A high temperature heating device for the study of fission product release from nuclear fuel

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Abstract – *At the Paul Scherrer Institute a high temperature inductive heating furnace, which can heat fuel samples up to 2300℃, has been developed in order to study the release of fission products. The furnace can be directly connected to an inductively coupled plasma mass spectrometer for online monitoring of the released elements and does not require their trapping before measurement. This paper describes the design of the inductive heating furnace, discusses its operating parameters, limitations and illustrates foreseen applications.*

A. INTRODUCTION

Removal of volatile and semi-volatile fission products from spent nuclear fuel by thermal and thermochemical treatment has been a subject of research for several decades. This topic focuses on the release of volatile elements induced by high temperatures, trapping the released products and finally their determination by inductively coupled plasma mass spectrometry (ICP-MS) or gamma analysis [1, 2, 3, 4].
The process of heating samples in air is known as voloxidation. The processing step employs high temperature and oxidizing gas to promote the oxidation of UO_2 to U_3O_8. This technique has been studied extensively in early 70's and has led to the development of several processes such as OREOX – oxidation and reduction of oxide, AIROX – Atomics International reduction oxidation and DEOX – decladding via oxidation. All these process applications can be used to prepare the fuel for hydrochemical, pyrochemical or DUPIC (direct reuse of PWR fuel in CANDU reactors) processes [5, 6, 7] However, none of these processes have been operated on a commercial scale so far. In the past decade these processes have returned to favor, due to concern about the effective management of spent nuclear fuel. To address this issue various development concepts of head-end reprocessing are under investigation by national research laboratories and by international cooperation.
The Paul Scherer Institute (PSI) in Switzerland started recently a research project called HERACLES (head-end reprocessing studies by thermal and thermochemical treatment of fuels). Objectives of the project are to study the release of the fission products during the high temperature treatment of spent oxide fuel, to perform real time measurements of fission products and to carry out the thermodynamic modeling to support these actions. This paper focuses on the design and implementation of a high temperature heating device for the study of fission product release and presents first experimental results.

B. EXPERIMENTS AND RESULTS

B.1. InVap design

The inductive heating device (InVap) was designed as successor of the heated laser ablation cell (HeLAC), which had a temperature limitation of about 700℃ and is described elsewhere [8]. The design of the InVap was carried out in a computer aided engineering (CAE) approach. This approach is based on the definition of boundary conditions followed by the selection of the best candidate technique for the given purpose. After the technique is selected, a 3D model is created and optimized by modeling of gas flows in the apparatus and maximum feasible temperature.
The following boundary conditions were predefined for the device:

- maximum sample temperature greater 2000℃
- ramping of the temperature with heating rates as low as 10 K/min

- capability to handle irradiated fuel
- oxidative (for pre-oxidation) and reductive gas atmosphere
- direct connection to an ICP-MS

In order to meet these criteria laser heating, electrothermal vaporization and inductive heating were assessed. Since emission of infrared light is the dominating effect at temperatures >2000℃ the power loss due to radiation has to be considered. This led to exclusion of a heating by laser, because the power loss would demand a very powerful and costly laser or make an infrared reflector in the close vicinity of the sample mandatory. For electrothermal vaporization a graphite tube, holding the sample, is heated by the Joule effect. Very high electrical currents are necessary to heat the graphite tube and the commercially available devices are designed for pulse operation rather than slowly increasing the power over a long time. Further the sample handling is hampered by the fact that the sample has to be placed on the L'Vov platform in the graphite tube. For this procedure the tube has to be removed from the furnace and later carefully be realigned.

The technique selected as most promising candidate is inductive heating of a graphite crucible. Inductive heaters are available in nearly any power range and the shape of the load coil can be freely selected. Further, the load coil can be covered with silver to act as a reflector for the infrared radiation. The devices are designed for continuous operation at full power and can ramp the power at almost any rate.

The materials for the device were carefully selected since they have to stand high temperatures but must not interact with the inductive heating, except the crucible. A schematic and picture of the InVap are given in

Figure 1. A quartz tube (30 mm ID) was selected as outer wall in the heated region. Quartz can stand temperatures of >1000℃ at almost full mechanical strength and is not prone to thermal shock. To support the crucible a MgO ceramic pillar is used. The material has a maximum working temperature of 2400℃ and is not affected by the inductive heater. Even though first experiments revealed that the high temperature gradient in the pillar caused cracking due to high thermal tension, this issue could be circumvented by stacking two crucibles on each other to reduce the temperature gradient in the insulating pillar. The base and the lid of the device are made from aluminum and serve as connection units for gas and cooling water. A quartz window in the lid is used as observation port for temperature measurement by a pyrometer. The void of the device is flushed with argon at different flow rates. The first stream at a low flow rate of 0.5 L/min enters at the base and flows as carrier gas around the crucible. The carrier gas can be mixed with pure oxygen or a hydrogen/argon mixture to adjust for oxidative or reductive atmosphere. A second argon stream at a flow rate of 0.8 – 1.0 L/min is used to quench the hot carrier gas and is introduced beneath the quartz window. The ICP-MS (Element 2, ThermoFisher, Bremen, Germany) is connected via a 2 mm ID PTFE tubing from the lid of the InVap. The load coil of the inductive heater is made from silver plated copper with a rectangular cross section and has 35 mm ID. The coil is positioned at the same level as the sample crucible and is directly connected to the high frequency matching network. The matching network itself is connected to the generator (TNX5 compact, Plustherm Point GmbH, Wettingen, Switzerland) which provides the 105 kHz high frequency. The heater is operated in an open control circuit, meaning no feed back from the pyrometer is used for the control. This was necessary because the pyrometer has only a measurement range of 750 – 2500℃. 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 as shown in Figure 2.

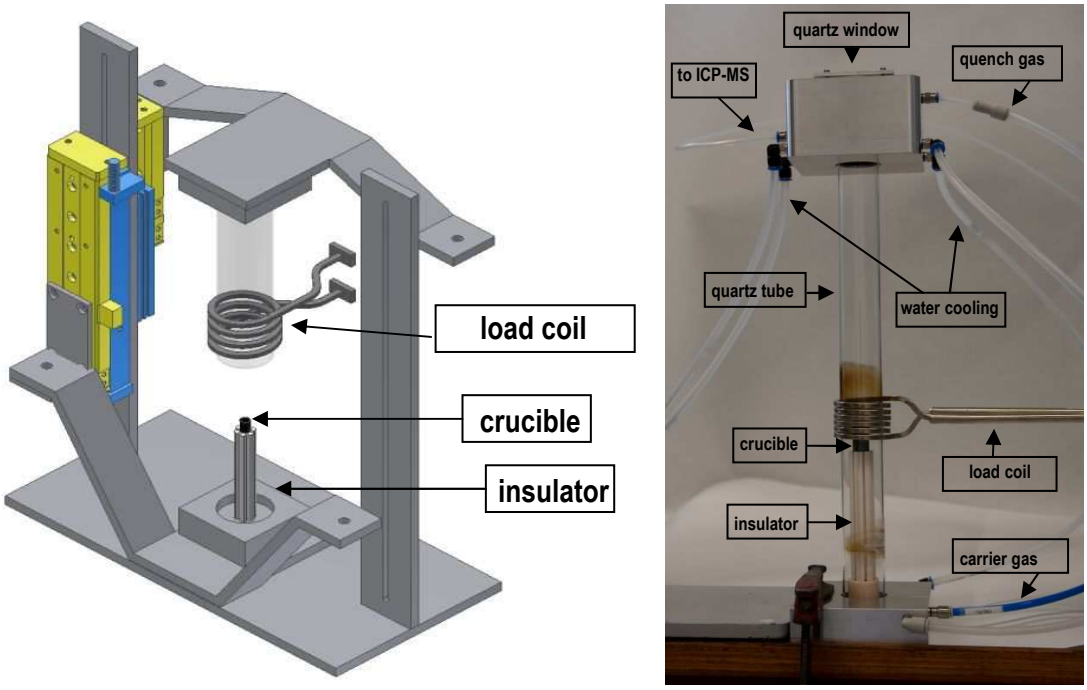

Figure 1: Schematic and picture of the InVap device

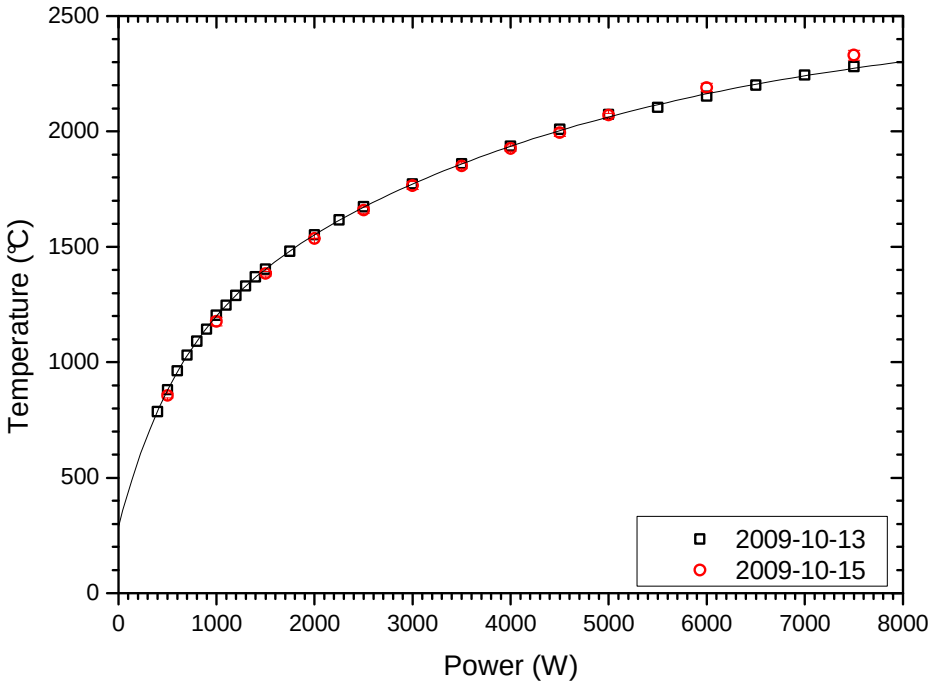

Figure 2: Calibration of the temperature with the forward power of the inductive heater

B.2. Samples used for experiments

The simulated fuel (SIMFUEL) used in this study was prepared at Chalk River Laboratories, Canada, as described elsewhere [9, 10]. The UO_2 based SIMFUEL composition, additives and impurities with concentrations greater than 10 µg/g, are listed in Table 1.

Table 1: Composition of the SIMFUEL from Chalk River Laboratories

Element	Concentration (µg/g)
Mg	10 ± 3
Al	36 ± 7
Cr	11 ± 2
Ni	10 ± 2
Ga	29 ± 6
Sr	1600 ± 200
Zr	2200 ± 200
Mo	180 ± 40
Ru	50 ± 10
Rh	13 ± 6
Pd	260 ± 50
Ba	1000 ± 100
La	900 ± 200
Ce	2700 ± 300
Nd	4500 ± 500
Th	18 ± 4

B.3. Temperature measurements

Figure 3 shows the sample temperature as a function of the applied generator power. At maximum power a temperature of about 2300℃ can be achieved. The heater temperature profile, a ramp-up and hold function, is easily programmable and fully controlled using a LabVIEW program. The InVap can heat a sample to the maximum temperature within a couple of minutes. Therefore, the temperature and time parameters can be changed depending on the needs of a particular experiment.

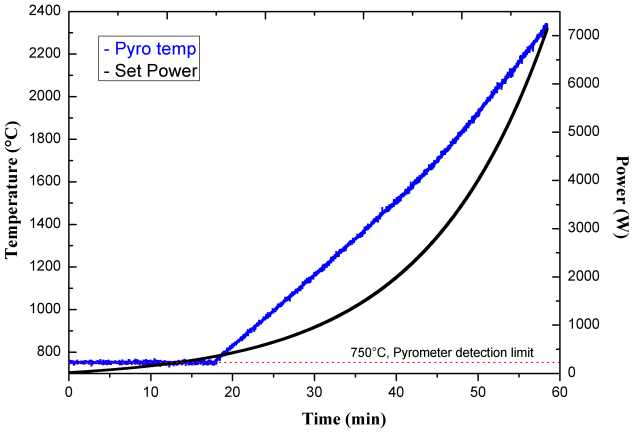

Figure 3: Power and temperature vs. time

B.4. Release measurements by ICP-MS

Samples are put into the graphite crucible which is then placed on the insulator in the InVap (Fig. 2). Once the InVap is closed and flushed with the carrier gas to remove air the optimization of the ICP-MS parameters has to be performed. ICP-MS optimization is critical as instrument signals are a function of a variety of parameters. Therefore, ICP-MS was optimized to ensure best instrument stability instead of the maximum signal intensity. Instrumental parameters are listed in Table 2. Due to current experimental set-up, the impurity of Xe in Ar gas was used for optimization. The modification

of experimental set-up, which will allow to introduce an internal standard, is currently in progress. After the ICP-MS optimization the samples were heated for the first test measurements with a ramp-up of 50 K/min to the maximum temperature, then the maximum temperature was hold for 30 min.

Table 2: ICP-MS operating parameters

Instrument type	Element 2
Coolant gas flow	16 L/min
Auxiliary gas flow	1 L/min
Sample gas	1 L/min
Additional gas	0.25 L/min
Extraction voltage	1800 V
SEM voltage	2200 V
Sampling cone	Aluminum

During the heating the ICP-MS measures the elemental release from SIMFUEL. The release of various elements versus temperature and time is shown in Figure 4. The plotted data were smoothed to capture release pattern as the ICP-MS had signal stability problems. The signal noise might be related to the dry plasma conditions. From laser ablation ICP-MS experiments it is known that the moisturizing of carrier gas improves the overall signal stability [11]. This effect will need to be verified for the present experimental set-up by repeating the experiments with a moisturized carrier gas. The addition of an internal standard must also be implemented via the addition of a standard solution to the gas stream.

Reproducibility of the results was checked by repeating the experiments under the same conditions several times. The outcome obtained showed that the intensities were reproducible; however the release curves were shifted to lower temperatures. This indicates that some material may condense on the walls of the InVap and in the transfer lines.

Additional experiments were done with ^{134}Cs and ^{99m}Tc in order to identify these possible memory effects due to condensation. These elements were chosen since they have different evaporation temperatures and are gamma emitters, which make identification of condensation on different parts of equipment much easier. Solutions of ^{134}Cs or ^{99m}Tc were placed in a graphite crucible and dried on a hot plate. After the sample was dried a gamma measurement was performed to obtain the starting activity of the sample. The samples were then placed in the InVap and heated using the same heating profile used for the release experiments. Once heating of the sample was done, gamma measurements on the graphite crucible were performed again. The results showed that the Cs is completely evaporated whereas 50% of the Tc remains in the crucible for the applied temperature regime. That is expected since the evaporation temperature of Tc is much lower than for Cs. Severe ^{134}Cs condensation of around 55% was found on the quartz tube and around 10% on the transfer line. For ^{99m}Tc condensation on the quartz tube is around 10% and around 1% on the transfer line.

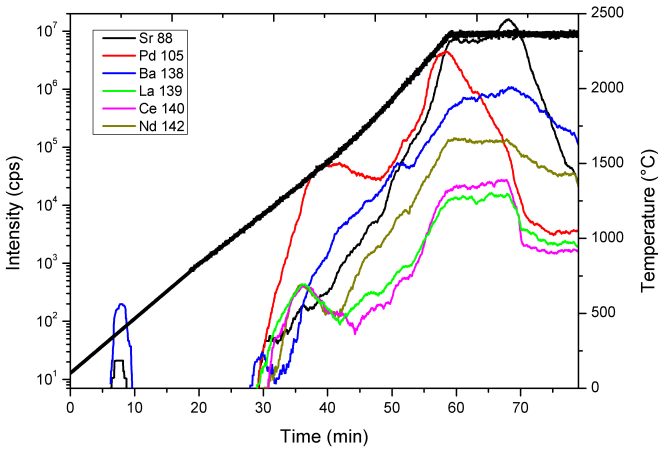

Figure 4: Elemental release from SIMFUEL

C. CONCLUSION AND OUTLOOK

This paper presents the design and first applications of the InVap. It has been demonstrated that this device is capable of heating samples up to 2300°C and can be successfully used for the release of elements, as well as it can be dedicated to heat treatment on other kind of samples. The experimental setup can be used for online measurement of released elements. However, condensation of the elements on the quartz tube and transfer line needs to be reduced.
Modifications of the set-up, such as moisturizing of the carrier gas and addition of an internal standard, will be implemented as soon as necessary equipment will be delivered. Afterwards experiments of fission products release from SIMFUEL will be repeated. Results obtained from those tests will demonstrate if the signal stability can be improved by moisturizing the carrier gas. As soon as problems concerning condensation and signal stability are under control experiments with active materials will be performed.

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