

## Electrochemical Reduction of $U_3O_8$ Powder and an Oxide Mixture in ACPF

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### 1. Introduction

It is well known that pyroprocessing technology based on a molten salt electrolysis is a promising option that satisfies the requirements of an economic advantage, environmental safety, and high proliferation resistance to treat spent nuclear fuels (SFs).<sup>1-3</sup> An electrochemical reduction or an electrolytic reduction of the spent oxide fuels has been developed to replace a conventional metallothermic reduction between metal oxides and lithium metal dissolved in a LiCl pool, which has some drawbacks such as a process complexity, a solubility limit of a reactant and product, a handling of the chemically active lithium metal and so on.<sup>4</sup>

The Korea Atomic Energy Research Institute (KAERI) has developed an Advanced Spent Fuel Conditioning Process (ACP) on the basis of a pyroprocessing for the purpose of a reduction in the volume, the radiotoxicity and the heat load of spent nuclear fuels (SFs) discharged from commercial pressurized water reactors (PWRs). The final product forms of the ACP are a metallic ingot for a disposal and a pellet of a waste salt.<sup>5,6</sup> The ACP consists of several steps such as a slitting, a voloxidation, an electrolytic reduction, a smelting, a waste salt conditioning process and so on as shown in Fig. 1. Our research group has employed an integrated cathode assembly with a porous magnesia diaphragm as a cathode basket to contain fine  $U_3O_8$  powder and to carry out an electrochemical reduction in the ACPF.

In this work, we will present the reduction characteristics of pure  $U_3O_8$  powder and the oxide mixture.

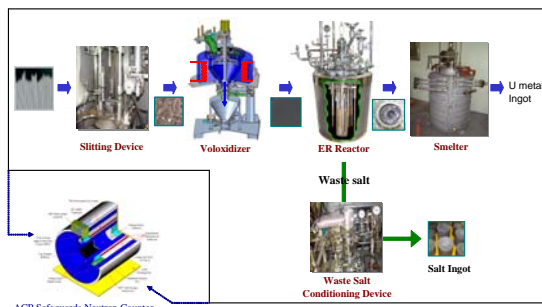


Fig. 1. Process stream of the advanced spent fuel conditioning process (ACP).

### 2. Experimental Section

The electrolysis cell was flushed with high purity argon gas while it was heated to the required temperature. The electrochemical reduction was carried

out at 650 °C under an Ar atmosphere to remove the oxygen gas from the cell, which produced at the anodes. A line for cooling air was installed at a flange to prevent the evolution of a salt fume from the reactor by condensing the salt and to protect the seal materials of the flange. The mixture of oxide powders prepared beforehand and LiCl were introduced into the reactor. The reactor was heated up and maintained at 650 °C. And then  $Li_2O$  was fed into the reactor to reach a concentration of *ca.* 3 wt% of the total weight of the LiCl- $Li_2O$  molten salt. After a complete dissolution of the  $Li_2O$  in LiCl molten salt, the electrolysis cell was operated by applying a desirable current with a potentiostat. When the  $Li_2O$  concentration reached a lower limit ( $\approx$  0.5 wt%) for a stable operation, a certain amount of  $Li_2O$  was additionally introduced to the electrolysis cell. After a completion of the reaction, the molten salt was transported to the salt treatment system and the cathode part was separated from the electrolysis cell. And then the reduced metallic product was taken out of the magnesia membrane. The product was sampled for quantitative and qualitative analyses. The sample was washed and dried in a vacuum oven and it was kept in a glove box under an inert Ar atmosphere to avoid a re-oxidation. The crystalline structure of the metallic product was characterized by an X-ray diffraction (XRD) method and a quantitative analysis of each element was performed by an Induced Coupled Plasma-Atomic Emission Spectrometer (ICP-AES).

### 3. Results and Discussion

An electrochemical reduction technology has been developed as a key unit process of the ACP for the efficient disposal of oxide spent fuels. In the present work, a mixture of metal oxide powders as a surrogate of a spent oxide fuel was used as a feed material to investigate the effect of the fission products on the reduction of uranium oxide and the diffusion behavior of the salt-soluble fission products. Uranium oxide was successfully reduced at 650 °C but the reduction degree and the current efficiency decreased due to the hindrance effect of the unreduced metal oxide, compared to those in the electrochemical reduction of pure  $U_3O_8$ . The diffusion behaviors of Cs, Sr and Ba as high heat-generating FPs from a cathode basket to an electrolyte phase have been investigated during an electrochemical reduction. A small amount of salt was taken from the electrolyte bulk phase during the run to determine the concentration of each element by ICP-AES. The concentration of those three elements increases with the reaction time. Thus, this result

indicates that the alkali and the alkaline earth metal such as Cs, Sr and Ba were diffused into and accumulated in the salt phase from the oxide mixture in the cathode basket as predicted from a thermodynamic consideration. However, the diffusion rate of the oxygen ions, which has a strong effect on a scale-up and the reduction conversion of FPs, were very slow when porous magnesia was used as a cathode basket.

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