INDUCTIVE HEATING FOR PARTITIONING OF FISSION PRODUCTS FROM SPENT NUCLEAR FUEL

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Summary

Among the concepts of reprocessing of spent nuclear fuel (SNF) currently used world-wide the recovery of uranium and transuranium elements by solvent extraction is the only technology applied on industrial scale. Non-aqueous reprocessing based on pyrochemical processes is considered to be an alternative way of partitioning for future transmutation purposes. Both approaches are dealing with the separation of fission products (FPs), like cesium or strontium, and of minor actinides, which are the primary heat generating elements and limit the amount of material that can be disposed. In an alternative approach for separation of FPs, recently developed at Paul Scherrer Institut (PSI), high temperature conditions are utilized to promote the release of volatile and semi-volatile FPs from SNF. This technology is proposed to be introduced as a head-end step of the fuel reprocessing that could help to decrease the radiotoxicity and downsize the amount of secondary waste streams.

The treatment of SNF is performed in an inductive heating device coupled to an inductively coupled plasma mass spectrometer (ICP-MS) to detect the FP release. Using this device it is possible to perform fuel annealing at maximum temperatures of 2300°C under various redox conditions (oxidizing, inert, reducing) by using different gas mixtures. The redox conditions control the fuel stoichiometry and the FP speciation in the fuel matrix that defines the FP release into the gaseous phase. Experimental studies show a distinct difference in the commencements of Cs and Sr/Ba release that becomes even larger under reducing conditions due to the shift of the Cs release towards lower temperatures. Thermodynamic modelling of the FP speciation under applied conditions demonstrated Cs stabilization in ternary compounds (as Cs_2MoO_4) with increasing oxygen potential. Differences in the thermochemical properties of FPs and, consequently, in the release behaviour can be useful for partitioning of FPs into the gaseous phase from irradiated oxide fuel.

Introduction

The concept of a closed nuclear fuel cycle is highly discussed as an alternative to the open fuel cycle in order to minimize nuclear waste. Closing the fuel cycle can be achieved through partitioning of uranium and transuranium elements (TRU) and conversion into the forms suitable for reuse as nuclear fuel. Long-lived minor actinides (Np, Am and Cm) are to be used for energy production [OECD, 1994; Burgazzi, 2007], while short-lived radioactive and neutron-absorbing fission products (FPs) are needed to be removed and converted into forms suitable for safe and long-term storage. In this context separation of Sr and Cs is important for safe disposal of high level waste (HLW), as they are main heat-generating nuclides. In both approaches of SNF reprocessing (hydro-metallurgical and pyro-chemical) irradiated fuel is separated from the cladding and dissolved either in an acid solution or in a molten salt, correspondingly. During further treatment (extraction steps of electrolysis) accumulated FPs are known to induce a number of problems, like the temperature increase during extraction steps or worsening the selectivity during the electrolysis in the molten salts [Souček, 2010]. At this point FP separation from irradiated fuel prior the fuel dissolution would favor reducing the waste volumes of extractions steps and improve separation efficiency for pyro-chemical partitioning.

An alternative way of FP separation from SNF, investigated at Paul Scherrer Institute (PSI), is based on thermochemical treatment procedures. With the aim of partitioning the FPs from U and TRU into the gaseous phase, irradiated fuel is treated in an inductive heating device under controlled gas atmosphere. Using a stepwise temperature increase on predefined redox conditions, it might be possible to promote the release of different FPs at different time intervals. Recently at Oak Ridge National Laboratory a similar idea of SNF treatment (Voloxidation) has been tested, that allows fuel de-cladding and pulverization when exposed to oxygen-rich atmosphere at 500–700°C. The approach demonstrated effective partitioning of volatile FPs, however, due to the low temperature a separation of semi- and low-volatile FPs has not been achieved [Westphal, 2005]. The present work demonstrates how the developed technique of inductive heating can be potentially used in partitioning of FPs from SNF for the purpose of advanced reprocessing technology. For results interpretation of the FP release observed under different annealing conditions the thermodynamic modeling of the FP speciation is performed. It is supposed to provide the better understanding of the FP behavior in the SNF as well as to predict the conditions on which the most efficient partitioning of FP from SNF can be achieved.

Experimental Procedure

InVap design and operational conditions

The design of the Inductive Vaporization (InVap) device was carried out in a computer aided engineering (CAE) approach. The final setup consists of a quartz tube (30 mm ID) closed from both sides with aluminum lids that serve as connection units for gas and cooling water. The upper lid is provided with a quartz window used as observation port for the temperature measurement by a pyrometer. The sample is placed inside the quartz tube in the carbon crucible. Additionally, MgO ceramic pillars are used to support the crucible. Such a holder system is able to withstand temperatures up to 2400°C and is not affected by the inductive heater. The void of the device is flushed with argon at different flow rates, however any other gas mixtures can be used instead of Ar to create required redox conditions. Via PTFE tubings (2 mm ID) from the upper lid the InVap is connected to an ICP-MS (Element 2, Thermo Fisher, Bremen, Germany). The load coil of the inductive heater (35 mm ID) is positioned at the same level as the carbon crucible containing the sample and is directly connected to the high frequency matching network (generator TNX5 compact, Plustherm Point GmbH, Wettingen, Switzerland). The pyrometer has a measurement range of 750 – 2500°C. In order to cover the lower temperature range the output power was calibrated to the temperature of the crucible during the installation and qualification of the device. The maximum working temperature of the described setup is 2300°C. The device is capable to handle irradiated fuel under various gas atmosphere to create oxidizing or reducing conditions. The direct connection to an inductively ICP-MS allows on-line detection of the transient signals of the elements in a wide range of mass units. Details of the design and the operational parameters of the InVap are described elsewhere [Švedkauskaitė-Le Gore, 2010; Kivel, 2012].

Investigated materials

In the annealing experiments irradiated uranium oxide fuel samples from a PWR with a burn-up of 3.8% FIMA (Fission per Initial Metal Atom) were investigated. The optimization of the InVap operational parameters was performed with a non-active material simulating irradiated oxide fuel (SIMFUEL) provided by Chalk River Laboratory (Canada). It has an FP inventory corresponding to the composition of 6% FIMA burn-up UO_2-based fuel. The constituents were mixed and sintered afterwards in order to provide homogeneous distribution of FPs within the pellet [Lucuta, 1991; Lucuta, 1992].

Since the operation of the InVap system at PSI is performed outside the hot cell, the amount of sample that can be handled in the device is limited by the dose rate. Furthermore, the amount of material used has to be low enough to avoid saturation of the ICP-MS detector during the release studies. These requirements have defined the sampling procedure as followed:

1. Roughening of the fuel pellet using sand paper (SP1000) to produce particles with an average size of 30 μm;
2. Imprinting of the roughened sample on a kapton tape: the generated particles are transferred and fixed onto the sticky kapton tape surface;
3. Encapsulation of fuel particles between the kapton tape and a cellulose nitrate filter with pore diameter of 0.4 μm (Millipore^{TM}) that enables a complete sealing of the fuel particles without the risk of contamination;
4. Dividing the encapsulated sample area into several representative subsamples.

The first two steps were performed in a hot cell. Afterwards, the imprints were taken out of the cell and further sample manipulations were carried out in a shielded fume hood.

Experimental conditions and data evaluation

The thermal treatment of the samples was carried out with the following temperature regimes:

1. Temperature ramp (24°C/min) up to 2300°C;
2. Annealing during 30 – 150 min at the maximum temperature;
3. Temperature drop without external cooling.

Different redox conditions (oxidizing, inert and reducing) were maintained by using different gas mixtures as carrier gas for the InVap. Inert atmosphere was created by using high purity Ar as carrier gas. Oxidizing conditions were created by flushing the quartz tube of the InVap with air at 500°C during 10 min prior the measurement. Preliminary experiments with SIMFUEL have shown that these conditions cause uranium oxide matrix destruction with formation of fine powder of U_3O_8. After the sample oxidation has finished, Ar was used as a carrier gas for detection of FP release during the temperature ramp of 24°C/min. Reducing conditions were maintained by a mixture of H_2/Ar with 0.7% of hydrogen volume fraction as carrier gas.

Solution of In (1 μg/g) in 5% HNO_3 was used as internal standard (IS) in order to account for the signal drifts over time or depending on the annealing conditions of the InVap. The IS was introduced via continuous nebulisation of the In solution into the plasma. Introduction of other IS into the solids (irradiated fuel, SIMFUEL) is not possible without distortion of the sample microstructure. It was also not possible to use additional standards along with the sample gas coming through the quartz tube in order to account for the transport efficiency of the InVap. When H_2/Ar mixture (reducing atmosphere) is used the traces of water at 2300°C become very corrosive for the quartz tube. Therefore, only the signal drifts due to the ICP-MS and InVap hardware are accounted for and only semi-quantitative analysis of the FP release in the InVap was possible.

The data evaluation procedure consists of the following steps: The acquired transient signals were analyzed to exclude any kind of interference and to choose the isotopes representing a certain FPs. After background subtraction and smoothing, signals were normalized to that of In-115 used as IS.

Thermodynamic modelling of FP speciation

Thermodynamic modelling is performed by Module of Fission Product Release (MFPR) code developed at the Nuclear Safety Institute of Russian Academy of Science (IBRAE, Russia) [Dubourg, 2003; Veschunov, 2006]. The code self-consistently describes the kinetics of various defect evolutions in the pellet, bubbles growth and their migration to the grain edges, diffusion of chemically active elements and formation of separate phases in the form of solid precipitates. With use of MFPR code the inventory of FPs in the irradiated fuel was calculated regarding to the fuel irradiation history. The code also assumes possible chemical interaction between FPs in the multicomponent U-O-FP system in the temperature range of 298 – 3000 K. Speciation of FPs was calculated using Gibbs energy minimization approach. Generally speaking, the code estimates equilibrium chemical speciation and activities/partial pressure of compounds in all co-existing phases at given pressure *P* and temperature *T.* The detailed description of the model and its validation can be found elsewhere [Barrachin, 2009; Ozrin, 2011].

Results and discussion

InVap signal reproducibility

The optimization of the InVap operational parameters was performed before the experiments with irradiated material using SIMFUEL due to the known speciation and homogeneous distribution of the component in the uranium oxide matrix. Intrinsic signals of Ba-138 (Fig. 1), typical for most FPs, demonstrate the reproducibility of the experiments in terms of temperature conditions. The signals were acquired during three independent annealing experiments and were normalized on the In-115 signal in order to account for the drop of the intensity at high temperatures. For the better visual comparison the signals were additionally normalization to maximum Ba-138 intensity.

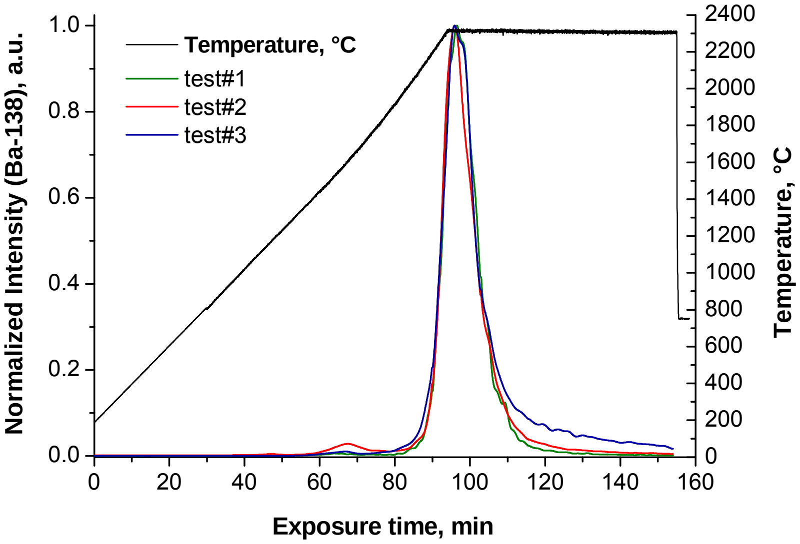


Figure 1: Normalized signal of Ba-138 release from SIMFUEL during annealing: results from three independent experiments with SIMFUEL.

The Ba-138 peaks were observed at the same time interval corresponding to a certain temperature of release. Fig. 1 demonstrates that the release of FPs can be very good reproduced in the InVap, if FPs in different samples are stabilized at the same chemical form. Consequently, if the FP speciation in the fuel changes and leads to different release behavior, this can be detected using the applied experimental system.

Mechanisms of FP release from irradiated fuel

Heating experiments using the InVap system have demonstrated that release of different FPs from irradiated fuel occurs over a wide temperature range (Fig. 2). However, the release kinetic for each FP is a characteristic parameter under equal conditions. Certain FPs have their specific release mechanisms because of the broad range of physical and chemical properties they possess. In other words, chemical properties in conjunction with migration ability in the fuel matrix having a certain structure make release mechanisms characteristic for every FP. Therefore, it is very important to have information about both chemical speciation and FP distribution in the solid phase.

On the very first stage of reactor operation FPs are dispersed in the fuel matrix on the atomic scale. With increase of burn-up or temperature fission gases (FGs) coalesce into gas bubbles. Further increase of burn-up causes the nucleation of small gas bubbles and their growth. It was found out that at temperatures below 1300 K the mobility of FG atoms is too low to diffuse to the sites where the bubbles can form [Orlander, 1976]. At temperatures between 1300 and 1900 K atomic motion of gas atoms becomes significant to promote FG escape through diffusion mechanisms. At these temperatures bubbles are formed, but they are not sufficiently mobile to migrate over considerable distances driven by the temperature gradient. However, FGs can be released if the bubble density is large enough to cause interlinkage that provides a pathway to open porosity or to weaken the grain boundaries so that stress in the fuel causes cracking.

Only if the open porosity has been created, volatile and semi-volatile FPs migrate through the interlinked bubbles and escape from the fuel matrix. The rapid diffusion in the gas phase allows the volatile elements to distribute uniformly within the matrix voids. Taking into account the critical temperature of opened porosity formation (1900 K) mentioned above, it could be suggested, that below this temperature release of FPs occurs only from the surface of the fuel. As soon as the temperature exceeds this level, FPs from the sample void contribute to the release.

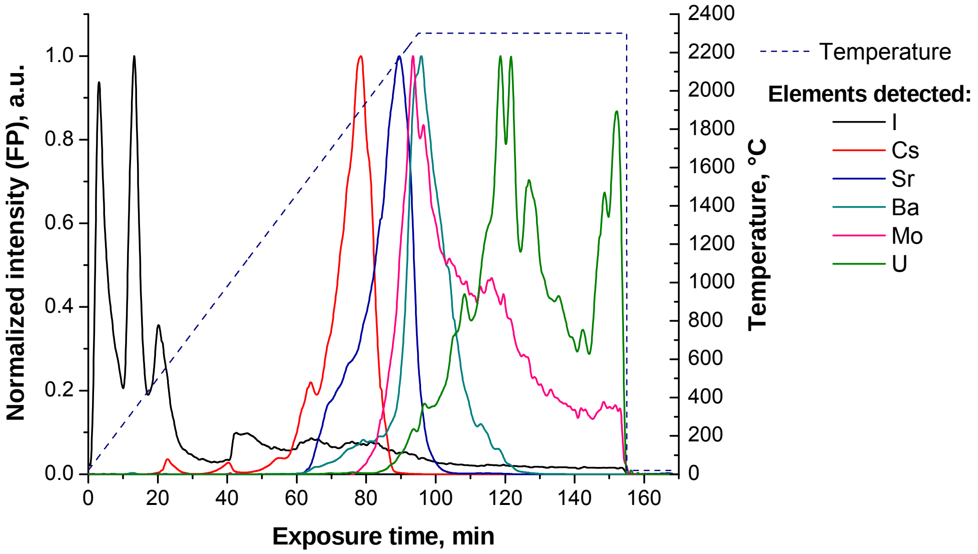
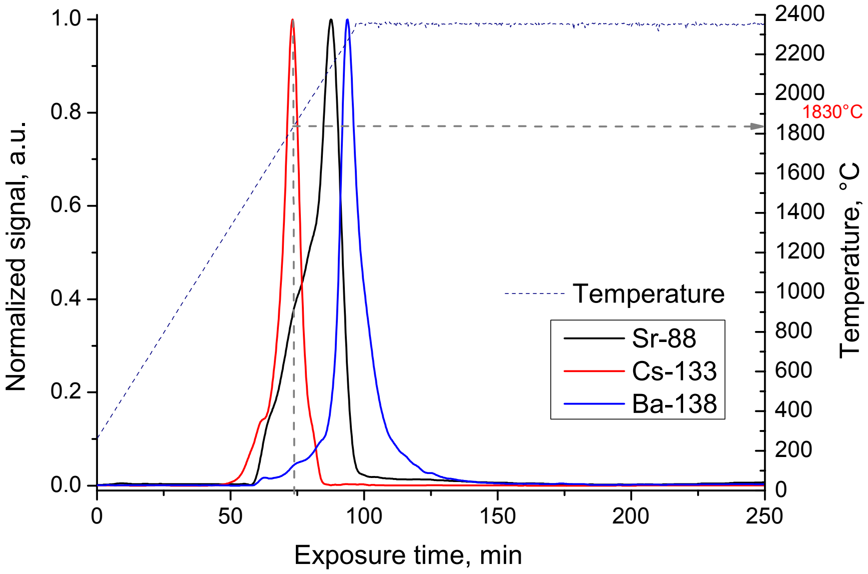


Figure 2: Normalized signals of FPs and U released from irradiated oxide fuel during thermal treatment.

Thus, the diffusion mechanism is unique for every FP. It depends on the initial chemical state of the FP after it has been created in the fuel, on its thermochemical properties and on the microstructure of SNF that has been established during irradiation period.

Release of Cs, Ba and Sr: experiment vs. modelling

Release of FPs in different temperature intervals shows the possibility of partitioning of certain FPs in the gaseous phase, when thermal treatment is performed at the “characteristic release temperature”. As an example, the release of only iodine can be promoted at the T < 800°C. Cs release commences at about 1800°C. In the temperature interval from 1900°C to 2300°C most of the semi-volatile FPs, like Sr, Ba, Mo etc., are released. Since the release profiles are rather broad, it is not possible to separate certain FPs from each other under given conditions. However, the release is mainly defined by the chemical speciation of FPs in the solid matrix, hence can be changed when other redox conditions are applied. In order to prove this suggestion, annealing experiments were performed under H_2/Ar atmosphere or after the fuel sample pre-oxidation. The results given in Fig. 3A and B demonstrate how release profiles of Cs, Ba and Sr change when the annealing atmosphere is switched from inert (A) to reducing (B). It has to be noticed, that signals shape obtained under oxidizing and inert conditions are almost identical. This signifies that PWR irradiated fuel was already oxidized before thermal treatment in the InVap, therefore further oxidation did not entail significant changes in the FP speciation.



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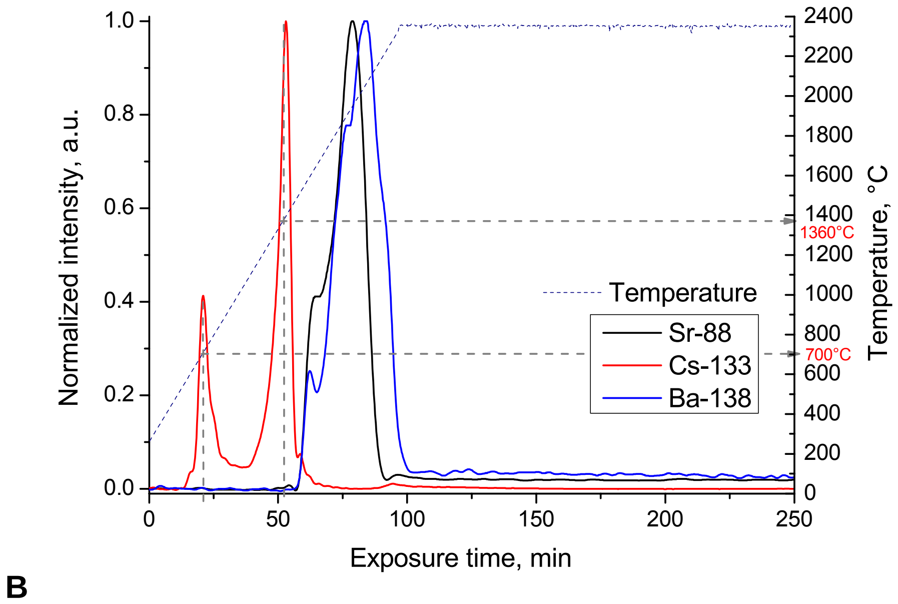

Figure 3: Normalized signals of Cs-133, Ba-138 and Sr-88 observed during thermal treatment of irradiated uranium oxide fuel in InVap under inert (A) and reducing conditions (B).

The thermodynamic calculations have shown that initially in solids Cs is mostly distributed between the so-called “grey phase” (ternary compounds of Cs and Mo/Zr/U oxides) and CsI (see Fig. 4). Speciation in the grey phase was calculated by MFPR model taking into account three main forms Cs_2MoO_4, Cs_2ZrO_3 and Cs_2UO_4. The composition of the grey phase is strongly dependant on the redox conditions. Under reducing conditions at low temperature the dominant species is Cs_2UO_4, which amount is diminishing with the temperature ramp and Cs is stabilized as Cs_2MoO_4. When oxidizing conditions are applied, Cs_2MoO_4 becomes the dominant form at already 400°C and is present in significant amounts in the gaseous phase until the Cs release occurs. In other words, stabilization of Cs as a molybdate is the reason of Cs retarded release on oxidized conditions. Thus the decrease of the experimentally observed release commencement on about 450°C when the annealing atmosphere is changed from oxidized to reduced is in a quite good agreement with theoretically calculated Cs speciation, given in Fig. 4. Thermochemical calculations demonstrated 550°C difference in the Cs release, whereas the retarded release under oxidizing conditions is the result of Cs stabilization in the grey phase, probably in the form of Cs_2MoO_4. However, the low temperature Cs release at 700°C, experimentally observed on reducing conditions, cannot be reproduced by the MFPR model and its origin is not clear so far.

The Cs distribution in the irradiated fuel was found to be in agreement with the data published before [Cordfunke, 1988; Moriyama, 1997]. In a number of studies one of the main species of Cs in fuel was determined to be CsI. However, in thermodynamic calculations cesium molybdate (Cs_2MoO_4) was predicted to be the most stable compound of Cs in the fuel with oxygen potential higher than -524 kJ/mol. This phase was found in FBR fuels in abundant concentrations precipitated on the fuel-cladding gap. Cs_2MoO_4 is quite stable in the gaseous state and is supposed to exist in the gas phase in FBR fuels. Besides molybdate, a more complex phase of $Cs_2U_4O_{12}$ was also observed in post-irradiation examination of highly irradiated fuel [Kleykamp, 1985]. Formation of Cs_2ZrO_3 was predicted to occur at very low oxygen potential, i.e. less than -620 kJ/mol. However, such a low oxygen potential is below the average conditions of a water-cooled reactor, therefore zirconate is expected to be present only in minor concentrations [Cordfunke, 1988].

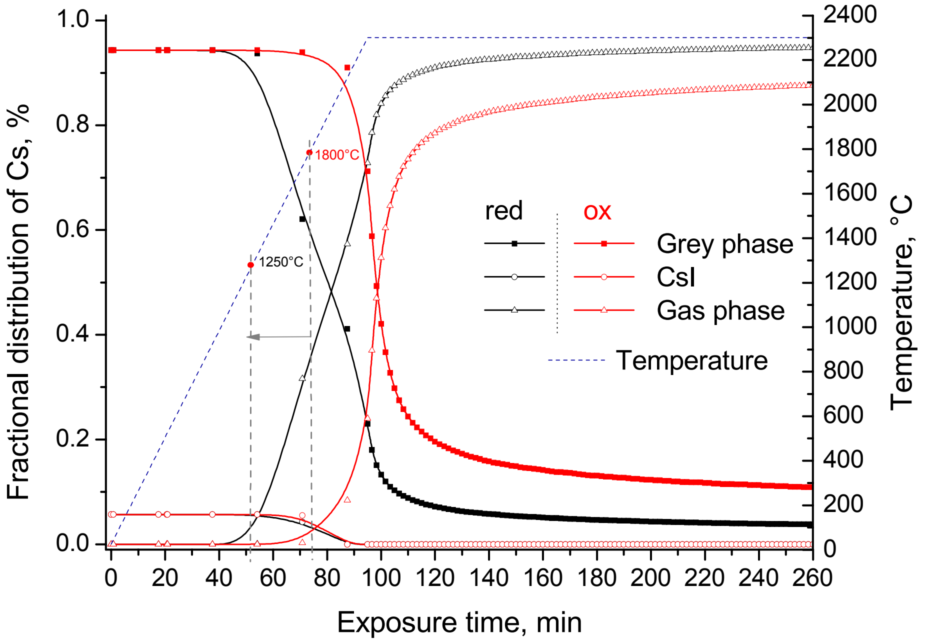

Figure 4: Cs fractional distribution between phases under reducing (black markers) and oxidizing (red markers) conditions simulated by MFPR.

Experimentally observed release of Sr and Ba is also consistent with speciation and distribution calculated by MFPR. No significant changes were detected in the acquired signals for both elements when redox conditions were changed. Results of the thermodynamic modelling, summarized in Table 1, show Ba to remain in the solid phase under any redox conditions. The only difference was found for Sr, which has higher solubility in uranium oxide (up to 21%) under reducing conditions. Oxidizing conditions cause a stabilization in the grey phase. Similar results were reported by Kleykamp and Brillant, who showed that Sr solubility in fuel reaches 12 %(n/n) at 1773 K [Kleykamp, 1993; Brillant, 2011]. Reducing conditions favor higher Sr dissolution in the fuel matrix, while oxidizing conditions promote its stabilization in the form of $SrZrO_3$ and $SrMoO_4$ in the grey phase. At low oxygen potential, e.g. on reducing conditions, $SrZrO_3$ was reported to be the most stable form below 1000 K.

Ba distribution is only slightly affected by redox conditions because of limited dissolution in the fuel matrix [Kleykamp, 1985; Cordfunke, 1988]. BaO, which is the stable form, has a very low solubility in SNF. The largest fraction of Ba is precipitated in the grey phase, consisting of $BaMoO_3$, $BaZrO_3$ and $BaUO_3$ and, possibly, of $Ba_2U_2O_7$ and Ba_3UO_6. The two dominant phases $BaZrO_3$ and $BaUO_3$ have a perovskite structure with the melting points of 2450°C and 2705°C, respectively. Oxidation of fuel promotes formation of $BaMoO_4$: at an oxygen potential higher than -400 kJ/mol, $BaMoO_3$ appears to be the most stable barium phase. Reducing conditions result in an almost even distribution of Ba within three perovskite structures: $BaMoO_4$, $BaZrO_3$ and $BaUO_3$. These ternary oxides form an eutectic with UO_2 and were demonstrated to be completely miscible.

Table 1: Release and fractional distribution of Cs, Ba and Sr in irradiated fuel PWR at burn-up of 3.8% FIMA after annealing at 2300°C on different redox conditions, calculated by MFPR, % (n/n).

Phase	Solid solution		Grey phase		Release into gas phase	
Conditions	*reduced*	*oxidized*	*reduced*	*oxidized*	*reduced*	*oxidized*
Cs	0	0	5	12	95	88
Sr	21	7	79	93	0	0
Ba	4	1	96	99	0	0

To summarize, earlier Cs release from SNF is promoted on reducing atmosphere, while stabilization of Cs in the grey phases retards its release when preoxidation is performed. Furthermore, almost no differences in Sr and Ba release were observed at any redox conditions applied. Such a significant shift of the Cs release temperature is fundamentally proven by thermodynamic modelling and demonstrates the possibility to separate Cs from Ba, Sr and the fuel matrix. A two-step approach has to be used to achieve this goal: 1) The annealing temperature is kept at about 1800°C to promote only Cs release. 2) The annealing temperature can be increased up to the maximum of 2300°C. Generally speaking the number of stages could be as much as the required number of FPs to be separated. However, the capability of the InVap system in this case is limited so far because some FPs possess rather similar chemical properties. This causes the simultaneous release of certain FPs that is not desirable in the separation technology.

Conclusions

The inductive heating approach applied in the InVap system was shown to be effective in selective partitioning of Cs from irradiated PWR fuel. Good reproducibility of the intrinsic signals detected by ICP-MS demonstrated the capability of the InVap system to promote certain volatile and semi-volatile FPs release at different time intervals, e.g. at “characteristic” release temperature. This temperature is based on the chemical speciation of FPs in the fuel, which may change when different redox conditions are applied during annealing. The commencement of Cs release was observed to decrease from 1830°C to 1360°C when the annealing atmosphere was switched from oxidizing to reducing. In other words, reducing conditions favour the selective separation of Cs from SNF and other heat generating FPs, like Ba and Sr. These InVap experiments are an example, how various annealing temperatures in conjunction with different redox conditions can be used for FPs partitioning for advanced reprocessing flowsheets.

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