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Rhenium solubility in borosilicate nuclear waste glass

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Abstract

The immobilization of ^{99}Tc in a suitable host matrix has proved to be an arduous task for the researchers in nuclear waste community around the world. At Hanford site in Washington, the total amount of ^{99}Tc in low activity waste (LAW) constitutes to be ~ 1300 kg. The current strategy at Hanford is to stabilize the ^{99}Tc by vitrification of LAW in borosilicate glasses. In this context, the present article reports on the solubility/retention of rhenium in a LAW borosilicate glass. Due to the radioactive nature of technetium, rhenium has been used as its simulant owing to the similarity between their ionic radii and other chemical aspects. The glasses containing Re (0 – 10,000 ppm by mass) were synthesized in vacuum sealed quartz ampoules in order to minimize the loss of Re by volatilization during melting at $1000\text{ }^{\circ}\text{C}$. The rhenium was found to predominantly exist as Re (VII) in all the glasses as observed by X-ray absorption near-edge structure (XANES). The solubility of Re in borosilicate glasses was determined to be ~ 3000 ppm by mass using inductive coupled plasma-optical emission spectroscopy (ICP-OES), and at higher rhenium concentrations some additional material was retained in the glasses in the form of crystalline inclusions as detected by x-ray diffraction (XRD) and laser ablation-ICP mass spectrometry (LA-ICP-MS). The implications of these results on the immobilization of ^{99}Tc from radioactive wastes in borosilicate glasses have been discussed.

Keywords: radioactive waste; technetium; rhenium; inductive coupled plasma; borosilicate glass

1. Introduction

The Hanford site in Washington is home to approximately 55 million gallons (~208,000 m³) of radioactive and chemically hazardous wastes stored in 177 underground tanks ¹. The wastes were generated as a result of more than 30 years of plutonium production in support of the nation's defense programs. The tank wastes are planned to be separated into high-volume low-activity waste (LAW) and low-volume high-level waste (HLW) fractions, which will then be vitrified into separate glass waste forms for long-term storage. The LAW vitrification product will be stored at the on-site integrated disposal facility while HLW glass will be transported to a deep-geologic repository whenever it becomes available.¹

The LAW at Hanford primarily consists of aqueous solutions containing Na⁺, K⁺, Al(OH)₄⁻, Cl⁻, F⁻, NO₂⁻, NO₃⁻, OH⁻, CO₃²⁻, and organics as well as other minor ionic species, including radionuclides. Some of the main radionuclides found in Hanford LAW include technetium-99 (⁹⁹Tc), iodine-129 (¹²⁹I), cesium-137 (¹³⁷Cs), and strontium-90 (⁹⁰Sr). The long-lived ⁹⁹Tc and ¹²⁹I radionuclides are of a matter of concern in comparison to ¹³⁷Cs and ⁹⁰Sr that are short-lived and predominantly fractionated into HLW. According to a recent estimate, the Hanford site tanks contain ~25,000 Ci (~1,500 kg) of ⁹⁹Tc and ~32 Ci (~180 kg) of ¹²⁹I.² The current flowsheet calculations estimate that more than 90% of the ⁹⁹Tc inventory in the tanks will be immobilized in the LAW glass whereas only about 20% of the ¹²⁹I inventory will be incorporated into the LAW glass.³ According to the performance assessments conducted for providing the guidance to the storage and disposal project for Hanford LAW, ⁹⁹Tc is the major dose contributor during the first 30,000 years following disposal.^{2; 4}

The major environmental concern with ⁹⁹Tc is its high mobility in addition to a long half-life (213,000 years). The highly soluble TcO₄⁻ does not adsorb well onto the surface of minerals

and, thus, migrates nearly at the same velocity as groundwater.^{5; 6} On the other hand, the primary concern with processing the Tc-containing waste into a glass is its volatility and hence the low retention.⁷ Other sources of Tc-loss may include entrainment with volatilized solvent, formation of aerosols, dust particles in scrubber systems, and other similar sources that can be partially mitigated by engineering systems and recycling.⁸ According to the current flowsheet >90% Tc is being estimated to be immobilized in the LAW glass based on the assumption that all the Tc collected through off-gas is recycled back to the vitrification system. Some recent studies have focused on the issue of Tc volatility from the glass melt with and without cold cap.⁹ Partitioning to the molten salt phase has also been suggested as a mechanism for low retention of Tc in the glass.¹⁰ Volatilization of Tc can occur from the salt layer more readily than from the glass, especially if sulfate is present.¹¹ Therefore, it is critical to understand the mechanism of Tc retention in or escape from glass melt for the management of Tc in LAW vitrification. One of the potential factors that can affect the retention of Tc is its solubility in LAW glass. To the best of authors' knowledge there is no published data on the solubility of Tc in borosilicate glasses for nuclear waste vitrification. The ultimate goal of the present study is to determine the solubility of Tc in a borosilicate glass for vitrification of Hanford LAW.

Rhenium (Re) has been used as a non-radioactive surrogate material for Tc because similarities in chemistry, ionic size, and other aspects, are stronger than other considered candidates such as Mn and W.⁸ Although, many studies have been reported depicting the dissimilarities in the chemistry of Tc and Re,¹²⁻¹⁵ still there exist sufficient similarities in their chemistry to make it a best known non-radioactive surrogate.^{15; 16} Rhenium compounds should be chemically similar to those expected for technetium in LAW simulants (KReO_4) as well as those in liquid (CsReO_4 , NaReO_4 , and KReO_4) and vapor [Re_2O_7 and $\text{ReO}_3(\text{OH})$] phases during

vitrification.⁸ To facilitate development of test procedures, Re was chosen as a non-radioactive surrogate for Tc as a first step before testing the solubility/retention of radioactive Tc in glasses. This paper reports the results on the solubility of Re in a simulated waste glass specifically designed for one of the Hanford's representative LAW streams. The testing with radioactive Tc is in progress and the results will be present in a follow-on article.

2. Experimental

In order to determine the true solubility of Re in a borosilicate glass, the volatilization loss of Re species above the melt was eliminated by heat treating the glasses mixed with Re source material in vacuum sealed ($\sim 10^{-4}$ Pa) fused quartz ampoules so that even the Re species in the gaseous phase would still remain in contact with the glass melt surface. This paper describes the unique experimental procedure designed to perform these solubility experiments along with the results obtained from various characterization techniques in order to quantify the solubility and retention of rhenium in the glasses.

2.1 Glass synthesis

2.1.1 Synthesis of baseline glass

The borosilicate LAW glass with nominal composition shown in [Table 1](#) was synthesized with the melt-quenching technique. The *baseline glass*, or the glass without any Re additions, was made in a large batch from the appropriate amount of oxides (MgO, Al₂O₃, H₃BO₃, SiO₂, Cr₂O₃, ZrO₂, TiO₂, ZnO, Fe₂O₃), carbonates (CaCO₃, Na₂CO₃, K₂CO₃) and sulfates (Na₂SO₄). The glass batch was homogenized in a vibrating agate mill and melted in a platinum alloy crucible at 1200 °C for 1 h. The resulting glass was quenched on a steel plate and crushed inside a tungsten carbide mill within a vibratory mixer yielding a fine glass powder.

2.1.2 Synthesis of rhenium containing glasses

Since the predominant form of Tc in the dried Hanford LAW will most likely be KTcO_4 ,⁸ we chose KReO_4 (Alfa Aesar, 99% metal basis, Re 64%) as the primary source of Re for our experiments. Re_2O_7 (NOAH Tech., 99.99%, -4 mesh) was used in one experiment as an alternative Re-source in order to assess the influence of different Re precursors (with the same oxidation state) on Re solubility in glass under a controlled environment. Note that in the former case K_2O and Re_2O_7 are added, whereas in the latter case only Re_2O_7 is added. The concentration of Re added to the baseline glass was varied between 0 and 10000 ppm (see [Table 1](#)), defined as parts per million mass of Re atoms in the glass. The fractions of the other components in the glasses with Re additions were kept in constant ratios with those in the baseline glass, normalized to the remaining mass fraction after accounting for the Re-source.

The LAW glass powder (as obtained from the experimental procedure mentioned in section 3.1) and the specified amount of Re-source powder were mixed in the tungsten carbide mill to prepare a mixture with a final batch size of 50 g, of which 30 g was used for the Re-solubility study, while the remaining 20 g was set aside for additional experiments. It should be noted that Re-free LAW glass powder (0 ppm Re) was also re-melted under similar conditions and will be considered as the *baseline experiment* in this study.

Each 30 g glass batch was placed into a flat-bottomed fused quartz tube and a fused quartz end cap was then inserted into the tube ([Fig. 1](#)). The tube was then connected to a vacuum system with compression fitting and evacuated. Once the pressure was $\sim 10^{-4}$ Pa ($\sim 10^{-6}$ Torr), the tube was sealed with an oxygen-propane torch. This vacuum sealed tube will hereafter be referred to as the *ampoule*. The ampoule containing powdered glass batch was inserted in the furnace pre-heated at 700 °C. The temperature of the furnace was increased from 700 °C to 1000

°C at a heating rate of 5 K min⁻¹ followed by a dwell of 2 h at 1000 °C to ensure the complete melting of glass batch. The ampoule containing glass melt was finally quenched in air within a stainless steel canister.

2.2 Characterization of glasses

2.2.1 *X-ray diffraction (XRD)*

XRD was performed on all the glasses and selected crystalline samples with a Bruker[®] D8 Advance (Bruker AXS Inc., Madison, WI) equipped with a Cu K_α target at 40 kV and 40 mA. The instrument had a LynxEye[™] position-sensitive detector with an angle range of 3° 2θ. Scan parameters used for sample analysis were 5–110° 2θ with a step of 0.015° 2θ and a 0.3-s dwell at each step. In order to high quality XRD data, the glass samples with Re concentration of 10000 ppm were analyzed in the 2θ range of 10-60° with a step of 0.015° 2θ and a 2.5-s dwell at each step. JADE 6[©] (Materials Data, Inc., Livermore, CA), software was used to identify phase assemblages.

2.2.2 *Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS)*

The microstructure was analysed on select samples with a JEOL scanning electron microscope (SEM, JSM-5900, JEOL Ltd., Tokyo, Japan) equipped with a tungsten filament and a Robinson backscatter electron detector. Additionally, an EDAX Si-drift detector was used to conduct energy dispersive spectrometry (EDS, Apollo XL, AMETEK, Berwyn, PA) for compositional distribution dot mapping. A 20 kV acceleration voltage was used for all imaging and analysis. Since the baseline glass contained both Si (K_α = 1.739 keV) and Zn (K_α = 8.628 keV) with comparable X-ray energies to Re energies (M_α = 1.842 keV, L_α = 8.650 keV), EDS could not be reliably used for semi-quantitative Re determination.

2.2.3 *X-ray Absorption Near Edge Structure (XANES) spectroscopy*

The Re L₂-edge (11959 eV) XANES data were collected at Stanford Synchrotron Radiation Laboratory beamline 11-2 using a Si (220) double crystal monochromator. The harmonic content of the beam was reduced with a harmonic rejection mirror or by detuning the monochromator by 50%. The powdered glass samples were contained in aluminum holders sealed with Kapton tape. Data were recorded in transmission using Ar-filled ion chambers or in fluorescence using a four-element Ge detector and were corrected for detector dead time effects. XANES data analysis was performed by standard procedures¹⁷ using the program Artemis.¹⁸ The Re XANES spectra were also analysed by principal component analysis using program SixPack.

Three reference spectra, ReO₂, ReO₃ and KReO₄ have been used for data fitting. The data has been fit using the locally written program “fites,” which performs a non-linear least squares fit of the data. Six parameters have been used in the fit: the amplitudes of the three standards, one global energy shift, and slope and offset (linear correction to account for differences in background correction). Data have been fit between 11940 and 12040 eV and the data resolution is estimated to be 6.5 eV based on the width of the white line at the Re L₂-edge. Therefore, there are 15 independent data (spectral range divided by the resolution) in the spectrum. The energy calibration of the spectrum is allowed to vary during fitting, so absolute energy calibration is not required. The actual improvement of the fit due to incorporation of the ReO₂ and ReO₃ standards has been examined using an F-test by comparing χ -squared with and without the ReO₂ standard. The null hypothesis in the F-test is that including the additional standard does not improve the fit, and a probability of F, p(F), < 0.05 indicates that the standard improved the fit to better than two times the standard deviation. No F-test has been performed on the ReO₄-soda standard as

this is the main component in all spectra. Additional data on the goodness-of-fit is included in the [Supplementary Material](#).

2.2.4 *Laser ablation-Inductive coupled plasma-Mass spectrometry (LA-ICP-MS)*

The LA-ICP-MS was used to analyze the chemical nature of bulk (polished) glass samples and to detect the presence of any crystalline/metallic Re inclusions in the samples. Glass samples were embedded in resin and polished to a 1- μm finish prior to LA-ICP-MS analysis. The polished glass samples were mounted in a laser system sample holder (UP-266 Macro, New Wave Research Inc, USA) coupled to a quadrupole ICP-MS (PQ Excell, VG Elemental, England). The rhenium sensitivity for ^{187}Re was ~ 1000 cps/ppm, based on a raster ablation with a 20- μm diameter laser spot, rising to ~ 8200 cps/ppm with a 70- μm diameter laser ablation spot. These values were determined by ablating the National Institute of Standards and Technology (NIST) “50 ppm” trace elements in a Standard Reference Material (SRM) 612 glass standard.¹⁹ Additionally, comparative measurements were made with the “500 ppm” trace elements in glass standard SRM 610.¹⁹ These standards are not certified for Re concentration, but by dissolution methods, SRM 612 has been reported at 6.57 ppm and SRM 610 at 49.9 ppm.²⁰

Rhenium distribution studies on the fabricated glasses were performed by ablating a grid of 100 spots, typically 0.5×0.5 mm total area, repeating the measurement over five to six sites across a sample. Single point feature studies such as probing intact gas bubbles were performed by allowing the laser to ablate into the glass to reach the subsurface feature of interest. For these types of analysis the ICP-MS was run in time-resolved analysis mode. More details on the depth profiling using LA-ICP-MS is provided in the [Supplementary Material](#).

During semi-quantitative Re analysis the laser was scanned over the surface of the sample in a raster pattern (scan speed 25 $\mu\text{m}/\text{sec}$) for a period >3 minutes while the ICP-MS collected the intensities of target analytes averaged over three one-minute blocks. Similar laser ablation measurements were performed on the SRM 612 and/or SRM 610 standard under identical conditions and the Re levels in the test glasses estimated by relative signal ratios assuming the reported Re concentration in these standard as stated above. These SRM glasses were run before and often in the midst of the unknown Re concentration glasses each day that the LA-ICP-MS was run, to account for variations in set-up, laser power drift, and other uncontrolled factors.

2.2.5 Inductive coupled plasma-Optical emission spectroscopy (ICP-OES)

The ICP-OES was employed to quantify the Re concentration (irrespective of its solubility or retention) in the as synthesized glasses. Fragments of glass samples weighing 20–40 mg were dissolved in 2 mL of concentrated hydrofluoric acid (HF) by mild heating (no boiling) at ~ 100 $^{\circ}\text{C}$ on a hot plate in 15 mL volume, capped Teflon[®] crucibles for 2–3 hours. This procedure left a small amount of un-dissolved white powder. The bulk Si was then slowly evaporated off with the HF until it was completely dry. Then, 2 mL of concentrated hydrochloric acid (HCl) was added and evaporated. Then, a mixture of 0.5 mL HCl and 1.5 mL HNO_3 was added to the Teflon crucible and heated gently for 1 h. Once the glass dissolution was completed and the crucible was allowed to cool down to room temperature, the contents of each crucible were transferred to test tubes and 1 wt.% HNO_3 was added to each test tube, thus, yielding ~ 10 g of total solution. From this solution, a weighed volume was further diluted by a factor of ten in 1 wt.% HNO_3 to prepare the final solution for ICP-OES analysis (ICAP 6500 Duo, Thermo-Fisher

Inc., England). Typical sample Re concentrations were in the range 0.1–2 ppm after final dilution. Quantitative analysis was performed by generating a calibration curve at three Re emission wavelengths (197.3, 221.4 and 227.5 nm), by serial weight dilution of a Re 999 ± 2 ppm solution concentration standard (Inorganic Ventures, USA) in 2 wt.% HNO₃. The calibration plots for all three wavelengths showed a linearity of 0.99 or better.

3. Results

3.1 Structural characterization of glasses

Melting at 1200 °C for 1 h was sufficient to produce a homogenous baseline (no Re) LAW glass with dark brown color. The absence of crystalline inclusions was also confirmed by XRD and SEM analyses. The glass transition temperature (T_g) determined from the DSC thermograph for this glass was ~530 °C while no exothermic crystallization curve could be observed until 1100 °C (see [Supplementary Material](#)). Magic angle spinning-nuclear magnetic resonance (MAS-NMR), Fourier Transform Infrared (FTIR) spectroscopy, and Raman spectroscopy were also conducted to characterize glasses as a function of Re source additions. Details of these measurements can be found in the [Supplementary Material](#). In general, these techniques showed a glass composed of primarily Q² and Q³ structural units, with Si, Al, or B tetrahedra, due to the large sodium content causing non-bridging oxygens. Aluminum is present 4-coordinated, and boron is present mostly as 3-coordinated with some 4-coordinated. Rhenium source additions did not appear to have clear effects on the glass structure as evidenced by MAS-NMR, FTIR, and Raman spectroscopy. Based on additional evidence from XANES (below), Re is thought to be present in the glass “in solution” as ReO₄⁻ isolated anions.

3.2 Crystallinity in Re glasses

The rhenium containing glass melts exhibited different physical and chemical features during the glass synthesis depending on their initial rhenium concentration. A brief account of visual observations that were made during synthesis of these glasses along with the results obtained from characterization of these glasses by XRD and SEM-EDS has been presented below.

Re-melting of the baseline glass (with 0 ppm Re) in the quartz ampoule resulted in a cylindrical shaped glass that cracked and shattered upon cooling into small pieces due to the stresses from a thermal expansion mismatch between glass and fused quartz. No significant interfacial reactions between glass melt and walls of quartz ampoule were observed. The addition of Re (100–2500 ppm) in the baseline glass with KReO_4 as its source resulted in amorphous glasses as revealed by XRD analysis (Fig. 2). Further increase in the Re concentration to ~6400 ppm (source: KReO_4) led to the formation of a separate low viscosity (estimated to be $< 0.1 \text{ Pa s}$) liquid phase floating on the top of the glass surface during cooling that gradually solidified to a white-colored superficial powdered layer. The XRD analysis of this superficial white powder revealed its highly crystalline nature with the dominance of alkali perrhenates along with a some minor phases, notably sulfates (Fig. 3), while the glass itself remained amorphous (Fig. 2). Similar observations were made for the glass with 10000-ppm Re (source: KReO_4) where a low viscosity liquid phase floated on the top of the glass and gradually solidified to form a highly crystalline white powder on the surface of the solidified glass with a dominance of NaReO_4 phase along with some minor phases including KReO_4 plus SiO_2 , likely attributed to impurity addition from the walls of quartz ampoule (Fig. 3). However, unlike the 6415 ppm (source: KReO_4) sample, the glass obtained with the 10000-ppm Re concentration exhibited the presence

of NaReO_4 phase. In order to obtain an insight into the distribution of crystalline inclusions in the sample, the glass was cut in three sections (bottom, middle, top) relative to the cooled white salt phase. The powder XRD analysis on three different parts of the glass sample revealed the heterogeneous distribution of crystalline inclusions in the sample as the top and middle sections of the glass exhibited the strong crystallinity while the bottom section of glass was only weakly crystalline (Fig. 2).

With respect to the synthesis of glass with Re_2O_7 as the rhenium source and Re concentration of ~ 6400 ppm, we did not observe any significant interaction between the glass melt and walls of the quartz ampoule. In XRD, the resulting glass did show Re-containing crystalline phases (Fig. 2) similar to the 10000 ppm KReO_4 sample, Also similar to its KReO_4 containing counterpart, a low-viscosity liquid phase was observed floating on the top of glass surface that gradually solidified to white-colored superficial powdered layer. The XRD analysis of the white powder revealed its crystalline nature (Fig. 3) with NaReO_4 as the major crystalline phase with minor phases including KReO_4 and alkali sulfate. The bottom part of the quartz ampoule cracked after a few minutes of air-quenching due to the thermal stresses, leading to the release of a plume of gas in the canopy hood.

The SEM images of the white powder at different locations on the glass surface illustrate their highly crystalline microstructure with dendritic morphology as shown in Fig. 4. The EDS elemental mapping of the dendritic crystals found on a fracture surface reveals the dominance of sodium, sulfur and rhenium in these crystals as is evident from Fig. 5. It is noteworthy that although the crystalline microstructure of the white powders is enriched in sulfur along with Re and Na, we did not observe any Re-S containing phase in XRD (Fig. 3). Additionally, the EDS confirms that the sulfur is associated with sodium (probably Na_2SO_4 with some K), while the

rhenium appears to be mostly associated with potassium (probably KReO_4 with some Na). It is likely that the perrhenate and sulfate salts were intimately mixed in the low viscosity liquid on top of the glass, and then deposited in the crack upon cooling where they formed separate crystalline phases.

3.3 Rhenium valence and coordination in glasses

The Re-XANES spectra of the studied glass compositions are presented in Fig. 6 while the fitting results are presented in Table 2. Fitting results of glasses at the two extremes of Re loading are shown in Fig. 7. Other than the glass with 100 ppm Re concentration (Fig. 7a), the spectra obtained from all the glasses have good signal – to- noise ratio. The F-test reveals that rhenium predominantly exists as six-coordinated Re^{7+} in the glasses with Re concentration varying between 0 – 6415 ppm, irrespective of the Re source. However, for glass with Re concentration = 10000 ppm (Fig. 7b), some of the rhenium has been also detected in four-coordinated Re^{4+} along with the dominance of Re^{7+} species. These results are in agreement with those reported by Lukens et al.¹² except that the 10000 ppm results in the appearance of Re (IV) species, which is unlikely according to their study. Even in the 10000 ppm case, the Re (VII) is ~90% of the Re sites.

3.4 Rhenium solubility in glasses

In agreement with the XRD results (Fig. 3), the presence of rhenium-rich crystalline inclusions in the glass with target Re concentration 6415 ppm (source: Re_2O_7) was confirmed by LA-ICP-MS data as presented in Fig. 8. A sharp increase in the intensity counts for ^{187}Re in imply that the laser beam ablated a Re-containing crystalline inclusion that was likely in the form

of NaReO_4 as detected by XRD analysis (Fig. 3). Depth profiling to identify bubbles versus inclusions is described in the [Supplementary Material](#).

Quantitative ICP-OES results are shown in Table 3. Each glass was sampled at least twice, and up to six times where various locations in the glass ingot were studied. Heterogeneity in the Re_2O_7 glass and 10000 ppm KReO_4 glass was further confirmed by ICP-OES taken from different regions of the sample (top, middle, or bottom) (Fig. 9). ICP-OES analysis on the different pieces of glass revealed the higher concentration of rhenium in top and middle parts of glass sample in comparison to the bottom part of sample. Similar results were obtained for glass with 10000 ppm of target Re concentration (source: KReO_4) as ICP-OES showed that experimental rhenium concentration varied between 3000-4000 ppm in different pieces of glasses. These results are in good agreement with the XRD results presented in Fig. 3. By contrast, the 4000 ppm (source: KReO_4) glass, produced last as a test case, showed relatively uniform Re concentration \sim 3000 ppm in all portions of the glass.

LA-ICP-MS data should be considered semi-quantitative, as proper quantification depends strongly on choosing a proper standard with the element of interest in the right range within a matrix which ablates similarly to the unknown sample.²¹ The SRM standard glasses available had very low Re concentration and gave unreasonably low numbers when used as the only calibration. Therefore, we chose to scale the LA-ICP-MS to the truly quantitative ICP-OES data as follows. The average value of the LA-ICP-MS results obtained using the SRM for 100, 1000, 2500, and 6415 ppm KReO_4 samples was plotted against the average ICP-OES results for these same glasses and a scale factor of 1.798 was found to be reasonable to apply to the LA-ICP-MS individual values. As an independent check, two samples were analysed with electron probe microanalysis with wavelength dispersive spectroscopy (EPMA-WDS), and the quantified

trend followed for variation in rhenium concentration in glasses is similar to that observed for the data obtained from ICP-OES and LA-ICP-MS (see [Supplementary Material](#)).

The ultimate solubility of Re in the borosilicate LAW glass was determined as follows. The individual sample quantitative data from 4000 ppm target (6 data points), 6415 ppm target KReO_4 source (2 data points), and 10,000 ppm (2 data points with lower values) were averaged to obtain a value of 3004 ppm. The justification for using the two lower values of the 10,000 ppm sample was that these points likely represented the bulk glass, whereas the two points with the higher Re measured values likely contained Re salt inclusions resulting in larger measured Re concentrations. The results of this analysis are shown in [Fig. 9](#), which is considered the key result of our work. Here the “equality line” is shown representing where solubility is equal to retention of the Re, and the “solubility line” is shown representing the maximum incorporation of Re in the glass under these conditions without forming inclusions.

3.5 Rhenium retention in glasses

With respect to ‘*solubility*’ and ‘*retention*’ of rhenium in the LAW glass, the ‘solubility’ is defined as the concentration (in mass fraction) of Re at an established equilibrium between dissolved and atmospheric Re. However, the glass-making process generally does not allow the glass melt to reach equilibrium. While the portion of a component dissolved in the amorphous phase(s) may be unsaturated (i.e. below the solubility), a substantial portion may simultaneously exist in the form of inclusions (i.e. inhomogeneities). Therefore, the retention ratio is a dynamic quantity that depends on the glass-making conditions.²² The retention ratio for of a particular element, i , is defined as

$$R_i = \frac{g_{i,r}}{g_{i,o}} \quad (1)$$

where $g_{i,0}$ is the target mass fraction of the element i (Re in present case) in the glass (i.e., the mass fraction of Re that would be present in glass if the total amount added with the feed were retained) and $g_{i,r}$ is the mass fraction of rhenium actually retained in the glass (here, as determined by ICP-OES analysis). Since $g_{i,0} \geq g_{i,r}$, therefore, $R_i \leq 1$. The difference between $g_{i,0}$ and $g_{i,r}$ is caused by losses to the atmosphere due to volatility and by the formation of surface salt phase enriched with Re. Fig. 10 presents the retention ratio for Re in the investigated glasses. The following observations can be made from the obtained results:

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- The Re concentration in glasses as obtained from ICP-OES varies almost linearly with the target Re concentration in the range of 100-2500 ppm as shown in Fig. 9. This shows that most of the rhenium (80 - 90%) added to the borosilicate glasses has been retained in them, the rest presumably being lost to volatilization. Further, the absence of any crystalline inclusions in these glasses confirms that at least up to 2500 ppm Re concentration, retention \leq solubility.
- An increase in target Re concentration beyond 2500 ppm led to the deviation in retention behavior from linearity. The maximum amount of Re retained in glass with target Re concentrations of 6415 ppm (source: KReO_4) and 10000 ppm were \sim 3000 ppm and 3000-4000 ppm, respectively. In the latter case, the 4000 ppm was likely due to the presence of inclusions.
- The difference in Re-precursors (Re_2O_7 and KReO_4) used in the glass melting showed its effect on Re-retention as the Re_2O_7 containing glass exhibited the Re-concentration of 2100-4000 ppm while \sim 3000 ppm Re concentration was detected for KReO_4 glass (Fig. 9).

- The significant spread in the values of retained Re concentration in glasses with target Re concentration > 6000 ppm is due to the heterogeneous distribution of rhenium rich inclusions in the glass matrix as has been already shown by XRD (Fig. 2).
- As is evident from Fig. 10, the retention ratio varied between 0.8 - 1 for glasses with target Re-concentration \leq 2500 ppm while beyond that, retention ratio decreased considerably. This decrease in retention ratio in glasses with higher target Re concentration may be attributed to the: (i) volatility of rhenium from the glass melt and subsequent deposition on the walls of quartz ampoule; ii) reaction between rhenium and the components from the glass melt resulting in deposition of highly crystalline white salt on the surface of glass. The white salt layer was removed from the glass surface before analysing the glasses by ICP-OES.

4. Discussion

4.1 Re versus Tc

Although Re has been widely accepted as a surrogate for Tc, it is important to highlight some important differences between the two species regarding their chemistry within glass environment. Rhenium has a bulk silicate Earth abundance of 0.2 ppb and is the rarest of all the naturally occurring elements, apart from the noble gases,²³ thus there have been few comprehensive studies on its behavior outside of the geochemistry literature. The most prominent difference between Tc and Re is their contrasting reduction-oxidation (redox) behavior. Rhenium commonly occurs in the +7 oxidation state as Re_2O_7 or ReO_4^- (perrhenate ion) as well as in the +4 state in ReO_2 and the +6 state in ReO_3 , whereas Tc occurs only in the 7+ or 4+ oxidation states.^{8; 24} Tc is more easily reduced from $\text{Tc}^{7+} \rightarrow \text{Tc}^{4+}$ compared to $\text{Re}^{7+} \rightarrow \text{Re}^{4+}$,⁸ and thus it has been suggested that Re may not be a representative substitute for Tc under reducing conditions, at least in borosilicate LAW glasses.¹² Additionally, in a particular chemical

durability test, the vapor hydration test (VHT),²⁵ Tc has always been observed to reduce to Tc⁴⁺ regardless of the starting Tc valence distribution, whereas Re⁷⁺ species has always been dominant in the Re glass analogues.²⁶ Furthermore, Tc is enriched at the outer corroded gel-layer of amorphous silica while almost absent at the center, while Re concentrations are lower near the surface of comparable samples and approach that of unreacted glass near the center, thus highlighting the difference in mobility of Re and Tc in hydrothermal environments. Also, a series of recent melter tests suggest that the retention of Re is 8 to 10% higher than Tc for similar glasses.^{9; 27}

According to the literature, solubility/retention and volatility of Tc/Re compounds in silicate and borosilicate glasses is strongly dependent on the oxidation state of the glass¹² as well as on the feed chemistry.⁸ For example, Tc and Re tend to be more volatile when present as Tc⁷⁺/Re⁷⁺ (TcO₄⁻/ReO₄⁻) than when present as Tc⁴⁺/Re⁴⁺ (TcO₂/ReO₂). On the other hand, KTcO₄ and KReO₄ precursors are expected to produce lower Tc and Re volatilization at higher temperatures compared to Tc₂O₇ and Re₂O₇, respectively.^{8; 28} Thus, the calculated or predicted solubility of Tc/Re in these studies may not be considered as the true *solubility* but, rather, is the *retention* of residual Tc/Re retained in the glass melt after volatilization of these species during melting.

One estimate for the solubility of Tc in borosilicate glass might be made based on a comparison of the solubility of Re measured in this study with the solubility of sulfur in borosilicate glass measured in various studies (~0.6 mol% SO₃²⁹ or ~3000 ppm wt S). On a part per million atom basis for a glass with composition studied here, however, sulfur shows about a six-fold higher solubility than rhenium in borosilicate glass, presumably due in part to its smaller

ionic radius ($S^{6+} = 43$ pm, $Re^{7+} = 67$ pm, $Tc^{7+} = 70$ pm³⁰). By this argument, then, Tc^{7+} should have a slightly lower solubility (by atoms) than Re^{7+} .

4.2 Re valence

A number of studies have focused on the differences between Tc or Re species in silicate/borosilicate glasses synthesized under different conditions in order to determine the effect of the starting material on the solubility/retention and volatility in glass.^{12; 31-33} However, the results from most of these studies tend to contradict each other, thus providing a vague and uncertain picture regarding the solubility of these species in glass melts. For example, according to O'Neill et al.³¹ and Richter and Drake,³² Re dissolves in silicate melts as species with unusually low valence states (Re^+ or Re^{2+}) while on the other hand Ertel et al.³³ demonstrated that Re dissolves in silicate melts as ReO_2 (Re^{4+}) and ReO_3 (Re^{6+}). Further, the results of Ertel et al.³³ were again contradicted by Lukens et al.¹² where it has been reported that Tc might exist in glasses as Tc^0 , Tc^{4+} , and Tc^7 , and in no case was Re found to exist as Re^{4+} and Re^{6+} , but rather in borosilicate glasses as Re^0 and Re^{7+} . Studies of Re diffusion heated in air under oxidizing conditions have shown that Re^{7+} in the melt is reduced to Re^{6+} near the surface of the melt to oxidize Fe^{2+} to Fe^{3+} in a redox couple, with Re^{6+} species diffusing faster than Re^{7+} species resulting in a surface layer reduced in Re.²⁴ The main reason behind this disparity in results may be attributed to the experimental procedure, because, in most of these studies, experiments were performed in an open crucible. We found some support through XANES for Re^{4+} in the highest $KReO_4$ target glasses, but no other oxidation state than Re^{7+} .

The initial motivation for undertaking LA-ICP-MS was that it had been reported that Re could concentrate in reduced metallic form in “micronuggets” in silicate melts which would

skew the assessed solubility of a glass containing them.³³ Reports on the homogeneity of Re in silicates have been inconsistent, however, with anorthite-diopside eutectic haplobasaltic melts evidencing ubiquitous micronuggets of Re as ReO_2 and ReO_3 .³³ On the contrary, Re was found to be homogenous, especially when compared to Os, in basaltic silicate melt which had previously crystallized out olivine.³⁴ In other study, Re distribution was homogenous in glass but heterogeneous in crystals precipitating from it, including clinopyroxene and garnet.³⁵ Indeed, even the NIST SRM 610 and 612 glasses have been denoted “moderately inhomogeneous” for Re distribution by quantitative geochemistry studies using LA-ICP-MS.¹⁹ Other than the evidence of inclusions, most probably sodium and potassium perrhenate, we did not see any evidence of the “micronuggets” causing small but measurable fluctuations in Re concentration suggested by these previous authors. Inclusions containing Re in our samples were indicated by very large excursions of Re concentration and were very spatially confined, different than the results reported by the geochemists.

4.3 Implications for waste processing

From the standpoint of ultimate disposition of radioactive Tc in a glass waste form, a few considerations should be made. First, assuming that the solubility of Re^{7+} is substantially similar to Tc^{7+} in glass, 3000 ppm solubility is more than adequate given current estimates of Tc concentrations in LAW glass of ~10 ppm with the recycle loop [ref]. The more important issue, then, becomes Tc retention. As shown by this study with Re, retention can be substantially lower than solubility even at low concentrations due to kinetic factors such as volatility. Here future work will be needed to understand the details of the interaction between formation of a low-melting salt phase in LAW glass (which may contain pertechnetate, sulfate, chromate,

chloride, nitrate, and nitrite along with various alkali metals), and volatilization from the cold cap where the slurry feed comes in contact with the melt pool. Here, previous work has shown that despite the estimated solubility of sulfate in borosilicate glass (~0.6 mol%), salt formation occurs at lower sulfate concentrations than solubility would indicate [ref]. Additionally, despite low concentrations of ^{137}Cs in LAW less than that estimated for pertechnetate (most ^{137}Cs is partitioned to HLW), pertechnetate has been shown to enhance the volatility (and hence retention) of Cs as well,⁸ causing additional concern for release of this short half-life, high dose contributor. Controlling the redox of the cold cap, then, to prevent formation of Tc^{7+} has been an area of intense research, though some authors are skeptical of success given the strongly oxidizing potential of nitrates that are ubiquitous in glass feed.³⁶

5. Conclusions

We have determined that the solubility of rhenium in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ simulated nuclear waste glass is ~3000 ppm by mass when glass is equilibrated at 1000 °C for the particular composition studied, a high sodium borosilicate representative of Hanford Low Activity Waste glass. In all the glasses studied, the primary Re valence was +7, with a possible small fraction (<10%) of +6 in the glass where the most KReO_4 was added. We expect the solubility of Tc^{+7} to be substantially similar to that shown for Re^{+7} in this study, and reduced scope test program is underway to verify this. Given the high solubility of Re/Tc in borosilicate glass, it is concluded that this is not a limiting factor in processing nuclear waste into glass given the currently estimated scenarios. Rather, it is the retention in glass that is the bigger concern, which is a more complex kinetic problem involving volatilization, phase separation, and complexing with alkali in the cold cap.

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