



Wet chemical processing for nuclear waste glass to retrieve radionuclides

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GRAPHICAL ABSTRACT

Retrieval from Nuclear Waste Glass



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ABSTRACT

Here, we show unexpected and significant elution behavior of various elements from simulated nuclear waste glass (NWG) in $\sim 10^0$ mol dm⁻³ acidic solutions below 100 °C, where a borosilicate-based glass matrix has been believed to be chemically durable. Most elements like glass main components (Li, B, Na, Ca, Al, and Zn, but except for Si) and simulated radionuclides (Rb, Cs, Sr, Ba, Se, Te, Mn, Pd, Mo, rare earths, Cr, Fe, and Ni) were remarkably eluted from the simulated NWG in $\sim 10^0$ M HNO₃ aq with Cl⁻ at 90 °C. Especially, the elution of Pd is governed by its coordination chemistry including a redox reaction, because Pd(0) present in the simulated NWG has to be oxidized to Pd²⁺ which forms [PdCl₄]²⁻ for its dissolution. While Zr in simulated NWG is sparingly eluted even in this treatment, its elution actually proceeds in 1–3 M H₂SO₄ aq at 90 °C thanks to strong coordination of Zr(IV) with SO₄²⁻. Through design and optimization of the leaching conditions, a protocol of the wet chemical process to retrieve the radionuclides from simulated NWG has been proposed and demonstrated.

1. Introduction

Nuclear power is much more energetically dense and cleaner compared with other energy sources, and therefore it is undoubtedly one of the main options to supply electric power in our current energy-

demanding society. However, we also have to be aware that generation of radioactive wastes cannot be avoided through operation of the nuclear energy systems. High-level nuclear wastes (HLW) are resulted from the reprocessing process for spent nuclear fuels, and the most cumbersome due to their strong radiotoxicity lasting for extremely long

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time ($> 10^5$ years) governed by half-lives of long-lived fission products (LLFPs; e.g., ^{106}Pd , ^{79}Se , ^{93}Zr , ^{135}Cs) and minor actinides (MAs; Am, Cm) [1–7]. Immobilization of radionuclides is the most important to consider the safe disposal of HLW. As a current trend, HLW is confined into a borosilicate-based matrix through mixing it with the glass melt to give a nuclear waste glass (NWG). High chemical durability of the borosilicate glass is widely known and accepted, which is a reason why this material has been selected. Indeed, there are numerous reports regarding assessment of elution behavior of NWG in neutral and basic conditions simulating environments at the actual waste repository sites [8–16]. Through these studies, the stability and durability of NWG have already been well established. This situation, however, also means that there is little chance to retrieve radionuclides from NWG unless its glass matrix is fully decomposed or digested under extreme conditions like hydrofluorination and alkali fusion. In the current status, there are no choices for NWG other than its long-term storage in deep underground, i.e., geological disposal.

As another trend, nuclear transmutation is attracting a special interest to bring an innovation for reduction of the radiotoxicity and lifetime of LLFPs and MAs in HLW to mitigate the nuclear waste issues [4,17,18]. While we still have to wait for the social implementation of the nuclear transmutation process for some decades, most HLW present today have already been solidified into borosilicate glass matrix to give NWG, and planned to be transferred to long term disposal in deep underground. To apply the transmutation process to the current nuclear energy system, LLFPs and MAs must be recovered somehow from NWG. However, nothing is considered to retrieve the radionuclides from NWG, even if the nuclear transmutation process is finally implemented. This task has been believed to be extremely challenging because of the well-known chemical durability of NWG, and therefore, no realistic retrieval methods have been proposed to date.

Here, we show unexpected and significant elution behavior of various elements from simulated NWG in $\sim 10^{-3}$ mol dm $^{-3}$ (= M) acids below 100 °C under ambient atmosphere and pressure, where the borosilicate-based glass has been believed to be chemically stable. These conditions are much milder than ordinary processing methods for glass dissolution. The important points are selection and combination of acids on the basis of coordination and solution chemistry of elements to be eluted.

2. Experimental

2.1. Materials

The glass cullet (granular, < 1 mm diameter) manufactured by IHI Inc. was employed as simulated NWG. To control the grain size of the sample on demand, the simulated NWG was ground with the mixer mill (Retsch MM200), followed by sieving. The nominal content of each element was listed in Table S1 (SI). Other chemicals were of reagent grade and used as received.

2.2. Methods

A typical acid leaching experiment was performed through the following procedure. The glass cullet of the simulated NWG was loaded to an acid aqueous solution preliminarily heated to a certain temperature in a thermostat oven. The solution/solid ratio was always kept at 15/1 mL/g. The supernatants were diluted with 1.5 M HCl aq, and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Scientific iCAP7200 Duo). To determine Cs in the solution phase, the inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700) was utilized. The normalized mass loss (NL_i , g m $^{-2}$) of element i was evaluated in accordance with,

$$NL_i = C_i / (X_i S / V) \quad (1)$$

where C_i and X_i are the concentration of element i in a solution phase and its mass fraction in the pristine simulated NWG. The surface-to-volume ratio (S/V) was estimated to be $6.5 \times 10^2 \text{ m}^{-1}$ on the assumption of spherical glass particles of 225 μm diameter in average (150–300 μm granules subjected to the elution experiment of Fig. 4), 2.7 g cm $^{-3}$ density of the simulated NWG, and 15/1 mL/g solution/solid ratio in the current elution experiments.

Each solid sample was ground, mixed with cellulose, pressed to make a pellet, and analyzed by wavelength-dispersive X-ray fluorescence (WDXRF, Rigaku ZSX PrimusII or Rigaku Supermini200). The recorded intensity of WDXRF was normalized by that of Si-K α line because of its negligible elution to the solution phase. Optical microscope photographs and the SEM backscattering electron images of solid samples were taken under the stereoscopic microscope (Olympus SZ61) and JEOL JCM-6000Plus, respectively. Prior to capturing the SEM images, the glass samples were coated by carbon deposit in VC-100 Carbon Coater (Vacuum Device). The BET analysis was performed by volumetric N $_2$ gas adsorption method with BELSORP-max (MicrotracBEL Co.). The MEDUSA program was employed to calculate the speciation diagrams with input of the stability constants obtained from the databases.

3. Results and discussion

3.1. Acid leaching of simulated NWG

Fig. 1a shows appearance of glass cullet of the simulated NWG (granular, < 1 mm) investigated in this work which consists of non-radioactive elements simulating radionuclides in HLW together with glass main components like SiO $_2$, B $_2$ O $_3$, Na $_2$ O, CaO, Al $_2$ O $_3$, ZnO, and Li $_2$ O. Its nominal content is summarized in Table S1 (Supplementary Information, SI). We preliminarily confirmed the stability of this glass sample in distilled water. As a result, no significant elution of the glass main components was detected even at 90 °C up to 7 h as shown in Fig. S1 (SI). When this simulated NWG was immersed in 2 M HCl aq for 5 h at 90 °C, color of the solution phase gradually turned to yellow, indicating elution of some heavy metals initially present in the simulated NWG. Indeed, most of the elements present in the simulated NWG except for Zr, Rh, Ru, and Si were more or less detected in the solution part (Table S2, SI). This finding was surprising and never expected from a common knowledge about chemical durability of the borosilicate glass and NWG.

To further understand the acid leaching phenomenon in detail, we focused on the elution behavior of Pd and Se, the typical LLFP elements, under different acidic conditions. In 2 M HCl aq (Fig. 1c and d), the elution of Pd and Se more or less proceeded with elapse of time at any of temperatures tested. While more than 90% of Se was eluted within 7 h, the elution of Pd was slower and not very significant. The majority of Pd in NWG is believed to be Pd(0) or its alloy with Te and Rh [6,14], and therefore must be oxidized to Pd $^{2+}$ for dissolution. This should be the reason why Pd is not eluted very efficiently in non-oxidizing HCl aq.

It is straightforward to utilize an oxidizing reagent for enhancing the Pd elution from the simulated NWG. Hence, we repeated the leaching experiments in 2 M HNO $_3$ aq. The results for Pd and Se are shown in Fig. 1e and f, respectively. Consequently, the major part of Pd still remained in the simulated NWG even at the highest temperature examined here. However, the Pd elution seems to be enhanced gradually with elevating temperature, implying that Pd(0) has actually reacted with HNO $_3$ to give Pd $^{2+}$. In contrast, the Se elution seems not to be very sensitive to the selection of acids.

Looking at Fig. 1c again, the elution of minor part of Pd from the simulated NWG has been detected despite absence of any of oxidizers. This fact can be ascribed to strong complexation of Cl $^-$ with Pd $^{2+}$ initially present in the simulated NWG to solubilize Pd $^{2+}$ as [PdCl $_4$] $^{2-}$ (Table S3, SI) [19]. Furthermore, it was also confirmed in Fig. 1e that HNO $_3$ is strong enough to oxidize Pd(0) to Pd $^{2+}$. Accordingly, the

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