Tellurite glasses for vitrification of technetium-99 from pyrochemical processing

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HIGHLIGHTS

- Alkali-alumino tellurite glass is developed to immobilize [99]Tc.
- Tellurite glass can incorporate up to 7 mass% of Re (used as a surrogate for Tc).
- Re ions in the tellurite glasses are in the form of Re(VII)O_4^- tetrahedra.
- The product consistency tests satisfied the requirements for the low activity wastes.

GRAPHICAL ABSTRACT
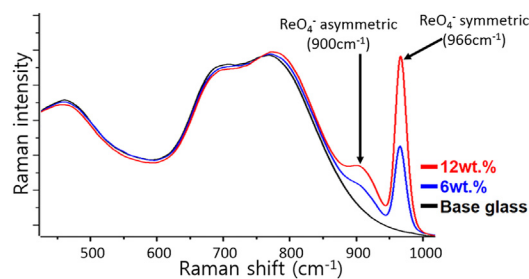
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ABSTRACT

A new alkali-alumino tellurite glass composition was developed to immobilize highly-volatile technetium (Tc) wastes generated from the pyrochemical processing technology. Tellurite glass can incorporate up to 7 mass% of rhenium (Re, used as a surrogate for Tc) with an average retention of 86%. Normalized elemental releases evaluated by seven-day product consistency test (PCT) satisfied the immobilized low activity waste requirements of United States when concentration of $Ca(ReO_4)_2$ in the glass was <12 mass %. Re ions form Re^{7+} and are coordinated with four oxygens to form ReO_4^- tetrahedra. These tetrahedra bond to modifiers such as Ca^{2+} or Na^+ that are further connected to the tellurite glass network by Ca^{2+} (or Na^+) — non-bridging oxygen bonds.

1. Introduction

Pyrochemical processing has been developed to extract and recycle the remaining uranium and transuranic elements from the spent fuel of fission reactors [1]. This process does not involve plutonium separation, and can therefore reduce the proliferation risk of nuclear weapons compared to traditional reprocessing methods such as Plutonium Uranium Redox EXtraction (PUREX). One of the first steps of pyrochemical processing is voloxidation, during which the spent UO_2 pellets are oxidized into U_3O_8 and

pulverized [2,3]. At the same time, fission product such as Tc, I, Kr, Xe and Cs are evaporated and captured by the off-gas treatment system. In particular, technetium-99 (^{99}Tc) is converted to Tc_2O_7 ($T_b = 310$ °C) during voloxidation, then evaporates. Then, these Tc_2O_7 vapors are captured by filters made of calcium granules and converted to $Ca(TcO_4)_2$ or $Ca_5Tc_2O_{12}$ [4].

^{99}Tc is a long-lived ($\tau_{1/2} = 2.1 \times 10^5$ years) fission product of uranium and has a high yield (6.13%) in nuclear reactors [5]. The stable oxidized species of Tc, pertechnetate anion (TcO_4^-), is highly water-soluble and freely migrates in groundwater. Therefore, to avoid environmental contamination, ^{99}Tc must be firmly immobilized in stable waste form such as glass. However, immobilization of Tc-containing wastes by vitrification has been challenging due to the high volatility of TcO_4^- during the glass-melting process [6]. In addition, solubility of Tc in low-activity waste (LAW) glass is < 3000 ppm by weight [7]. Therefore, new waste form must be specifically designed for wastes that contain Tc. Nonradioactive rhenium (Re) is used as a surrogate for ^{99}Tc because they have similar ionic size and volatility at high temperature [8]. Local atomic structure of Tc and Re in the borosilicate glasses were analyzed by X-ray absorption spectroscopy (XAS); Tc ions form $Tc(IV)O_6$ octahedra and $Tc(VII)O_4$ tetrahedra, and Re ions form $Re(VII)O_4$ tetrahedra [9]. Magic angle spinning (MAS) nuclear magnetic resonance (NMR), infrared and Raman spectroscopy analyses suggest that Re ions exist as ReO_4^- anions in the interstitial sites of the glass network [10].

Tellurite glasses have low melting temperature ($600 \leq T_m \leq 800$ °C) and high solubility of halides and therefore have been considered for immobilization of wastes that contain alkali chlorides [11,12]. The glasses achieve chloride retention of ~90%, which is considerably higher than the 60% retention achieved by borosilicate glasses [13]. The primary structural units that compose tellurite glass are TeO_4 trigonal bipyramids (tbp) and TeO_3 trigonal pyramids (tp). Pure tellurite (TeO_2) glass consists of TeO_4 tbp only, but they are converted to TeO_3 tp with non-bridging oxygens (NBO) when network modifiers are added [14,15]. Objectives of the current work were to investigate the potentials of tellurite glasses to immobilize Re, as a surrogate for Tc. Re was added in excess of 8 mass%, and the retention during the vitrification was as high as 90%. Re ions form (ReO_4^-) tetrahedra that are connected to the glass network by an oxygen single-bond.

2. Experimental methods

2.1. Preparation of tellurite glass

Tellurite glasses that contained Al_2O_3, B_2O_3, Na_2O and CaO were prepared (Table 1). Al_2O_3 and B_2O_3 improve the chemical durability of the glass, and Na_2O and CaO decrease its temperature for melting [13,16]. Tellurite glass frits without $Ca(ReO_4)_2$ were prepared first: 20-g batches were melted at 800 °C in alumina crucibles for 40 min.

Table 1
Nominal and analyzed compositions of tellurite glass prepared. All elements were analyzed by X-ray fluorescence (XRF) except for B analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Component	Nominal Composition		Analyzed (mass%)
	(mol%)	(mass%)	
TeO_2	64	79.06	79.21 ± 0.27
Al_2O_3	11	8.68	8.71 ± 0.22
B_2O_3	10	5.39	5.42 ± 0.10
Na_2O	8	3.84	3.84 ± 0.12
CaO	7	3.04	2.82 ± 0.07
Total	100	100	100.0

The melts were quenched by pouring onto a brass mold; after cooling, the glasses were crushed into fine powders (<150 μm in size), which were then mixed with $Ca(ReO_4)_2$ powders to prepare compositions of (100-x)[glass frits]-x$Ca(ReO_4)_2$ where $x = 3$ (glass RT3), 6 (RT6), 9 (RT9) or 12 (RT12) mass%. Batches of 12 g of powder were melted in covered alumina crucibles at 730 °C for 20 min under the ambient atmosphere without stirring.

Formation of glasses was confirmed by the featurelessness of the X-ray diffraction patterns recorded by an X-ray diffractometer (XRD) with a Cu-Kα source. The standard Archimedes method was used to measure the densities of glasses. Glass transition temperatures and thermal expansion coefficients were measured using a thermomechanical analyzer (TMA-60, Shimadzu, Japan). The compositions of glasses were analyzed by X-ray fluorescence spectrometer (XRF, S8 Tiger, Bruker, Germany). The B contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 8300, PerkinElmer, USA) after dissolving the glass powders in a mixed HF and HNO_3 solutions. The distributions of Re in glasses were analyzed by the energy dispersive X-ray spectroscopy (EDS, Aztec EDS, Oxford instruments, UK) attached to the scanning electron microscope (SEM, JSM-7100F, JEOL, Japan).

2.2. Chemical durability test

A Product Consistency Test (PCT) was performed following the procedures in American Society for Testing and Materials (ASTM) C 1285-02 [17]. Glasses were powdered and sieved to 100−200 mesh (0.149−0.074 mm). Powders were washed twice with deionized (DI) water in an ultrasonic cleaner, then washed three times using ethanol to remove organic impurities. Powders were dried at 90 °C overnight and 2 g of glass powders was mixed with 20 mL of DI water in a Teflon vessel and kept in an oven for 7 d at 90 °C. The solution was filtered through a 0.45-μm syringe filter to remove particulates, then the concentrations of ions in the solution were analyzed by ICP-AES. Normalized releases, r_i (g/m^2) of element i, were calculated as

$$r_i = \frac{c_i(soln)}{(f_i)\left[(SA)/V\right]}, \tag{1}$$

where $c_i(soln)$ is the concentration (g/L) of element i in the solution, f_i (unitless) is the fraction of element i in the unleached waste form, and (SA)/V (m^2/L) is surface area of the glass powders per volume leachate.

2.3. Raman and X-ray absorption spectroscopy (XAS)

Raman spectra were recorded in the range 50−4500 cm^{-1} at 9−15 cm^{-1} resolution using a Bruker dispersive Raman microscope equipped with a 532-nm laser. Slit aperture was fixed to 50×1000 μm and the integration time was 20 s with a laser power of 10 mW. The glass specimens for Raman spectroscopy were thin (~2.5 mm) disks, which had been polished to optical quality.

Rhenium L_1-edge (12.527 keV) and L_3-edge (10.535 keV) XAS spectra were collected in fluorescence mode at the 10C beamline of the Pohang Light Source (Pohang, Korea) with a ring current of 300 mA at 2.5 GeV. A monochromatic X-ray beam was obtained from the X-ray photons by using a Si (111) double-crystal monochromator. The XAS data were recorded for powdered RT6 and RT12 specimens attached to polyimide film. Reference data were collected from crystalline ReO_2, ReO_3, $Ca(ReO_4)_2$ and $KReO_4$. XAS data were analyzed using the programs ATHENA and ARTEMIS as reported in detail earlier [18,19]. The extended X-ray absorption