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Electrochemical reduction behavior of simplified simulants of vitrified radioactive waste in molten $CaCl_2$

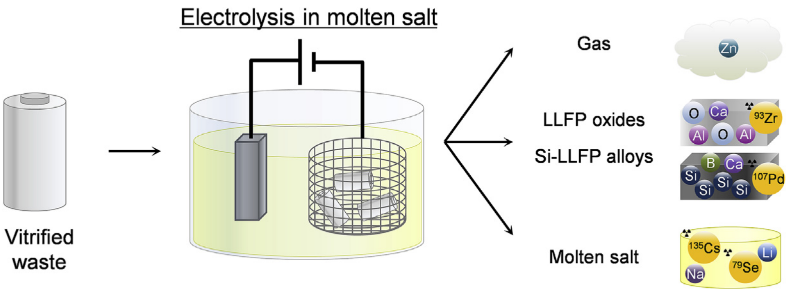
Yumi Katasho [a], Kouji Yasuda [b, c], Toshiyuki Nohira [a, *]

[a] Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan
[b] Agency for Health, Safety and Environment, Kyoto University, Yoshida-hommachi, Sakyo-ku, Kyoto, 606-8501, Japan
[c] Department of Fundamental Energy Science, Graduate School of Energy Science, Kyoto University, Yoshida-hommachi, Sakyo-ku, Kyoto, 606-8501, Japan

HIGHLIGHTS

- Two simplified simulants of vitrified waste were electrolyzed in molten $CaCl_2$.
- The dissolution of Na, Li, and Cs into molten $CaCl_2$ was confirmed.
- The main component, SiO_2, was reduced to Si by the electrolysis of the glass.
- Al, Zr, and Pd remained in the solid phase after the electrolysis.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrochemical reduction of two types of simplified simulants of vitrified radioactive waste, simulant 1 (glass component only: SiO_2, B_2O_3, Na_2O, Al_2O_3, CaO, Li_2O, and ZnO) and simulant 2 (also containing long-lived fission product oxides, ZrO_2, Cs_2O, PdO, and SeO_2), was investigated in molten $CaCl_2$ at 1103 K. The behavior of each element was predicted from the potential–pO^{2-} diagram constructed from thermodynamic data. After the immersion of simulant 1 into molten $CaCl_2$ without electrolysis, the dissolution of Na, Li, and Cs was confirmed by inductively coupled plasma atomic emission spectrometry and mass spectrometry analysis of the samples. The scanning electron microscopy/energy dispersive X-ray and X-ray diffraction analyses of simulants 1 and 2 electrolyzed at 0.9 V vs. Ca^{2+}/Ca confirmed that most of SiO_2 had been reduced to Si. After the electrolysis of simulants 1 and 2, Al, Zr, and Pd remained in the solid phase. In addition, SeO_2 was found to remain partially in the solid phase and partially evaporate, although a small quantity dissolved into the molten salt.

1. Introduction

Nuclear power generation has several advantages: it is a low-carbon energy production method and yields a stable energy supply. With an increasing global population and consequent increasing energy demands, nuclear power is becoming more important. However, a serious problem affecting the nuclear power industry concerns site selection for the disposal of radioactive waste. In particular, in Japan, frequent earthquake tremors increase the risk of the leakage of radioactive materials from disposal sites. Therefore, new methods for the disposal of radioactive waste are required.

An alternative disposal process to geological disposal is shown in Fig. 1a. This process was proposed for the treatment of radioactive waste from nuclear power plant known as one of the

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* Corresponding author.
E-mail address: nohira.toshiyuki.8r@kyoto-u.ac.jp (T. Nohira).

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ImPACT programs (Impulsing Paradigm Change through Disruptive Technologies) in 2015 [1]. From high-level radioactive waste (HLW) and vitrified radioactive waste produced in the past, long-lived fission products (LLFPs) such as ^{135}Cs, ^{79}Se, ^{93}Zr, and ^{107}Pd are separately recovered. In the next step, they are converted into short-lived or stable nuclides by nuclear transmutation [2,3]. A recent study shows that ^{93}Zr (half-life period:1.53 million yr) was converted to stable nuclides with 39.1% and short-lived nuclides (half-life period: $\leqq$ 1 yr) with 56.8% [3]. Then, some of these species are disposed of as stable waste, and the others are recovered as valuable metals such as Pd and Ru. The recovered platinum group metals can be utilized as catalysts for automobile exhaust gas and fuel cells. If this process were realized, the large quantities of HLW and vitrified waste currently produced would be significantly reduced, and the problems regarding site selection for geological disposal would be mitigated. To achieve this, the recovery of each LLFP from the vitrified wastes is a necessary key technology.

The decomposition of the Si–O network structure of glass is required to recover LLFPs from the vitrified waste composed of SiO_2, B_2O_3, Na_2O, Al_2O_3, and oxides of LLFPs such as Pd, Zr, Cs, and Se. Recently, we proposed a method to electrochemically reduce the vitrified wastes to decompose the glass network structure, as shown in Fig. 1b [4,5] and Eq. (1):

$$MO_x + 2\,x\,e^- \rightarrow M + x\,O^{2-}\ (\text{in molten } CaCl_2) \tag{1}$$

where M is the component element in the vitrified waste. After the glass network of the vitrified radioactive waste has decomposed, the recovery of LLFPs becomes easier in the subsequent steps using molten salt electrolysis compared with the recovery from the original vitrified waste. For the decomposition of the vitrified waste, molten salt electrolysis is superior to conventional wet process using HF acid because of its high processing rate, the small amount of secondary radioactive waste. In the wet process, the produced HF acid solution containing fluorosilicic acid needs to be converted to nitric acid solution in order to separate and recover LLFPs. Since the recycling of HF acid is not easy, a large amount of secondary liquid waste is produced whether or not the HF acid is recycled. On the other hand, the recycling of molten salt is relatively easy after the recovery processes of LLFPs and other components by electrolysis and vaporization.

Many studies have been conducted for electrochemical reduction of solid oxides in molten salts, especially for $CaCl_2$-based molten salts [6–22]. In 2000, Chen et al. firstly reported the electrochemical reduction of TiO_2 to Ti in molten $CaCl_2$ [6]. In 2003, Nohira et al. reported the electrochemical reduction of solid SiO_2 to Si in molten $CaCl_2$ [7]. The electrochemical reductions of SiO_2 occurs at the three-phase interface among SiO_2, conductive metal, and molten salt.

$$\text{Cathode: } SiO_2\ (s) + 4\ e^- \rightarrow Si\ (s) + 2\ O^{2-} \tag{2}$$

The $CaCl_2$-based electrolytes were used because of the high solubility of O^{2-} ions [23]. Various groups have investigated that the electrochemical reduction of SiO_2 for the clarification of reaction mechanisms, the production of solar-grade Si etc. [8–14]. So far, electrochemical reductions of various oxides (Ti, Cr, Ce, Nb, Ta, W, Ni, Zr, Dy, and U) have been widely investigated in $CaCl_2$-based molten salts [15,16]. The reductions of oxides mixtures ($NiTiO_3$ [17], TiO_2+SiO_2 [18,19], TiO_2+SiO_2+other oxides [20], $ZrSiO_4$ [21], CaB_2O_4 [22], etc.) have been also studied to develop a new production process of materials.

Moreover, the electrochemical reduction of spent oxide fuels has been studied by many research groups [24–32]. Sakamura et al. reported the electrochemical reduction of UO_2 in molten $CaCl_2$ or LiCl [24]. Hur et al. investigated the solubility of lanthanoid oxides under electrolytic reduction in molten LiCl–Li_2O to form mixed oxides and electrochemical behavior of Br^-, I^-, and Se^{2-} in LiCl [29]. Yoo et al. reported the conceptual study of preprocessing for recovering actinoids from spent oxide fuels using the electrochemical reduction in molten LiCl [28].

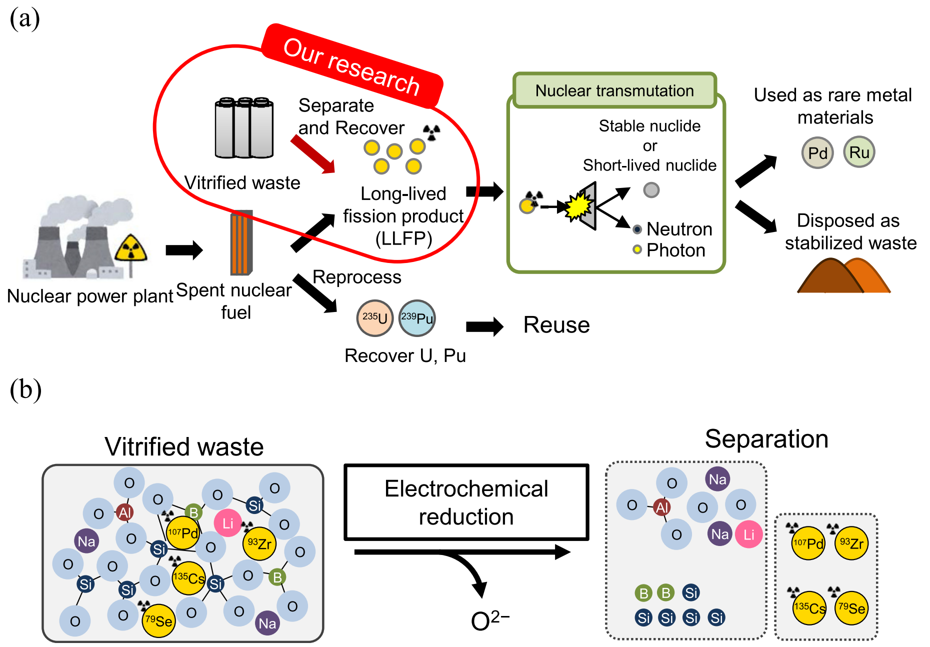

Fig. 1. (a) Our research target for the processing of spent nuclear fuel. (b) Schematic illustration of the separation of the elements by the decomposition of the glass network structure by electrochemical reduction in molten $CaCl_2$.