ABSTRACT

The Advanced Spent Fuel Conditioning Process (ACP) has been under development at Korea Atomic Energy Research Institute (KAERI) since 1997. The concept is to convert spent oxide fuel into metallic form and to remove high heat-load fission products such as Cs and Sr from the spent fuel. The heat power, volume, and radioactivity of spent fuel can decrease by a factor of a quarter via this process. For the realization of ACP, a concept of electrochemical reduction of spent oxide fuel in Li2O-LiCl molten salt was proposed and several cold tests using fresh uranium oxides have been carried out. In this new electrochemical reduction process, electrolysis of Li2O and reduction of uranium oxide are taking place simultaneously at the cathode part of electrolysis cell. The conversion of uranium oxide to uranium metal can reach more than 99% ensuring the feasibility of this process.

INTRODUCTION

In Korea, spent fuels, the natural by-product from electricity generation by nuclear energy systems, will be stored at each nuclear power plant site until interim storage facilities are constructed in 2016. So, Korea’s demand for advanced spent fuel treatment service has continuously increased with the expansion of its nuclear power capacity and the accumulation of spent fuels. The worldwide trend for the management of spent fuel is to develop spent fuel conditioning technologies that enhance environmental friendliness, cost viability, proliferation resistance, and have the potential to maximize the use of natural resources. A globally recognized approach that meet these criteria is the “Dirty Fuel and Clean Waste” concept, which involves the effective management of spent fuel through the development and application of innovative nuclear technologies for electricity generation and the subsequent destruction of long-lived nuclides of the transuranic elements by transmutation. A prominent variation on this concept involves adopting the dry processing technology for conditioning spent fuel and immobilizing the radioactive constituents for eventual deep geological disposal (1-3).

A new approach to spent fuel treatment technology based on the pyrochemical processing has been proposed and developed at KAERI since 1997 (4). The concept is to convert spent oxide fuel into metallic form and to remove high heat-load fission products such as Cs and Sr from the spent fuel. The generalized flowsheet of ACP is shown in Fig. 1. The PWR spent fuel assemblies are disassembled and the spent fuel rods are chopped. The chopped spent fuel that consists mainly of UO2 pellets is put into the voloxidation unit. Pulverization of spent fuel pellets by oxidation under high temperature air environment and separation of spent fuel from zircaloy cladding are conducted. Most of volatile fission products are removed during this voloxidation
operation. The oxidized spent fuel powders are transferred to reduction unit and react with Li in LiCl molten salt at 650 °C. Metal powders, chlorides, complex oxides are produced depending on their relative stability in Li/LiCl molten salt system. The metallized spent fuel and complex oxide compounds are separated from the salt phase by filtration and transferred to the casting unit for the manufacture of spent fuel rods to be packed in the storage canister. The remaining salt is transferred to the Li recovery unit and regenerated by electrowinning to convert the Li2O to Li. Both Li and LiCl are recycled to the metallization unit.

The criteria for the main unit operations were as follows:
1) 20 kgHM of the PWR spent fuel is introduced into the process. Voloxidation is carried out under air atmosphere at 500 °C to produce oxidized spent fuel powders. All the volatile fission products can be removed in the disassembling and the voloxidation operations.
2) 15% excess Li is put into the reduction step and the final concentration of Li2O in the LiCl salt is 3.2 wt%. The amount of LiCl salt contained in the filtered metal powders is 2.3% and this salt is recycled to the Li recovery operation.
3) In the electrochemical Li recovery step, 95% Li is recovered and recycled to the reduction step with LiCl.

Thermal power and radioactivity of the reduced metal were calculated by using ORIGEN2 computer code. The radioactivity of the reduced metal ingot is ascribed mostly to Pu. Most of thermal power is produced from Pu, Am and Cm. Mass, radioactivity, and thermal power of the reduced metal which is converted from the 20 kgHM of oxide spent fuel are 19.76 kgHM, 1,764 Ci, and 4.7 W respectively. These quantities of radioactivity and thermal power are 24.27% and 24.24% respectively of those of spent fuel oxide.

However, the conventional Li reduction process for the reduction of oxide fuel powder demands...
a highly pure inert gas atmosphere inside hot cells to prevent unwanted Li oxidation and explosion. Such a handling problem of chemically active Li in hot cell environments makes the reduction process complicated and expensive. Actually, various issues have been identified from handling and recovery of metallic Li during the mock-up tests of the ACP.

**CONCEPT OF ELECTROCHEMICAL REDUCTION TECHNOLOGY**

In the conventional Li process, the reactant spent fuel oxide is coated with lithium oxide, thus shutting the reaction completely if the reaction could not be promoted by fluxing away the product oxide by LiCl molten salt. However, the solubility of Li₂O in 650 °C LiCl is only 8.7% and the reoxidation of transuranic elements occurs above the concentration of 5.1% Li₂O in LiCl molten salt. So, large amount of LiCl molten salt is needed for the conventional Li process. Also, the density difference between Li (d 0.534) and UO₂ (d 10.97), U₃O₈ (d 8.30) demands vigorous stirring. So, these problems with handling of chemically active Li give rise to severe process limitations and stringent reaction system design requirements.

Recently, Chen et al. reported direct electrochemical reduction of TiO₂ to Ti in molten CaCl₂ salt. The feasibility and applicability of this electrochemical reduction technology for spent oxide fuel treatment in molten LiCl salt was studied in this study. As calculated in table 1 using literature data (7), the reduction of uranium oxides to U metal is thermodynamically easier than that of Li₂O. However, the semiconductive properties of uranium oxides make their direct reduction impossible as experimentally verified using linear sweep voltammetry method. Since the standard reduction potentials for Li₂O and LiCl are –2.47 V and –3.46 V, respectively, at 650 °C, there is an operating window which allows for the selective decomposition of Li₂O. So, new electrochemical reduction technology based on the catalytic reaction of Li₂O in molten Li₂O-LiCl salt system has been proposed and studied.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>ΔG_f (kcal/mol)</th>
<th>Reduction Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O(s) → 2Li(s) + 1/2O₂(g)</td>
<td>114.0</td>
<td>-2.47</td>
</tr>
<tr>
<td>2Li₂O(s) + C(s) → 4Li(s) + CO₂(g)</td>
<td>133.5</td>
<td>-1.45</td>
</tr>
<tr>
<td>LiCl(s) → Li(s) + 1/2Cl₂(g)</td>
<td>79.8</td>
<td>-3.46</td>
</tr>
<tr>
<td>UO₂(s) → U(s) + O₂(g)</td>
<td>221.1</td>
<td>-2.40</td>
</tr>
<tr>
<td>U₃O₈(s) → 3UO₂(s) + O₂(g)</td>
<td>44.4</td>
<td>-0.48</td>
</tr>
</tbody>
</table>

This electrochemical reduction technology is based on the integration of a Li reduction process and subsequent electrowinning of Li₂O into one electrolytic reduction step where electrolysis of Li₂O and reduction of spent oxide fuel are taking place simultaneously at the cathode part of electrolysis cell. In this case, both the oxide and the reduced metal are insoluble in molten LiCl, thus enabling the reduction and recovery of spent fuel. Li₂O instead of active Li is a feeding material in this concept. So, the safety of the ACP can be improved by this direct electrolytic reduction technology. Li produced via Li₂O electrolysis at cathode part reacts with spent oxide fuel resulting in the formation of Li⁺ and O²⁻ which originates from spent oxide fuel. The O²⁻ ion is directed to anode by potential and concentration gradient and eventually evolved as oxygen gas. The resultant Li⁺ may be rereduced and this regenerated Li can be used for the further reduction
of spent oxide fuel. This catalytic behavior of Li\(^+\) via oxidation and reduction cycle can decrease the amount of Li\(_2\)O in the molten LiCl salt. So, relatively small amount of LiCl is needed in this electrochemical reduction system compared to that in conventional Li process. Consequently, the reduction of system size can be achieved because the amount of LiCl is a ruling factor of reactor volume. In addition, the reoxidation of transuranic elements is prevented because the Li\(_2\)O concentration could not exceed the initial feeding value in this reduction system. The schematic diagram of electrolytic reduction system via catalytic (EC) reaction is shown in Fig. 3.

RESULTS OF FRESH TESTS USING URANIUM OXIDES

The chopped PWR spent fuel consists mainly of UO\(_2\) pellets. So, the applicability of electrolytic reduction technology to metallization of uranium oxides should be conducted to verify the feasibility of this reduction process. Fresh tests using U\(_3\)O\(_8\) powder have been carried out in this study.

The reaction system consisted of resistive heater, k-type thermocouple, dual type reactor, cathode, anode, a reference electrode, Ar gas and reactants supplying system, and oxygen detector. Alumina crucible was used to insulate the inner reactor from the outer reactor. The structural material for inner reactor was SUS 304. A cooling jacket was installed at the upper part of the reactor to prevent discharge of molten salt vapor. The cathode part of electrolysis cell consisted of a SUS conductor, U\(_3\)O\(_8\) powder, and non-conductive porous magnesia membrane as a container for uranium oxide. U\(_3\)O\(_8\) powder was filled between the SUS conductor and the magnesia membrane and its tap density was 2.8 ~ 2.9 g/cm\(^3\). Anode and a quasi reference electrode were made of Pt tube (outer diameter 8 mm) and Pt rod (outer diameter 3 mm), respectively. Reactivity test of electrochemical reduction process was performed in 650 °C, Li\(_2\)O-LiCl molten
salt system. Ar gas flow was applied to maintain an inert atmosphere in the reactor. Uranium oxide (U₃O₈ powder) and LiCl (Alpa, 99%) were supplied to the inner reactor at room temperature. Li₂O (Cerac, 99.5%) was treated carefully to prevent the formation of LiOH and fed to the inner reactor at 650 °C. During the reduction reaction, the variation of Li₂O concentration in molten salt was measured by titration method using a phenolphthalein indicator and 0.1 N HCl. After the electrochemical reduction reaction, the cathode part of electrolysis cell was cooled to room temperature in inert atmosphere to prevent the reoxidation of uranium metal and then separated from the reaction system. The residual molten salt in the product was washed away using distilled water and methanol, and then the product was vacuum dried. The conversion of uranium oxide to uranium metal was determined by thermogravimetry analysis.

In this electrolytic reduction concept, U₃O₈ powder is a constituent unit of cathode part. A significant issue for designing of a cathode is to find an innovative concept to contain oxide powder effectively. The containment structure should be porous, and stable against thermal and mechanical shocks. Porous Magnesia membrane was adopted as a container for U₃O₈ powder in this study. Li⁺ in molten salt is attracted to cathode through a porous magnesia membrane and reduced and deposited on uranium oxide for a chemical reaction with it to form uranium metal. O²⁻ comes out through the porous magnesia membrane and discharges at the anode as oxygen gas. Chronopotentiometry method was adopted to measure potential variation and reduction yield. The cell voltage of electrolytic reduction reaction was 2.7-2.8 V. When the oxide content of the molten salt was nearly depleted due to complete metallization of U₃O₈ and Li₂O, the anode voltage increased rapidly because of concentration polarization. The electrochemical reduction reaction was stopped at that point. The reduction yield of U₃O₈ to U metal reached more than 99% as shown in Table 2 when the loaded currents were lower than 1.5 A. These results indicate the possibility of application of electrochemical reduction technology to ACP of KAERI. However, when 2.0 A was applied to reduce U₃O₈ powder to U metal, only 93.0% reduction yield was observed implying relatively lower rate of chemical reaction compared to that of electron transfer in that case.

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>0.8</th>
<th>1.2</th>
<th>1.5</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction Yield (%)</td>
<td>~100</td>
<td>99.2</td>
<td>~100</td>
<td>93.0</td>
</tr>
</tbody>
</table>
The variation of Li$_2$O concentration in molten salt was measured. As shown in Fig. 3, the amount of Li$_2$O in LiCl molten salt decreased according to Faraday’s law of electrolysis at the initial stage of the reduction reaction suggesting that the electrochemical reduction reaction proceeds via electrolysis of Li$_2$O and then chemical reaction between Li and U$_3$O$_8$ powder. As the reaction proceeded, the concentration of Li$_2$O in LiCl came to steady value. In this stage, the rate of O$^{2-}$ formation from chemical reaction is similar to that of O$^{2-}$ depletion at anode. In this experiment, the chronopotentiometry was conducted by using 40 g of U$_3$O$_8$ and 7.87 g of Li$_2$O. For the reduction of 40 g of U$_3$O$_8$ to U metal, 0.76 mol of Li is needed. However, 7.87 g of Li$_2$O corresponds to only 0.53 mol of Li. So, the complete reduction of U$_3$O$_8$ to U metal proves the catalytic behavior Li$^+$ via oxidation and reduction cycle.

**SUMMARY**

A concept of electrochemical reduction of spent oxide fuel in Li$_2$O-LiCl molten salt was experimentally verified using fresh U$_3$O$_8$ powder. In this new electrochemical reduction process, electrolysis of Li$_2$O and reduction of spent oxide fuel are taking place simultaneously at the cathode part of electrolysis cell. Li produced via Li$_2$O electrolysis reacts with spent oxide fuel resulting in the formation of Li$^+$ and O$^{2-}$ which originates from spent oxide fuel. The resultant Li$^+$ is rereduced and the regenerated Li is used for further reduction of spent oxide fuel. The cell potential of electrolytic reduction reaction was 2.7-2.8 V and the conversion of uranium oxide to uranium metal can reach more than 99% in this electrolytic reduction system.

**ACKNOWLEDGEMENT**

This work was funded by the National Mid- and Long-term Atomic Energy R&D Program.
REFERENCES