Effect of Redox Conditions on the Fission Products Release from Irradiated Oxide Fuel

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Abstract

An in-house designed system for inductive vaporization (InVap) enables the investigation of the fission product (FP) release from irradiated fuel at temperatures up to 2300°C and under different redox conditions. Via the direct connection of the InVap device to an inductively coupled plasma mass spectrometer (ICP-MS) the on-line monitoring of the FP release is possible. Theoretically modeled and data experimentally determined on thermal treatment of irradiated fuel and release of volatile FPs (Cs, I), semi-volatile FPs (Sr, Ba, Tc, Mo, Ru) and actinides (U, Pu or Am) are discussed regarding to the nuclear fuel reprocessing technology.

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1. Introduction

The concept of a closed nuclear fuel cycle is highly discussed as a possible way to minimize the amount of nuclear wastes. Closing the fuel cycle can be achieved through partitioning of uranium and transuranium elements and their conversion into forms suitable for reuse as a nuclear fuel. In this regard partitioning of heat generating FPs, like Cs or Sr (and their short-lived decay products Ba and Y), is highly advisable prior fuel dissolution. These FPs may cause degradation of extraction agents due to radiological effects or overheating, as

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well as worsening the selectivity of electrochemical separations in molten salts [1, 2]. Near-term benefits hence include the significant drop in the thermal load of the wastes that, in turn, can reduce the costs for the spent nuclear fuel disposal.

Similar to DEOX (DEcladding via OXidation) process, an alternative method of FP separation from irradiated fuel under high temperature conditions has been developed at PSI. The proposed method is aimed to promote FP release at elevated temperatures created by inductive heating [3]. The Inductive Vaporization device (InVap), designed to handle irradiated nuclear fuel at temperatures up to 2300°C [4, 5], is directly connected to ICP-MS, that enables on-line tracing of the release of the vast variety of FPs. Different gases or gas mixtures were used to maintain and control redox conditions during annealing, as it has been previously reported to have a significant impact on FP speciation [6, 7]. The present paper is focused on the influence of redox conditions on the FP release from irradiated oxide fuel from pressurized water reactor (PWR) during annealing in InVap. To support the experimental work with information on chemical processes in the fuel during treatment, the Module of Fission Product Release (MFPR) was applied [8, 9]. Initially designed to assess the behavior of FPs during severe accidents in the single rode performance, the MFPR code is presently used for the needs of fuel reprocessing technology.

2. Experimental

2.1. Annealing procedure

The system consists of a vertically positioned quartz tube fixed between two aluminum bodies, serving as connection units for gas and cooling water. The sample is placed on a carbon holder on a ceramic support inside the tube. The load coil of the inductive heater is adjusted at the same level as the sample and is directly connected to the high frequency matching network (TNX5, Plustherm Point GmbH, Switzerland). Such setting provides the sample heating from room temperature up to 2300°C at almost any rate. The sample temperature is monitored through a quartz window in the upper lid by a pyrometer. The following annealing regime was used in the present study: (1) - temperature ramp with a constant heating rate of 24°C/min, (2) – annealing at 2300°C during 165 minutes, (3) – temperature drop back to room temperature without external cooling.

The void of the device is continuously flushed with Ar or gas mixtures (0.7% H\textsubscript{2} in Ar; air), that are used to transport the released products to the ICP-MS system (Element 2, Thermo Fischer Scientific, Germany), as well as to maintain different redox conditions in the InVap. The direct connection to an ICP-MS is used for on-line detection of the transient signals of the released elements in mass range of 79 to 241. More detailed description on the design and operational parameters of the InVap can be found elsewhere [4, 5].

2.2. Materials and Methods

Samples of uranium oxide fuel from PWR irradiated up to 39.6 MWd/kgHM were provided by the PSI hot-cell facility. The fuel pellets were sampled by imprinting the roughened pellet surface on adhesive kapton tape and covering of the tape with a cellulose nitrate filter (Millipore\textsuperscript{TM}). To prevent detector saturation during the measurement and to follow the dose rate limitations for the amount of material that can be handled outside a hot cell, the obtained imprint (Ø 35 mm) was divided into representative subsamples. Each subsample was used for a single experiment.

Inert and reducing conditions were created using pure Ar and a 0.7% H\textsubscript{2}/Ar gas mixture, respectively. Oxidizing conditions were achieved by sample pre-oxidation with air at 500°C during 10 minutes prior to the measurement.

The release of selected FPs and actinides was detected by means of ICP-MS via the corresponding isotopes: Sr-88, Mo-98, Tc-99, Ru-101, I-127, Cs-133, Ba-137, U-238, Pu-239 and Am-241. A solution of In (1 mg/g in
5% HNO₃) was used as internal standard in order to account for the signal drifts over time or caused by pressure change in the InVap. To assess the efficiency of the release for some products gamma-spectrometry measurements of the samples before and after annealing were performed using semi-conductor Ge-detector (Canberra GmbH).

2.3. Modeling approach

The calculation of the release kinetics for selected FPs was performed with use of the Module of Fission Product Release (MFPR, IBRAE, Russia). This code is designed to describe the release of the chemically active elements driven by their diffusion out of grains, as well as micro-structural defects evolution, bubbles growth and migration to the grain faces and edges [8]. With use of MFPR code the inventory of FPs in the irradiated fuel is calculated taking into account the fuel irradiation history (flux, irradiation time and conditions) and cooling time. The code accounts for possible chemical interactions in the multi-component U-O-FP system including the fuel stoichiometry. Speciation for selected FPs and actinides is calculated by minimizing the total Gibbs energy of the system in the temperature range of 298 – 3000 K [8, 9].

3. Results and Discussion

3.1. Simulation of FP release under different redox conditions

The mechanism of FP release from irradiated fuel is rather complex and is considered to be dependant on following factors: (1) fuel microstructure (developed during the irradiation period), (2) inventory of FPs and their speciation, (3) thermal diffusion properties of FPs and their precursors.

As a burn-up increases, fission gases coalesce into gas bubbles that lead to the fuel swelling and volume expansion. At a certain bubble density the interlinkage of bubbles creates the pathways to open porosity. After this special porous structure has been established, the volatile and semi-volatile FPs migrate through the interlinked bubbles and escape from the fuel matrix. The second factor - FPs speciation - is the one that can be affected by conditions applied either within the reactor operation period or during fuel handling after it’s discharge. According to the chemical state in the fuel accumulated FPs are commonly classified into four groups, namely: fission gases (Xe, I, Br etc.), metallic precipitates (Mo, Tc, noble metals etc.), oxide precipitates (Rb, Cs, Ba, Mo, Ru etc.) and solid solutions with fuel matrix (Sr, Zr, Ln etc.). Depending on the oxygen potential some FPs, like Mo and Ru, are oxidized or reduced, resulting in a continuous transport between metallic and oxide precipitates buffering the oxygen potential of the fuel matrix [10, 11]. Such phase transitions in turn affect the speciation of other FPs, like Ba and Cs that form stable ternary compounds with Mo, Zr or U [12].

In order to understand the behaviour of FPs under conditions applied in the InVap, the speciation and release of FPs was simulated by MFPR code. The released amount of some elements was calculated (and further experimentally detected) to be a few orders of magnitude different from each other. That is why, for better clearness, the values of fractional release in Fig. 1 (and consequently in Fig. 2) are demonstrated as normalized on the overall amount of corresponding element released within the annealing time. Under reducing conditions the release of Cs was calculated to start at 1450°C and 100% release should be achieved below 2000°C. However, an application of oxidizing atmosphere resulted in a retarded release with a maximum released Cs fraction of 95%. Thermodynamic calculations predicted Cs to be distributed between Cs₂MoO₄, Cs₂ZrO₃, and CsI phases, and the fraction of each species dependant on the redox and temperature conditions. Among these phases Cs₂MoO₄ is more refractory at high oxygen potential and high temperature and was suggested to retard the release of Cs on oxidizing conditions [13].
Commencement of U release was calculated to be almost independent on redox conditions and to start at about 1850°C. The total U release calculated for both conditions comprises less than $10^{-5}$ % of its inventory. Similarly to Cs, changes in the release of other FPs, like Ba, Mo and Ru were theoretically predicted. The influence of oxidizing atmosphere resulted in 99% of Ba being stabilized in form of ternary compounds BaMoO$_4$, BaZrO$_3$ and BaUO$_3$, and hence in significantly lower release. On contrary, oxides of Mo and Ru possess significant volatility that, in turn, will result in their enhanced release under oxidizing conditions [13].

3.2. InVap annealing experiments on irradiated fuel

Results of MFPR calculations identified, that reducing atmosphere favors earlier Cs release. The same tendency of accelerated Cs release under reducing atmosphere was observed during annealing in the InVap (Fig. 2). Noticeable, that Cs release in the InVap was detected earlier than it was predicted. Probably during simulation some cesium species were not taken into account, but yet have remarkable volatility at high temperature. Besides the delayed commencement, much higher Cs signal was detected on oxidizing conditions that is inconsistent with simulated data. One of the possible explanations of this difference between modeled and experimental results may be FP deposition in the experimental setup. This effect was earlier observed in VERCOR experiments for high temperature treatment of single rods for simulation of severe accidents in a PWR, when significant deposits on the cladding were found for Ba as well as for Cs [6, 7]. The quantification of the absolute amount of FPs released in the gaseous phase is not possible so far, since an internal standard can not be introduced into the fuel samples without distortion of the fuel structure. The only possibility to account for the efficiency of Cs release was to monitor Cs-137 as a tracer for Cs transport by means of gamma-spectrometry. Post-annealing analysis showed no detectable activity of Cs-137, hence the complete Cs release from the fuel was assumed.
As an example of our experimental findings Fig. 2 represents an impact of the gas atmosphere on Cs release. The difference between the commencement temperatures of Cs and U release is about 800°C. Complete Cs release was detected in both cases; however for U fractional release does not exceed 10^-6% if treatment is performed under reducing atmosphere, which is two orders of magnitude lower than that for oxidizing conditions. Taking into account differences in amount and temperature of the release, the separation of more than 95% of Cs inventory can be achieved at 1800°C under reducing conditions. At the same time this temperature is low enough to prevent substantial evaporation of uranium. The results on a few other FPs and actinides are summarized in Table 1.

Iodine release is almost instantaneous and occurs on 100%. The release of Ba and Sr was detected at relatively high temperature. Theoretical calculations defined the total release of 9 and <1% correspondingly. Therefore it’s unlikely, that the complete partitioning of Sr and Ba can be achieved by under proposed conditions. Delayed release of Mo and Ru was detected under oxidizing conditions, however released fractions were found to be a few orders of magnitude higher if compared to reducing conditions. Finally, relatively low amount of actinides was detected shortly before maximum working temperature and the release was only minor influenced by redox conditions.

Table 1. The temperature (°C) of the commencement of the release for selected FPs and actinides observed in the InVap

| Conditions   | Cs  | I   | Sr  | Ba   | Mo  | Ru  | U   | Pu  | Am  |
|--------------|-----|-----|-----|------|-----|-----|-----|-----|-----|
| Reducing     | 600 | 300 | 1550| 1540 | 1000| 750 | 1400| 2000| 1900|
| Oxidizing    | 900 | 650 | 1600| 1500 | 1760| 2000| 1700| 1900| 1850|
4. Conclusions

The experimental setup of InVap coupled to an ICP-MS was demonstrated to be a powerful analytical tool for investigation of FP release from irradiated fuel. The application of different gas mixtures during high temperature annealing allows the separation of FPs from the fuel matrix. This effect was suggested to have an actual application in the reprocessing technology for spent nuclear fuel, when a number of FPs can be selectively removed by thermal treatment of the fuel. Theoretical modeling using MFPR code was applied to assess the FP speciation in the fuel, as well as to predict the conditions for effective removal of selected FPs from the fuel. Release of more than 95% of the Cs inventory was achieved by annealing of the fuel at 1800°C on reducing atmosphere without significant actinides evaporation.

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