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Structural Behavior of Tc and I ions in Nuclear Waste Glass

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Abstract

Technetium-99 (Tc) and iodine-129 (I) are two long-lived fission products of high volatility, which makes their study in glass structure challenging. Both technetium and iodine have broad ranging multivalent chemistry and complex reactivity dependent on redox conditions; technetium and iodine redox may vary from Tc^0 to Tc^{7+} and from I^- to I^{7+}. Relatively few studies have been done on their speciation in glass, in part because of their low retention at the temperatures required for glass melting. To better understand the redox and structural behavior of Tc and I in various nuclear waste glasses, a series of technetium- and iodine-containing borosilicate glasses of varied chemistry were prepared at scales ranging from a few grams to hundreds of kilograms. Technetium was included in both high-level and low-level nuclear waste glass formulations under a variety of redox conditions at concentrations ranging from 0.003 wt% to 0.06 wt%. Non-radioactive iodine glass samples were prepared in crucible melts using excess amounts of sodium or potassium iodide salts or ammonium iodate that resulted in concentrations ranging from 0.04 to 1.27 wt% iodine. These samples were also compared to glasses prepared in pilot-scale experiments in which the overall retentions reached 48% and 34% for technetium and iodine, respectively. Tc and I speciation in the resulting glasses were determined by X-ray absorption spectroscopy (XAS). While technetium was found as Tc^0, Tc^{4+}, and Tc^{7+}, only I^- was identified in these glasses. Previous studies of Tc local environment information inferred from K-edge XAS and Raman spectroscopy identified pertechnetate tetrahedra surrounded by network-modifying cations in oxidized glasses and octahedral TcO_6 units in glasses prepared under reducing conditions. Conversely, iodine K-edge XAS of all glasses studied indicate iodide environments with lithium or sodium nearest-neighbors resembling disordered versions of octahedral sites in crystalline lithium or sodium iodide.

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1. Introduction

^{99}Tc and ^{129}I are two long-lived isotopes (211,000 years and 15.7 million years half-life, respectively) and beta emitters of a few hundred keV presenting a significant problem for nuclear waste management. Both Tc and I isotopes are of high yield (about 6% and 0.8%, respectively) in the thermal fission of ^{235}U and ^{239}Pu, therefore contributing large quantities of these radionuclides to the waste inventory (Salvatores, 2011). In the US, decades of plutonium production during the Cold War has generated more than 80 million gallons of high level nuclear waste, currently stored in large underground tanks at Hanford, Washington and Savannah River, South Carolina. Ongoing generation of spent nuclear fuel worldwide also continuously adds about 810 g/ton fuel of ^{99}Tc and 170 g/ton of ^{129}I.

Both elements have wide-ranging multivalent chemistries, from -1 in iodide to +7 in periodate and pertechnetate. While iodide I^- is the most stable iodine species, Tc^{7+} (as the pertechnetate oxyanion, TcO_4^-) is the most stable technetium species; both are mobile anions of concern in waste-site remediation (Muramatsu, 1995). Finally, the added considerations of their high solubility and environmental mobility cause them to dominate the relative contribution to projected peak doses at 10,000 years (Piet et al, 2007). The potential contamination concern by inhalation or ingestion is compounded by the fact that both mobile anions, I^- and TcO_4^-, can concentrate in living organisms (Luykx, 1986).

The challenge of these radionuclides is not limited to the long-term disposal, but is also a primary concern in vitrification of the nuclear waste, generally carried at 1100 ºC to 1200 ºC. At such temperatures, most Tc and I compounds are highly volatile and their retention in the glass averages about 20% of the target for I and 35% of the the target for Tc. Glass melt retention for Tc is generally improved in more reducing melt conditions which favor the less volatile Tc^{4+}. Iodine retention also increases under more reducing redox conditions but remains low. As a result, the study of either element in glass is challenging, due to this low retention issue.

The present paper attempts to provide a better understanding of the redox and structural behavior of Tc and I in nuclear waste glasses; the Tc results have been previously reported and are consolidated here for the purpose of comparison to I. The I results are findings from recent XAS and Raman studies on simulated Hanford nuclear waste glasses prepared in small crucible and pilot vitrification melter tests.

2. Experimental

A series of technetium- and iodine-containing borosilicate glasses of varied chemistry were prepared at scales ranging from a few grams to hundreds of kilograms. ^{99}Tc was included in both high-level and low-level nuclear waste glass formulations under a variety of redox conditions, at concentrations measured in the range of 0.003 wt% to 0.06 wt%. Technetium was introduced in the vitrification feed as a sodium pertechnetate, the predominant species in most high alkaline Hanford tank wastes. Two tank wastes were simulated: AN-105, which has a low content of organic complexants, and AN-107, which has high contents of organic material and complexants such as EDTA, NTA, citrate, and oxalate. As discussed by Lukens et al. (2000), pertechnetate is also the likely species to be considered in the cold-cap of a glass melter. The glasses formulated for tank AN-105 include 16 to 20 wt% Na_2O, 3 to 4 wt% K_2O but no lithium and little calcium (2 wt% CaO); the formulations for tank AN-107 are lower in sodium (12-16 wt% Na_2O) and include ~2 wt% Li_2O and ~5 wt% CaO. Other glass former additives remain similar (~6 wt% Al_2O_3, 10 wt% B_2O_3 and 40-47 wt% SiO_2); and both glasses include 6-7 wt% Fe_2O_3, which is also used to monitor the glass redox via Mössbauer spectroscopy. Other principal glass components include MgO, TiO_2, ZnO, and ZrO_2. The samples were prepared under different redox conditions by changing the melt atmospheric composition from air to N_2, to 1:1 CO_2/CO or 100 ppm O_2 in N_2; detailed description of the sample preparation is provided in Lukens et al. (2007).

Eleven non-radioactive iodine bearing glass samples were also recently prepared; nine in small (10 ml) crucible melts under air, and two in a continuously-fed DuraMelter 10 (DM10) ceramic-lined Joule-heated melter where the ~ 8 kg melt pool is maintained at 1150ºC and agitated with air-sparging (Matlack et al, 2012). The glass formulations tested can be divided into three types of compositions. In the first series, lithium dominates the glass modifiers, closely followed by sodium with high amounts of calcium, and only trace amounts of potassium present. In the second series, sodium dominates the glass modifiers but some potassium is also present. In the last series, neither potassium nor lithium is present. All three series use a similar blend of glass formers (~6-10 wt% Al_2O_3, 10-13 wt% B_2O_3 and 43-50 wt% SiO_2). Other principal glass components include TiO_2, ZnO, and ZrO_2; both DM10

glasses have Fe_2O_3, used to monitor the glass redox by Mössbauer spectroscopy. In crucible melts, iodine was over-batched to compensate for its very low retention (~12% retained on average in covered, unsealed crucibles melted at 1150ºC); the glasses were prepared from reagent-grade chemicals including excess amounts of sodium or potassium iodide salts, or ammonium iodate (Table 1). X-ray fluorescence, measured against a PANalytical Omnian calibration M standard at 5.94±0.03 wt% I, determined concentrations for iodine in the glasses that range from 0.05 to 1.27 wt% (0.04 to 0.66 mol%). These samples were also compared to glasses prepared in pilot-scale experiments in which the overall retentions reached 48% and 34% for technetium (as ^{99m}Tc) and iodine, respectively. ^{99m}Tc is an excellent substitute for ^{99}Tc in pilot tests, allowing rapid analysis by gamma spectroscopy, but its short half-life of 6 h prevents any Tc XAS analysis on these samples. Only the non-radioactive iodine results are reported here on DM10 glasses

Table 1. Composition (mole%) of iodine glasses prepared in pilot tests and in over-batched crucible metls.

Glass	I	SiO_2	B_2O_3	Al_2O_3	CaO	K_2O	Li_2O	MgO	Na_2O	Others[(a)]	Sum
KI-1	0.10	51.05	9.00	6.15	11.17	0.17	9.43	-	8.59	4.34	100
KI-2	0.41	48.96	9.24	6.31	11.46	0.68	9.68	-	8.82	4.45	100
Pilot-1	0.04	50.83	9.03	3.36	8.25	0.43	9.00	4.98	5.42	8.66	100
KI-3	0.38	52.11	10.52	4.31	2.61	**3.11**	-	-	21.86	5.09	100
KI-4	0.11	52.29	10.50	4.32	2.62	3.12	-	-	21.94	5.10	100
KI-5	0.11[(b)]	55.51	10.46	4.31	2.76	2.81	-	-	19.34	4.70	100
Pilot-2	0.03	48.56	9.84	4.05	2.51	4.03	-	2.50	19.32	9.16	100
NaI-1	0.13	53.80	11.32	4.50	2.92	-	-	-	22.78	4.55	100
NaI-2	0.60	52.39	11.55	4.60	2.99	-	-	-	23.23	4.65	100
NaI-3	0.66	48.97	12.37	4.93	3.20	-	-	-	24.90	4.97	100
NaI-4	0.02	49.28	12.45	4.96	3.22	-	-	-	25.06	5.01	100
NaI-5	0.57[(b)]	49.01	12.37	4.93	3.20	-	-	-	24.92	4.98	100
NaI-6	0.63	49.20	12.42	4.95	3.21	-	-	-	25.01	4.57	100

[(a)]The other principal components are 1.5 to 2 mol% ZrO_2, and 2.3 to 3 mol% ZnO, plus Fe_2O_3 (2 mol%) and TiO_2 (1 mol%) in the two pilot melter glasses. Formulation NaI-6 also includes 2 mol% SnO_2 in place of ZrO_2.
[(b)]Ammonium Iodate used as the source of iodine in these glass melts.

Tc K-edge (21,044 eV) XAS experiments were conducted on Beam Lines 4-1 and 11-2 at the Stanford Synchrotron Radiation Lightsource. The iodine K-edge (33,170 eV) spectra were collected on Beam Line X-18B at the National Synchrotron Light Source, Brookhaven National Laboratory. Glass spectra were collected up to 40 times for each sample to improve signal-to-noise levels in the averaged data. Crystalline standards I_2, KI, $NaI{\bullet}2(H_2O)$, $CaI_2{\bullet}4(H_2O)$, $NaIO_3$, $Ca(IO_3)_2$ and KIO_3 were also run in triplicate with the details of all the measurements to be reported in McKeown et al. (2015). Tc X-ray absorption near-edge structure (XANES) fitting was performed as previously described in Lukens et al. (2004). X-ray absorption fine structure (EXAFS) data analysis using IFEFFIT was performed by standard procedures described in Lukens et al. (2004) and McKeown et al. (2015) for Tc and I, respectively.

Raman spectra were also measured for some of these glasses using 5145 Å Ar^+ laser excitation and a single-grating spectrometer notch-filter system. The Raman spectra were recorded in parallel using a Peltier cooled CCD detector (McKeown et al. 2007).

3. Results

3.1 Technetium XANES and EXAFS results

Comparison of the various Tc K-edge spectra for the glasses with Tc^0 (technetium metal foil), Tc^{4+}, and Tc^{7+} standards showed that the melt redox conditions significantly affect the technetium species found in the glass

(Table 1). The AN-105 glass melted in air was found to be fully oxidized (Tc^{7+}) but the AN-107 glass, which initially included many organic reagents, yielded a glass with 47% Tc^{4+} when melted in air. When melted in N_2, a similar result was obtained for AN-105 glass, while the AN-107 glass produced more reduced Tc (78% Tc^{4+}). Further reduction in CO/CO_2 atmospheres produced metallic inclusions.

Table 2. Summary of XAS Findings on Technetium Glasses.

Redox conditions	Waste Type	Tc XANES	Dominant Species	Coordination number	Tc-O distance
Air	AN-105	100% Tc^{7+}	Pertechnetate Tetrahedral TcO_4^-	4	1.72 Å
Air	AN-107	47% Tc^{4+} + 53% Tc^{7+}			
N_2	AN-105	48% Tc^{4+} + 52% Tc^{7+}			
N_2	AN-107	78% Tc^{4+} + 22% Tc^{7+}			
100 ppm O_2 in N_2	AN-105	100% Tc^{4+}	Tc^{4+} in octahedral TcO_6 and some TcO_2 (cr) inclusions	6	2.00 Å
100 ppm O_2 in N	AN-107	100% Tc^0			
1:1 CO/CO_2	AN-105	100% Tc^0	Metallic inclusion	Not applicable	
1:1 CO/CO_2	AN-107	100% Tc^0			

EXAFS data and analyses indicate two types of Tc sites in the glass structure: in the most oxidized glasses, technetium is in the form of Tc^{7+} pertechnetate tetrahedral sites, while in the more reduced glasses, Tc^{4+} is in octahedral sites. In pertechnetate Tc^{7+} tetrahedra, Tc-O distances near 1.72 Å are found, compared with longer Tc-O distances near 2.00 Å in Tc^{4+} octahedral sites.

In other work (McKeown et al. (2007) and Buechele et al. (2012)) two samples synthesized under different redox conditions were studied by Tc XANES before and after 24.9 days of alteration in the Vapor Hydration Test (VHT) at 238 ºC. The first glass, II-121, included 20% Tc^{7+} + 80% Tc^{4+} while the more oxidized second glass, II-118, included 80% Tc^{7+} + 20% Tc^{4+}. XANES and EXAFS of both altered glass coupons after VHT found Tc to be fully reduced with Tc^{4+} in octahedral sites with Tc-O at 2.00 Å. EXAFS data and analyses showed that in the altered II-118 sample, the Tc^{4+} octahedra were polymerized to form dimers, by having a Tc-Tc correlation, with Tc-Tc at 2.56 Å. This local Tc environment in the altered II-118 VHT is similar to Tc^{4+} octahedra in a-TcO_2•xH_2O (Fig. 1) that polymerize to form chains as previously reported by Lukens et al. (2002). Cross section profiles studied by Scanning Electron Microscopy (SEM) in McKeown et al. (2007) and Buechele et al. (2012) generally found altered sample cores to be depleted of technetium, while Tc^{4+} can concentrate near the surface of the glass alteration layer.

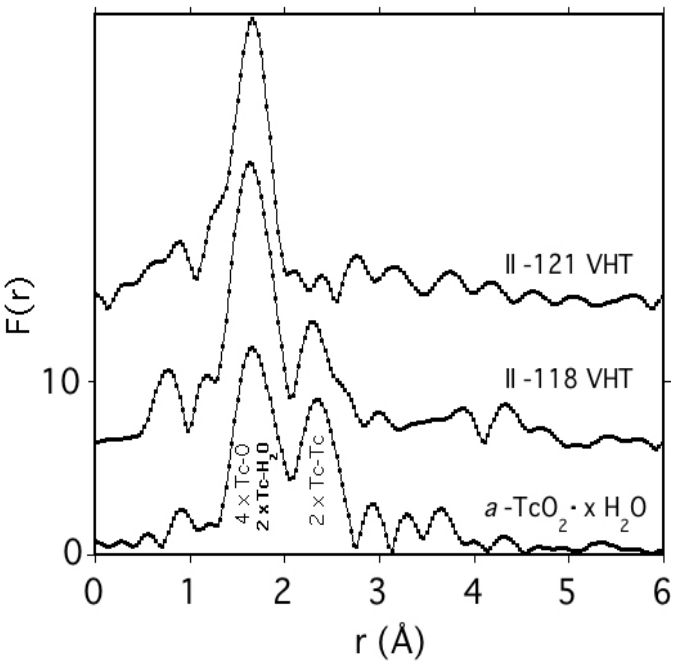

Fig. 1. Tc EXAFS Fourier transforms of VHT altered glasses II-121 and II-118 compared with a-TcO_2•xH_2O.

Raman results for five Tc-containing glasses, including AP-101 formulation II-118 glass and AN-107 formulation II-121 glass, show Tc-O stretch modes diagnostic of isolated pertechnetate tetrahedra that appear to be surrounded by network modifying cations (McKeown et al. 2007). The Raman spectra for these glasses did not contain any features due to the reduced Tc^{4+} species in TcO_6 octahedral environments.

3.2 Iodine XANES and EXAFS Results

XANES features for all eleven iodine glasses are most similar to those of the iodide standards, especially KI and NaI•2(H_2O) (Figure 2). No evidence of iodate was seen in XANES, EXAFS, or Raman spectroscopy. While iodate, periodate, iodine (I_2) and calcium iodide are all Raman active compounds, no iodine dependent Raman features could be seen in any of the glasses studied, even when the glasses were prepared with sodium iodate as the source of iodine. The lack of any iodine-dependent Raman modes indicates that iodide is the most likely iodine species in the glass and confirms that iodine is likely surrounded by network-modifier cations such as Li, Na, or K. This is further confirmed by EXAFS where the amplitudes are nearly ten times weaker for the glasses and iodide standards than for the iodate standards.

EXAFS analyses indicate that the glasses can be divided into two groups: one group where sodium dominates the network modifiers, and the other group where lithium dominates the network modifiers. EXAFS fitting indicates iodide environments, where nearest neighbors to iodine are either lithium or sodium with average I-Li and I-Na distances near 2.80 Å and 3.04 Å, respectively; these distances are shorter than equivalent distances in the crystalline LiI and NaI. The numbers of neighboring alkali cations around iodine in these glasses are also lower than in LiI and NaI as can be seen in Figure 3. These findings indicate that iodine sites in these glasses can be considered as disordered versions of the octahedral iodine sites in crystalline LiI and NaI. EXAFS fitting also indicated no evidence for K, Ca, or I as nearest neighbors to iodine in the glasses investigated.

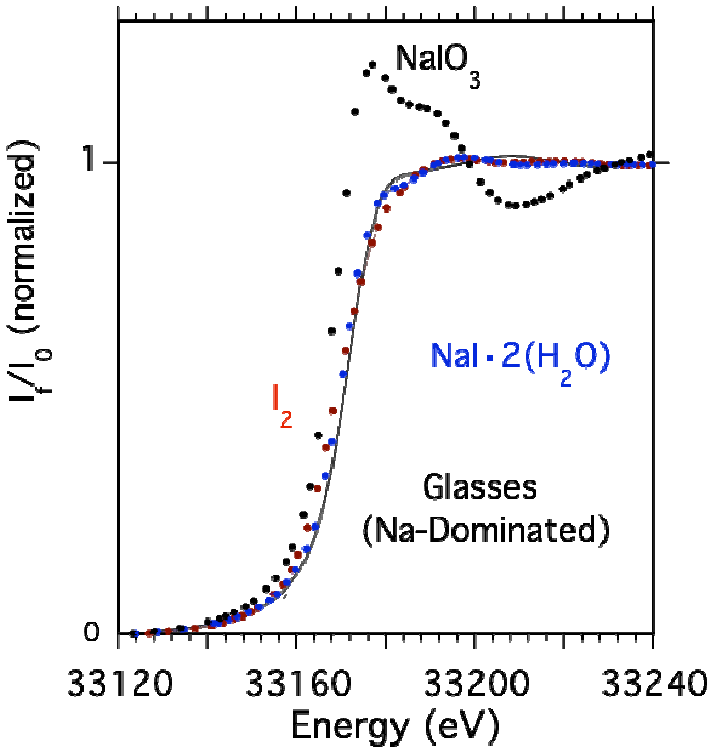

Fig. 2. Iodine in glass XANES spectra (black lines) compared with I_2 (dark red points and line) NaI•2(H_2O) (blue points and line), and $NaIO_3$ (black points and line) standards.

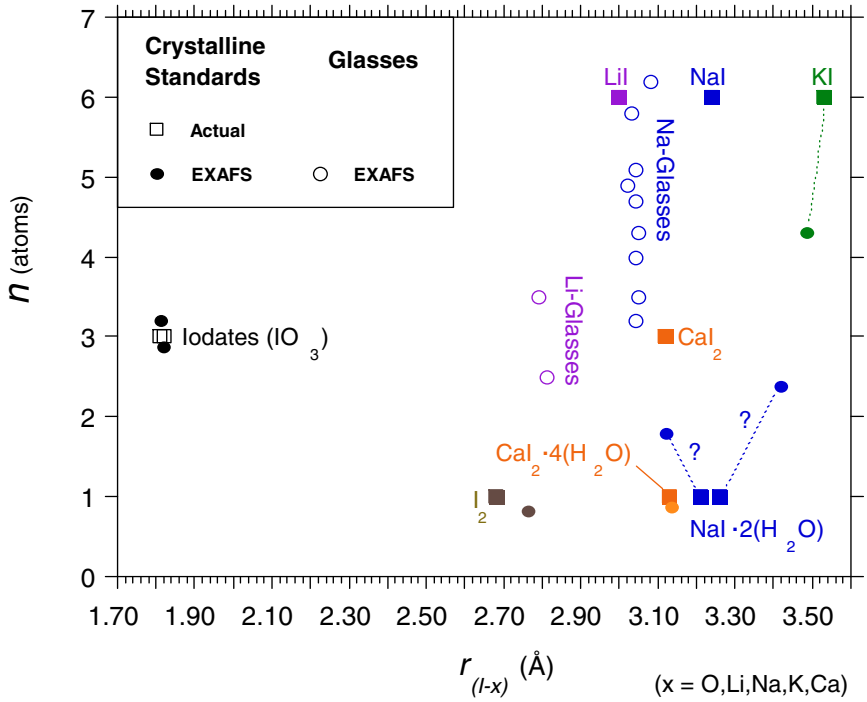

Fig. 3. Summary of the iodine EXAFS findings (distance r and number of nearest neighbors n) for both standards and glasses.

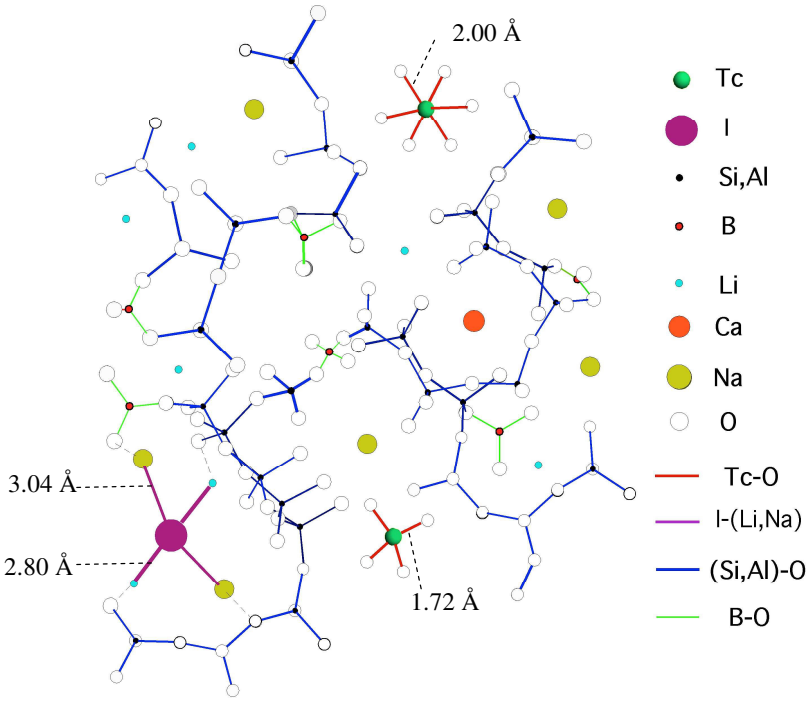

Fig. 4. Hypothetical borosilicate glass structure with iodine and technetium sites.

4. Conclusions

The low retention of technetium and iodine during vitrification can be understood from the structural information inferred from XAS and Raman studies. As an anion, pertechnetate is more stable in oxidizing melting conditions, and resides in the glass as a tetrahedral anion that seeks charge balance among the glass modifiers. As a result, pertechnetate is not strongly bonded to the borosilicate network. Likewise, iodine is in the glass as an iodide ion, situated near sodium or lithium network-modifiers for charge balance, and is also not strongly bonded to the glass structure. On the other hand, reduced Tc in glass, as $Tc^{4+}O_6$ octahedra, is less mobile, which may be caused by $Tc^{4+}O_6$ octahedra bonding to themselves, as seen in one VHT altered sample, or by $Tc^{4+}O_6$ bonding to the borosilicate network, which has not yet been clearly observed. Using the XANES, EXAFS, and Raman findings above, technetium and iodine environments in the glass are portrayed in Figure 4: technetium is in either $Tc^{7+}O_4$ pertechnetate tetrahedra or $Tc^{4+}O_6$ octahedra, while iodine is shown as in an average site with lithium and sodium nearest-neighbors. Note that both elements occur much less frequently in the actual glass structure than the major chemical components shown in this hypothetical structure.

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