Immobilization of Technetium Waste from Pyro-processing Using Tellurite Glasses

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1. Introduction

Pyro-processing was developed for the recycling of the spent fuel from pressurized water reactors. The uranium and trans-uranium extracted from the spent fuel can be reused in the sodium-cooled fast reactor [1]. During the voloxidation process of pyroprocessing, volatile fission products evaporate due to the high processing temperatures. Technetium-99 (^{99}Tc) is oxidized to the Tc_2O_7 ($T_b = 310^oC$) during voloxidation process and evaporated Tc_2O_7 is captured to form $Ca(TcO_4)_2$ or $Ca_5Tc_2O_{12}$ in the calcium granule filters of an off-gas treatment system [2]. ^{99}Tc is an important radionuclide, because its high fission yield (6.13%) and it has a long half-life ($\tau_{1/2} = 2.1 \times 10^5$ years) . Pertechnetate anion (TcO_4^-), the dominant species of Tc in natural aqueous solution, is highly soluble and mobile in the environment. Rhenium is generally used as a surrogate for Tc because of similarity in volatility at high temperature, ionic size, and redox potentials [3].
Vitrification of Tc wastes has been challenging because of the low solubility in the silicate glass and high volatility in the melting process.

In previous studies, the measured solubility of Tc and Re was ~3000 ppm at 1000^oC in low activity waste (LAW) glass. And retention of Tc has been reported within 12 ~ 77% during the borosilicate vitrification process [3].

Tellurite glasses have been studied for halide waste immobilization due to low melting temperatures ($T_m = 600$-$800~^oC$) and flexibility of network with foreign ions. Tellurite glasses offered higher halide retention than borosilicate glasses [4].

The structure of pure tellurite (TeO_2) consists of TeO_4 trigonal bipyramids (tbp), but TeO_4 units are converted to TeO_3 trigonal pyramids (tp) having non-bridging oxygen (NBO) as the modifiers added [5].

Objectives of this study are to investigate the tellurite glasses for Tc immobilization using Re as a surrogate. Retention and waste loading of Re were analyzed during the vitrification process of tellurite glass. We investigated local structures of Re ions in glasses by Raman and X-ray absorption spectroscopies.

2. Experimental Methods

2.1 Preparation and melting of tellurite glass

The compositions of tellurite glass frit are presented in Table I. Al_2O_3 and B_2O_3 are known to provide tellurite glass with chemical durability and Na_2O and CaO give stable against devitrification [4]. The base glass frits were first melted in alumina crucibles for 30 min at 800^oC. The melts were quenched by pouring onto a brass mold and the glass was crushed into fine powders. After which glass frits were mixed with different amounts of $Ca(ReO_4)_2$ (3, 6, 9 and 12 mass%), symbols of the composition were given as RT3, RT6, RT9 and RT12. The batches melted in covered alumina crucibles at 730^oC for 20 min, poured into a brass mold.

Table I: Nominal and analyzed glass composition. All elements were analyzed by XRF except for B analyzed by ICP-AES.

Component	Nominal Composition		Analyzed
	(mol%)	(mass%)	(mass%)
TeO2	64	79.06	79.21
Al2O3	11	8.68	8.71
B2O3	10	5.39	5.42
Na2O	8	3.84	3.84
CaO	7	3.04	2.82
Total	100	100	100.0

2.2 Characterization of tellurite glass

Formation of glasses was analyzed using the X-ray diffractometer (XRD). Formation of glasses was amorphous by X-ray diffractometer (XRD) analysis. The chemical composition of glasses was analyzed with X-ray fluorescence (XRF) and the boron content was analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES). Glass transition temperature and thermal expansion coefficient was determined by thermomechanical analysis (TMA).

2.2 Chemical durability test

The Product Consistency Test (PCT) was performed according to ASTM standard test method C1285-02 [6]. The glasses were crushed and then sieved to obtain the particle size of 75-150 μm. Powders were ultrasonically washed with water and ethanol to remove any organic impurities. Powder were dried at $90 \pm 5~^oC$ overnight and 2 g of glass powders were mixed with 20 mL of deionized water in a Teflon vessel and maintained for 7 days at $90~^oC$. The solution was filtered using a 0.45 μm syringe filter and the concentrations of elements in the solution were measured by ICP-AES. The normalized releases, r_i (g/m^2), were calculated by;

$$r_i = \frac{c_i(soln)}{(f_i)[(SA)/V]} \quad (1)$$

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

2.3 Raman and X-ray absorption spectroscopy (XAS)

Raman spectra were obtained between 54 and 4466 cm^{-1} with a 532 nm laser and 10 mW power. The glass specimens for Raman spectroscopy were flattened by mechanical polishing with a thickness of 2.5 mm. $Ca(ReO_4)_2$ and $KReO_4$ were used to obtain the reference spectra.

X-ray absorption spectroscopy (XAS) of the Rhenium L_1-edge (12.527 keV) and L_3-edge (10.535 keV) of the sample powders was carried out in fluorescence mode at the 10C beamline of the Pohang Light Source (PLS) in the 2.5 GeV with a ring current of 300 mA. The X-ray beam was monochromatized using a double Si (111) monochromator. The crystalline ReO_2, ReO_3, $Ca(ReO_4)_2$ and $KReO_4$ were used to obtain the reference spectra were collected. The XAS data were analyzed with the ATHENA and ARTEMIS software programs [7]. The extended X-ray absorption fine structure (EXAFS) spectra were converted to $k(Å^{-1})$ after background removal and normalization. The k-space range was set to 3–13 $Å^{-1}$, and EXAFS data were obtained by performing a Fourier transform to the real space within R = 1–3 Å range. The interatomic distances, Debye-Waller factor and the coordination numbers were obtained. S_0^2 was fixed at 0.9.

3. Results and discussion

3.1 Glass Composition and Basic Characteristics

The analyzed composition of the glass remains comparable to the nominal composition. (Table I) Formation of all glasses was amorphous by XRD analysis Density of the base glass is 4.2 g/cm^3 measured by Archimedes method and increased slightly with the addition of $Ca(ReO_4)_2$. Glass transition temperature and thermal expansion coefficient of the base glass are 390 ºC and 14.5 x 10^{-6} /K respectively.

3.2 Re retention

Re concentrations in glasses were analyzed by XRF, as shown in Table II. Re retention (analyzed content/nominal content) in all glasses were >82% with an average of 86%.

3.3 Chemical durability

Fig. 1 shows the normalized elemental releases r_i from the 7 day PCT from glasses containing $Ca(ReO_4)_2$.

Normalized elemental releases for all elements in the base glass are below 0.53 g/m^2. As the $Ca(ReO_4)_2$ content increased, these values increased. However, all r_i values except for r_{Na} of RT12 are below the safety guideline of <2 g/m^2 for the immobilized low activity waste (ILAW) requirement in U.S.

Table II: Re retention in glasses with various $Ca(ReO4)_2$ additions analyzed by XRF.

$Ca(ReO_4)_2$ addition (mass%)	Re addition (mass%)	Retained Re (mass%)	Retention (%)
3	2.07	1.70	82.36
6	4.13	3.74	90.41
9	6.20	5.47	88.17
12	8.27	7.00	84.68

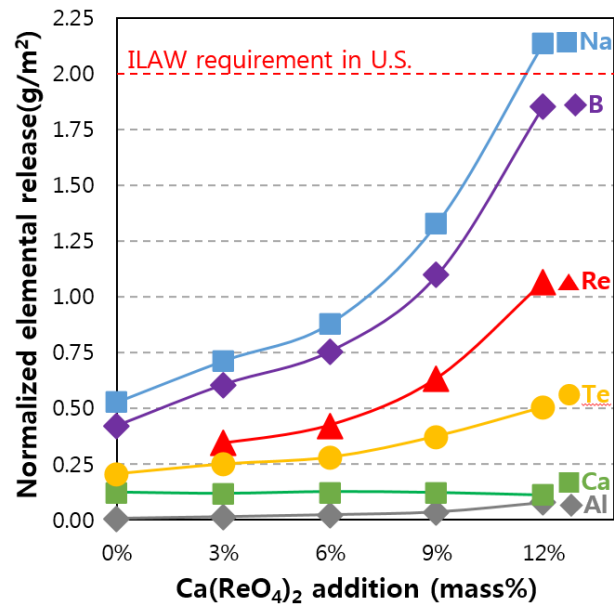Fig. 1. Normalized releases for 7 day PCT from samples with various $Ca(ReO_4)_2$ additions.

3.4 Raman spectroscopy

The Raman spectra of the base glass is shown in Fig.2. The band between 400 and 500 cm^{-1} (band A) is assigned to the stretching and bending vibrations of Te-O-Te linkage. The bands at 650-700 cm^{-1} (band B) and 750-800 cm^{-1} (band C) are due to the stretching vibrations of TeO_4 and TeO_3 units respectively. Raman spectra of RT6 and RT12 glasses have three sharp peaks of 334, 900 and 980 cm^{-1} and intensities of three peaks increase as the $Ca(ReO_4)_2$ content increases. The three additional peaks are due to the stretching and bending vibration of ReO_4^- and correspond similarly to the Raman peak of $Ca(ReO_4)_2$ crystal. In addition, intensity of the band A slightly decreased and the peak position is not changed as the $Ca(ReO_4)_2$ amount increased. It suggests that the addition of modifiers break Te-O-Te linkages however formation of new linkage such as Re-O-Te is not

generated. Intensity of the band C also increased whereas intensity of the band B decreased at the same time because the addition of $Ca(ReO_4)_2$ transforms a portion of TeO_4 units into TeO_3 units.
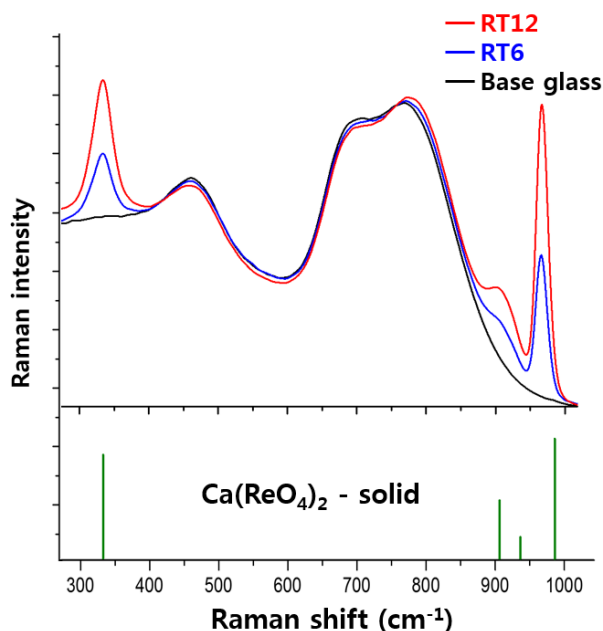

Fig. 2. Raman spectra of base glass, RT6, RT12 and $Ca(ReO_4)_2$.

3.5 XAS analysis

The oxidation state and local structure of Re in tellurite glass have been investigated by the X-ray absorption near edge structure (XANES) spectroscopic method at the Re L_1-edge (Fig. 3). The reference spectra for Re^{7+} was obtained from $Ca(ReO_4)_2$ and $KReO_4$ crystals. ReO_2 and ReO_3 crystals were used to obtain the reference spectra for Re^{4+} and Re^{6+}, respectively. Chemical states of Re in glasses were determined by nonlinear least-squares fits to XANES spectra of references. The result from fitting the XANES spectra show that only Re^{7+} is present neither Re^{4+} nor Re^{6+}. The Re L_3-edge EXAFS structural parameters are summarized in Table III. The Re-O distance and the coordination number are ~1.72 Å and ~4.3 respectively. Since all Re in glass are Re^{7+}, the fitting parameters are similar to the reference crystals and physically reasonable (Fig. 4).

Table II: The EXAFS structural parameters obtained from the references, RT6 and RT12 glasses.

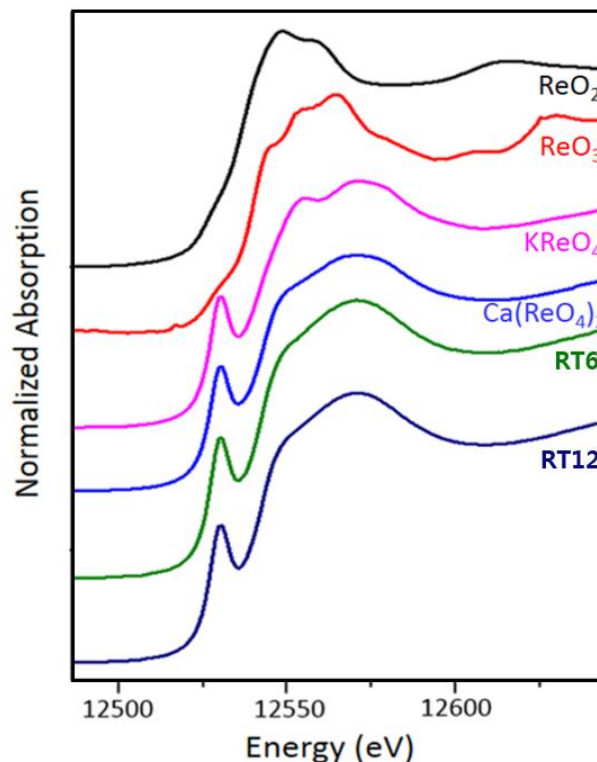|	CN	Distance(Å)	Debye-Waller Parameter(Å^2)
$Ca(ReO_4)_2$	4.0	1.72	0.0001
$KReO_4$	4.0	1.73	0.0002
RT6	4.3	1.73	0.0008
RT12	4.4	1.73	0.0001

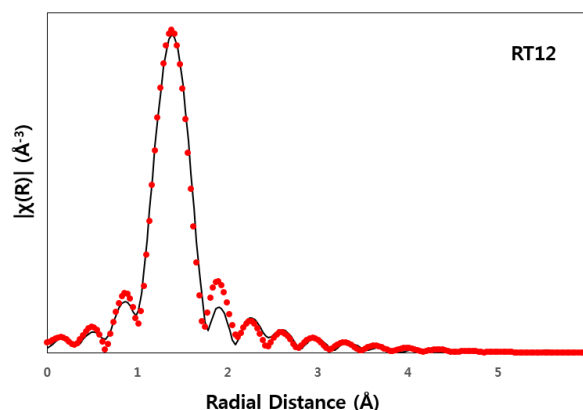Fig. 3. Re L_1 XANES spectra of reference crystals, RT6 and RT12

Fig. 4. Fourier transformed radial distribution function (RDF) of k^2-weighted EXAFS spectrum for Re in RT12(solid lines) and fits(dot). Fit range: 1<R<3.

3.6 Proposed structural model

All of Re ions in the tellurite glass are Re^{+7} and exist as a ReO_4^- anion was determined by XAS analysis. ReO_4^- in tellurite glass can be organized in two possible forms. The first is to bond directly with the glass network and the second is to connect to the glass modifier. In Raman spectra analysis, however, the addition of $Ca(ReO_4)_2$ nearly didn't change the glass structure and Re-O-Te linkage was not generated. Therefore, ReO_4^- anion was bonded with modifier related NBO of glass network and didn't directly connect to tellurite glass network.

3. Conclusions

The tellurite glass was investigated to immobilize the $Ca(TcO_4)_2$, surrogated by $Ca(ReO_4)_2$. The average of Re retention in tellurite glass was 86%. The 7-day PCT results were satisfied with U.S requirement up to 9 mass% of $Ca(ReO_4)_2$ content. Re in the tellurite glass exists +7 oxidation state and was coordinated with 4 oxygen. Re was not directly bonded with the glass network of tellurite and ReO_4^- exists with modifier related with NBO of glass network.

REFERENCES

[1] H. Lee, G. Park, K. Kang, J. Hur, J. Kim, D. Ahn, Y. Cho, and E. Kim, Pyroprocessing technology development at KAERI, Nuclear Engineering and Technology, Vol.43.4, p.317, 2011.

[2] S. Frank, W. Ebert, B. Riley, H. Park, Y. Cho, C. Lee, M. Jeon, J. Yang, H. Eun, Waste Stream Treatment and Waste Form Fabrication for Pyroprocessing of Used Nuclear Fuel, INL, INL/EXT-14-34014 (2015).

[3] J.G Darab, P.A. Smith, Chemistry of Technetium and Rhenium Species during Low-Level Radioactive Waste Vitrification, Chemistry of Materials, Vol.8.5, pp.1004-1021, 1996

[4] B.J. Riley, B.T. Rieck, J.S. McCloy, J.V. Crum, S.K. Sundaram, J.D. Vienna, Tellurite glass as a waste form for mixed alkali–chloride waste streams: Candidate materials selection and initial testing, Journal of Nuclear Materials, Vol.424.1, pp.29-37, 2012

[5] Y. Dimitriev, V. Dimitrov, M. Arnaudov, IR spectra and structures of tellurite glasses, Journal of Materials Science, Vol.18.5, pp.1353-1358, 1983.

[6] Standard test methods for determining chemical durability of nuclear, hazardous, and mixed waste glasses and multiphase glass ceramics: The Product Consistency Test (PCT), C 1285-02, ASTM International, West Conshohocken, PA, 2008 <www.astm.org>.

[7] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, Journal of Synchrotron Radiation, Vol.12.4, pp.537-541, 2005.