



Redox-dependent solubility of technetium in low activity waste glass



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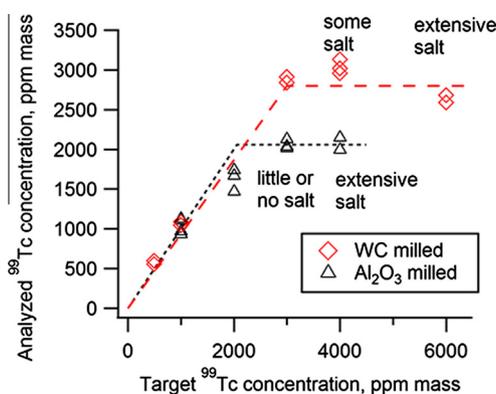
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HIGHLIGHTS

- Hanford low activity waste glass spiked with KTCO_4 500–6000 ppm Tc by mass.
- Tc solubility varied with glass redox, 2000–2800 ppm, higher when slightly reduced.
- Tc mostly present as Tc(IV) with some Tc(VII) and rarely TcO_2 inclusions.
- Small amounts of WC from ball mills can be strongly reducing for Fe and Tc.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 11 November 2013

Accepted 3 March 2014

Available online 11 March 2014

ABSTRACT

The solubility of technetium was measured in a Hanford low activity waste (LAW) glass simulant, to investigate the extent that technetium solubility controls the incorporation of technetium into LAW glass. A series of LAW glass samples, spiked with 500–6000 ppm of Tc as potassium pertechnetate, were melted at 1000 °C in sealed fused quartz ampoules. Technetium solubility was determined in the quenched bulk glass to be 2000–2800 ppm, with slightly reducing conditions due to choice of milling media resulting in reductant contamination and higher solubility. The chemical form of technetium obtained by X-ray absorption near edge spectroscopy is mainly isolated, octahedrally-coordinated 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. Salts formed at the top of higher technetium loaded glasses during the melt. The results of this study show that technetium solubility should not be a factor in technetium retention during melting of Hanford LAW glass.

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1. Background

Radioactive waste from decades of plutonium production is currently stored in large underground tanks at the Hanford Site in eastern Washington State, USA. 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, and chromium and manganese may be present up to several percent. Certain tanks have percent levels of sulfate, fluoride, chloride, and chromate, and many other compounds may be present. The radioactivity of the tanks is mostly due to ⁹⁰Sr and ¹³⁷Cs, with a much smaller contribution by the long-lived fission products including ⁹⁹Tc, ¹²⁹I, ⁹³Zr, and ⁷⁹Se. Some of the waste components do not incorporate well into

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silicate glasses, and 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 partition to the low-activity waste and will be vitrified in that fraction.

Technetium typically incorporates poorly into silicate glass in traditional glass melting as it 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]. Proposed mitigation efforts include an offgas recycle loop which would reintroduce the technetium into the melter, such that over time all the Tc will be immobilized in glass. To effectively manage technetium retention in the Hanford LAW glass, it is critical to understand whether the solubility of technetium is a controlling factor. The speciation of technetium in glass has been previously studied and reported [8–11], but the solubilities of these Tc species in representative waste glass were previously unknown.

The solubility in glass of technetium and many other waste constituents depends partly on their chemical forms, as this may influence its incorporation in glass. The chemical form of technetium in the unprocessed 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 from the waste will oxidize all of the organic compounds and will oxidize technetium to Tc(VII), as 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 is likely to 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 the fugacity of oxygen in the glass as determined by iron redox [8] and can change depending on the melt temperature and oxidation environments [17–19].

In this paper we report the measured solubility of technetium in a Hanford LAW glass simulant and its redox sensitivity, taken under controlled conditions. In contrast, the solubility of technetium obtained by actual manufacture of LAW glass in a full-scale melter involves other considerations not discussed in this paper, including overpressure of the volatile compounds, total concentration of anions and oxyanions, presence of surface salts, and overall alkali content [20,21]. Retention of technetium in melters depends primarily on the volatility, which is influenced by the glass chemistry, redox, cold cap, and other factors [22,23].

2. Materials and methods

2.1. Glass synthesis

Simulant glass for this work was formulated for one of the projected LAW streams to be processed at the Hanford Waste Treatment and Immobilization Plant [24,25]. The glass components were mixed as oxides or carbonates (boron as H_3BO_3), fused, and then crushed to a fine, free flowing powder in a tungsten carbide mill. The crushed glass is not particularly hygroscopic and does not generate gas pressure when it is re-melted. The stock crushed glass 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.

Table 1

Composition of low activity waste (LAW) 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_2O_3	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

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. About 3 g of freshly recrystallized, dry ammonium pertechnetate was accurately weighed, and then dissolved in water. A 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 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. The particle size was not measured due to potential hazards associated with Tc, but the crystalline KTcO_4 settled quickly out of solution yet was not large enough to plug a plastic transfer pipette tip, which places the particle size around 100–600 μm . Note that finely powdered pure technetium compounds are easily dispersed by static charges and constitute a high radioactive contamination hazard.

For each glass melt, 20.00 g of powdered glass was 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 in a ball mill 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 a fused quartz ampoule and keep glass powder off the walls of the ampoule.

Some technetium compounds are volatile at 1000 °C, the temperature of the glass melts [26]. Many salts have significant vapor pressure at this temperature and may extensively evaporate out of the glass. To avoid volatilization losses, which would compromise the solubility measurement, the glass samples spiked with technetium for this work were melted in a sealed fused-quartz ampoule [20]. Components volatile at 1000 °C may move to the headspace above the glass, but cannot escape the quartz ampoule. In the method used here, each powdered glass sample blended with the technetium salt is placed in the bottom of the fused-quartz

ampoule. A fused-quartz end cap is placed in the ampoule about 11 cm above the bottom of the ampoule (see Fig. 1), and sealed to the quartz ampoule wall with an oxypropane flame while under vacuum, after the air is evacuated to 4×10^{-4} Torr so that the ampoule does not pressurize at temperature. A wad of quartz wool was pushed into the top of the fused quartz ampoule for thermal insulation, and 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 protruded 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} . Fig. 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.

Each technetium-spiked glass sample was melted at 1000 °C for two hours, then withdrawn from the furnace 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 fused salt layer, when present, diffused into the cracks as they formed on cooling. Cracking continued after the salts had solidified, so that some cracks are free of salts. The cooled glass appeared nearly black, and was transparent only in thin (~ 1 mm thick) pieces.

2.2. Glass characterization

Qualitatively, when the solubility was reached, a clearly visible fluid salt layer appeared on the surface of the molten glass, while

below the solubility limit no salt layer formed. The cooled bulk glass was then analyzed to measure the technetium solubility, and pieces were taken from various locations in the bulk glass and from the salt cake on top of the glass. The quantitative measurement of true chemical solubility 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 also be found in more than one chemical form, each with a different solubility.

Samples of bulk glass were analyzed for total technetium by ICP-mass spectrometry (MS), and for Fe(II)/Fe(III) ratio to provide an indication of the oxidation potential in the glass. The iron oxidation state was measured by a spectrophotometric method [27]. In this method, 0.1 mL of a 0.85 M ammonium metavanadate, 0.5 mL of concentrated H_2SO_4 , and 1 mL of HF are added to 10–30 mg finely ground glass sample. After analyzing the Fe(II) concentration, ascorbic acid is added to the sample and the total iron concentration can be determined from the same sample. Samples of bulk glass were analyzed by X-ray diffraction (XRD) for selected glasses to investigate the presence of any crystalline inclusions.

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, and a single large fragment from each sample was placed in a 2 mL screw cap centrifuge tube. To prevent contamination, the tube was heat-sealed inside a low-density polyethylene bag, which was sealed inside a polyester bag. Data were obtained at the Stanford Synchrotron Light Source Beamline 11-2 at room temperature.

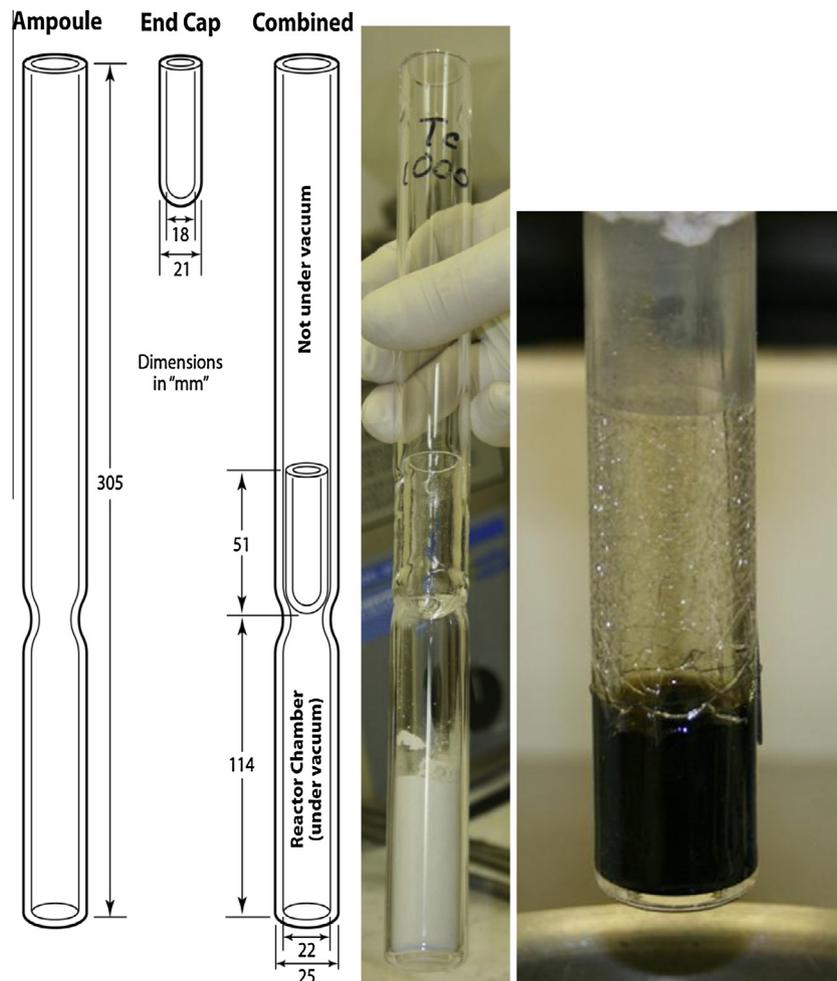


Fig. 1. Diagram of fused quartz ampoule and end cap (left), glass powder before melting (middle), and melted and cooled glass (right).

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 aluminum filter and was corrected for dead-time effects. The monochromator was energy-calibrated to 21,044 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.

The XANES data were averaged using the software package SIX-Pack [28]. Data were normalized and corrected for self-absorption using the ARTEMIS program [29]. Sample spectra were convolved with a 1.2 eV Gaussian peak to match the resolution of the reference spectra. XANES data were fit with a locally written program, “fites”, using the standard spectra as follows. Standard reference spectra included TcO_4^- (adsorbed on ion exchange resin), $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, 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.

Extended X-ray absorption fine structure (EXAFS) data were also collected on two samples which XANES indicated contained crystalline TcO_2 (as opposed to isolated Tc(IV) octahedra in glass [9]). EXAFS data were fit using the programs ATHENA and ARTEMIS [29,30] using theoretical scattering curves calculated using FEFF 7.0 [31] and the atomic positions of Tc and O in crystalline TcO_2 reported by Rodriguez et al. [32].

3. Results and discussion

3.1. Solubility of Tc and dependence on 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 and mix it with 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. All the frit glass (without technetium) was originally ground and homogenized in a different tungsten carbide mill, and by ICP-OES performed on one sample it was determined that this introduced ~ 200 ppm tungsten. After the effect of tungsten carbide became apparent, ~ 20 g of the frit glass (already containing ~ 200 ppm tungsten) was pulverized in the tungsten carbide ball mill jar and the raw pulverized glass (not melted) was examined by XRD. Tungsten carbide was clearly evident in the XRD spectrum (not shown) and the semi-quantitative analysis (using a spike of 5 wt% CaF_2) estimated ~ 0.1 wt% tungsten carbide was present in this glass milled for ~ 5 min in the ball mill jar. However, the amount of tungsten carbide introduced into each sample is not accurately known because of semi-quantitative nature of the XRD analysis and not-well-controlled method of mixing in the ball mill jar.

To produce comparable samples without the reducing conditions caused by tungsten carbide in the ball mill jar, 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. This second series of technetium-spiked glass samples contained 1000, 2000, 3000, and 4000 ppm technetium. 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 compo-

ments and will not change the redox potential in the glass melt. The two sets of data, one for glass made with tungsten carbide and one for glass made with alumina, showed distinct differences from the effect of a reducing agent in the glass melt. Note that all these samples contained the ~ 200 ppm tungsten from the initial LAW glass homogenization before mixing with pertechnetate in the respective ball mill jars.

Fig. 2 shows the measured technetium concentrations in the glass samples, and the raw data is presented in Tables 2 and 3 along with experimental observations. A salt layer on top of the glass melt appeared on both 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-MS) was about 2800 ppm for the tungsten carbide milled samples, and 2000 ppm for the alumina milled samples. Crystalline phase was not detected by XRD performed on the bulk glasses of 4000 and 6000 ppm target tungsten carbide-milled and 3000 and 4000 target alumina-milled.

The glass samples prepared from blends mixed in tungsten carbide have a greater Fe(II)/Fe_{tot} ratio than the samples mixed in alumina. Fig. 3 shows the fraction of reduced iron plotted against the quantity of oxidizing agent (target ppm technetium, which is proportional to the quantity of KTCO_4 added). Fig. 3 also includes the iron redox on the as-prepared glass powder and the glass melted 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. This can be understood as follows: by giving oxygen gas a place to go, the vacuum can push the reaction to the reduced side of the equilibrium. 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)/Fe_{tot} ratio is highest in the sample with the smallest amount of KTCO_4 and decreases as KTCO_4 addition increases with the exception for 3000 ppm glass. The 3000 ppm tungsten carbide glass that had the longest mixing time had a higher Fe(II)/Fe_{tot} ratio than the 1000 ppm tungsten carbide glass, apparently because of the larger amount of tungsten carbide introduced. The sample with the largest amount of KTCO_4 (the 6000 ppm sample milled in tungsten carbide) had only 5% of its iron in the divalent state, presumably because the KTCO_4 oxidized all the tungsten carbide, leaving none to reduce the iron.

The XANES data are shown in Fig. 4. The results of fitting the data (given in Table 4) indicate that tungsten carbide reduces technetium, and apparently increases its solubility in glass (see Fig. 5).

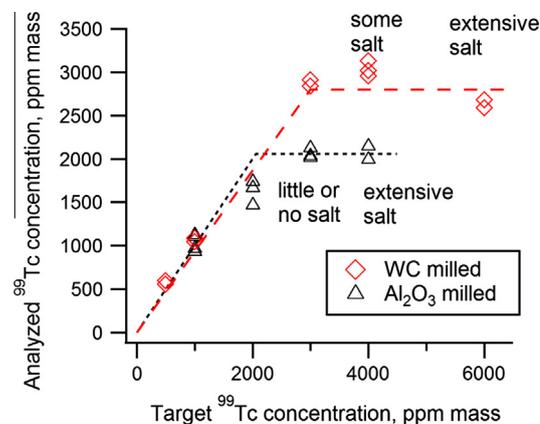


Fig. 2. Analyzed Tc concentration as a function of target concentration for tungsten carbide (WC) and alumina (Al_2O_3 , corundum) milled samples. Multiple samples were collected from different locations of the bulk glass and analyzed.

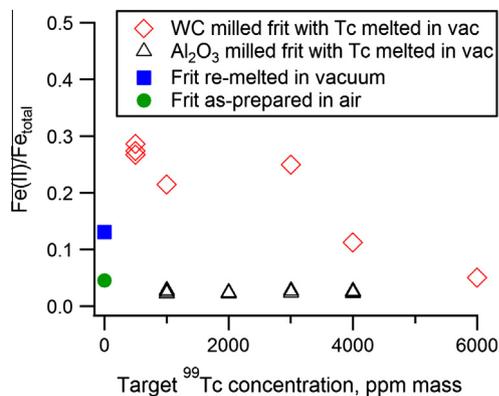
Table 2

Experimental conditions and results for samples ball milled in tungsten carbide (WC). “top”, “middle”, and “bottom” refer to positions in the melt. Percent in XANES is mole%.

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	83% isolated Tc(IV), 17% TcO ₂ Crystalline inclusions
3000 ppm Tc	WC ~10 min	Large meniscus, lots of bubbling	Top 2840 Bottom 2910	Middle 0.25	20% isolated Tc(IV), 80% 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)

Table 3Experimental conditions and results for samples ball milled in alumina (Al₂O₃). “top”, “middle”, and “bottom” refer to positions in the melt. Percent in XANES is mole%.

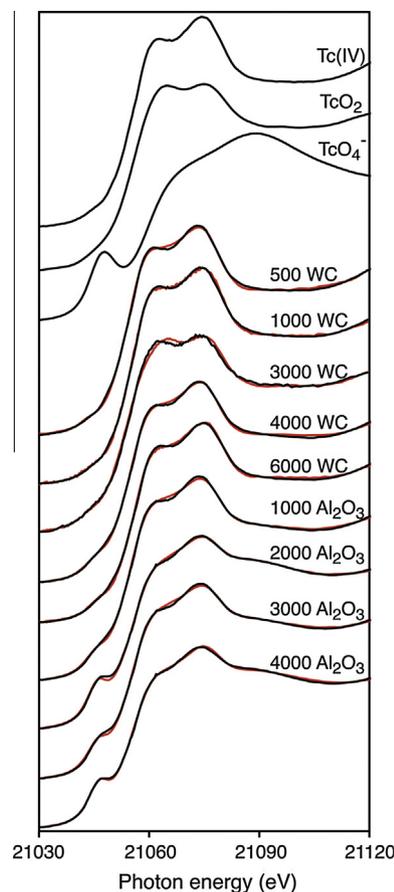
Sample	Mixing time	Notes on melt	ppm Tc by ICP-MS	Fe(II)/Fe(III) ratio	Tc oxidation state by XANES
1000 ppm Tc	Alumina 5 min	No visible salt, some bubbles in meniscus	Top 1130 Middle 1042 Bottom 933	Top 0.022 Middle 0.025 Bottom 0.028	83% isolated Tc(IV), 17% Tc(VII), middle sample
2000 ppm Tc	Alumina 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	Alumina 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	Alumina 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

**Fig. 3.** Fe redox as a function of target Tc concentration.

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 the notion that technetium is reduced from Tc(VII) to Tc(IV) by tungsten carbide.

Reduction of TcO₄⁻ was observed even for samples mixed in alumina, which is due in part to reduction of TcO₄⁻ by Fe(II) in the glass frit (oxidation of Fe(II) by TcO₄⁻). The Fe(II)/Fe_{tot} ratio decreases from 13% in the remelted frit glass to 2–3% in samples remelted with added pertechnetate. For samples mixed in tungsten carbide, the mill introduces tungsten carbide (estimated at ~0.1 wt% but not accurately known for each sample), which reduces TcO₄⁻ (TcO₄⁻ oxidizes the tungsten carbide as discussed earlier).

In the graph of the relative amounts of technetium species observed by XANES shown in Fig. 4, and in Tables 2–4, it can be seen that in all glasses at least ~40% of the technetium was 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 Fig. 5. It can be seen that for Tc(IV) in glass, the maximum concentration in glass is similar at ~1000 ppm regardless of milling media (redox) for 1000 and 3000 ppm target

**Fig. 4.** XANES fitting standards and glass spectra (shown as ppm target Tc with milling media used). Data are in red, fits are in black. Fit results shown in Table 4.

WC-milled glasses (Fig. 5a) and 1000 and 2000 ppm target Al₂O₃-milled glasses (Fig. 5b). Tc(VII), on the other hand, is completely absent in WC-milled glasses up to 3000 ppm target. However, for

Table 4
XANES fitting results.

Sample	Tc(IV) ^a	<i>p</i> ^b	TcO ₄ ⁻	<i>p</i>	TcO ₂ ·2H ₂ O	<i>p</i>
500 WC	1.00(1) ^c	<0.001	0.00(1)	1		
1000 WC	0.83(7)	<0.001	0.00(2)	1	0.17(8)	0.028
3000 WC	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 Spectrum of Tc(IV) gluconate complex.

^b *p* is the probability that the improvement to the fit from 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.

the 4000 ppm target glasses, the Al₂O₃-milled glass contains ~44% (~900 ppm) of the technetium as Tc(VII), while for the WC-milled glass only ~11% (~330 ppm) is Tc(VII). By taking the data of all the glasses, the total solubility is ~2800 ppm in WC-milled glasses (average of 4000 and 6000 ppm samples excluding 3000 target glass that contains TcO₂), while it is ~2000 ppm in Al₂O₃-milled glasses (average of 3000 and 4000 ppm samples). The average Fe(II)/Fe_{tot} ratio was 8% for the WC-milled glasses and 2.5% for the Al₂O₃-milled glasses. It should be emphasized that the solubility line here should be taken as approximate, since the glasses were not all at the same redox state, and the ratios of Tc(IV) and Tc(VII) varied. It is not possible to extrapolate the present results to estimate the solubility of technetium at different redox states outside the range tested in this study because there are only two data points. During planned operation of Hanford LAW vitrification facility, sucrose will be added to the melter feed to reduce the nitrates and nitrites from waste in the amount that are estimated to keep the iron redox approximately at 4% Fe(II)/Fe_{tot} ratio [23]. This suggests that the Hanford LAW glasses are likely to have the technetium solubility roughly between 2000 and 2800 ppm measured in the this study assuming there is no significant effect of glass composition on Tc solubility within the range of borosilicate glasses to be produced at Hanford.

Some comments on the aforementioned results and interpretations regarding the dependence of solubility on redox are warranted. Some readers may be concerned that the oxygen fugacity is not buffered and the experiments may not have been long enough to reach equilibrium, resulting in a perceived limitation of

applicability of the data. While the oxygen fugacity was not deliberately buffered (e.g., using the magnetite/hematite buffer), it is still controlled by the presence of Fe, WC, and Tc. Moreover, the oxygen fugacity in this sealed system can be determined from the Fe(II)/Fe(III) ratio using published data by Schreiber et al. [33]. Additionally, while a longer hold time than 2 h at temperature would have been preferable, a shorter time was chosen due to procedural and facility constraints. However, justification that the reactions have reached equilibrium can be made as follows. First, the hold time above the liquidus is similar to that used in studying Fe partitioning in basalt/amphibole melts [34]. More importantly, the relationship between the Fe oxidation state and the Tc oxidation state, and the fact that this is similar to that seen in previous studies, strongly implies that the system has reached equilibrium at least with respect to the Fe and Tc redox. The redox data provided can be extended beyond this particular system using the Fe(II)/Fe(III) couple, which is the usual redox state indicator in nuclear waste glass. Since the relationship between the Fe(II)/Fe(III) couple and the Tc(IV)/Tc(VII) couple is known, the Tc oxidation state distribution can be estimated from the Fe oxidation state distribution for the glasses with similar composition used in this study.

3.2. Crystalline inclusions containing Tc

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

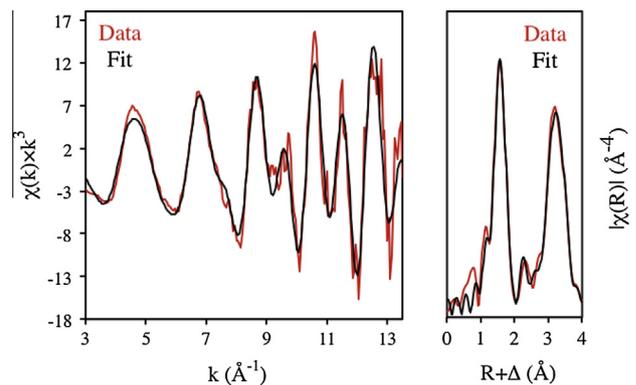


Fig. 6. Tc K-edge EXAFS spectrum of glass containing 3000 ppm Tc (WC milled). Fit parameters shown in Table 5.

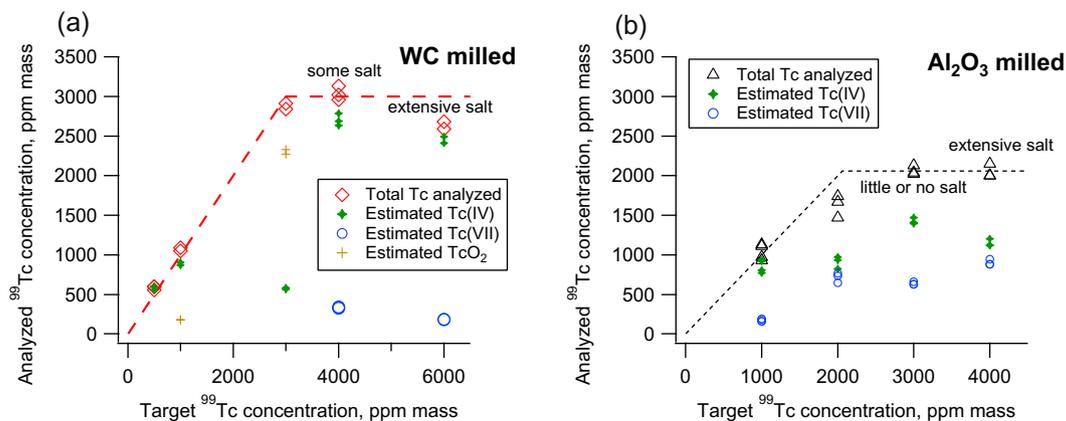


Fig. 5. Estimated technetium speciation in glass by mass as a function of target concentration for (a) tungsten carbide (WC) milled samples and (b) alumina (Al₂O₃) milled samples.

Table 5Best fit^a 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 (<i>p</i>)
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, $\chi^2 = 28.6$, $\chi^2_\nu = 2.1$, $R = 0.008$.^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.

the identity of the Tc(VII) species. Preliminary investigations using micro-Raman spectroscopy indicate that at least some of the Tc(VII) may be present as NaTcO₄ or KTcO₄ crystalline salts, in concentrations too low for detection with X-ray diffraction [35].

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 TcO₂ crystals. The presence of this species was confirmed by EXAFS. The spectrum of technetium in 1000 ppm glass (tungsten carbide milled) 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 milled) resembles that of TcO₂ crystallites in glass [9] with the caveat that the previously reported spectrum also includes a contribution from TcO₄⁻, which means it cannot be used as standard spectrum in XANES fitting. Therefore, the spectrum of TcO₂·2H₂O was used instead (the local structure of Tc in TcO₂·2H₂O is almost identical to that of Tc in crystalline TcO₂). 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 TcO₂ inclusions in a ratio of roughly 1:4. Fitting the XANES spectra for these samples produces large errors for the amounts of isolated Tc(IV) octahedra versus TcO₂ crystallites since the XANES spectra of Tc(IV) in glass and TcO₂·2H₂O are very similar. However, the errors for the total amount of Tc(IV) (TcO₂+isolated Tc(IV)) and the amount of Tc(VII) are comparable to those for the other XANES fits.

The EXAFS spectrum of technetium in 3000 ppm Tc glass (WC) is shown in Fig. 6. 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 TcO₂; however, a scale factor was 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 TcO₂ inclusions (the scale factor is 0.54). The distances to the neighboring atoms are in excellent agreement with those reported by Rodriguez et al. [32], which strongly supports the hypothesis that the spectrum is due to TcO₂ inclusions. Likewise, an F-test of the scattering shells shows that all neighboring atoms except the more distant oxygen neighbors are observed in the EXAFS experiment. Fitting results for EXAFS for this 3000 ppm Tc (tungsten carbide) glass are shown in Table 5. EXAFS analysis suggests that this sample contains a 1:1 ratio of Tc(IV) in isolated octahedra and TcO₂ inclusions. It is well known that EXAFS analysis presents a systematic error of 25% in the coordination number due to the strong correlation of the coordination numbers with the Debye–Waller thermal parameters, and it is independent of concentration of the scatterer. XANES analysis does not have the same systematic error

as EXAFS, and the error is well represented by the standard deviations of the fraction of species in the fits. Therefore, the error in the ratio of isolated Tc(IV) to TcO₂ inclusions in this sample is approximately the same by both EXAFS and XANES.

4. Conclusions

The apparent solubility of technetium in a representative Hanford low activity waste sodium borosilicate glass melted at 1000 °C is determined to be about 2000 ppm Tc by mass, and rises to about 2800 ppm if the glass is made under slightly reducing conditions. These reducing conditions were realized in this work by milling the pertechnetate salt with the glass frit in a tungsten carbide ball mill, as opposed to an alumina ball mill. These average solubilities should be taken as approximate, since the Tc(IV)/Tc(VII) ratios were different in each case, as the glasses were at different oxygen fugacities, particularly for the WC-milled samples. It should not be assumed that the solubility of Tc(IV) should be directly related to that of Tc(VII), as their respective environments in glass are different. Given that the estimated concentration of technetium in LAW glass at Hanford is ~3 ppm [24], the technetium solubility in glass should not be a factor in technetium retention regardless of its oxidation state.

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 six-coordinated ion, but in some cases it forms crystalline inclusions of TcO₂. The chemical form of the Tc(VII) in the glass is currently ambiguous, and could be dispersed isolated TcO₄⁻ and/or inclusions of crystalline pertechnetate salts.

Acknowledgements

This work was supported by the Department of Energy's Waste Treatment & Immobilization Plant Federal Project Office under the direction of Dr. Albert A. Kruger. The authors thank Jaehun Chun and two anonymous reviewers for comments on the manuscript. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. DOE under contract DE-AC05-76RL01830. Portions of this work were supported by U.S. Department of Energy, Basic Energy Sciences, Chemical Sciences, Biosciences, and Geosciences Division, Heavy Element Chemistry Program and were performed at Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. DOE Office of Science by Stanford University.

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