**Products of Pertechnetate Radiolysis
in Highly Alkaline Solution:
Structure of TcO$_2$•xH$_2$O**

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1

Abstract. The behavior of technetium in certain high level nuclear waste (HLW) tanks at the Hanford reservation creates challenges for the treatment and vitrification of the HLW. The main problem is the presence of unidentified, lower-valent technetium species, which are difficult to separate from the waste. To understand which species are formed under conditions analogous to HLW, radiolytic reduction of TcO_4^- in alkaline solution containing selected organic compounds has been examined. Insoluble $TcO_2 \bullet xH_2O$ is the primary radiolysis product in the presence of most of the organic compounds examined including citrate, dibutylphosphate, and aminopolycarboxylates. $TcO_2 \bullet xH_2O$ has a well-defined local structure, which is very similar to that reported for $RuO_2 \bullet xH_2O$. When diols, such as ethylene glycol, are present, only soluble, lower-valent technetium compounds are produced. The XAFS and UV-visible spectra of these compounds are consistent with a structure similar to $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$ in which the diolate ligands take the place of the EDTA ligands. The properties of the Tc(IV) alkoxide complexes are consistent with those of the soluble, lower-valent technetium complexes that complicate the disposal of CC waste at the Hanford site. The Tc(IV) alkoxide complexes are stable in alkaline solution and can be generated by the reduction of TcO_4^- in alkaline solution.

Introduction

The disposition of the high-level nuclear waste (HLW) located at the U.S. Department of Energy's (DOE's) Hanford Reservation is among the largest, and most expensive, remediation projects in the U.S.(*1*) Approximately 200,000 m^3 of HLW, stored in large underground storage tanks, must be retrieved and processed for disposal.(*1,2*) This heterogeneous waste consists of three major phases: sludge, supernate and saltcake.(*3,4*) The sludge, composed mainly of oxides, aluminates and silicates that are insoluble in the highly alkaline waste, contains the majority of the radionuclides. The supernate, a concentrated salt solution composed largely of sodium nitrate, sodium nitrite and sodium hydroxide, contains ^{137}Cs, ^{90}Sr, and ^{99}Tc. Saltcake is a mixture of water-soluble salts that have precipitated from the supernate due to evaporation of the water. The current plan for treating HLW involves separating this waste into high and low activity streams.(*1*) The high activity waste (HAW) stream will consist of sludge plus the radionuclides ^{137}Cs, ^{90}Sr, and ^{99}Tc that have been separated from the low activity waste (LAW) stream. This material will be vitrified and sent to a long term waste repository. The LAW stream will consist of the supernate and dissolved salt cake from which ^{137}Cs, ^{90}Sr, and ^{99}Tc have been removed. The LAW stream will be vitrified and stored at the Hanford Reservation. To meet the regulatory requirements for vitrified LAW, removal of sufficient ^{137}Cs, ^{90}Sr, and ^{99}Tc from the LAW stream is required.

The treatment of the Hanford HLW is greatly complicated by the behavior of technetium in certain tanks. The separation of the technetium from the supernate and dissolved saltcake is based upon ion exchange of pertechnetate, TcO$_4^-$.(*5,6*) However, certain waste tanks, the Complexant Concentrate (CC) or Envelope C tanks, contain a large percentage of soluble, lower-valent technetium species.(*7*) These tanks also contain

3

a relatively high concentration of organic compounds including dibutylphosphate, 2-hydroxyethylethylenediaminetriacetate (HEDTA), nitrilotriacetate (NTA), citrate, and glycolate.(*4,8*) In addition, the tanks contain iminodiacetate (IDA) and low concentrations of glyoxylate and formaldehyde, which result from the decomposition of the aminopolycarboxylate compounds.(*8,9*) These organic compounds, either singly or in combination, form soluble complexes with lower-valent technetium. These complexes greatly complicate the separation of technetium from the LAW stream because they are not separated by the ion exchange processes developed for pertechnetate.(*7*) Thus, the technetium concentration in the LAW stream from these tanks could exceed the limits for LAW, which would require a reduced waste loading or disposal of the vitrified LAW as HAW. Either of these alternatives is undesirable since both would greatly increase the overall cost.

The soluble, lower-valent technetium species present in CC tanks have not been identified. Investigations using X-ray absorption near edge spectroscopy (XANES) suggested that the lower-valent technetium species are Tc(IV); however, no further information was reported.(*10*) Identifying these species is complicated by the fact that few soluble, lower-valent technetium complexes are stable in highly alkaline environments except for Tc(V) dithiolate complexes(*11*) and some Tc(IV)(*12,13*) and Tc(V)(*14*) alkoxide complexes. The insoluble Tc(IV) complex, $TcO_2 \cdot xH_2O$(*15,16*) is produced when TcO_4^- is reduced in aqueous solution if ligands capable of forming other complexes are not present. $TcO_2 \cdot xH_2O$ does not pose a major problem for the separation of Hanford's HLW since it will be present in the sludge.

This paper addresses the role of selected organic compounds relevant to CC waste in the formation of lower-valent technetium species when TcO_4^- is reduced in alkaline solution and discusses the characterization of these lower-valent species.

4

Experimental Section

General. In the alkaline solutions used in this work, radiolysis of TcO_4^- produced either

$TcO_2 \cdot xH_2O$ or soluble products depending upon which organic compounds were present.

Radiolysis enables the facile reduction of TcO_4^- in highly alkaline solution without the

addition of chemical reductants that could produce unwanted technetium species,

especially technetium nitrido complexes.[17] Irradiation of these solutions with [60]Co γ

radiation produces reactive $HO^{\bullet}$, $H^{\bullet}$, and e_{aq}^- radicals from the radiolysis of water.[18]

Molecular radiolysis products, H_2 and H_2O_2, are produced in much smaller yield.[18] In

highly alkaline solution, $HO^{\bullet}$ and $H^{\bullet}$ react quickly with HO^- to yield O^- and e_{aq}^-,

respectively.[19] The oxidizing O^- radicals then react with the organic molecules present

in these solutions, protecting the reduced technetium species from oxidation by O^-.[19]

The hydrated electrons, e_{aq}^-, react quickly with TcO_4^-.[20-22] Based upon known

chemistry, radiolysis of TcO_4^- requires three reducing equivalents and produces Tc(IV) as

shown in Scheme 1.[20-24]

Scheme 1

$$TcO_4^- + e_{aq}^- \rightarrow TcO_4^{2-} \qquad\qquad k = 2.5\times10^{10}\ M^{-1}\ s^{-1}$$

$$2\ TcO_4^{2-} \rightarrow TcO_4^- + Tc(V) \qquad\qquad k = 1.5\times10^{5}\ M^{-1}\ s^{-1}$$

$$2\ Tc(V) \rightarrow TcO_4^{2-} + Tc(IV) \qquad\qquad k = 2.4\times10^{3}\ M^{-1}\ s^{-1}$$

The use of radiolysis to reduce TcO_4^- in this investigation does not imply that the

mechanism shown in Scheme 1 is responsible for the reduction of TcO_4^- in the actual

HLW since the high concentrations of nitrate and nitrite prevent reduction of TcO_4^- by

hydrated electrons.[19,25] Furthermore, both thermal chemistry and radiolysis (by a

5

different mechanism) have been reported to reduce TcO_4^- in highly alkaline solutions containing excess nitrate.(*26,27*) Radiolysis is used here only as a convenient method of reducing TcO_4^- cleanly.

Procedures. *Caution: ^{99}Tc is a β-emitter (E_{max} = 294 keV, $\tau_{1/2}$ = 2 × 10^5 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}).(*28*) UV-visible spectra were obtained using an Ocean-Optics ST2000 spectrometer. EPR spectra were obtained with a Varian E-12 spectrometer equipped with an EIP-547 microwave frequency counter and a Varian E-500 NMR gaussmeter. The XY plots of the EPR spectra were digitized and fit using the computer code POWFIT.(*29*) 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 spectra 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.(*30-32*)

The spectra were energy calibrated using the first inflection point of the pre-edge peak of the Tc K edge 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.

The data analysis was performed by standard procedures[33] using the EXAFSPAK suite of programs developed by G. George of SSRL. The background was removed by fitting a polynomial to the pre-edge of the data such that the post-edge spectrum followed the Victoreen function μ_{Vic}. The polynomial was subtracted from the data to give the spectrum μ_{exp}. A spline function, μ_{spline}, was chosen to minimize low R peaks in the extended X-ray absorption fine structure (EXAFS) Fourier transform. The EXAFS spectrum was obtained by the following function: $\chi(k)=(\mu_{exp}-\mu_{spline})/\mu_{Vic}$ where k, the electron energy in Å^{-1}, is $[(2m/h^2)(E-E_0)]^{1/2}$, and E_0 was defined as 21060 eV. The ΔE_0 parameter was allowed to vary during fitting of the EXAFS spectra; for a given fit, ΔE_0 was constrained to be the same for all scattering shells.

Fitting of the spectrum was done on the k^3 weighted data using the EXAFS equation where S_0^2 is the amplitude reduction factor, fixed at 0.9; N_i is the coordination

$$\chi(k) \cong S_0^2 \sum_{i=1}^{n} \frac{N_i S_i(k,R_i)F_i(k,R_i)}{kR_i^2} \exp\left(\frac{-2R_i}{\lambda(k,R_i)}\right)\exp\left(-2\sigma_i^2 k_i^2\right)\sin\left[2kR_i + \phi_i(k,R_i) + \phi_c(k)\right]$$

number of shell I; S_i is the central atom loss factor for atom i; F_i is the EXAFS scattering function for atom i; R_i is the distance to atom i from the absorbing atom; λ_i is the photoelectron mean free path; σ_i is the Debye-Waller factor; ϕ_i is the EXAFS phase function for atom i; and ϕ_c is the EXAFS phase function for the absorbing atom.[33] The program FEFF6[34] was used to calculate theoretical values for S_i, F_i, λ_i, ϕ_i, and ϕ_c based on atomic positions taken from the crystal structure of a similar complex.

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.

TcO$_2$•xH$_2$O. Under an argon atmosphere, NaOH (6 ml, 7M, 42 mmol) was added to a solution of TcCl$_6^{2-}$ (3 ml, 6.6 × 10^{-3}M, 20 μmol) in conc. HCl. The yellow TcCl$_6^{2-}$ solution immediately became warm and turned dark brown. Dark brown, flocculent solid began to precipitate after approximately half of the NaOH had been added. The solution was allowed to sit for 1 hour, and the supernatant was removed with a pipette. The sample was then centrifuged, and the remaining supernatant was removed with a pipette. To prepare the XAFS sample, boron nitride (100 mg) was thoroughly mixed with the damp solid. The mixture was heat sealed inside a polyethylene tube under Ar, and the tube was then doubly contained in Ar filled, heat sealed polyethylene bags.

Radiolysis Experiments. The stock solutions for radiolysis experiments were 0.1M or 0.5M in the organic compound and 2M in NaOH as shown in Table 1. To each of ten 2 ml polypropylene centrifuge tubes, 970 μl of this stock solution was added. NaTcO$_4$ (3.9×10^{-2}M in water) was then added to five of these tubes as listed in Table 1; an equal volume of water was added to the other five tubes. A Cu(II)/Fe(II) chemical dosimeter (Hart dosimeter), also in a 2 ml centrifuge tube, recorded the radiation dose.(*35*) A set of three tubes (sample with TcO$_4^-$, Hart dosimeter, sample without TcO$_4^-$) was placed equidistant from a 600 Ci ^{60}Co source. In a given experiment, three different sets of tubes placed at varying distances from the ^{60}Co source and irradiated for the same period of time, generally 16 hours. The tubes were housed in a heavy aluminum box with a 0.25 in. thick polycarbonate window. Two sets of reference samples, with and without

TcO_4^- were not irradiated. No reduction of TcO_4^- was observed in any of the unirradiated samples.

Results and Discussion

These experiments characterized the species produced by reduction of TcO_4^- in alkaline solution in the presence of selected organic compounds. The identities of the lower-valent technetium products, especially the soluble ones, are necessary to address problems caused by soluble, lower-valent complexes in the separation of technetium from the LAW. A summary of the results is given in Table 1, which lists the organic component, its concentration, the concentration of TcO_4^-, and whether the technetium containing radiolysis product is soluble or insoluble. The nature of the insoluble and soluble radiolysis products is discussed below.

Table 1: Results of radiolysis experiments

Organic Compound	[Organic] (M)	[TcO$_4^-$] (mmol)	Radiolysis Product
EDTA	0.5	1.1	Insoluble
NTA	0.5,0.1	1.1, 0.2	Insoluble
IDA	0.5,0.1	1.1, 0.2	Insoluble
Citrate	0.5	1.1	Insoluble
Diphenylphosphate	0.1	0.2	Insoluble
Dibutylphosphate	0.1	0.2	Insoluble
Ethanol	0.5	1.1	Insoluble
Ethylene glycol	0.5	1.1	Soluble
Glyoxylate	0.1	1.1,0.2	Soluble
Formaldehyde	0.1	0.2	Soluble

Insoluble radiolysis product. As summarized in Table 1, for nearly all of the organic compounds examined, radiolysis of alkaline solutions of TcO_4^- containing organic compounds produced a dark, insoluble precipitate, presumably $TcO_2 \cdot xH_2O$. For comparison, authentic $TcO_2 \cdot xH_2O$ was prepared by hydrolysis of $TcCl_6^{2-}$. Figure 1a shows the EXAFS spectrum of the insoluble product produced by radiolysis of TcO_4^- in

2M NaOH containing 0.5M ethylenediaminetetraacetic acid (EDTA). This spectrum

closely resembles the spectrum of $TcO_2 \cdot xH_2O$ obtained by hydrolysis of $TcCl_6^{2-}$, which is

shown in Figure 1b. The parameters obtained from fitting the two EXAFS spectra are

similar and are reported in Table 2. The major differences in the fit parameters are that

for the insoluble radiolysis product, the coordination numbers and Debye-Waller factors

are greater than those of $TcO_2 \cdot xH_2O$ obtained by hydrolysis. These differences are

attributable to different degrees of hydration of the two samples of $TcO_2 \cdot xH_2O$, which

produces discernibly different coordination environments for the Tc-centers. The

radiolysis sample has a less well-defined local geometry than the hydrolysis sample. The

heterogeneity of the radiolysis sample affects the EXAFS spectrum in the same way as

static disorder in that the Debye-Waller factors increase significantly. The coordination

numbers and Debye-Waller factors are positively correlated, and can be affected by a

number of variables, especially disorder.(*33*) In contrast to the coordination numbers, the

bond distances determined from EXAFS analysis are more precise.(*33*) As seen in Table

2, the bond distances in the insoluble radiolysis product and $TcO_2 \cdot xH_2O$ are not
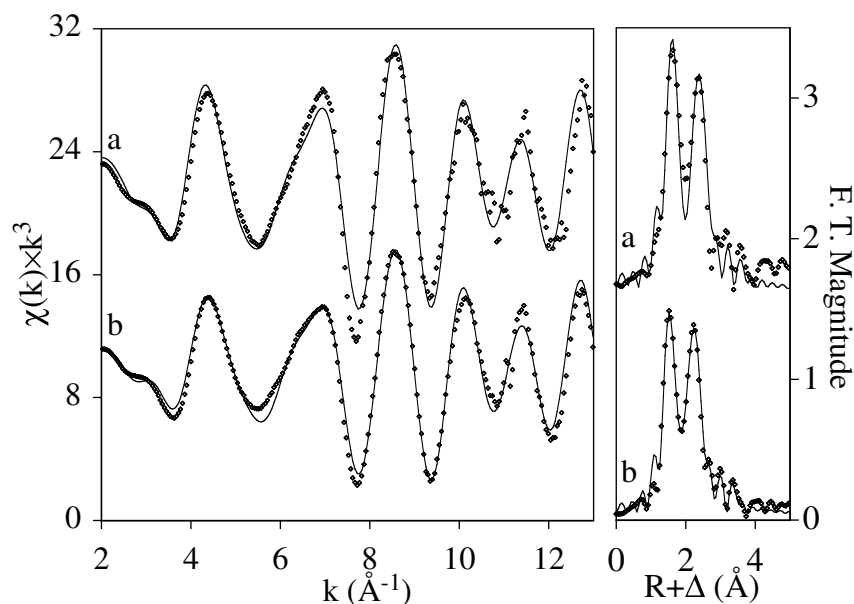
statistically different.

Figure 1: EXAFS spectra (left) and their Fourier transforms (right) for a) product of radiolysis of TcO_4^- in 0.4M Na_2EDTA and 2M NaOH and b) $TcO_2 \cdot xH_2O$ from the hydrolysis of $TcCl_6^{2-}$. The data are shown by the diamonds and fits by the solid trace.

Table 2: Structural parameters of the insoluble radiolysis product derived from EXAFS analysis

Scattering Path	Coordination Number	Distance (Å)	Debye-Waller Parameter ($Å^2$)	ΔE_0 (eV)[b]
TcO_4^- radiolysis in 0.4M Na_2EDTA and 2M NaOH				
Tc-O	5.9(3)	2.005(3)	0.0048(5)	-9.94
Tc-Tc	2.4(2)	2.570(2)	0.0059(5)	-9.94
Tc-O-Tc-O[c]	5(2)	4.05(2)	0.006(6)	-9.94
$TcO_2 \cdot xH_2O$ from $TcCl_6^{2-}$ hydrolysis				
Tc-O	3.9(3)	2.017(2)	0.0022(5)	-7.5
Tc-O	1.4(9)	2.47(2)	0.005(12)	-7.5
Tc-Tc	1.7(2)	2.57(2)	0.0029(6)	-7.5
Tc-O-Tc-O[c]	3.6(8)	4.07(2)	0.001(3)	-7.5

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) 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.

c) This scattering path is a 4-legged multiple scattering path between the *trans* ligands of the technetium coordination sphere.

Figure 2 shows the EPR spectra of the insoluble products produced by the radiolysis of TcO_4^- in the presence of several organic compounds. The spectra are observable only at low temperatures (<10 K). $TcO_2 \cdot xH_2O$ from the hydrolysis of H_2TcCl_6 yields the same EPR signal, which is shown in Figure 2 along with a spectrum simulated using an effective S'=1/2 spin Hamiltonian.(*36*) The similarity of the spectra of the radiolysis product and the product of hydrolysis of $TcCl_6^{2-}$ provides evidence that the insoluble radiolysis product is $TcO_2 \cdot xH_2O$.
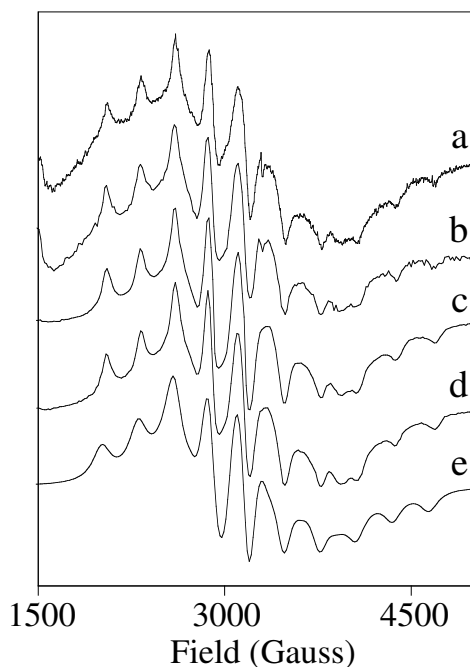
Figure 2: X-band EPR spectra (9.2 GHz, 1.8 K) of $TcO_2 \cdot xH_2O$ derived from a) hydrolysis of $TcCl_6^{2-}$, and radiolysis in 2M NaOH with 0.5M of b) citrate, c) Na_2EDTA, d) ethanol, and e) EPR spectrum simulated using an effective S'=1/2 spin Hamiltonian with g_1 = 2.145, g_2 = 2.034, g_3 = 1.979, $|A_1|$ = 4.8 × 10^{-3} cm^{-1}, $|A_2|$ = 13.0 × 10^{-3} cm^{-1}, $|A_3|$ = 26.1 × 10^{-3} cm^{-1}, line-width = 102 G peak to peak, 110 G perpendicular, Lorentzian lineshape.

Local structure of $TcO_2 \cdot xH_2O$. Because $TcO_2 \cdot xH_2O$ is generally amorphous,(*16,37*) its local structure was anticipated to be ill-defined, consisting of technetium atoms linked by a mixture of oxide and hydroxide bridges. However, the EXAFS results show that coordination environment of $TcO_2 \cdot xH_2O$ is well-defined. The EXAFS results from

$TcO_2 \cdot xH_2O$ prepared by hydrolysis of $TcCl_6^{2-}$ reveals a single coordination geometry about the technetium center. The technetium atom has 4 oxygen neighbors at 2.02 Å, 1.5 oxygen neighbors at 2.47 Å, and 2 technetium neighbors at 2.57 Å. In addition, a contribution from 4 *trans*-O-Tc-O-Tc multiple scattering paths requires a square planar arrangement of the 4 oxygen atoms at 2.02 Å since each set of *trans*-oxo ligands provides two multiple scattering paths. Except for the two O atoms at 2.47 Å, the Debye-Waller factors are reasonably small, which indicates that little disorder exists in any given shell of coordinating atoms. The contribution of the two O atoms at 2.47 Å to the fit is small, and the accuracy of the bond distance and the coordination number for these atoms is lower than for the other atoms. These structural parameters are similar to those previously reported for the reduction of TcO_4^- by NaH_2PO_2.(*38*)

The proposed coordination geometry of technetium is consistent with a 1-dimensional chain structure consisting of edge-sharing TcO_6 octahedra with *trans* water ligands. This structure, illustrated in Figure 3, is analogous to the $MX_2 \cdot 2H_2O$ structure of the first-row transition metal chlorides and bromides.(*39*) The same, one dimensional chain structure has been observed for $RuO_2 \cdot xH_2O$.(*40*) This structural motif is also present in the distorted rutile structure of crystalline TcO_2(*41*) in which the *trans*-water ligands are replaced by the bridging oxo ligands of the neighboring chains.
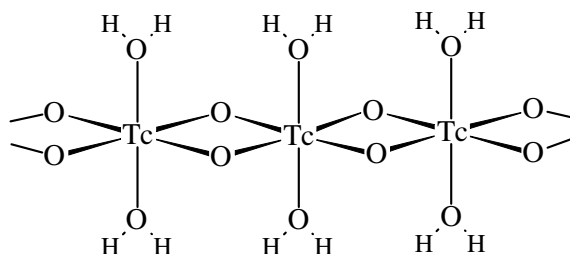

Figure 3: Proposed structure of the $TcO_2 \cdot xH_2O$ product.

The Tc-O bond distance found in $TcO_2 \cdot xH_2O$ corresponds to the 1.94-2.08 Å Tc-O distances of crystalline TcO_2.(42) The Tc-Tc distance also is similar to the short 2.48 Å Tc-Tc distance in $TcO_2(cr)$(42) and is consistent with M-M bonding resulting from the half-occupied orbitals of the Tc(IV) centers as in TcO_2.(42) A similar situation exists for $RuO_2 \cdot xH_2O$ where the 1.90-1.99 Å Ru-O bond distances correspond to those of $RuO_2(cr)$, and the 3.10 Å Ru-Ru distance is similar to the shorter Ru-Ru distance of 3.11 Å in $RuO_2(cr)$.(40) Furthermore, the EXAFS study of $RuO_2 \cdot xH_2O$ revealed that as x decreases from ~2, the structure of the solid changes as a water ligand is replaced with the bridging oxide ligand of a neighboring chain.(40) This change is responsible for the differences observed between the EXAFS spectra of $TcO_2 \cdot xH_2O$ produced by hydrolysis and radiolysis.

Soluble Radiolysis Products. Small amounts of soluble radiolysis products are detected by UV-visible spectroscopy during the radiolysis of TcO_4^- in the presence of IDA or NTA. Although the identity of these species has not been determined, they are not the known $Tc_2(\mu\text{-}O)_2$ complexes since their UV-visible spectra are different.(43-46) In fact, it is possible that these radiolysis products do not contain technetium and may result from slightly different radiation chemistry of the aminopolycarboxylates in the absence and presence of TcO_4^-. As shown above, when EDTA, NTA, and IDA are present, the dominant technetium containing radiolysis product is $TcO_2 \cdot xH_2O$.

Soluble, pink technetium complexes are the sole products of radiolytic reduction of TcO_4^- in the presence of ethylene glycol, glyoxylate, or formaldehyde. While glyoxylate and formaldehyde are formally aldehydes, in water, they exist as geminal diols with two hydroxyl groups on the same carbon.(47,48) The observation of the soluble technetium complexes in the presence of these ligands suggests that the soluble radiolysis

products are Tc(IV) diolates, which is consistent with the known stability of lower-valent technetium alkoxide complexes in alkaline aqueous solution.(*12-14,49*)

These pink radiolysis products are EPR silent and have similar UV-visible spectra characterized by an absorption at ~500 nm. The UV-visible spectra of these complexes and of $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$ are shown in Figure 4. All known Tc(IV) complexes that have a $Tc_2(\mu\text{-}O)_2$ core (see Figure 5) possess a similar peak at 500 nm,(*43-46*) which has been assigned to a $\delta^*\text{-}\delta$ transition within this core.(*45*) The similarity between these spectra and those of the radiolysis products suggests these compounds possess a $Tc_2(\mu\text{-}O)_2$ core as illustrated in Figure 5.
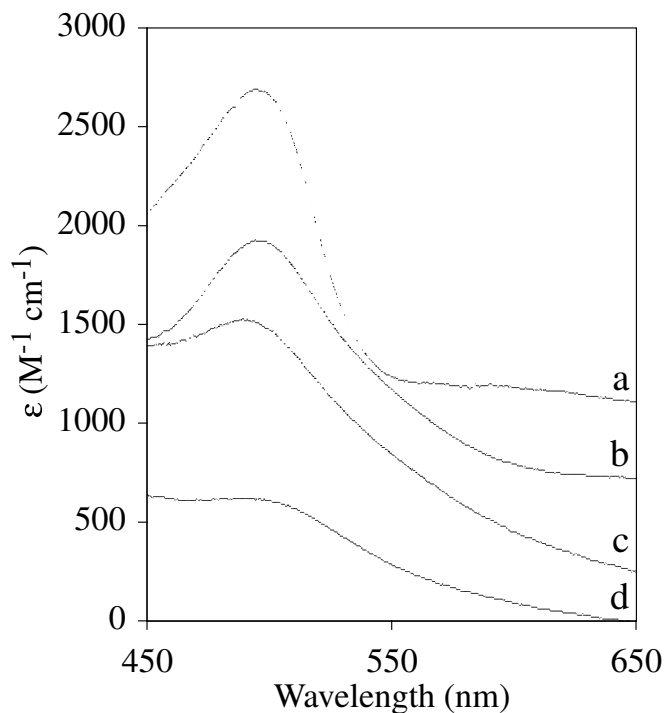

Figure 4: UV Visible spectra of the products of radiolysis of TcO_4^- in a) 0.2M Na_2EDTA, pH = 5. b) 0.1M glyoxylic acid and 2M NaOH, c) 0.1M formaldehyde and 2M NaOH, and d) 0.1M ethylene glycol and 2M NaOH.
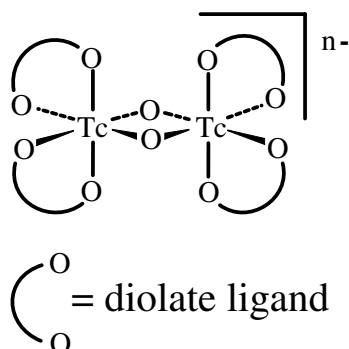
Figure 5: Proposed structure of the soluble radiolysis product.

To test this postulate, radiolysis product was examined in solution by XAFS. The EXAFS spectrum and its Fourier Transform for the product of radiolysis of TcO_4^- in 2M NaOH and 0.1M glyoxylic acid is shown in Figure 6, along with those from $(H_2EDTA)_2Tc(\mu\text{-}O)_2$ for comparison. The parameters obtained by fitting the data are given in Table 3. The structural parameters for $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$ in solution are in excellent agreement with those determined by crystallography.(*45*) The structural information for the radiolysis product suggests a simple coordination environment of six oxygen nearest neighbors and a single technetium neighbor. These results are consistent with the structure of the radiolysis product proposed in Figure 5. The Tc K-edge charge state shift for the soluble radiolysis product relative to TcO_4^- is –5.3 eV, which agrees with the shifts of –5.6, -5.3, and –5.5 eV for other Tc(IV) complexes, $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$, $TcO_2 \cdot xH_2O$, and crystalline TcO_2, respectively. The charge state shift results strongly supports the assignment of Tc(IV) as the oxidation state of the soluble radiolysis product.
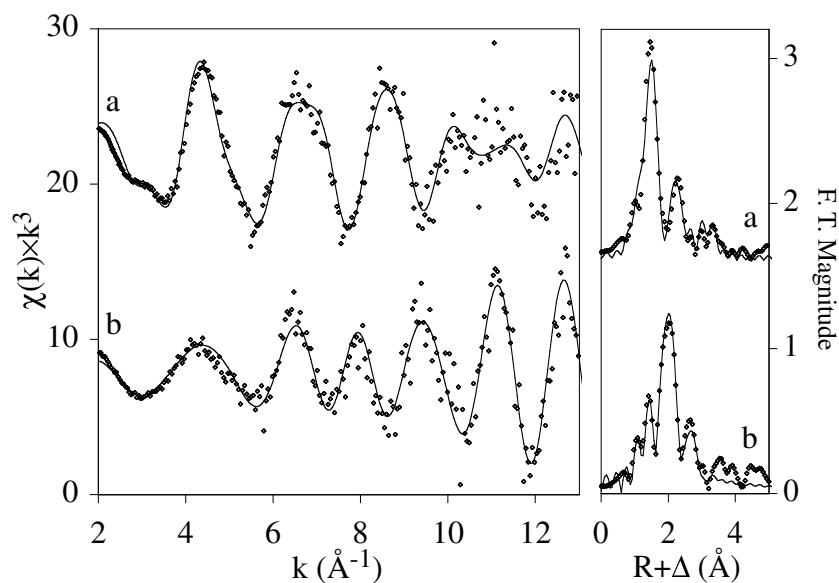
Figure 6: EXAFS spectra (left) and the respective Fourier transforms (right) for b) radiolysis of 1.1 mM TcO_4^- a) 2M NaOH and 0.1M glyoxylic acid and b) in 0.2M Na_2EDTA, pH = 5. The data are shown by the diamonds, and fits by the solid trace.

Table 3: Structural parameters of soluble radiolysis products derived from EXAFS analysis[a]

Scattering Path	Coordination Number[b]	Distance (Å)	Debye-Waller Parameter $(Å^2)$[b]	ΔE_0 (eV)[c]
TcO_4^- radiolysis in 0.1M glyoxylate and 2M NaOH				
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	6*	4.06(2)	0.002(3)	-7.9
TcO_4^- radiolysis in 0.2M Na_2EDTA, pH = 5.4				
Tc-O	2*	1.93(1)	0.003(1)	-7.2
Tc-O	2*	2.06(3)	0.002*	-7.2
Tc-N	2*	2.27(4)	0.004(3)	-7.2
Tc-Tc	1*	2.350(7)	0.0015(4)	-7.2
Tc-C	2*	2.99(2)	0.001*	-7.2
Tc-O	2*	3.28 (2)	0.004(2)	-7.2

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.
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.

Relatively high technetium concentrations (1 mM) were necessary to obtain the EXAFS spectrum shown in Figure 6a. At lower concentrations, it is probable that monomeric alkoxide complexes, similar to those described by Anderegg(*50*) would be formed rather than dinuclear complexes.

One striking result of this study is that the principal, soluble, lower-valent technetium species observed during radiolysis in highly alkaline solution are alkoxide complexes. The well-known Tc(IV) aminopolycarboxylate complexes, typified by $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$, are not formed in highly alkaline conditions. Instead, only the hydrous oxide is formed in the presence of aminopolycarboxylates. The trend in stabilities of the Tc(IV) radiolysis products in alkaline solution (diolate complexes > hydrous oxide > aminopolycarboxylate complexes) can be explained by the π-donor strength of the ligands. The strongest π-donors, alkoxides, form the strongest bonds with the Tc(IV) center, while the weakly π-donating aminopolycarboxylates form the weakest bonds. This trend is countered by the trend in the acidities of the ligands; carboxylates are the strongest acids while alcohols are the weakest. Consequently, at low pH, where only the aminopolycarboxylates are deprotonated, the Tc(IV) aminopolycarboxylate complexes are most stable. When the concentration of hydroxide increases sufficiently, the more strongly π-bonding hydroxide (and oxide) ligands form $TcO_2 \bullet xH_2O$ rather than the aminopolycarboxylate complexes. At still higher pH, where the diols are deprotonated, stable, soluble Tc(IV) diolate complexes are stable(*12-14,49*) since the alkoxides form stronger bonds than hydroxide with Tc(IV).

The difference in π-donor strength of the ligands has one additional effect. Since the valence electrons of the Tc(IV) center are destabilized by strongly π-bonding ligands, complexes with such ligands are much more sensitive to oxidation. For example,

$(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$ is extremely stable with respect to oxidation at the pH at which it forms.(*51*) In contrast, when exposed to air, the soluble Tc(IV) radiolysis products oxidize to TcO_4^- over a period of one week; other Tc(IV) alkoxides display similar air sensitivity.(*13*) Air also oxidizes the hydrous oxide to TcO_4^- but over a longer period. The soluble, lower-valent technetium species in actual HLW is also reported to be air sensitive.(*52*)

This research has elucidated and described the nature of lower-valent technetium species produced by the reduction of TcO_4^- in highly alkaline solution. In short, if only citrate, dialkylphosphates, or aminopolycarboxylates are present, insoluble $TcO_2 \bullet xH_2O$ is produced. Soluble, lower-valent species are produced when diolate ligands (and possibly other alkoxides) are present. The knowledge gained from these results enables research into the problems caused by lower-valent technetium complexes in HLW tanks at Hanford without having to use real HLW. Since Tc(IV) alkoxide complexes can be prepared in the laboratory, potential treatment schemes, such as selective oxidation or separation of the Tc(IV) species, may be developed in the laboratory using waste surrogates rather than tank waste. The more difficult and expensive experiments using actual tank waste can then be performed using the best techniques developed in the laboratory.

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