

Review

Electrochemical processing of spent nuclear fuels: An overview of oxide reduction in pyroprocessing technology

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Received 28 August 2015; accepted 30 October 2015

Available online 24 December 2015

Abstract

The electrochemical reduction process has been used to reduce spent oxide fuel to a metallic form using pyroprocessing technology for a closed fuel cycle in combination with a metal-fuel fast reactor. In the electrochemical reduction process, oxides fuels are loaded at the cathode basket in molten Li_2O – LiCl salt and electrochemically reduced to the metal form. Various approaches based on thermodynamic calculations and experimental studies have been used to understand the electrode reaction and efficiently treat spent fuels. The factors that affect the speed of the electrochemical reduction have been determined to optimize the process and scale-up the electrolysis cell. In addition, demonstrations of the integrated series of processes (electrorefining and salt distillation) with the electrochemical reduction have been conducted to realize the oxide fuel cycle. This overview provides insight into the current status of and issues related to the electrochemical processing of spent nuclear fuels.

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Keywords: Pyroprocessing; Electrochemical reduction; Electrorefining; Molten salt; Spent oxide fuel

1. Introduction

Nuclear energy is one of the global energy sources that can be used to meet the growing energy demand while avoiding CO_2 emissions into the environment. However, the accumulation of the spent fuel from nuclear power plants is a major hurdle in the use of nuclear energy. In Korea, about 700 t of spent fuel is produced from nuclear power plants every year. The total amount of spent fuel at the end of this century is anticipated to be more than 100,000 t [1]. Hence, recycling this spent fuel is part of the central focus of nuclear energy technology.

Pyroprocessing is a high-temperature electrochemical fuel processing technology for recycling the spent fuel into metal fuel for a nuclear fast reactor. In other words, pyroprocessing treats spent oxide fuels from light water reactors and produces metal fuels, which will

be irradiated in a nuclear fast reactor. The recycling of the fuel is expected to increase the uranium usage efficiency and decrease both the radiotoxicity and amount of the radioactive waste generated [2–9]. The process flow diagram of pyroprocessing in Korea consists of head-end processes, electrochemical processes (electrochemical reduction, electro-refining, and electro-winning), and waste treatment processes, as shown in Fig. 1 [10]. The purpose of the head-end processes, which consist of decladding, voloxidation, and oxide feed preparation, is to convert a spent fuel assembly into a suitable feed material that can be used in the electrochemical reduction process. In the voloxidation process, the dense oxide pellet discharged from the cladding hull is oxidized and pulverized to the powder form of U_3O_8 at a higher temperature than 500 °C under air atmosphere. The oxide feed with proper porosity and shape for the electrochemical processing is prepared with the voloxidized U_3O_8 powder.

Then, in the electrochemical reduction process (or oxide reduction process) based on a molten Li_2O – LiCl salt, the spent oxide fuel is reduced to supply metal feed to the electro-refining process. Additionally, high-heat-load fission products are dissolved into the molten Li_2O – LiCl salt, thus decreasing the heat load of the spent fuel.

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Peer review under responsibility of Chinese Materials Research Society.

In electro-refining, pure uranium from the fuel is recovered in a molten LiCl–KCl eutectic salt, while uranium, transuranic elements, and rare earth elements are dissolved into the LiCl–KCl salt. The electrowinning process is used to recover the uranium and transuranic elements from the remaining salt after electrorefining [10–12].

This overview focuses on the electrochemical reduction process, which is the first step of the electrochemical fuel processing; it is organized as follows. First, the basic principles and related reports on the electrode reactions (cathode and anode) are reviewed. Second, the factors that affect the speed of the electrochemical reduction are discussed, which are required for the process optimization. Finally, a demonstration of the integrated series of processes (electrorefining and salt distillation) with the electrochemical reduction is introduced.

2. Electrode reactions of spent fuel in electrochemical reduction process

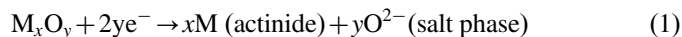
2.1. Cathode reactions

The electrochemical reduction process has been used to reduce the spent oxide fuel to the metallic form using pyroprocessing technology [13–16]. Conventionally, metal-thermic reduction using lithium metal dissolved in a LiCl pool as a reductant (the so-called lithium reduction process) was used to reduce the spent oxide fuel, which had some drawbacks such as process complexity, solubility limit of the reactant and product, and handling of the chemically active lithium metal [17,18]. To tackle these problems, the electrochemical reduction method has been used for the reduction of the spent oxide fuel since a pioneer study by Chen et al. in the early 2000s [19]. This novel electrochemical reduction technology, so-called FFC-Cambridge process or electro-deoxidation process, made it possible to convert metal oxides directly into their parent metals by solid state electrolysis in a molten salt medium [20,21]. Although both the electrochemical reduction and the electro-deoxidation terms have been widely used in the literature [20,22,23], the electrochemical reduction has been preferred term in the nuclear field. Various advantages of electrochemical reduction have been reported for fuel processing [18,24,25]: (1) it involves no troublesome handling of lithium metal; (2) the concentration of oxide ions in the electrolyte medium can be maintained at a low level, which is thermodynamically favorable for the reduction of actinide and lanthanide elements; and (3) the process is much simpler and easier than the metal-thermic reduction process.

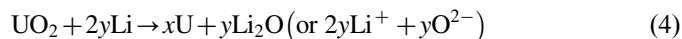
Extensive studies on the electrochemical reduction of uranium oxide, mixed oxide (MOX) fuel, and spent oxide fuels have been performed not only to measure the extent of the reduction of each element in the spent fuel or simulated fuel (SIMFUEL) [17,26–28], but also to understand the cathodic reaction pathways [13,24,29–31]. Although several molten salt systems have been tested for the reduction of oxide fuel [30–32], it seems that molten LiCl is the most promising option for the electrochemical reduction process for the following reasons: (1) the operating temperature can be lowered with LiCl salt because of its melting point, 605 °C

(e.g. melting point of CaCl₂, 772 °C); (2) a high current efficiency can be achieved with LiCl [30]; (3) O²⁻ has high solubility; and (4) in terms of its compatibility with the next electrochemical process, where the eutectic salt of LiCl–KCl is employed as the electrolyte, LiCl might be more suitable than any other salt.

In the electrochemical reduction process, oxides fuels are loaded at the cathode basket in molten LiCl, and some amount of Li₂O is added to speed up the reduction rate and prevent the anodic dissolution of the platinum anode by providing oxide ions to the salt [28]. The concentration of Li₂O added to LiCl is usually less than 3 wt% because a reaction between the produced uranium metal and Li₂O is not feasible even at such high concentrations. However, a concentration of 1 wt% of Li₂O is usually used by considering the corrosion resistance and degree of reduction in other oxides such as Pu₂O₃ and most of the rare earth oxides that occur in the spent fuel [33,34]. Based on the strategy of the head-end process, the spent oxide fuel can be loaded in various physical forms such as rod-cut, crushed particles, powder, and porous pellets [25,26,28,35,36], along with different oxidation states of uranium oxide, UO₂ or U₃O₈ [13,37]. The overall cathode reaction for the oxide fuel, mainly actinide oxides, is as follows:



Because uranium is a major element of the spent fuel, it is important to understand the electrochemical behavior of uranium oxide as a representative of actinide elements. When U₃O₈ is employed as a cathode material in the molten LiCl salt, various reaction intermediates appear during the electrochemical run [13,24]. Based on X-ray diffraction analysis, Jeong et al. reported that intermediates such as LiUO₃, U₄O₉, and UO₂ were formed at the beginning stage of the run (Fig. 1), and concluded that the reduction was started by the direct ionization mechanism lowering the oxidation states of the uranium and perovskite lithium uranate [13,38]. Then, the reduction of UO₂ was caused by two different reduction paths: the direct reduction and an electro-lithiothermic reduction assisted by the lithium metal produced in the fuel basket, as follows:



It is believed that both cathodic mechanisms occur because the decomposition voltages of the active actinide oxides are comparable to that of Li₂O [29,39].

While most of the previous studies have been conducted with unirradiated fuel, Idaho National Laboratory (INL, US) investigated the electrochemical reduction of spent oxide fuel in their hot cell facility [26,27]. These reports are valuable because they provide information on the reduction extent of each oxide in the spent fuel and the distribution of the fuel constituents between the salt and fuel phase (Table 1). Table 1 apparently suggests that 1) alkali and alkali earth metals such

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