

Fluorination of UO_2 and CeO_2 Under the Atmosphere of HF and H_2

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Abstract: In this study, hydrofluorination of UO_2 and CeO_2 was carried out at 550 °C under the atmosphere of H_2 and HF . Uranium dioxide was used as the main constituent of spent oxide fuel and CeO_2 used as a surrogate of transuranic oxides. Two hydrofluorination methods were presented: one is a direct hydrofluorination method in a molten fluoride salt and the other is that by gas solid reaction. In the former case, a fluoride mixture of 67% LiF -33% BeF_2 was used as carrier molten salt. It was thermodynamically confirmed that UO_2 was converted to UF_4 and CeO_2 to CeF_3 . As results of the experiments, in the case of UO_2 , fluorination took place in both systems. In the case of CeO_2 , however, hydrofluorination in the molten fluoride salt occurred only slightly because of the extremely low solubility of HF and H_2 in the molten fluoride salt. Based on this result, when fluorinating minor actinide oxides in a spent oxide fuel, hydrofluorination by gas solid reaction was predicted to be far superior to that in molten fluoride salt.

Keywords: hydrofluorination, molten salt, gas-solid reaction, uranium dioxide, cerium dioxide

Introduction

Spent nuclear fuel from commercial power plants contains many kinds of long-lived nuclides (minor actinides and fission products) including uranium and plutonium as fissile materials. It was well known that these elements, if released, would present a possible hazard that would have an impact on the environment for a long period of time. Hence, studies on partitioning and transmutation of long-lived nuclides from spent nuclear fuel have been carried out since the 1990's [1,2]. Various methods were introduced for the effective removal of long-lived nuclides from spent nuclear fuel: reprocessing followed either by wet partitioning [3-6] or by pyrochemical partitioning [7,8] using molten salt, and direct pyrochemical partitioning from spent nuclear fuel [9-11]. The pyrochemical method has an advantage over the wet process in the aspects of generation of secondary waste, proliferation, etc. Accordingly, many countries have studied various kinds of pyrochemical processes to treat spent nuclear fuel [7-14]. Among them, pyrochemical partitioning techniques using fluoride method has been

investigated by USA, France and Russia [8,10,12,14].

This study investigated which method is more favorable for the hydrofluorination of oxide: hydrofluorination in molten salt or hydrofluorination by gas-solid reaction. For this purpose, two reactor systems were prepared and results of hydrofluorination were compared. In this study, UO_2 was used as a main constituent of spent oxide fuel and CeO_2 used as a surrogate of transuranic oxides.

Experimental

Reagents

Anhydrous hydrogen fluoride, hydrogen and argon gases were taken directly from cylinders. Uranium dioxide and cerium dioxide are sintered pellets and fused type, respectively, and were used in the form of small pieces 3-5 mm in diameter. Uranium dioxide, which is used as a fuel of pressurized heavy water reactor (PHWR), was supplied by the ammonium uranyl carbonate (AUC) facility at Korea Atomic Energy Research Institute (KAERI) [15]. Cerium dioxide, as well as lithium and beryllium fluorides used as the molten salt carrier, was supplied by Aldrich Co. The used amounts of UO_2 and CeO_2 are about 1 g in every experiment.

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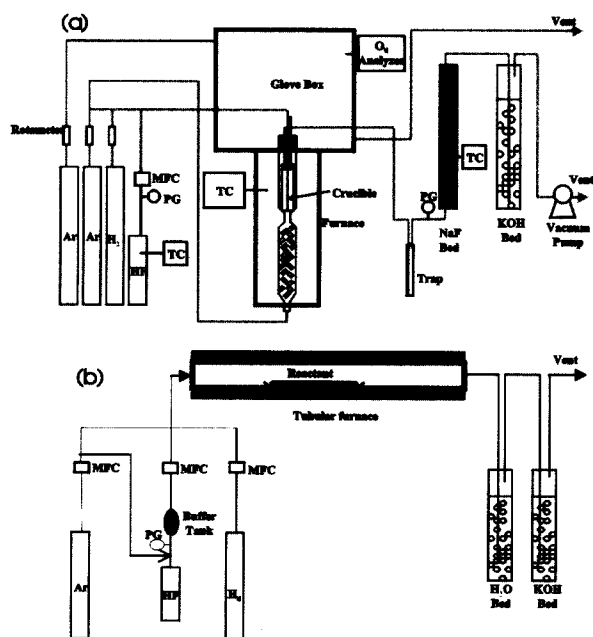


Figure 1. Schematic diagram of fluorination reactor (a: fluorination in the molten fluoride, b: fluorination by the gas-solid reaction).

Equipment and Procedure

Two systems were used for the fluorination of both UO_2 and CeO_2 : hydrofluorination in molten fluorides and hydrofluorination by a gas-solid reaction.

In the case of the hydrofluorination in the molten salt, experimental equipment is shown in Figure 1-(a). The system consists of three parts: the supply of reactant gases, hydrofluorination in the reactor containing the molten fluorides ($67\%\text{LiF}-33\%\text{BeF}_2$) and absorption of off-gases. Materials of the reaction vessel and the tubes are all monels. All the gas lines are $3/8$ inches. Both hydrogen fluoride and hydrogen gases were fed into the reactor controlled by an MFC (mass flow controller). The cylinder with anhydrous hydrogen fluoride was kept at higher than 50°C to prevent the HF from being liquefied during gas supplier (dew point of anhydrous HF: 28°C) and the tubes that the HF gas passed were also heated to 100°C using a line heater. The total gas flow rate was 330 mL/min in all the experiments and the mole ratio of $[\text{HF}]$ to $[\text{H}_2 + \text{HF}]$ be 0.33 . The fluorination reactor consists of two parts: the reactor placed in the down part and upper part was constructed to resemble a glove box for sampling the molten salt. The sampling port was made of an acrylic resin and was always kept under an argon atmosphere to prevent the molten salt from being oxidized with either O_2 or H_2O . The reactor consisted of two cylindrical compartments. The outside reactor having an ID of 15 cm was directly heated by an electrical furnace of 5 kw and the inside reactor having an ID of 3 cm contains molten salts. The heights of both

reactors were 15 cm and 5 cm , respectively. The outside reactor was designed to protect the inside reactor containing the molten salt. The amount of molten salt used in this work was 15 g batch. It was designed so that the gas line was inserted in the molten salt and then a mixture gas ($\text{HF}+\text{H}_2$) was bubbled through the molten salt to fluorinate the oxides. The inside reactor was constantly kept at 550°C because the co-melting point of the mixed fluoride ($67\%\text{LiF}-33\%\text{BeF}_2$) is 495°C . When the temperature of the molten salt approached to 550°C and become stable, the pieces of uranium dioxide or cerium dioxide were fed into the reactor for the fluorination experiment through the glove box. Meantime, the atmosphere of the reactor was kept in the atmosphere of Ar (200 mL/min). After addition of oxides into the reactor, both HF and H_2 were simultaneously fed into the reactor. Off-gases generated during the reaction were completely removed by using a gas absorption system. The off-gas absorption system consists of three parts: a condenser, an absorber and a scrubber. The absorber and scrubber contain a 6 M KOH solution. These equipments were made with acrylic resin and Teflon. As the reaction proceeded, a small amount of molten salt was taken out with a spoon for an analysis of the concentrations of uranium fluoride and cerium fluoride.

In case of fluorination by the gas-solid reaction, the system is identical to the system of molten salt except for the reactor part. The reactor part in the gas-solid reaction consists of a tubular furnace and a gas-solid reactor as shown in Figure 1-(b). The reactor was made with a monel alloy tube 3 inch in diameter (schedule #80) and 70 cm in length. The gaseous reactants were supplied via mass flow controller to the gas-solid reactor. Argon gas was used to dilute the hydrogen fluoride gas in the case of uranium dioxide, whereas hydrogen gas was used for cerium oxide. The flow rate of hydrogen fluoride and argon (hydrogen) gas were 100 and 200 mL/min , respectively. At each run, 1 g of solid reactant containing in a $3 \times 4\text{ cm}$ monel boat was put into the center of the reactor. The temperature of the reactor was slowly increased to the reaction temperature (550°C) in the argon or hydrogen atmosphere. After being kept for more than 1 h at the reaction temperature, hydrogen fluoride gas was fed into the reactor

Analysis

The yields of Fluorination of UO_2 and CeO_2 were measured by both an inductively coupled plasma atomic absorption spectrophotometer (ICP, ISA Jobin-Yvon JY 50P) and the weigh difference method. First, in the case of concentration analysis of U and Ce in the molten fluoride salt, as the reaction proceeded, a small amount of molten fluoride was taken out with a spoon. The resulting molten fluoride salt was crushing by a mortar

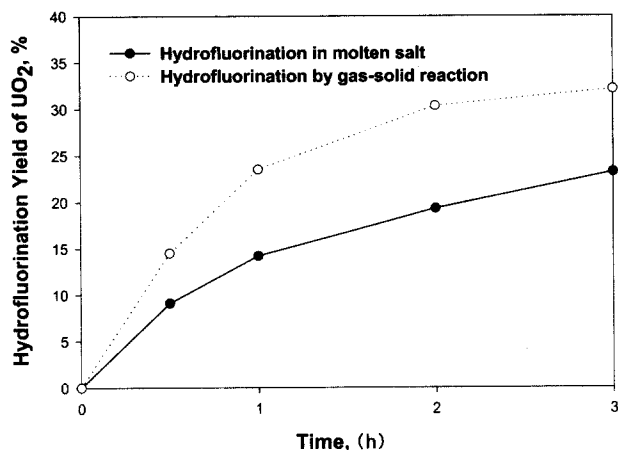


Figure 2. Hydrofluorination of UO_2 with time for 0.323 HF mole fraction at 550°C .

and exactly 0.1 g of this was weighed. Then, the sampled 0.1 g of molten fluoride was completely dissolved into 1 M HNO_3 solution for 2 days. The dissolved solution was measured by ICP for determination of U and Ce concentrations. Second, in the case of gas solid reaction, fluorination yields of UO_2 and CeO_2 were determined by the weigh difference method as follows:

$$\text{Weigh of solid after reaction} = \text{weigh of reactant solid} + \text{weigh of product solid.}$$

Thus, fluorination yield (α) is expressed as follows:

$$\alpha = R/(P-R) \times (A-B)/B$$

where R, P, A, and B represent the molecular weigh of the reactant solid, the molecular weigh of the product solid, the weigh of the solid after fluorination, and the initial weight of the reactant solid, respectively. Compositions of samples taken during fluorination were examined by the X-ray diffraction method to find the existence of intermediate compounds. Results of X-ray diffraction detected no other phase except for UO_2 , UF_4 , CeO_2 and CeF_3 phases.

Results and Discussion

It is well known that UO_2 is converted to UF_4 by HF through the following reaction [16,17]:

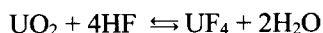


Figure 2 shows the results of the fluorination of UO_2 in the molten salt and by gas solid reaction. As shown in Figure 2, the fluorination rate of UO_2 is far faster in the gas-solid reaction than in the molten salt. In general, UF_4 formed as the product layer is soluble in molten fluoride salt because UF_4 dissolve to 15 mole % in the 67% LiF -33% BeF_2 molten salt at 550°C [18], but acts as diffusion resistance of the reactant gas in the gas-solid

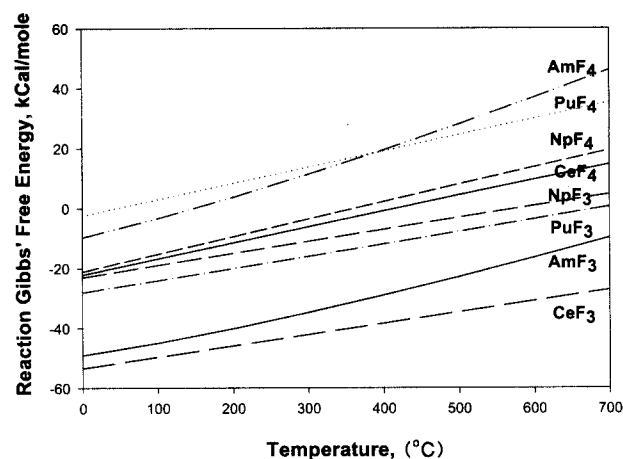


Figure 3. Reaction gibbs' free energy for reaction of oxides with HF to fluorides.

reaction [19]. This implies that the fluorination reaction in molten fluoride salt can progress far faster than that in gas-solid reaction. Nevertheless, the fluorination rate by the gas-solid reaction appeared faster. Such a phenomenon was considered to be due to the solubility of HF in the molten fluoride salt. Shaffer and Watson [20] reported that a solubility of HF is about 20 ppm at 550°C in molten fluoride salt, 67% LiF - 33% BeF_2 . In fact, this value is not sufficient for the fluorination of UO_2 and thus other factors such as pressure should be considered to increase the solubility of HF in the fluoride molten. In this connection, Shaffer, and coworkers [21] showed that HF solubility is increased at a given temperature by pressuring system containing a fluoride molten salt, NaF - ZrF_4 . However, this study did not examine an effect of pressure on hydrofluorination rate of UO_2 in molten fluoride salt. Objective of this study is to show which methods are more effective for hydrofluorination of metal oxide, hydrofluorination in molten salt or in gas-solid reaction under approximately 1 atm. In this respect, it was found that gas-solid reaction was more effective for hydrofluorination of UO_2 . On the other hand, cerium dioxide was selected as the surrogate material of transuranic oxides such as PuO_2 , NpO_2 , AmO_2 . These oxides including CeO_2 are reduced from tetra-valence to tri-valence during fluorination. This can easily be predicted considering Gibbs' free energy for fluorination reactions. In Figure 3, the reaction Gibbs' free energy for the fluorination of oxides into fluorides with temperature was presented using a thermodynamic database [22]. As seen in Figure 3, it is impossible for tetravalent fluorides of minor actinides to be formed above 500°C . In particular, the temperature of 550°C is suitable for stable operation because the eutectic point of the molten fluoride salt used in this study is 495°C . Accordingly, when based on the temperature of 550°C , all of the oxides (CeO_2 , PuO_2 , NpO_2 , AmO_2) are converted

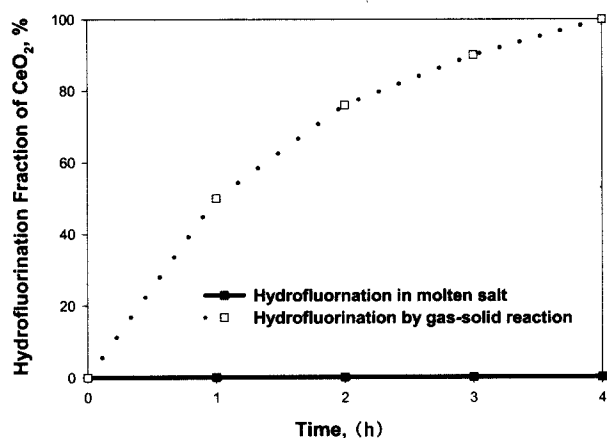


Figure 4. Hydrofluorination of CeO₂ with time for 0.323 HF mole fraction at 550 °C.

to the trivalent fluorides. Therefore, the fluorination reactions can be expressed as follows:

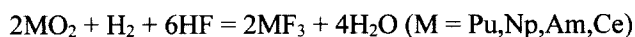


Figure 4 shows the results of the fluorination of CeO₂ in the molten salt and by gas solid reaction. In the case of the gas solid reaction, the fluorination reaction of CeO₂ was completely finished within 4 h. However, surprisingly, in the case of the reaction in the molten fluoride salt, the fluorination reaction of CeO₂ hardly occurred. Unlike the fluorination of UO₂, the fluorination rate of CeO₂ depends on the concentrations of H₂ and HF. Richardson and Malinauskas [23] reported that the solubility of H₂ was 0.2 ppm in the molten salt of 67% LiF-33% BeF₂ (1 atm, 550 °C). Since the solubility of both gases in the molten fluoride salt were very low, it is clear that the fluorination of CeO₂ is impossible in the molten fluoride salt. In particular, as the solubility of H₂ in the molten fluoride salt is extremely low, a fluorination reaction using H₂ should be carried out by a gas-solid reaction, not by the reaction in the molten fluoride salt. In addition, fluorination of the minor actinide oxides by gas solid reaction is possible at a lower temperature than that in molten fluoride salt, because the gas solid reaction does not use molten fluoride salt. Accordingly, when fluorinating spent oxide fuel containing various kinds of elements, a gas-solid reaction is far superior to the reaction in the molten salt.

Conclusions

Results of Hydrofluorination of UO₂ and CeO₂ used as a surrogate material of transuranic elements were as follows;

(1) Since the solubility of H₂ and HF in the molten

fluoride salt were very low, hydrofluorination by gas-solid reaction was far effective than that in molten fluoride salt.

(2) Tetravalent CeO₂ was hydrofluorinated to trivalent CeF₃ with an aid of H₂. This implies that tetravalent transuranic oxides can be also converted to trivalent fluorides as predicted thermodynamically. Thus, spent oxide fuel containing various kinds of radionuclides in the form of metal oxides should be hydrofluorinated under the H₂ and HF atmosphere.

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