Dissimilar Behavior of Technetium and Rhenium in Borosilicate Waste Glass as Determined by X-ray Absorption Spectroscopy

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Technetium-99 is an abundant, long-lived ($\tau_{1/2}$ = 213 000 years) fission product that creates challenges for the safe, long-term disposal of nuclear waste. Although ^{99}Tc receives attention largely because of its high environmental mobility, it also causes problems during its incorporation into nuclear waste glass because of the volatility of Tc(VII) compounds. This volatility decreases the amount of ^{99}Tc stabilized in the waste glass and causes contamination of the waste glass melter and off-gas system. The approach to decreasing the volatility of ^{99}Tc that has received the most attention is the reduction of the volatile Tc(VII) species to less volatile Tc(IV) species in the glass melt. On engineering scale experiments, rhenium is often used as a non-radioactive surrogate for ^{99}Tc to avoid the radioactive contamination problems caused by volatile ^{99}Tc compounds. However, Re(VII) is more stable toward reduction than Tc(VII), so more reducing conditions would be required in the glass melt to produce Re(IV). To better understand the redox behavior of Tc and Re in nuclear waste glass, we prepared a series of glasses under different redox conditions. The speciation of Tc and Re in the resulting glasses was determined by X-ray absorption fine structure spectroscopy. Surprisingly, Re and Tc do not behave similarly in the glass melt. Although Tc(0), Tc(IV), and Tc(VII) were observed in these samples, only Re(0) and Re(VII) were found. In no case was Re(IV) (or Re(VI)) observed.

Introduction

The production of plutonium in the United States during the Cold War has generated approximately 80 million gallons of high-level nuclear waste, which is currently stored in large underground tanks at the Savannah River Site in South Carolina and at the Hanford Site in eastern Washington.[1] Treatment and safe disposal of this waste is among the most challenging remediation projects in the United States. The current plan for stabilization of this waste includes separation into a high-activity and a low-activity waste stream.[1] The high-activity waste stream, which contains the bulk of the radioactivity but only a small volume of the waste, will be converted into glass (vitrified) and sent to the high-level waste repository, currently planned at Yucca Mountain. The low-activity waste stream contains most of the chemical constituents of the waste, including large amounts of sodium nitrate, sodium nitrite, sodium hydroxide, and small amounts of organic compounds such as EDTA, formate, and acetate. The low-activity waste stream will also contain 20 and 80% of the ^{99}Tc present in the waste tanks at the Savannah River and Hanford Sites, respectively. At the Savannah River Site, the low-activity waste stream is currently stabilized in a grout waste form, Saltstone, and at the Hanford Site, the low-activity waste stream will be vitrified.[1] In both cases, the resulting low-level waste form will be interred in an on-site repository.

The radionuclides ^{237}Np, ^{127}I, and ^{99}Tc are of particular concern in the high-level waste repository because of their long half-lives and high environmental mobility.[2] In the low-activity waste repositories at the Savannah River and Hanford Sites, ^{99}Tc is generally the radionuclide of greatest concern, since it dominates the dose received by people living off-site who drink groundwater or use it for agriculture.[3−5] The main reasons that ^{99}Tc is so important in determining the off-site dose are its high fission yield (∼6%), which results in a large inventory of ^{99}Tc in nuclear waste, its long half-life, 213 000 years, and the high solubility and environmental mobility of pertechnetate, TcO_4^-, the most stable form of Tc in aerobic environments.

In addition to creating challenges for the long-term disposal of nuclear waste, technetium also creates significant

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problems for vitrification of nuclear waste due to its volatility under these conditions.[6−10] During vitrification, the volatile technetium compounds that are lost from the glass melt must be captured in the off-gas treatment equipment. Secondary wastes from the off-gas treatment systems must then be either recycled or stabilized in alternative waste forms, which increases the amount of waste created. Under the conditions present in the glass melt, only Tc(VII) and Tc(IV) are expected to be present because Tc(V) and Tc(VI) are unstable with respect to disproportionation under these conditions. A number of Tc(VII) compounds have significant volatility at the temperatures (typically 1100−1200 °C) at which waste is vitrified.[6,9,10] On the other hand, lower-valence Tc compounds are less volatile under these conditions, because reducing conditions reduce the amount of Tc lost during vitrification.[6,11,12] Consequently, one of the major factors in controlling Tc volatility during vitrification is the redox state of the melt. Since iron is typically the most abundant redox-active element in the glass, the redox state is generally expressed as the ratio of iron that is present as Fe(II) to the total amount of iron, Fe(II)/ΣFe. Most nuclear waste vitrification processes operate under relatively oxidizing conditions, typically Fe(II)/ΣFe < 0.3, to prevent the formation of separate metallic and metal sulfide phases,[13] which can compromise the operation of the glass melter.

In addition to presenting problems for the vitrification of waste, Tc volatility also creates practical challenges for the development of waste-glass formulations. Whereas the preparation of Tc-bearing glasses on the small, crucible scale is relatively straightforward, preparation of Tc-bearing glasses at larger scales is much more difficult due to the problems caused by Tc contamination of the melter and associated equipment, especially the effluent gas treatment system. For this reason, Re is often used as a non-radioactive surrogate for Tc in such large-scale experiments.[6,9] In analogy to Tc chemistry, Re(VII) and Re(IV) are assumed to be stable in the glass melt. Although ReO_3 is known, it is unstable towards disproportionation above 300 °C.[14] However, Re is substantially different from Tc in one respect: the standard reduction potentials, in water, for the reduction of TcO_4^- and ReO_4^- to Tc(IV) and Re(IV) are significantly different, 0.74 and 0.51 V, respectively.[15,16] This difference is of great practical importance when using Re as a surrogate for Tc in the development of conditions used to vitrify waste.

Since Tc(IV) is less volatile than Tc(VII), reducing conditions decrease technetium volatility. Because of the difference in reduction potentials for TcO_4^- and ReO_4^-, a substantially more reducing redox environment would be required to reduce ReO_4^- in comparison to TcO_4^-. To investigate the effect of Tc redox state on Tc volatility, as well as the behavior of Re as its surrogate under the conditions present during vitrification, it is necessary to know the redox conditions that are required to produce Tc(IV) or Re(IV) in nuclear waste glass. The redox behavior of Tc and Re in a borosilicate melt has been studied previously by square-wave voltammetry, and quite different results were obtained for Tc and Re.[17]

The goal of the present study is to better understand the effect of redox environment on Tc and Re during vitrification. Toward that end, a series of glass samples was prepared under a range of redox conditions. Among these glasses are examples that contain only Re, only Tc, and both Tc and Re, the latter of which allows the direct comparison of the behavior of the two elements under identical redox conditions. The formulations of these glasses are similar to those that will be used to stabilize the low-activity waste stream at the Hanford Site.[5] The glasses reported here were prepared from the same solid glass formers as planned for the Hanford facility (SiO_2, $B(OH)_3$, Fe_2O_3, etc.) together with a chemical simulant of the anticipated low-activity waste stream to which Tc and/or Re was added as TcO_4^- or ReO_4^-.

The speciation of Tc and Re was determined using X-ray absorption fine structure (XAFS) spectroscopy. In glasses where either element was present as a single species, extended X-ray absorption fine structure (EXAFS) was used to determine the local structure of the metal ion and to identify the species. The X-ray absorption near edge structure (XANES) spectra of these species were used as standards to determine the speciation in glasses that contained a mixture of species.

Experimental Section

Reagent-grade chemical stock compounds were used for glass synthesis. Water was deionized using a MilliQ system. Oxide components of the prepared glasses were determined by X-ray fluorescence (XRF) spectroscopy with a relative uncertainty of 4%. XRF analyses utilized an ARL 9400 X-ray fluorescence spectrometer with XRF composition values determined using NIST standard glasses as standards. Technetium concentrations were determined by liquid scintillation measurements on acid-dissolved glass samples and have an uncertainty of 4%. B_2O_3 and Li_2O values were determined by direct-coupled plasma atomic emission spectroscopy on acid-dissolved glass samples. The purity of all crystalline standards used in this study was verified by powder X-ray diffraction. Fe(II)/Fe(total) ratios were determined colorimetrically using a manual adaptation of the method described by Whitehead and Malik, and have an absolute uncertainty of 0.4%.[18,19]

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Table 1. Compositions (wt %) Determined by XRF of Crucible Glasses[a] (all glasses prepared in air)

sample	glass type	Tc[d]	ReO_2	SiO_2	Fe_2O_3	Al_2O_3	B_2O_3	Li_2O	Na_2O	K_2O	MgO	CaO	other[c]
II-118	LAWA	0.005	[b]	44	7.5	5.9	9.1	0.23	16.0	2.7	2.1	2.1	8.4
II-121	LAWC	0.003	[b]	46	5.9	6.2	10.7	2.4	12.4	0.36	1.7	4.9	7.9
II-127	LAWC	0.048	0.04	45	5.9	6.2	10.3	2.2	15.6	0.38	1.6	4.7	7.6
II-128	LAWC	0.057	0.04	47	6.6	6.5	9.9	2.2	16.1	0.25	1.6	5.1	7.6
II-129	LAWA	0.02	0.01	40	6.6	5.9	8.7	[b]	19.5	4.1	1.9	1.9	7.2

[a] There was a relative uncertainty of 6% for the analyses on this sample. [b] Element was either not present or present below the detection limit. [c] The other principal components are TiO_2, ZrO_2, and ZnO. [d] Tc concentrations determined by liquid scintillation.

Table 2. Samples Prepared under Different Redox Conditions

sample	glass type	atmosphere	appearance
II-206	LAWA	air	brown
II-205	LAWC	air	brown
II-210	LAWA	N_2	dark brown
II-212	LAWC	N_2	dark green
II-214	LAWA	1:1 CO_2:CO	dark green w/ metallic film
II-216	LAWC	1:1 CO_2:CO	dark green w/ metallic film
II-218	LAWC	100 ppm O_2 in N_2	dark green
II-219	LAWA	100 ppm O_2 in N_2	green-brown

Two groups of borosilicate glasses were investigated. The first group, crucible glasses, was prepared in a vertical tube furnace by suspending a Pt/4% Au crucible in the center of the tube. The top of the tube was externally cooled and contained quartz wool to trap the volatilized Tc species. Prior to heating, the furnace was purged with gas (60 mL min^{-1} for 2 h, total volume of the furnace is 360 mL) through a long needle. During the glass synthesis, gas was slowly passed over the top of the tube and through a set of bubblers to trap any escaping Tc. These glasses were formulations developed for the low-activity waste Envelope C (LAWC) (specifically, for tank AN-107) and Envelope A (LAWA) (specifically, for tanks AP-101 or AN-105) at the Hanford Site.[20] The glasses were prepared by spiking a tank waste simulant (1.55 mL for LAWC glasses and 1.60 mL for LAWA glasses) with $NaTcO_4$ (0.32 mL, 0.106 M, 34 μmoles) and NH_4ReO_4 (0.54 mL, 0.20 M, 0.11 mmol), stirring to create a homogeneous mixture, and then adding the glass components (1.63 g for LAWC glasses and 1.93 g for LAWA glasses) to form a slurry, which was then heated according to the following schedule

$$30\ °C \xrightarrow{10\ min} 110\ °C \xrightarrow{2\ hr} 140\ °C \xrightarrow{3\ hr} 700\ °C$$

$$700\ °C \xrightarrow{2\ hr} 770\ °C \xrightarrow{2\ hr} 1150\ °C \xrightarrow{4\ hr} 1150\ °C$$

The glass was cooled to room temperature in the furnace and then removed from the crucible. The compositions of the examples of LAWA and LAWC glasses are given in Table 1, and the synthesis conditions are given in Table 2. The compositions of the glass components and the waste simulants are given in the Supporting Information.

The second group, melter glasses (Table 3), contains two sets of glasses. One set (LAWA1) was synthesized under oxidizing conditions and used a LAW Sub-Envelope A1 waste simulant.[21] The other glass set (HLWAZ-102) was synthesized under more reducing conditions and used a HLW AZ-102 waste simulant.[21] Rhenium-bearing waste glasses were synthesized in two similar continuously-fed DuraMelter 100 (DM100) ceramic-lined, Joule-heated melters, where the melt pools (∼110 kg for LAW and ∼180 kg for HLW) were maintained at 1150 °C and agitated using an air bubbler. Glass production rates of up to 220 kg glass per day were used for each production run of about 100 h in duration. Glass samples from the melter were extracted at various times during the melter run as Re concentrations were changed in the melt pool.

Tc K-edge (21044 eV) and Re L_2-edge (11959 eV) XAFS data were collected at the Stanford Synchrotron Radiation Laboratory beamlines 4-1 and 11-2 using a Si (220) double crystal monochromator. The harmonic content of the beam was reduced with a harmonic rejection mirror or by detuning the monochromator by 50%. Samples were mounted in polycarbonate holders sealed with Kapton tape. The holders were doubly contained in heat-sealed polyethylene pouches. Data were recorded in transmission using Ar-filled ion chambers or in fluorescence using a four-element Ge detector and were corrected for detector dead time effects. For crucible glasses, the top surface of the intact glass ingot, which was in contact with the tube furnace atmosphere, was probed with the exception of sample II-219, which shattered. The top surfaces of the glass pieces were examined in this case. The information depth, above which 68% of the observed fluorescence photons originate, is 0.26 mm at the Tc K-edge and 0.06 mm at the Re L_2-edge.[22]

EXAFS data analysis was performed by standard procedures[23] using the programs ifeffit[24] and Athena/Artemis;[25] theoretical EXAFS phases and amplitudes were calculated using FEFF7.[26] EXAFS data analysis and XANES fitting were performed as previously described.[27,28] The XANES fitting errors are extremely sensitive to the slope of the spectrum produced by the pre-edge correction; to minimize the errors, we included the slope of the XANES spectra in the fit. The Tc and Re XANES spectra were also analyzed by principal component analysis using the program SixPack.[29] The Tc spectra were spanned by 3 eigenvectors, which produced good fits for the spectra of TcO_4^-, Tc(IV), and Tc(0) in glass. The Re spectra were spanned by 2 eigenvectors, which produced good fits for the spectra of ReO_4^- and Re(0) in glass.[30]

The Tc XANES data for the glass samples had higher resolution than the reference spectra, so the spectra of the glasses were convolved with a 1 eV wide Gaussian. In addition, Tc K-edge XANES spectra for glasses II-205 through II-219 were smoothed using three iterations of simple three-point smoothing. The Tc

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Table 3. Composition (wt %) Determined by XRF of Rhenium Glasses Prepared in a Continuous Melter

sample	type	Re_2O_7	SiO_2	Fe_2O_3	Al_2O_3	B_2O_3[c]	Li_2O[c]	Na_2O	K_2O	MgO	CaO	other[a]
WVT-G-128b	LAWA1	0.52	42	6.4	6.2	9.0	[b]	18.8	0.45	1.51	2.1	9.5
WVT-G-126b	LAWA1	0.83	46	5.9	6.4	9.0	[b]	19.1	0.49	1.58	2.0	8.7
WVT-G-125c	LAWA1	0.48	47	5.5	6.5	9.0	[b]	18.7	0.49	1.36	2.1	9.0
WVT-G-150a	LAWA1	0.22	45	6.6	6.4	9.0	[b]	19.5	0.51	1.94	1.90	8.6
BLG-G-113a	HLW AZ−102	0.41	48	11.6	6.0	12.5	3.3	10.9	0.16	0.08	0.37	6.2
BLG-G-85a	HLW AZ−102	0.22	49	11.5	6.1	12.5	3.3	10.8	0.18	0.10	0.37	6.7
BLG-G-79a	HLW AZ−102	0.07	48	11.4	6.1	12.5	3.3	11.2	0.13	0.11	0.40	6.5

[a] The other principal components are TiO_2, ZrO_2, and ZnO. [b] Element was either not present or present below the detection limit. [c] Target compositions, actual composition not determined.

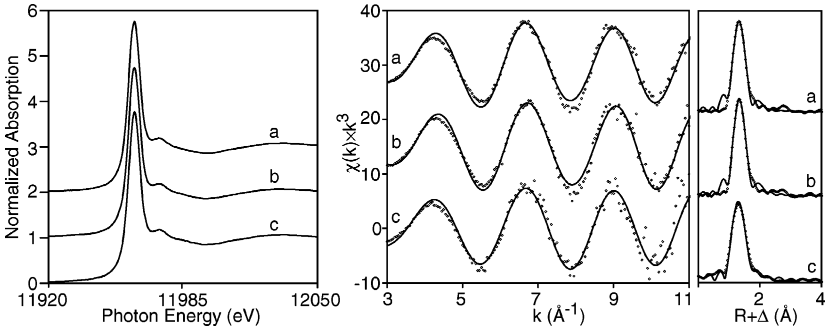

Figure 1. Re L_2 XANES spectra (left), EXAFS spectra (center), and Fourier transforms (right) for Re(VII) in glass (a) WVT-G-126b, (b) BLG-G-113a, and (c) II-205. Data are depicted as points; fit is indicated by the solid line. Fit range: $3 < k < 11$; $0.8 < R < 2.5$.

K-edge experimental resolution was ∼3 eV and the Tc K-edge core-hole broadening is ∼6 eV (from FEFF7) yielding a spectral resolution of ∼7 eV; the fit had a range of 150 eV (21 independent data points) and used six parameters (energy shift, *y*-axis shift, *y*-axis slope, and contribution of three standards). The fit for sample II-219 had a range of 120 eV due to noise in the pre-edge region. The Re L_2-edge XANES experimental resolution was ∼2 eV and the Re L_2-edge core-hole broadening is ∼5 eV, yielding a spectral resolution of ∼6 eV. The fit had a range of 120 eV (20 independent data points) and used seven parameters (as above, but with four standards). The fitting process was done in two stages. First, the XANES spectra were fit including all of the reference spectra. Whenever the contribution of the reference spectrum was within one standard deviation of zero, the spectra were fit again with that spectrum excluded. The final fit therefore includes only reference spectra that have non-zero contributions to the fit. The results of initial fitting are included in the Supporting Information.

Table 4. EXAFS Parameters for Re(VII) in Glass ($S_0^2 = S$)

sample	ΔE_0 (eV)	*R* factor[a]	no. of O neighbors	*R* (Å)	σ^2 (Å^2)
NH_4ReO_4	6(4)	0.038	4(1)	1.73(1)	0.002(2)
II-205	2(3)	0.023	4.7(8)	1.75(1)	0.002(1)
WVT-G-126b	−2(3)	0.031	4.5(8)	1.73(1)	0.003(1)
WVT-G-125c	−1(2)	0.015	4.1(5)	1.72(1)	0.002(1)
WVT-G-150a	0(2)	0.008	4.3(6)	1.73(1)	0.003(1)
BLG-G-113a	1(3)	0.018	4.3(9)	1.73(1)	0.002(1)
BLG-G-85b	5(1)	0.012	4.5(9)	1.74(1)	0.001(1)

[a] $R\text{ factor} = \sum(y_i(\text{data}) - y_i(\text{fit}))^2/\sum(y_i(\text{data}))^2$.

Results

Identities of the Technetium and Rhenium Species in the Glass. One spectroscopic technique that has been very useful for determining the speciation of Tc in samples that contain a mixture of species is fitting the Tc K-edge XANES spectra of samples using the XANES spectra of known Tc compounds as standards.[27,28] To determine the speciation of Tc and Re in glass samples in this manner, it is necessary to obtain standard spectra corresponding to the specific species present in the glass. This can be accomplished by using pure compounds, such as ReO_2, or by demonstrating that the reference sample contains only a single species. The reference spectra for Tc(VII) and Tc(IV) in glass were previously obtained,[27] but the reference spectra for metallic Tc in glass and for the Re species have not been reported. In this study, ReO_2 and ReO_3 were used to obtain the reference spectra for Re(IV) and Re(VI). The other standard spectra were from glass samples that contained a single species as determined by EXAFS.

NH_4ReO_4 was initially used as the Re(VII) standard, but its Re L_2 XANES spectrum is somewhat different from that of Re(VII) in the glass in that the large peak at the absorption edge (white line) of Re(VII) in glass is broader than that of NH_4ReO_4. The EXAFS spectra of Re(VII) in glasses prepared in both crucibles and melters are shown in Figure 1, and the fit parameters are given in Table 4. In all of these cases, the only important Re species in the glass is Re(VII), and the fitting parameters are similar. The XANES spectrum of II-205 was used as the standard for Re(VII) in glass.

The identities of the metallic Tc and Re species in the glass, Tc(0) and Re(0), were determined from the EXAFS spectra of the LAWA and LAWC glass samples prepared under highly reducing conditions generated using a 1:1 CO:CO_2 atmosphere. In both cases, a metallic film formed on the surface of the glass sample. The Tc K edge and Re L_2 edge EXAFS spectra of these samples are shown in Figure 2 and the fitting results are in the Supporting Information. The distances determined from fitting the EXAFS are in good agreement with the hcp structure of the metals.[31,32] Both samples are actually Tc:Re alloys: sample II-216 has a Tc:Re ratio of 6:1 and sample II-214 has a ratio of 1:3. Because II-216 contains mainly Tc in the metallic phase, it is referred to as Tc(0), and II-214 is referred to as Tc/Re. The very different appearance of the spectra of II-214 compared with that of II-216 is due to the Ramsauer−Townsend effect,

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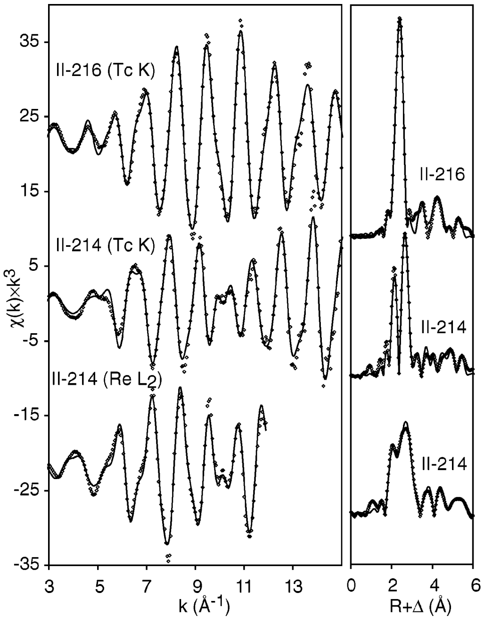

Figure 2. EXAFS spectra and Fourier transforms for Tc and Re metal standards: II-216 is the Tc(0) standard and II-214 is the Re(0) standard. Data are indicated by points; fit is indicated by the solid line. Fit range, Tc K edge: $3 < k < 15$; $1.9 < R < 6$; Re L_2 edge: $3 < k < 11.8$; $1.2 < R < 5.9$. Note: the Re L_2 edge EXAFS are truncated at 12 $Å^{-1}$ because of the presence of the Re L_1 edge at 12 527 eV.

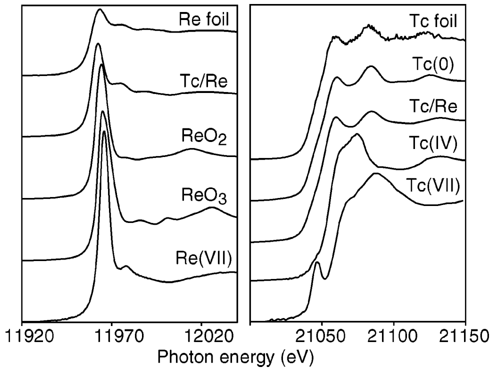

Figure 3. Re L_2-edge XANES standard spectra (left) and Tc K-edge standard spectra (right) used to determine Re and Tc speciation in glass samples. Tc(0), Tc/Re, and Re(VII) correspond to II-216, II-214, and II-205, respectively.

which makes peaks corresponding to the scattering from Re atoms appear to be split.[33] Despite the difference in appearance of the spectra, the structural parameters derived from the fitting the spectra are very similar in both samples. The EXAFS data are otherwise unremarkable. Most importantly, the lack of a peak at $R < 2$ shows that no O neighbors are present in either the Re or Tc coordination environment.

The XANES spectra of the standards are shown in Figure 3 along with the XANES spectra of Tc and Re metal foils. Although the Tc K-edge XANES spectra of metallic Tc in glass, Tc(0) (II-216) and Tc/Re alloy (II-214), are similar to the spectrum of bulk Tc metal, the spectra are not identical. In particular, the intensity of the transition at the absorption edge is slightly larger in the Tc(0) and Tc/Re alloy spectra than in Tc foil, and the position of the feature at ~21 125 eV changes as a function of the Re content of the alloy. In contrast, the Re L_2-edge XANES spectra of Re foil and Tc/Re are significantly different. Compared to the XANES spectrum of Re foil, the white line of the Tc/Re XANES spectrum is significantly larger, although the edge shift is only slightly different from that of Re foil (11957.6 eV versus 11958.2 eV). The white line is due to the $2p_{1/2}$ to $6d_{3/2}$ transition, and its intensity is proportional to the number of vacancies in the $6d_{3/2}$ level.[34] In a Tc/Re alloy, the intensity of this transition is expected to be greater than in pure Re metal. Tc is more electronegative than Re and will lower the Fermi level at Re in a Tc/Re alloy relative to Re in the metal, which would create more vacancies in the $6d_{3/2}$ level of the Tc/Re alloy. This effect has been previously observed in Pt alloys.[34,35] Apart from the intensity of the white lines, the XANES spectra of Re foil and Tc/Re in glass are similar.

Table 5. Re Speciation in Melter Glass Samples Determined from Analysis of the Re L_2 XANES Spectra

sample	type	Fe(II)/ΣFe	Re(0)	Re(VII)
WVT-G-128b	AZ-102	0.019	0	0.985(6)
WVT-G-126b	AZ-102	0.043	0	0.965(2)
WVT-G-125c	AZ-102	0.108	0	0.982(3)
WVT-G-150a	AZ-102	0.034	0	0.971(3)
BLG-G-113a	LAWA1	0.105	0.025(8)	0.967(5)
BLG-G-79a	LAWA1	0.128	0	0.986(5)
BLG-G-85b	LAWA1	0.058	0	0.989(4)

Rhenium Speciation in Melter Glasses. As noted in the introduction, Re is used as a non-radioactive surrogate for Tc in large-scale melter studies to avoid the hazards created by Tc volatilization. For this reason, the redox state and Re speciation in a series of Re-containing nuclear waste glasses prepared in a large melter were examined. The results from fitting the EXAFS spectra of these samples are reported in Table 4. In all cases, the number of oxygen neighbors and the Re−O bond lengths are consistent with the presence of only Re(VII). In both ReO_2 and ReO_3, the Re center has six oxygen neighbors, and the Re−O distances are much longer, 2.00 and 1.87 Å, respectively, whereas in ReO_4^-, the Re center has only four oxygen neighbors and a shorter Re−O distance, as seen in Table 4.[36,37] The results from fitting the XANES spectra are reported in Table 5. Both techniques show that the only important Re species in these samples is Re(VII), which is not surprising in light of the anticipated stability of Re(VII) in alkali-rich glass melts, suggested by its aqueous reduction potential under alkaline conditions, −0.59 V at pH 14.

Tc and Re Speciation in Crucible Glasses. The Tc and Re species present in the glasses were determined by fitting the XANES spectra of the samples using a linear combination of the XANES spectra of the standard species shown in Figure 3. The XANES spectra and fits for the glass samples are shown in Figure 4, and the fitting results are given in Table 6 along with redox potential (as Fe(II)/ΣFe) for each sample. Because metallic rhenium and technetium are present as films on the surfaces of the samples, the XANES analysis overstates the relative amounts of Tc(0) or Re(0) present in

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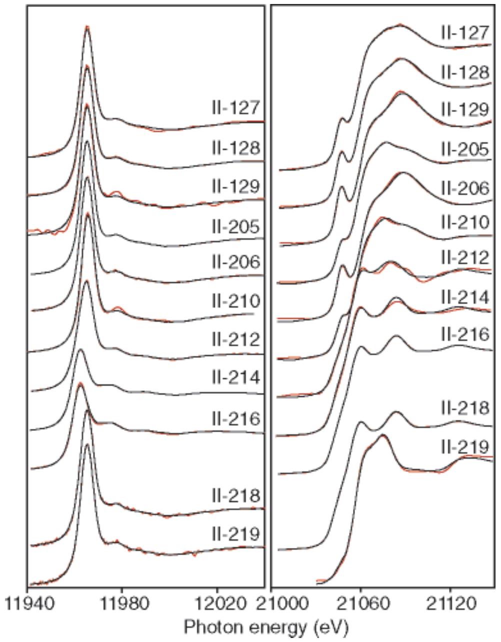

Figure 4. XANES spectra (red) and fits (black) for glass samples at the Re L_2-edge (left) and Tc K-edge (right). Sample numbers are given above the corresponding spectrum.

the sample. These results show that Tc(0), Tc(IV), and Tc(VII) may be observed in the samples, depending upon the redox conditions present during vitrification. In marked contrast, the results from fitting the Re L_2 XANES spectra show that only Re(0) and Re(VII) are present. The fraction of Re(IV) or Re(VI) observed in any of the samples was not statistically different from zero. The absence of these oxidation states is most obvious in sample II-212, which contains both Re(0) and Re(VII) but not Re(IV) or Re(VI).

Discussion

The redox environment of the crucible glasses is a function of both the atmosphere under which the glasses were prepared and the composition of the mixture used to prepare the glass, which contains both organic compounds that create reducing conditions and high concentrations of nitrate that create oxidizing conditions during vitrification of the samples. From this standpoint, the main difference between the LAWA and LAWC glasses is that the LAWC waste surrogate contains a higher concentration of organic compounds, which produces a more reducing environment than the LAWA glasses during vitrification.

Table 6. Tc and Re Speciation in Crucible Glass Samples Determined by XANES Analysis

sample	Fe(II)/ΣFe[a]	Re(0)	Re(VII)	Tc(0)	Tc(IV)	Tc(VII)
II-118	0.119	[b]	[b]	0	0.21(1)	0.80(1)
II-121	0.237	[b]	[b]	0	0.78(3)	0.17(4)
II-127	0.139	0	0.98(1)	0.06(1)	0.27(1)	0.67(1)
II-128	0.081	0	0.98(1)	0	0.13(1)	0.87(1)
II-129	0.089	0	0.98(2)	0	0	1.00(1)
II-205	0.223	0	1[c]	0	0.47(1)	0.52(1)
II-206	0.179	0	1.00(1)	0	0	1.00(2)
II-210	0.162	0	1.02(3)	0	0.48(2)	0.51(3)
II-212[d]	0.988	0.41(1)	0.63(1)	0.78(5)	0.23(4)	0
II-214[d]	0.998	1[c]	0	1.00(1)	0	0
II-216[d]	0.994	1.05(1)	0	1[c]	0	0
II-218[d]	0.843	0.09(3)	0.98(2)	1.00(1)	0	0
II-219	0.283	0	1.05(1)	0	1.00(4)	0

[a] Standard deviation: 2% of the value, determined from duplicate measurements. [b] Sample contains no Re. [c] Spectrum used as a standard in fitting. [d] The relative amounts of metalic Tc and Re present in the samples is overstated since they are present as films on the surfaces of the samples.

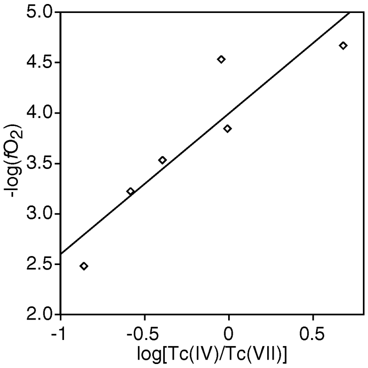

Figure 5. Relationship of the Tc redox state to oxygen fugacity determined from Fe(II)/ΣFe. Data are indicated by diamonds, and the least-squares fit is indicated by the solid line.

The speciation of Tc in glasses is expected to vary with oxygen fugacity, fO_2, during the preparation of the glass because the Tc species present in the glass are in equilibrium with O_2, as shown in eq 1, where n is the charge of the oxidized species and m is the difference in the number of electrons in the two oxidation states.[38−40] Schreiber and coworkers showed that this equilibrium can also be represented by eq 2, where E^* is the $-\log(fO_2)$ at which the concentrations of the two oxidation states are equal, to obtain a straightforward relationship between the fO_2 and the redox state of the metal ion.[39] This equilibrium is obeyed by a wide variety of transition metals in borosilicate glasses prepared by equilibrating the glass melt with an atmosphere of known fO_2. Using these results, we can determine fO_2 for glasses listed in Table 6 from eq 2 and the measured ratio of Fe(II) to Fe(III) in the glass. The ratio of Tc(IV) to Tc(VII) as a function of fO_2 can then be compared, as shown in Figure 5 for samples that contain observable quantities of Tc(IV) and Tc(VII).

$$4\mathrm{M}_{\mathrm{melt}}^{n+} + 2m\mathrm{O}_{\mathrm{melt}}^{2-} \leftrightarrow 4\mathrm{M}_{\mathrm{melt}}^{(n-m)+} + m\mathrm{O}_2(\mathrm{g}) \tag{1}$$

$$-\log(fO_2) = \frac{4}{m}\log\left(\frac{[\mathrm{M}^{(n-m)+}]}{[\mathrm{M}^{n+}]}\right) + E^* \tag{2}$$

The data shown in Figure 5 are consistent with the anticipated behavior of Tc(VII) and Tc(IV) in the glass. The least-squares linear fit to the data has a slope of 1.4 versus the expected value of 4/3, and E^* is 4.0. The value of E^* may be compared to previous work in a somewhat different system by Freude et al. in which the reduction potential, E_0', of the Tc(VII)/Tc(IV) couple was determined to be −0.18 V in a borosilicate melt at 1000 °C by square wave voltammetry.[17] The relationship between E^* and E_0' is given by eq 3

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$$E^* = \left(\frac{-4F}{R\ln(10)}\right)\frac{E_0'}{T} - \log(0.21) \qquad (3)$$

where F is the Faraday constant, R is the gas constant, and T is the absolute temperature. The value measured by voltammetry, $E_0' = -0.18$ V at 1000 °C, is equivalent to $E^* = 3.6$, which is in good agreement with the value obtained here. It should be noted that E^* for Tc is expected to change somewhat as the glass sample cools because the Tc(IV)/Tc(VII) couple has a different potential than the Fe(II)/Fe(III) couple,[41] which is consistent with the slightly higher value of E^* determined here: E_0' of -0.18 V is equal to $E^* = 4.0$ at 825 °C. Overall, the behavior of the Tc(IV)/Tc(VII) couple in the crucible glasses is consistent with the $f\mathrm{O}_2$ present during the formation of the melt as determined from the Fe(II)/Fe(III) ratio in the resulting glass.

As anticipated from their reduction potentials, Re(VII) is more stable towards reduction in the glass than is Tc(VII). This difference limits the conditions under which Re is a good surrogate for Tc. For Fe(II)/ΣFe $< \sim 0.1$, the speciation of Tc and Re is similar because >90% of both elements are heptavalent under these relatively oxidizing conditions. Similarly, for Fe(II)/ΣFe > 0.95, the speciation of Tc and Re is again identical as both elements are present as the metal; however, such highly reducing conditions are not very relevant to nuclear waste glass. Between these extremes, the Re and Tc species present in the glass are generally quite different. As noted above, a difference in speciation is anticipated because of the difference between the reduction potentials of Re(VII) and Tc(VII), and the speciation of Tc and Re reflects this difference. When the speciation of Tc and Re are different, the average oxidation state of the Tc species is lower than that of the Re species, as expected. However, Tc and Re do not behave congruently as a function of redox state.

In particular, neither Re(IV) nor Re(VI) appears to be stable in the glass. In contrast, the behavior of Tc is quite different, as Tc(0), Tc(IV), and Tc(VII) all appear to be stable. This difference between the behavior of Tc and Re was unanticipated. It had been assumed that the speciation of Re in glasses created under more reducing conditions would mimic the speciation of Tc in glasses created under more oxidizing conditions. However, the observation that only Re(0) and Re(VII) are present in the glass shows that Re may not be a good surrogate for Tc under certain redox conditions, namely $0.1 <$ Fe(II)/ΣFe < 0.95.

The failure to observe Re(IV) and Re(VI) in these samples suggests that these species might not be stable under conditions present in the melter. Evaluation of this hypothesis is hampered by a lack of thermodynamic data, especially for M(IV) dissolved in the glass melt, where M = Tc or Re. However, the stability of Re(IV) and Tc(IV) in the melt can be approximated using thermodynamic parameters of the tetravalent compounds ReO_2 and TcO_2. For the purposes of this discussion, two disproportionation reactions, eqs 4 and 5, are of interest. The first is disproportionation of M(IV) to M(0) and M(VII), which has already been analyzed in detail by Migge.[9,10] Because the glass melt is sodium-rich, the second reaction may be a better approximation of the behavior of Tc and Re in the melt.

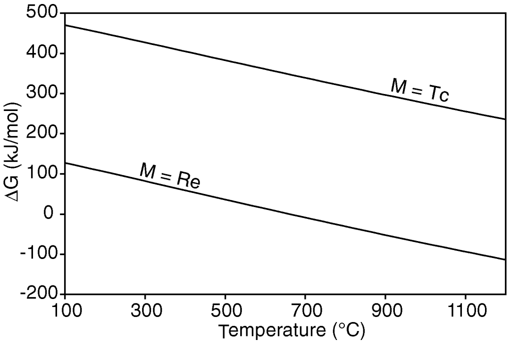

Figure 6. Plot of the Gibbs free energy of reaction 5 as a function of temperature. Disproportionation of Re(IV) becomes exothermic at high temperatures.

$$7MO_2 \rightarrow 3M + 2M_2O_7(g) \qquad (4)$$

$$7MO_2 + 2Na_2SiO_3 \rightarrow 3M + 2SiO_2 + 4NaMO_4 \qquad (5)$$

A plot of the Gibbs free energy of reaction 5 as a function of temperature is given in Figure 6.[42] A number of assumptions were necessary to calculate the energy of reaction 5. The heat capacities of $NaTcO_4$ and TcO_2 were assumed to be the same as those of $NaReO_4$ and ReO_2 and the heat capacity of Re was assumed to be the same as W, because the heat capacity of Re at high temperature was not available. However, the main assumption is that reaction 5 is a good approximation of the behavior of these species in the glass melt. Because of the last assumption in particular, the trends shown in Figure 6 are qualitative rather than quantitative. Nevertheless, the trends shown in Figure 6 are consistent with the observed behavior of Tc and Re in this study as well as with previous observations. In particular, the previous voltammetric study of the behavior of Tc and Re in glass showed that two reduction peaks were present in the Tc system, which could be assigned to the Tc(VII)/Tc(IV) and Tc(IV)/Tc(0) couples. However, in the Re system, only one reduction peak was observed at all square-wave frequencies. This observation was explained by a superposition of the Re(VII)/Re(IV) and Re(IV)/Re(0) couples, and the suggestion that Re(IV) was unstable under these conditions was forwarded. Previous thermochemical calculations of the rhenium−oxygen system also have suggested that Re(IV) may be unstable under these conditions.[9,10]

Conclusions

The speciation of Re and Tc has been examined in a series of nuclear waste glasses prepared under different redox conditions. To a large extent, Tc behaves as expected on the basis of its known chemistry. On the other hand, Re behaves very differently under these conditions, and Re(IV) appears to be unstable with respect to disproportionation. Calculation of the Gibbs free energy of the disproportionation reaction using the thermodynamic values of ReO_2 and TcO_2 as estimates for those of Re(IV) and Tc(IV) dissolved in the

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melt suggests that Re(IV) will disproportionate at high temperatures but Tc(IV) will be stable. This difference limits the applicability of Re as a Tc surrogate. Although Re is a good surrogate for Tc under oxidizing conditions, it is a poor surrogate for Tc under even slightly reducing conditions, including those intended to limit Tc volatility by converting volatile Tc(VII) into less volatile Tc(VI). It should be noted that these conclusions are only valid for the borosilicate glasses examined in this study, and Tc and Re may behave differently in other glasses, such as iron phosphate glasses.

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Supporting Information Available: Compositions of the LAWA and LAWC waste surrogates and glass precursors; EXAFS fitting results for Figure 3; initial XANES fitting results; thermodynamic parameters used to generate Figure 6; derivation of eq 3. This information is available free of charge via the Internet at http://pubs.acs.org.

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