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Recovery of palladium, cesium, and selenium from heavy metal alkali borosilicate glass by combination of heat treatment and leaching processes

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HIGHLIGHTS

- A separation technique of both noble and less noble metal from glass is studied.
- Via reductive heat treatment, 80% of palladium is extracted in liquid bismuth.
- Sodium–potassium-rich materials with cesium and selenium are phase separated.
- From the materials, over 80% of cesium and selenium are extracted in water.

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ABSTRACT

Reductive heat-treatment and leaching process were applied to a simulated lead or bismuth soda-potash-borosilicate glass with palladium, cesium, and selenium to separate these elements. In the reductive heat treatment, palladium is extracted in liquid heavy metal phase generated by the reduction of the heavy metal oxides, whereas cesium and selenium are concentrated in phase separated Na–K-rich materials on the glass surface. From the materials, cesium and selenium can be extracted in water, and the selenium extraction was higher in the treatment of the bismuth containing glass. The chemical forms of palladium in the glass affected the extraction efficiencies of cesium and selenium. Among the examined conditions, in the bismuth glass treatment, the cesium and selenium extraction efficiencies in water were over 80%, and that of palladium in liquid bismuth was over 80%.

1. Introduction

High-level liquid waste (HLLW) from reprocessing facilities of spent nuclear fuels is vitrified to immobilize radioactive nuclides. Borosilicate glass is well known as a suitable matrix for immobilizing radioactive nuclides, and it is used for vitrification of HLLW to prevent the release of the nuclides into the environment during its storage [1]. Various vitrification methods have been studied to convert HLLW into a durable solid for disposal [2–6]. In Japan, the vitrified materials are stored in the reprocessing facility in Rokkasho village before disposal, and the storage will increase along with the generation of the vitrified materials. However, the disposal sites of the vitrified materials are limited in Japan, and long-term storage is necessary for the solid after disposal because the radioactive nuclides contain long-lived fission products (LLFPs) with long half-lives [7]. In order to resolve the problem of the existing vitrified materials, an important option will be to separate LLFPs from the glass and transmute them to short-lived or stable nuclides using nuclear transmutation techniques [7–9] in future. We focused on the vitrified glass as a target material, which is already stored and will be generated from the reprocessing facility, not the liquid waste. For the LLFP recovery, we are studying the LLFP separation technique under the “Impulsing Paradigm Change through Disruptive Technologies (ImPACT)” program in Japan [8], and one of target LLFPs in the program are platinum group metals (PGMs). The PGMs in LLFPs can be recycled as valuable resources if the separated radioactive PGMs are transmuted to stable PGMs. The potential applications of fission PGMs in the chemical, pharmaceutical, petroleum, and electronic industries, as well as in research institutes were previously documented [10]. Since the natural abundance of PGMs in the Earth’s crust is limited, in order to conserve this resource, the recovery of fission PGMs by LLFP separation and transmutation has attracted particular attention.

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To separate PGMs from the glass, liquid metals are useful media, into which PGMs can be extracted from the glass in a melting process [11–14]. Naito et al. extracted PGMs in liquid metallic lead using a glass melting process [11]. Jensen et al. melted a mixture of glass-forming chemicals with noble metals, lead oxide, and charcoal to generate liquid metallic lead, in which the noble metals were extracted [12]. Jena et al. reported the extraction of PGMs in liquid metallic tin from a simulated borosilicate glass [13]. Uruga et al. examined liquid metallic copper for the extractions of PGMs and Mo as a solvent metal [14,15]. However, in these processes, it was difficult to extract less noble metals such as cesium, selenium, and zirconium which are also target LLFPs in the ImPACT program, because they were more stably present in the oxide phase than PGMs. Among such LLFPs, these three radioactive nuclides release radiation at higher doses compared to other radioactive nuclides [16], and they should be also separated from the glass and transmuted to short-lived or stable nuclides together with PGMs. The current glass vitrification process for stabilization of the radioactive materials is effective, and it would be difficult to extract such nuclides from the vitrified glasses. Therefore, the glass should be converted to a material from which the nuclides can be easily extracted and the extraction technique is applied to the material.

Reductive heat treatment using heavy-metal-containing media was applied to separate PGMs, cesium, and selenium. In this process, a heavy metal soda-potash-borosilicate glass, where PGMs, cesium, and selenium were present, was melted at 1000 °C under a CO-containing reductive atmosphere. During melting, the heavy metal oxides in the glass were reduced to metallic states by CO [17–19], and PGMs were extracted in the generated liquid metal, which was separated from the molten oxide phase as an agglomerate. The PGM can be further separated from the metal and purified by electrolytic refining method. Then, the molten oxide was annealed at 700 °C to separate Na–K-rich materials on the surface of the oxide that was in contact with the gas phase (referred to as the "contact surface") [20]. Simultaneously, cesium was transferred to the Na–K-rich materials. In our previous study, we reported that the leachability of cesium in water was enhanced by the phase separation technique [21]. From the Na–K-rich phase, therefore, cesium was extracted in water. We hypothesize that if LLFP-containing borosilicate glass is converted to heavy metal soda-potash-borosilicate glass and heated under a reductive atmosphere, the PGMs, cesium, and selenium in the glass may be effectively extracted. From the solution, cesium can be selected recovered by adsorbents [22] and selenium can be done by electrowining. However, in the above-mentioned previous study [21], the separation of PGMs, cesium, and selenium in the CO-containing reductive heat-treatment was not examined.

Our objective is to propose the separation process of palladium, cesium, and selenium from glass materials in the reductive heat treatment. To select heavy metal species in the glass, a simulated lead or bismuth soda-potash-borosilicate glass containing non-radioactive palladium, cesium, and selenium was heated under a CO-containing reductive atmosphere. The extraction efficiencies of the metals from the glass were evaluated at different chemical forms of palladium in the glass.

2. Materials and method

2.1. Simulated glass

Three types of the simulated glass were prepared using a mixture of standard reagents. Table 1 shows the batch compositions of the reagent mixtures. These reagents (purchased from Wako Chemical Co. Ltd., Osaka, Japan) were non-radioactive and mixed uniformly. In the preparation of the simulated glass, a 30 mL alumina crucible containing the reagent mixture was first placed in an electric furnace, and then the temperature in the furnace was elevated from room temperature to 1000 °C for more than 30 min. At that temperature, the mixture was melted for 2 h under atmospheric conditions. After that, the crucible was removed from the furnace using fire tongs, and the melt in the crucible was allowed to cool naturally and rapidly at room temperature. The obtained glassy material is referred to here as the "simulated glass." Palladium and selenium are possibly present as different chemical forms (oxides or metallic states) in the glass [23,24]. Therefore, in the glass preparation, the chemical forms of the palladium and selenium reagents were changed from oxides (ball-like PdO with diameter of 200–600 nm and rod-like SeO_2 with diameter of 150–500 nm) to metallic states (ball-like Pd with diameter of 0.35–1.5 μm and bulky Se with diameter of 0.5–1.5 μm) as shown in Table 1. When the reagent mixture with Se was melted under atmospheric conditions, the added Se was possibly oxidized. Although such oxidation may occur, a part of the selenium can exist in its metallic state in the glass [24].

Table 1
Compositions of reagent mixtures used for the preparation of simulated glass-batches (unit: g).

Chemical compounds	Simulated glass		
	Pb-glass	Bi-glass 1	Bi-glass 2
SiO_2	0.50	0.50	0.50
H_3BO_3	0.27	0.27	0.27
Na_2CO_3	0.50	0.50	0.50
PbO	0.50	0	0
Bi_2O_3	0	0.50	0.50
K_2CO_3	1.0	1.0	1.0
$CaCO_3$	0.179	0.179	0.179
Cs_2CO_3	0.050	0.050	0.050
ZrO_2	0.025	0.025	0.025
PdO	0.050	0.050	0
Pd	0	0	0.050
SeO_2	0.010	0.010	0
Se	0	0	0.010

Fig. 1 shows the XRD patterns of the Bi-glass 1 and Bi-glass 2. The Bi-glass 1 showed the amorphous glassy structure without the detection of the PdO and SeO_2 phases. This indicates that the palladium and selenium were incorporated in the glass matrix as oxides. On the other hand, for the Bi-glass 2, besides the main amorphous glassy structure, there were two minor peaks at 40° and 47°, which were indexed as the crystalline Pd phase. The detection of Se was not observed because most of the added Se was oxidized and incorporated in the glass matrix.

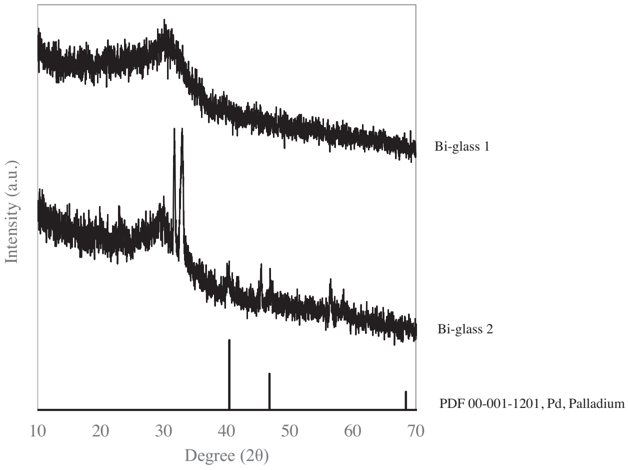

Fig. 1. XRD patterns of the Bi-glass 1 and Bi-glass 2.