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## DELIVERABLE (D-N°:4.1)

# STATUS OF MODELLING OF MIGRATION/RETENTION PROCESSES OF FISSION PRODUCTS IN THE SPENT FUEL STRUCTURE

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**ABSTRACT**

This report gives an overview of the chemical composition of the fission products in irradiated $UO_2$ fuels. Special attention has been made in their chemical state and the chemical compounds formed in reactor operation. Localization of fission products in different parts of the fuel such as gap, rim, grain boundary and grain is also discussed. Finally, migration and retention processes in the fuel structure can be modeled by using different approaches, empirical models which correlate fission gas release with the release of other radionuclides; thermodynamic models based on phase diagrams and thermochemistry; and mechanistic models which consider intragranular fission product transport from the bulk to the grain boundary, accompanied by both formation of precipitates and gaseous species in the intergranular bubbles.

## 1. INTRODUCTION

Performance assessment (PA) of the final spent fuel disposal requires a definition of the source term, this term is usually described as the combination of both radionuclides release instantaneously and radionuclides released congruently with the matrix dissolution process. The so called, instant release fraction (IRF) represents the fraction of the inventory of safety-relevant radionuclides that may be rapidly released from the fuel and fuel assembly at the time of canister breach [Johnson et al. 2005]. PA exercises considered the IRF to be the main source of radiological risk in geological disposal.

In spent fuel leaching experiments, the problem is how to establish a leaching time to determine IRF. Currently this time is arbitrary, for example in [Serrano-Purroy et al. 2012] IRF was calculated at 10 days while Roudil et al. [2007] established this time at 60 days. In both works, the release of selected radionuclides followed after more than one year of leaching time but a lower rate.

Probably, an important process in IRF is related to water contact to the different parts of the fuel but also which is the chemical state and location of the fission products.

In this contribution a review of migration and retention processes of fission products in the structure of the spent fuel is given. This will be focused in radionuclides different from fission gases since these have been discussed in detail in Deliverable D-

Nº: 4.2 (2013). Fission gas release modeling has been investigated for a long time and it is well understood.

## 2. CHEMICAL COMPOSITION

The chemical composition evolution in the spent fuel during irradiation is due to the following processes:

a) Uranium decrease content due to the fission processes.
b) Neutron capture processes to produce different Uranium and Plutonium isotopes; and minors actinides such as Americium, Neptunium and Curium.
c) Production of many fission products.

Actinides and Fission Products inventory during irradiation can be calculated by using neutronic calculations codes. Different institutions apply different codes, in France reported inventories are normally calculated by CESAR5; in Germany the most used code is the KORIGEN which is based on the Oak Ridge Isotope Generation and Depletion code ORIGEN. The ORIGEN-ARP code is generally used in the inventory calculations of Spanish nuclear fuels.

Data obtained by using different codes indicates no important differences between them. As an example, CESAR and ORIGEN2 results are compared in Table 1.

*Table 1. Inventory comparison (in terms of fraction) obtained by [POINSSOT, C. et al., 2001] using the CESAR code and those obtained by [KUROSAKI, K. et al., 1999] using the ORIGEN-2 code*

| Elements (%) | ORIGEN-2 | CESAR |
|---|---|---|
| Uranium | 0.881 | 0.92 |
| Plutonium | 0.011 | 0.013 |
| Zr + Nb | 0.014 | 0.016 |
| Mo + Tc | 0.013 | 0.018 |
| Pt group | 0.019 | 0.018 |
| Cd + Sn | $8 \cdot 10^{-4}$ | $6.25 \cdot 10^{-4}$ |
| Te + Se + Sb | $1.7 \cdot 10^{-3}$ | $1.91 \cdot 10^{-3}$ |

| Elements (%) | ORIGEN-2 | CESAR |
|---|---|---|
| I + Br | $8 \cdot 10^{-4}$ | $8 \cdot 10^{-4}$ |
| Cs + Rb | $8.8 \cdot 10^{-3}$ | 0.010 |
| Alkaline earth | $7.4 \cdot 10^{-3}$ | $8.8 \cdot 10^{-3}$ |
| Rare earth | 0.027 | 0.037 |

The reliability of these calculations can be compared to experimental inventory determination. Recently [Gonzalez-Robles, E., 2012], this comparison was carried out for a PWR fuel pellet with a burn-up of 52 MWd/kgU (cooling time 6 years), results are shown in Table 2.

*Table 2. Comparison between experimental and calculated element determination ($\mu g_{element}/g_{SNF}$) in a 52 MWd/kgU PWR $UO_2$ fuel.*

| **Element** | **52BU experimental** | **52BU theoretical (ORIGEN-ARP)** |
|---|---|---|
| Rb | 640 ± 130 | 500 |
| Sr | 2180 ± 440 | 1190 |
| Y | 800 ± 200 | 660 |
| Zr | 7600 ±1500 | 5100 |
| Mo | 4400 ± 900 | 4700 |
| Tc | 1200 ± 250 | 1100 |
| Ru | 4100 ± 800 | 2900 |
| Rh | 800 ± 200 | 600 |
| Cs | 4700 ± 200 | 3500 |
| Ba | 3500 ± 700 | 2300 |
| La | 2100 ± 400 | 1700 |
| Nd | 7000 ± 1400 | 5500 |
| U | 870000 ± 87000 | 823000 |
| Np | 1200 ± 300 | 700 |
| Pu | 7300 ± 1500 | 9700 |
| Am | 1100 ± 200 | 400 |
| Cm | 140 ± 30 | 60 |

The values obtained during the experimental determination of the inventory for 52BU nuclear fuel taking the uncertainties into account were in the same range as the theoretical values. The exceptions were Ba, Pu, Am and Cm, as it can be seen in Figure 1. In spite of these discrepancies, it is clear that theoretical calculations are good enough to be used when experimental determinations are not available, even for burn-ups higher than 40 MWd/kgU.

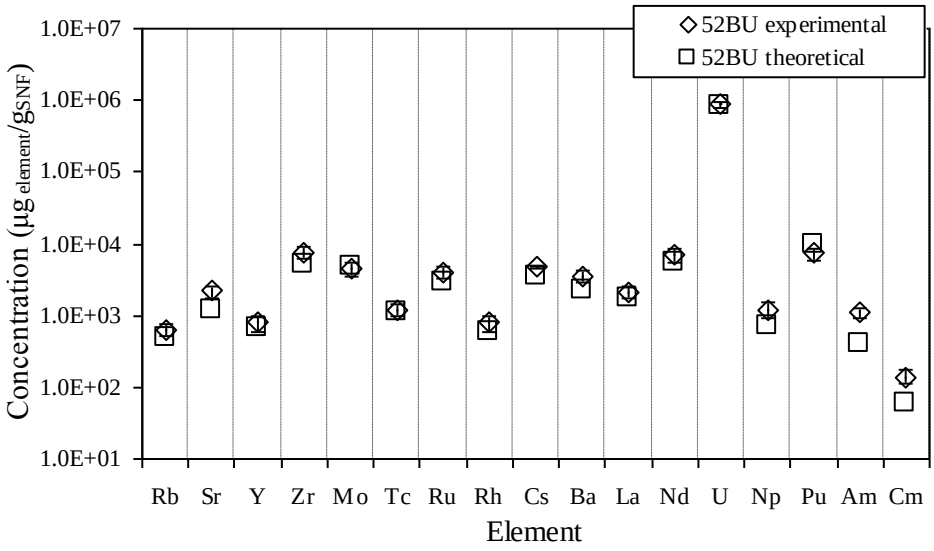


*Figure 1. Comparison of concentration ($\mu g_{element}/g_{SNF}$) from experimental and theoretical determinations, for 52BU Nuclear Fuel.*

## 3. CHEMICAL STATE

Classification of the chemical state of the fission products (FP) was carried by Kleykamp [1985], he divided them into four groups:

1) Fission gases and other volatile FP
2) Fission products forming metallic precipitates
3) Fission products forming oxide precipitates
4) Fission products dissolved as oxides in the fuel matrix

FP chemical state depends basically on the relative partial molar Gibbs free energy of oxygen. At the conditions of $UO_2$ fuel sintering, the oxygen potential is around -450 kJ/mol, this value is more or less constant as a function of the reactor temperature as

it is discussed by Matzke (1995) for fuels for medium burn-up (34.5 MWd/kgU). This value is similar to the oxygen potential of the $Mo/MoO_2$ equilibrium indicating that this fission product could play the role of oxygen buffer; in Matzke (1994) this role is studied, observing that several fuel compositions have lower oxygen potential than the couple $Mo/MoO_2$ at 750°C.

To understand the continuous transitions between metallic and oxide precipitates due to similar oxygen potentials and the fuel which changes its composition during irradiation and fission product formation is very helpful the use of Ellingham diagrams as shown in Figure 2 [Kleykamp, 1985].

As it can be seen in Figure 2, fission products with Gibbs free energies ($\Delta G^o$) lower than the oxygen potential of the different fuel composition ($UO_{2+x}$ and $U_{0.8}Pu_{0.2}O_{2\pm x}$) are present in fuel as oxide precipitates. On the contrary, if $\Delta G^o$ is higher, then fission products forms metallic precipitates.

Regarding the fission products dissolved in the fuel matrix, cesium, barium and tellurium are soluble in the fuel in small quantities [Kleykamp, 1985; Sari et al., 1979). Strontium, zirconium and niobium are, in some extent, soluble [Kleykamp, 1985] whereas large solubilities are observed for rare earth elements in $UO_2$ fuels in both $UO_2$-$ReO_2$ and $UO_2$-$Re_2O_3$ systems.

For high burn-up fuels, six different groups of elements can be considered as constituents of spent fuels [Ferry et al. 2005]. Taking into account the mass fraction of each group, the following order can be established:

1) Actinides
2) Lanthanides
3) Metallic precipitates
4) Oxides precipitates
5) Gases and volatiles
6) Metalloids

The most important elements, for the different groups mentioned above, present in the $UO_2$ fuel can be seen in Figure 3, a detail description of the chemical compounds formed during irradiation is commented below (see 4.).

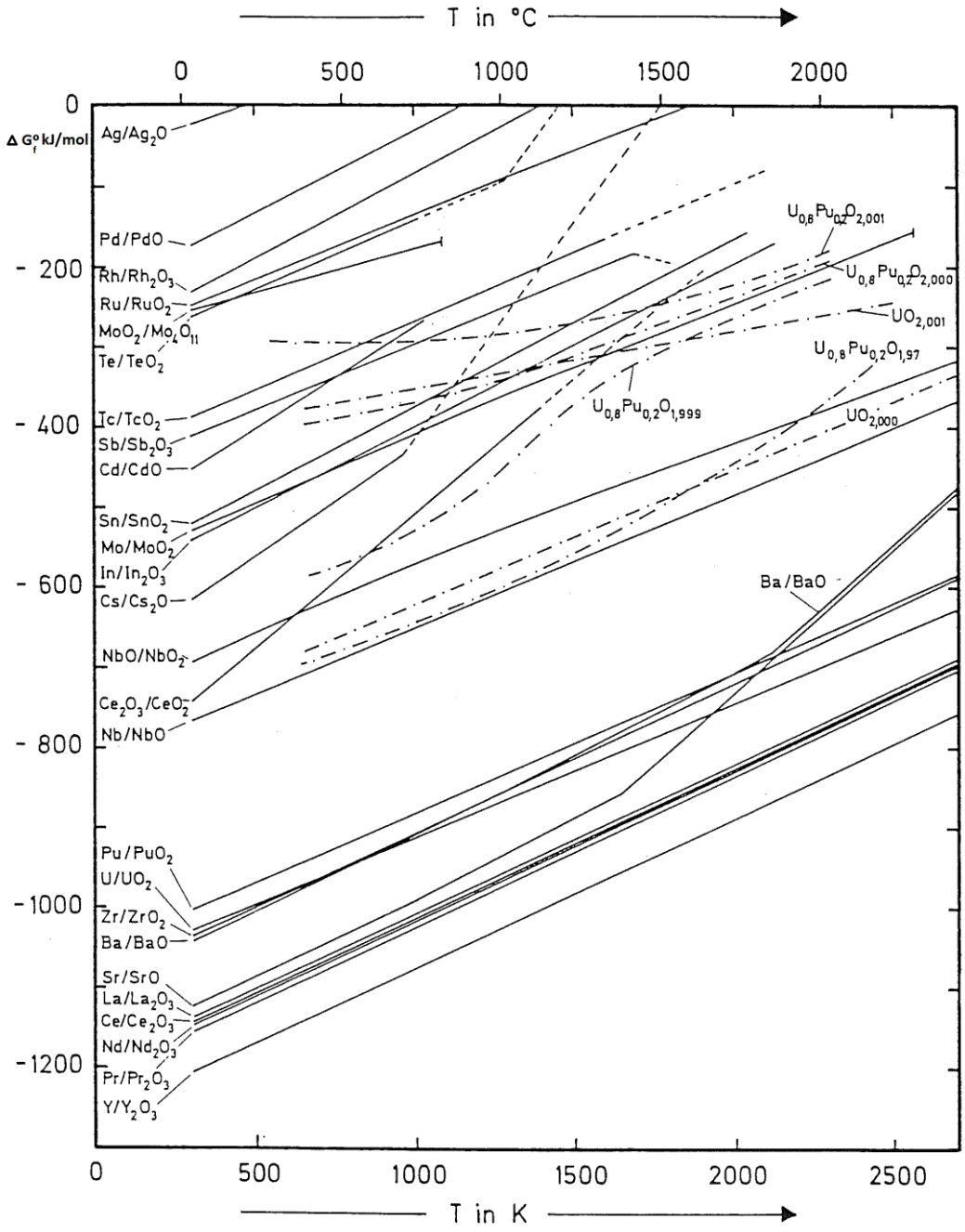


*Figure 2. Gibbs free energy ($\Delta G^o$) of fission products and $UO_{2+x}$ and $U_{0.8}Pu_{0.2}O_{2\pm x}$*

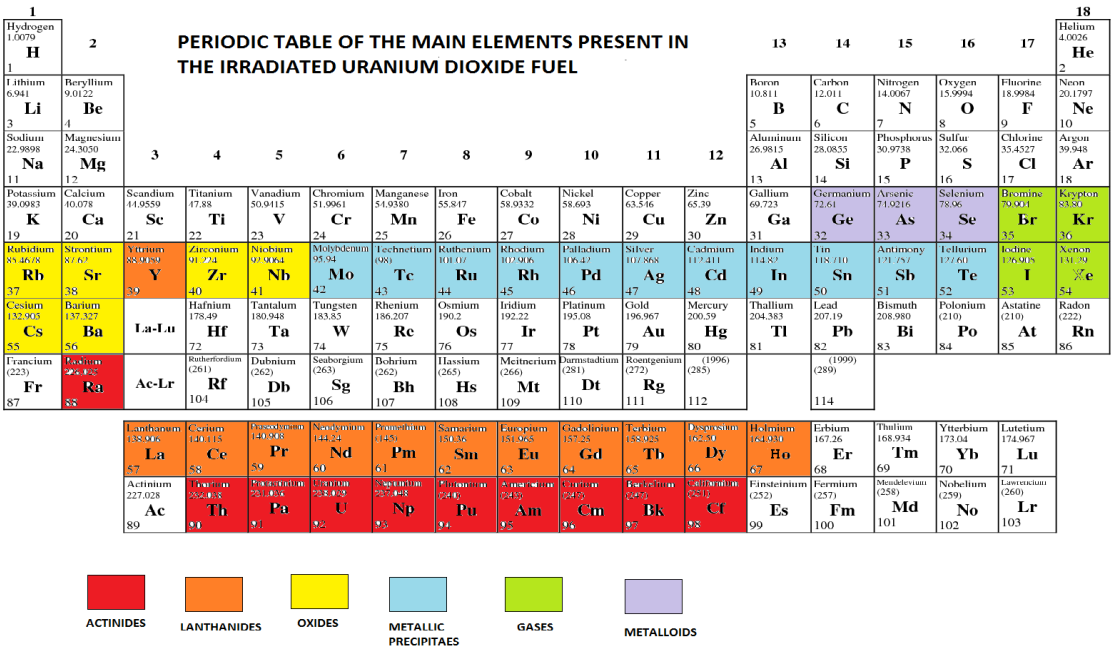


*Figure 3. Main elements present in high burn-up $UO_2$ fuels.*

The mass fraction of each group calculated for a fuel with a burn-up of 60 MWd/kgU after 50 years' cooling time is shown in Table 3 (Ferry et al. 2005).

*Table 3. Mass distribution for a $UO_2$ fuel (60 MWd/kgU) after 50 years' cooling time.*

| | mass (%) |
|---|---|
| ACTINIDES | 93.780 |
| LANTHANIDES | 1.860 |
| METALLIC PRECIPITATES | 1.679 |
| OXIDE PRECIPITATES | 1.606 |
| GAS & VOLATILES | 1.063 |
| METALLOIDS | 0.00961 |

## 4. CHEMICAL COMPOUNDS

The knowledge of the chemical compounds in the spent fuel can be important in order to understand the radionuclide release when water contacts the fuel. As discussed above, main compounds are oxides and metallic precipitates, however other types of compunds have been detected in $UO_2$ fuels.

The behavior of fission gases formed during irradiation are discussed in the frame of the First Nuclide project elsewhere [ Pekala et al. 2013].

### 4.1. Cesium

The chemistry of both cesium and rubidium in $UO_2$ fuels is very important because they react with the matrix, with cladding components and with other fission prodcuts leading to swelling and cladding corrosion at high oxigen potentials.

Based on thermodynamic equilibrium and solubility studies of cesium in $UO_2$, part of this fission product can be found as $(U,Pu,Cs,FP)O_{2-x}$ oxides, such as $Cs_2(U,Pu)_4O_{12}$ or $Cs_2(U,Pu)O_4$ [Kleykamp, 1985].

In general, the existence of $Cs_2M_4O_{12}$ in equilibrium with $MO_2$ and liquid Cs was proven, where $M=U_{0.8}Pu_{0.2}$ while the formation of $Cs_2(U,Pu)O_4$ has not been proven in irradiated $UO_2$ fuels.

Reactions with other FP give the following compounds: $Cs_2MoO_4$ [Imoto, 1986; Kurosaki et al., 1999; Dehaudt, 2000]; $Cs_3Te_2$ [Dehaudt, 2000]; $Cs_2Te$ [Imoto, 1986; Kurosaki et al., 1999] and CsI [Kurosaki et al., 1999; Dehaudt, 2000].

### 4.2. Iodine

Iodine chemical state within the fuel is not completely clear. It is reported that iodine release from $UO_2$ tends to surpass that of Xe a temperatures above 300°C, however chemical models predict a fractional release rate of iodine orders of magnitude below that of the fission gases, since models indicate that iodine exists in a less volatile chemical state, for example CsI [Kleykamp, 1985].

The formation of CsI in the spent fuel is already controversial, CsI traces were detected in parts of the pellets with temperatures around 500°C inside the cladding [Kleykamp, 1985]. By using microestructural analysis of $UO_2$ fuels with burn-ups from 44 to 48 MWd/kgU, it was not possible to detect CsI [Thomas et al., 1992]. Moreover

radial analysis of both radionuclides indicates that iodine migrates slightly faster than cesium which contraditcs an excessive CsI formation during distribution [Peehs et al. 1981].

### 4.3. Selenium and Tellerium

In spite of Selenium has been considered relevant in the safety analysis of the final spent fuel disposal, no data of selenium compounds in the fuel has been described. Taking into account thermodynamic equilibrium calculations, $Cs_2Se$ has been proposed [Cubbicciotti & Sanecki, 1978], with similar properties to CsI.

Thermodynamic equilibrium calculations indicate that Tellerium should be forming $Cs_2Te$ and $Cs_3Te_2$ [Dehaudt et al. 2000]. However, $Cs_2Te$ has never been detected [Thomas, 1992].

The oxygen potential of the $Te/TeO_2$ equilibrium is higher than that of LWR oxides, see Figure 2. Therefore, Tellurium can form metallic phases (with U, Pd, Sn), can be a constituent of multi-component fuel-fission oxides (Cs-Ba-U-Pu-O-Te) and can be dissolved in the oxide fuel $(U\text{-}Pu,Te,FP)O_{2-x}$ [Kleykamp, 1985].

Some recent results by using the Knudsen cell seem to indicate that a fraction of Tellerium is released at a temperature lower than 1500°C [Serrano-Purroy, personal communication].

### 4.4. Molybdenum, Technetium, Ruthenium, Rhodium and Palladium

These five elements are the components of the so-called “white inclusions” which corresponds to metallic precipitates, these phases are mostly hexagonal. The composition of this phase is given in Table 4.

*Table 4. Metallic precipitate composition*

| Mo | Ru | Tc | Rh | Pd | |
|---|---|---|---|---|---|
| 55-60 | 26-32 | 12 | 5-6 | 2-4 | (Kohli, 1987) |
| 35 | 30 | 10 | 5 | 20 | (Thomas et al., 1992) |

As it can be observed, Mo and Ru are the main components of the metallic phases within the fuel. Pd is one of the fission products which forms compounds with many FPs, from both the fuel and the cladding. Phases such as Pd-Ag-Cd and Pu(Pd, In, Sn, Te) [Thomas, 1992; Kleykamp, 1985].

### 4.5. Strontium and Barium

Strontium oxide is predominantly disolved in $UO_2$ and $(U,Pu)O_2$, for this reason some authors proposed Sr as indicator of the spent fuel matrix disslution [xxx]. However, some discrepancies have been observed in leaching experiments where Sr is released 3-4 times faster than uranium.

In the case of Barium, only a smaller fraction of the oxide forms solid solution with the fuel. Barium forms $BaUO_3$ and $BaZrO_3$ in fuel, $BaZrO_3$ can incorporate small quantities of several radionuclides such as Sr, Cs, U, Pu,Mo and REE, the following precipitate has been proposed $(BaCs,Sr)(U,Pu,Zr,Mo,REE)O_3$ [Kleykamp, 1985].

### 4.6. Zirconium

Zirconium oxide is completely miscible with $PuO_2$ [Carroll, 1963]. The solubility in $UO_2$ is restricted and is strongly dependent on temperature (50% at 1700$^{o}$C), as it was mentioned above Zr forms the $BaZrO_3$ perovskite structure [Kleykamp, 1985].

### 4.7. Lanthanides

La, Ce, Pr, Nd, Pm, Sm and Eu oxides are very soluble in $UO_2$. At high burn-ups, small fractions of the REE can be found in the perovskite oxide phases.

Recently, Dehaudt et al. (2000) gave the compound percentatge for several FP, these results are collected in Table 5 for a spent fuel with a burn-up of 60 MWd/kgU.

*Table 5. Compound percentage for several fission products*

| Characteristics of the $UO_2$ fuel | Burn-up= 60 MWd/kgU<br>O/M=1.997<br>$\Delta G^{o}(O_2)$= -420 kJ/mol<br>T = 750$^{o}$C |
|---|---|
| Fission products | |
| Mo | 48 % Mo, 34 % $MoO_2$ (ss), 18 % $Cs_2MoO_4$ |
| Cs | 58 % $Cs_2MoO_4$, 32 % $Cs_3Te_2$, 10 % CsI |

| | |
|---|---|
| Te | 100 % $Cs_3Te_2$ |
| Ba | 100% $BaZr0_3$ |
| Zr | 51 % $BaZrO_3$, 49 % $ZrO_2$ (ss ) |
| I | 100 % CsI |

## 5. LOCALIZATION OF FISSION PRODUCTS IN THE FUEL

The location of radionuclides in the irradiated fuel depends on mechanisms and migration kinetics during operation. Fission gas release mechanism has been studied in detail, a summary of these studies are collected in Deliverable (D-N°:4.2) (*Models for fission products release from spent nuclear fuel and their applicability to the First Nuclides project).*

Diffusion is the main mechanism responsible for the mobility of fission products. It is possible to distinguish three areas of different behavior in the reactor as a function of the temperature [Matzke, 1983]:

a) Below 1000°C, diffusion coefficient is independent on T, mobility seems to be due to fission reactions.
b) Between 1000°C and 1600°C, diffusion is mixed, it depends on both Temperature and fission reactions.
c) Above 1600°C, diffusion depends on temperature.

Diffusion studies were carried out in detail by Matzke [1983, 1987, 1990].

The mobility of FPs in the fuel by the effect of temperature depends on the chemical properties of the element such as electronegavity and ion size, for example a cation forming a solid solution with the $UO_2$ is much less mobile than and interstitial neutral atom [Prussin, 1988]. Electronegativy elements non soluble in $UO_2$ as I and Te are released at higher rates than weak electronegativity elements as Cs and Ba.

FP diffusion due to irradiation has been observed in the reactor, and it is the responsible of the radionuclide mobility for temperatures below 800°C, which is the case of the periphery of the pellet.

FP migrate by diffusion to the different parts of the fuel due to changes of morphology during operation. It is possible to differentiate the following parts:

a) Free volumes such as bubbles, cracks and the gap.
b) Restructured zone, the increase of the burn-up, due to neutron capture of U-238 to produce Pu-239, generates an external layer on the fuel with a higher burn-up, increased porosity and fuel grain subdivision, which results on the formation of the so-called rim or High Burn-Up Structure (HBS) [Hiernaudt et al., 2008], which is observed at BU's higher than 40 MWd/kgU. The increase of BU can produce the contact between the pellet and the cladding by swelling and consequently, closing the gap.
c) Grain boundaries of the non restructured matrix, gases and volatiles can be easily released from them due to temperature transitions or fuel oxidation.
d) Grains, the so-called $UO_2$ fuel matrix.

From different studies [Ferry et al., 2004; Johnson & Tait, 1997; Johnson & McGinnes, 2002] a good summary of FP's location in $UO_2$ fuel can be found in [Johnson et al., 2004], results are collected in Table 6.

*Table 6. Distribution of Radionuclides in the different parts of the fuel*

| Components | Radionuclides |
|---|---|
| Gap | Fission gases, volatiles: $^{129}I$, $^{137}Cs$, $^{135}Cs$, $^{79}Se$, $^{126}Sn$ |
| Rim porosity | Fission gases, volatiles: $^{129}I$, $^{137}Cs$, $^{135}Cs$, $^{79}Se$, $^{126}Sn$, Sr |
| Rim grains | Actinides, FP |
| Grain boundaries | Fission gases, volatiles: $^{129}I$, $^{137}Cs$, $^{135}Cs$, $^{79}Se$, $^{126}Sn$, segretated metals: $^{99}Tc$, $^{107}Pd$ |
| Grains | Actinides, remaining FPs and activation products |

In Figure 4, a summary of the the location of radionuclides toghether with chemical compounds formed in the fuel can be observed.

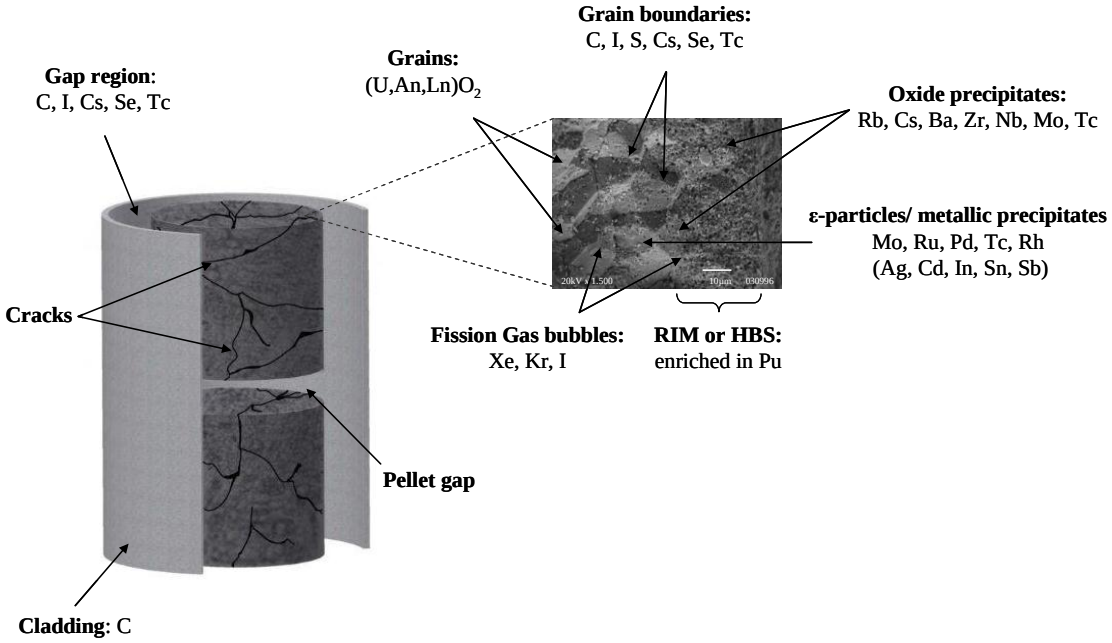


*Figure 4. Chemical composition and localization of the radionuclides in the $UO_2$ fuel*

## 6. MODELLING MIGRATION/RETENTION PROCESSES

Fission gas migration and modelling is discussed in detail in Deliverable (D-N°:4.2) (*Models for fission products release from spent nuclear fuel and their applicability to the First Nuclides project)* and references therein. A great number of fuel performance codes are available to predict the behaviour of a reactor rod during both normal and abnormal operation in the nuclear reactor. Capabilities of TRANSURANUS code were recently presented by Van Uffelen [2012], showing the combination of different aspects of the fuel in the reactor: thermal analysis; mechanical analysis; fission gas generation, transport and release; thermal and irradiation induced densification of the fuel; volume changes due to phase changes and neutronics.

### 6.1. Empirical Modeling

This model is based on establishing correlations between fission gas release (FGR) and other fission products normally the so-called volatiles such as iodine and cesium. In the case of $^{137}Cs$, a correlation with FGR equal to 1:3 has been found for FGR values higher than 1%, analyzing experimental results only a few experiments corroborate this correlation. Some authors [nagra] pointed out that this finding is consistent with

the fact that diffusion coefficient of Cs in the fuel is lower than that of FG [Poinssot et al. 2001]. No explanation is given in order to explain the similar release when FGR is around 1%.

In the case of $^{129}$I, the correlation with the FGR was suggested to be 1:1 [Gray, 1999]. This agrees with the observation of both iodine and xenon have similar diffusion coefficient in the fuel [Poinssot et al. 2001]. The major part of the iodine seems to be located in the grain boundaries, in contrast to cesium which is located in the gap. Recently, Johnson et al. [2012] have provided new data on short-term release of $^{137}$Cs and $^{129}$I for a number of fuels irradiated to burn-ups of 50–75 MWd/kgU. The results show that the fractional release of $^{137}$Cs is usually much lower than the FGR. Fractional $^{129}$I releases are somewhat larger, but only when the fuel was extracted from the cladding.

The different behaviour of $^{129}$I and $^{137}$Cs is also contradictory if CsI is considered the main compound formed in the fuel.

No other empirical correlation with FGR has been proposed for other fission products.

### 6.2. Thermodynamic Models

These models are based on the assessment of Gibbs energy parameters for the individual phases as functions of temperature, composition and pressure. For the more of 30 years, the CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) method has demonstrated to be a useful tool for solving problems in the field of materials and thermochemistry.

In Table 7, selected software is shown [Schmid-Fetzer et al., 2007] for thermodynamic and phase diagram calculations. Different capabilities are included in most software, for example several types of calculations: point calculation, line calculation, two-dimensional section, liquidus projection and Scheil solidification simulation. Phase models such as substitutional solution, gas molecules and stoichiometric compounds are also included.

*Table 7. Selected software* for thermodynamic and phase diagram calculations*

| | |
|---|---|
| FactSage | www.factsage.com |
| TDATA | www.npl.co.uk/data |
| Pandat; WinPhad | www.computherm.com |
| Thermo-Calc | www.thermocalc.com |
| Thermosuite | www.thermodata.free.fr |

*Discussed in detail in the special issue of CALPHAD 26 (2002)

Specific Database for a number of compounds of reactor materials and fission products is the so-called NUCLEA [2007] which is a thermodynamic database for in and ex-vessel applications containing 18 + 2 elements:

**O-U-Zr-Ag-In-B-C-Fe-Cr-Ni-Ba-La-Sr-Ru-Al-Ca-Mg-Si + Ar-H**

and including the 15 oxide system :

**$UO_2$-$ZrO_2$-$In_2O_3$-$B_2O_3$-FeO-$Fe_2O_3$-$Cr_2O_3$-NiO-BaO-$La_2O_3$-SrO-$Al_2O_3$-CaO-MgO-$SiO_2$**

Quality of thermodynamic data has been determined by comparison between calculation and available experimental data. In NUCLEA data, four different categories have been established:

- Estimated: No experimental data available
- Perfectible: Some domains need more experimental information
- Acceptable: The system is known and satisfactorily modeled
- High quality: The system is quite well known and modeled

## 6.3. Mechanistic Models

Advanced mechanistic codes in order to descript FGR and fuel swelling as a function of fuel fabrication and in a wide range of reactor operation are FASTGRASS [Rest and Zawadki, 1994] and VICTORIA [Heames et al., 1992]. Both are essentially

based on consideration of the equilibrium state of the bubbles, this is a simplification since defect structure of the crystal is almost completely excluded.

Recently, to avoid these problems the development of the code module for FP release (MFPR) has been carried out [Veshchunov et al., 2006].

The code considers that the most important FPs created in the fuel matrix are the following: Cs, Ce, I, Eu, Mo, Nd, Ru, Nb, Ba, Ss, Sr, Te, Zr, Xe and La and assumes that all these elements are in the matrix in atomic form. All impurity atoms formed due to fission processes migrate to grain boundaries. In this way, fission-gas atoms can be captured by intragranular gas bubbles, which can also migrate to grain boundaries. Part of the captured atoms can escape from bubbles by irradiation-induced and thermal re-solution processes.

In the MFPR model, the FP release from the matrix is divided into two steps:

- Intragranular FP transport from the bulk to the grain boundary, accompanied by both formation of precipitates and gaseous species in the intergranular bubbles.
- Accumulation of gases in the intergranular bubbles, and release to open porosity through the system of bubbles an the grain boundaries and the network of channels and tunnels

Processes modeled by the MFPR code:

a) Intragranular transport of FP elements:
- Diffusion and release of chemically active FPs
- Transport of fission gas

b) Evolution of point defects in the irradiated fuel.

c) Evolution of extended defects:
- Pore evolution
- Dislocation-loop evolution

d) Evolution of intragranular gas bubbles
- Intragranular bubbles under steady irradiation conditions at low temperatures $\leq 1500^{o}C$ (irradiation effects)
- Intragranular bubbles under steady irradiation conditions at high temperatures $\geq 1500^{o}C$ (thermal effects)
- Intragranular bubbles under transient conditions

e) Intergranular FP transport, release and swelling models
- Model of FP release by bubble interlinkage
- Model for Xe grain-face diffusion transport
- Intergranular-swelling process

f) Fuel oxidation in steam/hydrogen mixtures

The principal phases that appeared in the irradiated fuel and considered in the code are the following:

- The fuel-FP oxide solid-solution: Cs(c), alkaline earth metals Ba(c) and Sr(c) and their oxides BaO(c), SrO(c), zirconium and niobium in the forms Zr(c), ZrO2(c), Nb(c), NbO(c), $NbO_2$(c), rare earth elements La(c), Ce(c), Eu(c), Nd(c), and their oxides $La_2O_3$(c), $Ce_2O_3$ (c), $CeO_2$(c), $Eu_2O_3$(c), EuO(c), $Nd_2O_3$(c), metalloid Sb(s) and $Sb_2O_3$(c), noble metals Mo(s), Ru(s) and their oxides $MoO_2$(c), $RuO_2$(c).

- The metal phase composed of Mo(c) and Ru(c).

- The phase of complex ternary-compounds (grey phase) including molybdates, zirconates and uranates of Ba, Sr and Cs in the form: $BaUO_4$(c), $SrUO_4$(c), $Cs_2UO_4$(c), $BaMoO_4$(c), $SrMoO_4$(c), $Cs_2MoO_4$(c), $BaZrO_3$(c), $SrZrO_3$(c) and $Cs_2ZrO_3$(c).

- The separate solid-phase of CsI(c).

- The gas phase with the main components: Xe(g), Te(g), I(g), Cs(g), CsI(g), $Cs_2MoO_4$(g), $MoO_3$(g), $(MoO_3)_2$(g), $(MoO_3)_3$(g), RuO(g), $RuO_2$(g), $RuO_3$(g),Ba(g), Sr(g), ZrO(g), LaO(g), CeO(g), NdO(g), NbO(g), $O_2$(g).

## 7. CONCLUSIONS

Currently, mechanistic models can simulate FP release from irradiated $UO_2$ fuel, as it is the case of the MFPR code. This code is based on self-consistent consideration of evolution of various point defects (gas atoms, vacancies and interstitials) and extended defects (gas bubbles, dislocations, vacancy clusters and pores) and their mutual interactions under various irradiation and annealing regimes of $UO_2$ fuel operation.

The main question is how to understand leaching experiments from the information obtain from mechanistic models in order to predict the Instant Release Fraction (IRF) from $UO_2$ fuels. As it is mentioned in Deliverable 4.2 [Pekala et al., 2013], IRF from the fuel requires the contact with water, therefore the release of these fission products would be related to the rate of wetting of the different parts of the fuel. Numerical modeling of fuel pellet saturation with water has been attempted as part of the First Nuclides project [Pekala et al., 2012].

Another interesting point is to know the behavior of the different compounds, showed above, when water contact the fuel. Solubilities of molybdates, zirconates and uranates and also of some oxides and metallic precipitates could allow to a general picture of the fast radionuclide release, combining both mechanistic models and leaching experiments.

## 8. REFERENCES

Carroll, D.F. J. Am. Ceram. Soc. 46 (1963) 195

Dehaudt, P. (2000) Le combustible nucléaire et son état physico-chimique à la sortie des reàcteurs. Rapport CEA-R-5923

González-Robles, E. (2011) Study of Radionuclide Release in commercials $UO_2$ Spent Nuclear Fuels. Effect of Burn-up and High Burn-up Structure. PhD Thesis, UPC-Barcelona Tech.

Gray, W.J. Inventories of I-129 and Cs-137 in the gaps and grain boundaries of LWR spent fuels. *In Scientific Basis for Nuclear Waste Management XXII, (D. J. Wronkewiecz and J.H. Lee, Editors),* Mat. Res. Soc. Symp. Proc. 556 (1999) 487-494.

Heames, T.J. et al. VICTORIA: A Mechanistic Model of Radionuclide Behavior in the Reactor Coolant System Under Severe Accident Conditions, NUREG/CR-5545 SAND90-0756 Rev 1 R3, R4, 1992.

Hiernaut,J.-P., Wiss, T., Colle, J.-Y., Thiele, H., Walker, C.T., Goll, W., Konings, R.J.M. Fission product release and microstructure changes during laboratory annealing of a very high burn-up fuel specimen. J. Nucl. Mater. 377 (2008) 313–324.

Imoto, S. Chemical state of fission products in irradiated $UO_2$. J. Nucl. Mater. 140 (1986) 19-27.

Johnson, L.H., Tait, J.C. (1997) Release of Segregated Radionuclides from Spent Fuel, SKB Technical Report 97-18.

Johnson, L.H., McGinnes, D.F. (2002) Partitioning of radionuclides in Swiss power reactor fuels. NAGRA Technical Report NTB 02-07.

Johnson L., Poinssot C., Ferry C. and Lovera P. (2004) Estimates of the instant release fraction for UO2 and MOX fuel at t=0, in: A Report of the Spent Fuel Stability (SFS) Project of the 5th Euratom Framework Program, NAGRA Technical Report 04-08.

Johnson, L., Ferry, C., Poinssot, Ch., Lovera, P. Spent fuel radionuclide source-term model for assessing spent fuel performance in geological disposal. Part I: Assessment of the instant release fraction. J. Nucl. Mater. 346 (2005) 56–65.

Johnson, L., Günther-Leopold, I., Kobler Waldis, J., Linder, H.P., Low, J., Cui, D., Ekeroth, E., Spahiu, K., Evins L.Z. Rapid aqueous release of fission products from high burn-up LWR fuel: Experimental results and correlations with fission gas release. J. Nucl. Mater. 420 (2012) 54–62.

Kleykamp, H. The chemical state of the fission products in oxide fuels. J. Nucl. Mater. 131(1985) 221-246.

Kohli, R. The chemical state of fission products in LWR fuels related to long-term dry storage. in *Proceedings of a Workshop on the Chemical Reactivity of Oxide Fuel and Fission Products Release*. Berkeley (UK) April 1987

Kurosaki, K., Uno, M., Yamanaka, S. Chemical states of fission products in irradiated uranium-plutonium mixed oxide fuel. In Technology Reports of the Osaka University, 49 (1999) 29-35.

Nuclear Thermodynamic Database (NUCLEA) Version 2007-01, THERMODATA, 6, rue du Tour de l'Eau - 38400 Saint Martin d'Heres (F) 2007.

Matzke, H.J. Radiation enhanced diffusion in $UO_2$ and $(U,Pu)O_2$. Radiation effects 75 (1983) 317-325.

Matzke, H.J. Atomic transport properties in $UO_2$ and mixed $(U,Pu)O_2$. J. Chem. Soc. Faraday Trans. 2, 83 (1987) 1121-1142.

Matzke, H.J. Atomic mechanisms of mass transport in ceramic nuclear fuel materials. J. Chem. Soc. Faraday Trans. 8, 86 (1990) 1243-1256.

Matzke, H.J. Oxygen potential in the rim region of high burn-up $UO_2$ fuel. J. Nucl. Mater. 208(1994) 18-26.

Peehs, M., Manzel,R., Schweighofer, W., Haas, W., Haas, E., Würtz, R. On the behavior of cesium and iodine in light water reactor fuel rods. J. Nucl. Mater. 97 (1981) 157-164

Pekala, M., Riba, O., Duro, L. Models for fission products release from spent nuclear fuel and their applicability to the First Nuclides project. Deliverable (D-N°:4.2) First Nuclide project 2013.

Pekala, M., Idiart A., Duro, L., Riba, O., Modelling of spent fuel saturation with water-approach preliminary results and potential implications. In *1st Annual Workshop Proceedings of the Collaborative Project "Fast / Instant Releaseof Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides)*. Budapest (H), October 2012.

Poinssot, C., Toulhoat, P., Grouiller, J. P., Pavageau, J., Piron, J. P., Pelletier, M., Dehaudt, P., Cappelaere, C., Limon, R., Desgranges, L., Jegou, C., Corbel, C., Maillard, S., Faure, M. H., Cicariello, J. C., Masson, M. (2001) Synthesis on the long term behavior of the spent nuclear fuel, Vol. I (ed. CEA).

Prussin, S.G., Olander, D.R., Lau, W.K., Hansson, L. Release of fission products (Xe, I, Te, Cs, Mo and Tc) from polycrystalline $UO_2$. J. Nucl. Mater. 154 (1988) 25-33.

Rest, J., Zawadzki, S.A. FASTGRASS, A Mechanistic Model for the Prediction of Xe, I, Cs, Te, Ba and Sr release from Nuclear Fuel under Normal and Severe-Accident Conditions, NUREG/CR-5840 TI92 040783, 1994.

Roudil, D., Jégou, C., Broudic, V., Muzeau, B., Peuget, S., Deschanels, X. Gap and grain boundaries inventories from pressurized water reactors spent fuels. J. Nucl. Mater. 362 (2007) 411-415.

Sari, C., Walker, C.T., Schumacher, G. Solubility and migration of fission product barium in oxide fuel. J. Nucl. Mater. 79 (1979) 255.

Schmid-Fetzera, R., Andersson, D., Chevalier, P.Y., Eleno, L., Fabrichnaya, O., Kattner, U.R., Sundman, B., Wang, C., Watson, A., Zabdyr, L., Zinkevich, M. Assessment techniques, database design and software facilities for thermodynamics and diffusion. Computer Coupling of Phase Diagrams and Thermochemistry 31 (2007) 38–52

Serrano-Purroy, D., Clarens, F., González-Robles, E., Glatz, J., Wegen, D., de Pablo, J., Casas, I., Giménez, J., Martínez-Esparza, A. Instant release fraction and matrix release of high burn-up UO2 spent nuclear fuel: Effect of high burn-up structure and leaching solution composition. J. Nucl. Mater. 427 (2012) 249-258

Thomas, L. E., C.E.Beyer, Charlot, L. A. Microstructural analysis of LWR spent fuels at high burnup. J. Nucl. Mater. 188 (1992) 80-89.

Van Uffelen, P. The potential of TRANSURANUS code for source term calculations of spent. In *1st Annual Workshop Proceedings of the Collaborative Project "Fast / Instant Releaseof Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides)*. Budapest (H), October 2012.

Veshchunov, M.S. , Ozrin, V.D., Shestak, V.E., Tarasov, V.I., Dubourg, R., Nicaise, G. Development of the mechanistic code MFPR for modeling fission-product release from irradiated $UO_2$ fuel. Nuclear Engineering and Design 236 (2006) 179–200.