Behavior of Technetium in Alkaline Solution: Identification of Non-Pertechnetate Species in High-Level Nuclear Waste Tanks at the Hanford Reservation

Wayne W. Lukens,*,[1] David K. Shuh[1], Norman C. Schroeder[2], and Kenneth R. Ashley[2]

1) Actinide Chemistry Group, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720.
2) Chemical Science Technology, Los Alamos National Laboratory, Los Alamos, NM 87545.
3) Department of Chemistry, Texas A&M University-Commerce, Commerce, TX 75429.

Abstract. Technetium is a long-lived (^{99}Tc: 213,000 year half-life) fission product found in nuclear waste and is one of the important isotopes of environmental concern. The known chemistry of technetium suggests that it should be found as pertechnetate, TcO_4^-, in the extremely basic environment of the nuclear waste tanks at the Hanford site. However, other chemical forms of technetium are present in significant amounts in certain tanks, and these non-pertechnetate species complicate the treatment of the waste. The only spectroscopic characterization of these non-pertechnetate species is a series of X-ray absorption near edge structure (XANES) spectra of actual tank waste. To better understand the behavior of technetium under these conditions, we have investigated the reduction of pertechnetate in highly alkaline solution in the presence of compounds found in high-level waste. These results and the X-ray absorption fine structure (XAFS) spectra of these species are compared to the chemical behavior and XANES spectra of the actual non-pertechnetate species. The identity of the nonpertechnetate species is surprising.

* Author to whom correspondence should be addressed. Email: wwlukens@lbl.gov.

Introduction The Hanford Reservation in eastern Washington State is the site of one of the largest and most costly remediation efforts in the U.S. Years of plutonium production has generated 53 million gallons of high-level nuclear waste, which is now stored in 177 underground tanks.[1] The waste consists of three distinct fractions, supernate, saltcake, and sludge.[2,3] The supernate is an aqueous solution of sodium nitrate, nitrite, and hydroxide, and various organic compounds including citrate, gluconate, formate, oxalate, EDTA, and NTA; in addition, appreciable quantities of ^{137}Cs, ^{90}Sr, ^{127}I, ^{237}Np and ^{99}Tc are present in the supernate. Saltcake consists of water-soluble salts that have precipitated during reduction of supernate volume by evaporation and consists mainly of sodium nitrate and nitrite. Sludge consists of the waste components that are insoluble under strongly alkaline conditions and includes most of the fission products and actinides plus large quantities of aluminum and iron oxides and aluminosilicates.

The current plan for immobilizing this waste requires separating it into high and low activity streams, which will be vitrified separately to form high and low activity waste glasses.[1] The low activity waste stream mainly consists of supernate and dissolved saltcake, and the high activity waste stream is mainly sludge. Due to the previous performance requirements for the low activity glass, almost all of the ^{137}Cs and ^{90}Sr and approximately 80% of the technetium (^{99}Tc) needed to be removed from the low activity waste stream and sent to the high activity waste stream as illustrated in Scheme 1.[4] This technetium separation was to be accomplished by ion exchange of pertechnetate, TcO_4^-, the most thermodynamically stable form of technetium at high pH. Although ion exchange was effective for many tanks, work by Schroeder showed that it failed for Complexant Concentrate (CC) waste tanks, including tanks SY-101 and SY-103,

which contain a high concentration of organic complexants including nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), citrate, and gluconate.[4,5] In these tanks, the vast majority of technetium is present as a soluble, lower-valent, non-pertechnetate species (NPS) that is not removed during pertechnetate ion exchange. [4,5]
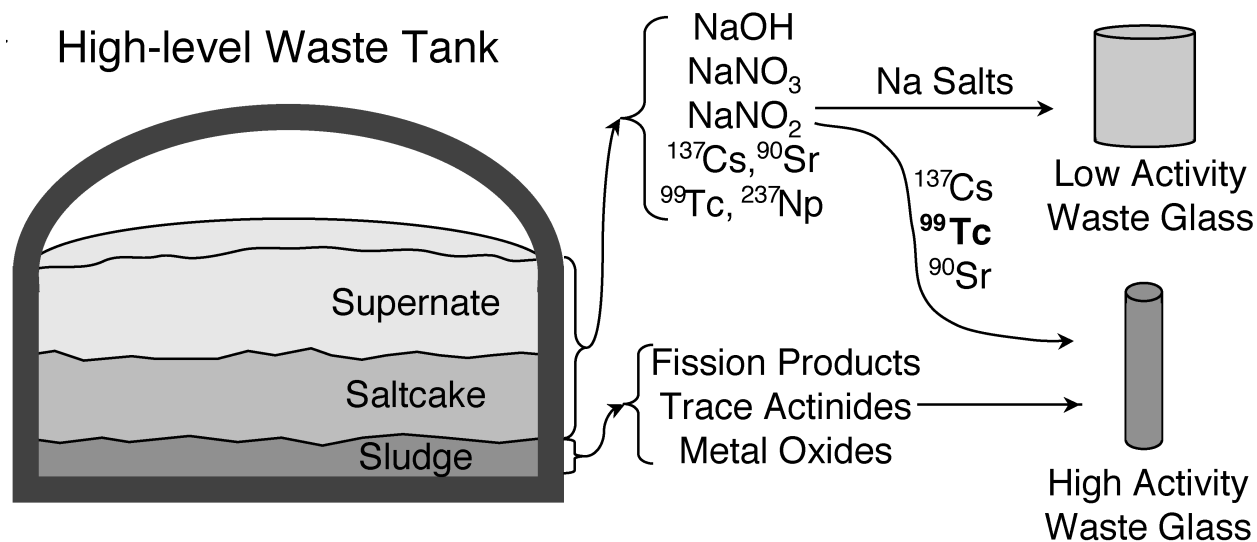
Scheme 1. Simplified illustration of immobilization of high-level nuclear waste at the Hanford Site illustrating the role of ^{99}Tc separation.

The identity of this species is unknown, and its behavior has hampered removal efforts. It is not readily removed by ion exchange, and although the NPS is air-sensitive (it slowly decomposes to pertechnetate), it is difficult to oxidize in practice.[5,6] The only spectroscopic characterization of the NPS is a series of Tc K-edge X-ray absorption near edge structure (XANES) spectra of CC samples reported by Blanchard (Fig. 1).[6] Although its identity can not be determined directly from these spectra, the NPS was believed to be Tc(IV) based upon the energy of its absorption edge, 7.1 eV lower than that of TcO_4^-. This edge shift is similar to that of TcO_2, 6.9 eV lower

than that of TcO_4^-.[7] The presence of soluble, lower-valent technetium species is unexpected in light of the known chemistry of technetium; under these conditions, insoluble $TcO_2 \cdot 2H_2O$ would be expected rather than soluble complexes. This work identifies the potential candidates for the non-pertechnetate species and identifies technetium complexes that have XANES spectra identical to that of the NPS shown in Fig. 1.
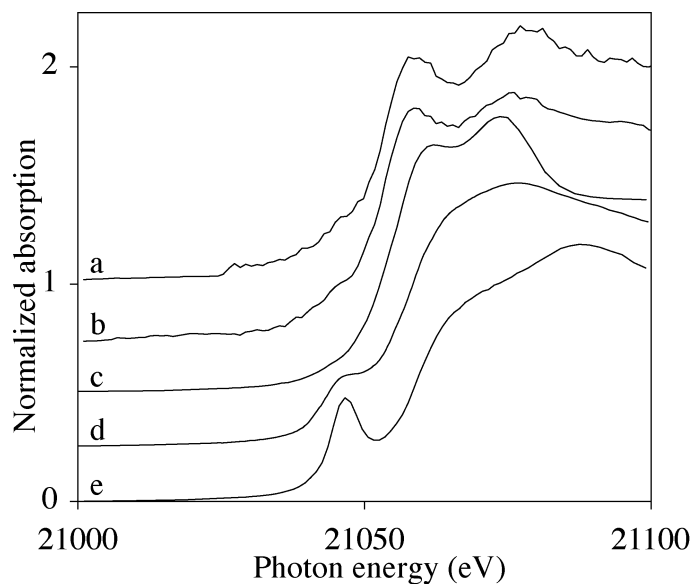
Figure 1: Tc K-edge XANES spectra of the non-pertechnetate species (NPS) in tanks a) SY-103, b) SY-101 reported by Blanchard in Ref. [6].

Experimental Section

Procedures. *Caution: ^{99}Tc is a β-emitter (E_{max} = 294 keV, $\tau_{1/2}$ = 2 × 10⁵ years).* All operations were carried out in a radiochemical laboratory equipped for handling this isotope. Technetium, as $NH_4^{99}TcO_4$, was obtained from Oak Ridge National Laboratory. The solid $NH_4^{99}TcO_4$ was contaminated with a large amount of dark, insoluble material. Prolonged treatment of this

sample with H_2O_2 and NH_4OH did not appreciably reduce the amount of dark material. Ammonium pertechnetate was separated by carefully decanting the colorless solution from the dark solid. A small amount of NaOH was added to the colorless solution, and the volatile components were removed under vacuum. The remaining solid was dissolved in water, and the colorless solution was removed from the remaining precipitate with a cannula. The concentration of sodium pertechnetate was determined spectrophotometrically at 289 nm (ε = 2380 M l^{-1} cm^{-1}). UV-visible spectra were obtained using an Ocean-Optics ST2000 spectrometer. X-ray absorption fine structure (XAFS) spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) at Beamline 4-1 using a Si(220) double crystal monochromator detuned 50% to reduce the higher order harmonic content of the beam. All ^{99}Tc samples were triply contained inside sealed polyethylene vessels. X-ray absorption fine structure spectra (XAFS) were obtained in the transmission mode at room temperature using Ar filled ionization chambers or in fluorescence yield mode using a multi-pixel Ge-detector system.[8] The spectra were energy calibrated using the first inflection point of the pre-edge peak from the Tc K edge spectrum of an aqueous solution of NH_4TcO_4 defined as 21044 eV. To determine the Tc K edge charge state shifts, the energies of the Tc K edges at half height were used.

EXAFS analysis and radiolysis experiments were carried out as previously described.[9]

All operations were carried out in air except as noted. Water was deionized, passed through an activated carbon cartridge to remove organic material and then distilled. Iminodiacetic acid was recrystallized three times from water. All other chemicals were used as received. The $Tc(CO)_3(H_2O)_3^+$ stock solution was prepared from $TcOCl_4(n\text{-}Bu_4N)$[10] by the procedure developed

by Alberto[11] then dissolving the reaction product in 0.01M triflic acid. The ^{99}Tc concentration was determined by liquid scintillation.

Solutions for NMR spectroscopy were prepared by addition of 0.10 mL aliquots of the $Tc(CO)_3(H_2O)_3^+$ stock solution to 0.90 mL of D_2O solutions of 1.1M NaOH with and without 0.11M organic complexant. NMR samples were contained inside a Teflon tube inside a 10 mm screw cap NMR tube. Solutions for XAFS spectroscopy were prepared by addition of 0.20 mL aliquots of the $Tc(CO)_3(H_2O)_3^+$ stock solution to 0.80 mL of D_2O solutions of 1.1M NaOH with and without 0.11M organic complexant. The Tc(IV) gluconate complex was prepared by reducing a solution of TcO_4^- (2mM, 1 mL, 2 μmol) in 0.1M potassium gluconate and 1M NaOH with sodium dithionite (2M, 10 μL, 20!μmol). Solutions were sealed under Ar inside 2 mL screw-cap centrifuge tubes, which were placed inside two consecutive heat sealed, heavy walled polyethylene pouches. Pouches were stored under Ar in glass jars sealed with PTFE tape until their spectra were recorded.

Results and Discussion

Tc(IV) Alkoxide Complexes. As a first step in investigating the behavior of technetium in highly alkaline solutions relevant to high-level waste, solutions of TcO_4^- in alkaline solution containing organic compounds, including complexants, were irradiated to reduce the TcO_4^-, and the lower-valent technetium products produced were identified.[9] The use of irradiation in these experiments does not imply a similar mechanism for reduction of TcO_4^- in high-level waste tanks. Both chemical[12] and radiolytic[13] pathways exist for reduction of TcO_4^- under these

conditions, but the radiation-chemical pathway is different from the pathway that is operative here, direct reduction of TcO_4^- by hydrated electrons from the radiolysis of water.

The initial results of the radiolysis experiments showed that none of the carboxylate complexants, citrate, EDTA, or NTA, form stable complexes with Tc(IV) in alkaline solution. Under these conditions, only $TcO_2 \cdot 2H_2O$ is produced.   However, soluble, lower-valent complexes are produced by the radiolytic reduction of TcO_4^- in alkaline solution containing the alcohols, ethylene glycol, glyoxylate, and formaldehyde. Although glyoxylate and formaldehyde are aldehydes, they exist as geminal diols in aqueous solution and therefore can act as alkoxide ligands. The EXAFS spectrum and structure of the Tc(IV) glyoxylate complex are shown in Fig.!2, and the structural parameters are given in Table 1. The structure is very similar to that of the well known $(H_2EDTA)_2Tc_2(\mu-O)_2$ complex with the EDTA ligands replaced by glyoxylate ligands, presumably acting as diolate ligands.
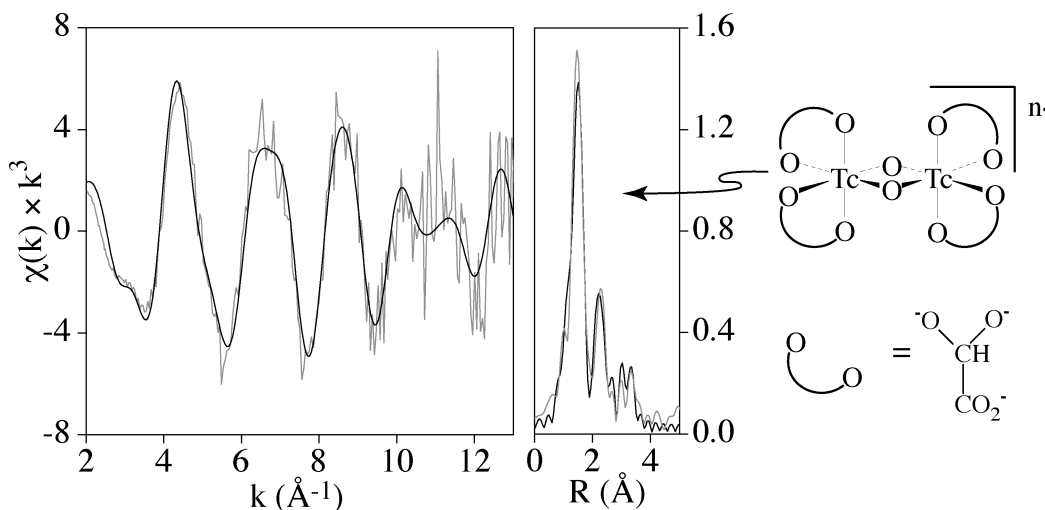
Figure 2. EXAFS spectrum and Fourier transform of the Tc(IV) species formed by radiolysis of TcO$_4^-$ in a solution of 0.1 glyoxylic acid in 1M NaOH; data are shown in gray and the fit in black. The structure of the complex consistent with the EXAFS spectrum is shown on the right.

Table 1. Structural parameters of soluble radiolysis product derived from EXAFS[a].

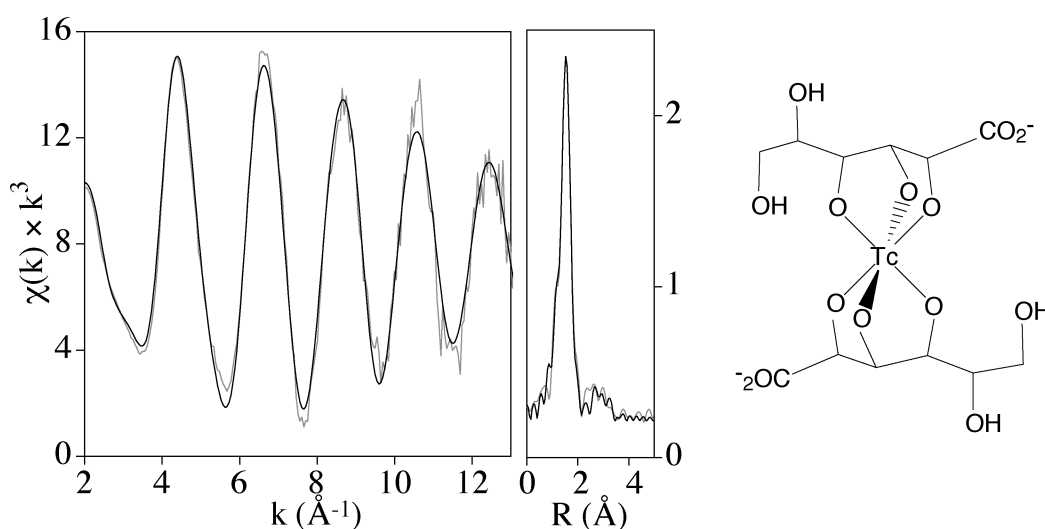| Scattering Path	Coordination Number[b]	Distance (Å)	Debye-Waller Parameter (Å^2)[b]	ΔE_0 (eV)[c]
Tc-O	6.7(3)	2.008(3)	0.0058(5)	-7.9
Tc-Tc	0.7(1)	2.582(4)	0.003*	-7.9
Tc-O-Tc-O[d]	6*	4.06(2)	0.002(3)	-7.9

a) Numbers in parenthesis are the standard deviation of the given parameter derived from least-squares fit to the EXAFS data. The standard deviations do not indicate the accuracy of the numbers; they are an indication of the agreement between the model and the data. In general, coordination numbers have an error of ±25% and bond distances have an error of ±0.5% when compared to data from crystallography.
b) Parameters with an asterisk were not allowed to vary during analysis.
c) E$_0$ was refined as a global parameter for all scattering paths. The large negative value results from the definition of E$_0$ in EXAFSPAK.
d) This scattering path is a 4-legged multiple scattering path between the *trans* ligands of the technetium coordination sphere.

These radiolysis experiments clearly show that soluble Tc(IV) alkoxide complexes can be formed in highly alkaline solution under conditions similar to those found in high-level waste. However, none of the potential ligands examined are present in high-level waste in sufficient concentrations to account for the formation of the soluble non-pertechnetate species.[3] The potential alkoxide ligand present in large quantities in CC waste is gluconate.[14] Moreover, gluconate can act as a tridentate alkoxide ligand (using the hydroxyl groups on carbon atoms 2-4). The resulting Tc(gluconate)$_2^{4-}$ complex would presumably be very similar to an analogous complex of Tc(IV) with two tridentate alkoxide ligands described by Anderegg.[15] This complex,

Tc[(OCH$_2$)$_3$CN(CH$_3$)]$_2$, is the most hydrolytically stable of the Tc(IV) alkoxide complexes. While most Tc(IV) complexes are stable only above pH 10, Tc[(OCH$_2$)$_3$CN(CH$_3$)]$_2$ is stable towards hydrolysis above pH 4. Consequently, an analogous Tc(IV) gluconate complex would be expected to be quite hydrolytically stable.

The colorless Tc(IV) gluconate complex was prepared in situ by reducing TcO$_4^-$ with dithionate in a solution of 0.1M gluconate and 1M NaOH. The EXAFS spectrum and its Fourier transform of Tc(IV) gluconate are shown in Fig. 3; fit parameters are given in Table 2. The coordination environment of the Tc center is simple: 6 O neighbors at 2.01 Å and 6 C neighbors at 3.37 Å. The bond distances are similar to the aforementioned Tc[(OCH$_2$)$_3$CN(CH$_3$)]$_2$.[15] Although the coordination geometry of the coordinated gluconate ligand cannot be determined directly from the EXAFS data, the similarity between the Tc-O distances in Tc(IV) gluconate and in Tc[(OCH$_2$)$_3$CN(CH$_3$)]$_2$ strongly suggests that the gluconate ligand is coordinated to the Tc center by three hydroxyl groups, as illustrated in Fig. 3, rather than a carboxylate and two hydroxyl groups.

Figure 3. EXAFS spectrum and Fourier transform of the Tc(IV) gluconate complex; data are shown in gray and the fit in black. The structure of the complex consistent with the EXAFS spectrum is shown on the right.

Table 2. Structural parameters of Tc(IV) gluconate derived from EXAFS[a]

Scattering Path	Coordination Number[b]	Distance (Å)	Debye-Waller Parameter (Å^2)[b]	ΔE_0 (eV)[c]
Tc-O	6*	2.010(1)	0.0045(1)	-5.2(3)
Tc-C	6*	3.37(2)	0.015(3)	-5.2
Tc-O-Tc-O[d]	6*	4.03(2)	0.008(3)	-5.2

a) Numbers in parenthesis are the standard deviation of the given parameter derived from least-squares fit to the EXAFS data. The standard deviations do not indicate the accuracy of the numbers; they are an indication of the agreement between the model and the data. In general, coordination numbers have an error of ±25% and bond distances have an error of ±0.5% when compared to data from crystallography.
b) Parameters with an asterisk were not allowed to vary during analysis (scale factor was varied instead; S^O_2=1.38(3)).
c) E_0 was refined as a global parameter for all scattering paths. The large negative value results from the definition of E_0 in EXAFSPAK.
d) This scattering path is a 4-legged multiple scattering path between the *trans* ligands of the technetium coordination sphere.

Although the EXAFS experiment establishes the existence of Tc(IV) gluconate, it does not establish whether Tc(IV) gluconate is the NPS observed in CC waste. In fact, as shown in Fig. 4, Tc(IV) gluconate is not the NPS in Tanks SY-101 and SY-103. Although the XANES spectra of Tc(IV) gluconate and the NPS are superficially similar, the energies of their absorption edges differ by 1.6 eV. More importantly, no combination of the spectra of Tc(IV) gluconate, Tc(V) gluconate, and TcO_4^- will fit the spectrum of the NPS. Not only is the NPS not Tc(IV) gluconate, the NPS cannot be any kind of Tc(IV) alkoxide complex. The energies of the Tc-K edges of Tc(IV) alkoxide complexes and other Tc(IV) complexes with oxygen neighbors,

including $TcO_2 \bullet 2H_2O$, fall within a very narrow range around 5.5 eV below the energy of the TcO_4^- absorption edge.[9] For comparison, the Tc-K edge of the NPS occurs at 7.1 eV below the TcO_4^- absorption edge.
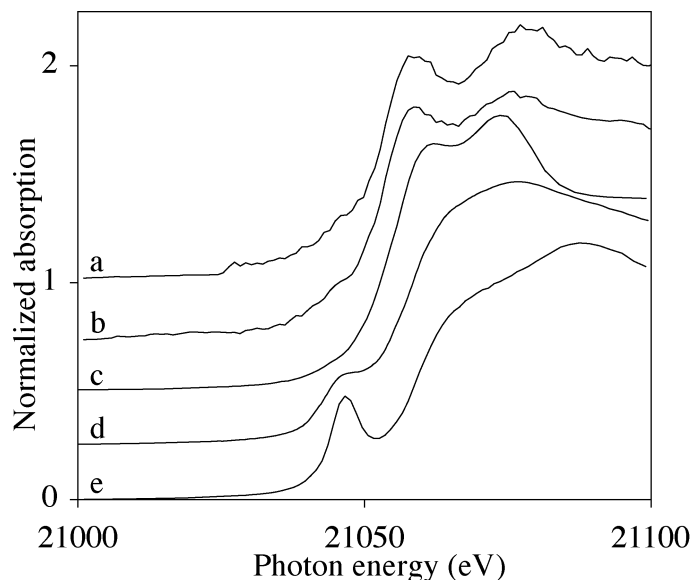
Figure 4. Tc K-edge XANES spectra of a) NPS in tank SY-103, b)!NPS in tank SY-101, c) Tc(IV) gluconate, d) Tc(V) gluconate, e)!TcO_4^-. The spectra of the non-pertechnetate species in tanks SY-101 and SY-103 are from Ref. [6].

The fact that Tc(IV) gluconate is not the NPS is surprising. The radiolysis experiments clearly show that Tc(IV) alkoxides can be formed and are stable in highly alkaline solution. In fact, the Tc(IV) gluconate complex is so stable that it can be prepared by dissolving $TcO_2 \bullet 2H_2O$ in 1M NaOH containing 0.1M gluconate, which may have implications for treating high-level waste. If CC waste containing gluconate is added to tanks containing $TcO_2 \bullet 2H_2O$, soluble Tc(IV) gluconate will be formed. Like the NPS, Tc(IV) gluconate would not be removed by the ion

exchange resins that remove TcO_4^-. However, Tc(IV) gluconate is fairly air-sensitive (much more so than the NPS), and should be easy to oxidize unlike the NPS. This sensitivity to oxidation could be the reason that Tc(IV) gluconate is not observed in CC waste. Another possibility is that the thermodynamic stability of the NPS is greater than that of Tc(IV) gluconate.

***fac*-Tc(CO)$_3$ Complexes**. A different approach was taken since the systematic investigation described above seemed unable to yield the identity of the NPS. Theoretical XANES spectra were calculated[16] for a variety of lower valent technetium complexes regardless of whether the ligands were present in high-level waste and disregarding the oxidation state of the technetium center. The complex that had a calculated XANES spectrum most similar to that of the non-pertechnetate species was *fac*-Tc(CO)$_3$(H$_2$O)$_3^+$.[11,17-19] Since the crystal structure of this complex has not been reported, the Tc-C and Tc-O distances for the carbonyl and water ligands were taken from the crystal structure of *fac*-Tc(CO)$_3$\{[OP(OCH$_3$CH$_3$)$_2$]$_3$Co(C$_5$H$_5$)\}.[20] The synthesis and chemistry of *fac*-Tc(CO)$_3$ complexes are the subject of extensive research, largely due to Alberto, since *fac*-Tc(CO)$_3$ complexes are potentially useful as ^{99m}Tc radiopharmaceuticals.[11,17-19] Of particular importance is the fact that *fac*-Tc(CO)$_3$ complexes can be prepared from TcO_4^- in alkaline solution at low CO concentrations. This characteristic, along with the fact that CC waste tanks contain CO (the head space gas consists of 0.25 to 0.5 mol % CO),[21] suggests that *fac*-Tc(CO)$_3$ could have formed in the Hanford high-level waste tanks.

The behavior of *fac*-Tc(CO)$_3$ complexes in alkaline solution has previously been investigated, and the species formed at different hydroxide concentrations have been identified by Gorskov

using ^{99}Tc-NMR spectroscopy.[22] Fig. 5 shows the ^{99}Tc-NMR spectra of the *fac*-Tc(CO)$_3$ species produced by adding *fac*-Tc(CO)$_3$(H$_2$O)$_3^+$ to different alkaline solutions. In 1M NaOH, the only species present is *fac*-Tc(CO)$_3$(H$_2$O)$_2$(HO), which has a chemical shift of −1060!ppm. As with Tc(IV), the carboxylate complexants do not form complexes with *fac*-Tc(CO)$_3$ in alkaline solution. Only *fac*-Tc(CO)$_3$(H$_2$O)$_2$(HO) was observed in 1M NaOH solutions containing 0.1M EDTA, NTA, or citrates. However, gluconate does form a complex with *fac*-Tc(CO)$_3$, which is indicated by the presence of a new peak in the ^{99}Tc-NMR spectrum at −1240 ppm of *fac*-Tc(CO)$_3$ in a solution of 0.1M gluconate and 1M NaOH. When *fac*-Tc(CO)$_3$(H$_2$O)$_3^+$ is added to an SY-101 simulant, both *fac*-Tc(CO)$_3$(H$_2$O)(HO) and *fac*-Tc(CO)$_3$(gluconate)$^{n-}$ are observed. However, after one week, the only observable technetium species are *fac*-Tc(CO)$_3$(gluconate)$^{n-}$ and TcO$_4^-$. These NMR experiments demonstrate that *fac*-Tc(CO)$_3$ species are stable in alkaline solutions approximating the composition of high-level waste. For comparison, solutions of Tc(IV) alkoxides are more air-sensitive, and will oxidize to TcO$_4^-$ in less than a week if exposed to air.
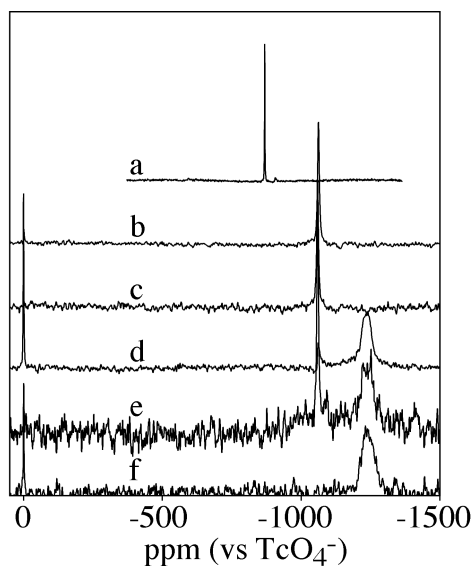
Figure 5. ^{99}Tc-NMR spectra of *fac*-Tc(CO)$_3$(H$_2$O)$_3$$^+$ dissolved in a) dilute triflic acid, b)!1M!NaOH, c) 1M NaOH with 0.1M EDTA, d) 1M NaOH with 0.1M gluconate, e) SY-101 simulant, f) SY-101 simulate after 1 week in air.

Several of the *fac*-Tc(CO)$_3$ complexes were also characterized by EXAFS spectroscopy as shown in Fig. 6 and the structural details are summarized in Table 3. It is not surprising that their spectra and the parameters derived from fitting their spectra are very similar. The main differences among these complexes are Tc-C and Tc-O distances of the carbonyl and water, hydroxide or gluconate ligands. Since the scattering atoms are identical and the bond distances change little among the complexes, the spectra differ only slightly. The change in bond distances is systematic and consistent with the nature of the ligands. The Tc-O distances for the first shell oxygen decrease in order from *fac*-Tc(CO)$_3$(H$_2$O)$_3$$^+$ to *fac*-Tc(CO)$_3$(H$_2$O)$_2$(OH) to *fac*-Tc(CO)$_3$(gluconate)$^{n-}$, in agreement with the observation that gluconate forms the most stable complex with *fac*-Tc(CO)$_3$ followed by hydroxide, and then followed by water. In addition, the CO distance is shorter in *fac*-Tc(CO)$_3$(H$_2$O)$_3$$^+$ than in the other two complexes as water is a weaker π−donor than the other two ligands. Overall, the EXAFS data are consistent with the known stabilities of these three complexes and clearly show that these are three distinct complexes, in agreement with the ^{99}Tc-NMR data.
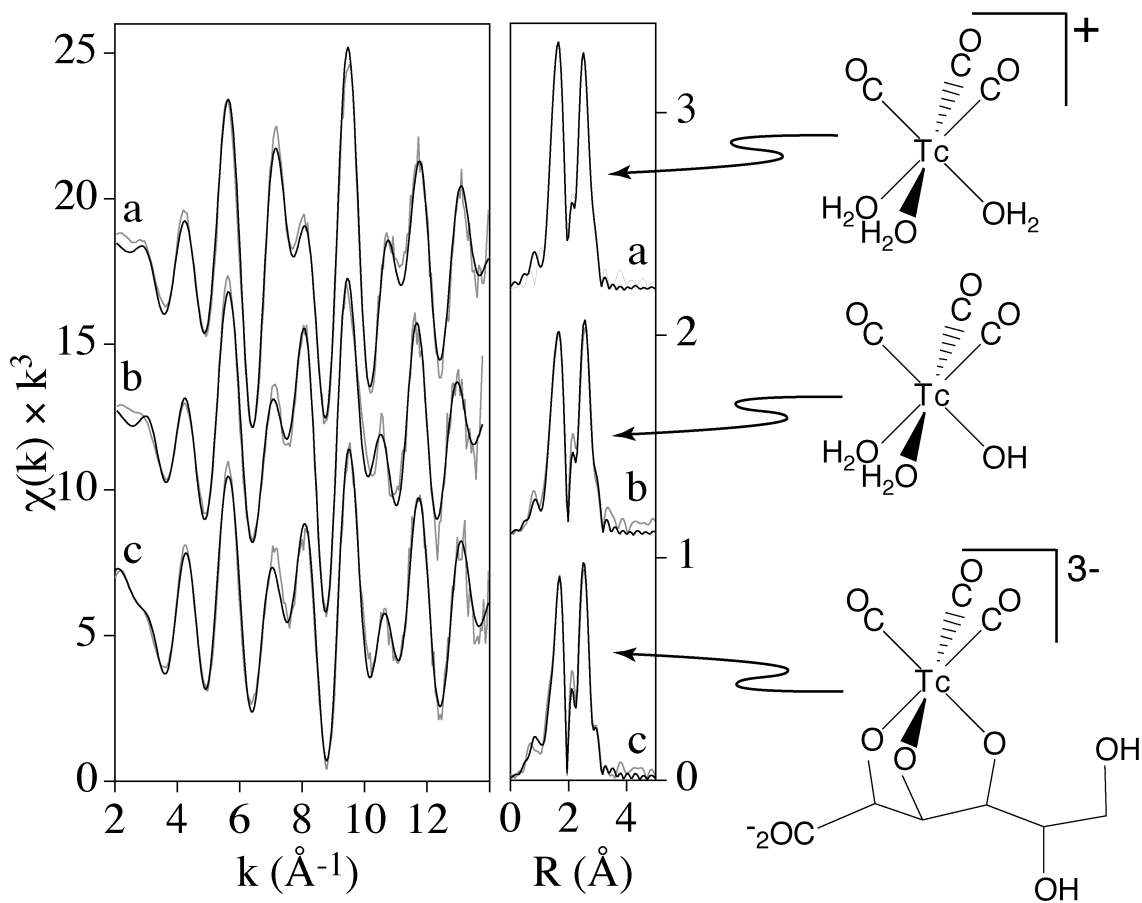
Figure 6. EXAFS spectra and Fourier transforms of a) $Tc(gluconate)_2^{2-}$, b)*fac*-$Tc(CO)_3(H_2O)_3^+$, c) *fac*-$Tc(CO)_3(HO)(H_2O)_2$, and d) *fac*-$Tc(CO)_3(gluconate)^{2-}$. Data are illustrated in gray, and the least squares fits are black. The structures of the complexes consistent with the EXAFS spectra are to the right of the spectra.

Table 3: EXAFS fitting results for *fac*-Tc(CO)$_3$ complexes.

Scattering Path		Tc(CO)$_3$(H$_2$O)$_3^+$	Tc(CO)$_3$(H$_2$O)$_2$(OH)	Tc(CO)$_3$(gluconate)$^{2-}$
Tc-C̲O	N	3	3	3
	R(Å)	1.904(2)	1.886(3)	1.911(2)
	σ^2(Å^2)	0.0041(2)	0.0058(3)	0.0062(2)
Tc-O̲	N	3	3	3
	R(Å)	2.163(2)	2.155(3)	2.137(2)
	σ^2(Å^2)	0.0052(2)	0.0047(5)	0.0068(3)
Tc-CO̲[a]	N	3	3	3
	R(Å)	3.045(9)	3.083(8)	3.09(3)
	σ^2(Å^2)	0.0050(2)	0.0046(2)	0.0015(2)
Tc-OC̲	N			3
	R(Å)			3.44(2)
	σ^2(Å^2)			0.011(2)
4 leg MS path with *trans* ligands coordinated to Tc	N	6	6	6
	R(Å)	3.96(2)	4.01(2)	3.96(1)
	σ^2(Å^2)	0.017(4)	0.010(3)	0.019(3)
ΔE_0		-14.8(4)	-11.6(6)	-11.1(3)
Scale Factor		1.39(4)	1.19(6)	1.68(7)

The results described above show that *fac*-Tc(CO)$_3$ complexes are stable under conditions found in high-level waste, but do not establish whether they are actually the NPS. As shown in Fig. 7, the XANES spectra of the *fac*-Tc(CO)$_3$ complexes are very similar, if not identical, to those of the NPS. The Tc K-edge energies of the XANES spectra of *fac*-Tc(CO)$_3$ complexes occur at 7.5 eV below that of TcO$_4^-$, in excellent agreement with the observed edge shift of 7.1 eV for the NPS. Most convincing is the fact that the spectrum of the NPS in tank SY-103 can be fit using only the spectrum of *fac*-Tc(CO)$_3$(gluconate)$^{n-}$, and the spectrum of the NPS in tank SY-101 can be fit using the spectrum of *fac*-Tc(CO)$_3$(gluconate)$^{n-}$ containing 7% TcO$_4^-$, presumably due to oxidation. The spectra of the NPS can also be fit using the spectrum of *fac*-Tc(CO)$_3$(H$_2$O)$_2$(HO), but the fit is of slightly poorer quality. Given the similarity of the EXAFS spectra of the *fac*-

Tc(CO)$_3$ complexes, it is not possible to definitively assign the spectra to a specific *fac*-Tc(CO)$_3$

complex, but XANES spectra in Fig. 1 are clearly to a *fac*-Tc(CO)$_3$ species.
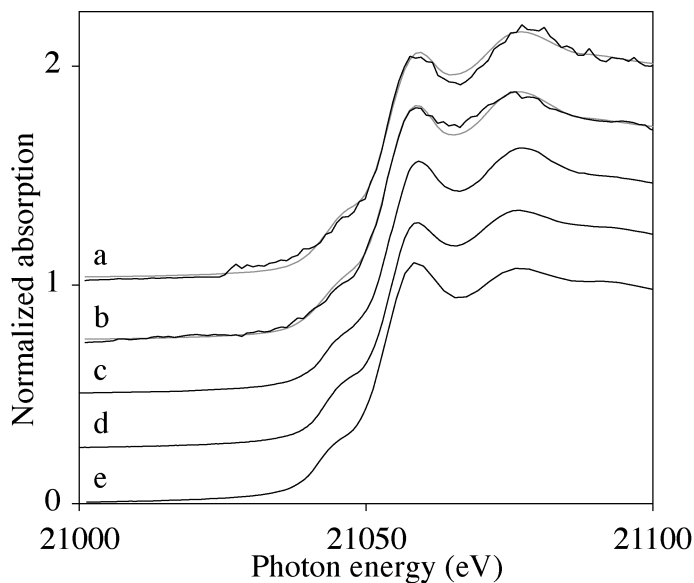
Figure 7. Tc K-edge XANES spectra of a) NPS in tank SY-103 (black) and

Tc(CO)$_3$(gluconate)$^{2-}$ (gray), b) NPS in tank SY-101 (black) and 93% Tc(CO)$_3$(gluconate)$^{2-}$ with

7% TcO$_4^-$ (gray), c) Tc(CO)$_3$(gluconate)$^{2-}$, d)!Tc(CO)$_3$(HO)(H$_2$O)$_2$, e) Tc(CO)$_3$(H$_2$O)$_3^+$. The

spectra of the NPS in tanks SY-101 and SY-103 are from Ref.![6].

The identity of the NPS explains some of its behavior. Simplest to explain is the fact that it is

not removed by the cationic resins used to separate TcO$_4^-$ from the waste. The most weakly

solvated anion (TcO$_4^-$ in this case) are the most strongly bound by the resins used to separate

TcO$_4^-$. Although *fac*-Tc(CO)$_3$(gluconate)$^{n-}$ is anionic, it should be more strongly solvated than

NO$_3^-$, which is present in much higher concentrations, consequently anionic Tc(CO)$_3$(gluconate)$^{n-}$

cannot be separated in the presence of excess nitrate using these resins. Of course, if uncharged *fac*-Tc(CO)$_3$(H$_2$O)$_2$(HO) is present, it too would not be removed by ion exchange.

The seemingly strange behavior of the NPS with regard to oxidation is largely explained by its identity. The *fac*-Tc(CO)$_3$ complexes are not thermodynamically stable with respect to oxidation to TcO$_4^-$; however, they are kinetically inert due to their low-spin d^6 electronic structure. As a result, they will react slowly with potential oxidizing agents, such as oxygen. The kinetic inertness of these complexes also affects oxidation by strong oxidizers. Since *fac*-Tc(CO)$_3$ complexes will react relatively slowly with strong oxidizers (although presumably much faster than they react with oxygen), the strong oxidizers will preferentially react with the compounds, such as nitrite or organic molecules, that are present in much higher concentrations and are much more reactive.

One aspect of the chemistry of *fac*-Tc(CO)$_3$ in CC waste that has not been addressed is the mechanism of its formation. As noted above, *fac*-Tc(CO)$_3$ complexes can be prepared from TcO$_4^-$ in alkaline solution at elevated temperature at low CO concentration; however, the formation of *fac*-Tc(CO)$_3$ complexes from TcO$_4^-$ in waste simulants remains to be investigated.

Stanford Synchrotron Radiation Laboratory, which is operated by the Director, U. S. DOE, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences.

References

(1)   Council, N. R. *Research Needs for High-Level Waste Stored in Tanks and Bins at U.S. Department of Energy Sites: Environmental Management Science Program*; National Acadamy Press: Washington, D.C., 2001.

(2)   Gephart, R. E.; Lundgren, R. E. "Handford Tank Clean Up: A Guide to Understanding the Technical Issues," Pacific Northwest National Laboratory.

(3)   Agnew, S. F.; Boyer, J.; Corbin, R. A.; Duran, T. B.; FitzPatrick, J. R.; Jurgensen, K. A.; Ortiz, T. P.; Young, B. L. "Hanford Tank Chemical and Radionuclide Inventories: HDW Model Rev. 4," LA-UR-96-3860, Los Alamos National Laboratory, 1996.

(4)   Schroeder, N. C.; Radzinski, S. D.; Ball, J. R.; Ashley, K. R.; Cobb, S. L.; Cutrel, B.; Whitener, G. "Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Waste (101-SY and 103-SY) Using Reillex^{TM} -HPQ Resin.," LA-UR-95-4440, Los Alamos National Laboratory, 1995.

(5)   Schroeder, N. C.; Radzinski, S. D.; Ashley, K. R.; Truong, A. P.; Sczcepaniak, P. A. In *Science and Technology for Disposal of Radioactive Tank Wastes*; Schulz, W. W., Lombardo, N. J., Eds.; Plenum Press: New York, 1998, p 301.

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

(7)   Almahamid, I.; Bryan, J. C.; Bucher, J. J.; Burrell, A. K.; Edelstein, N. M.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Shuh, D. K.; Nitsche, H.; Reich, T. *Inorg. Chem.* 1995, *34*, 193.

(8)   Bucher, J. J.; Allen, P. G.; Edelstein, N. M.; Shuh, D. K.; Madden, N. W.; Cork, C.; Luke, P.; Pehl, D.; Malone, D. *Review of Scientific Instruments* 1996, *67*, 4.

(9)   Lukens, W. W.; Bucher, J. J.; Edelstein, N. M.; Shuh, D. K. *Env. Sci. Tech.* 2002, *36*, 1124.

(10)   Davison, A.; Trop, H. S.; DePamphilis, B. V.; Jones, A. G. *Inorg. Synth.* 1982, *21*, 160.

(11)   Alberto, R.; Schibli, R.; Egli, A.; Schubiger, A. P.; Herrmann, W. A.; Artus, G.; Abram, U.; Kaden, T. A. *J. Organomet. Chem.* 1995, *493*, 119.

(12)   Bernard, J. G.; Bauer, E.; Richards, M. P.; Arterburn, J. B.; Chamberlin, R. M. *Radiochimica Acta* 2001, *V89*, 59-61.

(13)   Lukens, W. W.; Bucher, J. J.; Edelstein, N. M.; Shuh, D. K. *J. Phys. Chem. B* 2001, *105*, 9611.

(14)   Golcar, G. R.; Colton, N. G.; Darab, J. G.; Smith, H. D. "Hanford Waste Tank Simulants Specification and Their Applicability for the Retrieval, Pretreatment, and Vitrification Process," PNWD-2455, Pacific Northwest National Laboratory, 2000.

(15)   Alberto, R.; Albinati, A.; Anderegg, G.; Huber, G. *Inorg. Chem.* 1991, *30*, 3568.

(16)   Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. *Phys. Rev. B* 1995, *52*, 2995.

(17)   Alberto, R.; Schibli, R.; Egli, A.; Schubiger, A. P.; Abram, U.; Kaden, T. A. *J. Amer. Chem. Soc.* 1998, *120*, 7987.

(18)   Alberto, R.; Schibli, R.; Waibel, R.; Abram, U.; Schubiger, A. P. *Coord. Chem. Rev.* 1999, *192*, 901.

(19)   Alberto, R.; Ortner, K.; Wheatley, N.; Schibli, R.; Schubiger, A. P. *J. Amer. Chem. Soc.* 2001, *123*, 3135.

(20)   Kramer, D. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* 2001, *312*, 215.

(21)   Johnson, G. D. "Flammable Gas Program Report," WHC-SP-1193, Westinghouse Hanford Company, 1996.

(22)   Gorshkov, N. I.; Lumpov, A. A.; Miroslavov, A. E.; Suglubov, D. N. *Radiochemistry* 2000, *43*, 231.