



Silver phosphate glasses for immobilization of radioactive iodine



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ABSTRACT

Management of radioactive ^{129}I is a challenging issue due to its significantly long half-life and negative health effects. In this study, silver iodide (AgI)-incorporated silver phosphate glasses were prepared to immobilize ^{129}I for a long time. A melt-quenching method was employed to synthesize the glasses at 450 °C to prevent the evolution of I during the heat treatment. Characterization of the AgI-Ag₂O-P₂O₅ specimens revealed that the addition of AgI was possible up to 60 mol% into the glassy matrix although there were some amounts of Ag₄I(PO₄) and AgI clusters. This result was supported by the structural analysis which showed that the major iodine environment was composed of Ag and O regardless of the specimen compositions. The normalized leaching rates obtained by the 7-day PCT-A test showed that the chemical stability of iodine was satisfactory with the lowest leaching rate of $1.7 \times 10^{-4} \text{ g m}^{-2}/\text{d}$. Our findings in this study demonstrate the potential of silver phosphate glass for the immobilization of radioactive ^{129}I .

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1. Introduction

Nuclear energy is beneficial to the environment in terms of not-producing greenhouse gases unlike fossil-fuel based energy. However, nuclear energy production is inevitably accompanied by radioactive waste that must be managed for at least hundreds of thousands of years as a by-product. Among the many fission products produced by nuclear fission reactions, beta-emitting ^{129}I with a half-life of $1.57 \times 10^7 \text{ y}$ is the most problematic radioisotope when considering the dramatically long half-life and negative health effects. Accumulating in the thyroid with a biological half-life of 80 days in adults, ^{129}I could cause diseases such as thyroid nodules or cancer (Lind et al., 1998). Therefore, safe disposal of ^{129}I for a long time is a big issue in the field of radioactive waste management.

Several schemes have been suggested for the long-term disposal of ^{129}I . Ocean disposal is one of them (Burger, 1980; Burger et al., 1981). It is based on the principle that the concentration of ^{129}I is diluted to the background level by the vast amount of stable isotope (^{127}I) present in the ocean. It is reported that the annual production of ^{129}I by nuclear energy generation and the total amount of ^{127}I in the oceans are about 10^{10} and 10^{17} g , respectively (Exter, 2004). Although this method has been performed to dispose of radioactive iodine waste, actually gaining the public acceptance of ocean dumping is difficult due to the changed perception on

nuclear waste especially after the Fukushima Daiichi nuclear accident. Disposal in space with artificial satellites has also been suggested (Schneider and Platt, 1974): if the ^{129}I waste orbited around the earth or solar system permanently, the waste could be perfectly isolated from humans. However, technology for this strategy has yet to be developed, and extremely high costs are expected for extraterrestrial disposal. Another method is to transmute ^{129}I into stable elements such as ^{130}Xe by neutron irradiation (IAEA, 1987). Unfortunately, the feasibility of transmutation is very low with the current technology. Thus, a viable scheme for ^{129}I disposal is to bury the waste deep in the ground. Currently, high-level radioactive waste is destined to be buried in mined repository systems at depths within several hundred meters (Werme et al., 1992).

Radioactive iodine stored in subterranean regions could leach into the surface soil due to the existence of lateral and longitudinal movement of groundwater (Ko et al., 2014). Thus, the mobility of ^{129}I by groundwater transport is a serious concern. Iodine has various oxidation states including -1 , 0 , $+1$, $+3$, $+5$, and $+7$. When dissolved in water, iodine mostly exists as I^- , HOI , I_2 , and IO_3^- in normal environmental conditions (Hou et al., 2009). Among them, I^- is the prevalent species under reducing conditions which is common in deep groundwater. This anion is not readily adsorbed in silicate-based soils (Sazarashi et al., 1994) and becomes highly mobile along groundwater flow paths. Thus, the chemical durability of iodine-incorporated materials must be improved to guarantee the safe disposal of ^{129}I for extensive periods of time, which means at least 10 or 11 half-lives.

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Many researchers have investigated the potential immobilization forms for ^{129}I that include glasses, glass ceramics, cement, and inorganic minerals such as sodalite and apatite (Burger, 1980; Burger and Scheele, 1981; Riley et al., 2016; Sava et al., 2012; Scheele et al., 1984; Scheele and Wend, 2015; Strachan and Babad, 1979; Winters, 1980). In addition, silver iodide (AgI) is known to be an iodine compound with an excellent chemical stability in iron-rich soils (Exter, 2004; Inagaki et al., 2008). Iodine is not easily leached out from AgI due to its chemical resistance to aqueous media ($K_{sp} = 8.52 \times 10^{-17}$), which suggests that AgI could be a candidate phase for the long-term disposal of iodine waste (Yim, 1998; Vance et al., 2016). However, the release of Ag is also regulated by the Resource Conservation and Recovery Act (RCRA) due to its toxicity (40 CFR 261, 2012). Therefore, AgI must be safely immobilized by durable matrices to satisfy regulatory requirements. The incorporation of AgI within glass structures has also been studied by some researchers. Minami et al. investigated the glass forming characteristics of the AgI-Ag₂O-P₂O₅ system (Minami et al., 1977). The basic properties of the AgI-Ag₂O-P₂O₅ glass were evaluated by Japanese researchers (Fujihara et al., 1999; Sakuragi et al., 2008). A work by Lemesle et al. also included silver phosphate glass studies (Lemesle et al., 2014).

The aim of the present study was to investigate the synthesis of iodine waste forms using AgI-Ag₂O-P₂O₅ glasses and the characteristics of the initial leaching behavior of the glasses. Different specimens based on AgI-Ag₂O-P₂O₅ compositions were prepared with a melt-quenching method. Characterizations were performed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) techniques to study how AgI was incorporated into the glass. Elemental leaching was investigated with the Product Consistency Test (PCT-A) to see short-term leaching behavior of the AgI-Ag₂O-P₂O₅ systems (Jantzen and Bibler, 2006).

2. Materials and methods

Specimens based on AgI-Ag₂O-P₂O₅ compositions were prepared with AgI (Sigma-Aldrich, 99.9%, USA), AgNO₃ (Kojima Chemicals Co., Ltd., 99.9%, Japan) and NH₄H₂PO₄ (Kanto Chemical, INC., 99%, Japan), and all raw materials were reagent grade. The glass-forming regions of the AgI-Ag₂O-P₂O₅ system were investigated by Minami et al., and their results showed that glassy or crystalline structures are obtained depending on the molar ratios of AgI, Ag₂O and P₂O₅ (Minami et al., 1977). Based on the study by Minami et al., the molar ratios of AgI, Ag₂O and P₂O₅ that are expected to enable amorphous structures were determined for our specimens. Herein, total six samples were fabricated with varying compositions of AgI, Ag₂O and P₂O₅. Each mass for the three reagents (AgI, AgNO₃, and NH₄H₂PO₄) was determined to adjust the molar ratios of the specimens. The reagent powders were homogeneously mixed using an alumina pestle, and the mixtures were poured into alumina crucibles. These materials were then thermally elevated to 450 °C with a heating rate of 10 °C/min in an electric furnace. The heat-treatment was maintained for 2 h in an air atmosphere, and the specimens were quenched by pouring them out into a rectangular stainless steel (SUS) tray at the end of the heat-treatment.

The PCT-A test was employed to investigate the initial leaching behavior of the specimens. The procedure for the leaching test is described elsewhere (Jantzen and Bibler, 2006). Typically, the specimens were pulverized, and particles of 75–150 μm were only collected by a sieving process. The powders were placed into polypropylene plastic bottles manufactured by Wheaton Co., and purified water was poured into the bottles with a powder to purified water ratio of 10⁻¹ g/mL. Then, the bottles were tightly sealed and maintained at 90 °C in a drying oven for 7 d. At the end of the test, the leaching solutions were sampled to analyze the elemental

concentrations of the solutions by inductively coupled plasma-optical emission spectroscopy (ICP-OES, iCAP6300 Duo, Thermo Scientific Co., U.K.) or mass spectroscopy (ICP-MS, 7700x, Agilent Technologies, U.S.A.). The normalized leaching rates were calculated with Eq. (1) as follows:

$$NR_i (\text{g} \cdot \text{m}^{-2}/\text{d}) = C_i / (f_i \cdot SA/V \cdot t), \quad (1)$$

where C_i is the concentration of the i element (unit: mg/L); f_i is the mass fraction of the i element in the specimen (unitless), and SA/V is the ratio of the sample surface area (SA) to the leachant volume (V). Generally, the density and SA/V for a borosilicate glass specimen are 2.7 g/cm³ and 2000 m⁻¹, respectively (Ebert, 1994). Herein, the density of our specimens was assumed to be 5.9 g/cm³ following the typical density of AgI-Ag₂O-P₂O₅ glasses (Fujihara et al., 1999). In this regard, the SA/V was determined to be 915 m⁻¹ due to the high density of our specimens. Finally, t is the duration of the PCT-A test (unit: d).

Differential scanning calorimetry (DSC, Netzsch DSC 214) was employed to examine the glass transition temperatures of the specimens. The temperature was elevated from room temperature to 500 °C with a heating rate of 10 °C/min in an air atmosphere. The powder X-ray diffraction technique (D8 Advance A25, Bruker) was used to analyze the crystalline structure. Data collection was performed at each step of 0.01° for 0.1 s. The binding structure of the specimens was investigated with an X-ray photoelectron spectroscopy system (XPS, Axis Nova, Kratos). The system was operated with an accelerating voltage and filament current of 15 keV and 10 mA, respectively. Data calibration was performed with the 1 s binding energy of carbon (284.8 eV) as a reference value. The morphology of the specimens was examined with a scanning electron microscope (SEM, SU-8010, Hitachi). Energy dispersive spectroscopy (EDS, Horiba, X-MAX) was also employed to qualitatively analyze the elemental distribution. The specimen surfaces were polished, and a platinum coating was applied to the surfaces prior to the microscopic observation.

3. Results and discussion

Fig. 1 shows the morphological shapes of the quenched specimens with different compositions. Name and composition of each sample were presented in Table 1. Our aim was to synthesize a glassy structure in which the AgI particles are uniformly dispersed in the amorphous matrix. The phase separation of AgI from the matrix would increase the exposed surfaces of AgI in the event of waste form degradation resulting in the high possibility of groundwater intrusion by increased permeability (Spence and Shi, 2005). In this regard, heat-treated melts were taken out of the electric furnace and poured out into a SUS tray at room temperature. The quenching process reduces the time required for the arrangement of particles and the formation of ordered structures, which helps to make an amorphous structure in the specimens (Shelby, 2005). Visual observation of the specimens showed that there were two kinds of specimens with respect to transparency. The 30AgI-50Ag₂O-20P₂O₅ and 60AgI-20Ag₂O-20P₂O₅ specimens were relatively opaque and had many specks on their surfaces. In contrast, it was observed that the others were generally clear and transparent. There might be some relationship between transparency and structural characteristics. Therefore, XRD analysis was performed to reveal the structural difference among the specimens.

Fig. 2 shows the XRD patterns of the AgI-Ag₂O-P₂O₅ specimens. The results indicate that most peaks were found in the 30AgI-50Ag₂O-20P₂O₅ specimen and a few peaks were seen in the 60AgI-20Ag₂O-20P₂O₅ specimen. However, the XRD patterns of the other specimens did not have any clear peaks with strong intensity. The peaks of 30AgI-50Ag₂O-20P₂O₅ were divided into

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