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

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ABSTRACT

This report is an update of DELIVERABLE (D-N°:4.1) STATUS OF MODELLING OF MIGRATION/RETENTION PROCESSES OF FISSION PRODUCTS IN THE SPENT FUEL STRUCTURE based on the work performed during the project. Chemical compounds of ^{14}C are discussed taking into account thermodynamic considerations. Laser Ablation ICP-MS and Knudsen Cell MS have shown the capabilities to experimentally study the location of fission products in the fuel. Experimental results have been modelled by using thermodynamic and mechanism approaches. Leaching experiments have demonstrated to be a good tool to understand the location of fission products in different parts of the fuel such as gap, rim and grain boundary.

1. INTRODUCTION

This contribution is an update of the migration and retention processes of fission products in the structure of the spent fuel. This was the goal pursued in the work performed during the First-Nuclides project as well as in studies recently published.

The use of techniques such as Laser Ablation-ICP-MS and Knudsen cell allowed investigating the location of fission products in the fuel.

Moreover chemical speciation of ^{14}C was performed taking into account thermodynamic considerations.

2. Carbon Chemical Compounds in the Fuel

In this Project, chemical speciation of 14C was studied [Kienzler et al., 2013]. ^{14}C in the fuel can be formed by neutron reaction from ^{17}O, ^{14}N and ^{13}C. Calculations performed with a KIT fuel sample (assembly ID N0206, rod ID SBS1108) gave a concentration of this element equal to 0.016 mol/t_{HM}. The carbon may react with oxygen and a variety of mono-, di-, and trivalent elements giving carbon oxides and carbides, respectively.

Carbon Oxides

Taking into account Oxygen Potentials [Olander, 1976; Glassner, 1957] for actinides and fission products, the only elements which may compete for oxygen with carbon are Cs and Mo in a small area between 850 K and 1100 K where ΔG_f of the carbon oxides are below the ΔG_f(MoO2). Under these conditions, CO or CO_2 could be formed.

However comparing experimental results to theoretical carbon oxides formation, it seems that only a minor part of ^{14}C is released as CO_2 into the plenum.

Carbides

Gibbs free energy of formation (ΔG_f^0) of carbides of the most abundant additives, actinides and fission products in SNF are collected elsewhere [Wicks and Block, 1961; Shatynski, 1979]. The formation of oxides or carbides depends on fuel redox conditions.

Therefore, the speciation of ^{14}C is not yet resolved by theoretical considerations. Measurements, especially of the isotopic composition of the CO_2 in the gas phase and the redox state of the fuel are required. Equilibrium data between carbides and oxides as function of the temperature are needed.

3. Location of Fission Products in the Fuel

Location of fission products on the surface of a fuel pellet can be experimentally determined by using LA-ICP-MS. Roth et al. [Roth et al., 2013] applied this technique to two spent fuel samples 52A (standard UO_2 fuel) and C1 (doped with Cr and Al).

In 52A sample, the cesium and iodine profiles follow each other. Both cesium and iodine peaks are typically associated with visible cracks in the fuel. Overall, cesium, iodine and xenon profiles are rather flat in the interior of the pellet which means no excessive linear heat rates during operation. However, the profiles showed a clear increase near the outer boundary of the pellet.

A comparison between ^{133}Cs and ^{140}Ce profiles indicates that they are very similar; taking into account that ^{140}Ce is a rather immobile lanthanide, redistribution of ^{133}Cs seems to be very limited during operation in this sample.

In C1 sample, cesium, iodine and xenon profiles are rather flat too. The Al additive shows a very heterogeneous distribution, due to the low solubility of Al_2O_3 in the UO_2 matrix. The chromium additive appears to be rather homogenously distributed in the fuel. Both additives seem to be located in grain boundaries. For this sample profiles of cesium and cerium are also very similar.

Modelling carried out by KIT [Kienzler et al., 2014] with C1 sample gave that the calculated total concentration in the colder region of the pellet corresponds to Roth et al. [201] measurements. Besides, calculated release of volatile radionuclides into the gap regions corroborate with the fission gas release (FGR). Finally, after discharge from the reactor, diffusion processes of volatiles do not play any role due to the negligible diffusion coefficients at interim storage temperature.

Location of Xe in the rim zone was calculated for a fuel with a burn-up of 50.4 GWd/t_{HM}. Calculations showed that the percentage of Xe in the rim matrix and in rim pores were 0.026 wt.% and 0.953 wt.%, respectively [Kienzler et al. 2012]. Almost the complete Xe inventory of the rim is located in pores.

Location of fission products on the fuel can be also studied from leaching experiments [Casas et al. 2014], taking into account the conceptual model shown in Figure 1. The availability of the different radionuclides to be released depends on the way the studied sample has been pretreated, because the availability to water will be different in each case. According to that, separate contributions could be differentiated based on the sample pretreatment. In the real case, the three situations may take place as the water is reaching the different areas and the release of the RN's might show it.

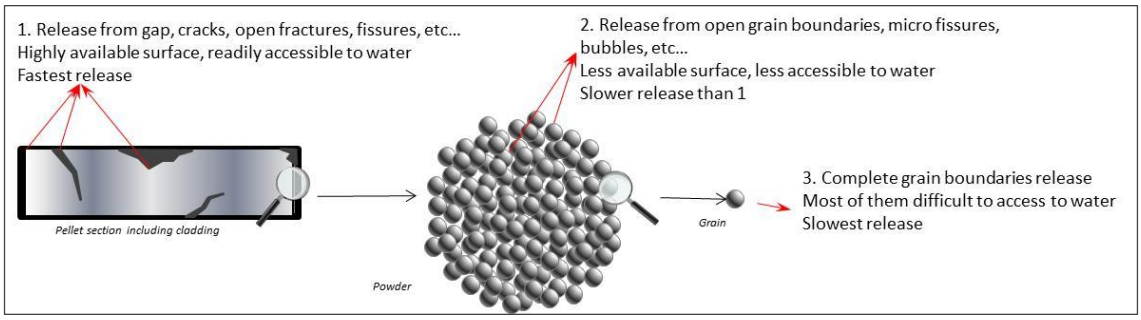

Figure 1. Conceptual model of the location of radionuclides depending on fuel samples

Casas et al. [2014] pointed out that the percentage of radionuclide released is higher for powdered than for cladded samples, except in the case of Cs in PWR samples. In those cases similar values are obtained. It can be assumed that for Cs its content in gaps and fractures is similar than its content in grain boundaries and micro fissures, which is not the case for the rest of radionuclides (Mo, Tc, Sr, Rb), that show greater content in grain boundaries due to their lower migration once segregated from the matrix. This general observation is also supported by the results obtained for the other high mobile radionuclide studied, Rb, which for some samples show behaviors that

closely follow those of Cs. Modelling of the Cs release from four segmented fuel samples is shown in Figure 2, initial release is attributed to Cs migrated to the gap, and the second step of the modelling to release from grain boundaries.

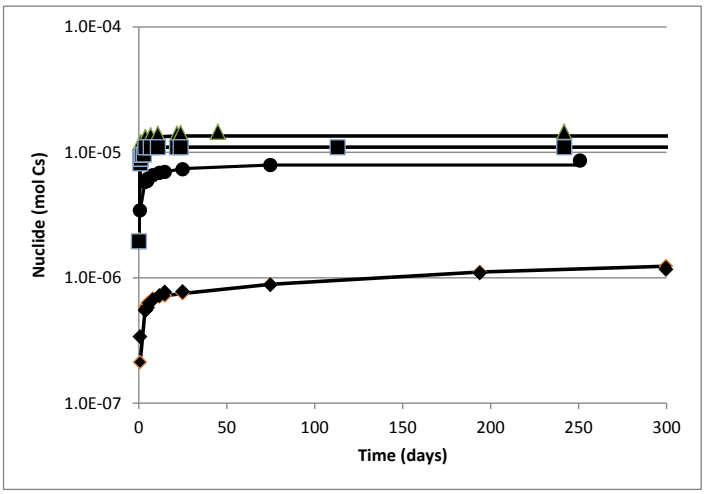

Figure 2. Fitting of Cs release from four segmented fuel samples

As mentioned above, Cs concern is due to its mobility. Because of that the behavior of Cs in a core powered spent fuel sample (PWR, 60 Mwd/kgU) before and after leaching was studied by using the Knudsen Cell Mass Spectrometry (KEMS) [Serrano-Purroy et al., 2014], and results were modelled by two mechanistic approaches: MFPR (Module for Fission-Product Release), and MEPHISTA (Multiphase Equilibria in Fuels via Standard Thermodynamic Analysis).

From the KEMS effusion curves for ^{137}Cs, before and after leaching, vs. temperature (see Figures 3 and 4), when we try to reproduce the experimental results by MFPR it is necessary to include the possible formation of Cs compounds like Cs_2MoO_4 and CsI. In addition, the MEPHISTA database was used to calculate the Cs speciation as a function of the fuel pO_2 and temperature.

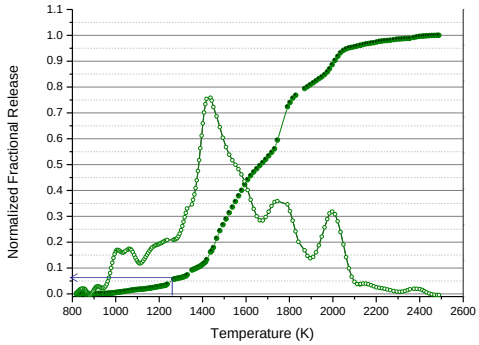

Figure 3. Cs location in the fuel before leaching

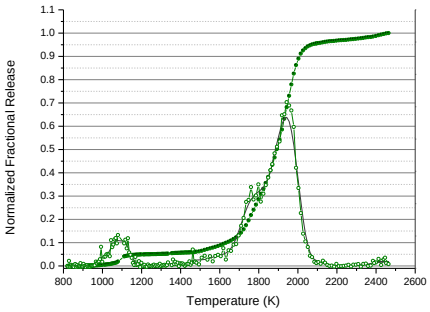

Figure 4. Cs location in the fuel after leaching

Five different migration steps were identified in the samples before leaching, corresponding to:

(I) and (II) release from Cs trapped in intergranular positions either as

(I) oxides form (Cs_2O, CsO, CsO_2…) (800-1150K) or

(II) in gas intergranular bubbles (1150-1250K),

(III) Cs release by atomic diffusion in the bulk (1250-1750K).

(IV) Release from CsI and/or Cs_2MoO_4 vaporization (1750-2000K) and

(V) release from the gas trapped in intragranular bubbles (2000-2250K).

The Cs release behavior observed for the samples after leaching is mainly linked to the first two peaks:

(I) and (II), corresponding to the IRF, disappear. This fraction corresponds to approximately 6% of the total released Cs in the untreated sample.

(III) Changes in pO_2 will significantly change the migration mechanism of Cs through the bulk, either by speeding-up the diffusion mechanism and shifting the release from 1400 to 1100K or by increasing the trapping in intragranular bubbles and therefore shifting the release to the end of the experiment.

(IV) This peak is not different from the one found in the non-leached sample and could correspond to CsI and/or Cs_2MoO_4 release. MEPHISTA does not predict any formation

of other Cs ternary oxides in our conditions. It is also possible that part of the Cs that diffuses through the matrix will react with oxidized Mo to form Cs_2MoO_4.

(V) Finally, the remaining Cs, trapped in intragranular bubbles is released together with the matrix sublimation.

4. References

Casas, I., A. Espriu, D. Serrano-Purroy, A. Martínez-Torrents, A. Martínez-Esparza, J. de Pablo (2014). IRF Modelling from spent fuel leaching experiments. In 3rd Annual Workshop Proceedings of the Collaborative Project "Fast /Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides) Karlsruhe 01 - 02 September 2014

Glassner, A. (1957). The thermochemical properties of the oxides, fluorides, and chlorides to 2500°K. Chicago, USA, Argonne National Laboratory.

Kienzler, B., C. Bube, E. González-Robles, V. Metz (2012). Modelling of boundary and initial conditions for upscaling migration/retention processes of fission products in the spent nuclear fuel structure. In 1st Annual Workshop Proceedings of the Collaborative Project "Fast /Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides) Budapest 09 - 11 October 2012

Kienzler, B., E. Bohnert, E. González-Robles, M. Herm, X. Gaona, C. Borkel (2013). Thermodynamic considerations on the speciation of ^{14}C in Spent Nuclear Fuel. In 2nd Annual Workshop Proceedings of the Collaborative Project "Fast /Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides) Antwerp 05 - 07 November 2013

Kienzler, B., V. Metz, E. González-Robles, M. Herma, O. Roth (2014). Behavior of fission products in fuel rods. In 3rd Annual Workshop Proceedings of the Collaborative Project "Fast /Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides) Karlsruhe 01 - 02 September 2014

Olander, D. R. (1976). Fundamental Aspects of Nuclear Reactor Fuel Elements. National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Roth,O., A. Puranen, J. Low, M. Granfors, D. Cui, C. Askeljung (2013). Spen fuel leaching experiments and laser ablation studies performed in Studsvik – Status and preliminary results. In 2nd Annual Workshop Proceedings of the Collaborative Project "Fast /Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel" (7th EC FP CP FIRST-Nuclides) Antwerp 05 - 07 November 2013

Serrano-Purroy,D., L. Aldave de las Heras, J-P Glatz, O. Benes, J-Y. Colle, R. Sureda, E. González-Robles, J. de Pablo, I. Casas, M. Barrachin, R. Dubourg, A. Martínez-Esparza (2014). Interpretation of Knudsen Cell Experiments to determine the Instant Release Fraction in Spent Fuel Corrosion Scenarios by using a Mechanistic Approach: the Caesium Case. Scientific Basis for Nuclear Waste Management XXXVII, Volume 1665: 275-281.

Shatynski, S. R. (1979). "The Thermochemistry of Transition Metal Carbides." Oxidation of Metals 13(2): 105-118.

Wicks, C. E. and F. E. Block (1961). Thermodynamic properties of 65 elements -Their oxides, halides, carbides, and nitrides. Bulletin 605: Medium: X; Size: Pages: 150.