

Chemical and Mechanical Sustainability of Silver Tellurite Glass Containing Radioactive Iodine-129

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Silver tellurite glasses with melting temperature of approximately 700°C were developed to immobilize ¹²⁹I wastes. Long-term dissolution tests in 0.1 M acetic acid and disposability assessment were conducted to evaluate sustainability of the glasses. Leaching rate of Te, Bi and I from the glasses decreased for up to 16 d, then remained stable afterwards. On the contrary, tens to tens of thousands of times more of Ag was leached in comparison to the other elements; additionally, Ag leached continuously for all 128 d of the test owing to the exchange of Ag⁺ and H⁺ ions between the glasses and solution. The I leached much lower than those of other elements even though it leached ~10 times more in 0.1 M acetic acid than in deionized water. Some TeO₄ units in the glass network were transformed to TeO₃ by ion exchange and hydrolysis. These silver tellurite glasses met all waste acceptance criteria for disposal in Korea.

Keywords: Silver tellurite glass, Iodine, Long-term leaching behavior, Waste acceptance criteria

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1. Introduction

^{129}I has a long half-life (1.57×10^7 y), high volatility, and high solubility in water. Furthermore, ^{129}I does not adsorb onto most minerals, so it has high mobility in water. Therefore, immobilization of ^{129}I in stable waste forms is a significant requirement in management of nuclear wastes [1]. ^{129}I is generated by fission reactions in nuclear reactors and can be released during pyroprocessing of spent nuclear fuel [2]. Most ^{129}I is collected using Ag-coated filters in off-gas treatment facilities of pyroprocessing units. Ag^+ captures I $^-$ with good efficiency to form AgI, which has low solubility in water [3]. However, AgI is usually mechanically fragile, so it is unsuitable for disposal unless it is confined within solid hosts [4].

Borosilicate glasses are the most promising glass waste forms for sequestration of high-level wastes due to good chemical durability and thermal stability. However, these glasses are not suitable for immobilization of ^{129}I because of their high melting temperatures ($T_m > 1,000^\circ\text{C}$), and low iodine solubility ($< 1\text{wt}\%$) [5].

To overcome these limitations, we developed silver tellurite glass with a composition of $53\text{TeO}_2\text{-}23\text{Ag}_2\text{O-}5\text{Bi}_2\text{O}_3\text{-}19\text{AgI}$ (mol%) [6]. This glass has a melting temperature of 700°C , which is low enough to prevent volatilization of ^{129}I during melting. Furthermore, up to 96% of I inside the initial powder mixture remained in the glass after melting. The waste loading of I was 11.21wt%. Normalized elemental releases of all elements verified from product consistency test (PCT) were $< 0.01 \text{ g}\cdot\text{m}^{-2}$, which satisfies the US regulations ($< 2 \text{ g}\cdot\text{m}^{-2}$). This glass has glass transition temperature (165°C), which is higher than the control temperature of geological repositories (100°C) [7, 8], and therefore can maintain its amorphous phase when stored in them.

This study evaluates the sustainability of silver tellurite glass waste forms for long-term storage, focusing on long-term leaching characteristics and five waste acceptance criteria for a disposal in Korea [9]. The surface of the glass was not changed significantly even after leaching

for 256 d in deionized water (DIW). Therefore, we evaluated long-term leaching in 0.1 M acetic acid solution for up to 128 d. X-ray photoelectron and Raman spectroscopic analyses suggested that changes occurred in the molecular structure of the glasses as dissolution proceeded.

2. Experimental Methods

A glass with a nominal composition $53\text{TeO}_2\text{-}23\text{Ag}_2\text{O-}5\text{Bi}_2\text{O}_3\text{-}19\text{AgI}$ (mol%) was prepared using conventional melt-quenching. Powders of TeO_2 , Ag_2O , Bi_2O_3 and AgI (all purities $> 99\%$) were weighed and mixed for melting at 700°C for 30 min in an alumina crucible in ambient atmosphere. Glass specimens were prepared by pouring the melt onto a brass mold, then further heat-treated at 150°C for 2 h to remove residual stress.

2.1 Analysis of the Waste Acceptance Criteria for Disposal

For solid waste forms to be accepted in a repository, several waste acceptance criteria must be satisfied [10-13].

2.1.1 Compressive Strengths

Fracture strengths were measured for specimens as prepared, subjected to thermal cycling and electron irradiation [10-12]. Specimens were prepared as cylinders with diameter of 1.2 and height of 2.4 cm. Fracture strengths were measured using a uniaxial compressive testing machine (ST-1000C, Salt) for a total of twelve specimens, three for each test.

Thermal cycling test using American Society for Testing and Materials (ASTM) B553 was conducted using a thermal shock test chamber (TSA-71H-W, espec). Specimens were subjected to changes of temperature from -40°C and 60°C for 1 h, each. The ramp rate was $20^\circ\text{C}\cdot\text{min}^{-1}$ and 30 cycles were repeated. An electron accelerator (ELV-8, EB TECH) was used to irradiate specimens to a total of 10^7 Gy.

2.1.2 Leaching Test [13]

Glass specimens with a surface area of 11.31 cm² were immersed in 113 ml DIW at room temperature following the procedures in ANS 16.1. Leachate was collected after 2, 7, 24, 48, 72, 96, 120, 456, 1128 and 2160 h. Concentrations of Iodine in the leachates were analyzed using inductively coupled plasma-mass spectroscopy (ICP-MS, NexION 350D, Perkin-Elmer SCIEX). Leachability indexes L_i were calculated as

$$L_i = \frac{1}{10} \sum_i^{10} [\log(\beta/D_e)]_n \quad (1)$$

where

$$D_e = \pi \left[\frac{A_n/A_0}{(\Delta t)_n} \right]^2 \left(\frac{V}{S} \right)^2 T \quad (2)$$

D_e [cm²·s⁻¹] is the effective diffusion coefficient, A_n [g] is the n^{th} accumulated amount of nuclides in the leachate, A_0 [g] is a total amount of target nuclides in the pristine specimen, V [cm³] is the volume of the specimen, and A [cm²] is its surface area, T [h] is average time interval between t_n and t_{n-1} , and $\beta = 1 \text{ cm}^2 \cdot \text{s}^{-1}$ is a constant. The US regulations require Iodine to have a leachability index (L_i) of 11 or higher [13]. Fracture strengths of the specimens after ANS 16.1 test were also measured using the same method described in the previous section.

2.2 Evaluation of Long-term Dissolution

Glasses were cut to 1 × 1 × 0.3 cm in size and polished using 1200-grit sandpaper. Leftover glasses were crushed using mortar and pestle, then sieved to collect powders with diameters of 25–45 μm. Powders were washed with DIW and ethanol in an ultrasonic cleaner to remove fine particles and impurities, then dried at 90°C for 12 h. Powders (~0.2 g) and a bulk specimen were immersed in 29.2 ml of 0.1 M acetic acid (pH 2.88 ± 0.05 at 25°C). This concentration of acetic acid is the standard solution for toxicity characteristic leaching procedure (TCLP) tests to provide the organic environment of groundwater [14]. The leachates and specimens were collected after 8, 16, 24, 32, 40, 48 h, and 3, 4,

8, 16, 32, 64, and 128 d. Leachates were filtered through 0.45-μm syringe filters, then the liquid was analyzed using an inductively coupled plasma-mass spectrometer (ICP-MS, NexION 300X, Perkin-Elmer SCIEX). Normalized elemental release rates r_i [g·m⁻²], were calculated as

$$r_i = \frac{C_i}{f_i(A/V)}, \quad (3)$$

where c_i [ppm = g·m⁻³ in deionized water] is the concentration of element i in the solution, f_i is the mass fraction of element i in the glass, A [m²] is the surface area of the glass powder, and V [m³] is solution volume. The value of A/V was fixed at 200 m⁻¹ with the density ρ of glass being 6.31 g·cm⁻³.

Depth profiles of the pristine and the glass leached for 128 d in 0.1 M acetic acid specimens were obtained using a time of flight-secondary ion mass spectrometry (ToF-SIMS, ION-TOF, Germany) and a surface profiler (α -step, veeco dektak 3) up to a depth of 10 μm. Thin slabs of glass specimens that had been leached in DIW or 0.1 M acetic acid were prepared using a focused ion beam (FIB, Helios, Pegasus, FEI) to record the cross sectional scanning electron microscope (SEM, Helios, Pegasus, FEI) and transmission electron microscope (TEM, JEM-2200FS, JEOL) images. Raman (NRS-5100) and X-ray photoelectron spectroscopy (XPS, K-ALPHA+) spectra of pristine glass and the glass leached for 128 d in 0.1 M acetic acid were recorded to investigate structural changes of the glass surface during the dissolution.

3. Results and Discussion

3.1 Evaluation of the Waste Acceptance Criteria

As shown in Table 1, the results of compressive fracture strengths of specimens subjected to each test all satisfied the strength requirement of > 3.45 MPa. Thermal shock appeared to cause the most damage to the glass, followed by electron radiation. Both tests resulted in the formation of

Table 1. Compressive strength of glass after tests of waste acceptance criteria

Tests	Compressive strength (MPa)
None	15.0
Thermal cycling	5.0
Irradiation	8.6
ANS 16.1	14.2

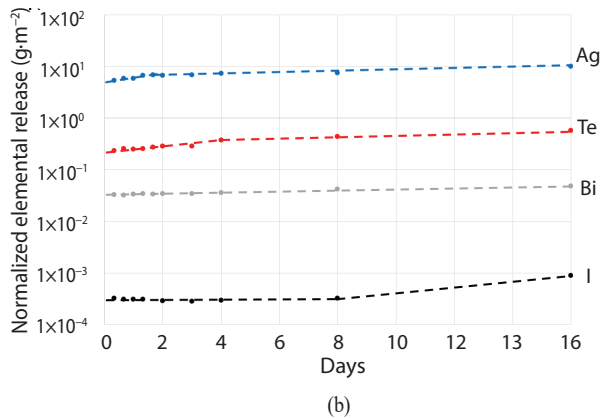
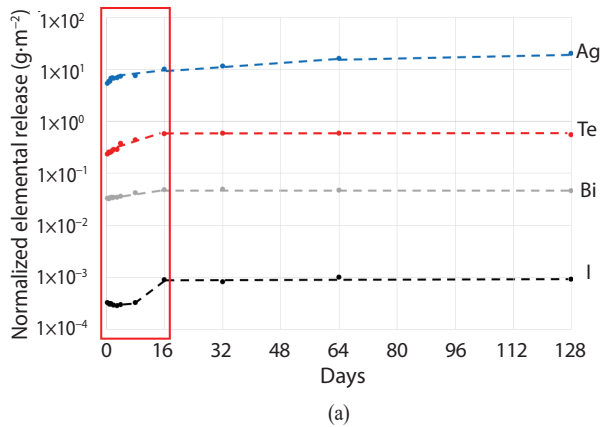


Fig. 1. Concentration of leached elements from the glasses in 0.1 M acetic acid for (a) 128 d and (b) 16 d at 90°C.

surface cracks, but compressive strengths still satisfied the regulation. The glass showed a leachability index of 17.58, which satisfies the regulation value of 11 or higher of ANS 16.1. Compressive fracture strength of tellurite glass is lower than that of ordinary silicate glasses (> 100 MPa) [15], but tellurite glass waste forms were not seriously affected by the external factors and clearly met the regulations and criteria imposed by authorities worldwide.

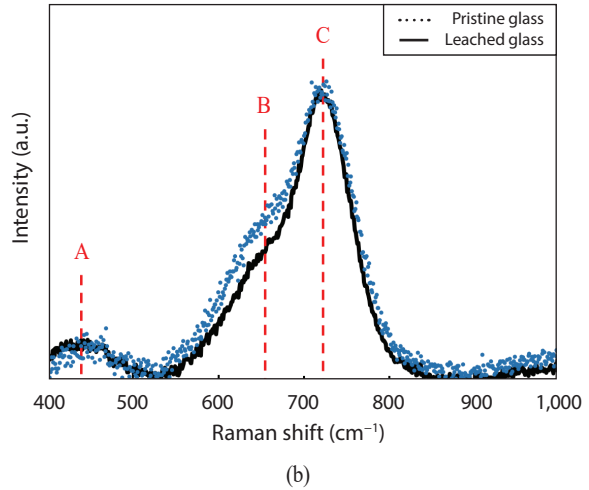
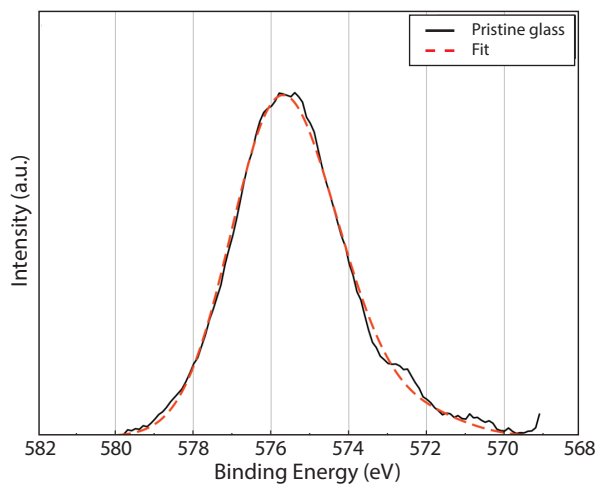


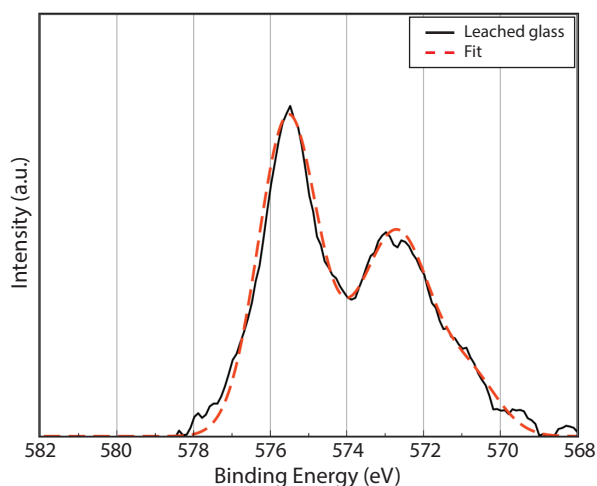
Fig. 2. Raman spectra of pristine glass (dotted line) and glass leached for 128 d in 0.1 M acetic acid (solid line).

3.2 Long-term Leaching Characteristics

Shape and surface of the glass specimens didn't show significant difference even when analyzed using ICP before and after leaching. Te, Bi and I contents in the glasses decreased for up to 16 d by leaching, then remained stable afterwards. On the contrary, Ag content continuously decreased by leaching for the full 128 d of the test, as a result of ion exchange between Ag^+ in the glass and H^+ in solution. As shown in Fig. 1, normalized elemental leaching of the glass until 128 d were in the range of $0.23 - 0.59$ for Te, $4.96 \times 10^{-2} - 3.22 \times 10^{-2} g \cdot m^{-2}$ for Bi, $3.06 \times 10^{-4} - 9.98 \times 10^{-4} g \cdot m^{-2}$ for I, and $5.39 - 20.32 g \cdot m^{-2}$ for Ag, respectively. The high leaching rate of Ag (tens to tens of thousands of times more than other elements) may occur because ion exchange occurs more actively than hydrolysis in acidic solution. The differences in leaching rates of Te, Bi and I, compared to Ag indicates that hydrolysis of the glass network gradually decreased from the early stage of leaching to the 16 d, then entered a stable state. Ion exchange of Ag^+ for H^+ occurred continuously until the 128 d, although the rate decreased. The I was leached ~10 times more in 0.1 M acetic acid than in DIW ($3.19 \times 10^{-5} - 7.76 \times 10^{-5} g \cdot m^{-2}$).



(a)



(b)

Fig. 3. XPS spectra of Te $3d_{5/2}$ in (a) pristine glass and (b) glass leached for 128 d in 0.1 M acetic acid.

However, this rate is still much lower than those of other elements, and remains in stable state after 16 d. These results suggest that leaching of I from waste will be very low, even if the silver tellurite glass is exposed to groundwater for a long period of time.

A TeO_2 glass network is made of $[\text{TeO}_4]^{4-}$ trigonal bipyramidal units (N_4) with two lateral Te-O bonds at a distance of 0.21 nm and two vertical bonds at a distance of 0.19 nm [16]. These $[\text{TeO}_4]^{4-}$ units transform to TeO_3 trigonal pyramidal structure with one or two non-bridging oxygens

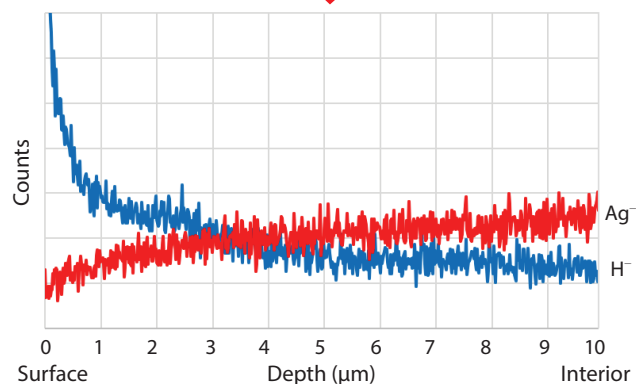
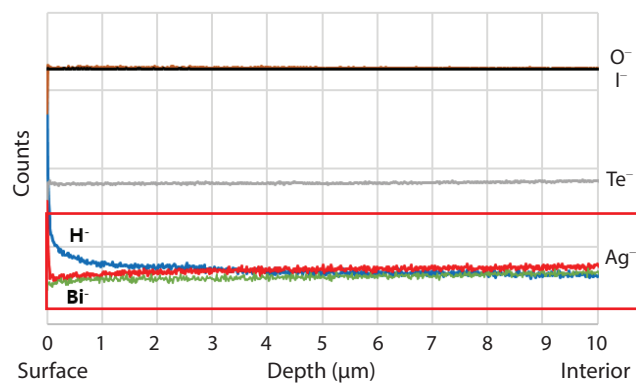


Fig. 4. Depth profiles of glass leached for 128 d in 0.1 M acetic acid at 90°C .

(NBOs) when network modifiers (or hydrolysis) are added [17]. Raman spectra of our silver tellurite glasses have three main bands associated with the vibration of Te-O bonds (Fig. 2). Band A centered at about 450 cm^{-1} is due to the bending vibration of the Te-O-Te linkage. Band B at about 660 cm^{-1} is attributed to symmetric stretching of TeO_4 units, and band C at about 740 cm^{-1} is attributed to symmetric stretching of TeO_3 units [18-20]. After leaching, intensities of bands A and C did not show any clear changes, but band B decreased slightly in intensity; i.e., the number of TeO_4 units decreased.

XPS spectra of Te $3d_{5/2}$ level were collected to provide evidence of the $\text{TeO}_4 \rightarrow \text{TeO}_3$ transformation during the hydrolysis. A large peak appeared at the low band-energy (BE)

side of the Te $3d_{5/2}$ band recorded from the glass leached for 128 d as shown in Fig. 3; this new peak is due to the Te in TeO_3 units. The peak at the high-BE side is associated with TeO_4 units [21-23]. A low-BE Te $3d_{5/2}$ peak appears when network modifiers are added [21]; this result suggests that the tellurite glass network in our glasses depolymerized during the leaching experiment.

As shown in Fig. 4, depth profiles of Ag^+ and H^+ ion concentrations of leached glass indicate that H^+ concentration is high near the surfaces, and Ag^+ concentration decreased slightly toward the surface, whereas concentrations of other ions remained largely constant. These results suggest that ion exchange occurred between Ag^+ in the glass and H^+ in the solution, together with the hydrolysis of tellurite glass network to form TeO_3 units. However, the largely constant Te concentration on the surface of glass indicates that this hydrolysis did not cause collapse of the glass network structure. TeO_4 and TeO_3 units seem to be connected to the glass network through their internal bridging oxygens. As shown in Fig. 1, the constant elemental release indicates that Te^{4+} ion dissolution was not large. However, we observed no evidence for formation of an altered layer that reduces leaching rate of elements, and that usually forms in silicate glasses [24-31].

4. Conclusions

Silver tellurite glasses were evaluated as hosts for the radioactive Iodine wastes. They showed fracture strengths were above 3.45 MPa after thermal cycling, electron radiation and ANS 16.1 that satisfy the requirements for a sustainable disposal. Leachability index of Iodine was 17.58 that is also larger than the regulation of > 11.0 . Long-term dissolution in 0.1 M acetic acid up to 128 d showed that Te, Bi and I leached out only during the first 16 d, whereas Ag^+ leached continuously for the 128 d, but at a very low rate. Analyses detected evidence of ion exchange between Ag^+ in the glass and H^+ in solu-

tion. TeO_4 units in the glass network transformed to TeO_3 with an ion exchange and hydrolysis. As inferred from the negligible amount of Te dissolved from the glass after initial period, both TeO_4 and TeO_3 units appear to be held in the network structure by the bridging oxygens.

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