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Solubility and Physical Form of Technetium in Low Activity Waste Glass

final draft

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Abstract

The solubility of technetium was measured in a Hanford low activity waste glass simulant. The simulant glass was melted, quenched and pulverized to make a stock of powdered glass. A series of glass samples were prepared using the powdered glass and varying amounts of solid potassium pertechnetate. Samples were melted at 1000°C in sealed fused quartz ampoules. After cooling, the bulk glass and the salt phase above the glass (when present) were sampled for physical and chemical characterization. Technetium was found in the bulk glass up to 2000 ppm (using the glass as prepared) and 3000 ppm (using slightly reducing conditions). The chemical form of technetium obtained by x-ray absorption near edge spectroscopy can be mainly assigned to isolated Tc(IV), with a minority of Tc(VII) in some glasses and TcO_2 in two glasses. The concentration and speciation of technetium depends on glass redox and amount of technetium added. Solid crystals of pertechnetate salts were found in the salt cake layer that formed at the top of some glasses during the melt.

1 Background

Radioactive waste from decades of plutonium production is currently stored in large underground tanks at the Hanford Site. This waste will be mixed with glass formers and then vitrified.[1]

The Hanford tank wastes vary widely in composition, but are typically largely sodium nitrate, nitrite, and carbonate with a small amount of hydroxide.[2; 3] Aluminum, iron and zirconium comprise 20% or more of the waste in some cases. Chromium and manganese may be present up to several percent. Certain tanks have percent levels of sulfate, fluoride, chloride, and chromate. Many other compounds may be present. The radioactivity of the tanks is mostly due to ^{90}Sr and ^{137}Cs, with a much smaller contribution by the long-lived fission products including ^{99}Tc, ^{129}I, ^{93}Zr, and ^{79}Se. The plutonium separation processes did not recover all of the plutonium from the irradiated uranium, and a small amount of plutonium, uranium and americium are also found in the tanks. Many of the waste components do not incorporate well into silicate glasses. A number of ionic compounds such as sulfates have low solubility in silicate glasses and may form a separate salt phase.

The current plan is to chemically separate the waste into a small volume of high-level waste, intensely radioactive from ^{90}Sr and ^{137}Cs, and a large volume of low-activity waste (LAW).[1] These two fractions will be vitrified separately. Technetium will report to the low-activity waste and will be vitrified in that fraction.

Technetium incorporates poorly into silicate glass in traditional glass melting. Technetium readily evaporates during melting of glass feeds (waste + additives) and out of the molten glass, leading to low retention in a final glass product.[4-7] To effectively manage technetium retention in the Hanford LAW glass, it is critical to understand if the solubility of technetium is a controlling factor. The speciation of technetium in glass has been previously studied, and the technetium species present in waste glass have been previously reported;[8-11] however, the solubilities of these species are unknown.

The solubility of technetium and many other waste constituents depends partly on their chemical forms. A particular constituent may be better incorporated into the glass if it is added in a specific chemical form. The chemical form of technetium in the raw tank waste is usually pertechnetate, but lower valent complexes may be present in some tanks.[12-16] When the waste is incorporated into glass, the nitrate and nitrite will oxidize all of the organic compounds and will oxidize technetium to Tc(VII) (fused nitrate is an extremely powerful oxidizing agent). At the maximum temperature of the glass melt, Tc(VII) can lose oxygen and drop to a lower oxidation state, which likely will have a different solubility in the glass than Tc(VII). The mechanism for the reduction of Tc(VII) in the glass is incompletely known. Technetium oxidation state is set by fugacity of oxygen in the glass as determined by iron redox[8] and can change depending on the post-melt temperature and oxidation environments.[17-19]

2   Experimental Section

2.1   Glass synthesis

Simulated glass for this work was formulated for one of the projected LAW streams to be processed at the Hanford Waste Treatment and Immobilization Plant.[20; 21] (Actual Hanford tank waste is radioactive and impractical to use.) The glass components were mixed as oxides or carbonates (boron as H_3BO_3), fused, then crushed to a fine, free flowing powder in an Angstrom mill using a tungsten carbide milling chamber. The crushed glass was stored in air in a capped container. The crushed glass is not particularly hygroscopic and does not generate gas pressure when it is re-melted. The stock crushed glass made this way was used in all subsequent glass experiments. The target weight percent of each glass component and the results of chemical analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) are shown in Table 1. This simulant glass does not contain nitrates, and experiments that use this glass do not have the extremely oxidizing conditions caused by nitrate in actual tank waste.

Some technetium compounds are volatile at 1000°C, the temperature of the glass melts.[22] Many salts have significant vapor pressure at this temperature and may extensively evaporate out of the glass. To avoid evaporation losses, which would compromise the solubility measurement, the glass samples spiked with technetium for this work were melted in a sealed fused quartz ampoule.[23] The powdered glass sample blended with the technetium salt is placed in the bottom of the fused quartz ampoule. The ampoule has a fused quartz end cap placed in the ampoule about midway (see Figure 1), which is fused to the quartz ampoule wall with an oxypropane flame, sealing the bottom chamber of the ampoule. The air is pumped out of the ampoule before it is sealed so that the ampoule does not pressurize at temperature. With this method, volatilization losses can be avoided and a more accurate solubility measurement can be made. Components volatile at 1000°C may move to the headspace above the glass, but cannot escape the quartz ampoule. A layer of salts in excess of the glass solubility may form at the top of the melt glass. The secondary salt phase typically contains alkali sulfate and alkali pertechnetate as determined by x-ray diffraction (XRD), Raman spectroscopy, and energy dispersive spectroscopy (details to be provided in a subsequent publication). Figure 1 shows the fused quartz ampoule and end cap with associated dimensions as well as photographs of the glass before and after melting with pertechnetate salt.

To measure the solubility of technetium in glass using this method, a series of samples was prepared and spiked with a range of technetium concentrations. When the solubility is reached, a clearly visible fluid salt layer appears on the surface of the molten glass. Below the solubility, no salt layer forms. The bulk glass must be analyzed to measure the technetium solubility accurately. The measurement is not necessarily straightforward, since the glass may have part of the analyte in true solution and part in the form of mechanical inclusions. The dissolved component being measured may be found in more than chemical form, each with a different solubility.

Solid, crystalline potassium pertechnetate ($KTcO_4$) was prepared for these tests and used to spike the powdered glass. Ammonium pertechnetate (NH_4TcO_4, obtained from Oak Ridge National Laboratory), partially decomposed from its own beta radiation, was dissolved in a solution of ammonium hydroxide and hydrogen peroxide and then heated to re-oxidize the technetium to pertechnetate and decompose the excess peroxide. The solution was evaporated to recrystallize ammonium pertechnetate as colorless crystals. The freshly crystallized compound was washed with dry ethanol to remove water, and then dried to constant weight. About 3 grams of freshly recrystallized, dry ammonium pertechnetate was weighed to the nearest 0.0001 g, and then dissolved in water. A carefully measured stoichiometric amount of K_2CO_3, dissolved in water, was added to the ammonium pertechnetate solution. The combined solution was evaporated to a low volume to expel ammonium carbonate and to precipitate crystalline $KTcO_4$. The final 2 mL of supernatant liquid was discarded. The solid $KTcO_4$ product was washed with ethanol to remove water and then dried to constant weight. Sub-samples of the $KTcO_4$ were assayed for total technetium by liquid scintillation and were found to be pure $KTcO_4$, within analytical uncertainty. The product was a free-flowing white crystalline powder, a little finer than table salt. This particle size is moderately coarse. (Finely powdered pure technetium compounds are easily dispersed by static charges and constitute a high contamination hazard).

Samples of powdered glass were spiked at 500, 1000, 3000, 4000, and 6000 ppm by weight technetium (as the element). For each glass melt, about 20 grams of powdered glass was accurately weighed, then

placed in a ball mill jar. A calculated amount of solid potassium pertechnetate was weighed to the nearest 0.0001 g, then added to the ball mill jar. The mixture was shaken for several minutes to pulverize the potassium pertechnetate and mix it thoroughly with the glass. The pulverized, spiked glass was poured through a tube of aluminum foil to direct the powder to the bottom of the fused quartz ampoule and keep glass powder off the walls of the ampoule. A fused quartz end cap was slid into the ampoule onto a small annulus about 11 cm above the bottom of the ampoule (see Figure 1), and then the ampoule was evacuated to 4×10^{-4} Torr. While the ampoule was still under vacuum, the ampoule was heated with an oxypropane flame to seal the ampoule to the end cap above the powdered glass, so that the glass would remain under vacuum during the melt process.

A wad of glass wool was pushed into the top of the fused quartz ampoule for thermal insulation. Three thermocouples were attached to the outside of the ampoule with wire. More quartz wool was wrapped around the outside of the ampoule to insulate the top portion of the ampoule, which protrudes through the top of the furnace. The quartz ampoule was then placed in the furnace at ~750°C and ramped to 1000°C at 5°C min^{-1}.

Each technetium-spiked glass sample was melted at 1000°C for 2 hours. Each sample was withdrawn from the furnace after two hours and allowed to cool in still air. As each ampoule cooled, the difference in thermal expansion between glass and fused quartz caused the glass sample and ampoule to shatter. The glass solidified and began to crack before the salts (if present) solidified. If a fused salt layer formed on the surface of the glass melt, then the liquid salts were drawn into the cracks in the glass as they form. The glass continued to crack after the salt cake had solidified, so that some cracks are free of salts.

2.2 Glass characterization

The cooled glass appears nearly black, and is transparent only in thin (~1 mm thick) pieces. Pieces were taken from various locations in the bulk glass and from the salt cake on top of the glass (see Figure 2). Samples of bulk glass were analyzed for total technetium by ICP-MS, and for iron(II) - iron(III) ratio to provide an indication of the oxidation potential in the glass. The iron oxidation state was measured by a spectrophotometric method.[24]

The oxidation state of the technetium was measured in the bulk glass by X-ray absorption near edge structure (XANES) spectroscopy. Glass samples were shattered with a large mortar and pestle. A single large fragment from each sample was placed in a 2 mL screw cap centrifuge tube. The tube was heat-sealed inside a LDPE bag, which was sealed inside a polyester bag. Data were obtained at SSRL BL 11-2 at room temperature. X-rays were monochromatized using a double crystal monochromator with Si (220) crystals. The second crystal was detuned by 50 % to reduce the harmonic content of the beam. Fluorescence data was recorded using a detector with a 0.1 mm Al filter and was corrected for dead-time effects. The monochromator was energy-calibrated to 21044 eV using the first inflection point of the pre-edge peak of TcO_4^- adsorbed on ion exchange resin. Incident beam intensity was measured using an inert gas filled ionization chamber.

Data were averaged using the software package SixPack.[25] Data were normalized and corrected for self-absorption using Artemis.[26] Sample spectra were convolved with a 1.2 eV Gaussian peak to match the resolution of the reference spectra. XANES data were fit with the locally written program "fites" using the standard spectra as follows. Standard reference spectra included TcO_4^- (adsorbed on ion exchange

resin), $TcO_2 \cdot 2H_2O$, and Tc(IV) gluconate complex, which has the same octahedral coordination environment as isolated TcO_6 coordination octahedra in glass. Individual scans are not energy calibrated and the energy of the spectrum was allowed to vary during the fit.

On two samples which XANES indicated contained crystalline TcO_2 (as opposed to isolated Tc(IV) octahedra in glass[9]), extended X-ray absorption fine structure (EXAFS) data was also collected. EXAFS data were fit using the programs Athena and Artemis[26; 27] using theoretical scattering curves calculated using Feff 7.0[28] and the atomic positions of Tc and O in crystalline TcO_2 reported by Rodriguez et al.[29]

As of this writing, samples are undergoing analysis by XRD, scanning electron microscopy, nuclear magnetic resonance, Raman spectroscopy, and x-ray photoelectron spectroscopy to determine the exact chemical form and distribution of technetium throughout the melt. Those results will be reported in a future publication.

3 Results and Discussion

3.1 Solubility and redox

The first series of technetium-spiked glass samples contained 500, 1000, 3000, 4000, and 6000 ppm technetium. A tungsten carbide ball mill jar was used to pulverize the potassium pertechnetate into the powdered glass. After the data was plotted and evaluated, it became apparent that the tungsten carbide ball mill jar had introduced milligram amounts of tungsten carbide into the glass samples, which created reducing conditions in the glass melt. The effect of tungsten carbide is apparent in the Fe(II)/Fe(III) ratio and in the measured technetium solubilities and speciation. The amount of tungsten carbide introduced into each sample is not accurately known, but can be approximately correlated with the length of time each sample was mixed (see Table 2, second column). After the effect of tungsten carbide became apparent, we pulverized more glass in the tungsten carbide ball mill jar and examined the raw pulverized glass (not melted) by XRD. Tungsten carbide was clearly evident in the XRD spectrum.

To produce comparable samples without the reducing conditions caused by tungsten carbide, additional technetium-spiked glass samples were prepared following the same method, except using an alumina ball mill to mix the pertechnetate salt with the powdered glass. The alumina ball mill also shed a small amount of material (evident from roughness and wear inside the ball mill jar), but alumina will not oxidize or reduce glass components and will not change the redox potential in the glass melt. The two sets of data, one made with tungsten carbide and one made with alumina, showed distinct differences from the effect of a reducing agent in the glass melt.

Figure 3 shows the measured technetium concentrations in glass samples, with the raw data presented in Tables 2 and 3 along with experimental observations. A salt layer on top of the glass melt appeared on the 4000 ppm samples, indicating that the solubility of technetium is less than 4000 ppm. The maximum total technetium in the bulk glass (measured by ICP-mass spectrometry) was about 3000 ppm for the tungsten carbide samples, and 2000 ppm for the alumina samples. The 3000 ppm tungsten carbide glass showed extensive bubbling in the melt, which is unusual in our experience with this LAW glass. The bubbling may have been caused by carbon monoxide from oxidation of tungsten carbide. The 3000 ppm

sample had the longest mixing time in the tungsten carbide ball mill jar, which probably introduced the largest amount of the tungsten carbide of all the affected samples.

The glass samples mixed in tungsten carbide have a greater $Fe(II)/Fe_{tot}$ ratio than the samples mixed in alumina. Figure 4a shows the fraction of reduced iron plotted against quantity of oxidizing agent (target ppm technetium, which is proportional to the quantity of $KTcO_4$ added). Figure 4a also includes the iron redox on the as-prepared glass powder used for solubility tests and the glass heat treated following the same procedure without technetium addition. The $Fe(II)/Fe_{tot}$ ratio was 4.5% in the as-prepared glass before heat treatment but increased to 13% after heat treatment. This increase of Fe(II) is likely a result of vacuum in the head space of the test ampoule. The fraction of Fe(II) is as high as 29% in samples mixed in tungsten carbide, but is consistently 2-3% for the corresponding samples mixed in alumina. The Fe(II) is highest in the samples with the smallest amount of $KTcO_4$, which is a mild oxidizing agent. The sample with the largest amount of $KTcO_4$ (the 6000 ppm sample) had only 5% of its iron in the divalent state presumably because the $KTcO_4$ oxidized all the tungsten carbide, leaving no tungsten carbide to reduce the iron. The 3000 ppm tungsten carbide glass that had the longest mixing time and showed extensive bubbling in the melt had a higher $Fe(II)/Fe_{tot}$ ratio than the 1000 ppm tungsten carbide glass, apparently because of larger amount of the tungsten carbide introduced.

The XANES data are shown in Figure 5. The results of fitting the data, given in Table 4, indicate that tungsten carbide reduces technetium, and apparently increases its solubility in glass. Technetium in the samples mixed in tungsten carbide was largely present as Tc(IV). The corresponding samples mixed in an alumina mill contained about 2/3 Tc(IV) and 1/3 Tc(VII). This result is consistent with reduction of technetium by tungsten carbide. Figure 4b shows the iron redox (log[Fe(II)/Fe(III)]) versus log[Tc(IV)/Tc(VII)] which shows nearly a linear relationship, similar to that observed by Lukens et al.[8] Note that Figure 4b involves the average values of iron and technetium redox ratio for each glass instead of using all results from multiple measurements from the same glass.

Since Tc(VII) to Tc(IV) is a three-electron transfer and Fe(III) to Fe(II) is a one-electron transfer, the equilibrium expression for these species will have a 3:1 mole ratio of Fe to Tc. Then, the relation between the redox ratios for iron and technetium can be expressed as

$$\log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) \approx \frac{1}{3}\log\left(\frac{[Tc^{4+}]}{[Tc^{7+}]}\right) \tag{1}$$

Figure 4b shows that the observed slope of the log[Fe(II)/Fe(III)] to log[Tc(IV)/Tc(VII)] agrees well with the expected value of 0.33 although there are large scatter of data, suggesting that the iron and technetium species in each glass are in general equilibrium.

~~The samples mixed in alumina had no significant amount of any reducing agent, but the TcO_4^- was still partially reduced, perhaps by thermal decomposition into Tc(IV) and oxygen at 1000°C.~~ Reduction of TcO_4^- was observed for samples mixed in alumina, which is due in part to reduction of TcO_4^- by Fe(II) in the glass frit. The Fe(II)/Fe(III) ratio decreases from 0.045 to 0.020 in samples prepared with added pertechnetate. In addition, the tungsten carbide chamber of the angstrom mill introduces small amounts of tungsten carbide (~200 ppm), which also reduces pertechneteate. The change in the Fe(II)/Fe(III) ratio and the tungsten carbide impurity account for the reduction of ~850 ppm TcO_4^-, which is consistent with

the results for the 1000 ppm and 2000 ppm samples. Additional reduction of TcO_4^- was observed in the 3000 ppm and 4000 ppm samples, possibly from thermal decomposition of TcO_4^- into Tc(IV) and O_2, which can escape into the evacuated ampoule.

It is not certain from this data what fraction of the technetium in the glass is in the form of inclusions and what fraction is truly dissolved. Further investigation is being carried out to confirm the identity of the Tc(VII) species. A graph of the relative amounts of technetium species observed by XANES is shown in Figure 5, and it can be seen that in all glasses at least ~40% of the technetium was in Tc(IV) and in most cases was >50%. The corresponding total amounts of each species, estimated by multiplying the ICP-MS measured technetium fractions by the technetium speciation fractions measured by XANES, are shown in Figure 6. It can be seen that for Tc(IV) in glass, maximum amount in glass is similar regardless of milling media (redox) for 1000 ppm target and 3000 ppm target (Figure 6a). Tc(VII), on the other hand, is completely absent in reduced glass until 4000 ppm target. At 4000 ppm target concentration, the total solubility of technetium for the reduced glasses was 3000 ppm where for oxidized glasses was only 2000 ppm. However, the oxidized glasses contain ~44% (~900 ppm) of the Tc as Tc(VII), while for the reduced glass only ~11% (~330 ppm) is Tc(VII). By taking the data of all the glasses, the best case Tc(IV) solubility appears to be ~2600 ppm (average of 4000 and 6000 ppm WC glasses Tc(IV) isolated in glass), while the best case Tc(VII) solubility appears to be ~900 ppm (average of 4000 ppm Al_2O_3 Tc(VII) samples). If this maximum amount of both oxidation states could be retained in glass, the total technetium solubility would be ~3500 ppm, which is not far off from the total solubility observed in reduced glass (~3000 ppm).

It is clear from the XANES data that the Tc(IV) is normally present as isolated species in glass, but that in two cases (1000 and 3000 ppm technetium with tungsten carbide milling) the XANES indicates TcO_2 crystals. The presence of this species was confirmed by EXAFS. The spectrum of technetium in 1000 ppm glass (tungsten carbide) is almost identical if not identical to that previously reported for isolated Tc(IV) octahedra in glass.[9] Likewise, the spectrum of technetium in 3000 ppm glass (tungsten carbide) resembles that of TcO_2 crystallites in glass[9] with the caveat that the previously reported spectrum also includes a contribution from TcO_4^-, which means it cannot be used as standard spectrum in XANES fitting. Therefore, the spectrum of $TcO_2 \cdot 2H_2O$ was used instead (the local structure of Tc in $TcO_2 \cdot 2H_2O$ is almost identical to that of Tc in crystalline TcO_2). As expected, XANES fitting shows that the 1000 ppm glass contains mainly isolated Tc(IV) octahedra, while the 3000 ppm glass contains both isolated Tc(IV) octahedra and crystalline TcO_2 inclusions in a ratio of roughly 2:3. Fitting the XANES spectra in this produces large errors for the amounts of isolated Tc(IV) octahedra and TcO_2 crystallites since the XANES spectra of Tc(IV) in glass and $TcO_2 \cdot 2H_2O$ are very similar. However, the errors for the total amount of Tc(IV) and the amount of Tc(VII) are comparable to the other XANES fits.

The EXAFS spectrum of technetium in 3000 ppm Tc glass (WC) is shown in Figure 7. The contribution due to scattering from neighboring technetium atoms is clearly visible in the peaks at 2.3 Å and 3.1 Å in the Fourier transform of the spectrum. The data can be fit using the structure of TcO_2; however, a scale factor applied to all scattering atoms except for the nearest oxygen neighbors to account for the fact that technetium in this sample appears to be a mixture of isolated Tc(IV) octahedra and TcO_2 inclusions (the scale factor is 0.54,). The distances to the neighboring atoms are in excellent agreement with those

reported by Rodriguez et al,[29] which strongly supports the hypothesis that the spectrum is due to TcO_2 inclusions. Likewise, an F-test of the scattering shells shows that all neighboring atoms except for the more distant oxygen neighbors are observed in the EXAFS experiment. Fitting results for EXAFS for this 3000 ppm Tc (WC) glass are shown in Table 5. While EXAFS suggest that this sample contains a 1:1 ratio of Tc(IV) in isolated octahedra and TcO_2 inclusions, EXAFS is notoriously inaccurate with a systematic error of 25% in the coordination number due to the strong correlation of the coordination numbers to the Debye-Waller thermal parameters. Therefore, the error in the ratio of isolated Tc(IV) to TcO_2 inclusions in this sample is approximately the same by both EXAFS and XANES.

3.2 Environmental impact

The apparent solubility of pertechnetate in Hanford LAW glass is ~2000 ppm under conditions that are neither reducing nor oxidizing (Fe(II)/Fe$_{tot}$ ~0.02). Some amount of reduction of Tc(VII) occurs during the melting process. The loading of technetium in LAW glass can be increased by using reducing conditions (Fe(II)/Fe$_{tot}$ ~0.25), up to ~3000 ppm total technetium. Contrary to our previous hypotheses,[20] the solubility of Tc(VII) (estimated to be ~900 ppm in these glass samples) is lower than predicted by arguments based on ionic radii, and the solubility of Tc(IV) (estimated to be ~2600 ppm in these glasses) appears to be quite high.

XANES data shows that the primary oxidation state of the technetium in the glass is Tc(IV). The Tc(IV) is present in the glass mostly as a well dispersed isolated 6-coordinated ion, but in some cases it forms crystalline inclusions of TcO_2. The chemical form of the Tc(VII) in the glass is unknown, and could be dispersed TcO_4^- or inclusions of crystalline pertechnetate salts. However, the latter is unlikely in light of the fact that a separate $KTcO_4$ phase is observed at high Tc concentrations. Further investigation of the glass by XPS, NMR and Raman are in progress to clarify the chemical form of the Tc(VII).

Given that the estimated concentration of technetium in LAW glass at Hanford is ~3 ppm,[20] the technetium solubility in glass should not be a factor in technetium retention regardless of its oxidation state. Likewise, at the Defense Waste Processing Facility in Aiken, South Carolina, the highest estimated Tc concentrations in actual glasses measured were ~33 ppm which most being <8 ppm, and >80% of the Tc was found to be retained (based on measured radioactivity) at a melt redox of Fe(II)/Fe$_{tot}$ ~0.2.[30]

Acknowledgements

ASSOCIATED CONTENT

Supporting Information. Plots for all the XANES data, including fits, are provided in the Supporting Information. This material is available free of charge via the internet at http://pubs.acs.org.

AUTHOR INFORMATION
Corresponding Author
<mark>TBD</mark>

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
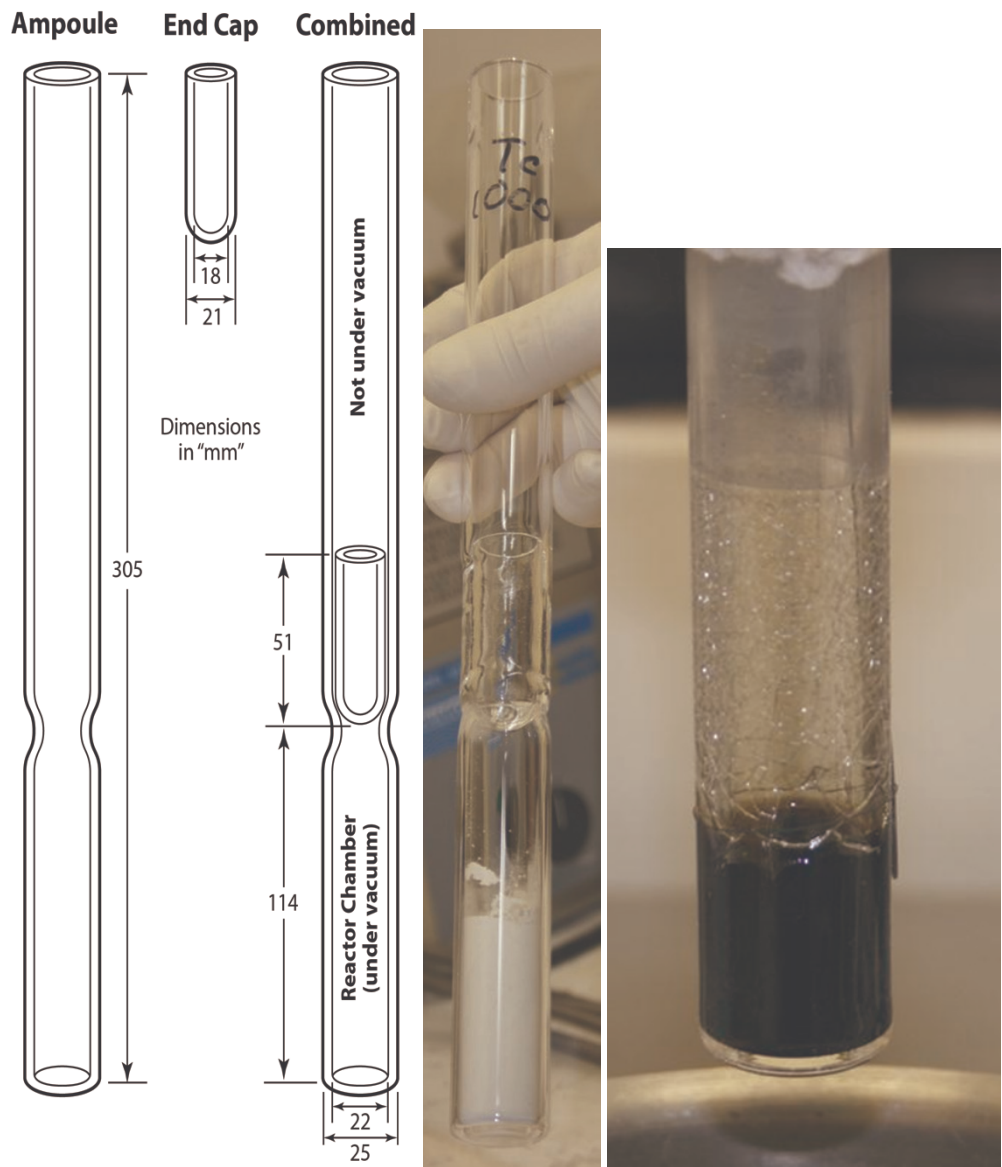
Figure 1. Diagram of Fused Quartz Ampoule and End Cap (left), glass powder before melting (middle), and melted and cooled glass (right)
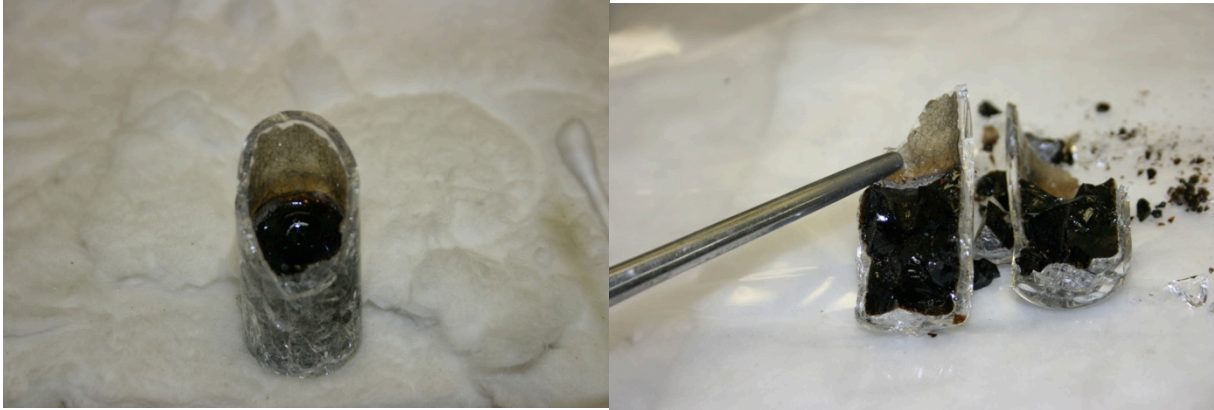
Figure 2. Glass after melt process. The picture on the left shows the glass melt, broken off the quartz ampoule. The picture on the right shows the same melt partially dissected to obtain samples.
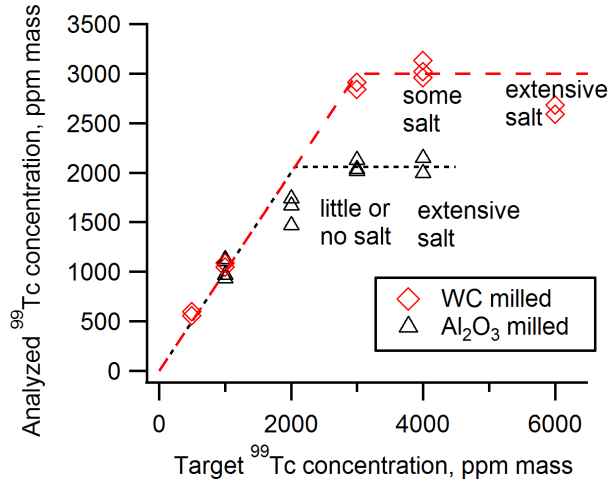
Figure 3. Analyzed Tc concentration as a function of target concentration for tungsten carbide and corundum milled samples (multiple samples were collected from different locations of the bulk glass and analyzed).
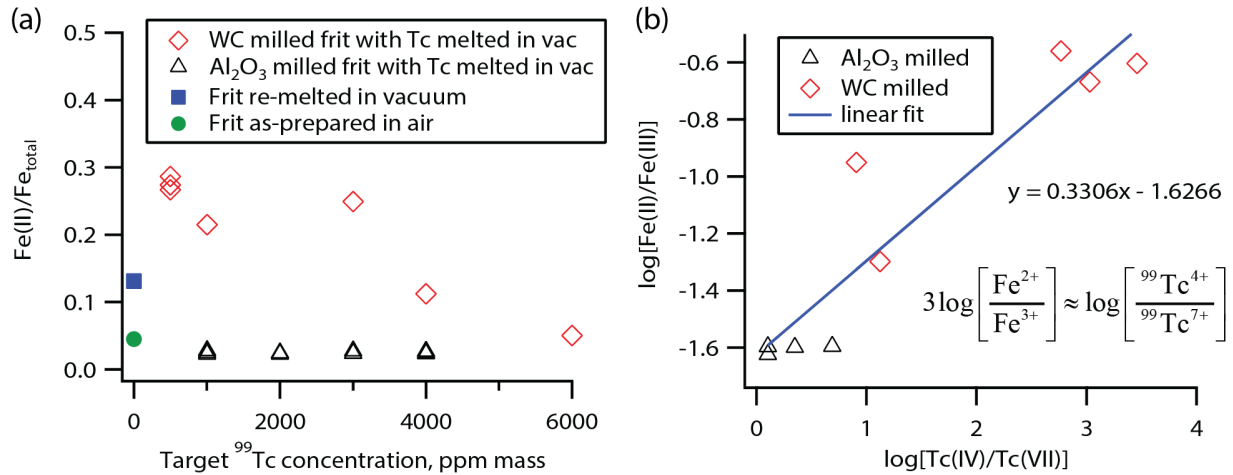
Figure 4. Fe redox as a function of target Tc concentration (left); Fe redox as a function of observed Tc redox from XANES (right).

Figure 5. XANES standards and spectra. Data are in red, fits are in black

Figure 6. Estimated technetium speciation in glass by mass as a function of target concentration for WC milled samples (left plot) and Al_2O_3 milled samples (right plot).

Figure 7. Tc K-edge EXAFS spectrum of glass containing 3000 ppm Tc (WC)

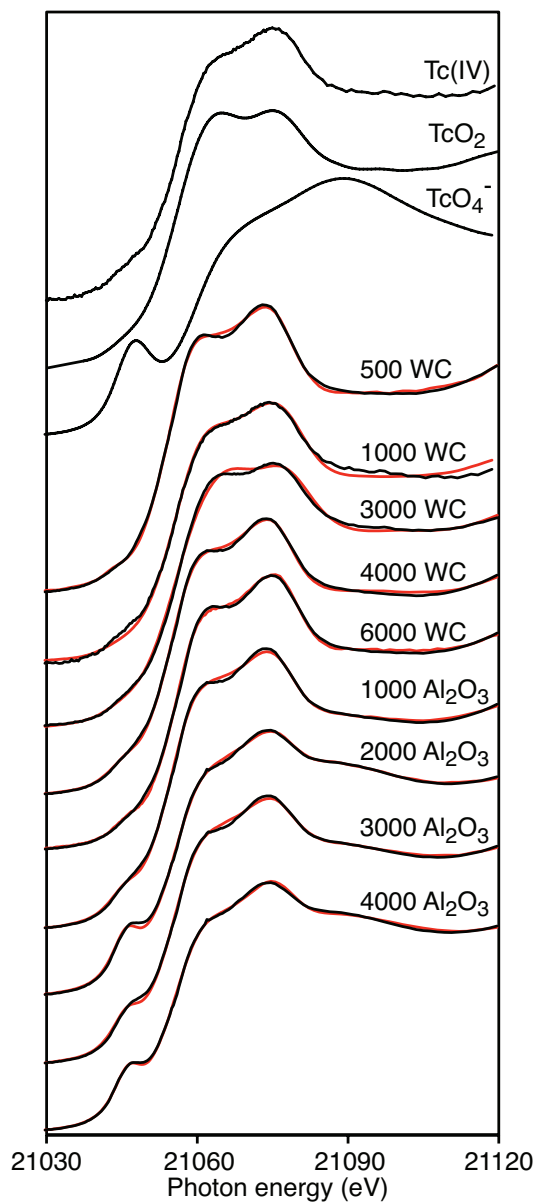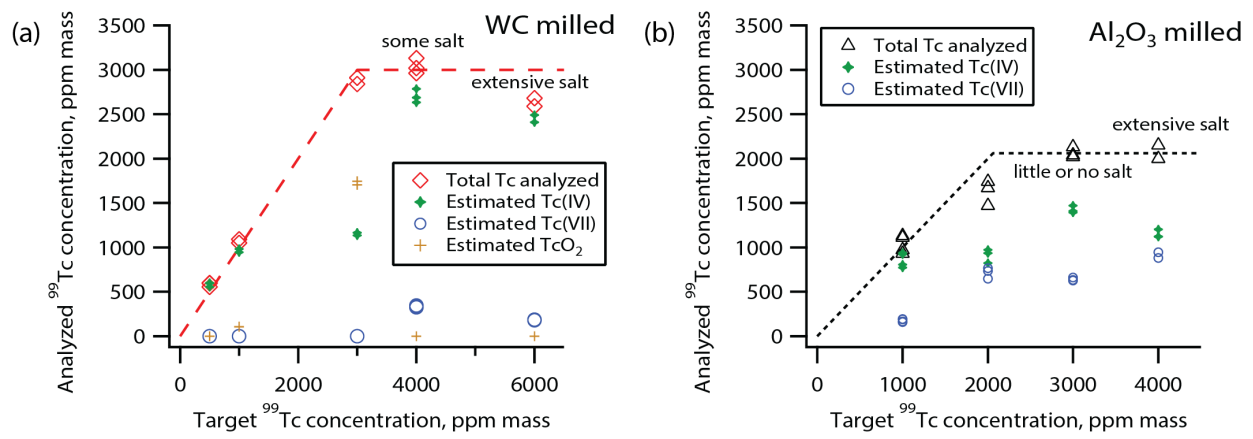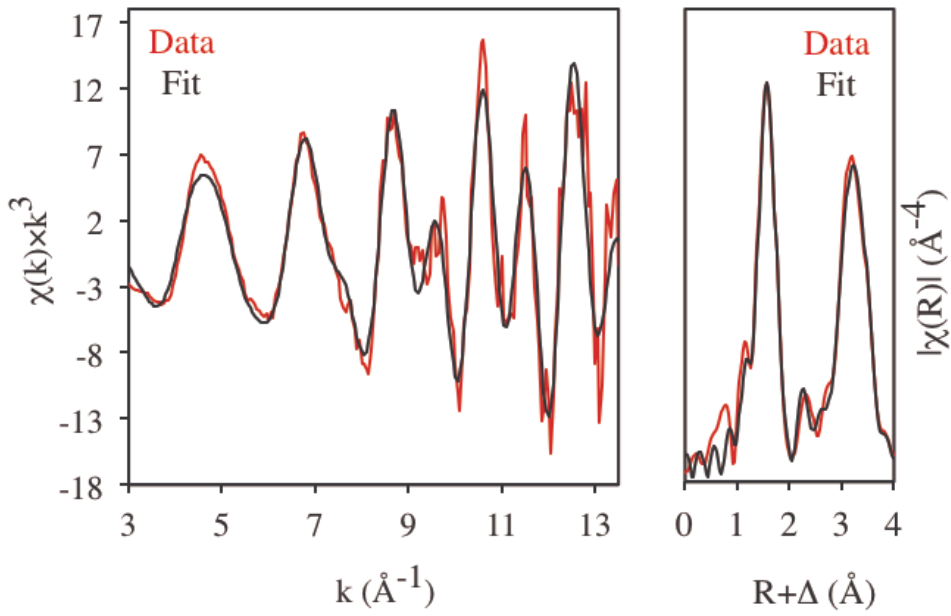**Table 1.** Composition of Low Activity Waste Glass with Chemical Analysis by ICP-OES; LOI indicates loss-on-ignition. (Measured SO_3 result is higher than expected, but has small net effect on glass.)

Oxide	Target wt%	ICP-OES Analysis wt%	Duplicate	Average
Al_2O3	6.10%	6.24%	6.15%	6.20%
B_2O_3	10.00%	9.18%	9.53%	9.35%
CaO	2.07%	2.05%	2.04%	2.05%
Cr_2O_3	0.02%	0.02%	0.02%	0.02%
Fe_2O_3	5.50%	5.23%	5.21%	5.22%
K_2O	0.47%	0.50%	0.51%	0.50%
MgO	1.48%	1.33%	1.32%	1.33%
Na_2O	21.00%	20.66%	20.39%	20.53%
SiO_2	45.30%	45.29%	44.77%	45.03%
SO_3	0.16%	0.24%	0.24%	0.24%
TiO_2	1.40%	1.38%	1.37%	1.37%
ZnO	3.50%	3.43%	3.42%	3.43%
ZrO_2	3.00%	2.68%	2.63%	2.66%
LOI @ 1000°C		3.89%	4.84%	4.37%
SUM	100.00%	102.13%	102.46%	102.30%

Table 2. Samples ball milled in tungsten carbide

Sample	Mixing time	notes on melt	ppm Tc by ICP-MS	Fe(II)/Fe(III) ratio	Tc oxidation state by XANES
500 ppm Tc	WC ~10 min	large meniscus, no salt, glass shattered	top 599 middle 555 bottom 597	top 0.29 middle 0.27 bottom 0.27	100% Tc(IV) , "middle" sample
1000 ppm Tc	WC ~4 min	large meniscus, no salt	top 1050 bottom 1090	middle 0.21	90% isolated Tc(IV), 10% TcO_2 crystalline inclusions
3000 ppm Tc	WC ~10 min	large meniscus, lots of bubbling	top 2840 bottom 2910	middle 0.25	40% isolated Tc(IV), 60% TcO_2 crystalline inclusions
4000 ppm Tc	WC several min	small meniscus, salt layer on meniscus	top 2960 bottom 3075	middle 0.11	89% isolated Tc(IV), 11% Tc(VII)
6000 ppm Tc	WC ~7 min	small meniscus, secondary salt layer on surface	top 2680 bottom 2590	middle 0.05	93% isolated Tc(IV), 7% Tc(VII); fit not good, Tc(VII) prob accurate

Table 3. Samples ball milled in alumina

Sample	Mixing time	notes on melt	ppm Tc by ICP-MS	Fe(II)/Fe(III) ratio	Tc oxidation state by XANES
1000 ppm Tc-Corundum	Corundum 5 min	no visible salt, some bubbles in meniscus	top 1130 middle 1042 bottom 933	top 0.022 middle 0.025 bottom 0.028	83% isolated Tc(IV), 17% Tc(VII) , "middle" sample
2000 ppm Tc-Corundum	Corundum 5 min	no visible salt, some bubbles in meniscus	top 1470 middle 1670 bottom 1740	top 0.024 middle 0.025 bottom 0.023	56% isolated Tc(IV), 44% Tc(VII) , "middle" sample
3000 ppm Tc-Corundum	Corundum 5 min	no visible salt, a little ring on meniscus	top 2020 middle 2040 bottom 2130	top 0.024 middle 0.024 bottom 0.028	69% isolated Tc(IV), 31% Tc(VII) , "middle" sample
4000 ppm Tc-Corundum	Corundum 5 min	lots of surface salt	top 2000 middle 2150 bottom 2000	top 0.023 middle 0.025 bottom 0.027	56% isolated Tc(IV), 44% Tc(VII) , "middle" sample

Table 4. XANES fitting results

Sample	Tc(IV) [a]	p [b]	TcO$_4^-$	p	TcO$_2$•2H$_2$O	p
500 WC	1.00(1) [c]	<0.001	0.00(1)	1		
1000 WC [d]	0.83(7)	<0.001	0.00(2)	1	0.17(8)	0.028
3000 WC [d]	0.2(1)	0.097	0.03(3)	0.408	0.8(1)	<0.001
4000 WC	0.89(1)	<0.001	0.11(1)	<0.001		
6000 WC	0.93(2)	<0.001	0.07(3)	0.041		
1000 Al$_2$O$_3$	0.83(1)	<0.001	0.17(1)	<0.001		
2000 Al$_2$O$_3$	0.56(1)	<0.001	0.44(1)	<0.001		
3000 Al$_2$O$_3$	0.69(1)	<0.001	0.31(1)	<0.001		
4000 Al$_2$O$_3$	0.56(1)	<0.001	0.44(1)	<0.001		

a) This is the spectrum of an isolated Tc(IV) center in glass (Tc dissolved in glass).
b) p,is the probability that the improvement to the fit due to adding a standard spectrum is due to noise. If the p-value is less than 0.05, the additional spectrum has significantly improved the fit.
c) Number in parentheses is the standard deviation in the last digit
d) Tc(IV) standard used was Tc(IV) in glass for these samples; other samples used Tc(IV) gluconate complex, which has the same octahedral coordination environment as isolated TcO$_6$ coordination octahedra in glass.

Table 5. Best fit EXAFS parameters for the 3000 ppm Tc (WC) sample

Neighboring Atom	# of Neighbors	σ^2 (Å^2)	Distance (Å)	Distance by Crystallography (Å)	F-Test [b] (p)
O [c]	6 [d]	0.0024(2)	1.999(4)	1.96-2.01	<0.001
Tc	0.54(9)	0.004(1)	2.62(1)	2.62	<0.001
Tc	0.54(9) [e]	0.001 [d]	3.10(1) [e]	3.08	<0.001
Tc	4.3(7) [e]	0.0026(7)	3.65(1)	3.60-3.65	<0.001
O	3.2(5) [e]	0.0026(7) [e]	3.49(3)	3.43-3.60	<0.001

a) Fit range: 3<k<13.5, 1<R<4; 21.8 independent data. 10 parameters, $S_0^2 = 1$, $\Delta E_0 = -4(1)$ eV, $\chi^2 = 28.6$, $\chi_v^2 = 2.1$, R = 0.008.
b) The F-test, p(F) determines the significance of the improvement to the fit created by adding an additional set of atoms. If the p-value is less than 0.05, the additional atoms have significantly improved the fit and can be considered "observed" in the EXAFS experiment.
c) Includes multiple scattering from trans oxygen atoms. The number of multiple scattering paths is constrained to equal the number of oxygen neighbors, the bond length and Debye-Waller parameters for multiple scattering are constrained to be twice those of this Tc-O bond.
d) Fixed (parameter not allowed to vary)
e) Parameter constrained to vary proportionally with parameter of preceding shell

References

(1) Certa, P. J. and Empey, P. A. River Protection Project System Plan, Office of River Protection, US Department of Energy, Richland, WA, ORP-11242 Revision 6, 2011.

(2) Toste, A. P., Osborn, B. C., Polach, K. J., and Lechner-Fish, T. J. Organic analyses of an actual and simulated mixed waste: Hanford's organic complexant waste revisited. *J. Radioanal. Nucl. Chem.,* **1995** *194*(1), 25-34; 10.1007/BF02037609.

(3) Golcar, G. R., Colton, N. G., Darab, J. G., and Smith, H. D. Hanford tank waste simulants specification and their applicability for the retrieval, pretreatment, and vitrification processes, BNFL, Richland, WA, BNFL-RPT-012, Rev 0, 2000.

(4) Kim, D. S., Bagaasen, L. M., Crum, J. V., Fluegel, A., Gallegos, A., Martinez, B., Matyas, J., Meyer, P. A., Paulsen, D. R., Riley, B. J., Schweiger, M. J., Stewart, C. W., Swoboda, R. G., and Yeager, J. D. Investigation of Tc migration mechanism during bulk vitrification process using Re surrogate, Pacific Northwest National Laboratory, Richland, WA, PNNL-16267, 2006.

(5) Darab, J. G. and Smith, P. A. Chemistry of Technetium and Rhenium Species during Low-Level Radioactive Waste Vitrification. *Chem. Mater.,* **1996** *8*(5), 1004-1021; 10.1021/cm950418+.

(6) Bibler, N. E. and Jurgensen, A. R. Leaching Tc-99 from SRP glass in simulated tuff and salt groundwaters. *Mat. Res. Soc. Symp. Proc.,* **1988** *112*, 585-593.

(7) Ebert, W. L., Wolf, S. F., and Bates, J. K. The Release of Technetium from Defense Waste Processing Facility Glasses. *Mater. Res. Soc. Symp. Proc.,* **1996** *412*, 221-227.

(8) Lukens, W. W., McKeown, D. A., Buechele, A. C., Muller, I. S., Shuh, D. K., and Pegg, I. L. Dissimilar Behavior of Technetium and Rhenium in Borosilicate Waste Glass as Determined by X-ray Absorption Spectroscopy. *Chem. Mater.,* **2007** *19*(3), 559-566; 10.1021/cm0622001.

(9) Lukens, W. W., Shuh, D. K., Muller, I. S., and McKeon, D. A. X-ray Absorption Fine Structure Studies of Speciation of Technetium in Borosilicate Glasses. *Mat. Res. Soc. Symp. Proc.,* **2004** *Vol. 802*, DD3.3.1-DD3.3.6.

(10) Antonini, M., Merlini, A. E., and Thornley, R. F. EXAFS structures of technetium in glasses prepared under different redox conditions. *J. Non-Cryst. Solids,* **1985** *71*(1-3), 219-225.

(11) Lanza, F., Cambini, M., Della Rosa, M., and Parnisari, E. *J. Trace Microprob. Techn.,* **1992** *10*, 257.

(12) Blanchard, D. L., Brown, G. N., Conradson, S. D., Fadeff, S. K., Golcar, G. R., Hess, N. J., Klinger, G. S., and Kurath, D. E. Technetium in Alkaline, High-Salt, Radioactive Tank Waste Supernate: Preliminary Characterization and Removal, Pacific Northwest National Laboratory, Richland, WA, PNNL-11386, 1997.

(13) Lukens, W. W., Bucher, J. J., Edelstein, N. M., and Shuh, D. K. Products of Pertechnetate Radiolysis in Highly Alkaline Solution: Structure of $TcO_2 \cdot xH_2O$. *Environ. Sci. Technol.,* **2002** *36*(5), 1124-1129; 10.1021/es015653+.

(14) Lukens, W. W., Shuh, D. K., Schroeder, N. C., and Ashley, K. R. Identification of the non-pertechnetate species in Hanford waste tanks, Tc(I)-carbonyl complexes. *Environ. Sci. Technol.,* **2004** *38*, 229-233; 10.1021/es034318d.

(15) Xia, Y., Hess, N. J., and Felmy, A. R. Stability constants of technetium(IV) oxalate complexes as a function of ionic strength. *Radiochim. Acta,* **2006** *94*(3_2006), 137-141; 10.1524/ract.2006.94.3.137.

(16) Hess, N. J., Xia, Y., and Felmy, A. R. *ACS Symp. Ser.,* **2006** *943*, 286-301.

(17) McKeown, D. A., Buechele, A. C., Lukens, W. W., Shuh, D. K., and Pegg, I. L. Tc and Re Behavior in Borosilicate Waste Glass Vapor Hydration Tests. *Environ. Sci. Technol.,* **2007** *41*, 431-436; 10.1021/es061306u.

(18) Buechele, A. C., Lukens, W. W., Shuh, D. K., McKeown, D. A., Muller, I. S., and Pegg, I. L. Comparison of the behavior of technetium and rhenium in low activity waste glass formulations subjected to the vapor hydration test. *Microsc. Microanal.,* **2010** *16*, 1628-1629; 10.1017/s143192761006232x.

(19)   Buechele, A. C., McKeown, D. A., Lukens, W. W., Shuh, D. K., and Pegg, I. L. Tc and Re behavior in borosilicate waste glass vapor hydration tests II. *J. Nucl. Mater.,* **2012** *429*(1–3), 159-165; 10.1016/j.jnucmat.2012.05.032.

(20)   McCloy, J. S., Riley, B. J., Goel, A., Liezers, M., Schweiger, M. J., Rodriguez, C. P., Hrma, P., Kim, D.-S., Lukens, W. W., and Kruger, A. A. Rhenium Solubility in Borosilicate Nuclear Waste Glass: Implications for the Processing and Immobilization of Technetium-99. *Env. Sci. Tech.,* **2012** *46*(22), 12616-12622; 10.1021/es302734y.

(21)   Goel, A., McCloy, J. S., Windisch, C. F., Riley, B. J., Schweiger, M. J., Rodriguez, C. P., and Ferreira, J. M. F. Structure of Rhenium-Containing Sodium Borosilicate Glass. *Intl. J. Appl. Glass Sci.,* **2013** *4*(1), 42-52; 10.1111/ijag.12003.

(22)   Gibson, J. K. High-Temperature Oxide and Hydroxide Vapor Species of Technetium. *Radiochim. Acta,* **1993** *60*, 121-126.

(23)   Riley, B. J., McCloy, J. S., Goel, A., Liezers, M., Schweiger, M. J., Liu, J., Rodriguez, C. P., and Kim, D.-S. Crystallization of Rhenium Salts in a Simulated Low-Activity Waste Borosilicate Glass. *J. Amer. Ceram. Soc.,* **2013** *96*(4), 1150-1157; 10.1111/jace.12280.

(24)   Baumann, E. W. Colorimetric determination of iron(II) and iron(III) in glass. *Analyst,* **1992** *117*(5), 913-916.

(25)   Webb, S. M. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. *Physica Scripta,* **2005** *2005*(T115), 1011.

(26)   Ravel, B. and Newville, M. ATHENA and ARTEMIS: Interactive graphical data analysis using IFEFFIT. *Phys. Scripta,* **2005** *T115*, 1007-1010.

(27)   Newville, M. IFEFFIT : interactive XAFS analysis and FEFF fitting. *J. Synchr. Rad.,* **2001** *8*, 322-324; doi:10.1107/S0909049500016964.

(28)   Rehr, J. J., Albers, R. C., and Zabinsky, S. I. High-order multiple-scattering calculations of x-ray-absorption fine structure. *Phys. Rev. Lett.,* **1992** *69*(23), 3397-3400.

(29)   Rodriguez, E. E., Poineau, F., Llobet, A., Sattelberger, A. P., Bhattacharjee, J., Waghmare, U. V., Hartmann, T., and Cheetham, A. K. Structural Studies of TcO2 by Neutron Powder Diffraction and First-Principles Calculations. *J. Am. Chem. Soc.,* **2007** *129*(33), 10244-10248; 10.1021/ja0727363.

(30)   Bibler, N. E., Fellinger, T. L., Marra, S. L., O'Drisscoll, R. J., Ray, J. W., and Boyce, W. T. Tc-99 and Cs-137 Volatility from the DWPF Production Melter during Vitrification of the First Macrobatch at the Savannah River Site, Westinghouse Savannah River Company, Aiken, SC, WSRC-MS-99-00860, 1999.