

High-Temperature Experimental Techniques for Nuclear Fuel Separate Effect Tests

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ABSTRACT

Many physical and chemical properties of nuclear fuel are currently modelled in the fuel performance codes with empirical correlations with several free parameters rather than exact models. On one hand, the macroscopic phenomena are so complex that it is difficult to come up with precise models for fuel performance codes, and on the other hand, the microscale physical and chemical phenomena are not understood well enough. We present here a concept for sintering simulated nuclear fuel samples for separate effect tests, which can help in the model development and understanding of underlying physics and chemistry. We also review previous work done at VTT with simulated fuels that has been the basis for the current work.

1 INTRODUCTION

Currently the light water reactor (LWR) fuel performance codes generally ignore or apply empirical adjustment for many chemical and physical phenomena of the nuclear fuel. These phenomena include fuel-clad bonding due to chemical reaction between the fuel pellets and the cladding, post failure oxidation of nuclear fuel, changes in the elemental composition of the fuel as irradiation proceeds, stress corrosion cracking of the cladding, and hydride precipitation and dissolution in the cladding. However, exceptions in the field can be found, such as SFPR [1], ALCYONE [2], and BISON [3, 4].

Even though the elemental composition of the fuel can be estimated accurately through burnup calculations, the constituent elements appear as part of different chemical species in the fuel. This chemical speciation has a direct impact on the fuel's chemical and physical properties. These chemical states of fission products can be classified into four main groups based on several elemental analysis of irradiated LWR and fast breeder reactor (FBR) fuels [5]: 1) fission gases and other volatile fission products (Kr, Xe, Br, and I), 2) fission products forming metallic precipitates (Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, and Te), 3) fission products forming oxide precipitates (Rb, Cs, Ba, Zr, Nb, Mo, and Te), and 4) fission products dissolved in the fuel matrix (Sr, Zr, Nb, Y, La, Ce, Pr, Nd, Pm, and Sm). The content of fission products is continuously changing due to increasing burnup and radioactive decay of isotopes in the fuel.

The chemical composition of metal oxides in the nuclear fuel contributes directly or indirectly to

the fuel's physical properties, such as thermal conductivity and fission gas release. However, the exact composition of oxides in the fuel when the burnup increases remains still to some extent unknown. This paper presents plans for the future experimental research at VTT Technical Research Centre of Finland related to fuel chemical composition analysis focusing on the manufacturing techniques of different fuel samples. First, the sintering process and further sample characterisation is discussed and then previous experiments related to the special uranium and plutonium particle preparation are shortly reviewed.

2 FUEL SINTERING IN CONTROLLED ATMOSPHERE

The oxygen potential of the fuel is defined as the standard Gibbs energy of formation of the oxide per mole of oxygen at a reference pressure in a given temperature. It is related to the oxygen equilibrium partial pressure, through $\Delta G_{O_2} = \Delta G_{O_2}^* + RT \ln(p_{O_2})$ [kJ.mol⁻¹ O₂]. In experimental studies, the standard oxygen potential term $\Delta G_{O_2}^*$ is often neglected as it is a relative quantity and dependent on the choice of the reference state. Generally it is thought that the oxygen potential in the fuel remains constant or increases with the increasing burnup [6]. In every fission event, oxygen is released, and the free oxygen atoms are mainly consumed by reaction with the cladding or with fission products. If the fuel has not enough sinks for oxygen, the oxygen potential (or oxygen partial pressure) increases in the

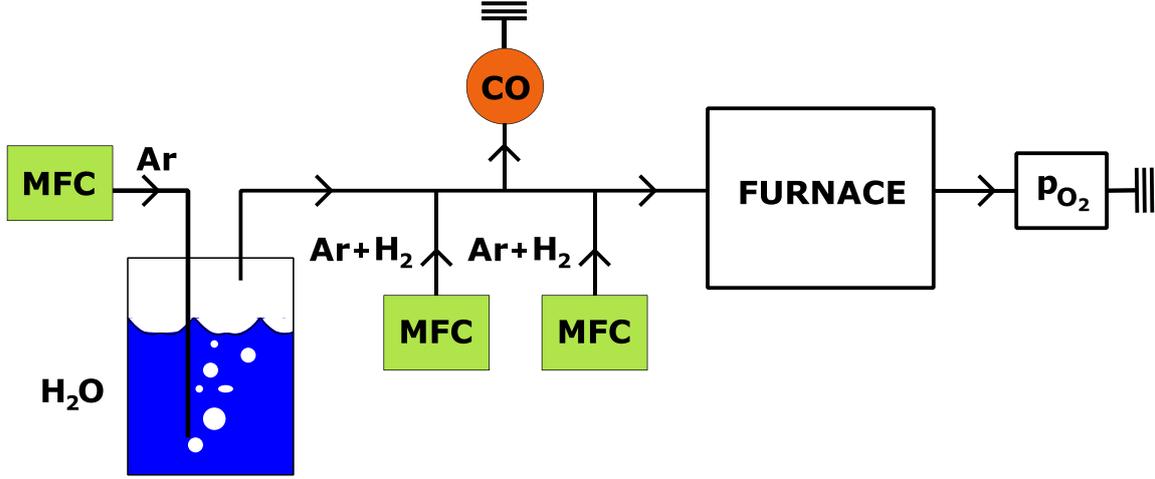


Figure 1. Fuel sintering in controlled atmosphere. The mass flow controllers (MFCs) adjust the flow of different gases to the furnace. Coupling suction through the critical orifice (CO) enables low enough oxygen partial pressure in the furnace. Oxygen partial pressure is measured during the annealing with a sensitive high temperature oxygen sensor.

fuel, signifying, for example, different oxide formation and new phases.

Sintering of a standard UO_2 sample requires in principle only reducing conditions in the furnace. This can be achieved with, for example, H_2 gas. In order to simulate the fuel characteristics as a function of burnup i.e. segregation of fission products and oxide states of fission products, and the fuel itself, the oxygen potential during the sample sintering have to be adjusted [7]. In Fig 1. we propose a controlled flow of steam into the sintering furnace with H_2 to create a sintering atmosphere with a known oxygen partial pressure. First argon is led through the water to get argon saturated with water. Then argon and hydrogen gas mixture is added to the line. In order to get low enough steam partial pressure for the fuel simulations, suction through the critical orifice and additional argon-hydrogen mixture are coupled to the pipeline.

The oxygen partial pressure can be obtained from the known pressures of steam and hydrogen in the furnace through the Gibbs free energy of the water dissociation reaction $\text{H}_2\text{O} \Leftrightarrow \text{H}_2 + 1/2\text{O}_2$. Above $1200\text{ }^\circ\text{C}$ $\Delta G_0(T = 1900\text{ K}) \sim -51\text{ kJ}\cdot\text{mol}^{-1}$ for the water dissociation reaction as calculated by thermochemical data from FACTSage [8]. Using the relationship between the Gibbs energy of reaction and the equilibrium constant, K , we get

$$\Delta G_0 = -RT\ln(K) = -RT\ln\left(\frac{p_{\text{H}_2}p_{\text{O}_2}^{0.5}}{p_{\text{H}_2\text{O}}}\right) \quad (1)$$

$$\rightarrow p_{\text{O}_2} = \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \exp\left(-\frac{\Delta G_0}{RT}\right)\right)^2.$$

However, it is difficult to estimate the final partial pressure of oxygen in the furnace according to equation (1) as it has to be very small to simulate the fuel state (10^{-9} bar). Therefore, the final oxygen partial pressure should be verified with an oxygen sensor sensitive to small oxygen partial pressures [9].

After preparing samples simulating a fuel state, they can be addressed to several separate effect tests to get more insight in the nuclear fuel performance during different kinds of scenarios. Possibilities for the separate effect experiments could be mechanical toughness tests for nuclear fuels containing fission products, fission product structural behaviour in the fuel as a function of oxygen partial pressure, pellet-cladding interaction: chemistry and mechanical studies, and early irradiation state characterization to name a few. Experiments like this together with modern microscopy and material characterisation techniques can bring additional information of the fuel properties. Along with the in-pile tests performed at research reactors, separate effect experiments can offer tools to improve existing nuclear fuel performance codes to a more sophisticated level taking accurately into account the microstructural phenomena in the fuel.

3 FUEL AEROSOL PARTICLE PREPARATION

Experimental research project of VTT on aerosols originating from nuclear fuel was ongoing in

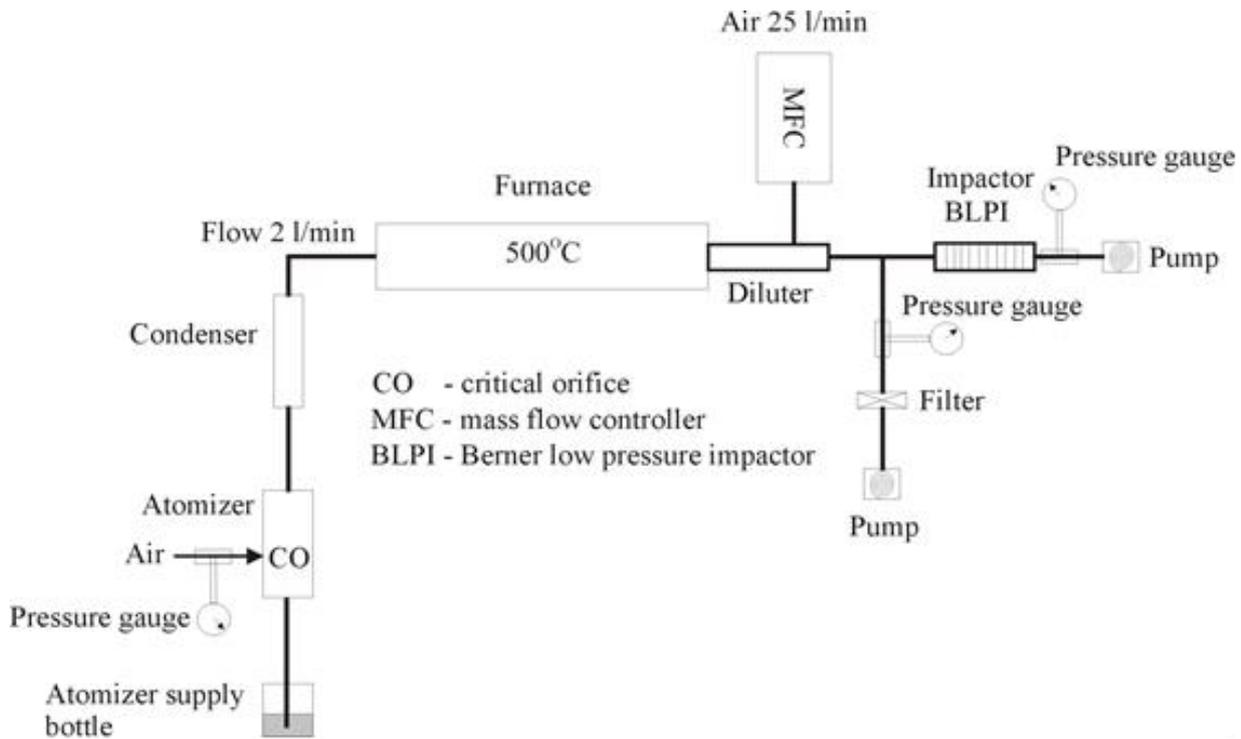


Figure 2. Facility for the production of uranium and plutonium oxides particles [11].

2006 to 2010. The objective of the project was to produce particles of uranium and plutonium oxides as a quality control material for safeguards purposes. The particles were required to be in a size range of 1 μm in diameter.

A method for the generation of particles included three main steps [10, 11]: 1) generation of droplets from U/Pu-nitrate precursor solutions, 2) drying of droplets / thermally decompose U/Pu nitrates / formation of oxides in a furnace and 3) sampling of the generated solid particles and classification of the particles by their aerodynamic diameter using an impactor (see Fig. 2).

The particles were size-classified using Berner Low Pressure Impactor (BLPI), which enabled to separate particles into 11 classes. Inside the impactor, the particles were collected on an aluminium foil attached to each collection stages. A Scanning Electron Microscopy image of the collected uranium oxide (UO_x) particles on the impactor stage 8 is shown in Fig. 3.

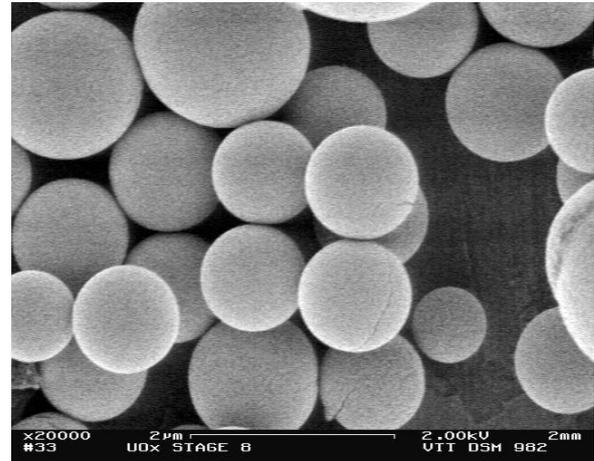


Figure 3. SEM image of the particles collected on the impactor stage 8 [11].

The distribution of particle sizes on stage 8 of BLPI was analysed. The number of particles with a specific diameter was determined from a SEM image. The total amount of particles in the analysis was 224. The resulting number size distribution is presented in Fig. 4. The mode of the distribution is around a particle diameter of 1 μm , thus the produced particles were corresponding to the requested size.

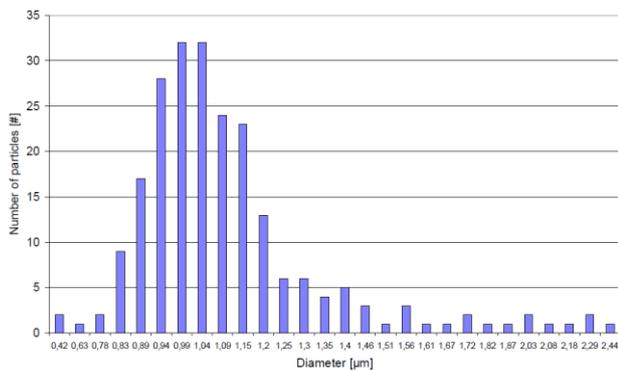


Figure 4. Distribution of particle sizes on stage 8 [11].

The developed method was suitable for the production of both uranium oxides and plutonium oxides particles with the requested particle diameter [12]. The same method could also be used for other purposes related to fuel research in the future.

4 CONCLUSIONS

Often the fuel performance codes are verified against in-pile experiments in which macroscopic phenomena are detected. This leaves, however, the underlying microscopic effects unnoticed. We present here an approach to sinter fuel samples in a furnace with controlled atmosphere to simulate a real fuel pellet with a selected burnup. These samples can be applied in separate effect tests to study microscale phenomena in the fuel, such as fission product clustering, phases and oxidation. Previous small fuel particle preparation project in VTT serves as a basis for the current work.

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