Development Status of Oxide Reduction Process for Pyroprocessing

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1. Introduction

The problem of spent fuel has still been unsolved in nuclear-power countries. The recycling of spent fuel can be a solution because approximately 96–97% of its components are recyclable materials; the spent fuel contains uranium of 94–96% (235: approx. 1%) and plutonium of 1–1.5% [1,2]. Hence, the recycling technologies have been intensively developed. Pyroprocessing is one of the recycling technologies; its aim is to electrochemically recover U and transuranic elements in the spent oxide fuel in high-temperature molten salts as electrolytes and recycle them as metal fuels for fast nuclear reactors. Through pyroprocessing non-recyclable fission products are separated from the spent oxide fuel and finally disposed of, which leads to reduction of their waste volumes [3-5].
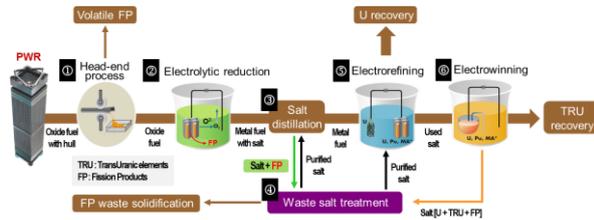

Fig. 1. Pyroprocessing flow diagram.

Fig. 1 shows a flow diagram of the pyroprocessing method developed by Korea Atomic Energy Research Institute (KAERI), which consists of a head-end process, electrochemical processes (electrolytic reduction, electrorefining, and electrowinning), and a waste-salt-treatment process. In the head-end process (① in Fig. 1), the spent oxide fuel is first separated from the hulls, and heat treated to have a proper size and density for the subsequent electrochemical processes. While the spent oxide fuel is heated, volatile and semi-volatile fission products are exhausted from the fuel to gas phase. Secondly, the spent-oxide fuel prepared through the head-end process is electrochemically reduced to a metallic form in molten Li_2O-LiCl salt at 650 °C through electrolytic reduction (② in Fig. 1); this is also known as "oxide reduction" (OR). The reaction of the OR is a kind of the decomposition reaction of MO_2 to M and O_2. In addition, the fission products such as Sr are dissolved in the salt to form their chlorides. The salt remaining in the metallic product is then removed by distillation (SD, ③ in Fig. 1) at a high temperautre (>800 °C) under vacuum, which is aimed to prevent changes in the eutectic composition of the electrorefining salt (LiCl–KCl at 500 °C) by the remaining Li_2O-LiCl salt. Then, the distilled salt is treated for recycling salt and separating the fission products (④ in Fig. 1). Finally, U and transuranic elements (TRU) are recovered during electrorefining (⑤ in Fig. 1) and electrowinning (⑥ in Fig. 1), respectively [6,7].
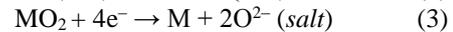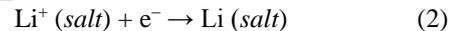
2. Oxide Reduction Process

Before the OR process was invented, a chemical reduction process using the lithium (Li) as a reductant (also called Li reduction process) in molten LiCl at 650 °C dissolved had been first developed by Argonne National Laboratory (ANL) to reduce actinide oxides into their metallic forms [8]. During the Li reduction process, the following reaction occurs:

$$4Li + MO_2 \rightarrow M + 2Li_2O \qquad (1)$$
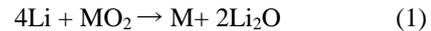
where M denotes a metal. However, the Li reduction process had some drawbacks such as process complexity, solubility limit of the reactant and product, and handling of the chemically active lithium metal [9].

Due to these problems, the electrochemical reduction method has been adopted for the reduction of the spent oxide fuel since a pioneer study by Chen et al. in the early 2000s [10]. Li_2O (typically 1.0 wt%)–LiCl salt, as described by the following reactions as well as the reaction 1 [11]:

Cathode:
$$Li^+ (salt) + e^- \rightarrow Li (salt) \qquad (2)$$
$$MO_2 + 4e^- \rightarrow M + 2O^{2-} (salt) \qquad (3)$$

Li_2O, which is produced by reaction (2) in molten LiCl, dissociates into Li^+ and O^{2-}:
$$Li_2O \rightarrow 2Li^+ + O^{2-} \qquad (4)$$

Platinum anode:
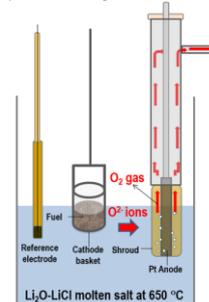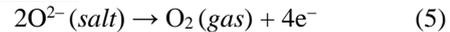$$2O^{2-} (salt) \rightarrow O_2 (gas) + 4e^- \qquad (5)$$

Fig. 2. Schematic diagram of OR cell containing salt, cathode, anode, and reference electrode [11].

3. Development Status of Oxide Reduction Process

3.1. Korea

KAERI conducted experiments using U_3O_8 as a feed and a magnesia basket as a cathode material at the beginning of OR development (before 2008) [12]. The reduction of U_3O_8 into metallic U was successful. However, after frequent breakage of the magnesia basket, the material of the cathode was changed to stainless steel to succeed in OR in a bench-scale experiment [13], and then concentrated on the scale up of the OR apparatus. Based on the experimental results obtained from the bench scale experiments, the influence of the components of the OR apparatus on its efficiency of the process has been continuously studied. As a result of these efforts, KAERI succeeded in the demonstration of the OR using scaled-up apparatus (0.6 kg (Fig.3 [14], 17 kg [15] and 50 kg [6]).
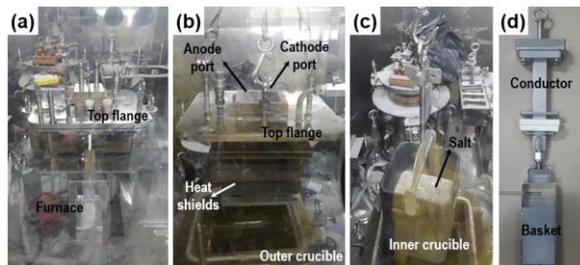

Fig. 3. Photographs of: (a) outer view of the OR apparatus, (b) top flange and outer crucible, (c) inner crucible containing OR salt, and (d) the cathode assembly of the basket and conductor [14].

In addition, efforts have been made to explore stable materials and operating conditions that can endure long-time operation of the OR process [14]. In recent years, it has also achieved significant results in the development of alternative anode that can replace expensive platinum [16].

3.2. Japan

In 2012, Central Research Institute of Electric Power Industry (CRIEPI) has reported a series of pyroprocessing tests involving head-end process, OR, and electrorefining processes using ~ 100 g of simulated spent oxide fuel [17]. Then, in 2013, they also reported a series of pyroprocessing tests using equipment of semi-industrial design. The scale of the OR equipment for the test was 5 kg/batch. It is notable that the equipment used in their study was aimed to operate pyrochemical treatment in a hot cell suitable for 1 ton HM/yr throughput [18].

In 2015, a feasibility study on the pyrochemical treatment of damaged fuel debris (corium) generated by severe accidents at light water reactors was reported. It was experimentally demonstrated that uranium in synthetic corium specimens of $(U,Pu,Zr)O_2$ could be reduced [19].

3.3. U.S.

Idaho National Laboratory (INL) reported separation and recovery of uranium and group actinide products from both irradiated fast reactor MOX Fuel [20] and spent light water reactor fuel [21] via OR (50 g/batch) and electrorefining. The extent of metal oxide conversion in the posttest fuel was 99.7% conversion of uranium oxide to metal. They observed that fission products partitioned into the salt phase with very low concentrations of U and Pu detected.

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