

Rhenium Solubility in Borosilicate Nuclear Waste Glass: Implications for the Processing and Immobilization of Technetium-99

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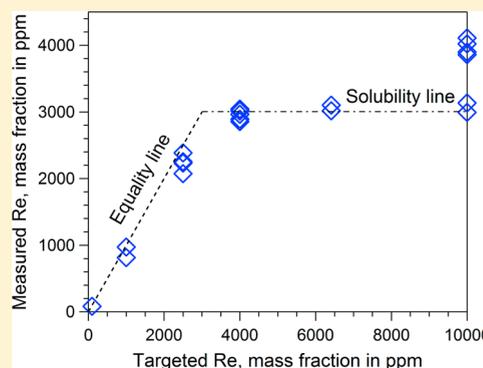
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Supporting Information

ABSTRACT: The immobilization of technetium-99 (^{99}Tc) in a suitable host matrix has proven to be a challenging task for researchers in the nuclear waste community around the world. In this context, the present work reports on the solubility and retention of rhenium, a nonradioactive surrogate for ^{99}Tc , in a sodium borosilicate glass. Glasses containing target Re concentrations from 0 to 10 000 ppm [by mass, added as KReO_4 (Re^{7+})] were synthesized in vacuum-sealed quartz ampules to minimize the loss of Re from volatilization during melting at 1000 °C. The rhenium was found as Re^{7+} in all of the glasses as observed by X-ray absorption near-edge structure. The solubility of Re in borosilicate glasses was determined to be ~ 3000 ppm (by mass) using inductively coupled plasma optical emission spectroscopy. At higher rhenium concentrations, additional rhenium was retained in the glasses as crystalline inclusions of alkali perrhenates detected with X-ray diffraction. Since ^{99}Tc concentrations in a glass waste form are predicted to be <10 ppm (by mass), these Re results implied that the solubility should not be a limiting factor in processing radioactive wastes, assuming Tc as Tc^{7+} and similarities between Re^{7+} and Tc^{7+} behavior in this glass system.



1. INTRODUCTION

The Hanford site in Washington is home to approximately 2.1×10^{11} m³ ($\sim 5.5 \times 10^7$ gallons) of radioactive and chemically hazardous wastes stored in 177 underground tanks.¹ The wastes were generated as a result of 45 years of plutonium production in support of the nation's defense programs. The current plan is to separate the tank wastes into high-volume, low-activity waste (LAW) and low-volume, high-level waste (HLW) fractions that 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 when such a location becomes available.¹

The LAW at Hanford primarily consists of aqueous solutions containing Na^+ , K^+ , $\text{Al}(\text{OH})_4^-$, Cl^- , F^- , NO_2^- , NO_3^- , OH^- , CO_3^{2-} , and organics as well as other minor ionic species, including radionuclides. Some of the main radionuclides found in Hanford LAW include ^{99}Tc , iodine-129 (^{129}I), cesium-137 (^{137}Cs), and strontium-90 (^{90}Sr). The long-lived ^{99}Tc and ^{129}I

radionuclides are a matter of concern in comparison to ^{137}Cs and ^{90}Sr , which are short-lived and predominantly fractionated into HLW. According to a recent estimate, the Hanford site tanks contain $\sim 9 \times 10^2$ TBq ($\sim 2.5 \times 10^4$ Ci or ~ 1500 kg) of ^{99}Tc and ~ 1 TBq (~ 32 Ci or ~ 180 kg) of ^{129}I .² The current flowsheet calculations estimate that more than 90% of the ^{99}Tc inventory in the tanks will be immobilized in the LAW glass, whereas only about 20% of the ^{129}I inventory will be incorporated into the LAW glass.³ According to the performance assessments conducted to provide guidance for the storage and disposal project for Hanford LAW, ^{99}Tc is the major dose contributor during the first 3×10^4 yrs following disposal.^{2,4}

The major environmental concern with ^{99}Tc is its high environmental mobility in addition to a long half-life (2.1×10^5

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years). The highly soluble TcO_4^- does not adsorb well onto the surface of minerals and, thus, migrates nearly at the same velocity as groundwater.^{5,6} The primary concern with processing the Tc-containing waste into a glass is its extreme volatility that results in low concentrations of Tc retained in the final product relative to the target.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 for the Hanford vitrification process, >90% Tc is estimated to be immobilized in the LAW glass based on the assumption that all of 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 of the Tc into 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 sulfates are present.¹¹ Therefore, it is critical to understand the mechanism of Tc retention in (or escape from) a 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 the 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^{7+} in a borosilicate glass for vitrification of Hanford LAW.

Rhenium has been the preferred nonradioactive ⁹⁹Tc surrogate material over other candidates such as Mn or W, because of rhenium's similarities to technetium in chemistry, ionic size, speciation in glass, volatility from glass, and other aspects.⁸ Although many groups have reported divergent behavior due to differences in the reduction potentials of Re^{7+} and Tc^{7+} ,^{12–15} the chemistry of the two elements is very similar when in the same oxidation state. In other words, while Re is not a perfect surrogate for Tc due to the differences in reduction potentials, Re^{4+} is a good surrogate for Tc^{4+} and Re^{7+} is a good surrogate for Tc^{7+} . This work addresses the behavior of Re^{7+} in Hanford LAW glass, which is formed under strongly oxidizing conditions due to the decomposition of nitrate. Consequently, the most important Tc species in Hanford LAW glass is hypothesized to be TcO_4^- . The similarities between ReO_4^- and TcO_4^- overwhelmingly argue for its utility in obtaining preliminary data in a nonradioactive environment that can later be corroborated with Tc.^{15,16} Moreover, Re^{7+} and Tc^{7+} have the same volatility issues in glass processing, and no other surrogate element has been found that can duplicate this important aspect. Additionally, rhenium compounds should be chemically similar to those expected for technetium in LAW simulants (KTcO_4) as well as those in liquid (CsTcO_4 , NaTcO_4 , and KTcO_4) and vapor (Tc_2O_7 and $\text{TcO}_3(\text{OH})$) phases during vitrification.⁸ This work reports 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 presented in a follow-up article.

2. EXPERIMENTAL SECTION

In order to determine the true solubility of Re in a borosilicate glass, the volatilization loss of Re species above the melt was greatly decreased by heat treating the glasses mixed with Re source material in vacuum sealed ($\sim 10^{-4}$ Pa, $\sim 10^{-6}$ Torr) fused

quartz ampules so that even the Re species in the gaseous phase would still remain in contact with the glass melt surface. This work 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. The borosilicate LAW glass was synthesized with the melt-quenching technique and is termed the *baseline* glass without any Re additions (Table 1). This glass

Table 1. Composition of Baseline LAW Glass

Oxide	Mass%
SiO_2	45.3
Al_2O_3	6.1
B_2O_3	10
Na_2O	21
CaO	2.07
Fe_2O_3	5.5
Cr_2O_3	0.02
K_2O	0.47
MgO	1.48
SO_3	0.16
TiO_2	1.4
ZnO	3.5
ZrO_2	3.5

composition is based on the AN-105 low-sulfur tank waste, one of the earliest planned to be processed into LAW glass, and has been used in recent glass formulation studies of Tc retention.^{9,17} The baseline glass was made in a large batch from the appropriate amount of oxides (MgO , Al_2O_3 , SiO_2 , Cr_2O_3 , ZrO_2 , TiO_2 , ZnO , Fe_2O_3), carbonates (CaCO_3 , Na_2CO_3 , K_2CO_3), sulfates (Na_2SO_4) and H_3BO_3 . The glass batch was homogenized in a vibrating agate mill and melted in a lidded 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.

Since the predominant form of Tc in the dried Hanford LAW will most likely be an alkali pertechnetate,⁸ we chose KReO_4 (Alfa Aesar) as the primary source of Re for our experiments. The concentrations of Re added to the baseline glass were 100, 1000, 2500, 4000, 6415, and 10 000 ppm (see Table 1), defined as parts per million of Re atoms in the glass, by mass. The fractions of the other components in the glasses with Re additions were kept in constant ratios with those in the baseline glass, renormalized to the remaining mass fraction after accounting for the rhenium source (see Supporting Information for detailed compositions).

The LAW glass powder (as obtained from the experimental procedure mentioned previously) and the appropriate amounts of KReO_4 powder were mixed in the tungsten carbide mill to prepare a 30 g batch for melting. The glass frit was prepared this way so that the sulfate would be well-mixed and soluble in the glass and so that the rhenium source powder could be well-mixed within the glass, and captured by the glass powder sintering at the maximum allowable solubility. Rhenium-free LAW glass powder was also remelted under similar conditions and will be considered as the *baseline experiment* in this study.

Each powder batch was placed into a flat-bottomed fused quartz tube and a fused quartz end-cap was then inserted into the tube. The tube was then connected to a vacuum system

with compression fitting and evacuated. Once the pressure was $\sim 10^{-4}$ Pa, the tube was sealed with an oxygen-propane torch. The vacuum sealed tube (ampule) containing powdered glass batch was inserted in the furnace preheated at 700 °C. The temperature of the furnace was increased to 1000 °C at a heating rate of 5 °C min⁻¹ followed by a dwell of 2 h at 1000 °C to ensure the complete melting of glass batch. Higher temperatures were attempted initially, but there were concerns with (1) dissolving the fused quartz due the high sodium content in the LAW glass, and thus changing the batch chemistry and (2) having the Re compound attack the ampule wall. At the end of the heating time, the ampule 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).** All of the glasses and selected crystalline samples were analyzed with a Bruker D8 Advance (Bruker AXS Inc.) XRD equipped with a Cu K_α target at 40 kV and 40 mA. The instrument had a LynxEye position-sensitive detector with a scan range of 3° 2θ. Scan parameters used for sample analysis were 5–60° 2θ with a step of 0.015° 2θ and a 0.3-s dwell at each step. In order to obtain counting statistics to resolve any additional weak crystalline peaks, the glass samples with Re concentration of 10 000 ppm were analyzed with a 2.5-s dwell at each step. For all scans, JADE 6 (Materials Data, Inc.) software was used to identify phase assemblages.

2.2.2. X-ray Absorption Near Edge Structure (XANES) Spectroscopy. For most of the glasses, XANES spectroscopic data were collected on powdered glasses representing an average of the glass sample, at the Re L₂-edge (11.959 keV) with the Stanford Synchrotron Radiation Laboratory 11–2 beamline using a Si (220) double crystal monochromator. The harmonic content of the beam was reduced by detuning the monochromator by 50%. The powdered glass samples were contained in aluminum holders sealed with Kapton tape. Data were recorded in transmission mode with Ar-filled ion chambers or in fluorescence mode with a 32-element Ge detector and were corrected for detector dead time effects. Data reduction was performed by standard procedures¹⁸ with Artemis software.¹⁹ The Re XANES spectra were also analyzed by principal component analysis with SixPack software.²⁰

Reference spectra for crystalline ReO₂, ReO₃, and KReO₄ were used for data fitting. Spectra of the reference data were taken with higher spectrometer resolution than the resolution used to record the glass data. The reference spectra were convolved with a 0.4 eV Gaussian curve prior to fitting the data as determined by fitting the spectrum of ReO₄⁻ doped sodalite that was measured at the same time as the glass data using a series of ReO₄⁻ reference spectra convolved with 0.1 to 1 eV Gaussians. The data fitting was based on a nonlinear least-squares method and was performed in a locally written program. Six parameters were used in the fit: the amplitudes of the three standards, one global energy shift, slope, and offset (linear correction to account for differences in background correction). Data were fitted between 11.940 and 12.040 keV and the data resolution is estimated to be 6.5 eV based on the width of the white line at the Re L₂-edge.

2.2.3. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). An ICP-OES technique (ICAP 6500 Duo, Thermo-Fisher Inc., England) 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

ultrapure (Optima grade, Thermo-Fisher Scientific) hydrofluoric acid (HF) with mild heating (no boiling) at ~ 100 °C on a hot plate in 15 mL, capped perfluoroalkoxy crucibles for 2–3 h. This procedure left a small amount of undissolved 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 HNO₃ was added to the crucible and heated gently for 1 h.

3. RESULTS AND DISCUSSION

3.1. Crystallinity in Re Glasses. Melting the initial glass frit at 1200 °C for 1 h was sufficient to produce a homogeneous baseline (no Re) LAW glass with dark brown color. The absence of crystalline inclusions was also confirmed by XRD. The rhenium-containing glass melts exhibited different physical and chemical features during the glass synthesis depending on their initial rhenium concentration.

Remelting of the baseline glass (with 0 ppm Re) in the quartz ampule resulted in a cylindrical shaped glass ingot that cracked and shattered into small pieces upon cooling (but remained as an intact cylinder). No significant interfacial reactions between glass melt and walls of quartz ampule were observed. The addition of Re (100–2500 ppm) in the baseline glass resulted in amorphous glasses as revealed by XRD analysis (Figures 1

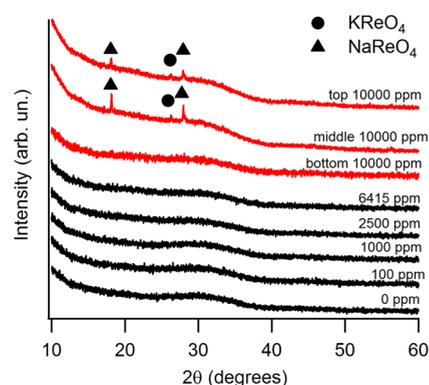


Figure 1. Powder XRD of glasses.

and 2). Further increase in the Re concentration to 6415 and 10 000 ppm led to the formation of a separate low viscosity liquid phase (visually estimated to be <0.1 Pa s) floating on top of the glass surface during cooling that gradually solidified to a white-colored superficial powdered layer. The XRD analysis of

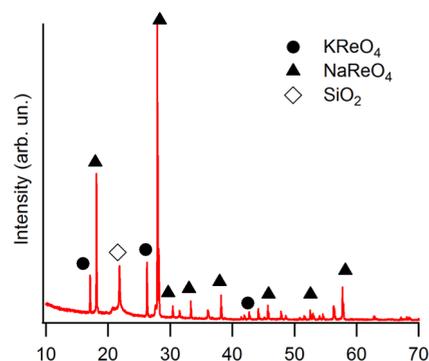


Figure 2. XRD of white salt from melt surface of 10 000 ppm target Re sample.

this superficial white powder revealed its highly crystalline nature with the dominance of alkali perrhenates (NaReO_4 and KReO_4) along with some minor phases, notably sulfates plus SiO_2 (cristobalite-high), the latter likely from the walls of quartz ampule (Figure 2).

Unlike the 6415 ppm glass sample, which exhibited no crystalline peaks, the glass obtained with the 10 000 ppm Re concentration showed evidence of KReO_4 and NaReO_4 phases (Figure 2). 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 vertically oriented ampule. The powder XRD analysis on three different parts of the glass sample revealed the heterogeneous distribution of crystalline inclusions of alkali perrhenates. The explanation for this spatial segregation of crystalline phases is not clear, but it may be related to the transport of supersaturated rhenium toward the surface in bubbles where a surface salt phase eventually forms.

3.2. Rhenium Valence and Coordination in Glasses.

The Re-XANES spectra of the studied glasses are presented in Figure 3 along with the reference spectra used in fitting. For the

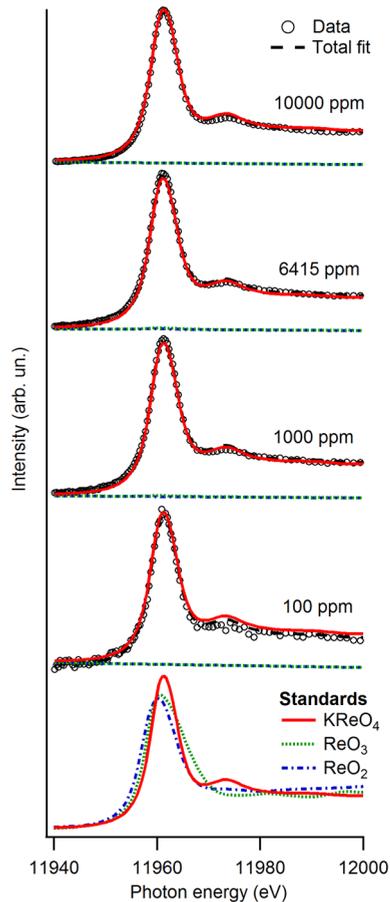


Figure 3. XANES results for the Re standards and some of the glasses (data are offset for clarity).

glasses prepared with 100 to 6415 ppm Re, the data were recorded in fluorescence to obtain better signal-to-noise. For the glass prepared with 10 000 ppm Re, transmission data were used due to self-absorption, which affected the XANES fitting. The results are given in Table 2. In all cases, the amounts of ReO_2 and ReO_3 are smaller than their standard deviations, and

Table 2. XANES Fitting Results

Re target (ppm)	ReO_2^a	ReO_3^a	KReO_4^a
100	0.0(2)	0.0(2)	1.0(1)
1000	0.00(9)	0.01(9)	0.99(6)
6415	0.01(7)	0.01(7)	0.98(4)
10000 ^b	0.00(6)	0.00(6)	1.00(4)

^aNumber in parentheses is the standard deviation and is in the same decimal place as the digit preceding it. ^bXANES data recorded in transmission rather than fluorescence.

the amount of Re^{7+} is within one standard deviation of 1.0. The XANES results show that Re^{7+} is the only significant species present in these samples. These results are in general agreement with those reported by Lukens et al.,¹² that predict only Re^{7+} at these oxygen fugacities.

3.3. Rhenium Solubility in Glasses. Quantitative ICP-OES results are shown in Figure 4. Each glass was sampled at

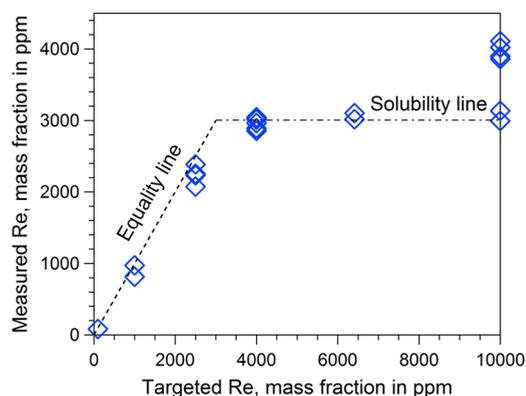


Figure 4. Quantitative assessment of Re solubility in borosilicate glass.

least two and up to six times where various locations in the glass ingot were studied. Heterogeneity in the 10 000 ppm Re glass was further confirmed by ICP-OES taken from different regions of the sample (top, middle, or bottom) (Figure 4). The ICP-OES analysis on the different pieces of glass revealed the higher concentration of rhenium in the top and middle parts of the glass sample in comparison to the bottom part of sample. This is in agreement with the result of higher crystallinity in the upper parts of the sample, and may be due to details of the transport of supersaturated rhenium to the surface of the melt such as in bubbles. Similar results were obtained for the glass with 10 000 ppm of target Re concentration as ICP-OES showed that the experimental rhenium concentration varied between 3000 and 4000 ppm in different pieces of glasses. These results are in good agreement with the XRD results presented in Figure 2. By contrast, the 4000 ppm glass, produced last as a test case, showed relatively uniform Re concentration ~ 3000 ppm in all portions of the glass.

The ultimate solubility of Re in the borosilicate LAW glass was determined as described below. The quantitative data from 4000 ppm target (6 data points), 6415 ppm target (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 measured Re values likely contained Re salt inclusions resulting in larger measured Re concentrations. Even if these 10 000 ppm points are not included, the average

solubility is 2990 ppm. The results of this analysis are shown in Figure 4. Here the “equality line” is shown representing where solubility is equal to the retention of Re, and the “solubility line” is shown representing the maximum incorporation of Re in the glass under these conditions without forming inclusions.

3.4. Rhenium Retention in Glasses. “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.²¹ The retention ratio of a particular element, i , is defined as follows:

$$R_i = \frac{g_{i,r}}{g_{i,0}} \quad (1)$$

where $g_{i,0}$ is the target mass fraction of 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, and presented in Supporting Information) and since $g_{i,0} \geq g_{i,r}$, $R_i \leq 1$. 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 a surface salt phase enriched with Re. In an actual glass melter application, the retention is strongly influenced by volatility. This is enhanced when there is absence of a cold cap (i.e., unconverted feed covering at least part of the melt surface).

The following observations can be made from the results obtained in this study:

- 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. This shows that most of the rhenium (80–90%) added to the borosilicate glasses has been retained and the rest was, presumably, lost to volatilization. Further, the absence of any crystalline inclusions in these glasses confirms that the retention was less than or equal to the solubility, at least up to 2500 ppm Re.
- An increase in the target Re concentration beyond 2500 ppm led to the deviation in retention behavior from linearity. The maximum amount of Re retained in the glass with target Re concentrations of 6415 ppm and 10 000 ppm were ~3000 ppm and 3000–4000 ppm, respectively. In the case of the 10 000 ppm target glasses where measured Re was ~4000 ppm, the higher concentration of Re was likely due to the presence of inclusions.
- The significant spread in the values of retained Re concentration in glasses with target Re concentration >6500 ppm is due to the heterogeneous distribution of rhenium-rich inclusions in the glass matrix as has been already shown by XRD (Figure 2).
- Some of the reduction in retention in the glasses with target Re > 6000 ppm was due to formation of white rhenium salts. Note that the salt layer was removed from the glass surface before analyzing the glasses by ICP-OES and thus its Re content is not included in the soluble

fraction of Re. The surface salts therefore represent a reduction in retention of the target Re concentration.

- The retention ratio varied between 0.8 and 1 for glasses with target Re concentration ≤ 2500 ppm while beyond that, R_i decreased considerably (see Supporting Information). The decreasing retention for low target Re concentrations can be attributed to volatility of rhenium from the glass melt and subsequent deposition on the walls of the quartz ampule. At higher Re target concentrations, Re salt could be lifted to the surface of the glass melt trapped in bubbles originating from the pores of the glass powder as it sintered or from redox reactions of Re or Fe.

3.5. Redox and Valence in Re and Tc. Although Re has been widely used as a surrogate for Tc, it is important to highlight some differences between the two species regarding their chemistry within the glass environment. Rhenium has a bulk silicate Earth abundance of 0.2 ppb and is the rarest of all of the naturally occurring elements, apart from the noble gases,²² 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^- 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.^{8,23}

Tc is more easily reduced from $\text{Tc}^{7+} \rightarrow \text{Tc}^{4+}$ compared to $\text{Re}^{7+} \rightarrow \text{Re}^{4+}$.⁸ Consequently, it has been suggested that Re may not be a representative substitute for Tc under reducing conditions, at least in borosilicate LAW glasses.¹² In the vapor hydration test used to assess chemical durability,²⁴ Tc has been observed to reduce to Tc^{4+} regardless of the starting Tc valence distribution, whereas Re^{7+} species remained dominant in the Re glass analogues.²⁵ Furthermore, in some hydrothermally altered borosilicate LAW glasses, Tc is enriched at the corroded outer amorphous silicate gel-layer, 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.²⁶ Also, a series of recent melter tests suggest that the retention of Re is 8 to 10% higher than Tc for similar glasses.²⁷ Despite the lack of precise correlation in the redox of Re and Tc, the assumption of 100% Tc^{7+} and use of Re^{7+} as a surrogate should lead to a conservative estimate for solubility of Tc in an oxidizing environment, such as that present in the high nitrate feed environment at Hanford. Since Tc^{4+} is not nearly as mobile in water as Tc^{7+} (as TcO_4^-) and not as volatile, the applicability of Re^{7+} data to Tc for these glasses should be reasonable. However, it should not be assumed that the solubility of Tc^{4+} (or Re^{4+}), which may be present in non-negligible quantities in other nuclear waste glasses, would be the same as the solubility of Tc^{7+} (or Re^{7+}).

According to the literature, volatility and retention of Tc and Re compounds in silicate and borosilicate glasses is strongly dependent on the oxidation state of the glass as well as on the feed chemistry.^{8,12} For example, Tc and Re tend to be more volatile when present as $\text{Tc}^{7+}/\text{Re}^{7+}$ ($\text{TcO}_4^-/\text{ReO}_4^-$) than when present as $\text{Tc}^{4+}/\text{Re}^{4+}$ ($\text{TcO}_2/\text{ReO}_2$). However, KTcO_4 and KReO_4 precursors are expected to produce lower Tc and Re volatilization at higher temperatures compared to Tc_2O_7 and Re_2O_7 , respectively.^{8,28} Thus, the calculated or predicted maximum content of Tc/Re in glass in these literature studies

is not the *solubility* but, rather, the *retention* of Tc/Re in the glass after volatilization of these species during melting, the value of which should be significantly lower than the true solubility.

An estimate for the solubility of Tc in borosilicate glass can 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 % SO_3 or ~ 3000 ppm by mass S).²⁹ This assumption is based on the fact that pertechnetate (and perhenate) salts tend to behave similarly to sulfates and segregate out of the melt into a low-melting salt phase.^{11,30} Using this value for sulfur solubility, the ppm mass value can be converted to a parts-per-million-atoms (ppma) basis, and for the sodium borosilicate LAW glasses with the compositions studied here, this equates to ~ 1900 ppma for sulfur. The equivalent value for Re in our LAW glass assuming 3000 ppm by mass solubility is ~ 333 ppma for rhenium, which is a 6-fold reduction in solubility compared to sulfur. This decreased solubility for Re compared to S, neither of which appear to participate in the glass network, may be due to the much larger ionic crystal radius of Re ($S^{6+} = 26$ pm, $\text{Re}^{7+} = 52$ pm, and $\text{Tc}^{7+} = 51$ pm for 4-coordinated species as would be expected in this case).^{30,31} By this argument, Tc^{7+} should have a comparable solubility (in ppma) to Re^{7+} . Assuming the same ~ 333 ppma solubility for Tc^{7+} as for Re^{7+} in this glass, Tc^{7+} solubility should be ~ 1500 ppm by mass.

From the standpoint of ultimate disposition of radioactive Tc in a glass waste form, a few considerations should be made. The required average maximum concentration of Tc to be immobilized in Hanford LAW glass can be approximated from (1) the total estimated Tc inventory in the underground tanks ($\sim 1.5 \times 10^3$ kg per Mann 2004)² and (2) the total estimated mass of LAW glass to be produced (5.3×10^8 kg per Certa et al 2011).¹ Assuming 100% retention of Tc and these numbers, the average expected Tc concentration in LAW glass is ~ 3 ppm by mass. Assuming that the solubility of Tc^{7+} on a per-atom basis in glass is similar to that obtained for Re^{7+} , and assuming the redox state in LAW glass favors Tc^{7+} , the solubility of Tc is orders of magnitude higher than current estimates of Tc concentrations in LAW (~ 3 ppm), even when recycle loops are taken into account that can ultimately result in 100% retention for volatile species. However, the apparent solubility of Re^{4+} in glass appears to be very low,³² and if the same is true for Tc^{4+} , then the solubility of Tc in silicate glass depends greatly on the redox state of the melt. Additionally, as previously stated, Tc^{7+} is much more easily reduced than Re^{7+} , so Tc^{4+} may indeed be present in non-negligible concentrations in LAW glass, a possibility that should be experimentally verified. If Tc^{4+} is present in significant quantities, then the solubility data obtained in the literature for Re^{4+} may not be relevant for Tc^{4+} since Re^{4+} is so difficult to form in realistic glass compositions, and another surrogate should be considered, such as Ti^{4+} or, preferably, Ru^{4+} .³³ In Tc^{4+} , the *d*-electrons are antibonding, which weakens the interaction between oxide ligands and the metal, a situation more closely replicated by Ru, which is adjacent to Tc on the periodic table. In general, however, Re is preferred as a surrogate for Tc, since Re has similar volatility to Tc, whereas other potential 4+ surrogates (Ti, Ru) are far less volatile (i.e., TiO_2 and RuO_2). Solubility of Ru^{4+} in borosilicate glass was previously found to be at the detection limit, ~ 10 ppm,³³ so solubility of Tc^{4+} is expected to be low as well. Additionally, Tc^{7+} is expected to be the most

important Tc valence for Hanford LAW glass due to the decomposition of nitrate and thus highly oxidizing environment in the melter, and some glass studies have shown production of substantial amounts of Tc^{7+} when glass is melted in air in platinum crucibles.²⁵ The same studies have shown, however, that Tc reduces to Tc^{4+} under conditions where Re does not reduce,^{12,25} so comparisons must be made with caution.

The more important issue, then, becomes Tc retention. As shown in this study with Re, even at low target concentrations, the retention can be substantially lower than the solubility due to kinetic factors such as volatility. Here, future work will be needed to understand the details of the interaction between the formation of a low-melting salt phase in LAW glass (that may contain TcO_4^- , SO_4^{2-} , CrO_4^{2-} , Cl^- , I^- , NO_3^- , and NO_2^- 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 its solubility.³⁴ Additionally, pertechnetate has been shown to increase the volatility (reduce the retention) of Cs, possibly due to the formation of the volatile compound, CsTcO_4 .⁸ This occurs despite low concentrations of ^{137}Cs in LAW (less than pertechnetate) as most ^{137}Cs is partitioned into HLW, resulting in additional safety concerns about the uncontrolled release of this high dose contributor during LAW processing. For the foregoing reasons, controlling the redox of the cold cap to prevent formation of Tc^{7+} (and thus TcO_4^-) has been an area of intense research; however, decomposition of nitrites during vitrification of LAW glass will create highly oxidizing conditions in the melt that may result in the formation of Tc^{7+} regardless of the initial oxidation state.³⁵

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional details about sample preparation and glass composition, XANES analysis, and calculation of retention ratio. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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