49	9,8%
<sup>108</sup> Pd	2005-04-29	0,153	0,015	9,8%	0,192	0,019	9,8%	0,192	9,8%
<sup>109</sup> Ag	2005-04-29	0,092	0,009	10%	0,116	0,012	10%	0,116	10%

## 4. Calculation of Burnup

### 4.1. Burn-up determination in radiochemistry

In radiochemistry burn-up is expressed as the number of fissions relative to the number of heavy metal atoms initially present in the fuel (FIMA = Fissions per Initial Metal Atom) and is calculated according to following the equation:

$$F = \frac{\sum \Delta N}{\sum N_0} \times 100 = \frac{\sum \Delta N}{\sum N_E + \sum \Delta N} \times 100 \quad (\text{eq 1-1})$$

F = atom percent burn-up FIMA

$\sum \Delta N$  = number of heavy atoms fissioned

$\sum N_0$  = number of heavy atoms initially present

$\sum N_E$  = number of heavy atoms at the end of irradiation

In irradiated fuel  $\sum N_E$  can be determined using a combination of mass-spectrometry and radiochemical measurement techniques.  $\sum \Delta N$  can be derived from an appropriate fission product monitor for which the concentration in the fuel is proportional to the number of heavy atom fissioned. Commonly used burn-up monitors are neodymium isotopes, cesium-137 and cerium-144<sup>(1),(2),(3)</sup>. In the literature neodymium-148 is recommended as an ideal burn-up monitor<sup>(4)</sup>.

#### 4.1.1. Calculation of $\sum N_E$

The concentrations of the different U, Pu, Am and Cm isotopes obtained from analysis are converted from the time of measurement ( $T_M$ ) to the end of irradiation ( $T_{EOL}$ ). For the uranium isotopes with half lives  $> 10^5$  years no corrections have to be made for decay. Pu, Am and Cm-isotopes are corrected for decay and/or for in buildup due to the decay of higher actinides. The radionuclides for which the concentration is influenced due to the decay of a parent radionuclide are  $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ , and to a lesser extent,  $^{240}\text{Pu}$ .

Combining the number of atoms of uranium, plutonium and minor actinides at EOL gives the total number of heavy atoms present in the sample at EOL or  $\sum N_E$ .

#### 4.1.2. Calculation of $\Sigma\Delta N$

The total number of heavy atoms that were fissioned,  $\Sigma\Delta N$ , is directly proportional to the number of atoms of a fission product monitor according to the relationship

$$\Sigma\Delta N = \frac{N_n}{MWFY_n} \quad (eq\ 4-1)$$

$N_n$  = total atom production of isotope n

$MWFY_n$  = mean weighted fission yield for fission product n

The total atom production  $N_n$  for stable fission products such as the Nd-isotopes can be derived easily from the chemical analyses without further corrections. The exception is the isotope  $^{144}\text{Nd}$ , which is the daughter product of  $^{144}\text{Ce}$  ( $t_{1/2} = 284.9$  days).

When using radioactive fission products as burn-up monitors such as  $^{137}\text{Cs}$  and  $^{144}\text{Ce}$ , an additional correction factor for in-pile and out-pile decay has to be determined taking into account the irradiation history of the fuel. These correction factors are calculated using the equations

$$F_{in-pile} = \frac{\lambda_n \times \Delta T_1}{1 - e^{-\lambda_E \times \Delta T_1}} \quad (eq\ 4-3)$$

$$F_{out-pile} = \frac{1}{e^{-\lambda_E \times \Delta T_2}} \quad (eq\ 4-4)$$

$T_1$  = duration of irradiation cycle

$T_2$  = time elapsed between end of cycle and EOL

Multiplying the number of atoms at EOL by these factors gives the actual number of fissions resulting in the formation of  $^{137}\text{Cs}$  and  $^{144}\text{Ce}$ .

Two of the neodymium isotopes that are formed as a result of fission show a relatively high cross-section for (n, $\gamma$ ) capture, namely  $^{143}\text{Nd}$  (325 barns) and  $^{145}\text{Nd}$  (42 barns) resulting in the formation of  $^{144}\text{Nd}$  and  $^{146}\text{Nd}$  respectively. To eliminate the impact on the burn-up calculations from the buildup and burnout due to thermal irradiation, these isotopes are summed for the actual burn-up calculations, i.e.  $^{143}\text{Nd} + ^{144}\text{Nd}$  and  $^{145}\text{Nd} + ^{146}\text{Nd}$ .

To calculate an accurate average weighted fission yield  $MWFY_n$  for each burn-up monitor the mean fissile composition at any given moment of the irradiation must be known. As this is virtually impossible a more practical approach is taken using the information concerning the

fissile composition at the beginning of irradiation obtained from the fuel producer and at the end of irradiation as derived from analysis.

A number of approaches can be used to the calculation of  $MWFY_n$ . One approach, which is applicable to commercial MOX as well as  $UO_2$  fuels, is to determine the fissile composition using the ratio of two isotopes of the same fission element with appreciable difference in fission yield for the different fissile species. This approach was adopted using the ratio of the  $^{148}Nd$  and  $^{150}Nd$  and assuming that all fissions are from  $^{235}U$ ,  $^{239}Pu$  and  $^{241}Pu$ .

The results of the burn-up calculation as %FIMA, including the calculated in-pile decay correction, mean weighted fission yield and number of fissions are given in Tables 4-1. The nuclear database ENDF-VI.8 was used for calculation of  $MWFY_n$ . An averaged value for %FIMA of 5,64% was obtained with a very good agreement between different fission product monitors of Nd and Cs.

**Table 4-7     % FIMA M11**

<b>Fission monitor</b>	<b>In-pile decay</b>	<b>MWFY (%)</b>	<b>Fission number</b>	<b>% FIMA <math>\pm 2s</math></b>
<b>Cs-137</b>	1,05761	6,391	1,944E+21	5,70 $\pm$ 0,23
<b>Ce-144</b>	5,71309	4,705	1,889E+21	5,54 $\pm$ 0,55
<b>Nd-143+Nd-144</b>		9,943	1,890E+21	5,55 $\pm$ 0,11
<b>Nd-145+Nd-146</b>		6,274	1,929E+21	5,66 $\pm$ 0,11
<b>Nd-148</b>		1,6828	1,942E+21	5,69 $\pm$ 0,11
<b>Nd-150</b>		0,8220	1,942E+21	5,69 $\pm$ 0,11
		<b>% FIMA average</b>	1,923E+21	<b>5,64</b>
		2s_average		0,013
		%2s_average		0,23%

An overall uncertainty budget was also derived for the burn-up calculations. The uncertainty of the obtained %FIMA for M11 at a 95% confidence level for Nd-isotopes, for  $^{137}Cs$  and for  $^{144}Ce$  is found to be 2%, 4% and 10% respectively.

#### **4.2. Mass balance**

As a measure of the overall quality of the burnup determination the mass balance MB is calculated. This is done by dividing the determined sum of heavy atoms and averaged number of

fissions (EOL = 1997-08-16) by the number of heavy atoms initially present in the fuel (BOL = 1993-08-24).

$$MB = \frac{(\sum N_E + \sum \Delta N)_{EOL}}{(\sum N_0)_{BOL}}$$

The mass balance calculated for the radiochemical analyses of the UO<sub>2</sub> sample M11 is 98,4%, which is quite acceptable in view of the overall uncertainties contributed to the radiochemical burnup analyses and burnup calculations.

## 5. References

- (1) P. De Regge, R. Boden  
Determination of Neodymium Isotopes as Burnup Indicator of Highly Irradiated (U,Pu)O<sub>2</sub> LMFBR fuel  
Journal of Radioanalytical Chemistry, vol. 35, pp 173-184 (1977).
- (2) P. De Regge, D. Huys, R. Boden  
Radiochemical Analysis Methods for Burnup Determination in Irradiated Fuel  
Paper presented at the "Vortragstagung : Kern-, Radio- und Strahlenchemie, Grundlagen und Anwendungen" Jülich 22 – 26 September 1980.
- (3) R. Boden  
Methodology, Calculation and Interpretation in the Destructive Burnup Determination of Nuclear Fuel  
NCS/72/D4301/RB/lr/1398, December 1992.
- (4) ASTM E321-96  
Standard Test Method for Atom Percent in Uranium and Plutonium Fuel (Neodymium-148 Method)

## APPENDIX: Nuclear Data

The nuclear data used for the calculations, such as half-lives, specific activities and fission yields are stated in the following Tables. The data bases used are

- Nuclides 2000: An electronic data chart of the radionuclides (version 1.2, European Communities, 2000)
- Janis 2.1: A Java-based Nuclear Data Display Program (NEA, June 2004)

	<b>half-life</b>		<b>SA Bq/g</b>
U-234	2,4587E+05	years	2,300E+08
U-235	7,0428E+08	years	7,996E+04
U-236	2,3432E+07	years	2,393E+06
U-238	4,4710E+09	years	1,244E+04
Pu-238	8,776E+01	years	6,336E+11
Pu-239	2,413E+04	years	2,295E+09
Pu-240	6,5675E+03	years	8,396E+09
Pu-241	1,441E+01	years	3,811E+12
Pu-242	3,7376E+05	years	1,464E+08
Am-241	4,3300E+02	years	1,268E+11
Am-242m	1,411E+02	years	3,876E+11
Am-243	7,3699E+03	years	7,389E+09
Cm-242	1,6294E+02	days	1,225E+14
Cm-243	3,0021E+01	years	1,814E+12
Cm-244	1,8112E+01	years	2,994E+12
Cs-134	2,0634E+00	years	4,791E+13
Cs-137	3,0021E+01	years	3,221E+12
Ce-144	2,849E+02	days	1,178E+14
Eu-154	8,6059E+00	years	9,993E+12
Eu-155	4,96E+00	years	1,723E+13

<b>fission product monitor</b>	<b>Fission Yields</b>		
	<b>i=U-235</b>	<b>i=Pu-239</b>	<b>i=Pu-241</b>
	<b>FYi (%)</b>	<b>FYi (%)</b>	<b>FYi (%)</b>
Cs-137	6,1883	6,6074	6,6507
Ce-144	5,4996	3,7394	4,2274
Nd-143	5,9558	4,4132	4,5780
Nd-144	5,4996	3,7397	4,2274
Nd-145	3,9334	2,9863	3,2629
Nd-146	2,9969	2,4581	2,7664
Nd-148	1,6735	1,6421	1,9321
Nd-150	0,65320	0,9663	1,2094