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REAL TIME MEASUREMENT OF FISSION PRODUCTS RELEASED FROM SPENT NUCLEAR OXIDE FUEL BY THERMAL TREATMENT

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Abstract – *The development of advanced reprocessing concepts for spent nuclear fuel is a challenging research topic worldwide. Various scenarios are being proposed and studied in order to improve the reprocessing efficiency and simplify the flowcharts for future aqueous or pyrochemical processes. The Paul Scherer Institut (PSI) in Switzerland has started a research project dedicated to the study of the removal of volatile and semi-volatile fission products by thermal and thermochemical treatment of spent oxide fuel.*

*For this study a HeLAC (**he**ated **l**aser **a**blation **c**ell), capable of heating samples up to 650 °C, was built. The HeLAC is designed so that the actual sample and cell temperatures are monitored independently. The cell can be directly connected to an inductively coupled plasma mass spectrometer (ICP-MS, Element 2, Thermo Fisher Scientific, Bremen, Germany) for online monitoring of the fission products released as a function of the increasing fuel temperature.*

Using this configuration various tests on simulated spent fuel have been performed to determine the optimal operating conditions necessary for the elemental release and for the ICP-MS specifications. Results obtained in this study will be presented along with the future concept for the thermal treatment of spent fuel up to 2000°C.

I. INTRODUCTION

For many decades the development of reprocessing technologies was focused on the recovery of unburned uranium and plutonium from spent nuclear fuel so that it may be put to further use. Whereas minor actinides and long lived fission products were of little interest and therefore remained trapped within the highly active waste.[1, 2.]

Due to problems related to the storage of radioactive waste as well as proliferation issues, an international interest in the advanced nuclear fuel cycle and in an alternative approach for handling radioactive waste has emerged. The partitioning and transmutation of long lived fission products and minor actinides to shorter lived products reduces the long term radioactivity of the waste and is therefore very attractive for advanced reprocessing.

Currently the dominant system of separating actinides from spent fuel uses aqueous processes, which are based upon differences in the chemical properties. To be able to accommodate the new types of fuels for the Generation VI reactors these aqueous processes need further development. At the same time there is a growing interest in non-aqueous processes which provide higher radiation resistance and produce smaller waste volumes than aqueous processes, but are more difficult to conduct.

Even though a wide range of research and development has been conducted in parallel for aqueous as well as non-aqueous treatments there is still no unanimous scenario for advanced reprocessing that has been adopted worldwide.

The head-end process, whose primary purpose is to convert the irradiated nuclear fuel into a form suitable for the separation of fission products, is needed for both the aqueous and the pyrochemical treatment of spent fuel.

The actual steps involved differ depending on the type of fuel, but can be divided into the following groups: removing the fuel cladding; dissolving the fuel; treating off-gases; clarifying solution from insoluble fission products; conditioning the solution for solvent extraction. Some of the steps, like removing the fuel cladding which commonly relies on the mechanical sharing of fuel rods, are the same for both processes.

Several laboratories around the world are currently investigating alternative pre-treatment step which involves the removal of fission products via direct release from the broken fuel structure or via oxidation and volatilization using a high temperature process.[3, 4, 5.] The Paul Scherrer Institut is one laboratory that has started a research program dedicated to the study of the removal of volatile fission products during head-end processing and the development of an analytical technique for online monitoring of the element separations and the speciation.

Research programs focusing on different steps of the reprocessing process are of key importance for enabling an effectual reprocessing. As the results of these works will enrich the understanding of minor actinides and long lived fission products behavior furthermore allow improvements in development of the flowcharts which aim is the actinide recoveries from the different type of fuels.

II. EXPERIMENTAL

II. A. Instrumentation

The design of the **he**ated **l**aser **a**blation **c**ell (HeLAC) is based upon a commercially available laser ablation cell; however, key modifications were necessary. The cell body is made of Inconel 600 and contains a quartz window. The heater element, which is mounted at the bottom of the cell, is capable of heating a sample to 650 °C. The cell floor separates the heater from direct contact with the radioactive sample. This not only makes heater element easy to replace, but also allows it to be handled as non-radioactive waste.

The heater temperature profile, a ramp-up and hold function, is easily programmable and fully controlled using LabVIEW. Temperatures of the sample and the carrier gas within the cell are measured with the aid of a pyrometer and thermocouples. The HeLAC is coupled to an ICP-MS Element 2 via Teflon (PTFE) tubing with a length of 70 cm and an internal diameter of 4 mm. Argon is used as the carrier gas, however other gases such as oxygen in a mixture with argon can be used if necessary.

The HeLAC cell is designed to be installed in a shielded glove-box if needed. A photo of the HeLAC is shown in Fig. 1.

II. B. Samples used for experiments

For the initial study simulated fuel (SIMFUEL) was used. The SIMFUEL was made in-house by mixing natural oxides corresponding to fission products present in spent fuel (see Table I).

TABLE I

SIMFUEL composition

Uranium and fission products	Surrogate oxides	Element composition (wt %)
U	UO_2	95.251
Y	Y_2O_3	0.107
La	La_2O_3	0.235
Nd (Pr, Sm)	Nd_2O_3	2.037
Sr	SrO	0.103
Ba	BaO	0.692
Ru(Tc)	RuO_2	0.575
Sb	Sb_2O_3	0.107
Cs	CsCl*	0.892

*CsCl was used since CsO is unstable in air.

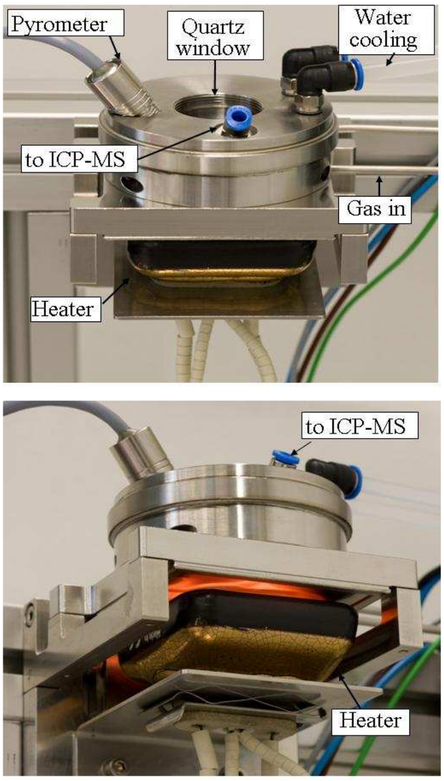

Fig. 1. A photo of the HeLAC.

III. FIRST RESULTS AND DISCUSSION

III. A. TGA

A thermo gravimetrical analysis (TGA) was performed in order to determine whether the ramp-up rate (time needed to reach the maximum temperature) has an influence on the release of volatile components. SIMFUEL samples between 140 to 270 mg were heated in the TGA (Mettler-Toledo AG, Greifensee, Switzerland) using three different heating rates to reach the maximum temperature of 650°C. Obtained results showed no significant difference in the release of volatile components using different heating rates (Table II).

TABLE II

Volatile components release during different heating rates

Sample name	Heating rate ^{o}C/min	Weight, mg	Weight loss, wt %
Sample-1	15	220.4	0.64
Sample-2	15	174.2	0.89
Sample-3	15	176.8	0.66
Sample-1	30	167.0	0.70
Sample-2	30	269.7	0.58
Sample-3	30	170.4	0.72
Sample-1	60	155.4	0.65
Sample-2	60	183.8	0.69
Sample-3	60	144.2	0.67

II. B. ICP-MS

ICP-MS optimization is complicated and time consuming as instrument signals are a function of a variety of parameters. However, it is critical to obtain the highest possible sensitivity for analytes of interest. Standard procedures were applied to ensure best instrument stability and to obtain the maximum signal intensity. Moreover, during measurements a standard indium solution was used to compensate for possible drifts due to changes in the plasma condition.

After the ICP-MS is optimized the samples are placed on a platinum foil and heated in the HeLAC to the maximum temperature. Between each sample the cell is washed to avoid any possible memory effect. In addition to this, after each opening, the cell is flushed with carrier gas to remove air which would otherwise cause a plasma extinguish.

So far only the release of Cs has been investigated as the temperatures reached in the HeLAC are too low for the volatilization of other elements.

A cesium chloride/sodium chloride powder mixture was used for the optimization of the thermal treatment parameters and for the verification of the analytical performance of the ICP-MS in combination with the HeLAC. Obtained results ascertained that the minimum amount of Cs necessary for an online analysis is about 10 ng. This corresponds to about 10 µg of SIMFUEL.

Non-reproducible release behaviour of Cs from both the SIMFUEL and from the CsCl/NaCl powder was observed (Fig. 2 and 3). Therefore additional experiments investigating the SIMFUEL powder were performed. The homogeneity of the SIMFUEL on a macro scale was proven to be better than 5 %; nevertheless, further characterization of the powder is continuing. On the other hand, the experiments performed so far, indicate that the origin of these non-reproducible results is the sample matrix itself and not the experimental equipment.

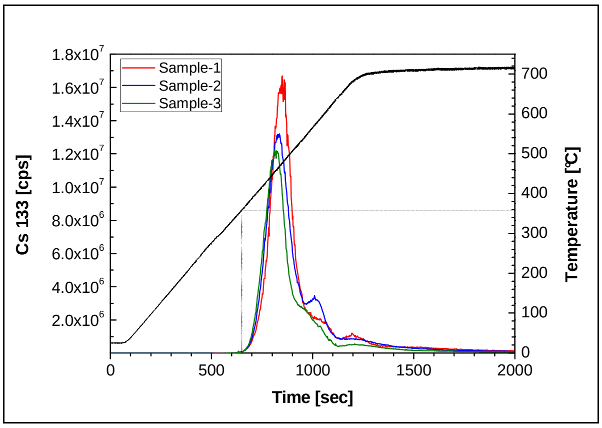

Fig. 2. Cs release from CsCl/NaCl powder subsamples versus sample temperature.

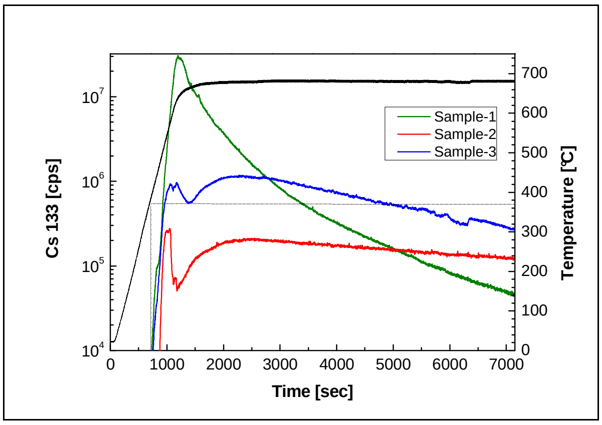

Fig. 3. Cs release from SIMFUEL subsamples versus sample temperature.

The ability to perform oxidation of fuel samples while the ICP-MS is running was also tested. Oxygen mixed with argon gas used as an oxidative carrier gas was applied during heating of natural uranium oxide pellet in the HeLAC. The flow rates were 0.25 L/min and 0.5 L/min respectively. Oxidation of the sample occurred when the sample temperature reached about 500^{o}C (Fig. 4). This corresponds with the data found in literature.[6.] However, the main focus was on the ICP-MS performance while the oxygen gas was applied. Tests showed that adding the oxygen gas had no influence on the ICP-MS performance and measurements results were equivalent to the results measured under non oxidative conditions.

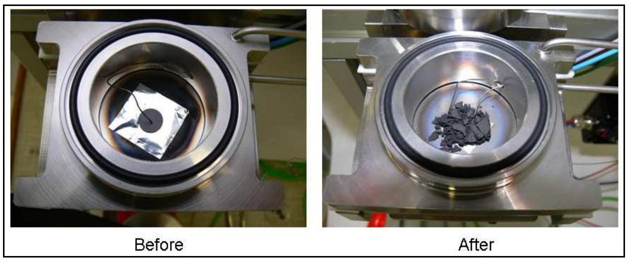

Fig. 4. Uranium oxide pellet before and after heating under oxidative conditions.

IV. OUTLOOK

In order to achieve a release of other volatile and semi-volatile elements during the thermal treatment of spent fuel, higher temperatures are required. Additional effort is now being focused on the construction of an inductive heating device able to heat samples up to 2000°C which also can be directly connected to ICP-MS.

Coupling of the HeLAC to an ICP-MS allows continuous online measurements of fission products release induced by thermal treatment. Know-how experience in online trace analysis of actinide and fission product release measurements can be used for better understanding of thermal and chemical behavior of volatile species in spent fuel.

V. CONCLUSIONS

The obtained results confirmed that the preliminary experimental setup can be successfully used for the release and online measurement of Cs. Additionally, no disadvantages in terms of the stability or the robustness of the setup were detected due to the coupling of the HeLAC to an ICP-MS. Finally, the oxidation of fuel samples while the ICP-MS is running is also possible.

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