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Authors

Lukens Jr., Wayne W.
Fickes, Michael J.
Bucher, Jerome J.
et al.

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FINAL REPORT
U.S. Department of Energy

RESEARCH PROGRAM TO INVESTIGATE THE
FUNDAMENTAL CHEMISTRY OF TECHNETIUM

Principal Investigator: David K. Shuh
Institution: Chemical Sciences Division, Lawrence Berkeley National Laboratory

Co-Principal Investigator: Norman M. Edelstein
Institution: Chemical Sciences Division, Lawrence Berkeley National Laboratory

Co-Principal Investigator: Carol J. Burns
Institution: Chemistry Division, Los Alamos National Laboratory

Collaborators: Wayne W. Lukens, Jerome J. Bucher
Institution: Chemical Sciences Division, Lawrence Berkeley National Laboratory

Collaborators: Michael G. Fickes, Brian L. Scott
Institution: Chemistry Division, Los Alamos National Laboratory

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Executive Summary

The chemistry of technetium, Tc, presents two separate problems that complicate the disposition of the high-level nuclear waste currently residing in tanks at the Hanford and Savannah River sites. The first is the presence of soluble lower valent technetium species, presumably tetravalent Tc(IV) complexes, in certain tanks, especially the complexant concentrate (CC) tanks, at the Hanford site. These reduced technetium species could adversely affect the composition of the low-level waste form because these species cannot be easily removed from the waste stream. Since the stable oxidation state of technetium at high pH is Tc(VII) as pertechnetate ion, TcO_4^-, the observation of reduced technetium species was surprising. Neither the identity of the reduced technetium species nor their origin was known. In addition, the only proposed method of removing these species is oxidation to TcO_4^-, which can be efficiently removed by ion exchange. Since the identity of the species is unknown, designing alternative methods to remove them from the waste is difficult.

The second problem associated with technetium chemistry is its behavior in the environment. Technetium forms the highly environmentally mobile pertechnetate ion, TcO_4^-, in aerobic environments. This ion is extremely soluble, does not readily sorb to soil components, and since ^{99}Tc has a long half-life of 213,000 years, its leaching from waste into water supplies is of great concern. Leaching could be prevented by providing a physical barrier to prevent TcO_4^- from migrating; however, the long half-life of ^{99}Tc raises the question whether a physical barrier would remain intact for the necessary period. Another strategy to prevent the leaching of technetium is to provide chemical containment by reducing the Tc to insoluble Tc(IV) as $TcO_2 \cdot xH_2O$, TcS_2, or incorporated into a host lattice. In this case, migration of Tc will be prevented as long as it remains

reduced or incorporated in the host lattice. Therefore, the major issue for chemical containment is preventing the oxidation of the immobile, reduced technetium species to highly mobile TcO_4^-.

The chemistry of technetium pertinent to the aforementioned issues has been addressed by fundamental research.. The results can be divided into three areas: the identity of technetium species produced by radiolysis in alkaline solution, the mechanism for radiolysis of pertechnetate in alkaline solution, and the evolution of reduced technetium species incorporated in slag-based grout.

The identity of technetium species that can be produced in alkaline solution has been investigated by the radiolysis of pertechnetate, TcO_4^-, in 2M NaOH. The major findings are as follows:

- Tetravalent technetium aminopolycarboxylates, such as the well-known $(H_2EDTA)_2Tc_2(\mu-O)_2$ are not stable in highly alkaline solution and cannot be formed in highly alkaline solution.

- Soluble, reduced technetium species are the major radiolysis product only when diols are present. Spectroscopic studies strongly suggest that these soluble species are Tc(IV) diolate complexes with structures similar to that of $(H_2EDTA)_2Tc_2(\mu-O)_2$.

- In the absence of diols (or presumably polyols), the reduced technetium species is $TcO_2 \bullet xH_2O$.

- All of the radiolysis products, both soluble and insoluble, are air-sensitive and are oxidized to TcO_4^- over a period of days to weeks.

The mechanism of TcO_4^- radiolysis was investigated with the following results:

- The reducing agent is NO_3^{2-} produced by the reaction of hydrated electrons with nitrate, NO_3^-.

- Reduction of TcO_4^- requires the presence of organic materials to scavenge the oxidizing O^- radical anions produced during radiolysis.

- The behavior of NO_3^{2-} suggests that other easily reduced oxoanions, such as CrO_4^{2-} will be reduced in tanks that contain high concentrations of ^{137}Cs and organic compounds.

Because radiolytic reduction of TcO_4^- is efficient in the presence of excess nitrate, reduced technetium species may be found wherever enough radioisotopes exist, especially ^{137}Cs, and wherever the concentration of organic material is sufficient to scavenge the O^- radicals produced during radiolysis. However, in the absence of certain organic molecules, such as, diols or polyols, the reduced technetium species will be $TcO_2 \cdot xH_2O$, which will precipitate. While reduced technetium species may be very prevalent, soluble reduced technetium species should form only in the presence of ligands capable of producing soluble Tc(IV) species in highly alkaline solution. These ligands are apparently present in a small number of tanks, in particular the Hanford CC waste tanks.

The radiolysis products produced in alkaline solution are air sensitive. In addition, the reduced technetium complexes in the CC wastes oxidize in air if the ^{137}Cs is removed. The air sensitivity of the reduced technetium species has two significant implications. First, old samples from the Hanford tanks will not accurately reflect the proportion of reduced technetium species, so experiments to measure the proportion of reduced

technetium species in a given tank must be carried out on freshly sampled material. Second, the reduced technetium species could be removed, albeit slowly, by aeration. However, the ^{137}Cs and ^{90}Sr would have to be removed as a prerequisite. The radiation produced by the nuclides has two effects. It reduces TcO_4^-, as described above. It also creates organic radicals, which rapidly scavenge oxygen and would prevent the oxygen from reacting with the reduced technetium species.

The behavior of technetium in slag-based, cement waste forms was followed over a three year period using x-ray absorption fine structure spectroscopy that yielded the following results:

- In cements exposed to air, one third of the technetium was oxidized to TcO_4^- after 25 months although all of the technetium was initially reduced to TcS_2.

- In cements that were sealed, TcO_4^- continued to be reduced over a period of 15 months although only half of the TcO_4^- was initially reduced to TcS_2.

These results strongly suggest that oxygen will oxidize the technetium in slag-based waste forms to TcO_4^-. However, the results do not provide information about the actual rate of oxidation in a real waste form. In small cement samples, oxidation is fairly rapid; however, in a large block, the rate of oxidation will be limited by the rate of diffusion of oxygen and its reaction with blast furnace slag. The ready oxidation of reduced technetium also raises doubt whether immobile, reduced technetium species can resist oxidation when incorporated into other waste forms.

Acknowledgements

1. Introduction

Technetium (^{99}Tc, β emitter, 0.29 keV max, $\tau_{1/2} = 2.1 \times 10^5$ yr) presents a number of problems that hinder the processing and ultimate disposal of the U. S. Department of Energy (DOE) legacy nuclear waste.

Technetium present in the waste tanks at the Hanford and the Savannah River sites has been assumed to be TcO_4^- because the chemically stable form of technetium in oxidizing environments is pertechnetate, TcO_4^-. Based upon this assumption, specific strategies were developed to remove TcO_4^- from liquid waste using anion exchange. While removal of an acceptable fraction of technetium from actual double shell slurry feed waste has been demonstrated on the laboratory scale, analogous separation techniques failed when actual complexant concentrate (CC) waste, which contains a high concentration of organic compounds, was used (Schroeder 1995). These results suggest that a large percentage of the technetium is present as soluble, reduced technetium species. The presence of these species contradicts the assumption that almost all of the technetium will be present as TcO_4^- and increases the difficulty in removing the technetium from the waste stream.

Once the technetium has been removed from the waste stream, the stability of pertechnetate presents difficulties for incorporation into waste forms. During waste vitrification, the stability of heptavalent technetium species leads to the volatilization of technetium (Darab 1996). Technetium forms volatile oxides, Tc_2O_7 and $CsTcO_4$, when heated under oxidizing conditions (Darab 1996, Migge 1990). Such conditions are present during the normal vitrification of both low-level and high-level waste and low level waste glasses. Volatilization of the technetium presents two challenges. The glass melter and associated equipment become heavily contaminated by technetium transported in the vapor phase. More importantly, little of the technetium is stabilized in the waste form. Volatilization of the technetium may be ameliorated by creating reducing conditions in the glass melt by adding additional organic material such as sugar or graphite. However, reducing conditions often adversely effect the performance of the glass (Darab 1996).

Volatilization of the technetium may be avoided by immobilizing it in a waste form, such as cement or grout, which are produced by low temperature routes (Gilliam 1990, Smith 1993, Allen 1997). However, cement waste forms present a different set of challenges. In cement, the technetium leach rate can be lowered by reducing TcO_4^- to Tc(IV) with blast furnace slag (Gilliam 1990, Smith 1993). As Tc(IV), technetium is extremely insoluble and is not environmentally mobile. The challenge is to prevent oxidation of Tc(IV) back to environmentally mobile TcO_4^-. Previous work has demonstrated that technetium does not remain reduced in some cement waste forms (Allen 1997). Theoretical studies have suggested that oxygen diffusing through the cement can oxidize Tc(IV) to TcO_4^- (Smith 1993). Since TcO_4^- does not strongly adsorb on oxide surfaces, it could conceivably leave the waste through pores in the cement or by weathering of the cement.

One of the impediments in dealing with these issues is the incomplete understanding of technetium chemistry under conditions important to DOE. For example, little information exits for the chemistry of technetium in alkaline solutions other than the elementary thermochemistry and electrochemistry.

Research Objectives

The purpose is to increase the basic scientific understanding of technetium chemistry to better understand the behavior of technetium in chemical environments relevant to DOE. Two important areas in need of study are the behavior of technetium in highly alkaline solutions similar to high-level nuclear waste, and its behavior in different waste forms. This research program addressed these two needs.

Approach

Two separate approaches were used in this program. The first focus was to understand the basic solution chemistry of technetium, which underlies its behavior in the highly alkaline environment of the nuclear waste tanks located at the Savannah River and Hanford Sites. The specific problems at these sites are related to the anomalous oxidation state of technetium (Schroeder 1995). Although, at high pH, technetium should exist in its highest oxidation state as TcO_4^-, soluble, lower-valent technetium species have been observed in certain wastes. The specific unknowns that this program sought to answer are the nature of lower valent technetium species that can be formed in highly alkaline solution and whether pertechnetate undergoes radiolytic reduction in highly alkaline solution when nitrate is present in excess.

The second focus area is the behavior of technetium immobilized in various waste forms. The behavior of technetium in cement wastes was examined to gain information about its long-term stability. Specifically, this research examined the oxidation of reduced technetium species by components present in high-level waste that are incorporated into cement waste along with technetium.

Background

The high-level wastes from the nuclear weapons production program are a significant and costly legacy of the cold war. Although the chemical processing of the fuel rods was performed in acid, the wastes were made highly basic to prevent corrosion of the storage tanks. Under these alkaline conditions, the chemistry of technetium is largely unknown. The radioactive wastes have been accumulating for over fifty years and contain a variety of chemicals and radionuclides in a complex, heterogeneous mixture. The waste consists of three physical forms: supernate, the liquid phase; saltcake, mixture of soluble salts that precipitated after the evaporation of the supernate; and sludge, a mixture of insoluble, inorganic compounds, mainly oxides, which precipitated when the wastes were made alkaline. The sludge contains the majority of the actinides and fission products. However, the supernate and saltcake contain large quantities of the fission products ^{99}Tc and ^{137}Cs. The chemical form of technetium in this liquid phase has been assumed to be pertechnetate, TcO_4^-, which is the most thermodynamically stable chemical form of technetium at high pH.

Work by Schroeder and coworkers reported that complexant concentrate (CC) waste contains a large portion of the soluble technetium species that are not TcO_4^- (Schroeder 1995). Their report suggested that the technetium might be present as soluble Tc(IV) complexes. X-ray absorption near edge spectroscopy (XANES) studies on CC waste performed by Blanchard and coworkers support this assertion (Blanchard 1995). While these XAFS studies strongly suggest that the soluble technetium complexes are Tc(IV), they are not able to define the nature of the complexes. Few technetium complexes are

known to be stable in basic solution. Dithiolate ($^-$SCH$_2$CH$_2$S$^-$) complexes of Tc(V) are extremely stable in aqueous solution including alkaline solutions (Davison 1980). Diolate ($^-$OCH$_2$CH$_2$O$^-$) complexes of Tc(V) (Davison 1987) and Tc(IV) (Alberto 1986) are stable *only* in alkaline aqueous solution; they decompose to TcO$_2$•xH$_2$O at pH < 10.

The process of incorporation of technetium into waste form matrices and the long-term stability of technetium in these waste forms are major concerns since little is known about technetium behavior in these solid phases. At present, incorporation of technetium into glass or cement waste forms is planned. Technetium presents specific challenges for the long-term isolation in these waste forms. In glass waste forms, a large portion of the technetium can be lost during vitrification. However, modifying the redox chemistry and melt conditions of the glass can lead to poorer glass properties (Darab 1996). Technetium can be easily encapsulated in cement; however, mobile TcO$_4^-$ must be reduced to immobile Tc(IV) species (Gilliam 1990). If Tc(IV) is reoxidized to environmentally mobile TcO$_4^-$, it may leave the cement waste form through the pores.

2. Products of radiolysis of TcO$_4^-$ in alkaline solutions

Introduction

The identity of the reduced technetium species that complicate the removal of technetium from the supernate of the CC wastes is subset of the broader issue of the nature of technetium complexes synthesized by the reduction of TcO$_4^-$ in highly alkaline ssolution. Previous work by Blanchard, et. al. strongly suggests that the Tc(IV) is the oxidation state of the soluble non-pertechnetate species present in CC waste (Blanchard 1995). In addition, as shown in the following section, Tc(IV) is the oxidation state of the technetium species produced by radiolysis in highly alkaline solution. However, few Tc(IV) complexes are stable in highly alkaline solution. With the exception of alkoxide and thiolate complexes, almost all Tc(IV) complexes decompose in alkaline solution to give the hydrous Tc(IV) oxide, TcO$_2$•xH$_2$O.

To determine whether soluble Tc(IV) complexes could be created in highly alkaline solution, γ-radiolysis was performed on 2M NaOH solutions containing TcO$_4^-$ and selected organic molecules. The organic molecules examined included formate, glycolate, glyoxylate, ethylene glycol, ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), iminodiacetate (IDA), diphenylphosphate, dibutylphosphate, and acetate. The organic molecules serve a dual purpose: as ligands for the reduced technetium species and as scavengers of the oxidizing O$^-$ radicals produced during radiolysis. The results of these experiments are reported in Table 2.1. The most interesting result reported in Table 1 is that an insoluble radiolysis product is the principal product in almost all cases. While small amounts of soluble radiolysis products are observed in some cases, soluble radiolysis products are the main products in only a few cases. These differences and the identities of the radiolysis products are discussed below.

Table 2.1: Survey of reductive radiolysis of TcO_4^- in 2M NaOH.

Organic Material	Insoluble	Soluble
EDTA	Yes	trace
NTA	Yes	trace
IDA	Yes	trace
Acetate	Yes	No
Citrate	Yes	No
Ethanol	Yes	No
Dibutyl phosphate	Yes	No
Ethylene Glycol	No	Yes
Glyoxylate	No	Yes
Formaldehyde	No	Yes

Results

Insoluble product of TcO_4^- radiolysis

   With the exception of ethylene glycol, glyoxylate, and formaldehyde, radiolytic reduction of TcO_4^- in the presence of organic molecules produced a dark, insoluble product. This product is spectroscopically identical to $TcO_2 \cdot xH_2O$ produced by the hydrolysis of $TcCl_6^{2-}$ in alkaline solution.

   Figure 2.1a shows the EXAFS spectrum of the insoluble product produced by radiolysis of TcO_4^- in 2M NaOH plus 0.5M EDTA. This spectrum is almost identical to the spectrum of $TcO_2 \cdot 2H_2O$ obtained by hydrolysis of $TcCl_6^{2-}$, which is shown in Figure 1b. The parameters obtained from fitting the two EXAFS spectra are similar. The major difference is that for the insoluble radiolysis product, the coordination numbers and Debye-Waller factors are greater than those of $TcO_2 \cdot 2H_2O$ obtained by hydrolysis. These differences between the spectra are attributable to a slight heterogeneity of the radiolysis product, presumably due to the presence of a small amount of another technetium species, TcO_4^-. Such heterogeneity increases the Debye-Waller factors, and consequently the coordination numbers, in the same way as static disorder. In EXAFS analysis, the coordination numbers and Debye-Waller factors are strongly, positively correlated, and can be affected by a number of variables, especially disorder (Koningsberger 1988, Teo 1986). In contrast to the coordination numbers, the bond distances determined from EXAFS analysis are more precise (Teo 1986). As shown in Table 2.2, the bond distances in the insoluble radiolysis product and $TcO_2 \cdot 2H_2O$ are nearly the same.

Figure 2.1. EXAFS spectra (left) and Fourier Transforms (right) of (a) insoluble material from the radiolysis of TcO_4^- in 2M NaOH and 0.4M EDTA, and (b) $TcO_2 \bullet xH_2O$ prepared from $TcCl_6^{2-}$. The data are represented by dots, the least squares fits are represented by lines.

Table 2.2: Structural parameters for $TcO_2 \bullet xH_2O$ derived from EXAFS analysis.

Scattering Path	Coordination Number	Distance (Å)	Debye-Waller Parameter ($Å^2$)	ΔE_0 (eV)
TcO_4^- radiolysis in 0.4M Na_2EDTA and 2M NaOH				
Tc-O	6.2(3)	2.014(3)	0.0048(5)	-8.87
Tc-Tc	3.2(3)	2.573(2)	0.0059(5)	-8.87
Tc-O-Tc-O	4(1)	4.08(2)	0.002(5)	-8.87
$TcO_2 \bullet 2H_2O$ 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	3.6(8)	4.07(2)	0.001(3)	-7.5

Figure 2.2: X-band (9.2 GHz) EPR spectra of $TcO_2 \bullet H_2O$ 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) simulated EPR spectrum with $g_1 = 2.145$, $g_2 = 2.034$, $g_3 = 1.979$, $|A_1| = 4.8 \times 10^{-3}$ cm^{-1}, $|A_2| = 13.0 \times 10^{-3}$ cm^{-1}, $|A_3| = 26.1 \times 10^{-3}$ cm^{-1}, line-width = 102 G peak to peak, 110 G perpendicular, Lorentzian lineshape.

Figure 2.2 shows the electron paramagnetic resonance (EPR) spectra of the insoluble products produced by radiolysis in the presence of several different organic molecules. The spectrum is only observable at low temperatures (<10 K). Hydrolysis of H_2TcCl_6 with NaOH produces the same EPR spectrum, shown, for comparison, in Figure 2.2. This spectrum was simulated using the parameters given in the caption of Figure 2. Since the EPR and EXAFS spectra of the radiolysis product and the product of hydrolysis of $TcCl_6^{2-}$ are virtually identical, we conclude that the radiolysis product is simply $TcO_2 \bullet xH_2O$. These results show that the well-known Tc(IV) aminopolycarboxylate complexes, such as $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$, are not are stable with respect to hydrolysis to $TcO_2 \bullet xH_2O$ at these pHs.

Local structure of $TcO_2 \bullet xH_2O$

Because $TcO_2 \bullet xH_2O$ is amorphous, we had anticipated that its local structure would be ill-defined, consisting of technetium atoms linked by a mixture of oxide and hydroxide bridges. However, the EXAFS and EPR data provide strong evidence that this assumption is incorrect. The EXAFS spectrum of $TcO_2 \bullet xH_2O$ shows a single, well-defined, coordination geometry about technetium. 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 that the 4 oxygen atoms at 2.02 Å form a square plane since each set of *trans*-oxo ligands produces two multiple scattering paths. The agreement between the model and the data is excellent. 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 simulated spectrum is small relative to the other 4 O atoms and the technetium atoms. Consequently, the accuracy of the bond distance and number of neighbors for the two O atoms at 2.47 Å is expected to be lower than for the other atoms.

The observed coordination geometry of technetium suggests that the local structure of $TcO_2 \cdot xH_2O$ is a 1-dimensional chain structure consisting of edge-sharing TcO_6 octahedra with *trans*-water ligands. This structure, illustrated in Figure 2.3, is similar to the commonly observed $MX_2 \cdot 2H_2O$ structure of the first-row transition metal chlorides and bromides (Morosin 1963). This structural motif is also present in the distorted rutile structure of crystalline TcO_2. In crystalline TcO_2, the *trans*-water ligands are replaced by the bridging oxo ligands of the neighboring chains.

Figure 2.3. Proposed structure of $TcO_2 \cdot xH_2O$.

In comparison to known, molecular species that possess a similar $Tc_2(\mu\text{-}O)_2$ core, the Tc-μ-O bonds are approximately 0.1 Å longer in $TcO_2 \cdot 2H_2O$ (Bürgi 1981, Anderegg 1983, Linder 1989, Alberto 1990). This increased bond length is consistent with the proposed structure since the μ-O ligands exert a much stronger *trans* influence than the ligands *trans* to the oxo bridge in any of the molecular species. The Tc-Tc distance is 0.2 Å longer in $TcO_2 \cdot 2H_2O$ than in the molecular species. The 2.47 Å Tc-O distance, assigned to the *trans*-water ligands, is quite long. This distance is substantially longer than the average Tc-N distance of 2.2 Å found in $(TCTA)_2Tc_2(\mu\text{-}O)_2$ (Linder 1989), $(NTA)_2Tc_2(\mu\text{-}O)_2$ (Anderegg 1983), or $(EDTA)_2Tc_2(\mu\, O)_2$ (Bürgi 1981). We are unable to find a systematic error which could account for increasing the distance of this shell of atoms; however, the contribution of this shell to the total simulated spectrum is quite small (~5 %).

The observed powder EPR spectrum is consistent with the proposed structure. The spectrum shows the 10-line pattern expected for hyperfine coupling to the ^{99}Tc nucleus, which has a nuclear spin of 9/2. The spectrum was fit using a Lorentzian lineshape with a peak to peak linewidth of 102 Gauss, a perpendicular linewidth of 110 Gauss, and the spin Hamiltonian given in equation 2.1 using an effective spin of 1/2.

$$= \beta \mathbf{H} \cdot \mathbf{g} \cdot \tilde{\mathbf{S}} + \tilde{\mathbf{S}} \cdot \mathbf{A} \cdot \mathbf{I} \qquad (2.1)$$

The derived parameters are $g_1 = 2.145$, $g_2 = 2.034$, $g_3 = 1.979$, and , $|A_1| = 4.8 \times 10^{-3}$ cm^{-1}, $|A_2| = 13.0 \times 10^{-3}$ cm^{-1}, $|A_3| = 26.1 \times 10^{-3}$ cm^{-1}. The rhombic symmetry of the spectrum is consistent with the low symmetry of the technetium coordination environment although the g-values, derived from the fit, are slightly greater than expected for Tc(IV) (Pieper 1975). However, the fact that the spectrum is observable only at very low temperature rules out the assignment of this species to Tc(VI), such as NTc^{3+}, since EPR spectra can be observed at room temperature for Tc(VI).

The linewidths of the peaks are much smaller than expected for such a magnetically concentrated sample. The extreme narrowing of the linewidths can be explained by strong magnetic exchange between the adjacent technetium centers (Abragam 1970, McGregor 1976, Bencini 1990). The contribution to the second moment of the EPR spectrum from dipolar coupling between neighboring spins can be calculated using equation 2.2, where θ is the angle that the line between the metal centers makes

$$M_2 = (\tfrac{3}{4})S(S+1)g^2\beta^2 \sum_k \frac{(3\cos^2\theta - 1)}{r_k^6} \qquad (2.2)$$

with the magnetic field, r is the distance between the metal centers, and the other symbols have their usual meanings (Abragam 1970). When the magnetic axis is aligned with the chains of TcO$_2$•2H$_2$O, dipolar coupling would produce a Gaussian lineshape with a full width at half-height of approximately 6300 Gauss (S = 3/2) or 1250 Gauss (S = 1/2). For exchange coupled systems, the lineshape is Lorentzian with a width of $\Gamma \sim M_2/J_0$, where J_0 is the isotropic exchange parameter. Based upon the assumption that exchange coupling does occur in TcO$_2$•2H$_2$O, to obtain the roughly 100 Gauss linewidth of the observed spectrum, J_0/k must be 55 K if S = 3/2 or 2 K if S = 1/2. While both of these values are similar to those reported for different MX$_2$•2H$_2$O compounds (Carlin 1977), the reported, low magnetic moment of TcO$_2$•2H$_2$O is more consistent with an effective S' = 1/2 (Nelson 1954). In light of the fact that all of the MX$_2$•2H$_2$O complexes display varying degrees of exchange, assuming that magnetic exchange occurs in TcO$_2$•2H$_2$O is reasonable. However, without either single crystal EPR data or magnetic susceptibility data over a larger temperature range than previously reported, the details of the magnetic interactions in TcO$_2$•2H$_2$O cannot be unequivocally determined.

Soluble radiolysis products

Small amounts of soluble radiolysis products are observed during the radiolysis of TcO$_4^-$ in the presence of IDA or NTA. Although the identity of these species has not been established, they are not the known Tc(IV)$_2$(μ-O)$_2$ complexes because their UV-Visible spectra are different (Bürgi 1981, Anderegg 1983).

In the presence of ethylene glycol, glyoxylate, or formaldehyde, radiolytic reduction of TcO$_4^-$ produces only soluble radiolysis products. These pink products are all EPR silent and have similar UV-Visible spectra characterized by an absorption peak at ~500 nm. The UV-Visible spectra of these complexes and that of known (H$_2$EDTA)$_2$Tc$_2$(μ-O)$_2$ (Bürgi 1981) are shown in Figure 2.4. The common feature of the organic compounds that yield soluble products from the radiolysis of TcO$_4^-$ in alkaline solution is that they are diols. In addition, none of the organic compounds, which yield insoluble radiolysis products, is a diol. While glyoxylate and formaldehyde are formally aldehydes, they

exist as hydrates in aqueous solution; these hydrates are geminal diols. These results are consistent with previous reports of the stability of lower-valent technetium diolate complexes in alkaline aqueous solution.
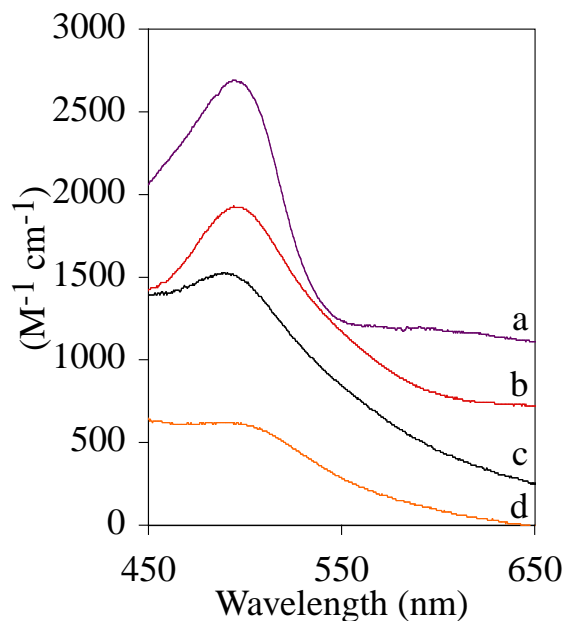
Figure 2.4. Visible spectra of the products of radiolysis of 0.2mM TcO_4^- in (a) 0.1M EDTA at pH = 5 and in 2M NaOH with 0.1M of (b) glyoxylate, (c) formaldehyde, and (d) ethylene glycol.

The radiolysis of TcO_4^- in the presence of ethylene glycol is particularly interesting since ethylene glycol complexes of both Tc(IV), $Tc(eg)_3^{2-}$ (Alberto 1986), and Tc(V), $OTc(eg)_2^-$ (Davison 1987) have been reported, where eg is the dianion of ethylene glycol. In both cases, the lower-valent technetium complex is stable in aqueous, alkaline solution. The spectrum of the radiolysis product does not resemble the spectrum of either the Tc(IV) or the Tc(V) complex. The Tc(IV) complex is colorless and has a single peak in the UV at 37040 cm^{-1}, and the Tc(V) complex is violet and has as strong peak at 40000 cm^{-1} and much weaker peaks at 28170 and 18690 cm^{-1}. In contrast, the final ethylene glycol radiolysis product has absorption peaks at 38460 and 19720 cm^{-1}, and its visible spectrum resembles that of $[(H_2EDTA)Tc(\mu\text{-}O)]_2$ more strongly than it resembles the spectra of the reported Tc(IV) and Tc(V) ethylene glycol complexes.

This apparent contradiction can be resolved by monitoring the evolution of the UV spectrum of the radiolysis product as a function of absorbed dose. Figure 2.5 shows the spectra of a solution of 0.2 mM TcO_4^-, 2M NaOH, and 0.2M ethylene glycol and 0.8M ethanol (ethanol acts as an O^- scavenger) with increasing absorbed dose. Figure 2.5 also shows the fitted spectrum along with two deconvoluted spectra showing the relative contributions of TcO_4^- and the radiolysis product. At low absorbed dose, and therefore, low concentration of the radiolysis product, the radiolysis product is characterized by a single peak in the UV spectrum between 36900 and 37310 cm^{-1}. The absorption energy is in good agreement with that reported for the Tc(IV) complex $Tc(eg)_3^{2-}$ and is not in good

agreement with that reported for the Tc(V) complex, $OTc(eg)_2^-$. So, at low concentrations, the radiolysis product appears to be $Tc(eg)_3^{2-}$.

Figure 2.5. UV spectra of the radiolysis of TcO_4^- in 2M NaOH and 0.5M ethylene glycol at absorbed doses of a) 0, b) 3.4, c) 6.8, and d) 19.6 kGy. The spectrum is represented by the diamonds; the fit is represented by the solid line, the contribution from TcO_4^- is represented by dots, and the contribution from the radiolysis product is represented by a solid line.

At higher absorbed doses, and therefore, higher concentrations, the spectrum of the radiolysis product changes and develops the characteristic absorption peak at 500 nm, shown in Figure 2.4. This peak is found in all of the radiolysis products at concentrations of ~0.1 mM. This peak is very similar to that found in all of the Tc(IV) complexes which have a $Tc_2(\mu\text{-}O)_2$ core, and has been assigned to a δ^*-δ transition within this core (Bürgi 1981, Anderegg 1983, Linder 1989). The similarity between these spectra and those of the radiolysis product at high concentrations suggests that these compounds all posses the $Tc_2(\mu\text{-}O)_2$ core as illustrated in Figure 2.6.

Figure 2.6. Compounds with $Tc_2(\mu\text{-O})_2$ cores. Left: $(H_2EDTA)_2Tc_2(\mu\text{-O})_2$. Right: Proposed structure of the product of radiolysis of TcO_4^- in alkaline solutions containing diols. The diolate ligand is represented by the curved line.

    To test this postulate, we examined the radiolysis product at high concentration by X-ray absorption fine structure spectroscopy (XAFS). The extended X-ray absorption fine structure (EXAFS) spectrum of the product of TcO_4^- in 2M NaoH and 0.1M gyloxylic acid is shown in Figure 2.7 along with the spectrum of $(H_2EDTA)_2Tc(\mu\text{-O})_2$ for comparison. The pertinent parameters derived from fitting the data are given in Table 2.3.   The parameters for $(H_2EDTA)_2Tc_2(\mu\text{-O})_2$ in solution are in excellent agreement with those determined by crystallography. The parameters for the radiolysis product suggest a very 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 2.6.

Figure 2.7.   EXAFS spectra (left) and Fourier Transforms (right) of (a) $(H_2EDTA)_2Tc_2(\mu\text{-O})_{22\backslash}$ (b) product of the radiolysis of 2mM TcO_4^- in 2M NaOH and 0.1M glyoxylate. The data are represented by dots, the least squares fits are represented by lines.

Table 2.2: Structural parameters for Tc(IV) complexes derived from EXAFS analysis.

Scattering Path	Coordination Number	Distance (Å)	Debye-Waller Parameter (Å^2)	ΔE_0 (eV)
(H$_2$EDTA)$_2$Tc$_2$(μ-O)$_2$ in water at pH = 5				
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	2.349(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
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

Discussion

The most striking result is that the principal, soluble, reduced technetium species observed during radiolysis are the diolate complexes. The well-known Tc(IV) aminopolycarboxylate complexes, typified by (H$_2$EDTA)$_2$Tc$_2$(μ-O)$_2$, are not formed during radiolysis in alkaline solution. Instead, only the hydrous oxide is formed if only aminopolycarboxylates are present. The explanation for the trend in stabilities of the Tc(IV) radiolysis products (diolate complexes > hydrous oxide > aminopolycarboxylate complexes) is straightforward.

The trend is due to differences in π-donor ability of the ligands: the strongest π-donors, alkoxides, form the strongest bonds with the Tc(IV) center, while the weakly π-donating aminopolycarboxylates will form the weakest bonds. This trend is balanced 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) polycarboxylate complexes are most stable. When the concentration of hydroxide increases sufficiently, the more strongly bonding hydroxide (and oxide) ligands will displace the aminopolycarboxylates to form TcO$_2$•xH$_2$O. At still higher pH, where the diols are deprotonated, stable, soluble Tc(IV) diolate complexes can exist due to the fact that alkoxides form stronger bonds with Tc(IV) than does hydroxide.

Interestingly, the difference in π-donor strength of the ligands has one additional effect. Since the complexes with strongly π-donating ligands are electron rich, they are much more sensitive to air oxidation. For example, (H$_2$EDTA)$_2$Tc$_2$(μ-O)$_2$ is air-stable at the pHs at which it forms (Bürgi 1981). In contrast, when exposed to air, the soluble Tc(IV) radiolysis products oxidize to TcO$_4^-$ over a period of one week. Similarly, when exposed to air, the hydrous oxide is oxidized to TcO$_4^-$ but over a longer period of time.

In addition to the changes in oxidation potential of the Tc(IV) complexes due to changing the ligand environment, the pH of the solution plays an important role. Tc(IV) complexes become increasingly easy to oxidize at higher pH. Therefore, at the high pHs where the Tc(IV) diolate complexes are stable towards hydrolysis, these complexes are

easily oxidized to TcO_4^-. On the other hand, if the pH of a solution containing Tc(IV) and aminopolycarboxylates is lowered, the resulting Tc(IV) aminopolycarboxylate complexes are difficult to oxidize.

One other Tc(IV) complex may be present in very highly alkaline solution: $Tc(OH)_6^{2-}$. Its existence is implied by the fact that the reduction of TcO_4^- at very high pH consumes hydroxide. In addition, Sn(IV), whose chemistry is closely analogous to Tc(IV) does form the complex hydroxide $Sn(OH)_6^{2-}$. However, although the existence of $Tc(OH)_6^{2-}$ has been implied, this complex has not been reported.

Conclusion

The radiolysis of TcO_4^- in 2M NaOH generates two classes of radiolysis products: soluble Tc(IV) diolates and insoluble $TcO_2 \cdot xH_2O$. Both of these products are appreciably air-sensitive at this pH. The existence of only these radiolysis products and their chemical behavior can be explained by the π-donating ability of the ligands.

Experimental

Caution: ^{99}Tc is a β-emitter (Emax = 294 keV, $\tau_{1/2}$ = 2 × 105 years). All operations were carried out in a radiochemical laboratory equipped and approved for handling this isotope. Technetium, as $NH_4^{99}TcO_4$, was obtained from Oak Ridge National Laboratory. The solid $H_4^{99}TcO_4$ 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. To the colorless solution, a small amount of NaOH was added, 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}) (Colton 1965). UV-visible spectra were obtained using an Ocean-Optics ST2000 spectrometer. EPR spectra were obtained on 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. EPR spectra were fit using the computer code POWFIT (Lazos). 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. XAFS spectra were obtained in the transmission mode at room temperature using argon filled ionization chambers or in fluorescence yield mode using a multi-element Ge-detector (Fabris 1999). 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 NH4TcO4 defined as 21044 eV.

The data analysis was performed by standard procedures (Koningsberger 1988) 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••Vic. The polynomial was subtracted from the data to give the spectrum •exp. A spline function, •spline, was chosen to minimize low R peaks in the EXAFS Fourier transform. The EXAFS spectrum was obtained by the

following function: $\chi(k)=(\mu_{exp}-\mu_{spine})/\mu_{Vic}$ where k, the electron energy in Å^{-1}, is $[(2m/\hbar^2)(E-E_0)]^{1/2}$, 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 following EXAFS equation where S_0^2 is the scale factor, fixed at 0.9; N_i is the coordination number

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

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. The program FEFF6 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 the most similar complex (Rehr 1992, Zabinski 1995).

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 crystallized three times from water. All other chemicals were used as received.

$TcO_2 \cdot 2H_2O$. 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 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 heat sealed polyethylene bags.

Results and Discussion Solutions for radiolysis experiments were prepared by weighing the appropriate amounts of sodium hydroxide and organic compound into a 10 ml volumetric flask then preparing 10 ml of solution. To each of ten 2 ml polypropylene centrifuge tubes, 970 μl of this stock solution was added. $NaTcO_4$ (30 μl, 3.9×10^{-2}M, 1.2 μmol) was then added to five of these tubes, and 30 μl of water was added to the other five. A Cu(II)/Fe(II) chemical dosimeter (Hart dosimeter), also in a 2 ml centrifuge tube, recorded the radiation dose (Hart 1955). A set of three tubes (sample with TcO_4^-, Hart dosimeter, sample without TcO_4^-) were placed on an arc such that the three tubes were 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 contained in a heavy aluminum box with a 0.25 in. thick polycarbonate window.

3. Mechanism of TcO4- Radiolysis in Alkaline Solution in the Presence of Organic Material and Excess Nitrate

Introduction.

The radiation chemistry of nitrate solutions has recently received increasing attention due, in part, to its relevance to the chemistry of high level nuclear waste (Fessenden 2000). Specifically, the high-level nuclear waste stored in underground tanks at the Savannah River and Hanford Sites is highly alkaline, and contains high concentrations of nitrate and nitrite In these tanks, the radiation source is the decay of ^{137}Cs and ^{90}Sr (Toste 1995). In addition, certain tanks also contain lower concentrations of several organic ions including formate, oxalate, glycolate, acetate, iminodiacetate (IDA), nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA) 2-hydroxyethylethylenediaminetriacetate (HEDTA), and citrate (Toste 1995, Agnew 1996). Because of this variety of ions and molecules, the thermal and radiation chemistry of these tanks are complex, and can produce unexpected chemical changes in the species present.

One example is the discovery of low valent technetium species in high-level waste (Schroeder 1995). Although the most stable form of technetium at pH>10 is pertechnetate, TcO_4^- (Meyer 1991), a large fraction of lower valent technetium complexes was found in certain waste tanks. These tanks contain relatively high concentrations of ^{137}Cs and aminopolycarboxylates including HEDTA, NTA, and IDA. This combination has aroused suspicion that radiolysis of TcO_4^- was responsible for the presence of reduced technetium species. However, these tanks contain concentrations of nitrate and nitrite up to five orders of magnitude greater than that of TcO_4^- (Agnew 1996). The large excess of nitrate prevents the reducing primary radiolysis product, e_{aq}^-, from reducing TcO_4^- at an appreciable rate. In addition, TcO_4^- cannot be readily reduced by organic radicals produced by radiolysis since nitrite reacts quickly with reducing organic radicals (Henglein 1980). For these reasons, direct reduction of TcO_4^- by the primary radiolysis products seems unlikely in the presence of high concentrations of nitrate and nitrite.

To improve the understanding of technetium chemistry relevant to high level tank waste, the radiolysis of TcO_4^- was studied in highly alkaline solutions containing selected organic molecules. In addition, the radiolysis of TcO_4^- was studied in solutions containing IDA or NTA and different concentrations of nitrate. The radiation chemical yields for loss of TcO_4^-, $G(-TcO_4^-)$, reported in molecules / 100 eV, was sensitive to the reduction potentials of the radicals produced during radiolysis. Surprisingly, in the presence of 0.2M $NaNO_3$ and 0.1M NTA or IDA , $G(-TcO_4^-)$ was large, 15-20% of the yield when only NTA or IDA were present. The results support a mechanism in which TcO_4^- is reduced by NO_3^{2-} at a much greater rate than hydrolysis of NO_3^{2-}.

Results and Discussion

To interpret the radiation chemical yield for the reduction of pertechnetate, $G(-TcO_4^-)$, the oxidation state of the technetium radiolysis product must be identified to determine the number of reducing equivalents needed to remove a pertechnetate ion from solution. Based upon known chemistry, radiolysis of TcO_4^- requires three reducing equivalents and produces Tc(IV) as the radiolysis product: Pertechnetate reacts very quickly with

hydrated electrons yielding technetate, TcO_4^{2-} (equation 3.1) (Pikaev, 1977, Deutsch 1978, Lisbon 1989). Technetate, TcO_4^{2-}, disproportionates with a bimolecular rate constant of 1.5×10^5 M^{-1} s^{-1} in alkaline solution (equation 3.2) (Kissel 1969, Founta 1987). Similarly, in the absence of stabilizing ligands, Tc(V) is known to disproportionate rapidly with a bimolecular rate constant of 2.4×10^3 M^{-1} s^{-1} (equation 3.3) (Koltunov 1984a). Alternatively, Tc(V) species could be reduced by TcO_4^{2-}, which is a moderately strong reducing agent, $E^0(TcO_4^-/TcO_4^{2-}) = -0.64$ V vs. NHE (equation 3.4) (Deutsch 1978, Founta 1987). For these reasons, Tc(IV), as $TcO_2 \bullet xH_2O$, is the likely radiolysis product in alkaline solutions in the absence of ligands capable of forming Tc(V) or Tc(IV) complexes that are stable at high pH. The supposition the Tc(IV) is the final oxidation state is strongly supported by the observation that the major radiolysis product is a dark precipitate in the absence of diolate ligands, which can form soluble, lower valent, technetium complexes in highly alkaline solution (Alberto 1986, Davison 1987). As reported in the previous section, the dark precipitate is spectroscopically identical to $TcO_2 \bullet xH_2O$ produced by hydrolysis of $TcCl_6^{2-}$ as determined by XAFS and EPR spectroscopy. Besides the insoluble radiolysis product, a minor, soluble radiolysis is usually observed. However, the principal radiolysis product is $TcO_2 \bullet xH_2O$.

$$TcO_4^- + e_{aq}^- \rightarrow TcO_4^{2-} \qquad\qquad k_1 = 2.5 \times 10^{10}\ M^{-1}\ s^{-1} \quad (3.1)$$
$$2\ TcO_4^{2-} \rightarrow TcO_4^- + Tc(V) \qquad\qquad k_2 = 1.5 \times 10^5\ M^{-1}\ s^{-1} \quad (3.2)$$
$$2\ Tc(V) \rightarrow TcO_4^{2-} + Tc(IV) \qquad\qquad k_3 = 2.4 \times 10^3\ M^{-1}\ s^{-1} \quad (3.3)$$
$$Tc(V) + TcO_4^{2-} \rightarrow Tc(IV) + TcO_4^- \qquad\qquad\qquad\qquad\qquad (3.4)$$

The effect of selected organic molecules upon the radiolytic reduction of TcO_4^- was examined in 2M NaOH; these results, plus data previously reported by Pikaev and coworkers (Pikaev 1996), are reported in Table 3.1. In 2M NaOH, hydroxyl radicals are rapidly converted to oxide radical anions, O^-; therefore, O^- can be treated as the primary oxidizing radical produced by radiolysis (Buxton 1988). The organic molecules studied rapidly scavenge O^- radicals yielding organic radicals and prevent oxidation of the reduced technetium species (Buxton 1988). The hydrated electrons produced during radiolysis reduce TcO_4^- removing TcO_4^- from solution with a radiation chemical yield, $G(-TcO_4^-)$, of $1/3g(e_{aq}^-)$. The deviation of $G(-TcO_4^-)$ from this value can be explained using the reduction potentials of the organic radicals.

When the organic scavengers are primary or secondary alcohols, α-hydroxyalkyl radicals are produced from H-abstraction. These radicals are strongly reducing, e.g., $E^0[(CH_3)_2CO,H^+/(CH_3)_2C^\bullet OH] = -1.7$ V, and are even more strongly reducing when deprotonated (Schwartz 1989). In fact, 2-hydroxy-2-propyl radical reduces TcO_4^- with a rate constant of 7×10^8 M^{-1} s^{-1} (Lisbon, 1989). Since these radicals reduce TcO_4^-, the predicted value of $G(TcO_4^-)$ is $1/3[g(e_{aq}^-) + g(R\bullet)]$, where $g(R\bullet)$ is the yield of organic radicals produced from H-abstraction by O^- and $H\bullet$. The first two entries in Table 3.1 show that the observed $G(-TcO_4^-)$ values are in good agreement with this prediction.

On the other hand, if the organic radicals are capable of oxidizing reduced technetium species, the observed $G(-TcO_4^-)$ values will be smaller than $1/3g(e_{aq}^-)$. For example, the calculated standard potential of the radical produced by H-abstraction from acetate, $E^0(\bullet CH_2CO_2^-,H^+/CH_3CO_2^-) = 1.7$ V (Yu 1994), is similar to that of O^- (Kläning 1985). Consequently, this radical can oxidize the reduced technetium species. As a result, $G(-TcO_4^-)$ will be smaller than $1/3g(e_{aq}^-)$, although the value of $G(-TcO_4^-)$ cannot be

predicted without knowing the rates of reaction of the organic radicals with each other and with the reduced technetium species. As shown by the lower entries in Table 3.1, H-abstraction from certain organic molecules produces radicals capable of oxidizing reduced technetium species. The fact that radicals produced from citrate are oxidizing is not surprising since the carbon centered radical is α to the carboxylate group as in the acetate radical. Similarly, the 1,2-dihydroxyethyl radical produced by H-atom abstraction from ethylene glycol rapidly dehydrates in alkaline solution to form the oxidizing formylmethyl radical (Bansal 1973, Steenken 1979).

Table 3.1: Observed radiation-chemical yields for the loss of TcO_4^- in the presence of selected organic molecules.

Organic	$[TcO_4^-]$ mM	[Organic] M	$G_{obs}(-TcO_4^-)$	$G_{calc}(-TcO_4^-)$	Reference
CH_2CH_2OH	5	0.1	2.7	2.4[a]	20
CH_3OH	5	0.1	2.5	2.5[a]	20
EDTA	5	0.04	1.2	1.2[b]	20
NTA	0.2	0.1	1.0	1.0[b]	this work
IDA	0.2	0.1	0.9	1.0[b]	this work
$CH_3CO_2^-$	1.2	0.5	0.1		this work
Citrate	1.2	0.5	0.5		this work
$HOCH_2CH_2OH$	1.2	0.5	0.4		this work

a) $G_{calc}(-TcO_4^-) = (g(e_{aq}^-)+g(R\bullet))/3$
b) $G_{calc}(-TcO_4^-) = g(e_{aq}^-)/3$

The radicals produced by the reaction of O^- with the aminopolycarboxylates EDTA, IDA, and NTA appear to be unreactive towards both pertechnetate and reduced technetium species. In the presence of these molecules, the $G(-TcO_4^-)$ can be attributed to reduction by e_{aq}^- alone, as shown in Table 3.11. However, a similar radiation chemical yield could be obtained if radicals produced from the aminopolycarboxylates both reduced TcO_4^- and oxidized reduced technetium species. Such a scenario is suggested by the known radiation chemistry of glycine (Bonifacic 1998, Hug 2000).

$$H_2NCH_2CO_2^- + HO\bullet \rightarrow HO^- + H_2NCH_2CO_2^{\bullet} \rightarrow H_2NCH_2^{\bullet} + CO_2 \tag{3.5}$$
$$H_2NCH_2CO_2^- + HO\bullet \rightarrow H_2O + H_2NC^{\bullet}HCO_2^- \tag{3.6}$$
$$H_2NCH_2CO_2^- + HO\bullet \rightarrow H_2O + HN^{\bullet}CH_2CO_2^- \tag{3.7}$$

Three different radicals are produced by the reaction of glycine with hydroxyl radicals (Bonifacic 1998, Hug 2000). Strongly reducing $H_2N-CH_2^{\bullet}$ radicals result from decarboxylation of the $H_2N^{+\bullet}-CH_2-CO_2^-$ radical produced by oxidation of glycine anion, equation 3.5. Weakly reducing, weakly oxidizing $H_2N-C^{\bullet}H-CO_2^-$ radicals are produced by H abstraction from the methylene group, equation 3.6. Strongly oxidizing $HN^{\bullet}-CH_2-CO_2^-$ radicals are produced by H-atom abstraction from the amino group, equation 3.7. Therefore, if the radiation chemistry of the aminopolycarboxylates is similar to that described for glycine, the observed $G(-TcO_4^-)$ of $1/3g(e_{aq}^-)$ could be due to oxidation of reduced technetium species by the $HN^{\bullet}-CH_2-CO_2^-$ radicals and reduction of TcO_4^- by H_2N-

$CH_2^{\bullet}$ radicals in addition to reduction of TcO_4^- by e_{aq}^-. However, this possibility can be eliminated.

Because EDTA and NTA are tertiary amines, they cannot react with O^- to produce strongly oxidizing radicals. Therefore, for EDTA and NTA, the observed $G(-TcO_4^-)$ of $1/3g(e_{aq}^-)$ is due only to the action of hydrated electrons. If strongly reducing $H_2N\text{-}CH_2^{\bullet}$ radicals were produced during radiolysis of NTA or EDTA at these pHs, $G(-TcO_4^-)$ would be greater than $1/3g(e_{aq}^-)$. So for EDTA and NTA, the only radicals produced must be C-centered radicals, $R_2N\text{-}C^{\bullet}H\text{-}CO_2^-$, produced by H-abstraction from the methylene groups. The situation is different for the secondary amine, IDA, since the oxidizing radical, $^{\bullet}N(CH_2CO_2^-)_2$, can be produced by H-atom abstraction from the amino group; however, this pathway cannot be very significant. In the reaction of glycine with hydroxyl radicals, $HN^{\bullet}\text{-}CH_2\text{-}CO_2^-$ radicals are generated in 17% yield relative to the total number of radicals (Hug 1998). Since the ratio of activated C-H bonds to N-H bonds is 4:1 in IDA versus 1:1 in glycine, the maximum yield of oxidizing radicals produced during the radiolysis of IDA is expected to be ~4%.

The difference between the reactivity of glycine and that observed here for the aminopolycarboxylates can be attributed to pH differences. At the pHs used in the glycine studies, hydroxyl radical was the prevalent oxidizing radical. Its standard potential is 1.91 V, slightly greater than that of O^-, $E^0(O^-,H^+:HO^-) = 1.7$ V (Kläning 1985). However, in 2M NaOH, $E^0(O^-,H^+:HO^-)$ is only 0.94 V. This difference is significant since the reduction potential for the $H_2N^{+\bullet}\text{-}CH_2\text{-}CO_2^-$ radical, which gives rise the to the strongly reducing $H_2N\text{-}CH_2^{\bullet}$ radical, is calculated to be 1.6 V (Armstrong 1995). So, oxidation of aminopolycarboxylates by O^- is unlikely to produce $R_2N\text{-}CH_2^{\bullet}$ radicals, but H-abstraction from H-C or H-N bonds can take place. A very similar situation has been observed in the reactivity of purines and pyrimidines with O^-: when the reduction potential of the substrate is small, electron transfer occurs from the organic base to O^-, but when the reduction potential is greater, H-abstraction occurs (Ioele 1998).

Radiolysis of TcO_4^- in the presence of NO_3^-. Since the C-centered radicals produced during radiolysis of IDA and NTA are unreactive towards technetium species, these molecules represent excellent scavengers for use in studying the radiolysis of technetium in the presence of nitrate. The basic radiation chemistry of nitrate is given in equations 3.8-3.10 (Fessenden 2000, Daniels 1967, Daniels 1969a, Daniels 1969b, Forni 1986)

$$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-} \qquad\qquad k_8 = 9.7\times10^9 \text{ M}^{-1}\text{ s}^{-1} \quad (3.8)$$
$$NO_3^{2-} + H_2O \rightarrow NO_2^{\bullet} + 2\,HO^- \qquad\qquad k_9 = 1\times10^3 \text{ M}^{-1}\text{ s}^{-1} \quad (3.9)$$
$$2\,NO_2^{\bullet} + H_2O \rightarrow NO_3^- + NO_2^- + 2\,H^+ \qquad\qquad k_{10} = 6\times10^7 \text{ M}^{-1}\text{ s}^{-1} \quad (3.10)$$

In solutions containing both NO_3^- and TcO_4^-, NO_3^- acts as a scavenger of e_{aq}^-, in competition with TcO_4^-. Since the reaction rates for NO_3^- and TcO_4^- with e_{aq}^- are known, the fraction of e_{aq}^- which react with TcO_4^- can be determined.

The observed radiation chemical yields for TcO_4^- reduction in solutions of 2M NaOH, 0.1M NTA or IDA, and various concentrations of nitrate are listed in Table 3.2. Surprisingly, at high nitrate concentrations, $G(-TcO_4^-)$ is much larger than can be explained by the reaction of TcO_4^- with e_{aq}^-. For example, in 0.1M $NaNO_3$ and 0.1M NTA, $G(-TcO_4^-)$ is 0.19; if only e_{aq}^- were reacting with TcO_4^-, the radiation chemical yield would be 0.01. Since the organic radicals produced from aminocarboxylates do not

react with technetium species, the only radical capable of reducing TcO_4^- is NO_3^{2-} ($E^0(NO_3^-/NO_3^{2-}) = -0.89$ V) (Fessenden 2000), equation 3.11.

$$TcO_4^- + NO_3^{2-} \rightarrow TcO_4^{2-} + NO_3^- \tag{3.11}$$

Table 3.2: Observed and calculated radiation-chemical yields for the loss of TcO_4^- in 2M NaOH, 0.1M IDA or NTA at various nitrate concentrations.

$[NO_3^-]$	$G(-TcO_4^-)$ NTA[a,b]	$G(-TcO_4^-)$ IDA[a,b]
0.20	--	0.13(1)
0.10	0.16(1)	0.12(2)
0.05	0.17(3)	0.13(1)
0.01	0.22(1)	0.17(1)
0.005	0.29(7)	0.21(1)
0.001	0.50(3)	0.50(3)
0	1.0(1)	0.90(3)

a) Standard error from fitting the radiolysis data is given in parentheses.
b) Radiation-chemical yields in ions/100 eV.

If only NO_3^{2-} and e_{aq}^- reduce TcO_4^- the mechanism for radiolysis of TcO_4^- is simple: TcO_4^- and NO_3^- compete for e_{aq}^-, and TcO_4^- and H_2O compete for NO_3^{2-}. The expected radiation chemical yield $G(-TcO_4^-)$ is then given by equation 3.12 where k_n is the rate constant for the reaction given in equation 3.n.

$$G(-TcO_4^-) = \frac{g(e_{aq}^-)}{3\left(k_1[TcO_4^-] + k_8[NO_3^-]\right)}\left\{k_1[TcO_4^-] + k_8[NO_3^-]\frac{k_{11}[TcO_4^-]}{\left(k_{11}[TcO_4^-] + k_9[H_2O]\right)}\right\} \tag{3.12}$$

The results in Table 3.22 are presented graphically in Figure 3.1 along with a least squares fit of the data to equation 3.12 using k_{11}, the rate constant for the reaction of TcO_4^- with NO_3^{2-}, as the only variable. The agreement between the data and the fit are good; however, the two sets of experiments give slightly different values for k_{11}. Radiolysis in the presence of NTA gives $k_{11} = 2.9(2)\times10^7$ M^{-1} s^{-1} while radiolysis in the presence of IDA gives the slightly lower value of $2.2(2)\times10^7$ M^{-1} s^{-1}; the standard errors are in parentheses. The difference in rate constants is due to the fact that values of $G(-TcO_4^-)$ in the presence of IDA are systematically lower than those in the presence of NTA. As noted above, the reaction of NTA with O^- cannot produce strongly oxidizing radicals; however, the reaction of IDA with O^- can produce such radicals. Based upon the assumption that $^\bullet N(CH_2-CO_2^-)_2$ radicals will be produced from IDA at 1/4 of the rate of production from glycine, the $G(-TcO_4^-)$ values observed with IDA can be corrected by adding 0.05 to account for lower valent technetium species oxidized by these radicals. A least squares fit of the corrected data to equation 3.12 yields a value of $3.2(2)\times10^7$ M^{-1} s^{-1} for k_{11}, which is in good agreement with that measured using NTA as the O^- scavenger.

Figure 3.1. Radiation chemical yield for loss of TcO_4^- in 2M NaOH with (a) 0.1M NTA, and (b) 0.1M IDA as a function of nitrate concentration. The data are represented by the circles with the standard error represented by vertical lines. A least squares fit of the data to equation 3.12 is represented by the solid line.

The reduction of TcO_4^- by NO_3^{2-} is considerably slower than the reduction of TcO_4^- by 2-hydroxy-2-propyl radical. The slower rate is consistent with the smaller equilibrium constant of reaction 3.11, based upon the reduction potentials of the species involved, and with the fact that reaction 3.11 involves two negatively charged substrates. The reaction of NO_3^{2-} with TcO_4^- may also be compared with other reactions of NO_3^{2-}. NO_3^{2-} reduces O_2, benzoquinone, and methylviologen with rate constants of 2.3×10^8, 7.6×10^8, and $3.3 \times 10^9 \, M^{-1} \, s^{-1}$, respectively. Again, these rate constants are considerably greater than k_{11}, for the reasons noted above.

Although the reaction of NO_3^{2-} with TcO_4^- is considerably slower than the other electron transfer reactions of NO_3^{2-}, the reaction of NO_3^{2-} with TcO_4^- is much faster than the hydrolysis of NO_3^{2-} (Fessenden 2000, Forni 1986). The significance of this difference in rate is the relatively high efficiency of the reduction of TcO_4^- in concentrated nitrate solution provided that molecules capable of scavenging O^- are present.

Conclusion

The γ-radiolysis of TcO_4^- in highly alkaline solution in the presence of selected organic compounds and nitrate has been examined. In highly alkaline solution, the radicals produced by radiolysis from the aminopolycarboxylates, EDTA, NTA, and IDA, are unreactive towards the technetium species present in solution. These observations suggest that only unreactive C-centered radicals are produced during radiolysis of aminopolycarboxylates under these conditions. In the presence of O^- scavengers, radiolysis of TcO_4^- in nitrate solutions is efficient due to reduction of TcO_4^- by NO_3^{2-}.

<u>Experimental</u>

The radiolysis experiments were performed as described in the previous section.
Radiolysis Data Treatment. All radiation-chemical yields are reported as molecules/100 eV. The radiation doses absorbed by the samples were determined from the Hart dosimeters and were corrected for the different compositions of the dosimeter and sample solutions, for the relative positions of the dosimeter and sample to the source. In addition, the response of the Fe(II)/Cu(II) dosimeter with a 5:1 Fe/Cu ratio was found to be slightly non-linear in comparison to the oxygen-saturated Fricke dosimeter; this non-linearity was corrected. At low absorbed doses, the Hart dosimeter was not accurate, and the absorbed dose was calculated using oxygen-saturated Fricke dosimeters (Fricke 1966). UV-visible spectra were collected from the pertechnetate containing solutions using the solutions without pertechnetate as references. The concentration of pertechnetate was determined by fitting the spectra. Unirradiated samples were used to determine the initial concentration of TcO_4^- and the position and linewidth of the TcO_4^- peaks. Only the heights of the TcO_4^- peaks were allowed to vary when fitting the spectra of irradiated samples. The presence of additional radiolysis products was treated by including additional peaks in the fit.

The radiation chemical yields for the primary radicals were calculated using the method derived by Schuler (Balkas 1970, Schuler 1981). The yield of hydrogen atoms g(H•) is 0.55. The yield of hydrated electrons $g(e_{aq}^-)$ was determined using equation 3.13 where the left-hand term is

$$g(e_{aq}^-) = \frac{g(H\bullet)k_{H\bullet+OH^-}[OH^-]}{k_{H\bullet+OH^-}[OH^-] + k_{H\bullet+RH}[RH]} + 2.55 + 2.33\frac{\sqrt{\sum k[S]/\lambda}}{1 + \sqrt{\sum k[S]/\lambda}} \qquad (3.13)$$

the fraction of hydrogen atoms which react with hydroxide to form hydrated electrons ($k_{H\bullet+OH}$ is the rate constant for the reaction of H• with OH-, and $k_{H\bullet+RH}$ is the rate constant for the reaction of H• with the organic species), and the right-hand side is the yield of hydrated electrons corrected for scavenging from spurs; k[S] is the rate of reaction of substrate S with hydrated electrons, and λ is 8×10^8 s^{-1} (Balkas 1970). Similarly, the yield of oxide radical ions was determined using equation 3.14 where k[S] is the rate of

$$g(O^-) = 2.7 + 1.5\frac{\sqrt{\sum k[S]/\lambda}}{1 + \sqrt{\sum k[S]/\lambda}} \qquad (3.14)$$

reaction of substrate S with hydroxyl radicals, and λ is 4.7×10^8 s^{-1} (Schuler 1981). Hydroxide was not included as a substrate in the calculation of g(O$^-$) since the reactivity of O$^-$ is comparable to that of HO•.

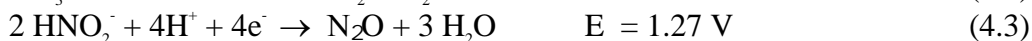## 4. Behavior of Technetium in Cementitious Waste Forms

Introduction

At the Savannah River Site, technetium is currently placed in a cementitious waste form that consists of a mixture of fly ash, blast furnace slag (BFS) and Portland cement plus the decontaminated supernate from the high level waste tanks (Langton 1988, Langton 1989). A similar waste form has been previously proposed for the Hanford site.

Cementitious waste forms have a number of very attractive properties including low cost and low temperature preparation. The latter is particularly important for technetium since Tc_2O_7 is volatile. In terms of technetium chemistry, the major drawback of cementitious waste forms is their porosity. This porosity poses challenges to the immobilization of technetium because TcO_4^- is highly soluble and does not sorb to the minerals that comprise the cement waste form (Gilliam 1990). The behavior of TcO_4^- in the cementitious waste should closely parallel that of NO_3^-; that is, TcO_4^- should slowly diffuse from the waste. Since TcO_4^- is the stable form of technetium at pH > 10 or in aerobic environments at all pHs, the migration of technetium from cement waste forms could be problematic if it is present as TcO_4^-.

To prevent migration of technetium from these waste forms, blast furnace slag is added to the grout (Langton 1988, Langton 1989, Gilliam 1990). Blast furnace slag reduces TcO_4^- to $TcO_2 \bullet xH_2O$ or TcS_2 (Allen 1997), which, unlike TcO_4^-, are insoluble. If the technetium is reduced to Tc(IV), it will remain immobilized in the cementitious waste; however, if the technetium is present as TcO_4^-, it will diffuse from the waste.

Our interest in the behavior of technetium in waste began with the studies of the effectiveness of different reagents for reducing TcO_4^- prior to and during the preparation of cement samples. While BFS was effective at reducing the technetium to TcS_2, the technetium was oxidized back to TcO_4^- over a period of time ranging from days to months (Allen 1997). Since these samples contained high concentrations of nitrate and nitrite, the oxidation of TcO_2 (or TcS_2) could result from reaction with these anions as shown in equations 4.1 through 4.6. This possibility is supported by reports that both NO_3^- and NO_2^- will oxidize lower-valent technetium species in acidic solutions (Koltunov 1984b, Koltunov 1988).

Acid

$$TcO_4^- + 4\,H^+ + 3e^- \rightarrow TcO_2 + \qquad\qquad E^0 = 0.74\ V \qquad\qquad (4.1)$$

$$NO_3^- + 3\,H^+ + 2e^- \rightarrow HNO_2 + H_2O \qquad\quad E\ = 0.94\ V \qquad\qquad (4.2)$$

$$2\,HNO_2 + 4H^+ + 4e^- \rightarrow N_2O + 3\,H_2O \qquad E\ = 1.27\ V \qquad\qquad (4.3)$$

Base

$$TcO_4^- + 2\,H_2O + 3e^- \rightarrow TcO_2 + 4\,OH^- \qquad E\ = -0.36\ V \qquad\quad (4.4)$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2\,OH^- \qquad\quad E\ = 0.01\ V \qquad\qquad (4.5)$$

$$2\,NO_2^- + 3\,H_2O + 4e^- \rightarrow N_2O + 6\,OH^- \qquad E\ = 0.15\ V \qquad\qquad (4.6)$$

Results and Discussion

To determine the effect of NO_3^- and NO_2^- upon the behavior of technetium in cement wastes, two sets of technetium containing cement samples were prepared, and the evolution of the technetium species was examined over a period of 3 years. The cement samples examined here were nominally equivalent to the formulation used in the SRS saltstone (Langton 1988, Langton 1989). The dry cement consisted of 46% fly ash, 46% BFS, and 8% Portland cement.

The first set of cements was prepared using solutions with and without nitrate and nitrite as shown in Table 4.1. The technetium in these samples was reduced with alkaline Na_2S prior to incorporation into the cement to insure that the TcO_4^- was completely reduced to TcS_2. The cement was allowed to set in polystyrene (PS) cuvettes, which were closed with vinyl tape and sealed inside to two concentric, thin-walled polyethylene (PE) bags.

Table 4.1. Components of aqueous solution (moles/L)[a]

Sample	NO_3^-	NO_2^-	PO_4^{3-}
Tc-1	2.0	0.62	0.12
Tc-2	none	none	0.12
Tc-3	2.0	0.62	0.2
Tc-4	none	none	0.2

a) In addition, each sample contains 0.35M $NaAl(OH)_4$, 0.17M Na_2CO_3, 0.15M Na_2SO_4, 0.93M NaOH, and 0.22M NaCl

The behavior of these samples over time was studied using XAFS spectroscopy. Initially, in all of the samples, all of the technetium was reduced to TcS_2. Figure 4.1 shows the EXAFS spectra of the cement samples shortly after their preparation. In addition, Figure 1 contains the least-squares fits to the spectra. The structural data derived from fitting the EXAFS are given in Table 4.2. To illustrate the differences in the EXAFS spectra of the different technetium species, Figure 4.2 contains the EXAFS spectra of cement sample Tc-1 plus the spectra of $TcO_2 \bullet xH_2O$ and TcO_4^-. As is clear from Figures 4.1 and 4.2, the vast majority of the technetium in these samples has been reduced to Tc(IV) as TcS_2. These results are in good agreement with earlier work (Allen 1997).

Figure 4.1. Technetium K-edge EXAFS spectra (left) and Fourier transforms (right) for technetium bearing cement samples Tc-1, Tc-2, Tc-3, and Tc-4. The data are represented by dots and the least squares fits are represented by lines.

Table 4.2. Structural parameters derived from fitting the EXAFS spectra of the freshly prepare technetium bearing cements.

Scattering Path	Coordination Number	Distance (Å)	Debye-Waller Parameter ($\mathring{A}^2$)	ΔE_0 (eV)
Tc-1				
Tc-S	4.4(2)	2.361(3)	0.0071(4)	-9.2
Tc-Tc	1.9(1)	2.775(3)	0.0071	-9.2
Tc-2				
Tc-S	4.8(2)	2.361(3)	0.0077(4)	-11.8
Tc-Tc	2.2(1)	2.775(3)	0.0077	-11.8
Tc-3				
Tc-S	3.9(2)	2.367(4)	0.0076(5)	-11.9
Tc-Tc	1.8(2)	2.783(4)	0.0076	-11.9
Tc-4				
Tc-S	3.9(2)	2.366(4)	0.0080(4)	-11.4
Tc-Tc	2.0(1)	2.778(3)	0.0080	-11.4

Figure 4.2. Technetium K-edge EXAFS spectra (left) and Fourier transforms (right) for technetium bearing cement samples Tc-1, $TcO_2 \cdot xH_2O$, and TcO_4^- (on Reillex-HPQ). The data are represented by dots and the least squares fits are represented by lines.

In addition to the large differences in the EXAFS spectra of different technetium species shown in Figure 4.2, the X-ray absorption near edge spectra (XANES) of TcS_2, $TcO_2 \cdot xH_2O$, and TcO_4^- are very different as shown in Figure 4.3. In addition, Figure 4.3 shows least squares fits of the spectra to the sum of an arctangent function and Gaussian peaks. Both the energies and the shapes of the near edge spectra of these compounds are quite different. This difference allows the fraction of technetium that consists of TcS_2, $TcO_2 \cdot xH_2O$, and TcO_4^- to be quantified by fitting the near edge spectra to the sum of simulated spectra of the components. Figure 4.4 shows the XANES spectrum of Tc-1, 25 months after preparation. This figure also shows the fitted spectrum and the deconvolution of the fitted spectra into spectra of the technetium species present in this cement sample. The excellent agreement between the actual and simulated spectra in Figure 4.4 show that the speciation of the technetium in these cement samples can be reliably quantified in a simple, straightforward manner.

Figure 4.3. Technetium K-edge XANES spectra of (a) TcO_4^-, (b) $TcO_2 \bullet xH_2O$, and (c) TcS_2 (initial Tc-1 spectrum). Data are represented by dots, least squares fits are represented by lines.

Figure 4.4. Technetium K-edge XANES spectrum of sample Tc-1 after 2 years. The data is represented by dots, and the fit is represented by the solid line. The deconvolution of the fit into its components is also shown.

As shown in the Figure 4.4, the speciation of the technetium in the cement samples has changed greatly after 25 months of aging. In particular, the fraction TcS_2, which was initially the only species present, has declined to roughly 25%. More importantly, roughly one third of the technetium has been oxidized to the highly mobile TcO_4^- ion. The evolution of the technetium speciation in the four cement samples is reported in Table 4.3. The most noteworthy result presented in Table 4.3 is that none technetium in any of the samples remains entirely TcS_2. While much of the loss of TcS_2 is due to hydrolysis to $TcO_2 \cdot xH_2O$, a large fraction is oxidized to TcO_4^- after 25 months. Interestingly, the technetium in sample Tc-4, which does not contain nitrate or nitrite, is also appreciably oxidized after 25 months.

The data in Table 4.3 appear to show that the fraction of specific technetium species fluctuates over time. For example, the percentage of TcS_2 in Tc-1 dips to 12% after 12 months then increases to 52% after 16 months. However, these fluctuations do not actually reflect fluctuations of technetium speciation in time. Rather, they represent differences in technetium speciation in different parts of the cement sample. Because of the way the cement samples are packaged, the X-ray beam interrogates different areas of the samples in different experiments. Since the cement samples are very much larger than the X-ray beam, different areas of the cement are examined during different experiments. This lack of spatial registry between experiments does not present any difficulty initially because the technetium speciation in the sample is homogenous: all of the technetium is TcS_2. However, as the sample ages the TcS_2 is oxidized at different rates in different regions of the cement, which produces a heterogeneous distribution of technetium species.

Table 4.3. Speciation of technetium in cement samples as a function of time in months

Sample	0	3	9	12	16	25
Tc-1						
TcS_2	100%	69%	83%	29%	52%	30%
$TcO_2 \cdot xH_2O$	0%	28%	15%	40%	35%	35%
TcO_4^-	0%	4%	3%	32%	13%	33%
Tc-2						
TcS_2	99%	97%	91%	91%	65%	40%
$TcO_2 \cdot xH_2O$	1%	2%	6%	6%	35%	56%
TcO_4^-	1%	1%	2%	3%	0%	4%
Tc-3						
TcS_2	98%	97%	41%	61%	30%	28%
$TcO_2 \cdot xH_2O$	2%	2%	38%	37%	40%	47%
TcO_4^-	1%	1%	21%	2%	29%	25%
Tc-4						
TcS_2	96%	93%	73%	85%	37%	27%
$TcO_2 \cdot xH_2O$	4%	5%	27%	13%	42%	42%
TcO_4^-	0%	1%	0%	2%	21%	31%

The data in Table 4.3 are presented graphically in Figure 4.5. From Figure 4.5, the oxidation of the technetium species over time is quite apparent. In addition, the presence or absence of nitrate/nitrite does not appear to be correlated with the oxidation of Tc(IV) to TcO_4^-. The technetium in all of the samples has been oxidized. Since nitrate and nitrite cannot be solely responsible for oxidation of the technetium, the only oxidant that can account for the oxidation of the Tc(IV) is oxygen.

Figure 4.5. Fraction of technetium which is Tc(IV) as a function of cement age for cement samples Tc-1 through Tc-4. The samples containing nitrate and nitrate are represented by triangles, the samples without nitrate and nitrite are represented by squares, and the average of all samples is represented by circles. A linear least squares fit is given by the bold line, and its parameters are given on the chart.

To test the postulate that oxygen is responsible for oxidizing the reduced technetium species, a new set of technetium bearing cements were prepared analogously to the first set with the following changes. The cement mixture was the same, but the liquid phases were different as reported in Table 4.4. In addition, reduction of TcO_4^- was attempted using the same Na_2S solution as the first set of cements. However, the sulfide solution had oxidized and did not completely reduce the TcO_4^- to TcS_2. The incomplete reduction of TcO_4^- was fortuitous, as discussed below. The major difference between the samples was the containment. In this latter set of cement samples, the polystyrene cuvettes were sealed by filling the headspace with liquid epoxy, which formed an airtight seal with the cuvettes. The samples were then sealed in concentric polyethylene bags as in the first set of samples.

Table 4.4. Components of aqueous solution (M)

Sample	Cl^-	NO_3^-	NO_2^-
Tc-A	4	none	none
Tc-B	none	4	none
Tc-C	none	none	4

In addition, each sample contained 4M NaOH.

The evolution of the technetium speciation for the sealed cement samples is given in Table 4.5 and presented graphically in Figure 4.6. These results are in marked contrast to the results from cement samples Tc-1 through Tc-4. While the TcO_4^- was not entirely reduced to Tc(IV) initially, the fraction of Tc(IV) steadily *increases* over time. The reductant responsible for converting the TcO_4^- to Tc(IV) is most likely BFS. The reductant cannot be the Na_2S solution since it is obviously oxidized as evidenced by the fact that it did not completely reduce the TcO_4^- during the preparation of the samples.

The results illustrated in Figures 4.5 and 4.6 clearly implicate oxygen as the species responsible for the oxidation of Tc(IV) to TcO_4^-. In addition, these results strongly suggest that nitrate and nitrite do not appreciably oxidize Tc(IV) in the cements. The latter result is not surprising. While NO_3^- and NO_2^- are capable of oxidizing reduced technetium species at low pH, the oxidizing species are NO_2^+ and HNO_2, respectively (Koltunov 1984b, Koltunov 1988). The concentrations of these species are vanishingly small at high pH. Consequently, neither nitrate nor nitrite are likely to oxidize Tc(IV) at any appreciable rate although oxidation is thermodynamically possible.

Table 4.5. Speciation of technetium in sealed cement samples versus age in months.

Sample	0	5	9
Tc-A			
TcS_2	40%	51%	46%
$TcO_2 \cdot xH_2O$	34%	29%	42%
TcO_4^-	26%	20%	12%
Tc-B			
TcS_2	40%	44%	51%
$TcO_2 \cdot xH_2O$	36%	41%	39%
TcO_4^-	24%	16%	10%
Tc-C			
TcS_2	40%	37%	41%
$TcO_2 \cdot xH_2O$	33%	38%	42%
TcO_4^-	27%	25%	17%

Figure 4.6. Fraction of technetium which is Tc(IV) as a function of cement age for sealed cement samples Tc-A (triangles), Tc-B (squares),and Tc-C (diamonds). The average is given by circles and a linear least-squares fit to the average is given by the bold line. The parameters from the fit are given on the chart.

The role of oxygen is not overly surprising since the instability of most reduced technetium species towards oxidation by air is well known. In addition, the role of oxygen in the release of technetium from cementitious waste forms has been addressed theoretically (Smith 1993). The results illustrated in Figures 4.5 and 4.6 strongly reinforce the main theoretical conclusions: atmospheric oxygen will oxidized Tc(IV) species in BFS containing cement, although at a reduced rate; and in the absence of oxygen, residual TcO_4^- will be reduced by BFS in the cement.

Conclusion

The main implication of these results is that adding BFS to cement waste forms will not permanently immobilize technetium. The technetium is likely to be immobilized until the BFS is oxidized. This means that the technetium may be released if the waste is weathered. In addition, technetium could be released without weathering if the BFS were oxidized to some depth within the waste.

The secondary implication of these results is that nitrate and nitrite will not oxidize the Tc(IV). Therefore, the technetium in the slag-based cement is likely to remain as immobile Tc(IV) as long as oxygen is excluded. The net result is that the technetium is likely to be immobilized within the waste form until the BFS has been oxidized. Since the diffusion of oxygen through the pore fluid is slow, it is unlikely that the oxidized region of the waste will penetrate far from contact with a source of oxygen (either aerated water or atmosphere). Consequently, release of technetium is likely to be limited by weathering of the waste form to expose a new surface to oxygen.

Experimental

Preparation of Cement Samples. The desired amount of TcO_4^- (300 µl, 1.2 mg ^{99}Tc) was added to the salt solution (300 µl) along with the Na_2S solution (60 µl). The mixture was stirred and allowed to age for 1 minute. The solution darkened upon standing. The liquid was then added to1 g of cement "Mix-2" consisting of 46% pulverized fly ash, 46% blast furnace slag and 8% Portland cement. The components were mixed until homogeneous (~1 minute) then transferred into polystyrene cuvettes by pipette. Samples Tc-1 through Tc-4 were capped with vinyl tape then sealed inside two thin polyethylene bags. Samples Tc-A through Tc-C were sealed by pouring freshly prepared epoxy into the cuvettes and allowing it to cure on top of the cement, sealing the top of the cuvette.

XAFS spectra were obtained as described in part 2. Data analysis was performed by first fitting the spectra of three standards, TcS_2, $TcO_2 \cdot xH_2O$ and TcO_4^- using the sum of an arctangent and Gaussian peaks. These standard spectra were then used to fit the actual data by allowing the origin of the X-ray energy and the contribution of each component to vary. The X-ray energies of the three components were fixed with respect to each other. They were allowed to vary to compensate for small errors in the calibration of the X-ray energy.

## 5. Molecular Chemistry of Technetium

Introduction

Two principal challenges are associated with the molecular chemistry of technetium in waste media: predicting and analyzing the chemical fate of complexes of technetium over time based upon sound knowledge of its chemical behavior, and exerting control over the distribution/dispersal of the element by stabilizing the coordination environment toward unwanted side reactions (e.g., hydrolysis, oxidation). For instance, questions may be raised regarding the performance of cement or glass waste forms containing technetium, as experimental studies have indicated reduced technetium sulfides or oxides in these waste forms can be oxidized as oxygen diffuses into the matrix, resulting in the release of TcO_4^-(Allen 1997, Smith 1993, Marples 1991). These concerns can only be addressed by devising means of better controlling the oxidation state of the technetium in the matrix, or by chemically "fixing" (coordinating) the technetium to the substrate in a manner resistant to hydrolysis.


Results and Discussion

To assess these approaches to stabilization of technetium, synthetic studies associated with this project involved both attempts to prepare molecular complexes of lower-valent technetium that would be more resistant to hydrolysis, and examination of the viability of strongly binding the metal to immobile supports (using organic polymers as prototype supports). In order to pursue these investigations, however, it was first necessary to devise improved methods for preparation of common starting materials. A number of technetium and rhenium complexes possessing terminal oxo or nitrido groups and halide ligands have been reported in the literature, but their widespread use has been hindered by difficult and low-yield syntheses (Cotton 1979, Davison 1982, Nelson 1954, Rulfs 1955, Liese 1981, Baldas 1991, Cotton 1966, Rose 1996, Baldas 1984). In the early

stages of this project, we were able to study the syntheses of complexes of the formulae $[MOX_4]^-$, $[MNX_4]^-$, and $[MX_6]^{2-}$ (M = Tc, Re; X = Cl, Br, I) and examine possible mechanisms for their interconversion. To avoid hydrolysis in the generation of these precursors, synthetic studies were carried out in non-aqueous media, utilizing a variety of halide transfer agents, including PX_5 and Me_3SiX in reactions with high-valent technetium and rhenium oxides.   Synthetic routes to a variety of complexes, including MO_3X, fac-$[MO_3X_2]^-$, cis-$[MO_2X_4]^-$, $[MOX_5]^-$, MOX_4, $MOX_4(L)$, $[MOX_4(L)]^-$, and $MOX_3(L)_2$ (M = Tc, Re; X = Cl, Br, I; L = THF, MeCN) were devised. Vibrational and electronic spectroscopies proved best suited to characterize the metal oxohalide complexes; EPR spectroscopy was also utilized to examine the paramagnetic species in the series. Though far less commonly employed, ^{17}O and ^{99}Tc NMR spectroscopies were powerful tools in the identification and study of interconversion of species in solution.

The reaction of high-valent metal complexes with phosphorus pentahalides or trimethylsilylhalides proved the most reliable synthetic routes to a variety of oxohalide species. Schemes 5.1 and 5.2 depict the interconversion of chloride-containing species for technetium and rhenium. Comparable schemes have been derived for bromide- and iodide-containing products, although these ligands are less likely to support high-valent metals. The molecular structures of several oxohalide complexes were examined by single crystal x-ray diffraction. Reactions of the permetallates $[MO_4]^-$ (M = Tc, Re) yielded solely anionic oxohalide complexes, while the use of neutral starting materials such as $MO_3(OSiMe_3)$ more often resulted in the formation of neutral oxohalide complexes.   The phosphorus pentahalide reagents react much more quickly than trimethylsilylhalides, but the phosphorus oxotrihalides formed as byproducts of metal halogenation can act as ligands, influencing the identity of the metal complex isolated from solution. Both phosphorus pentahalide and trimethylsilylhalide reagents react more readily with technetium oxo ligands than with the rhenium oxo analogs. These relative rates are consistent with the weaker metal-oxo bond strengths anticipated for second-row transition metals. Within a series of halide reagents (e.g., $SiMe_3X$, X = Cl, Br, I), the more electrophilic reagents (I >> Br > Cl) resulted in more facile halide metathesis.
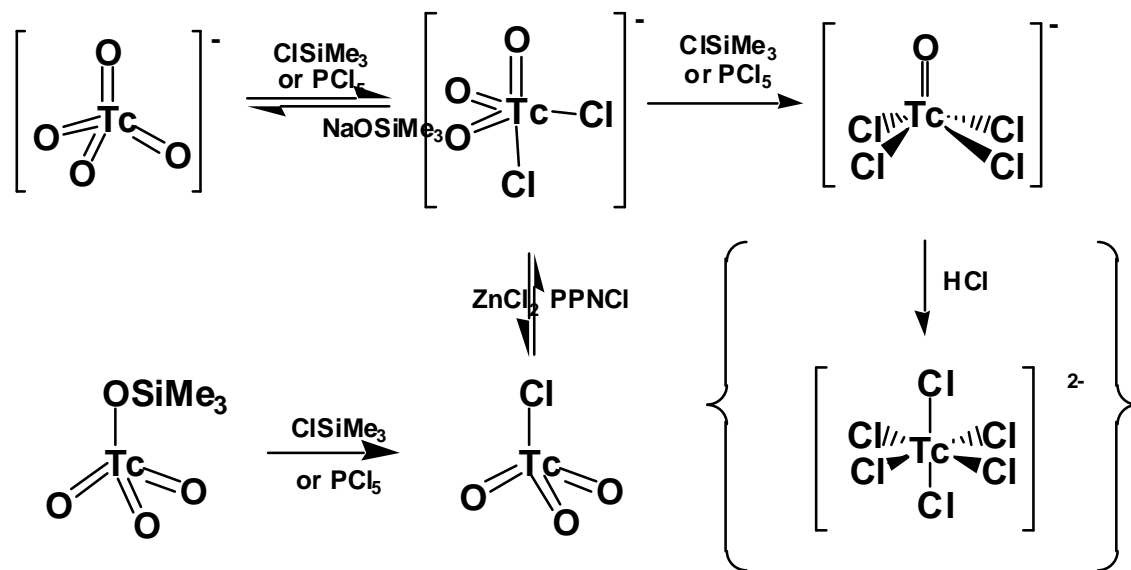
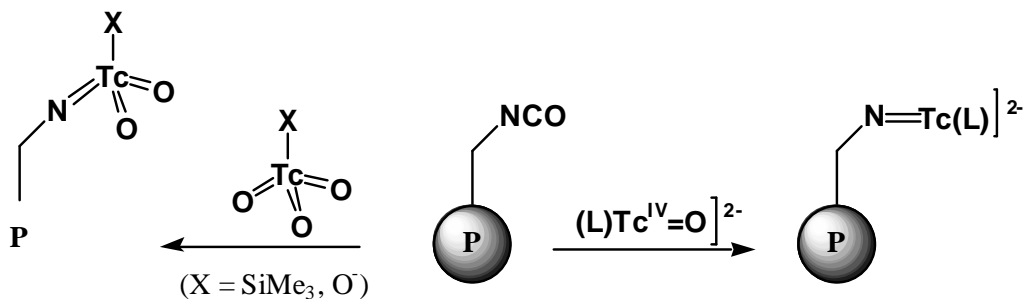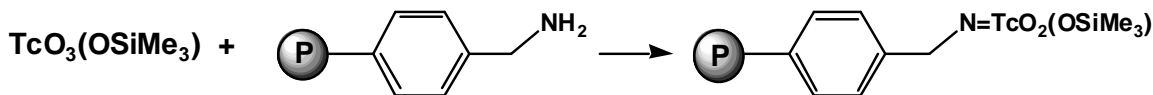**Scheme 5.1**: Synthesis of technetium oxychloride complexes.
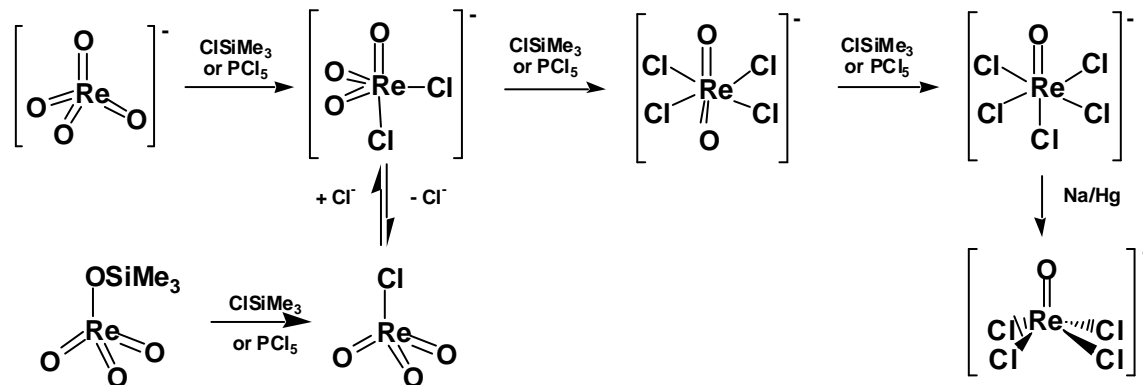
Scheme 5.2: Synthesis of rhenium oxychloride complexes.

With the availability of a broad range of precursors, the second phase of the studies involved attempts to prepare Tc(IV) complexes containing tank waste-relevant complexants such as EDTA, citrate, and phosphate. Any procedure employing the tetravalent starting material K_2TcCl_6 in aqueous media has generally resulted in hydrolysis rather than substitution when the reactions are conducted under neutral or basic pH conditions. Under acidic conditions, no reaction is observed between K_2TcCl_6 and the complexants. Attempts were made to generate species in alcoholic media, in the hopes of avoiding competitive hydrolysis pathways. K_2TcCl_6 did not react with EDTA in neutral methanol solutions, nor does a reaction take place in acidified methanol or ethanol. Subsequent investigations were directed at the use of the bromide analog, K_2TcBr_6; some literature precedent exists for reactivity of this species in methanol (Alberto 1986). Concurrently, reactions of the fluoride analog, K_2TcF_6 were pursued under aqueous conditions in the hopes that this species would be less sensitive to hydrolysis (Alberto 1990). These approaches did not prove fruitful in generating complexes amenable to characterization; either no reaction occurred (e.g., the fluoride complex K_2TcF_6 was found to be quite resistant to metathesis), or mixtures of products were generated.

The second approach to the synthesis of lower-valent Tc complexes was the use of reductants such as hydrazine and hydroxylamine on pertechnetate in the presence of the complexants. While these studies met with no more success in the preparation of coordination complexes of Tc(IV), they did yield important confirmation of literature reports that these reductants can under certain conditions generate metal nitride species (Chatt 1969). We have verified this by confirming isolation of a Tc(V) nitride complex by reduction of pertechnetate by hydrazine in the presence of dithiocarbamate as a complexing ligand (Baldas 1986). This observation is significant in light of the fact that nitrogen-based reductants such as hydrazine and hydroxylamine are commonly used to generate Tc(IV) *in situ* for environmental speciation and stability studies (Pikaev 1996). The technetium nitride moiety is quite robust under a range of conditions, and its behavior is very different from that of Tc(IV) (Baldas 1991, Baldas 1986, Baldas 1984). Reduction of pertechnetate with hydroxylamine in the presence of complexants appears to be significantly slower than reductions using hydrazine under comparable conditions.

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Further efforts to identify means of stabilizing technetium in "immobilized forms" were directed at the development of routes to append technetium to immobile "supports." In particular, studies were targeted at the condensation of pertechnetate and perrhenate with reactive sites on polymeric substrates. Organic polymers were chosen as the initial substrates for study based upon the commercial availability of samples with well-characterized dispersion of chemical sites of attachment, and because of their relative ease of chemical functionalization. A variety of polymer supports are now commercially available for solid phase synthesis from hydrocarbon media, with chemical functionality and the appropriate degree of cross-linking to insure adequate pore size and mechanical stability. The bulk of these are polystyrene-based polymers, often cross-linked with divinylbenzene. The most common family is directly functionalized polystyrene. The swelling properties of polystyrene have been modified in some commercial analogs by grafting other polymer chains (polyoxyethylenes, polyacrylamides) onto the polystyrene backbone.

The next step in development of the chemistry was selection of an appropriate strategy for metal attachment. The main goal in design of the system was to generate robust metal-support interactions that would provide a matrix for radionuclide entrainment resistant to leaching or oxidative degradation. Approaches to radionuclide capture have most often involved the use of multidentate coordinating anionic ligands. Unfortunately, the strength and specificity of metal ion attachment in these systems can often be oxidation state dependent, and competition with hydrolysis remains a problem (as was observed in attempts to prepare discrete molecular complexes as previously described). In order to circumvent these difficulties, chemical protocols were examined that generated a metal-functional group covalent bond. Methods were explored based upon their analogy to known solution chemistry (Bryan 1993, Chatt 1962, Chatt 1964). The most successful method of attachment of those explored was the generation of metal-imido (M=NR) ligands either by reaction of metal oxo species with pendant isocyanate groups (liberating carbon dioxide), or by direct condensation with amine functional groups (Scheme 5.3). A variety of approaches was examined to generate pendant isocyanate groups on polystyrene; the most effective was treatment of the amine-based polymer with triphosgene. To provide a baseline assessment of the degree of functionalization of the polystyrene beads (so that subsequent metal uptake could be quantified), a protocol was developed to react the functionalized polymer with a base, and subsequently titrate the supernatant. Employing functionalized polystyrene with a commercial specification of 1.5 mequiv NH_2/g resin, the resultant isocyanate-functionalized polymer was determined to have >0.7 mequiv. NCO/g resin.

$TcO_3(OSiMe_3)$ + **P**—⬡—CH_2NH_2 ⟶ **P**—⬡—$N=TcO_2(OSiMe_3)$

$$\underset{\textbf{P}}{\underset{|}{}}N=\overset{\overset{X}{|}}{Tc}\overset{O}{\underset{O}{\diagdown}} \longleftarrow \overset{\overset{X}{|}}{\underset{O}{Tc}}\overset{O}{\underset{O}{\diagup}} \quad \text{(X = SiMe}_3\text{, O}^-\text{)}$$

P—CH_2—NCO $\xrightarrow{\ (L)Tc^{IV}=O \big]^{2-}\ }$ **P**—CH_2—$N\!=\!Tc(L)\big]^{2-}$

Scheme 5.3. Binding of high-valent technetium species at polymer supports.

Reaction of the polymer with metal-containing species ($MeMO_3$ or Me_3SiOMO_3, M = Tc, Re) with polymer was carried out in organic media to permit maximum swelling of the polymer, and consequently maximum contact probability for reaction. Uptake of the metal by the polymer was rapid, as determined both by the color change of the polymer and by measurement of metal-containing species in the supernatant after contacting, in a once-through column configuration.

Characterization of the polymer-bound metal species was carried out principally by vibrational spectroscopy (indicating a metal-oxo species was present) and by EXAFS spectroscopy. While the data is fit well by a model in which the metal is appended to the polymer in the form of a complex of the formula **P**-N=MRO_2 (**P** = polymer support, M = Tc; Figure 5.1), the oxidation state stability of the metal differs between technetium and rhenium. Technetium is maintained in the heptavalent oxidation state throughout attachment. Rhenium is appended to the polymer either as Re(V) or Re(VII), depending on the nature of the starting material (Figure 5.2).

TcO_4^-

Atom	Coord. #	Distance	Debye-Waller	E_o
O(N)	4.97(12)	1.722(1) Å	0.0027(2) Å^2	-6 eV

Fourier Transform

OSiMe$_3$

Atom	Coord. #	Distance	Debye-Waller	E_o
O(N)	4.04(9)	1.717(1) Å	0.0030(1) Å^2	-10 eV
Si	1.6(2)	2.468(3) Å	0.0050(7) Å^2	-10 eV

Fourier Transform
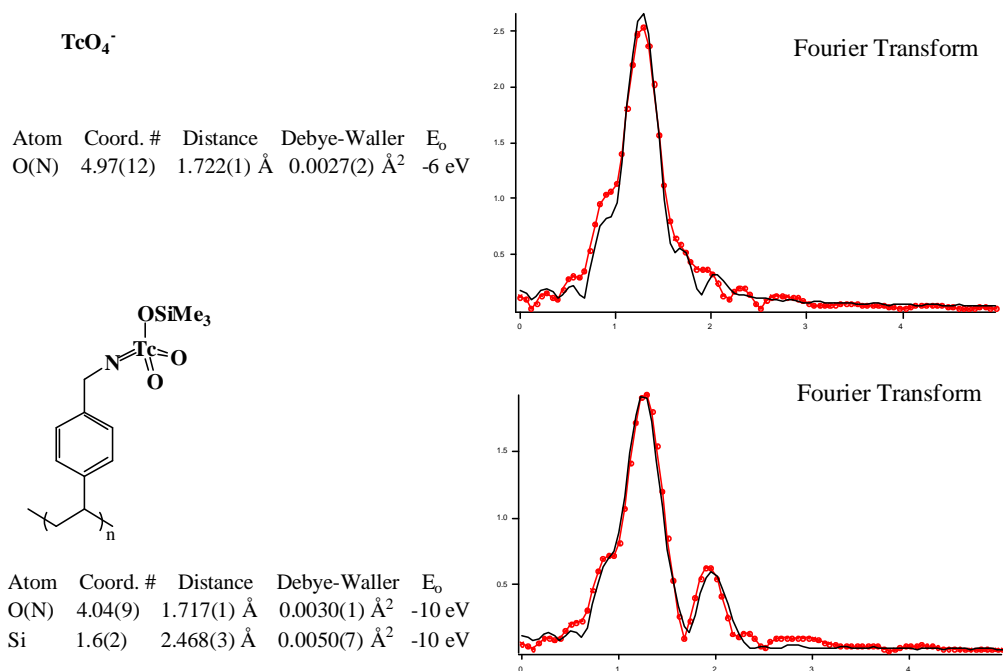
Figure 5.1. EXAFS of a polymer bound Tc(VII) species.

Atom	Coord. #	Distance	Debye-Waller	E$_o$
O(N)	1.39(7)	1.696(6) Å	0.0007 Å^2	-14 eV
O(N)	3.2(6)	2.09(2) Å	0.014(4) Å^2	-14 eV
O(N)	1.5(5)	2.275(7) Å	0.002(2) Å^2	-14 eV

(dark green-brown) Re(V)

Atom	Coord. #	Distance	Debye-Waller	E$_o$
O(N)	4.6(1)	1.724(1) Å	0.0009(1) Å^2	-10.3 eV

Re(VII)

(light lime green)

+ H$_2$O$_2$/THF

Atom	Coord. #	Distance	Debye-Waller	E$_o$
O(N)	4.4(2)	1.722(2) Å	0.0008(2) Å^2	-10.5 eV

Re(VII)

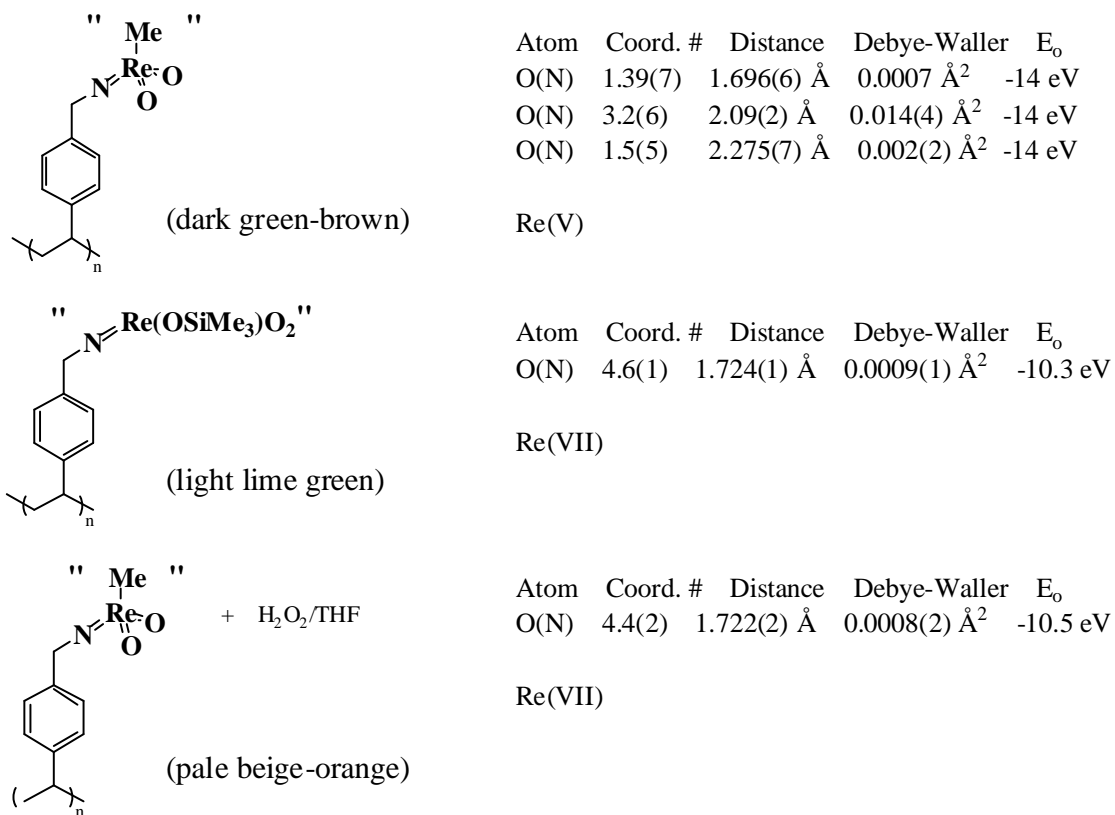(pale beige-orange)

Figure 5.2. EXAFS results for polymer-bound rhenium complexes.

Subsequent investigations have centered on evaluation of the chemical stability of the polymer–bound metal. The solid-support linkage is stable to large excesses of chlorotrimethylsilane and even aqueous solutions with high hydrogen peroxide concentrations. However, based on color changes incurred in this latter reaction in the case of rhenium, the polymer-bound complex appears to undergo a chemical transformation, presumably oxidation of a reduced metal complex bound to the support. This is confirmed by EXAFS data, which demonstrate oxidation to rhenium (VII) (Figure 5.2). The most rigorous of the leaching studies have been evaluation of the stability the metal-imido linkage to aqueous acid and base. Representative results for batch 24 hr leaching studies are presented in Figure 5.3. The resistance of the complex to leaching in aqueous media is largely due to the hydrophobicity of the polymer. Treatment with aqueous NaOH and HCl at 0.1 and 10mM concentrations result in no appreciable leaching. More forcing conditions were assessed by examining leaching in the presence of organic promoters (ethanol/toluene, tetrahydrofuran) to effect swelling of the polymer support. Only under the most forcing conditions (10mM base), was a significant fraction of the technetium removed from the support.
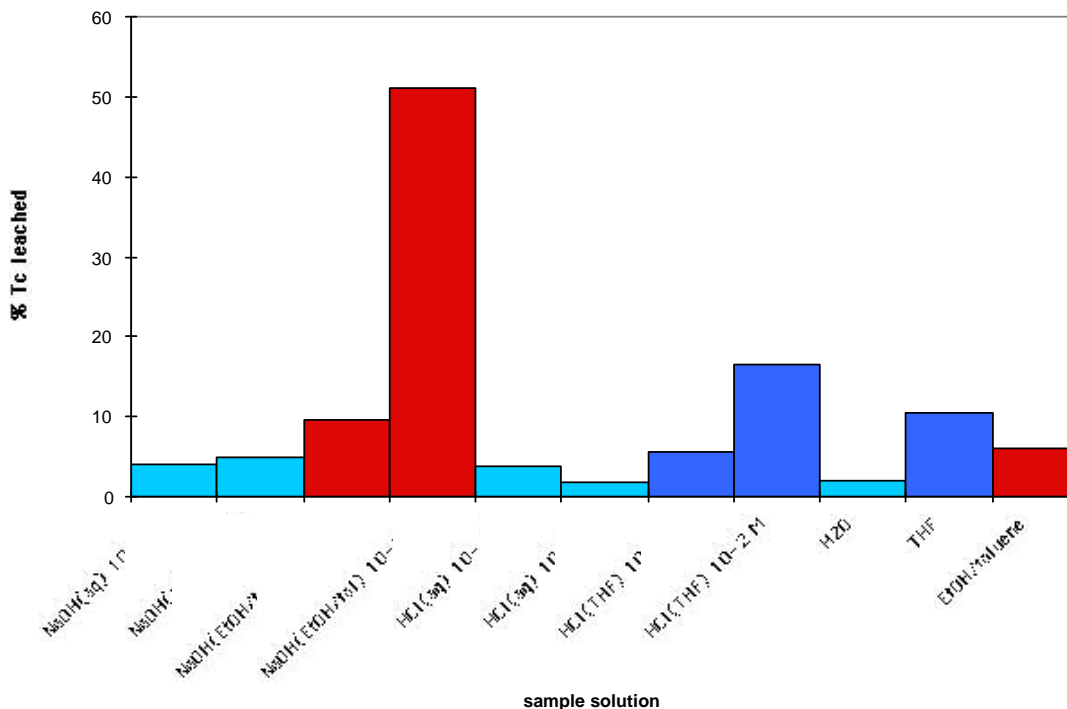
Figure 5.3. Leaching results from technetium bearing resins over 24 hours.

In molecular chemistry of technetium, one of the strategies that has been most effective in stabilizing metal-imido linkages to hydrolysis has been the imposition of steric congestion at the site of the nitrogen ligand (Bryan 1993). In order to suggest appropriate modifications to the polystyrene support, it will be necessary to develop a better understanding of the coordination of the metal to the polymer. To improve our ability to characterize the structural nature of the support-bound metal complexes and the linkage whereby the metal is attached to the polymer, we have extended our synthetic functionalization of polystyrenes to include the development of cleavable linkers, which can be selectively detached from the polymer after reactions with the metal complexes. A representative member employing a cleavable silyl linker has been prepared and is under evaluation for metal binding (the appropriate cleavage reaction is depicted in Scheme 5.4).

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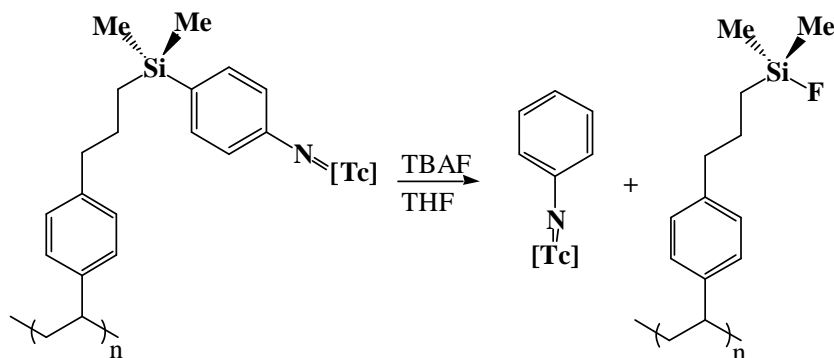
Scheme 5.4. Development of a cleavable linker.

Finally, we have begun to examine solid and soluble polymer substrates, particularly derivatives of polyethyleneimine (PEI) for use either directly as a water-soluble polymer additive, or as a solid substrate when supported on silica gel (Figure 5.4). This polymer may be readily modified at the secondary amine with the appropriate linkers. Various forms of PEI also have primary amine end groups that may be appropriate to derivative as isocyanate groups, to take advantage of comparable condensation routes to those previously demonstrated for metal attachment.
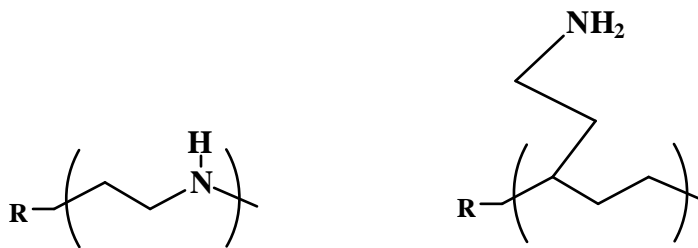
Figure 5.4. Soluble polymer substrates.

Experimental

All work was performed under inert atmosphere using conventional Schlenk and glove box techniques. Solvents were purified by distillation from standard drying agents under inert atmosphere. X-ray absorption fine structure spectroscopy was performed as described in section 2.

6. Relevance to EM Issues

Behavior of Technetium in High-Level Waste

This research has identified a facile route to radiolysis of TcO_4^-: reduction by NO_3^{2-}. If a suitable O^- scavenger is present to prevent oxidation of reduced technetium species back to TcO_4^-, radiolytic reduction of technetium is rapid. Scavengers capable of rapidly reacting with O^- are present both in the waste tanks at Hanford, oxalate, formate, glycolate, aminopolycarboxylates (Agnew 1996), and at the Savannah River Site, oxalate (Hester 2000). In addition, few species present in the supernate are capable of competing with TcO_4^- for NO_3^{2-}. These species are principally water, chromate, and permanganate; nitrite reacts very slowly, if at all, with NO_3^{2-}. However, chromate and permanganate will have little net effect upon the radiation chemical yield for TcO_4^- unless they are present in very high concentration. However, this does suggest that tanks containing high concentrations of ^{137}Cs and organic compounds will have correspondingly large amounts of Cr(III) in their sludge.

Much of the technetium present in certain high-level waste tanks may be reduced. For example, Table 6.1 shows the initial rate of reduction of TcO_4^- based upon the data reported by Agnew and including only competition from water. On average, TcO_4^- undergoes radiolysis at a rate of ~1% per day. In addition to radiolytic reduction of TcO_4^-, chemical reduction of TcO_4^- catalyzed by noble metal (Ru, Rh, Ir) colloids has also been reported by Schroeder and coworkers (Bernard 1999). This pathway may also be important for the reduction of TcO_4^- in tanks that have high concentrations of organic chelators and chelator fragments.

Table 6.1: Calculated initial rate of TcO_4^- radiolysis, Hanford Tanks

Tank	Initial $\%(-TcO_4^-)$ per day
SY-101	1.5%
SY-103	1.4%
AN-102	1.0%
AN-107	1.2%
AW-101	0.8%
AP-106	0.2%
AP-102	0.8%

Of greater relevance than the mechanism of TcO_4^- reduction is the nature of the reduced technetium species. In the absence of certain stabilizing ligands, the major reduced technetium species is $TcO_2 \cdot xH_2O$, which will be present in the sludge. Other than the potential for technetium volatilization during vitrification (Darab 1996), the presence of this reduced technetium species should not cause problems.

On the other hand, the presence of soluble, reduced technetium species does present problems. This research has identified Tc(IV) diolates as possible candidates for the reduced technetium species, which is in agreement with observations performed by Blanchard on actual tank waste (Blanchard 1995). In addition, research by Schroeder and coworkers has identified glycolate and gluconate complexes of technetium that are stable in aqueous alkaline solution (Schroeder 2000). The stability of the gluconate complex is in good agreement with the results presented here. Since gluconic acid is a polyol with

five hydroxyl groups, it should be capable of forming Tc(IV) complexes that are very stable in alkaline solution. The possibility of forming glycolate complexes in alkaline solution is of greater concern given the relatively high concentration of glycolate present in certain tanks. The results from radiolysis of TcO_4^- with added glycolate have not been conclusive, and are ongoing.

The soluble, reduced technetium species resulting from radiolysis in 2M NaOH are all air sensitive and are oxidized back to TcO_4^- over a period of one week at ambient temperature. Except for thiolate complexes (Davison 1980), all known reduced technetium complexes, which are stable to hydrolysis in alkaline aqueous solution, are air sensitive. However, at low pH, many Tc(IV) complexes, especially the aminopolycarboxylate complexes, are stable towards oxidation (Linder 1989); therefore, reduced technetium species are much easier to oxidize at high pH.

The oxidation of reduced technetium species has been addressed by Schroeder and coworkers for actual waste from tank AN-107 (Schroeder 1998). They find that oxidation of the reduced technetium species generally requires the oxidation of the nitrate and organic material present in the waste presumably due to the slow kinetics of oxidizing the reduced technetium species. However, based upon reports by Blanchard and Schroeder (Blanchard 1995, Schroeder 1998), the reduced technetium species in the CC waste are also air sensitive although they are oxidized slowly at ambient temperature. These species could conceivably be oxidized at a greater rate by aerating them at elevated temperatures in a manner analogous to that used to oxidize Cr(III) to CrO_4^{2-} (Rapko 1998). However, oxidation would need to be preceded by the removal of ^{137}Cs from the supernate to prevent radiolysis of TcO_4^-.

Behavior of Technetium in Cementitious Waste Forms

The research described in Section 5 underscores the role that oxygen plays in controlling the stability of reduced technetium species. In the absence of oxygen, the blast furnace slag will reduce TcO_4^- to immobile Tc(IV) species. However, if oxygen is present, these Tc(IV) species will be oxidized to the environmentally mobile TcO_4^- anion. The most important factor that determines the fate of the technetium is the rate of diffusion of oxygen through BFS loaded grout. While a single theoretical study has been reported (Smith 1993), to our knowledge, no experimental studies have been reported addressing the problem of air oxidation of the reduced technetium species back to TcO_4^-. All reported studies of technetium leaching from BFS loaded grout have used cement samples less than 3 months old.

The results from Section 5 show that BFS grout will not indefinitely immobilize technetium if the waste form is exposed to the atmosphere. The question is whether the rate of technetium release from the waste form will remain acceptable if the technetium is oxidized to TcO_4^-. This question has been largely addressed by Langton and coworkers. Although the reported technetium leach rate of BFS grout was very low, the technetium leach rate for grout without BFS was still below regulatory limits (Langton 1988). However, oxidized BFS grout is not identical to the cement grout used in the TcO_4^- release experiments.

Although the reduced technetium in BFS grout will eventually be oxidized to TcO_4^-, this fact alone does not mean that BFS grout is not the most suitable waste form for technetium. Few reports of the long term behavior of technetium in other waste forms exist, although technetium has been reported to readily leach from glass waste forms

(Ebert 1995). Since the resistance of technetium to oxidation in other waste forms has not been addressed in detail, the possibility exists that no ideal, simple waste form can prevent the oxidation of reduced technetium species to TcO_4^-.

Recommendations

If soluble reduced technetium species remain a problem for the disposition of the CC waste at the Hanford Site, further research could address whether aeration of the waste at elevated temperature, after removal of the ^{137}Cs and ^{90}Sr, can oxidize these species to pertechnetate. To our knowledge, this route has not been investigated. In addition, technetium reduction in the high-level waste may be more widespread than previously thought. This means that, apart from the CC waste, the sludge will contain greater amounts of $TcO_2 \cdot xH_2O$.

The long-term resistance of BFS grout to technetium leaching has not been addressed in actual waste packaging. The issue that may need to be addressed is the rate of technetium oxidation in actual saltstone. In addition, the behavior of technetium in alternative waste forms should be examined to determine whether other waste forms could prevent the oxidation of technetium to the mobile TcO_4^- ion.

Project Productivity

The objective of this research was to provide fundamental information to understand the behavior of technetium in two areas of interest to DOE: the complex environment of the high level nuclear waste tanks at the Hanford and Savannah River Sites and the behavior of technetium in solid state environments analogous to waste forms.

This project has successfully addressed scientific issues in both areas and has been most productive in addressing the solution chemistry. Section 5 addresses issues related to the synthesis of technetium model complexes. Section 2 identifies the Tc(IV) complexes that can be formed in highly alkaline solution by radiolysis. Section 3 describes the mechanism of TcO_4^- radiolysis in highly alkaline solution containing excess nitrate.

Some of the most pressing issues relevant to the chemistry of technetium in solid phases have been addressed. Specifically, the behavior of technetium in solid state materials analogous to slag-based waste forms has been investigated. The role of oxygen in the speciation of technetium is extremely important. The behavior of technetium in materials specifically designed to resist oxidation have also been examined. However, none of the materials investigated possess all of the qualities desirable for immobilizing technetium: low cost/easy synthesis, resistance to oxidation, low rate of technetium release. Answers to these questions will require research investigations and will have to be addressed in the future.

Personnel Supported

Jerome J. Bucher, Staff Scientist
Lawrence Berkeley National Laboratory

Dr. Carol J. Burns, Senior Staff Scientist
Los Alamos National Laboratory

Dr. Norman Edelstein, Senior Staff Scientist
Lawrence Berkeley National Laboratory

Dr. Michael G. Fickes, Postdoctoral Fellow
Los Alamos National Laboratory

Dr. Wayne W. Lukens, Scientist
Lawrence Berkeley National Laboratory

Dr. David K. Shuh, Senior Staff Scientist
Lawrence Berkeley National Laboratory

Publications. and Presentations

Publications

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Lukens WW, PG Allen, JJ Bucher, MN Edelstein, DK Shuh. 2000 "Radiation Chemistry of Technetium in Highly Alkaline Solution." American Chemical Society Meeting, San Francisco, California.

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Amonette AB, RD Orr, DS Burke, JG Darab, SM Ponder, TE Mallouk. PG Allen, JJ Bucher, DL Caulder, IM Craig, P Liu, WW Lukens, DK Shuh. 1999 "The Removal of Pertechnetate Anions from Simulated Aqueous Radioactive Tank Wastes Using Supported Zero-Valent Iron." American Chemical Society National Meeting, New Orleans, Louisiana. [Collaboration with other Technetium EMSP, Mallouk (Pennsylvania State University)]

Interactions

The interaction of technetium with ferragels (supported, colloidal iron metal) has been investigated by XAFS techniques at Stanford Synchrotron Radiation Laboratory (SSRL) with the Mallouk Group of the Pennsylvania State University and J. Darab of Pacific Northwest National Laboratory (PNNL). They have an EMSP to study the reduction of waste species, including pertechnetate, by ferragels. This collaborative venture was fostered by the first EMSP National Workshop at which both parties expressed mutual interest in the chemistry of technetium in the ferragel system and in using XAFS to characterize the technetium-ferragel interaction. Two SSRL XAFS runs have examined the technetium ferragel systems and have provided valuable information abut the nature of the reduced technetium species.

Future Work

Future work in this area will be performed under a renewal of this EMSP program. Two areas will be investigated: methods for removing reduced technetium species from highly alkaline solutions and incorporation of technetium into solid state materials. As illustrated by Schroeder, oxidation of reduced technetium species may require the oxidation of both the nitrite and organic materials in the waste unless the technetium species can be specifically oxidized (Schroeder 1998). As an alternative, methods for removing reduced technetium species, specifically Tc(IV) and Tc(V) will be investigated. Such techniques could greatly simplify the processing of CC wastes.

The incorporation of technetium into solid state materials will also be studied. One major question, which needs to be addressed, is whether Tc(IV) will remain reduced in any waste form when it is exposed to atmospheric oxygen. To answer this question, synthetic techniques will be developed for incorporating Tc(IV) in various hosts. The electronic structure of the technetium species and its resistance to oxidation will be investigated.

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