

The Current Status of Electrolytic Reduction Processes in Pyroprocessing Development

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1. Introduction

Pyroprocessing is a type of recycling technology that aims to use high-temperature molten salts as electrolytes to electrochemically recover U and transuranic elements from spent oxide fuel. These recovered elements can then be recycled as metal fuels for fast nuclear reactors. Additionally, pyroprocessing helps to separate non-recyclable fission products from the spent oxide fuel, resulting in a reduction in the volume of waste that needs to be disposed of.

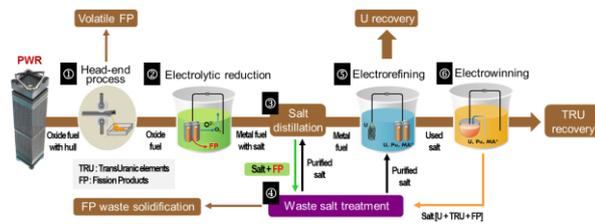


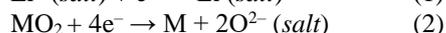
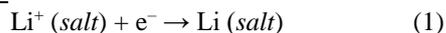
Fig. 1. Pyroprocessing flow diagram.

The pyroprocessing method presented in Fig. 1 illustrates the flow diagram developed by the Korea Atomic Energy Research Institute (KAERI). The process comprises a head-end process, several electrochemical processes (namely, electrolytic reduction, electrorefining, and electrowinning), and a waste-salt-treatment process [1-6].

2. Electrolytic reduction process

To convert spent-oxide fuel into its metallic form, the head-end process is used to prepare it before undergoing electrolytic reduction. This process, also known as oxide reduction (OR), occurs in molten $\text{Li}_2\text{O-LiCl}$ salt at a temperature of $650\text{ }^\circ\text{C}$. During the OR reaction, MO_2 is decomposed into M and O_2 , while fission products like Sr dissolve into the salt and form chlorides. The OR reactions are as follows (Fig.2) [7]:

Cathode:



Li_2O , which is produced by reaction (3) in molten LiCl , dissociates into Li^+ and O^{2-} :



Platinum anode:

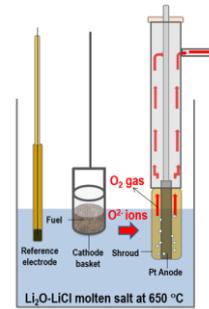
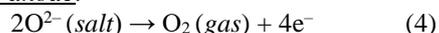


Fig. 2. Schematic diagram of OR cell containing salt, cathode, anode, and reference electrode [8].

KAERI has made significant progress in the development of pyroprocessing technology. One of our achievements has been the creation of electrolytic reducers in different sizes (0.6 kg, 17 kg [9] and 50 kg) to improve the efficiency and economics of the process. The 0.6 kg-scale electrolytic reducer (Fig.3) was designed for employment in hot cell experimentation involving spent nuclear fuel. The previous study [10] establishes the successful operation of an electrolytic reducer at a scale of 0.6 kg. The demonstration involved the conduct of ten successive runs utilizing simulated oxide fuel. The experimental setup remained unchanged, with the retention of the molten LiCl salt and Pt anode throughout the testing phase.



Fig. 3. Photographs of electrolytic reducer installed in M8 hot cell (KAERI).

The electrolytic reducer with capacity of 50 kg/batch (Fig. 4) was developed to facilitate the validation of engineering-scale equipment [11]. Additionally, we have been researching stable materials and operating conditions that can endure long-term operation of the OR process. An electrolytic reducer equipped with

automation features was developed to test the viability of unattended operation in industrial settings (Fig.5).



Fig. 4. Photographs of electrolytic reducer with a capacity of 50 kg/batch installed in PRIDE (KAERI) [11].



Fig. 5. Photographs of electrolytic reducer equipped with automation features (KAERI).

Another notable success in recent years has been the development of an alternative anode that can replace the costly Pt. Numerous candidates have undergone thorough scrutiny as potential substitutes for the Pt anode [12–17]. Carbon, in particular, has garnered attention due to its economical price point and commendable electrical and mechanical characteristics. The graphite anode has demonstrated its superiority over the conventional Pt anode of a comparable reactor in terms of its ability to facilitate a current that is 6-7 times greater [18].

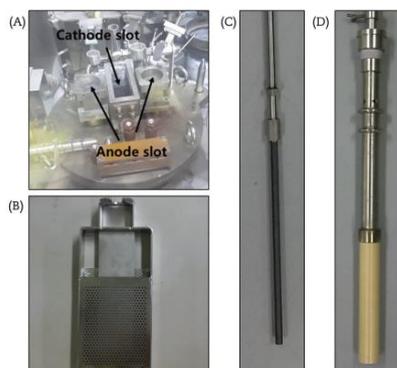


Fig. 6. Electrolytic reducer and electrodes. (A) Flange. (B) Cathode basket. (C) Graphite anode. (D) Anode shroud [18].

This presentation intends to provide a comprehensive overview of the electrolytic reduction research achievements of KAERI, while also presenting the current status of overseas research and development in the field.

REFERENCES

1. Silverio, LB, de Queiroz Lamas, W, An analysis of development and research on spent nuclear fuel reprocessing, *Energy Policy*, Vol. 39, p281, 2011.
2. Rodríguez-Penalonga, L, Moratilla Soria, BY, A review of the nuclear fuel cycle strategies and the spent nuclear fuel management technologies, *Energies*, Vol. 10 p1235, 2017.
3. Laidler, JJ, Battles, JE, Miller, WE, Ackerman, JP, Carls, EL Development of pyroprocessing technology. *Prog Nucl Energy*, Vol. 31, p131, 1997.
4. Ackerman, JP, Johnson, TR, Chow, LSH, Carls, EL, Hannum, WH, Laidler, JJ, Treatment of wastes in the IFR fuel cycle. *Prog Nucl Energy*, Vol. 31, p141, 1997.
5. Benedict RW, McFarlane, HF, EBR-II spent fuel treatment demonstration project status. *Radwaste Magazine*, Vol. 5, p23, 1998
6. Lee, H, Park, G-I, Lee, J-W, Kang, K-H, Hur, J-M, Kim, J-G, Paek, S, Kim, I-T, Cho, I-J, Current status of pyroprocessing development at KAERI. *Sci Technol Nucl Install*, Vol. 2013, p343492. 2013.
7. Choi, E-Y, Jeong, SM, Electrochemical processing of spent nuclear fuels: An overview of oxide reduction in pyroprocessing technology. *Prog Nat Sci Mater Int*, Vol. 25, p572, 2015.
8. Choi, E. Y., Won, C. Y., Cha, J. S., Park, W., Im, H. S., Hong, S. S., Hur, J. M, Electrochemical reduction of UO_2 in $LiCl-Li_2O$ molten salt using porous and nonporous anode shrouds. *Journal of nuclear materials*, Vol. 444, p261, 2014.
9. E.Y. Choi, J.M. Hur, I.K. Choi, S.G. Kwon, D.S. Kang, S.S. Hong, H.S. Shin, M.A. Yoo, S.M. Jeong, Electrochemical reduction of porous 17 kg uranium oxide pellets by selection of an optimal cathode/anode surface area ratio, *J. Nucl. Mater.* Vol. 418, p87, 2011.
10. Choi, EY, Lee, J, Heo, DH, Lee, SK, Jeon, MK, Hong, SS, Kim, S-W, Kang, HW, Jeon, S-CHur, JM, Electrolytic reduction runs of 0.6 kg scale-simulated oxide fuel in a $Li_2O-LiCl$ molten salt using metal anode shrouds. *J Nucl Mater*, Vol. 489, p1, 2017.
11. Lee, H., Park, G. I., Lee, J. W., Kang, K. H., Hur, J. M., Kim, J. G., Paek S., Kim I.-T., Cho I.-J., Current Status of Pyroprocessing Development at KAERI, *Science and Technology of Nuclear Installations*, Vol. 2013, 343492, 2013.
12. S.-W. Kim, E.-Y. Choi, W. Park, H.S. Im, J.-M. Hur, TiN anode for electrolytic reduction of UO_2 in

- pyroprocessing, *J. Nucl. Fuel Cycle Waste Technol.* Vol13, p229, 2015.
13. S.-W. Kim, E.-Y. Choi, W. Park, H.S. Im, J.-M. Hur, A conductive oxide as an O₂ evolution anode for the electrolytic reduction of metal oxides, *Electrochem. Commun.* Vol 55, p14, 2015
 14. S.-W. Kim, W. Park, H.S. Im, J.-M. Hur, S.-S. Hong, S.-C. Oh, E.-Y. Choi, Electrochemical behavior of liquid Sb anode system for electrolytic reduction of UO₂, *J. Radioanal. Nucl. Chem.* Vol 303 p1041, 2015
 15. S.-W. Kim, S.-K. Lee, H.W. Kang, E.-Y. Choi, W. Park, S.-S. Hong, S.-C. Oh, J.-M. Hur, Electrochemical properties of noble metal anodes for electrolytic reduction of uranium oxides, *J. Radioanal. Nucl. Chem.* Vol 311 (2017) p809
 16. J.-M. Hur, J.-S. Cha, E.-Y. Choi, Can carbon be an anode for electrochemical reduction in a LiCl-Li₂O molten salt? *ECS Electrochem. Lett.* Vol 3, pE5, 2014.
 17. S.-W. Kim, M.K. Jeon, H.W. Kang, S.-K. Lee, E.-Y. Choi, W. Park, S.-S. Hong, S.-C. Oh, J.-M. Hur, Carbon anode with repeatable use of LiCl molten salt for electrolytic reduction in pyroprocessing, *J. Radioanal. Nucl. Chem.* Vol 310, p463, 2016.
 18. Kim, S-W, DH, Lee, SK, Jeon, MK, W. Park, J.M. Hur, Hong, S.S., Oh S.C., E.Y. Choi, A preliminary study of pilot-scale electrolytic reduction of UO₂ using a graphite anode, *Nucl. Eng. Technol.* Vol. 49, p1451, 2017.