Fluorination of UO$_2$ and CeO$_2$ Under the Atmosphere of HF and H$_2$

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Received August 10, 2001; Accepted December 28, 2001

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 UO₂ and CeO₂: 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% LiF-33% BeF₂) and absorption of off-gases. Materials of the reaction vessel and the tubes are all monol. 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 [HF] to [H₂ + 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 O₂ or H₂O. 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 (HF + H₂) 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% LiF-33% BeF₂) 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 H₂ 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, 1g of solid reactant contained in a 3 × 4 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 UO₂ and CeO₂ 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
and exactly 0.1 g of this was weighed. Then, the sampled 0.1 g of molten fluoride was completely dissolved into 1 M HNO₃ 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 UO₂ and CeO₂ were determined by the weigh difference method as follows:

Weigh of solid after reaction = weigh of reactant solid + weigh of product solid.

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

\[ a = \frac{R(P-R) \times (A-B)}{B} \]

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 weigh 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 UO₂, UF₄, CeO₂ and CeF₃ phases.

**Results and Discussion**

It is well known that UO₂ is converted to UF₄ by HF through the following reaction [16,17]:

\[ \text{UO}_2 + 4\text{HF} \rightleftharpoons \text{UF}_4 + 2\text{H}_2\text{O} \]

Figure 2 shows the results of the fluorination of UO₂ in the molten salt and by gas solid reaction. As shown in Figure 2, the fluorination rate of UO₂ is far faster in the gas-solid reaction than in the molten salt. In general, UF₄ formed as the product layer is soluble in molten fluoride salt because UF₄ dissolve to 15 mole % in the 67% LiF-33%BeF₂ molten salt at 550 °C [18], but acts as diffusion resistance of the reactant gas in the gas-solid 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% BeF₂. In fact, this value is not sufficient for the fluorination of UO₂ 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-ZrF₄. However, this study did not examine an effect of pressure on hydrofluorination rate of UO₂ 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 UO₂. On the other hand, cerium dioxide was selected as the surrogate material of transuranic oxides such as PuO₂, NpO₂, AmO₂. These oxides including CeO₂ 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 (CeO₂, PuO₂, NpO₂, AmO₂) are converted...
to the trivalent fluorides. Therefore, the fluorination reactions can be expressed as follows:

$$2\text{MO}_2 + \text{H}_2 + 6\text{HF} = 2\text{MF}_3 + 4\text{H}_2\text{O} \quad (M = \text{Pu}, \text{Np}, \text{Am}, \text{Ce})$$

Figure 4 shows the results of the fluorination of CeO\textsubscript{2} in the molten salt and by gas solid reaction. In the case of the gas solid reaction, the fluorination reaction of CeO\textsubscript{2} was completely finished within 4 h. However, surprisingly, in the case of the reaction in the molten fluoride salt, the fluorination reaction of CeO\textsubscript{2} hardly occurred. Unlike the fluorination of UO\textsubscript{2}, the fluorination rate of CeO\textsubscript{2} depends on the concentrations of H\textsubscript{2} and HF. Richardson and Malinauskas [23] reported that the solubility of H\textsubscript{2} was 0.2 ppm in the molten salt of 67\% LiF-33\% BeF\textsubscript{2} (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 CeO\textsubscript{2} is impossible in the molten fluoride salt. In particular, as the solubility of H\textsubscript{2} in the molten fluoride salt is extremely low, a fluorination reaction using H\textsubscript{2} 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 UO\textsubscript{2} and CeO\textsubscript{2} used as a surrogate material of transuranic elements were as follows;

(1) Since the solubility of H\textsubscript{2} and HF in the molten fluoride salt were very low, hydrofluorination by gas-solid reaction was far more effective than that in molten fluoride salt.

(2) Tetravalent CeO\textsubscript{2} was hydrofluorinated to trivalent CF\textsubscript{3} with an aid of H\textsubscript{2}. 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 H\textsubscript{2} and HF atmosphere.

Acknowledgement

This project has been carried out under the Nuclear R & D program by MOST.

References


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