A STUDY ON THE DEVELOPMENT OF FLUORINATION PROCESS

Sang-Woon Kwon, Eung-Ho Kim, Joon-Bo Shim, Jae-Hyung Yoo and **Byung-Ho Kim**
Korea Atomic Energy Research Institute
Yusong P.O. Box105, Daejeon, 305-600 Korea

Abstract

As the high temperature electrorefining is carried out in the electrolyte medium of molten salt such as metal halide eutectic mixture, metal chlorides or metal fluorides should be prepared before the electrochemical operation. In this study, therefore, fluorination of various metals and metal oxides were studied. Two types of fluorination methods, that is, *fluorination in molten salt and fluorination by gas-solid reaction* were compared. It was found that the latter method was more effective for the fluorination of Zr, CeO_2, Nd_2O_3, and SrO. Noble metals, however, did not react with hydrogen fluoride and thus could be separated from other elements. In parallel with this, various reaction models were compared with the experimental results. As result, the phase boundary controlled-model was found to be suitable for CeO_2, whereas the nucleation and growth-model showed a good simulation for Nd_2O_3 and SrO.

Introduction

There are many kinds of long-lived radionuclides in high-level radioactive wastes including spent nuclear fuels. Generally, the wastes have been stored in an interim site or reposited in a deep geological formation. To reduce the burden of long-term risk during the storage, it was proposed to separate and transmute the long-lived elements into the short lived or stable elements.

Long-lived radionuclides should be partitioned from the high-level wastes or spent fuels to manufacture a fuel for a transmutation reactor. Partitioning processes can be discriminated into two categories; a wet type and a dry type. The dry process has some advantages over the wet process in compactness and reduction of secondary wastes, and reaction kinetics. The dry process is being studied in several countries with a focus on the establishment of proliferation resistant fuel cycle technology. In the dry process, electrochemical methods are used for the partitioning of the long–lived radioactive nuclides.

As the high temperature electrorefining is carried out in the electrolyte medium of molten salt such as metal halide eutectic mixture, metal halides should be prepared before the electrochemical operation. Fluoride molten salt can be manufactured in two ways: *fluorination in molten salt and fluorination by gas-solid reaction.* Spent nuclear fuel contains various kinds of metal and metal oxides such as actinide, rare earth, noble metal, alkaline, and alkaline earth elements. Their fluorination characteristics are expected more or less to be different from each other. Rare earth elements are major components to be partitioned for the manufacture of the transmutation reactor fuel.

In this study, above two fluorination methods were compared and the fluorination behaviour of some metals and metal oxides was investigated.

Experimental

Reagents

Solid reactants were cerium dioxide (CeO_2), neodymium dioxide (Nd_2O_3), strontium oxide (SrO), silver(Ag), and palladium(Pd). All of them were supplied by Aldrich Co. Two types of CeO_2 were used; powders with an average size of about 1.2 μm and pieces with a diameter of about 3 mm. The average sizes of Nd_2O_3 and SrO were about 1.7 and 4.5 μm, respectively. Anhydrous hydrogen fluoride (HF) and high purity (>99.999%) argon/hydrogen were used for gaseous reactants.

Experimental set-up and procedure

Two experimental systems were used to fluorinate metals and metal oxides for the fluorination in molten salt and for the fluorination by a gas-solid reaction. In the case of the fluorination in the molten salt, experimental equipment is shown in Figure 1-a. The system consists of three parts: the supply of reactant gases, fluorination in the reactor containing the molten fluorides (67%LiF-33%BeF_2) and absorption of off-gases. The experimental set-up for the gas-solid reaction is composed of a gas supply system, a gas- solid reactor system, and an off-gas treatment system, as shown in Figure 1-b. The gas-solid reactor system consists of a tubular furnace and a gas-solid reactor where the gas-solid reaction occurs. The reactor was made with a 3" diameter (schedule #80) monel alloy tube and the length of the reactor was 70 cm.

Figure 1. **Experimental systems for the fluorination reactions**
(a) fluorination in molten salt
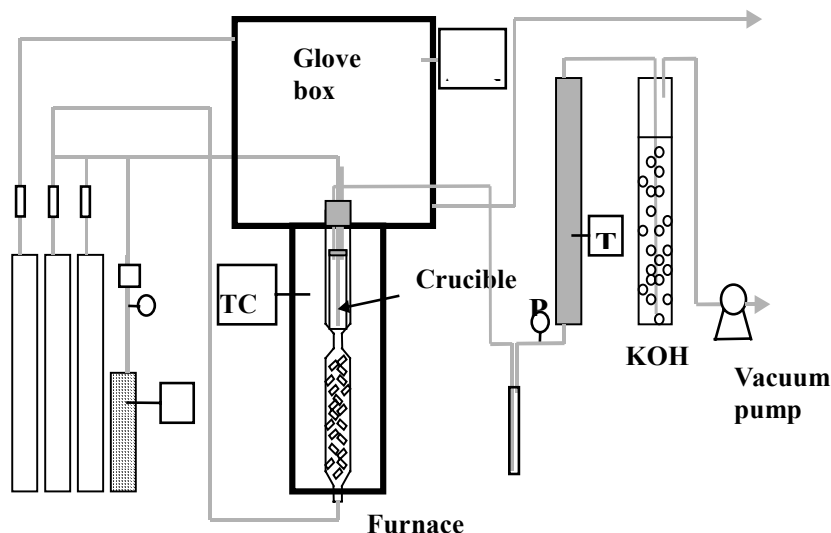
(b) fluorination by gas-solid reaction
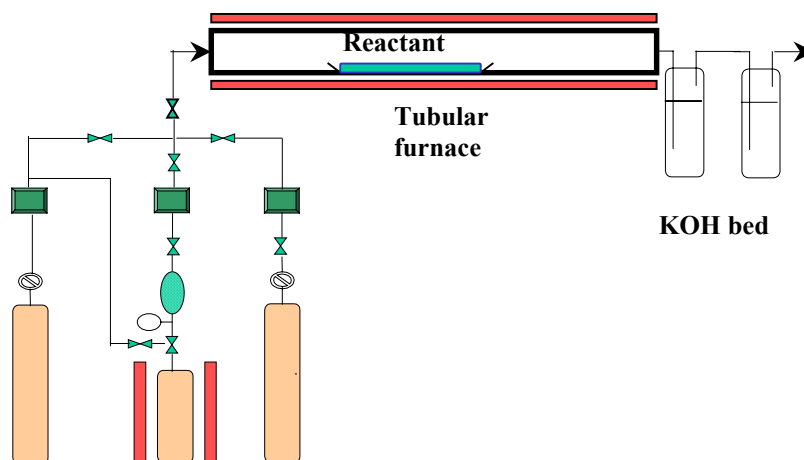
In both systems, the gaseous reactants were supplied via a mass flow controller to the reactor. Liquid hydrogen fluoride was vaporised and fed to a buffer tank to avoid the entrainment of the mist to the mass flow controller. Argon gas was used to dilute the hydrogen fluoride gas except CeO_2 in which hydrogen gas was used. The flowrate of hydrogen fluoride and argon/hydrogen gas were 100 and 200 ml/min, respectively, and the total gas flowrate of the mixed gas was kept at 300 ml in all experiments.

At each run, about 1g of solid reactant contained in a 3×4 cm monel boat was put into the centre of the reactor. Then, the temperature of the reactor was slowly increased to the reaction temperature in the argon or hydrogen atmosphere. After being kept for more than 1 hour at the reaction temperature, hydrogen fluoride gas was fed to the reactor. The reaction temperature was varied from 300 to 500°C. The resulting fluoride was analysed by X-Ray Diffractometry (XRD).

Results and discussion

Comparison of fluorination methods

It was studied experimentally on the fluorination of cerium and uranium oxides for the comparison of the two fluorination methods: fluorination in molten salt and fluorination by gas-solid reaction.

Cerium dioxide was selected as a 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 as expressed with following equation:

$$2MO_2+H_2+6HF = 2MF_3+4H_2O \quad (M=Pu,Np,Am,Ce) \tag{1}$$

Cerium dioxide particles were fluorinated by the above two fluorination methods. In the case of the gas-solid reaction, the fluorination reaction of CeO_2 was completely finished within several hours, whereas the fluorination reaction of CeO_2 hardly occurred in the molten fluoride salt as shown in Figure 2.

Figure 2. **Comparison of fluorination methods**
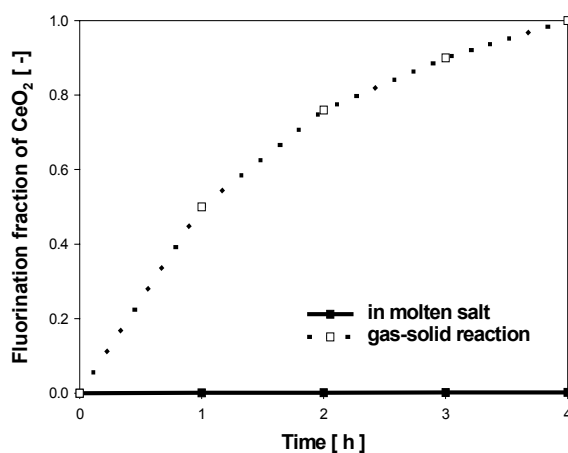
The fluorination rate of UO_2 was far faster in the gas-solid reaction than in the molten salt. In general, UF_4 formed as the product layer is soluble in molten fluoride salt, but acts as diffusion resistance of the reactant gas in the gas-solid reaction. This implies that the fluorination reaction 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.

Fluorination of some metals and metal oxides

Spent nuclear fuel contains various kinds of metals and metal oxides such as actinide, rare earth, noble metal, alkaline, and alkaline earth elements. Their fluorination characteristics are expected more or less to be different from each other. In this study, the gas-solid reaction was applied to investigate the fluorination behaviour of CeO_2, Nd_2O_3, SrO, Ag, and Pd.

It was verified by X-Ray Diffractometry that Nd_2O_3 powders were completely fluorinated by the gas-solid reaction. Reaction between Nd_2O_3 and HF is represented with the following equation:

$$Nd_2O_3+6HF = 2NdF_3+3H_2O \tag{2}$$

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As shown in Figure 3, Nd_2O_3 reacted fast with HF gas. At 300°C, the fluorination reaction was terminated within 15 minutes. The fractional conversion of Nd_2O_3 also increased with the increasing reaction temperature.

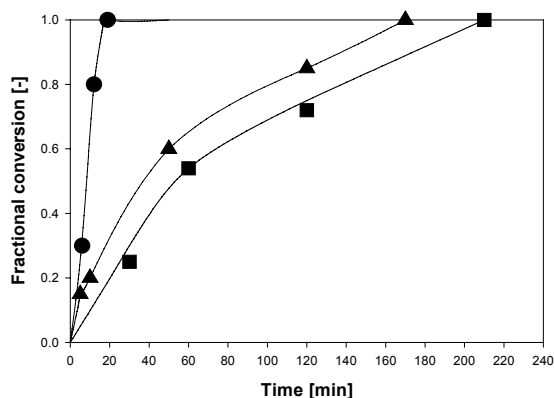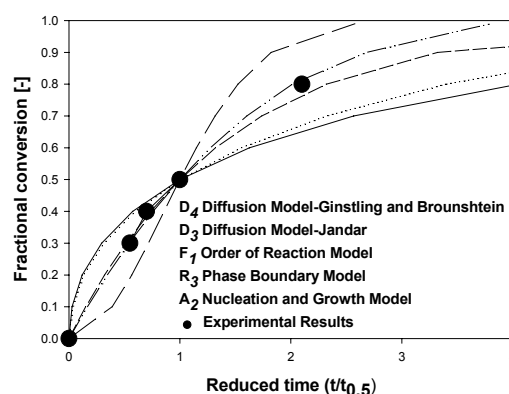Figure 3. **Fluorination fraction of Nd_2O_3**

Figure 4. **Reduced time – conversion curve powders at various temperatures of CeO_2**

SrO was used for the investigation of the fluorination behaviour of the alkaline earth elements. The fluorination reaction proceeded very fast. Strontium oxide powders were converted completely to strontium fluoride within 5 minutes at 300°C.

Noble metals are generally difficult to be fluorinated due to their stability against chemical reaction. It was experimentally verified that the noble metals could not be fluorinated at the conditions of this study. No fluorination reaction was preceded after 5 hours at 500°C and 700°C. Therefore, by using this result, noble metals can be separated from other elements during the dissolution step of the prepared fluorides after fluorination since the noble metals are heavier than the molten salt.

From the above results, it could be concluded that the gas-solid reaction is favourable for the fluorination of the metals and oxides except noble metals.

Reaction models

It is important to investigate the reaction model for the reaction kinetic study. Among the various gas-solid reaction models, the most suitable model can be selected by the comparison between the reduced time-fractional conversion curve and the experimental values. Some widely used gas-solid reaction models are the diffusion-controlled model, phase boundary model, order of reaction model, and nucleation and growth model.

Figure 4 shows the reduced time-conversion curve for the reaction of CeO_2. From the curve, the phase boundary controlled (reaction controlled) model was found to be suitable for the reaction. Similarly, from the reduced time-conversion curve, the nucleation and growth model is found to be most suitable for the fluorination reaction of both Nd_2O_3 and SrO.

Summary

The following conclusions can be drawn from this study on the fluorination of metals and metal oxides:

- Gas-solid reaction method was more effective over the method of fluorination in molten salt to fluorinate the metal and metal oxides.

- Noble metals did not react with HF gas and could be separated from other elements during the dissolution step.

- Among the various gas-solid reaction models, the phase boundary controlled (reaction controlled) model was suitable for the fluorination of CeO_2, whereas the nucleation and growth model was suitable for Nd_2O_3 and SrO.