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RESEARCH PROGRAM TO INVESTIGATE THE FUNDAMENTAL CHEMISTRY OF TECHNETIUM

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Executive Summary

The objective of this research is to increase the knowledge of the fundamental technetium chemistry that is necessary to address challenges to the safe, long-term remediation of high-level waste posed by this element. These challenges may be divided into two categories: unexpected behavior of technetium in high-level waste tanks at the Hanford and Savannah River Sites and the behavior of technetium in waste forms.

Unexpected technetium chemistry, which has caused concern about the remediation of high-level waste tanks, has been observed at both the Savannah River and Hanford Sites. At the Savannah River site, high concentrations of technetium were found in the insoluble sludge fraction of the waste, which was surprising since technetium was expected to exist only as soluble pertechnetate anion, TcO_4^-. Since the presence of technetium in the sludge greatly increases the amount of technetium in the residual waste that remains in tanks after closure, tank heels, the source term for technetium leaching from closed tanks could be greater than anticipated. Technetium (^{99}Tc) is one of the fission products of greatest concern for environmental contamination due to its long half-life, 213,000 yr., and the high solubility and mobility of pertechnetate, which is the stable form of technetium in aerobic environments.

At the Hanford Reservation, technetium posed a different challenge related to the separation of technetium from the water soluble fraction of the waste, which will be vitrified and placed in a repository at the Hanford Reservation. Initial performance assessments of this repository showed that ~80% of the technetium would have to be removed from this Low Activity Waste (LAW) stream. The technetium separation is currently believed to be unnecessary (as of January

2003) and may be removed from the process. However until this point, this technetium separation was thought to be necessary. The technetium separation was based upon ion-exchange of pertechnetate and worked well for a number of the high-level waste tanks, but worked poorly for certain tanks (Complexant Concentration waste) due to the presence of unknown, soluble, nonpertechnetate species.

The research goals in this area were to understand how pertechnetate could be reduced in high-level waste and to identify the problematic nonpertechnetate species. Our previous research identified a radiolytic pathway involving the reaction of nitrate with hydrated electrons that reduced pertechnetate under conditions similar to those found in high-level waste. This pathway explains both the presence of insoluble technetium species ($TcO_2 \bullet 2H_2O$) in tanks at the Savannah River Site and the presence of reduced technetium species at the Hanford Site. During this research period, the problematic, non-pertechnetate species were identified as Tc(I) carbonyl complexes derived from either $Tc(CO)_3^+$ or $Tc(CO)_2(NO)^{2+}$. While this is a surprising result, it is consistent with the known chemistry of technetium. Identification of the nonpertechnetate species enables rational investigation of methods to either oxidize these species to pertechnetate or remove them using appropriate separation techniques.

In addition, Tc(IV) gluconate was shown to be formed from the reaction of $TcO_2 \bullet 2H_2O$ with alkaline gluconate solutions. This reaction has important implications for one proposed method to overcome the separation problem posed by the presence of the nonpertechnetate species. The proposal involved diluting Complexant Concentrate waste using waste from other tanks to decrease the concentration of the nonpertechnetate species to acceptable levels. However, if

these tanks contain $TcO_2 \bullet 2H_2O$ due to radiolytic reduction, soluble Tc(IV) gluconate could be formed due to gluconate in Complexant Concentrate waste. Although Tc(IV) gluconate would not be removed by ion exchange, Tc(IV) gluconate is relatively easy to oxidize, unlike Tc(I) carbonyl complexes,. If technetium separation again becomes part of the process for vitrification of Hanford waste, the possibility of forming Tc(IV) gluconate should be investigated.

Another research area addressed by this program is the behavior of technetium in waste forms. As noted above, technetium is a fission product of great concern for environmental contamination due, in large part, to the stability and mobility of pertechnetate. Two waste forms, reducing grout and glass, are employed to immobilize technetium. Reducing grout is the low activity waste form, Saltstone, at the Savannah River Site and is also used to immobilize technetium in the tank heels of closed high-level waste tanks. Glass is used as the high-activity waste form at both the Savannah River and Hanford Sites and is also used as the low-activity waste form at the Hanford Site. The behavior of technetium poses different challenges to its long-term immobilization in these two waste forms.

In reducing grout waste forms, the main issue is the leach rate of technetium. Since the aqueous diffusion coefficients of pertechnetate and nitrate are similar, their effective diffusion coefficients from grout waste forms are also similar. However, the leach rate of technetium can be greatly decreased by reducing pertechnetate to Tc(IV) species that have small effective diffusion coefficients. This approach to chemical immobilization is employed in reducing grout waste forms to better immobilize technetium. However, the Tc(IV) species created in reducing grout waste forms are not stable towards oxidation under aerobic conditions and may not remain

reduced. Consequently, the technetium leach rate from reducing grout could increase as technetium is oxidized.

The results of our research clearly illustrate that the Tc(IV) species in reducing grout waste form are rapidly oxidized to pertechnetate by atmospheric oxygen. However, this result does not mean that all Tc(IV) in actual waste will be quickly oxidized since the oxidation rate is controlled by diffusion and reaction of oxygen with the reducing grout matrix. The rate of matrix oxidation was found to be consistent with the mechanism proposed by Smith and Walton, and is relatively slow. In an actual waste form, the degree of oxidation would depend upon the spacing between cracks that are accessible to oxygenated surface water. Very little of the Tc(IV) would be oxidized in an intact Saltstone monolith, but a much higher percentage could be oxidized if the monolith is heavily cracked and these cracks are accessible to surface water. Since the leach rate of technetium changes greatly depending upon its oxidation state, oxidation of Tc(IV) in the grout waste form could affect its performance.

In glass waste forms, the main concerns are loss of volatile technetium species during vitrification and leaching of technetium from the final waste form. Both topics have been previously studied; however, little is known about the actual speciation of technetium in borosilicate glass and the role of technetium speciation in volatility and leaching. Our research identified the technetium species present in borosilicate glass prepared under conditions analogous to those used to prepare DOE glass waste forms: vitrification of a mixture of glass precursors or glass frit and an alkaline waste surrogate. The species found in the glass are pertechnetate, crystalline TcO_2 inclusions, and Tc(IV) homogenously incorporated in a glass

matrix. The synthetic conditions determine which species is present. The routes that lead to technetium volatility are in agreement with previous work. Loss of a large fraction of the technetium is likely due to oxidation of TcO_2 to Tc_2O_7. The alkali metal salts of pertechnetate are also somewhat volatile, especially $CsTcO_4$.

Collaborations were important part of this research. Discussions with Dr. Norm Schroeder of Los Alamos National Laboratory about the chemistry of technetium and Hanford high-level waste were essential in identifying the nonpertechnetate species as Tc(I) carbonyl complexes. Development of the glass chemistry project was facilitated by discussions with Dr. Isabelle Muller and Dr. David McKeown of the Vitreous State Laboratory at The Catholic University of America who provided glass frit and representative glass compositions as well as experimental advise.

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We thank Dr. Norman Schroeder of Los Alamos National Laboratory for essential discussions about the behavior of technetium in the high-level waste at the Hanford Reservation. We also thank Dr. Isabelle Muller and Dr. David McKeown, both at the Vitreous State Laboratory of The Catholic University of America for helpful discussions about glass chemistry and for providing compositions of Hanford Low Activity Waste glasses as well as representative samples of glass frit. We thank Dr. Corwin Booth of Lawrence Berkeley National Laboratory for helpful discussions about EXAFS and XANES spectroscopy and for the use of the computer code "fites" used to fit the XANES data of the cement samples.

I. Introduction

Technetium (^{99}Tc, β emitter, 0.29 keV max, $\tau_{1/2} = 2.1\times10^5$ 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 pertechnetate, TcO_4^-, because the chemically stable form of technetium in oxidizing environments. 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, Radzinski et al. 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. Technetium forms volatile oxides, Tc_2O_7 and $CsTcO_4$, when heated under oxidizing conditions.(Migge 1990; Darab and Smith 1996) 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 proses 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 and Smith 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, Spence et al. 1990; Smith and Walton 1993; Allen, Siemering et al. 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, Spence et al. 1990; Smith and Walton 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, Siemering et al. 1997) Theoretical studies have suggested that oxygen diffusing through the cement can oxidize Tc(IV) to TcO_4^-.(Smith and Walton 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 fundamental 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 increased fundamental knowledge 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 addresses these needs to provide an improved basis for DOE to address its technetium-related problems.

Approach

An integrated approach was used to investigate the two distinct topics addressed by this research 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, Radzinski et al. 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. The speciation of technetium in vitreous waste forms was also examined using glasses prepared under conditions analogous to those use to prepare actual waste-form glasses.

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, Radzinski et al. 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, Brown et al. 1997) 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 ($^-SCH_2CH_2S^-$) complexes of Tc(V) are extremely stable in aqueous solution including alkaline solutions.(Davison, Orvig et al. 1980) Diolate ($^-OCH_2CH_2O^-$) complexes of Tc(V)(Davison, DePamphilis et al. 1987) and Tc(IV) (Alberto, Anderegg et al. 1986) are stable *only* in alkaline aqueous solution; they decompose to $TcO_2 \bullet xH_2O$ 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 a degradation of glass properties.(Darab and Smith 1996) Technetium can be easily encapsulated in cement; however, mobile TcO_4^- must be reduced to immobile Tc(IV) species.(Gilliam, Spence et al. 1990) If Tc(IV) is reoxidized to environmentally mobile TcO_4^-, it may leave the cement waste form through the pores.

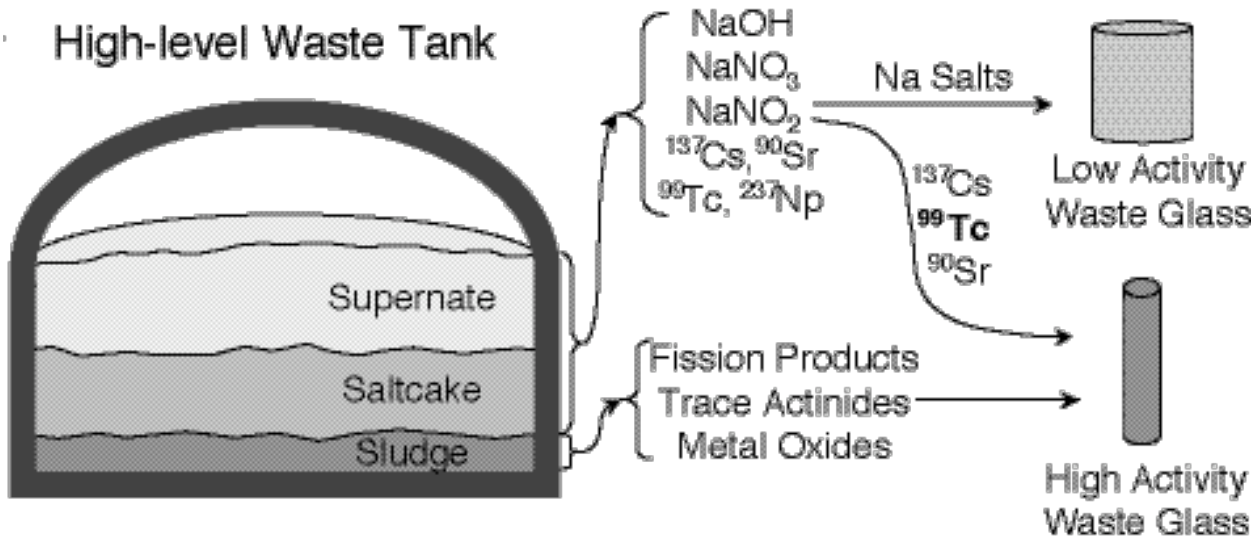
II. Identification of the nonpertechnetate species in Hanford waste

Introduction

The Hanford Reservation in eastern Washington State is the site of one of the largest and most costly remediation efforts in the U.S. Years of plutonium production has generated 53 million gallons of high-level nuclear waste, which is now stored in 177 underground tanks.(National Research Council 2001) The waste consists of three distinct fractions, supernate, saltcake, and sludge.(Gephart and Lundgren; Agnew, Boyer et al. 1996) The supernate is an aqueous solution of sodium nitrate, nitrite, and hydroxide, and various organic compounds including citrate, gluconate, formate, oxalate, EDTA, and NTA; in addition, appreciable quantities of ^{137}Cs, ^{90}Sr, ^{127}I, ^{237}Np and ^{99}Tc are present in the supernate. Saltcake consists of water-soluble salts that have precipitated during reduction of supernate volume by evaporation and consists mainly of sodium nitrate and nitrite. Sludge consists of the waste components that are insoluble under strongly alkaline conditions and includes most of the fission products and actinides plus large quantities of aluminum and iron oxides and aluminosilicates.

The current plan for immobilizing this waste requires separating it into high and low activity streams, which will be vitrified separately to form high and low activity waste glasses.(National Research Council 2001) The low activity waste stream mainly consists of supernate and dissolved saltcake, and the high activity waste stream is mainly sludge. Due to the previous performance requirements for the low activity glass, almost all of the ^{137}Cs and ^{90}Sr and approximately 80% of the technetium (^{99}Tc) needed to be removed from the low activity waste

stream and sent to the high activity waste stream as illustrated in Scheme 2.1.(Schroeder, Radzinski et al. 1995; DOE 2003) This technetium separation was to be accomplished by ion exchange of pertechnetate, TcO_4^-, the most thermodynamically stable form of technetium at high pH. Although ion exchange was effective for many tanks, work by Schroeder showed that it failed for Complexant Concentrate (CC) waste tanks, including tanks SY-101 and SY-103, which contain significant amounts of organic complexants including nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), citrate, and gluconate.(Schroeder, Radzinski et al. 1995; Schroeder, Radzinski et al. 1998) In these tanks, the vast majority of technetium is present as a soluble, lower-valent, non-pertechnetate species (NPS) that is not removed during pertechnetate ion exchange. (Schroeder, Radzinski et al. 1995; Schroeder, Radzinski et al. 1998)



Scheme 2.1. Simplified illustration of immobilization of high-level nuclear waste at the Hanford Site illustrating the role of ^{99}Tc separation.

The identity of the NPS is unknown, and its behavior has hampered removal efforts. It is not readily removed by ion exchange, and although the NPS is air-sensitive (it slowly decomposes to pertechnetate), it is difficult to oxidize in practice.(Blanchard, Brown et al. 1997; Schroeder, Radzinski et al. 1998) The only spectroscopic characterization of the NPS is a series of Tc K-edge X-ray absorption near edge structure (XANES) spectra of CC samples reported by Blanchard (Fig. 2.1).(Blanchard, Brown et al. 1997) Although its identity can not be determined directly from these spectra, the NPS was believed to be Tc(IV) based upon the energy of its absorption edge, 7.1 eV lower than that of TcO_4^-. This edge shift is similar to that of TcO_2, 6.9 eV lower than that of TcO_4^-.(Almahamid, Bryan et al. 1995) The presence of soluble, lower-valent technetium species is unexpected in light of the known chemistry of technetium; under these conditions, insoluble $TcO_2 \bullet 2H_2O$ would be expected rather than soluble complexes. This work identifies the potential candidates for the non-pertechnetate species and identifies technetium complexes that have XANES spectra identical to that of the NPS shown in Fig. 2.1.

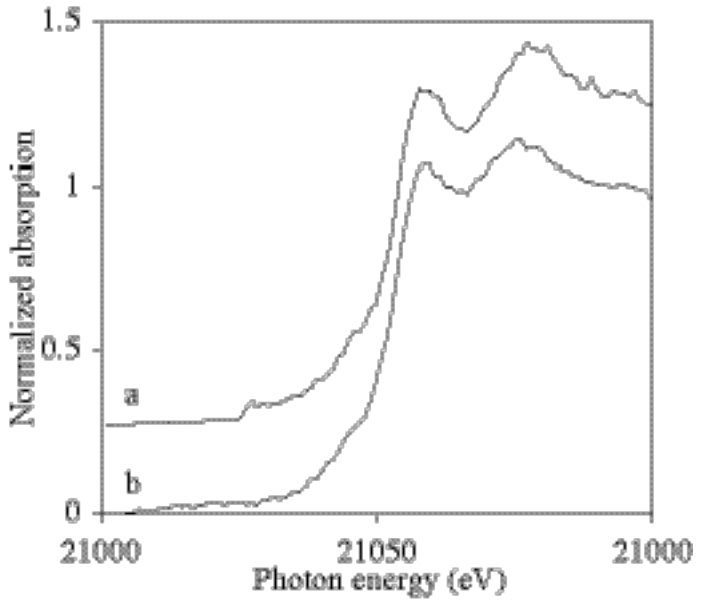


Figure 2.1. Tc K-edge XANES spectra of the non-pertechnetate species (NPS) in tanks a) SY-103, b) SY-101 reported by Blanchard in Ref. (Blanchard, Brown et al. 1997).

Results and Discussion

Tc(IV) Alkoxide Complexes. As a first step in investigating the behavior of technetium in highly alkaline solutions relevant to high-level waste, solutions of TcO_4^- in alkaline solution containing organic compounds, including complexants, were irradiated to reduce the TcO_4^-, and the lower-valent technetium products produced were identified.(Lukens, Bucher et al. 2002) The use of irradiation in these experiments does not imply a similar mechanism for reduction of TcO_4^- in high-level waste tanks. Both chemical(Bernard, Bauer et al. 2001) and radiolytic(Lukens, Bucher et al. 2001) pathways exist for reduction of TcO_4^- under these conditions, but the radiation-chemical pathway is different from the pathway that is operative here, direct reduction of TcO_4^- by hydrated electrons from the radiolysis of water.

The initial results of the radiolysis experiments showed that none of the carboxylate complexants, citrate, EDTA, or NTA, form stable complexes with Tc(IV) in alkaline solution. Under these conditions, only TcO_2•$2H_2O$ is produced. However, soluble, lower-valent complexes are produced by the radiolytic reduction of TcO_4^- in alkaline solution containing the alcohols, ethylene glycol, glyoxylate, and formaldehyde. Although glyoxylate and formaldehyde are aldehydes, they exist as geminal diols in aqueous solution and therefore can act as alkoxide ligands. The EXAFS spectrum and structure of the Tc(IV) glyoxylate complex are shown in Fig. 2.2, and the structural parameters are given in Table 2.1. The structure is very similar to that of the well known $(H_2EDTA)_2Tc_2(\mu\text{-}O)_2$ complex with the EDTA ligands replaced by glyoxylate ligands, presumably acting as diolate ligands.

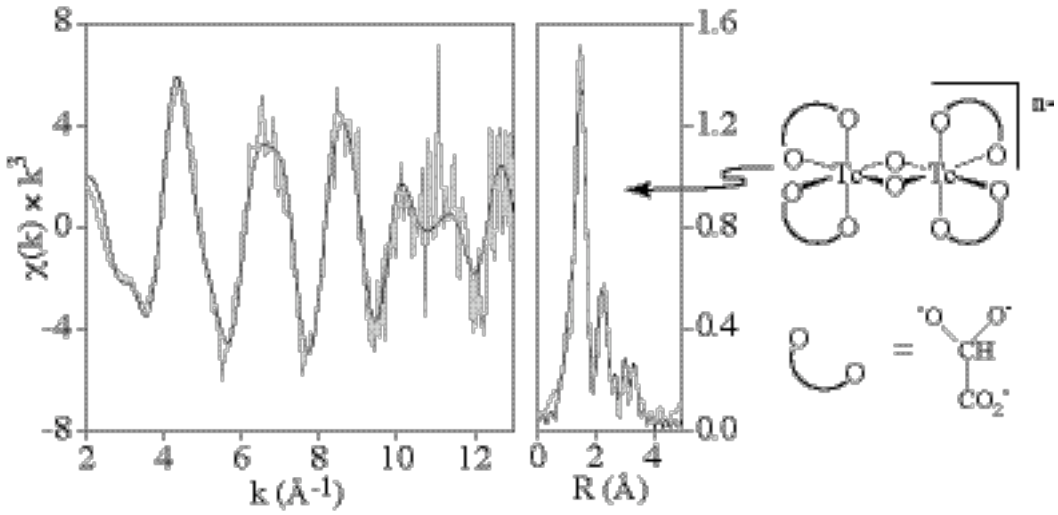


Figure 2.2. EXAFS spectrum and Fourier transform of the Tc(IV) species formed by radiolysis of TcO_4^- in a solution of 0.1 glyoxylic acid in 1M NaOH; data are shown in gray and the fit in black. The structure of the complex consistent with the EXAFS spectrum is shown on the right.

Table 2.1. Structural parameters of soluble radiolysis product derived from EXAFS.[a]

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

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

These radiolysis experiments clearly show that soluble Tc(IV) alkoxide complexes can be formed in highly alkaline solution under conditions similar to those found in high-level waste. However, none of the potential ligands previously examined are present in high-level waste in sufficient concentrations to account for the formation of the soluble non-pertechnetate species.(Agnew, Boyer et al. 1996) The potential alkoxide ligand present in large quantities in CC waste is gluconate.(Golcar, Colton et al. 2000) Moreover, gluconate can act as a tridentate alkoxide ligand (using the carboxylate group and hydroxyl groups on carbon atoms 2 and 3). The resulting $Tc(gluconate)_2^{2-}$ complex would presumably be similar to an analogous complex of Tc(IV) with two tridentate alkoxide ligands described by Anderegg.(Alberto, Albinati et al.

1991) This complex, $Tc[(OCH_2)_3CN(CH_3)]_2$, is the most hydrolytically stable of the Tc(IV) alkoxide complexes. While most Tc(IV) alkoxide complexes are stable only above pH 10, $Tc[(OCH_2)_3CN(CH_3)]_2$ is stable towards hydrolysis down to pH 4. Consequently, an analogous Tc(IV) gluconate complex would be expected to be quite hydrolytically stable.

The colorless Tc(IV) gluconate complex was prepared in situ by reducing TcO_4^- with dithionate in a solution of 0.1M gluconate and 1M NaOH. The EXAFS spectrum and its Fourier transform of Tc(IV) gluconate are shown in Fig. 2.3; fit parameters are given in Table 2.2. The coordination environment of the Tc center is simple: 6 O neighbors at 2.01 Å and 6 C neighbors at 3.37 Å. The bond distances are similar to the aforementioned $Tc[(OCH_2)_3CN(CH_3)]_2$.(Alberto, Albinati et al. 1991) Although the coordination geometry of the coordinated gluconate ligand cannot be determined directly from the EXAFS data, the large Debye-Waller parameter of the gluconate carbon atoms suggests that the gluconate ligand is coordinated to the Tc center by a carboxylate and two hydroxyl groups, as illustrated in Fig. 3, rather than three hydroxyl groups.

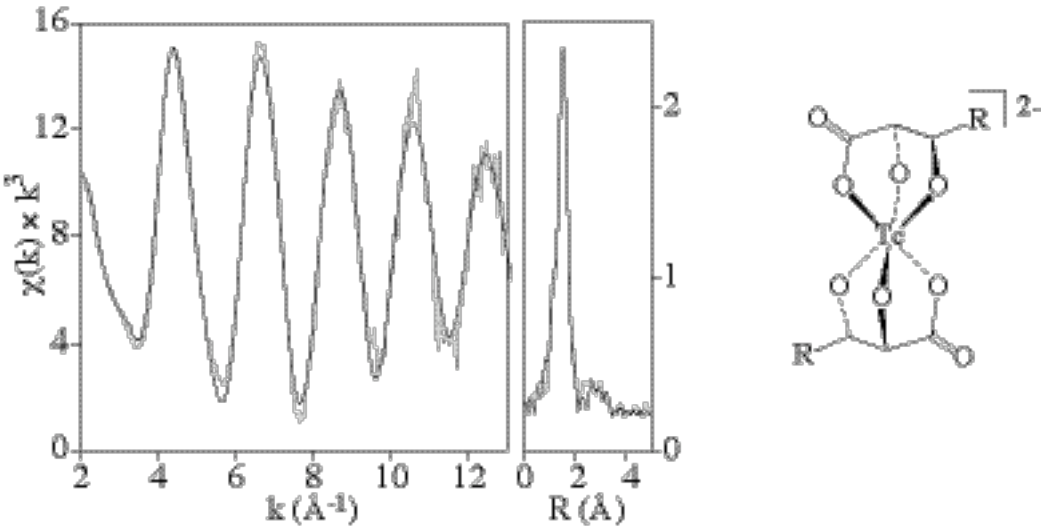


Figure 2.3. EXAFS spectrum and Fourier transform of the Tc(IV) gluconate complex; data are shown in gray and the fit in black. The structure of the complex consistent with the EXAFS spectrum is shown on the right, $R=C_3H_4(HO)_3$.

Table 2.2. Structural parameters of Tc(IV) gluconate derived from EXAFS[a]

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

a) Numbers in parenthesis are the standard deviation of the given parameter derived from least-squares fit to the EXAFS data. The standard deviations do not indicate the accuracy of the numbers; they are an indication of the agreement between the model and the data. In general, coordination numbers have an error of ±25% and bond distances have an error of ±0.5% when compared to data from crystallography.
b) Parameters with an asterisk were not allowed to vary during analysis (scale factor was varied instead; $S^O{}_2$=1.38(3)).
c) E_0 was refined as a global parameter for all scattering paths. The large negative value results from the definition of E_0 in EXAFSPAK.
d) This scattering path is a 4-legged multiple scattering path between the *trans* ligands of the technetium coordination sphere.

Although the EXAFS experiment establishes the existence of Tc(IV) gluconate, it does not establish whether Tc(IV) gluconate is the NPS observed in CC waste. In fact, as shown in Fig. 2.4, Tc(IV) gluconate is not the NPS in Tanks SY-101 and SY-103. Although the XANES spectra of Tc(IV) gluconate and the NPS are superficially similar, the energies of their absorption edges differ by 1.6 eV. More importantly, no combination of the spectra of Tc(IV) gluconate, Tc(V) gluconate, and TcO_4^- will fit the spectrum of the NPS. Not only is the NPS not Tc(IV) gluconate, the NPS cannot be any kind of Tc(IV) alkoxide complex. The energies of the Tc-K edges of Tc(IV) alkoxide complexes and other Tc(IV) complexes with oxygen neighbors, including TcO_2•$2H_2O$, fall within a narrow range around 5.5 eV below the energy of the TcO_4^- absorption edge.(Lukens, Bucher et al. 2002) For comparison, the Tc-K edge of the NPS occurs at 7.1 eV below the TcO_4^- absorption edge.

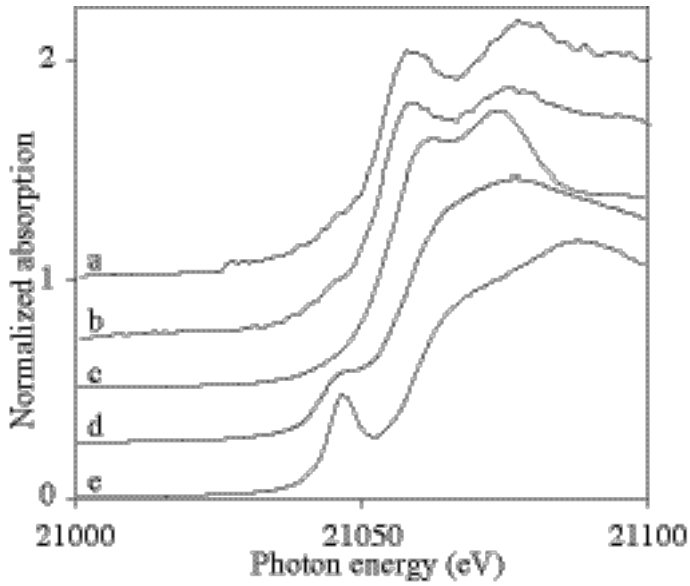


Figure 2.4. Tc K-edge XANES spectra of a) NPS in tank SY-103, b) NPS in tank SY-101, c) Tc(IV) gluconate, d) Tc(V) gluconate, e) TcO_4^-. The spectra of the non-pertechnetate species in tanks SY-101 and SY-103 are from Ref. (Blanchard, Brown et al. 1997).

The fact that Tc(IV) gluconate is not the NPS is surprising. The radiolysis experiments clearly show that Tc(IV) alkoxides can be formed and are stable in highly alkaline solution. In fact, the Tc(IV) gluconate complex is so stable that it can be prepared by dissolving $TcO_2 \bullet 2H_2O$ in 1M NaOH containing 0.1M gluconate, which may have implications for treating high-level waste. If CC waste containing gluconate is added to tanks containing $TcO_2 \bullet 2H_2O$, soluble Tc(IV) gluconate will be formed. Like the NPS, Tc(IV) gluconate would not be removed by the ion exchange resins that remove TcO_4^-. However, Tc(IV) gluconate is fairly air-sensitive (much more so than the NPS), and should be easy to oxidize, unlike the NPS. This sensitivity to oxidation could be the reason that Tc(IV) gluconate is not observed in CC waste. Another possibility is that the thermodynamic stability of the NPS is greater than that of Tc(IV) gluconate.

***fac*-Tc(CO)$_3$ Complexes**. An alternate approach was taken since the systematic experimental investigation just described seemed unable to yield the identity of the NPS. Theoretical XANES spectra were calculated(Zabinsky, Rehr et al. 1995) for a variety of lower valent technetium complexes regardless of whether the ligands were present in high-level waste and disregarding the oxidation state of the technetium center. The complex that had a calculated XANES spectrum most similar to that of the non-pertechnetate species was *fac*-$Tc(CO)_3(H_2O)_3^+$.(Alberto, Schibli et al. 1995; Alberto, Schibli et al. 1998; Alberto, Schibli et al. 1999; Alberto, Ortner et al. 2001) Since the crystal structure of this complex has not been reported, the Tc-C and Tc-O distances for the carbonyl and water ligands were taken from the crystal structure of *fac*-$Tc(CO)_3\{[OP(OCH_3CH_3)_2]_3Co(C_5H_5)\}$.(Kramer, Davison et al. 2001) The synthesis and chemistry of *fac*-$Tc(CO)_3$ complexes are the subject of extensive research, largely due to Alberto, since *fac*-$Tc(CO)_3$ complexes are potentially useful as ^{99m}Tc radiopharmaceuticals.(Alberto, Schibli et al. 1995; Alberto, Schibli et al. 1998; Alberto, Schibli et al. 1999; Alberto, Ortner et al. 2001) Of particular relevance is the fact that *fac*-$Tc(CO)_3$

complexes can be prepared from TcO_4^- in alkaline solution at low CO concentrations. This characteristic, along with the fact that CC waste tanks contain CO (the head space gas consists of 0.25 to 0.5 mol % CO),(Johnson 1996) suggests that *fac*-$Tc(CO)_3$ could have formed in the Hanford high-level waste tanks. In addition, the similar Tc(I) dicarbonyl nitrosyl complex $Tc(CO)_2(NO)(H_2O)_3^{2+}$ in which one CO ligand has been replaced by the isoelectronic NO^+ ligand has also been reported.(Rattat, Schubiger et al. 2001)

The behavior of *fac*-$Tc(CO)_3$ complexes in alkaline solution has previously been investigated, and the species formed at different hydroxide concentrations have been identified by Gorskov using ^{99}Tc-NMR spectroscopy.(Gorshkov, Lumpov et al. 2000) Fig. 2.5 shows the ^{99}Tc-NMR spectra of the *fac*-$Tc(CO)_3$ species produced by adding *fac*-$Tc(CO)_3(H_2O)_3^+$ to different alkaline solutions. In 1M NaOH, the only species present is *fac*-$Tc(CO)_3(H_2O)_2(HO)$, which has a chemical shift of –1060 ppm. As with Tc(IV), the carboxylate complexants do not form complexes with *fac*-$Tc(CO)_3$ in alkaline solution. Only *fac*-$Tc(CO)_3(H_2O)_2(HO)$ was observed in 1M NaOH solutions containing 0.1M EDTA, NTA, or citrate. However, gluconate does form a complex with *fac*-$Tc(CO)_3$, which is indicated by the presence of a new peak in the ^{99}Tc-NMR spectrum at –1240 ppm of *fac*-$Tc(CO)_3$ in a solution of 0.1M gluconate and 1M NaOH. When *fac*-$Tc(CO)_3(H_2O)_3^+$ is added to an SY-101 simulant, both *fac*-$Tc(CO)_3(H_2O)(HO)$ and *fac*-$Tc(CO)_3(gluconate)^{2-}$ are observed. However, after one week, the only observable technetium species are *fac*-$Tc(CO)_3(gluconate)^{2-}$ and TcO_4^-. These NMR experiments demonstrate that *fac*-$Tc(CO)_3$ species are stable in alkaline solutions approximating the composition of high-level waste. For comparison, solutions of Tc(IV) alkoxides are more air-sensitive, and will oxidize to TcO_4^- in less than a week if exposed to air.

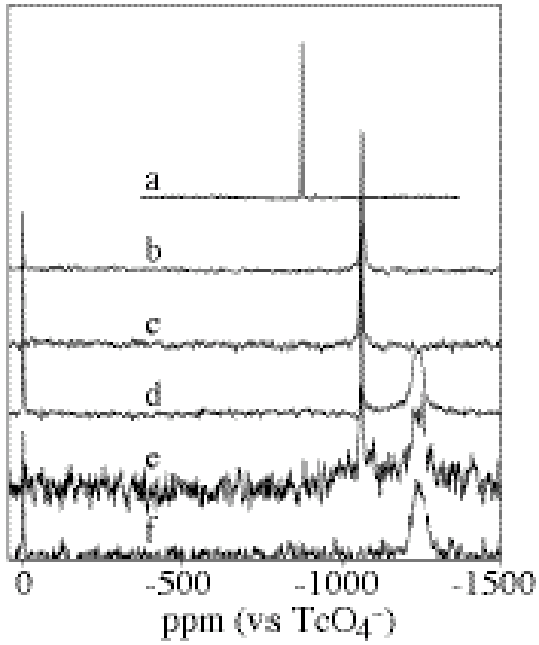


Figure 2.5. ^{99}Tc-NMR spectra of *fac*-$Tc(CO)_3(H_2O)_3^+$ dissolved in a) dilute triflic acid, b) 1M NaOH, c) 1M NaOH with 0.1M EDTA, d) 1M NaOH with 0.1M gluconate, e) SY-101 simulant, f) SY-101 simulate after 1 week in air.

Several of the *fac*-$Tc(CO)_3$ complexes were also characterized by EXAFS spectroscopy as shown in Fig. 2.6 and the structural details are summarized in Table 2.3. It is not surprising that their spectra and the parameters derived from fitting their spectra are very similar. The main differences among these complexes are Tc-C and Tc-O distances of the carbonyl and water, hydroxide or gluconate ligands. Since the scattering atoms are identical and the bond distances change little among the complexes, the spectra differ only slightly. The change in bond distances is systematic and consistent with the nature of the ligands. The Tc-O distances for the first shell oxygen decrease in order from *fac*-$Tc(CO)_3(H_2O)_3^+$ to *fac*-$Tc(CO)_3(H_2O)_2(OH)$ to *fac*-$Tc(CO)_3(gluconate)^{2-}$, in agreement with the observation that gluconate forms the most stable complex with *fac*-$Tc(CO)_3$ followed by hydroxide, and then followed by water. In addition, the CO distance is shorter in *fac*-$Tc(CO)_3(H_2O)_3^+$ than in the other two complexes as water is a weaker π–donor than the other two ligands. Overall, the EXAFS data are consistent with the known stabilities of these three complexes and clearly show that these are three distinct complexes, in agreement with the ^{99}Tc-NMR data.

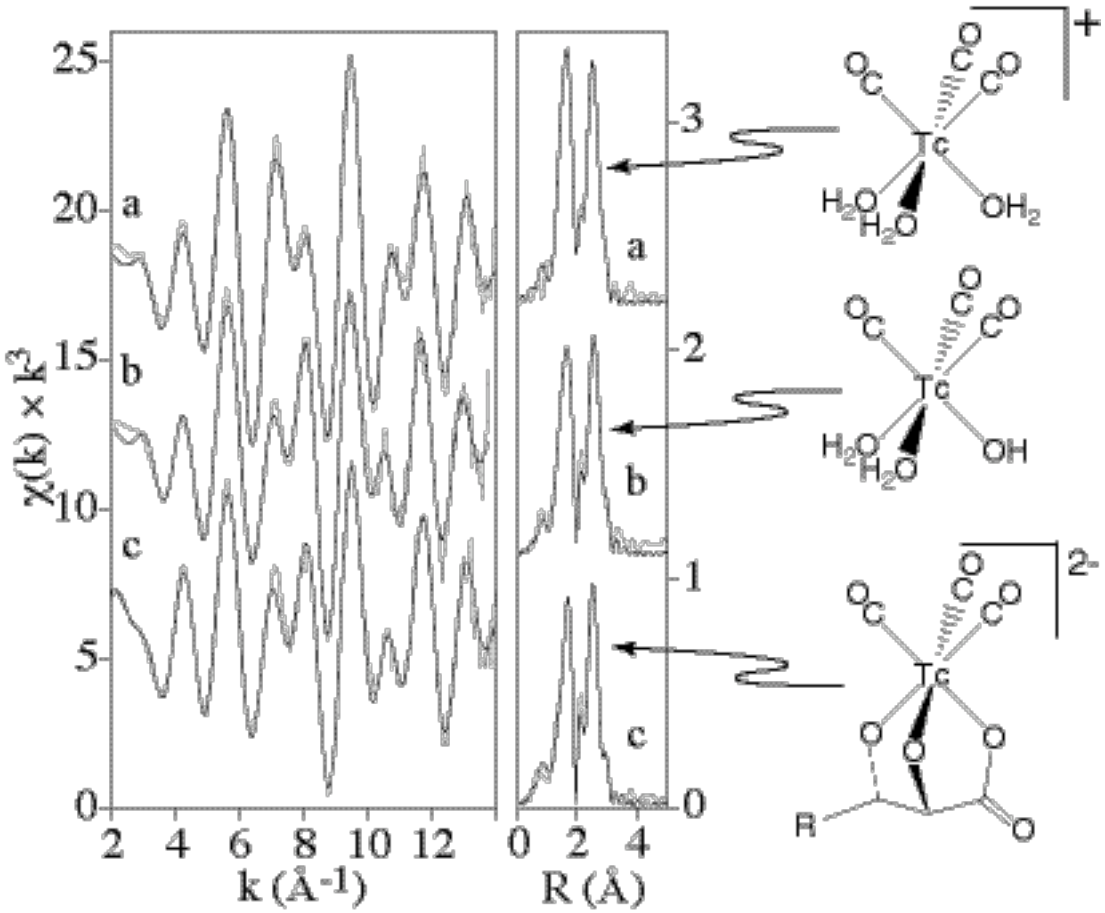


Figure 2.6. EXAFS spectra and Fourier transforms of a)*fac*-$Tc(CO)_3(H_2O)_3^+$, b) *fac*-$Tc(CO)_3(HO)(H_2O)_2$, and c) *fac*-$Tc(CO)_3(gluconate)^{2-}$. Data are illustrated in gray, and the least squares fits are black. The structures of the complexes consistent with the EXAFS spectra are to the right of the spectra.

Table 2.3. EXAFS fitting results for *fac*-$Tc(CO)_3$ complexes.

Scattering Path		$Tc(CO)_3(H_2O)_3^+$	$Tc(CO)_3(H_2O)_2(OH)$	$Tc(CO)_3(gluconate)^{2-}$
	N	3	3	3
Tc-<u>C</u>O	R(Å)	1.904(2)	1.886(3)	1.911(2)
	σ^2(Å^2)	0.0041(2)	0.0058(3)	0.0062(2)
	N	3	3	3
Tc-<u>O</u>	R(Å)	2.163(2)	2.155(3)	2.137(2)
	σ^2(Å^2)	0.0052(2)	0.0047(5)	0.0068(3)
	N	3	3	3
Tc-C<u>O</u>[a]	R(Å)	3.045(9)	3.083(8)	3.09(3)
	σ^2(Å^2)	0.0050(2)	0.0046(2)	0.0015(2)
	N			3
Tc-O<u>C</u>	R(Å)			3.44(2)
	σ^2(Å^2)			0.011(2)
4 leg MS path	N	6	6	6
with *trans* ligands	R(Å)	3.96(2)	4.01(2)	3.96(1)
coordinated to Tc	σ^2(Å^2)	0.017(4)	0.010(3)	0.019(3)
ΔE_0		-14.8(4)	-11.6(6)	-11.1(3)
Scale Factor		1.39(4)	1.19(6)	1.68(7)

The results described above show that *fac*-$Tc(CO)_3$ complexes are stable under conditions found in high-level waste, but do not establish whether they are actually the NPS. As shown in Fig. 2.7, the XANES spectra of the *fac*-$Tc(CO)_3$ complexes are very similar, if not identical, to those of the NPS. The Tc K-edge energies of the XANES spectra of *fac*-$Tc(CO)_3$ complexes occur at 7.5 eV below that of TcO_4^-, in excellent agreement with the observed edge shift of 7.1 eV for the NPS. Most convincing is the fact that the spectrum of the NPS in tank SY-103 can be fit using only the spectrum of *fac*-$Tc(CO)_3(gluconate)^{2-}$, and the spectrum of the NPS in tank SY-101 can be fit using the spectrum of *fac*-$Tc(CO)_3(gluconate)^{n-}$ containing 7% TcO_4^-, presumably due to oxidation. The spectra of the NPS can also be fit using the spectrum of *fac*-$Tc(CO)_3(H_2O)_2(HO)$, but the fit is of slightly poorer quality. As noted above, analogous Tc(I) dicarbonyl nitrosyl complexes, including $Tc(CO)_2(NO)(H_2O)_3^{2+}$, are known.(Rattat, Schubiger et al. 2001) The $Tc(CO)_2(NO)$ complexes are somewhat more stable then *fac*-$Tc(CO)_3$ complexes and could be generated in high level waste as a result of the radiolytic decomposition of nitrate and nitrite.(Cook, Dimitrijevic et al. 2001; Meisel, Camaioni et al. 2001) The XANES spectra of $Tc(CO)_2(NO)$ and *fac*-$Tc(CO)_3$ complexes would be similar. Given the similarity of the XANES spectra of the Tc(I) carbonyl complexes, assignment of the non-pertechnetate species to a particular species is not conclusive although $Tc(CO)_3(gluconate)^{2-}$ provides an excellent fit to the observed XANES spectrum of the non-pertechnetate species.

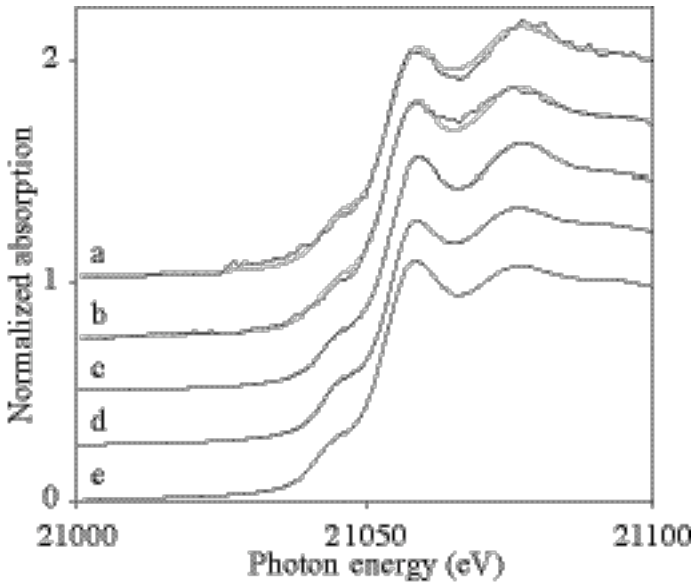


Figure 2.7. Tc K-edge XANES spectra of a) NPS in tank SY-103 (black) and $Tc(CO)_3(gluconate)^{2-}$ (gray), b) NPS in tank SY-101 (black) and 93% $Tc(CO)_3(gluconate)^{2-}$ with 7% TcO_4^- (gray), c) $Tc(CO)_3(gluconate)^{2-}$, d) $Tc(CO)_3(HO)(H_2O)_2$, e) $Tc(CO)_3(H_2O)_3^+$. The spectra of the NPS in tanks SY-101 and SY-103 are from Ref. (Blanchard, Brown et al. 1997).

The identity of the NPS explains some of its behavior. Simplest to explain is the fact that it is not removed by the cationic resins used to separate TcO_4^- from the waste. The most weakly solvated anion (TcO_4^- in this case) are the most strongly bound by the resins used to separate TcO_4^-. Although *fac*-$Tc(CO)_3(gluconate)^{2-}$ is anionic, it should be more strongly solvated than NO_3^-, which is present in much higher concentrations, consequently anionic $Tc(CO)_3(gluconate)^{2-}$ cannot be separated in the presence of excess nitrate using these resins. Of course, if uncharged *fac*-$Tc(CO)_3(H_2O)_2(HO)$ is present, it would not be removed by ion exchange.

The seemingly strange behavior of the NPS with regard to oxidation is largely explained by its identity. The *fac*-$Tc(CO)_3$ complexes are not thermodynamically stable with respect to oxidation to TcO_4^-; however, they are kinetically inert due to their low-spin d^6 electronic structure. As a result, they will react slowly with potential oxidizing agents, such as oxygen. The kinetic inertness of these complexes also affects oxidation by strong oxidizers. Since *fac*-$Tc(CO)_3$ complexes will react relatively slowly with strong oxidizers (although presumably much faster than they react with oxygen), the strong oxidizers will preferentially react with the compounds, such as nitrite or organic molecules, that are present in much higher concentrations and are much more reactive.

One aspect of the chemistry of *fac*-$Tc(CO)_3$ in CC waste that has not been addressed is the mechanism of its formation. As noted above, *fac*-$Tc(CO)_3$ complexes can be prepared from TcO_4^- in alkaline solution at elevated temperature at low CO concentration; however, the exact mechanism for the formation of *fac*-$Tc(CO)_3$ complexes from TcO_4^- in waste simulants remains to be investigated.

Experimental

Procedures. *Caution: ^{99}Tc is a β-emitter (E_{max} = 294 keV, $\tau_{1/2} = 2 \times 10^5$ years).* All operations were carried out in a radiochemical laboratory equipped for handling this isotope. Technetium, as $NH_4{}^{99}TcO_4$, was obtained from Oak Ridge National Laboratory. The solid $NH_4{}^{99}TcO_4$ was contaminated with a large amount of dark, insoluble material. Prolonged treatment of this sample with H_2O_2 and NH_4OH did not appreciably reduce the amount of dark material. Ammonium pertechnetate was separated by carefully decanting the colorless solution from the dark solid. A small amount of NaOH was added to the colorless solution, and the volatile components were removed under vacuum. The remaining solid was dissolved in water, and the colorless solution was removed from the remaining precipitate with a cannula. The concentration of sodium pertechnetate was determined spectrophotometrically at 289 nm (ε = 2380 M l^{-1} cm^{-1}). UV-visible spectra were obtained using an Ocean-Optics ST2000 spectrometer. X-ray absorption fine structure (XAFS) spectra were acquired at the Stanford Synchrotron Radiation Laboratory (SSRL) at Beamline 4-1 using a Si(220) double crystal monochromator detuned 50% to reduce the higher order harmonic content of the beam. All ^{99}Tc samples were triply contained inside sealed polyethylene vessels. X-ray absorption fine structure spectra (XAFS) were obtained in the transmission mode at room temperature using Ar filled ionization chambers or in fluorescence yield mode using a multi-pixel Ge-detector system.(Bucher, Allen et al. 1996) The spectra were energy calibrated using the first inflection point of the pre-edge peak from the Tc K edge spectrum of an aqueous solution of NH_4TcO_4 defined as 21044 eV. To determine the Tc K edge charge state shifts, the energies of the Tc K edges at half height were used. EXAFS analysis and radiolysis experiments were carried out as previously described.(Lukens, Bucher et al. 2002)

All operations were carried out in air except as noted. Water was deionized, passed through an activated carbon cartridge to remove organic material and then distilled. Iminodiacetic acid was recrystallized three times from water. All other chemicals were used as received. The $Tc(CO)_3(H_2O)_3^+$ stock solution was prepared from $TcOCl_4(n\text{-}Bu_4N)$(Davison, Trop et al. 1982) by the procedure developed by Alberto(Alberto, Schibli et al. 1995) then dissolving the reaction product in 0.01M triflic acid. The ^{99}Tc concentration was determined by liquid scintillation.

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

III. Behavior of Technetium in Cementitious Waste Forms

Introduction

Immobilization of the high-level nuclear waste created during plutonium production by the U. S. Department of Energy (DOE) is the most expensive and complex remediation project in the U. S.(Gray and Becker 1993; 2000) An important component of this effort is the use of grout based cementitious waste forms (CWFs) to immobilize the low-activity waste stream at the Savannah River Site and to stabilize the waste residues in high-level tanks at both the Savannah River and Hanford Sites.(Oblath 1984; Oblath 1989; Serne, Lokken et al. 1992; Council 2001) The long-term effectiveness of these measures to prevent the migration of radionuclides is described by performance assessments that depend on the leach rates of the radionuclides.(Oblath 1984; Serne, Lokken et al. 1992; Seitz, Walton et al. 1993; Kaplan and Serne 1998) ^{99}Tc is one of the radionuclides of greatest concern for leaching from CWFs because of the high mobility and lack of sorption of pertechnetate, TcO_4^-, the most stable form of technetium under aerobic conditions.(Gilliam, Spence et al. 1990; Kaplan and Serne 1998)

For soluble contaminants such as TcO_4^- or NO_3^-, leach rates from CWFs can be modeled using an effective diffusion coefficient, $D_{eff} = N_m D_m$ where D_m is the molar diffusion coefficient of the contaminant in water and N_m is the MacMullin number, a characteristic of the porous solid that is identical for solutes such as gases or anions that are highly soluble and not adsorbed by the matrix.(Taffinder and Batchelor 1993) Among potential CWFs, $D_{eff}(NO_3^-)$ varies 1.3×10^{-9} cm^2 s^{-1} to 6.2×10^{-8} cm^2 s^{-1}.(Langton 1988; Gilliam, Spence et al. 1990; Serne, Lokken et al. 1992) The D_{eff} values for NO_3^- and TcO_4^- are similar since their molar diffusion coefficients are almost identical, 1.53×10^{-5} and 1.48×10^{-5} cm^2 s^{-1}, respectively.(Yeh and Wills 1970; Rard, Rand et al. 1999) The leachability of technetium can be greatly decreased by reducing soluble TcO_4^- to insoluble Tc(IV) species by the addition of blast furnace slag (BFS) or other reductants to the grout. The $D_{eff}(^{99}Tc)$ values of reducing grouts are much smaller, 3×10^{-11} cm^2 s^{-1} to 4×10^{-12} cm^2 s^{-1}, because Tc(IV) how low solubility and readily sorbs to the grout matrix.(Langton 1988; Gilliam, Spence et al. 1990) Reducing conditions used in actual CWFs take advantage of this decreased leachability to create a more effective waste form.(Langton 1988; Council 2001)

Previous research showed that although TcO_4^- is reduced to Tc(IV) in reducing grouts, the degree of reduction varied with experimental conditions.(Allen, Siemering et al. 1997) In some cases, TcO_4^- was initially reduced to Tc(IV) but was later oxidized. Two species, NO_3^- and O_2, are present in large quantities in or around CWFs and are potentially capable of oxidizing Tc(IV) to TcO_4^-. Whether NO_3^- or O_2 is responsible for oxidizing Tc(IV) has a profound effect on the behavior and immobilization of technetium in CWFs.

Oxidation by NO_3^- or O_2 produces two very different scenarios for the speciation and leaching of technetium from reducing CWFs. If NO_3^- is chiefly responsible for the oxidation, Tc(IV) would be oxidized throughout the entire CWF. increasing the leachability of ^{99}Tc in the entire volume of the waste. In this scenario, the rate of oxidation of Tc(IV) to TcO_4^- would depend only on the reaction rate and the concentration of the reactants.

The scenario involving oxidation by O_2 is more complicated. In this case, diffusion of O_2 into the CWF would result in the formation oxidized surface region that would have greater technetium leachability. However, the leachability of technetium in the bulk of the waste form would remain low since it would remain Tc(IV). As shown by Walton and Smith, the thickness of the oxidized region depends mainly upon N_m and the reductive capacity of the CWF. Using typical parameters for reducing CWFs, the thickness of the oxidized region is small compared to the dimensions of the CWF, and oxidation by O_2 is less of a concern than oxidation by NO_3^-.

Therefore, the primary concern raised by the rapid oxidation of Tc(IV) species observed in the previous study was that NO_3^- rather than O_2 was responsible for the oxidation. Such rapid oxidation of Tc(IV) by NO_3^- would mean that all of the initially reduced technetium in actual CWFs would be quickly oxidized back to TcO_4^-. Under this research program, the evolution of ^{99}Tc speciation in a series of grout samples both sealed and unsealed and with and without NO_3^- was followed for an extended period by X-ray absorption fine structure (XAFS) to determine whether NO_3^- or O_2 was responsible for oxidizing Tc(IV) species in these grout samples.

Results and Discussion

Two series of cement samples, "sealed" and "unsealed" were prepared, the composition of which is shown in Table 3.1. The speciation of technetium in these samples was determined using XAFS as the samples aged over a period of 4 years.

Table 3.1. Composition of cement samples

Sample	Tc (mg)	Solution (ml)	Final Solution Composition	Cement (g)
			Unsealed Samples	
1	2	1.5	1.85M $NaNO_3$, 1.07M NaOH, 0.57M $NaNO_2$, 0.23M $NaAl(OH)_4$, 0.16M Na_2CO_3, 0.14M Na_2SO_4, 0.02M NaCl, 0.02M $Na_2C_2O_4$, 0.008M Na_3PO_4, 0.13M Na_2S	3
2	2	1.5	As Sample 1, but no $NaNO_3$, $NaNO_2$	3
3	2	0.95	As Sample 1, but 0.05M Na_3PO_4	1.5
4	2	0.95	As Sample 2, but 0.05M Na_3PO_4	1.5
			Sealed Samples	
A	1.2	0.66	2M NaOH, 2M NaCl	1.0
B	1.2	0.66	2M NaOH, 2M $NaNO_3$	1.0
C	1.2	0.66	2M NaOH, 2M $NaNO_2$	1.0

EXAFS studies of initial technetium speciation. A prerequisite for investigating the long-term behavior of technetium is identifying which technetium species are present. While it is obvious that TcO_4^- will be present under oxidizing conditions,(Colton 1965) the species present in grout under reducing conditions are less obvious. The hydrous Tc(IV) oxide, $TcO_2 \bullet xH_2O$, results from the reduction of TcO_4^- in the absence of other ligands both in solution and in grout samples.(Cartledge 1971; Allen, Siemering et al. 1997) In addition, sulfide, either added to the grout as Na_2S or BFS, reduces TcO_4^- to a lower-valent technetium sulfide species thought to be similar to TcS_2.(Allen, Siemering et al. 1997) Interestingly, the reaction of sulfide with TcO_4^- in alkaline solution is a known route to Tc_2S_7,(Lee and Bondietti 1983) which is generally believed to be the technetium species present in reducing CWFs.(Lee and Bondietti 1983; Smith and Walton 1993) While these results appear to be contradictory, the inconsistency is largely due to the Tc(VII) oxidation state implied by the stoichiometry of Tc_2S_7. If Tc_2S_7 is not actually a Tc(VII) sulfide complex but a lower-valent disulfide complex, no contradiction exists between these previous studies. Although Tc_2S_7 is generally assumed to be a Tc(VII) compound, this assumption has never been examined.(Rard, Rand et al. 1999)

To identify the technetium sulfide species present in reducing grouts, the Tc K-edge EXAFS spectra of the unsealed samples were examined shortly after they were prepared. Only these samples contained a single technetium species. All other samples, including these samples at later times, contained more than one technetium species. The unsealed samples initially had identical Tc K-edge EXAFS spectra, shown in Fig. 3.1. The parameters derived by fitting the spectra, listed in Table 3.2, are also comparable. Therefore, in addition to containing only one technetium species, all of these samples contain the same technetium species, which will be termed TcS_x.

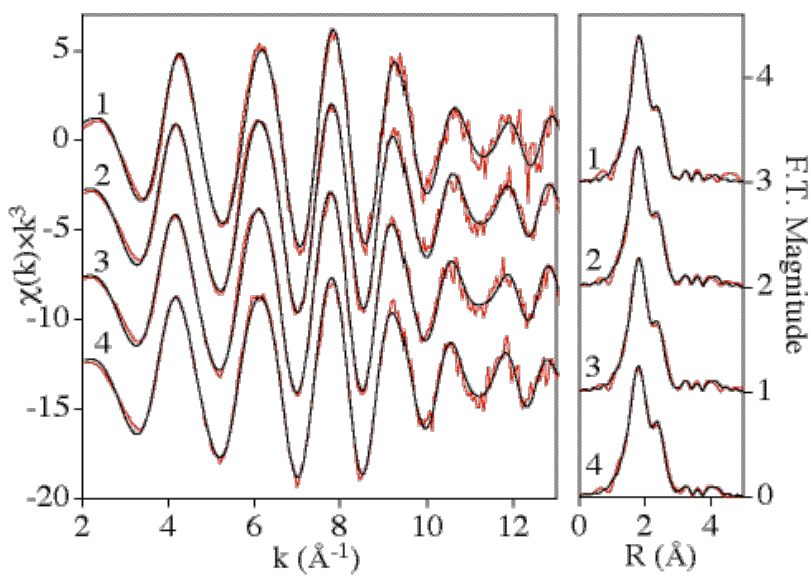


Figure 3.1. Tc K-edge EXAFS spectra (left) and their Fourier transforms (right) of the technetium species initially present in grouts prepared by initially reducing the TcO_4^- with excess sodium sulfide. Data is shown in red (gray in B/W) and the fits are shown in black. Sample numbers are indicated next to the traces.

Table 3.2. Initial technetium coordination environment in the unsealed samples

Scattering Atom		Sample 1	2	3	4
S	N	7.4(2)	7.9(2)	7.3(2)	7.8(2)
	R	2.367(2)	2.364(2)	2.371(2)	2.367(2)
	σ^2	0.0108(4)	0.0115(3)	0.0111(3)	0.0121(3)
Tc	N	2.1(1)	2.0(2)	2.0(2)	2.0(2)
	R	2.767(2)	2.766(2)	2.774(2)	2.770(2)
	σ^2	0.0073(6)	0.0071(4)	0.0074(4)	0.0071(4)
Tc	N	0.22(8)	0.25(4)	0.24(4)	0.25(5)
	R	3.82(2)	3.841(9)	3.840(9)	3.87(1)
	σ^2	0.003(1)	0.0023(5)	0.0023(5)	0.0023(6)
Tc	N	0.78[a]	0.75[a]	0.76[a]	0.75[a]
	R	4.28(1)	4.295(7)	4.291(1)	4.317(8)
	σ^2	0.003[a]	0.0023[a]	0.0023[a]	0.0023[a]
S	N	2.5(5)	2.9(3)	2.5(3)	2.7(4)
	R	4.41(2)	4.44(1)	4.44(1)	4.47(1)
	σ^2	0.005[b]	0.005[b]	0.005[b]	0.005[b]
ΔE_0		-7.1(4)	-10.0(3)	-9.9(3)	-9.7(4)

a) Parameter determined by the corresponding parameter in the preceding shell.
b) Parameter fixed.

The coordination environment of TcS_x can be described by considering the first two and last three coordination shells separately. The first two coordination shells, which comprise the large feature in the Fourier transformed EXAFS spectra, consist of ~7 sulfur neighbors at 2.37 Å and 2 technetium nearest neighbors at 2.77 Å. These distances and coordination numbers are similar to those of the molybdenum sulfide complex, $Mo_3S(S_2)_6^{2-}$, shown in Fig. 3.2, in which each molybdenum center has 7 sulfur and 2 molybdenum neighbors at 2.44 and 2.72 Å, respectively.(Müller, Pohl et al. 1979) The $Mo_3(\mu^3\text{-}S)(\mu\text{-}S_2)_3$ core of this complex forms the building block of the MoS_3 structure,(Weber, Muijsers et al. 1995) which has an EXAFS spectrum similar to that of TcS_x.(Cramer, Liang et al. 1984; Hibble, Rice et al. 1995) The nearest neighbor environments in both compounds are analogous; in MoS_3, each molybdenum center has ~6 sulfur neighbors at 2.44 Å and 2 molybdenum neighbors at 2.75 Å. The similarities of the distances and coordination numbers of the first two coordination shells of MoS_3, $Mo_3S(S_2)_6^{2-}$ and TcS_x strongly suggest that the TcS_x structure is built from the same triangular core, $Tc_3(\mu^3\text{-}S)(\mu\text{-}S_2)_3$ as shown in Fig. 3.2, with two additional sulfur-based ligands linking adjacent triangular clusters. Furthermore, the 2.77 Å Tc-Tc distance is typical for such a triangular complex composed of seven-coordinate metal centers; analogous triangular complexes with six-coordinate metal centers have substantially shorter metal-metal distances.(Müller, Jostes et al. 1980)

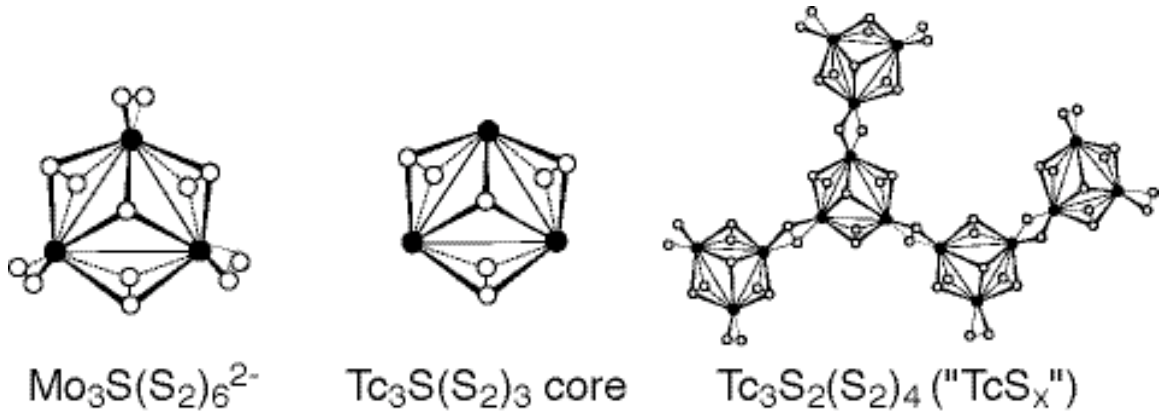


Figure 3.2. Structures of $Mo_3S(S_2)_6^{2-}$ and the analogous $Tc_3S(S_2)_3$ core that forms the building block of TcS_x metal atoms are illustrated by solid circles, sulfur atoms are illustrated by open circles.

The last three coordination shells, which form the small features at higher R in the Fourier transform, result from the next nearest neighbors of the technetium center. Each technetium has a next-nearest technetium neighbor at either 3.85 Å (~25% of the technetium centers) or 4.3 Å (~75% of the technetium centers), and has ~3 additional sulfur neighbors at 4.4 Å due to ligands on adjacent Tc centers. The two different Tc-Tc distances suggest that different ligands bridge the technetium centers. Since the 7 first shell sulfur neighbors require that each technetium center has an additional 2 sulfur ligands in addition to those that comprise the $Tc_3S(S_2)_3$ core, possible identities of the bridging ligands are two bridging sulfide (or hydrosulfide) ligands or an edge-bound disulfide similar to the bridging disulfide of the $Tc_3(\mu^3\text{-}S)(\mu\text{-}S_2)_3$ cluster without the Tc-Tc bond. The Tc-Tc distance of two technetium centers symmetrically bridged by an edge-bound disulfide ligand would be close to 4.3 Å. In a similar copper complex,(Fujisawa, Moro-oka et al. 1994) two Cu centers are separated by 4.03 Å, but the Tc-S bonds in TcS_x are 0.1 Å longer than the Cu-S bonds. Moreover, the S-S distance of this bridging disulfide, determined from the Tc-Tc and Tc-S distances, is 2.0 Å, typical for a bridging disulfide.(Müller, Pohl et al. 1979; Fujisawa, Moro-oka et al. 1994) For these reasons, the 4.3 Å Tc-Tc distance is assigned to two Tc centers symmetrically bridged by a disulfide ligand.

The 3.85 Å Tc-Tc distance could be due to either two bridging sulfide or hydrosulfide ligands. If the Tc and S atoms are coplanar, the Tc-Tc and Tc-S distances produce a Tc-S-Tc angle of 109°. Although few families of complexes exist in which the parameters for bridging sulfide and hydrosulfide ligands can be compared directly, a M-S-M angle of 109° is more typical of a bridging sulfide than of a hydrosulfide, which generally have M-(SH)-M angles of ~100°.(Mueting, Boyle et al. 1984; Bianchini, Mealli et al. 1986; Pleus, Waden et al. 1999) For this reason, the 3.85 Å Tc-Tc distance is assigned to two Tc centers symmetrically bridged by two sulfide ligands. Overall, the EXAFS data is consistent with a TcS_x structure composed of triangular $Tc_3(\mu^3\text{-}S)(\mu\text{-}S_2)_3$ clusters linked by either bridging disulfide or by two bridging sulfide ligands as shown in Fig. 3.2.

The structure of TcS_x derived from EXAFS, shown in Fig. 3.2, yields a stoichiometry of $Tc_3S_2(S_2)_4$ or Tc_3S_{10}, which is almost identical to that determined for Tc_2S_7 prepared under similar conditions, $TcS_{3.2}$.(Lee and Bondietti 1983) Since the conditions used to prepare these samples

are analogous to those used to prepare Tc_2S_7, it seems likely that TcS_x is actually Tc_2S_7. However, the technetium centers in TcS_x are clearly not heptavalent. As dictated by the ligands, TcS_x is a Tc(IV) compound, which is consistent with its Tc-K edge absorption energy, 6.5 eV below that of TcO_4^-. For comparison, the energies of the Tc-K edges of Tc(IV) complexes with oxygen coordination shells occur at ~5.5 eV below that of TcO_4^-.(Lukens, Bucher et al. 2002) Consequently, the technetium sulfide species present in reducing containing grouts, TcS_x, appears to be Tc_2S_7 as previously suggested;(Lee and Bondietti 1983; Smith and Walton 1993) however, the technetium centers in TcS_x are tetravalent in agreement with the previous XAFS analysis.(Allen, Siemering et al. 1997)

Evolution of technetium speciation determined by XANES spectroscopy. The speciation of technetium in the grout samples was determined by least squares fitting of the XANES spectra using the XANES spectra of $TcO_2 \bullet xH_2O$, TcO_4^-, and TcS_x as components. This method is analogous to those previously described by Ressler et al. and Sarrao et al., which have been shown to yield quantitative speciation information.(Sarrao, Immer et al. 1999; Ressler, Wong et al. 2000) The evolution of technetium speciation in the unsealed and sealed samples is addressed separately.

Unsealed samples. As described in the previous section, the technetium speciation in all the unsealed samples is initially identical since all samples contain only TcS_x. However, as the samples age, their XANES spectra change as shown in Fig. 3.3, which also shows the deconvolution of the XANES spectrum of an aged sample. As is clear from the figure, the agreement between the fit and data is excellent for the unsealed samples. The mole fraction of TcO_4^- in these samples is reported in Table 3.3 and shown in Fig. 3.4 as a function of the age of the sample. The scatter of the data shown in Fig. 3.4 is much greater than the error in the measurement and is believed to arise from the spatial inhomogeneity of the technetium speciation in these samples. The origin of this inhomogeneity will be discussed later. Unfortunately, this large degree of scatter results in a correspondingly large standard deviation in the rate of oxidation of Tc(IV) in the samples. The rates of oxidation of the technetium in samples 1-3 are statistically identical, and oxidation of sample 4, which contained no NO_3^- or NO_2^-, was slightly faster. The presence of NO_3^- and NO_2^- in these samples did not accelerate the oxidation of the Tc(IV) species.

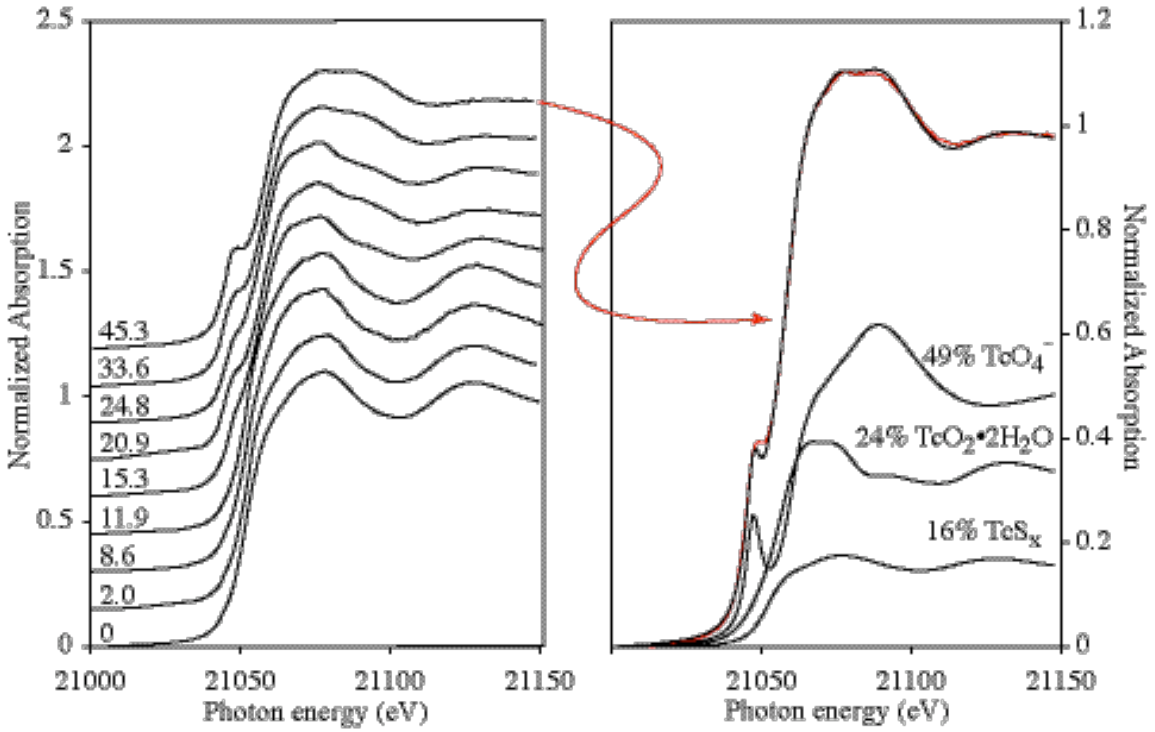


Figure 3.3. Left: Evolution of the Tc-K edge XANES spectra of unsealed sample 1 as a function of age. The age of cement (in years) is given next to the corresponding spectrum. Right Deconvolution of the XANES spectrum of a 45 month old sample. Data are shown in red (gray in B/W) and the least squares fit is shown in black.

Table 3.3. Mole fraction of TcO_4^- in the unsealed samples.

Age of sample (months)	Fraction TcO_4^- (percent) Sample 1	Sample 2	Sample 3	Sample 4
0.0	0.00(2)	0.5(4)	0.5(4)	0.4(5)
2.0	1(1)	0(2)	0(1)	0(2)
8.6	0(1)	0(2)	16(2)	0(1)
11.9	25(2)	0(2)	0(2)	0(2)
15.3	9(1)	0(5)	23(2)	16(2)
20.9	7(1)	26(1)	22(1)	31(1)
24.8	27(2)	1(7)	16(2)	24(1)
33.6	14(2)	39(1)	32(2)	42(1)
45.3	38(2)	27(1)	29(2)	49(2)
Rate of oxidation (% $month^{-1}$)	0.7(2)	0.8(3)	0.7(2)	1.3(2)

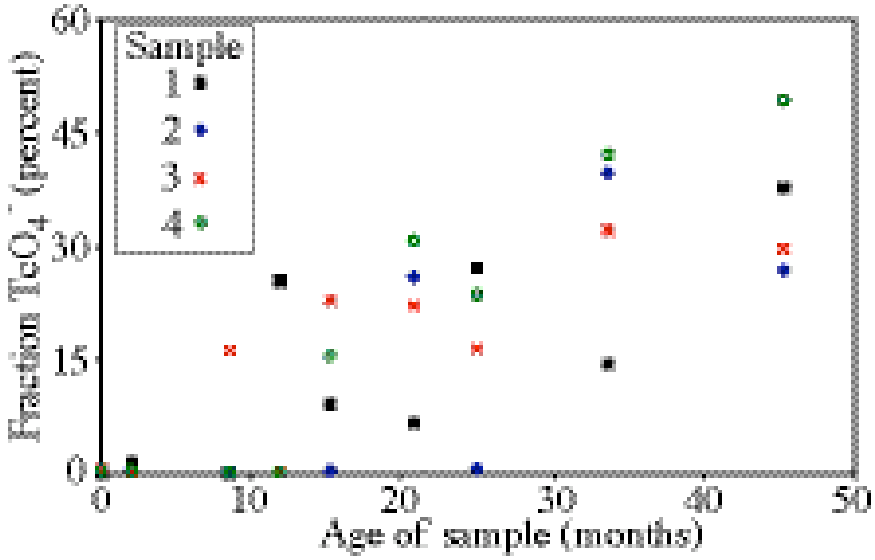


Figure 3.4. Evolution of the mol. fraction of TcO_4^- in the unsealed samples as a function of age.

Sealed samples. Unlike the unsealed samples, ~20% of the TcO_4^- in the sealed samples was not reduced to Tc(IV) at the beginning of the experiment. However, as the samples aged, the amount of TcO_4^- present decreased as shown in Fig. 3.5 and reported in Table 3.4. The quality of the fit is not as good for these samples as it was for the unsealed samples; however, the errors are small. Unlike the unsealed samples, very little scatter is present in the amount of TcO_4^- in these samples and the amount of TcO_4^- varies little among the samples until samples A and C were exposed to air. Unlike the unsealed samples, the sealed samples appear to be spatially homogenous. The large increase in the amount of TcO_4^- observed in samples A and C at 26 months is due to exposure of these samples to atmosphere at 22 months; sample B remained sealed. As in the unsealed samples, the presence of NO_3^- has no observable effect on the speciation of technetium in the sealed samples.

Table 3.4. Evolution of the mol. fraction of TcO_4^- in the sealed samples

Age of sample	Fraction TcO_4^- (percent)		
(months)	Sample A	Sample B	Sample C
0.0	19(3)	16(3)	20(3)
5.6	15(2)	8(3)	19(3)
9.5	5(2)	4(2)	9(3)
18.3	8(3)	5(2)	9(3)
30.0	41(2)	3(2)	56(2)

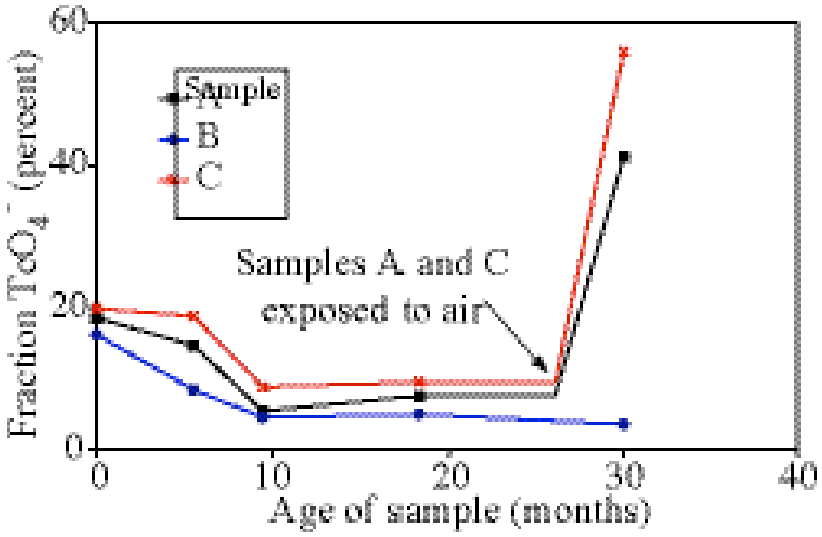


Figure 3.5. Evolution of the mol. fraction of TcO_4^- in the sealed samples as a function of age. Arrow indicates when samples A and C were opened (the fraction TcO_4^- at that point is assumed to be the same as previously determined at 18 months).

The data from both series of samples show that TcS_x is unstable towards oxidation in the high pH environment of grout. As noted previously, both NO_3^- and O_2 can oxidize the lower valent technetium species present in these grout samples. Since the presence of NO_3^- had no significant effect on the rate of oxidation of technetium in these samples, atmospheric O_2 is the likely oxidizing agent. This is also consistent with the spatial inhomogeneity of the technetium speciation present in the unsealed samples. The technetium speciation in the unsealed samples was initially homogenous: all of the technetium in each sample was present as TcS_x. However, as atmospheric O_2 diffused into the sample, TcS_x in the grout near the unsealed top of the cuvette was oxidized, while TcS_x further down in the sample remained reduced. Therefore, XANES experiments would reveal a different technetium oxidation state depending upon whether grout near the top of the cuvette was examined (TcO_4^-) or grout near the bottom was examined (TcS_x). The scatter of the data in Fig. 3.4 is consistent with this spatial inhomogeneity of technetium speciation combined with the fact that the portions of the cement examined using XANES were randomly chosen.

The premise that O_2 is the actual oxidizer is strongly supported by the results from sealed samples illustrated in Fig. 3.5. Although the TcO_4^- in these samples was not initially reduced to TcS_x, the amount of TcO_4^- in these samples declined in later months presumably due to reduction by BFS. Furthermore, the technetium speciation in the sealed samples was spatially homogeneous. Although the technetium speciation evolved and the portions of the samples probed by XANES were randomly chosen, little scatter exists in the technetium speciation among the different samples. Since these samples were sealed, atmospheric O_2 was not present to oxidize the technetium species near the top of the cuvette, and technetium speciation did not vary with position. However, the most dramatic evidence for O_2 oxidation is the 40-50 % increase in the amount of TcO_4^- in the initially sealed samples after 4 months exposure to atmosphere.

One unexpected result is the appearance of $TcO_2 \bullet 2H_2O$ in the aged samples. Formation of $TcO_2 \bullet 2H_2O$ cannot result from the hydrolysis of TcS_x since this compound is stable to hydrolysis under the conditions present during the synthesis of the grout samples. Rather, the observation of $TcO_2 \bullet 2H_2O$ implies that the oxidation of TcS_x proceeds by initial oxidation to $TcO_2 \bullet 2H_2O$ that is then oxidized to TcO_4^- as shown in equations 2-3. This mechanism is consistent with the potentials for the reduction of SO_4^{2-} to S^{2-} (-0.67 V) and of TcO_4^- to $TcO_2 \bullet 2H_2O$ (-0.28 V) at pH 13. Although the detailed mechanism is more complex than this simple picture, oxidation of TcS_x to TcO_4^- proceeds with $TcO_2 \bullet 2H_2O$ as an intermediate.

$$Tc_3S_{10} + 18\ O_2 + 20\ HO^- \rightarrow 3\ TcO_2 \bullet 2H_2O + 10\ SO_4^{2-} + 4\ H_2O \qquad (2)$$

$$4\ TcO_2 \bullet 2H_2O + 4\ HO^- + 3\ O_2 \rightarrow 4\ TcO_4^- + 10\ H_2O \qquad (3)$$

The thickness of the oxidized region formed in the initially sealed samples after exposure to atmosphere can be determined using a variation of the method used to calculate X-ray self-absorption developed by Tröger, et al.(Tröger, Arvanitis et al. 1992) The observed 40% increase in TcO_4^- content over 4 months corresponds to the oxidation of the outer 0.28 mm of the sample. This thickness can be compared with the thickness of the oxidized region determined using the model developed by Smith and Walton, which is based upon an oxidized region formed by the diffusion and reaction of O_2 with the reduced species in CWFs.(Smith and Walton 1993) The thickness of the oxidized region, X, can be modeled using equation 4 where C_{02} is the concentration of

$$X = \sqrt{\frac{8 N_m D_{O2} C_{O2} t}{C_{red}}} \qquad (4)$$

dissolved O_2 (3×10^{-7} mol mL^{-1}), C_{red} is the concentration of reducing equivalents in the CWF in moles of electrons (3.8×10^{-4} mol mL^{-1} for a CWF composed of 28% BFS with a measured reducing capacity of 0.81 meq g^{-1}), t is time in s, D_{O2} is the molar diffusion coefficient of O_2 in water (2×10^{-5} cm^2 s^{-1}) and N_m is the MacMullin number defined above.(Smith and Walton 1993) The observed thickness, 0.28 mm, of the oxidized region in grout samples exposed to air corresponds to a N_m of 5.7×10^{-4} or a $D_{eff}(NO_3^-)$ of 8.8×10^{-9} cm^2 s^{-1}, which is within the range of $D_{eff}(NO_3^-)$ reported for CWFs. The observed rate of oxidation of the grout sample exposed to air is consistent with the simple reaction/diffusion model.

The effect of oxidation by O_2 on an actual waste form, Saltstone, can be illustrated using this model. In comparison to the grout sample, Saltstone has a smaller $D_{eff}(NO_3^-)$, from 1.3×10^{-9} cm^2 s^{-1} to 5×10^{-9} cm^2 s^{-1}, but a similar C_{red} since Saltstone is prepared from the same BFS used to prepare the grout samples. Using a $D_{eff}(NO_3^-)$ of 5×10^{-9} cm^2 s^{-1}, the thickness of the oxidized region would be 17 cm after one ^{99}Tc half-life (213,000 yr), and after ten half-lives, the oxidized region would be 53 cm thick. For comparison, the dimensions of a Savannah River Saltstone cell are 30.5 m × 30.5 m × 7.5 m.(Seitz, Walton et al. 1993) Therefore, approximately 4% of the technetium in the waste form would be oxidized after one ^{99}Tc half-life, and approximately 14% would be oxidized after ten half-lives based on the assumption that oxidation occurs at the top and bottom of the Saltstone cell. Cracking and flow of surface water through the CWF could

greatly increase these numbers and the leaching of TcO_4^- by effectively decreasing the size of the Saltstone cell to the intercrack spacing,(Seitz, Walton et al. 1993; Kaplan and Serne 1998) so this discussion generally illustrates the difference between oxidation by O_2, which produces an oxidized surface region with an increased $D_{eff}(^{99}Tc)$, and oxidation by NO_3^-, which would result in an increased $D_{eff}(^{99}Tc)$ throughout the entire volume of the waste. All of the results in this study indicate that the oxidation of Tc(IV) species in these grout samples is due solely to O_2, and NO_3^- has no observable effect on the speciation of technetium in these samples. While these results do not show that NO_3^- is unreactive towards Tc(IV) in reducing grouts, this reaction occurs too slowly to be observed.

Experimental

Procedures. *Caution: ^{99}Tc is a β-emitter (E_{max} = 294 keV, $\tau_{1/2} = 2 \times 10^5$ years).* All operations were carried out in a radiochemical laboratory equipped for handling this isotope. Technetium, as $NH_4{}^{99}TcO_4$, was obtained from Oak Ridge National Laboratory. The solid $NH_4{}^{99}TcO_4$ was contaminated with a large amount of dark, insoluble material. Prolonged treatment of this sample with H_2O_2 and NH_4OH did not appreciably reduce the amount of dark material. NH_4TcO_4 was separated by carefully decanting the colorless solution from the dark solid. A small amount of NaOH was added to the colorless solution, and the volatile components were removed under vacuum. The remaining solid was dissolved in water, and the colorless solution was removed from the remaining precipitate with a cannula. The concentration of $NaTcO_4$ 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.

All operations were carried out in air. Water was deionized, passed through an activated carbon cartridge to remove organic material and then distilled. All other chemicals were used as received. The grout samples examined here are similar to those previously used for the study of chromium reduction in reducing grout samples and are similar to Saltstone, the CWF used to immobilize low activity waste at the Savannah River Site.(Langton 1988; Bajt, Clark et al. 1993) The dry cement consisted of 46% Type F fly ash, 46% BFS, and 8% Portland cement.(Bajt, Clark et al. 1993) The fly ash, BFS, and Portland cement are those used by the Savannah River Saltstone facility, and were provided by C. A. Langton. Two series of grout samples were prepared.

The first series was prepared using solutions with and without NO_3^- and NO_2^- as shown in Table 3.1. To the waste simulant was added TcO_4^- (0.02 mmol, 0.1 mL, 0.2 M NH_4TcO_4), which was then reduced with Na_2S (0.21 mmol, 0.1 mL, 2.1M Na_2S) in 1M LiOH forming a very dark solution with a black precipitate. The dry cement mixture was added forming a slurry that was placed in a polystyrene (PS) cuvette, which was capped and closed with vinyl tape and sealed inside two thin-walled polyethylene (PE) bags. This first series of samples will be referred to as "unsealed samples", and the final composition of the waste solution after addition of the TcO_4^- and Na_2S solutions is listed in Table 3.1.

The second series of samples was prepared analogously to the first. To the waste simulant was added TcO_4^- (0.012 mmol, 0.30 mL, 0.039 M $NaTcO_4$) and an oxidized Na_2S solution in 1M LiOH (0.065 mL), which formed a dark solution with a black precipitate. The dry cement

mixture was added, forming a slurry that was placed in an acrylic cuvette that was sealed with a plug of epoxy and further sealed inside two heavy-walled (PE) bags. This second series of samples will be referred to as "sealed samples", and the final composition of the waste solution after addition of the TcO_4^- and Na_2S solutions is also listed in Table 3.1. Samples A and C were opened after 26 months and placed in loosely capped jars that were opened weekly. Sample B remained sealed throughout the experiment.

The reductive capacity of the BFS was determined using a slightly modified version of the Angus and Glasser method.(Angus and Glasser 1985) The BFS (~0.5 g) was slurried in 5-10 mL of water to which was added 25.0 mL of 0.059 M $(NH_4)_4Ce(SO_4)_4 \bullet 2H_2O$ in 2 M sulfuric acid. After 1 hour, the solution was titrated with freshly prepared 0.050 M $(NH_4)_2Fe(SO_4)_2 \bullet 6H_2O$ in 0.75 M sulfuric acid. The end point was determined using 0.25 mL of 0.025 M Fe(II) tris-(1,10-phenanthroline) complex.(Walden, Hammett et al. 1931; Smeller 1999) The reductive capacity of the BFS sample was determined from the difference in the volume of Fe(II) solution needed to titrate 25.0 mL of the Ce(IV) solution alone and with the BFS. The reductive capacity of the BFS was 0.82(1) meq g^{-1}.

XAFS spectra were acquired and analyzed as described in the previous section.

The X-ray absorption near edge structure (XANES) spectra were fit using the spectra of TcS_x, TcO_4^-, and $TcO_2 \bullet 2H_2O$ as standards. The fitting was done using the code "fites" developed by C. H. Booth.(Sarrao, Immer et al. 1999) The fit used 4 parameters and the XANES spectra had 19 independent data points (8 eV resolution).

The determination of the thickness of the oxidized region in samples exposed to atmosphere was carried out using the probability of detecting an X-ray photon from within a sample as described by Tröger et al.(Tröger, Arvanitis et al. 1992) The contribution, c, of a surface region of thickness, d, to the total fluorescent XANES signal is given in Eq 1, where $\mu(E)$ and $\mu(F)$ are the total absorption coefficients of the sample at the incident photon energy and the fluorescent photon energy, respectively, and φ and θ are the angles of the sample with respect to the incident photon beam and the fluorescent detector, respectively. For these experiments, $\mu(E)$ and $\mu(F)$ are 5.3 and 7.8 mm^{-1}, respectively, and were determined from the elemental composition of CWF given by Serne, et al.(Serne, Lokken et al. 1992)

$$c = \frac{1}{K}\int_0^d e^{-Kx}dx \qquad K = \frac{\mu(E)}{\sin\varphi} + \frac{\mu(F)}{\sin\theta} \tag{1}$$

IV. Behavior of Technetium in Glass

Introduction.

Borosilicate glass is the major waste form for the immobilization of the legacy high level nuclear waste created by years of plutonium production by the DOE. Glass was selected for several reasons including good durability and the fact that vitrification is a mature technology. Although

most radionuclides present no challenges to the vitrification of high-level waste, certain radionuclides, especially ^{137}Cs and ^{99}Tc, are easily volatilized during vitrification.(Langowski, Darab et al. 1996)

The behavior of technetium and rhenium in borosilicate glasses has recently been reviewed,(Darab and Smith 1996) and will be discussed only briefly here. A number of Tc(VII) compounds have low boiling points. Both pertechnetyl chloride and fluoride (TcO_3Cl and TcO_3F) have boiling points under 100 °C. Tc(VII) oxide, Tc_2O_7, boils at 350 °C, and the alkali metal salts of pertechnetate, particularly $CsTcO_4$, are volatile at high temperature. A few, volatile, lower-valent technetium complexes, such as $TcOCl_3$ and $TcOF_4$ also exist, but are probably not important in this context. The technetium species with the greatest roles in Tc volatility are most likely Tc_2O_7 and the alkali pertechnetates, especially $CsTcO_4$.

Since the importance of the behavior of technetium during vitrification is well known, many studies of the incorporation of technetium in waste form glasses have been performed.(Lammertz, Merz et al. 1985; Freude, Lutze et al. 1989; Ebert, Wolf et al. 1995; Ebert, Bakel et al. 1997; Bibler, Fellinger et al. 1999) The results of these studies vary widely. In some cases, almost all of the technetium is lost during vitrification while other studies find that technetium is well retained. In the most relevant study, the retention of technetium in actual waste glass produced by the Defense Waste Processing Facility at the Savannah River Site,(Bibler, Fellinger et al. 1999) almost no technetium or cesium was lost during vitrification. A number of factors are responsible for the wide variation in degree of volatilization of technetium during vitrification. Most importantly, the experimental parameters vary widely. Many experiments involve mixing technetium compounds with glass frit and melting the mixture to form waste glasses with compositions representative of actual waste glasses. However, work by Darab and Smith showed that this method can yield results that are greatly different from mixing glass frit or precursor with simulated waste solution and then drying and vitrifying the mixture.(Darab and Smith 1996)

In addition to the difficulty in understanding the behavior of technetium during vitrification created by trying to correlate the results of experiments performed under different conditions, little is known about the speciation of technetium in these glasses. Two studies of the speciation of technetium in glasses have been reported. Lanza, et al. prepared glass samples in a graphite crucible under argon atmosphere (reducing conditions) and found that technetium was present as metal inclusions.(Lanza, Cambini et al. 1992) Antonini, et al. prepared glasses under reducing conditions and under air using both NH_4TcO_4 and $TcO_2 \bullet 2H_2O$.(Antonini, Merlini et al. 1985) Under reducing conditions, the glasses contained technetium metal as found by Lanza. Under oxidizing conditions, the glasses contained TcO_2 inclusions. In none of these experiments was Tc(VII) or isolated Tc(IV) centers observed. While these results may seem to imply that Tc(VII) is not stable in glass (presumably due to loss of volatile Tc(VII) species), the conditions used to prepare the glasses are not representative of those used to prepare actual waste form glasses, so the technetium speciation in these glasses may by different from those prepared under conditions more similar to those used for actual waste.

The main focus of this research thrust is to characterize the speciation of technetium in borosilicate glasses as a function of experimental conditions, especially conditions similar to

those used to prepare actual waste glasses: vitrification of mixture of glass precursors and simulated waste. This information will be used to better understand the behavior of technetium during vitrification.

Results and Discussion

Three different series of glass samples were prepared, and their compositions are given in Table 4.1. The first series are simple borosilicate glasses prepared from oxide and carbonate precursors plus a very simple waste simulant consisting of sodium hydroxide and sodium aluminate with and without added EDTA. Technetium was added as either $NaTcO_4$ or $TcO_2 \bullet 2H_2O$. The second series have compositions representative of Hanford Low Activity Waste (LAW) waste glasses, and the waste simulant is an SY-101 simulant in which technetium is the only radioactive component.(Golcar, Colton et al. 2000) The final series, test simulant glasses, has a composition similar to LAW glass minus zirconium and used a simple simulant containing selected additional components to determine their effects on technetium speciation and volatilization. The final composition of the glasses and the composition of the waste surrogates are given in Table 4.1. Rather than discuss each series individually, the speciation of technetium in borosilicate glass will be discussed first, then the speciation of technetium versus retention will be discussed.

Table 4.1. Composition of glasses and waste simulants

Final Glass Composition (wt %)	Waste Simulant Composition (M)
Simple Borosilicate Glasses	
63 SiO_2, 15 Al_2O_3, 14 Na_2O, 4 B_2O_3, 4 CaO, 0.2 TcO_2	4M NaOH, 1M $NaAlO_2$, 0.28M EDTA[a]
Simulated Hanford Low Activity Waste Glass	
40 SiO_2, 20 Na_2O, 6 B_2O_3, 6 Al_2O_3, 5 Fe_2O_3, 3 ZnO, 2 ZrO_2, 2 TiO_2, 2 CaO, 2 K_2O, 1 MgO, 0.2 TcO_2	5M NaOH, 0.5M $NaAlO_2$, 0.5M KOH, 0.2M KF, 0.05M Na_2SO_4, 0.02 CsCl, 0.02M Na_2HPO_4, 3.2M $NaNO_3$[a], 1.2M $NaNO_2$[a], 0.08M EDTA[a]
Test Simulant Glasses	
48 SiO_2 , 15 Na_2O, 10 B_2O_3, 8 Al_2O_3, 6 Fe_2O_3, 5 CaO, 3 Li_2O, 2 K_2O, 2 MgO, 1 TiO_2, 0.2 TcO_2	5M NaOH, 0.5M $NaAlO_2$, 0.5M KOH, 0.1M NaF[a], 0.1M NaCl[a], 0.1M CsOH[a], 0.1M $NaNO_3$,[a] 0.02M sucrose[a]

a) not present in all simulants

Speciation of technetium by EXAFS

Three different technetium environments were observed in these glass samples. In general, technetium was present as two of these three species in any given glass sample. However, in a few samples, the great majority of the technetium was present as a single species. In these cases, EXAFS was used to determine the local structure of the technetium species. The EXAFS spectra of these species are shown in Fig. 4.1 along with the local structure determined from the EXAFS data. Table 4.2 contains the structural parameters derived from the EXAFS data.

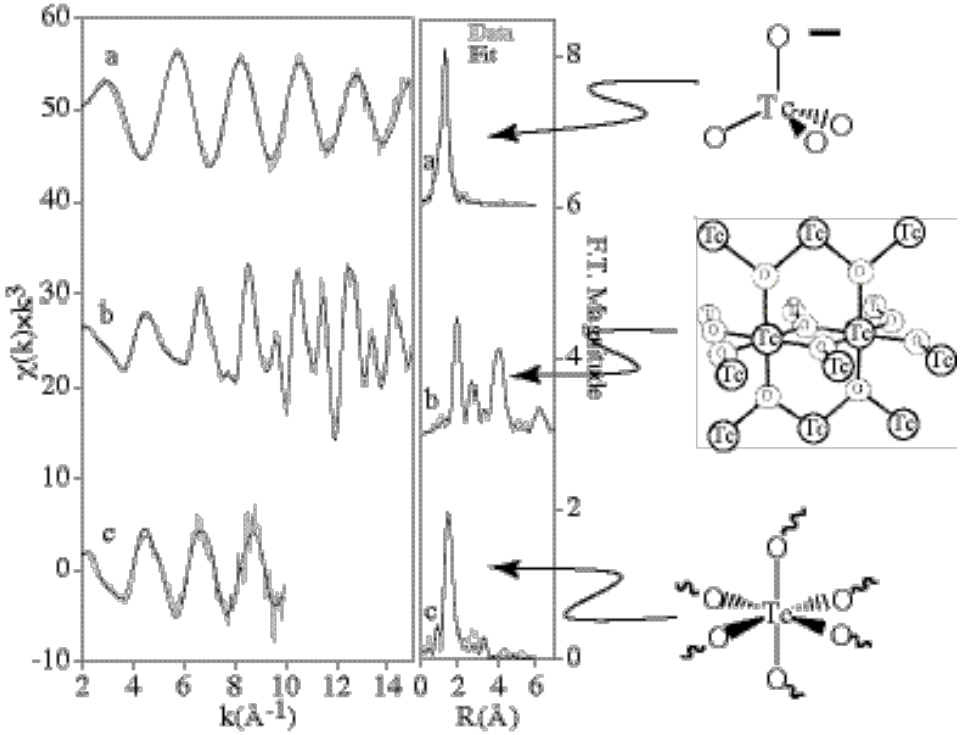


Figure 4.1. Tc K-edge EXAFS spectra and Fourier Transforms (left) and corresponding local environments (right) of (a) pertechnetate, (b) crystalline TcO_2 inclusions, and (c) isolated Tc(IV) centers in a glass matrix.

Table 4.2. EXAFS fitting parameter for technetium species in glass

Scattering Path	Coordination Number	Distance (Å)	Debye-Waller Parameter (Å^2)	ΔE_0 (eV)
TcO_4^- in glass, Scale Factor = 0.92(2)				
Tc-O	4[a]	1.723(1)	0.0024(1)	-6.3(5)
TcO_2 inclusions in glass, Scale Factor = 0.73(5)				
Tc-O[c]	1.3(3)	1.70(1)	0.003(1)	-11(4)
Tc-O	6[a]	1.994(3)	0.0019(3)	-6(1)
Tc-O-Tc-O[d]	6[a]	4.06(3)	0.0019[b]	-6[b]
Tc-Tc	1[a]	2.597(3)	0.0033(3)	-6[b]
Tc-Tc	1[a]	3.095(4)	0.0026(4)	-6[b]
Tc-Tc	9[a]	3.645(3)	0.0050(2)	-6[b]
Tc-Tc	3[a]	4.54(1)	0.0064(8)	-6[b]
Tc-Tc	9[a]	5.434(6)	0.0048(4)	-6[b]
Tc(IV) in glass, Scale Factor = 0.82(6)				
Tc-O	6[a]	2.031(4)	0.0045(7)	0.6(8)
Tc-O-Tc-O[d]	6[a]	4.17(3)	0.001(4)	0.6[b]

a) Coordination number fixed.
b) Parameter linked to previous parameter.
c) Separate Tc-O shell due to TcO_4^- in sample.
d) Four-legged multiple scattering path due to *trans* oxygen ligands.

The technetium environment most often observed among these samples is pertechnetate in glass, shown in Fig. 4.1a. The Tc-O distance is typical of pertechnetate. No other scattering paths are observed for this species, which is typical for pertechnetate even when pertechnetate is adsorbed on solid matrices. The least commonly observed environment is inclusions of crystalline TcO_2.(Almahamid, Bryan et al. 1995) The spectrum shown in Fig. 4.1b illustrates this environment, which is clearly identified by Tc-Tc scattering distances identical to those of crystalline TcO_2. In addition, the sample shown in Fig. 4.1b also contains some pertechnetate. Finally, Tc(IV) octahedra homogenously distributed in the glass matrix is illustrated in Fig. 4.1c. Unfortunately, the signal to noise ratio of the spectrum in Fig. 4.1c is poor due to the intense fluorescence of zirconium from this sample, which limited the technetium fluorescence signal. Consequently, the k-range of this data is severely limited. The only scattering paths observed for this species are due to the TcO_6 coordination environment. Scattering by more distant neighbors is not observed and is believed to be due to the truncation of the data.

Speciation of Technetium by XANES

As shown in the previous section, EXAFS is extremely useful for determining the local environment of technetium in glasses containing primarily a single species. However, the vast majority of the samples examined contained multiple species and are less amenable to this type of EXAFS analysis. In these cases, the technetium speciation was determined by fitting the TcK-edge XANES spectra using the XANES spectra of technetium in the three environments illustrated in Fig. 4.1 as standards.(Sarrao, Immer et al. 1999; Ressler, Wong et al. 2000) The XANES standards and three typical XANES spectra deconvoluted in this manner are illustrated in Fig. 4.2. As seen in Fig. 4.2a-b, the XANES spectra of TcO_2(cr) and Tc(IV) are very similar; the major difference is the increased height of the first post-edge feature, which is due to the *trans* Tc-O-Tc-O multiple scattering path, in the XANES spectrum of Tc(IV). As a result of this similarity, although the fraction of tetravalent technetium can be determined accurately, the exact contributions of Tc(IV) and TcO_2 are less accurate. The fraction of TcO_4^- in these glasses can also be accurately determined. It should be noted that the EXAFS spectra of the glasses can also by deconvoluted in the same manner, but acquisition of XANES spectra take approximately 10% of the time needed to acquire the EXAFS spectra shown in the previous section.

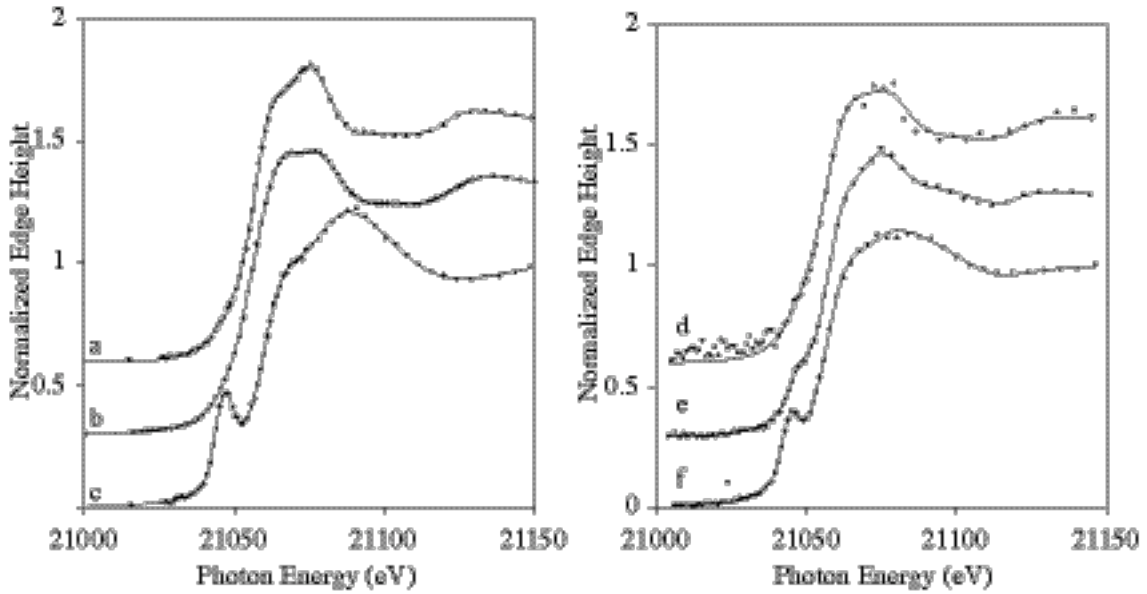


Figure 4.2. Tc K-edge XANES spectra of technetium in glass. Standard spectra (left): a) Tc(IV) in glass matrix, b) TcO_2 inclusion, and c) TcO_4^- in glass. Examples of XANES fits (right); d) poorest fit (14% TcO_4^-, 20% TcO_2, 66% Tc(IV)), e) best fit (30% TcO_4^-, 70% Tc(IV)), f) typical fit (65% TcO_4^-, 35% Tc(IV). Data are indicated by dots, fits are shown as lines.

While it is somewhat informative to examine the technetium speciation resulting from different vitrification conditions, comparing the volatilization of technetium versus technetium speciation is more interesting. The edge-height of the Tc K-edge XANES spectra in transmission, which is directly proportional to the amount of technetium in the X-ray beam, provides a method to compare the relative technetium retention in these glasses.(Koningsberger and Prins 1988) Fig. 4.3 shows the Tc-K edge height (in transmission) versus Tc(IV) fraction for the Simple Borosilicate Glasses and the Simulated Hanford Low Activity Glasses. As is clear from the figure, no simple correlation exists between technetium retention and oxidation state among these glasses. In fact, the glass sample that retained the most technetium contained 85% TcO_4^-. While no correlation exists between oxidation state and retention among these glasses, a strong correlation exists between technetium retention and synthesis conditions as shown in Fig. 4.4. Although it may not be completely clear from the figure, the glasses with the highest technetium retention were prepared using the simplified waste simulant containing only sodium hydroxide and sodium aluminate and sometimes EDTA.

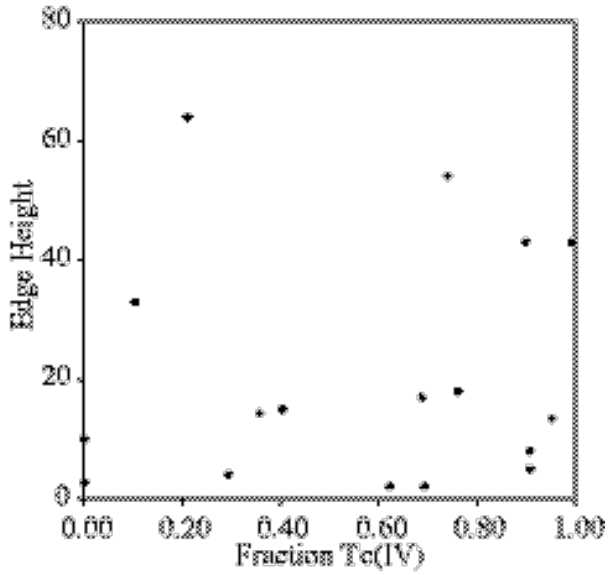


Figure 4.3. Tc K-edge XANES edge height, a rough estimate of Tc retention, versus fraction of Tc(IV) in glass samples.

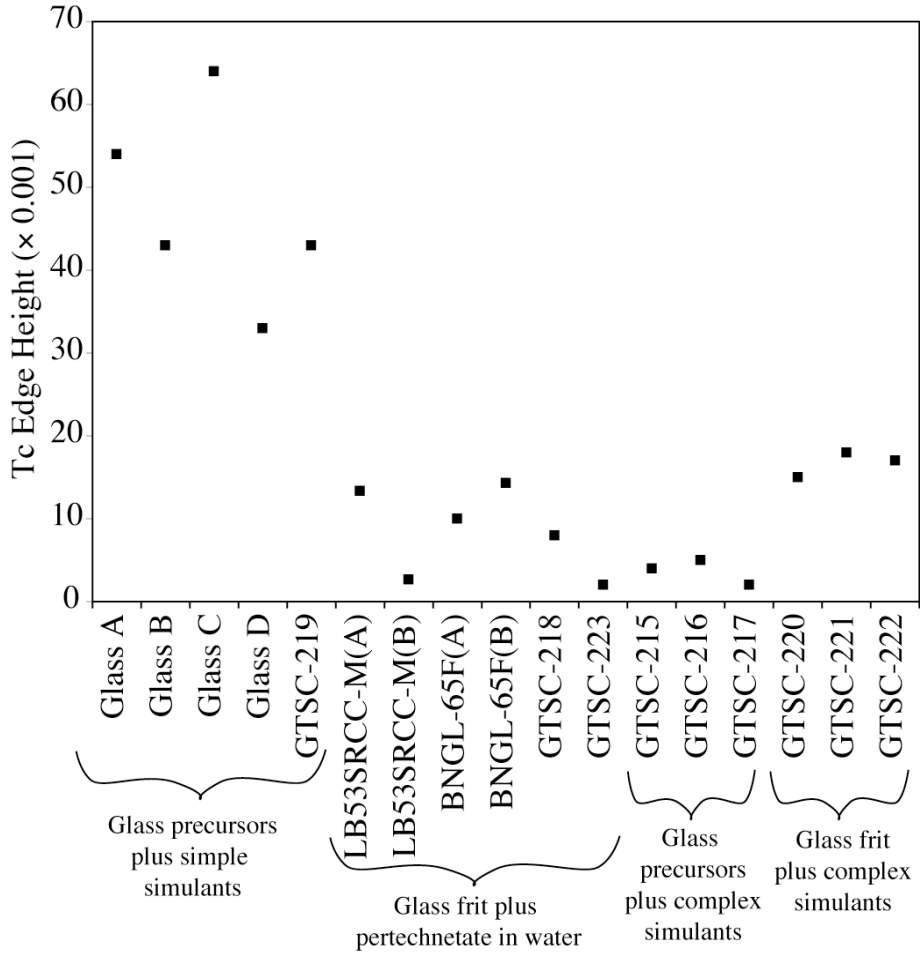


Figure 4.4. Tc K-edge XANES edge height in transmission, a rough estimate of Tc retention, versus synthesis conditions of glass samples.

The data shown in Fig. 4.3 and 4.4 strongly imply that some component of the representative simulant is responsible for increasing technetium volatility during vitrification. To obtain a more detailed understanding of the role of the components of the complex simulant in technetium volatility, glasses analogous to Hanford Low Activity Waste Glass were prepared using a simple simulant containing only sodium hydroxide, potassium hydroxide, and sodium aluminate plus one selected component of the complex simulant. The results are given in Table 4.3.

Table 4.3. Results of vitrification with selected components of the complex simulant[a]

Component[b]	Fraction TcO_4^-	Tc K-Edge Height (transmission)	Tc K-Edge Height (fluorescence)
nothing	50	46	1.81
0.1M NaF	52	84	1.80
0.1M NaCl	48	86	1.53
0.1M CsOH	22	51	0.86
0.1M $NaNO_3$	50	88	1.41
0.015M Sucrose	24	108	1.98

a) Simple simulant: 5M NaOH, 0.5M KOH, 0.5M $NaAlO_2$.
b) Concentration of added component in the waste simulant in addition to the NaOH, KOH, and $NaAlO_2$.

As shown in Table 4.3, NaF, NaCl, and $NaNO_3$ had little or no effect on either technetium speciation or retention in these glasses. The relatively low Tc K-edge height of the control sample with no additive is smaller than for the other glasses, this is believed to be due to an experimental problem (part of the X-ray beam bypassed the sample), and the fluorescence edge height is more useful for these glasses. Two additives, CsOH and sucrose, had an effect on both technetium speciation and retention. In both cases, technetium was present as mainly Tc(IV). However, the sample prepared with CsOH retained less technetium while the sample prepared using sucrose retained more technetium. In all of these glasses, the Tc(IV) was present as Tc(IV) homogenously distributed through the glass matrix rather than TcO_2(cr) inclusions.

Technetium Speciation

The identity of the technetium species found in the glasses is a simple function of the preparation conditions. Easiest to explain is origin of TcO_2 inclusions. These occur when the technetium compound used in the experiment is a precursor to TcO_2. The most obvious of these precursors is $TcO_2 \bullet 2H_2O$, which is converted to TcO_2(cr) at relatively low temperature, 300 °C.(Nelson, Boyd et al. 1954) The less obvious precursor is NH_4TcO_4, which is also converted to TcO_2(cr) by heating to 350 °C under an inert atmosphere.(Spitsyn, Kuzina et al. 1978) $TcO_2 \bullet 2H_2O$ can be generated either by initially reducing TcO_4^- using hydrazine or by including a large excess of organic material in the waste simulant. Both routes were observed to yield glasses containing TcO_2(cr) inclusions in these experiments. In addition, the work of Antonini, et al. illustrates the formation of TcO_2(cr) inclusions from the decomposition of NH_4TcO_4.(Antonini, Merlini et al. 1985)

The other two technetium environments observed in these experiments are believed to result from initial incorporation of pertechnetate in the melt. As illustrated in Fig. 4.1a and observed in

many of these samples, pertechnetate added to the glasses is incorporated as pertechnetate provided that it is not reduced, either by organic materials in the glass precursor or by other routes, such as decomposition of NH_4TcO_4. If the glass precursor contains a small amount of organic material, Tc(IV) homogeneously distributed in the glass matrix is observed. This species presumably results from initial incorporation of pertechnetate in the melt, which is later reduced. The identity of the reducing agent is currently unknown, but could be either residual carbonaceous material resulting from the pyrolysis of organic components of the waste or Fe(II) created by reduction by the same organic components.

Technetium Volatility

The most notable result of these experiments is that pertechnetate is well retained by borosilicate glasses. Although this result appears to contradict previous work that shows that reducing conditions increase technetium retention, no contradiction actually exists. Previous work shows that reducing conditions do increase technetium retention, but that does not imply that all Tc(VII) species are volatile. Previous studies, especially that of Darab and Smith,(Darab and Smith 1996) clearly show that the large degree of technetium volatilization observed in many studies is most likely due to oxidation of TcO_2 to Tc_2O_7 as shown by equations 1-3. Volatilization of technetium by this mechanism is most pronounced when either $TcO_2 \bullet 2H_2O$ or NH_4TcO_4 is added to either glass frit or glass precursors with a high melting point and vitrification is carried out under air. As noted before, Smith and Darab deliberately prepared glasses in this manner to illustrate this point and observed only ~3% retention of technetium in the glass.

$$TcO_2 \bullet 2\,H_2O \xrightarrow{300^\circ\,C} TcO_2 + 2\,H_2O \qquad (1)$$

$$NH_4TcO_4 \xrightarrow{300^\circ\,C} TcO_2 + 2\,H_2O + 0.5\,N_2 \qquad (2)$$

$$2\,TcO_2 + 1.5\,O_2 \longrightarrow Tc_2O_7 \qquad \Delta G = -146\,\text{kcal/mol} \qquad (3)$$

When technetium is present as an alkali pertechnetate, loss of Tc_2O_7 is extremely unlikely since the decomposition of alkali pertechnetate to form alkali oxide and Tc_2O_7 is extremely endothermic as shown in equations 4-6.(Rard, Rand et al. 1999) All of these data are at 25 °C, but the large magnitude of the Gibbs free energy of these reactions makes them extremely unlikely at the temperatures examined here. Consequently, when technetium is added to the glass precursors as pertechnetate in waste simulant, loss of technetium should be less than in the previous scenario. The good retention of technetium by glasses prepared with the simple simulant is in agreement with postulate; however, at least one of the components of the more representative Hanford simulant increases the volatility of the technetium.

$$2\,NaTcO_4 \longrightarrow Na_2O + Tc_2O_7 \qquad \Delta G = 109\,\text{kcal/mol} \qquad (4)$$

$$2\,KTcO_4 \longrightarrow K_2O + Tc_2O_7 \qquad \Delta G = 142\,\text{kcal/mol} \qquad (5)$$

$$2\,CsTcO_4 \longrightarrow Cs_2O + Tc_2O_7 \qquad \Delta G = 153\,\text{kcal/mol} \qquad (6)$$

A number of technetium compounds could be responsible for the technetium volatilization when more complex simulant was used, TcO_3Cl, TcO_3F, and $CsTcO_4$. The first two are extremely volatile while $CsTcO_4$ is only volatile at high temperature. The results from glasses prepared using selected components of simulant showed that only CsOH had any effect on the technetium volatilization and retention. Interestingly, the glass prepared with Cs also contained a higher percentage of Tc(IV). Both of these observations can be explained by loss of volatile $CsTcO_4$, which led to the loss of pertechnetate but not Tc(IV).

While it is somewhat surprising that a low concentration of CsOH (0.1 M) would have any effect on the volatility of technetium in the presence of 0.5 M KOH and 5 M NaOH, the effect of Cs is magnified by the thermodynamic stability of $CsTcO_4$. At the concentrations of sodium, potassium, and cesium hydroxide used in these experiments, >99% of the technetium is present at $CsTcO_4$ based upon the heats of formation of the pertechnetate salts. In addition, $CsTcO_4$ is the least soluble of the pertechnetate salts.(Rard, Rand et al. 1999) These two factors result in the precipitation of $CsTcO_4$ when water evaporates from the slurry at the start of the vitrification. Since $CsTcO_4$ is also the most volatile of the alkali pertechnetates, the increased volatilization of technetium is possible at low CsOH concentrations.

The final experiment shown in Table 4.3 shows the typical result that creating reducing conditions can increase technetium retention. However, the reduced technetium species present in the glass is Tc(IV) not TcO_2, which implies that the pertechnetate was likely reduced in the melt rather than reduced to TcO_2 at the beginning of the vitrification process. Since all of the alkali pertechnetates are volatile, it is not surprising that reduction to nonvolatile Tc(IV) increases technetium retention. The conditions necessary to produce Tc(IV) in the glass are only slightly more reducing, -0.18 V, than glass in contact with air.(Freude, Lutze et al. 1989)

The conclusions that can be drawn from this research are mainly the origin of technetium speciation in borosilicate glasses. Inclusion of TcO_2 occur if technetium is added to the glass as NH_4TcO_4 or $TcO_2 \bullet 2H_2O$ or if strongly reducing conditions occur at the start of the vitrification process, prior to formation of the melt. If pertechnetate is present when the melt is formed, either TcO_4^- or Tc(IV) homogenously distributed in the glass matrix is present depending on the electrochemical potential of the melt. The main results from technetium retention are similar to those of previous studies. The major route to technetium volatilization is oxidation of TcO_2 to Tc_2O_7. Technetium is lost due to the volatility of alkali pertechnetates, especially $CsTcO_4$. Consequently, reducing conditions are undesirable at the beginning stages of vitrification since they lead to the formation of TcO_2, but slightly reducing conditions are desirable in the melt since they lead to the reduction of TcO_4^- to isolate Tc(IV) sites. While this information is useful if technetium volatility is the only important parameter in vitrification, other, more important considerations exist. The most notable of these is the necessity to prevent reduction of the noble metal fission products, Ru, Rh, Pd, and Ag, to metal, which could short out the electrodes of a joule-heated melter. This requirement limits how reducing the melt environment can be. Whether incorporation of Tc(IV) in the glass is consistent with preventing reduction of the noble metal fission products to metal is unknown.

Experimental

Procedures General procedures are described in Section II.

All operations were carried out in air. Water was purified using a MilliQ system. All other chemicals were used as received. Several series of glass samples were prepared using similar conditions. A waste simulant containing $NaTcO_4$ was added to either powdered glass frit or glass precursors forming a thick slurry, which was transferred to a small 5%Au / Pt crucible. In some cases, the $NaTcO_4$ was initially reduced to $TcO_2 \bullet 2H_2O$ using hydrazine. In addition, certain components of the waste simulant, such as nitrate or EDTA, were omitted in selected experiments. The crucible was suspended in a vertical tube furnace. In a typical experiment, the furnace was heated to 90 °C at 6 °C/min then to 110 °C at 0.75 °C/min then to 1200 °C at 10 °C/min and held at 1200 °C for 30 min. The glass was allowed to cool to room temperature inside the furnace. The final glass compositions, and the compositions of the waste simulants are listed in Table 4.1.

XAFS spectra were acquired and analyzed as described in Section II.

Relevance to DOE Issues

Behavior of Technetium in High-Level Waste

Our previous research identified a facile route to radiolysis of TcO_4^-: reduction by NO_3^{2-}, which could result in reduction of TcO_4^- to lower-valent technetium compounds provided that the O^- radicals created by radiolysis were scavenged. This pathway could be important for waste tanks at both the Savannah River and Hanford Sites, and can explain the high levels of technetium found in the sludge of high-level waste tanks at the Savannah River Site. In addition, our previous work showed that soluble Tc(IV) alkoxide complexes could be created under highly alkaline conditions. However, the alkoxide ligands used for that research are not present in sufficient concentrations in high-level waste to account for the problematic soluble, nonpertechnetate species found in Hanford high-level waste tanks.

One potential alkoxide ligand, gluconate, is present in high concentrations in certain waste tanks and could be responsible for the formation of soluble lower valent species. In fact, Tc(IV) gluconate is easily prepared, and $TcO_2 \bullet 2H_2O$ rapidly dissolves in alkaline gluconate solution. This behavior could cause problems in one of the proposed scenarios for treating high level waste: mixing Complexant Concentrate (CC) waste with waste from other tanks to reduce the proportion of technetium present as the soluble nonpertechnetate species. However, if the waste from other tanks contains $TcO_2 \bullet 2H_2O$, which seems likely based upon the radiolysis experiments, the gluconate present in CC waste will form soluble Tc(IV) gluconate, which cannot be removed by ion-exchange. However, Tc(IV) gluconate is moderately air-sensitive and could potentially be oxidized.

While Tc(IV) gluconate could pose problems in potential treatment schemes, it is not the soluble nonpertechnetate species, which are apparently Tc(I) carbonyl complexes. Unfortunately, such complexes are kinetically inert, which explains why oxidation of the nonpertechnetate species is difficult. It may, however, be possible to remove these species using ion selective resins.

Behavior of Technetium in Cementitious Waste Forms

The results from work with the grout waste forms clearly show that oxygen will react quickly with the lower valent technetium species present in reducing grout waste forms. However, this does not mean that all of the lower valent technetium species in the grout will be rapidly oxidized to mobile pertechnetate. The observed rate of oxidation of the lower valent technetium species is in good agreement with the simple reaction/diffusion model of Smith and Walton. This model shows that oxidation will occur slowly and only at the surface of the waste form that is exposed to air (or water saturated with air). Oxidation of technetium at the surface will increase its leach-rate, but this is not the major concern. If oxidation of technetium occurs only at the surface of the waste form monolith, only a small percentage of the reduced technetium species will be oxidized. However, if surface water penetrates cracks within the waste form, oxidation of a much larger fraction of the technetium will occur, and the technetium leach rate for the waste form could be much higher.

Behavior of Technetium in Borosilicate Glasses

The results reveal which technetium species are present in borosilicate glasses prepared under conditions similar to those used to prepare actual waste glasses. Three technetium species are found in the glasses, pertechnetate, TcO_2(cr) inclusions, and Tc(IV) homogenously distributed in the glass matrix. The conditions that lead to each of these species is also discussed. Results from investigating the volatility of technetium agree with previous experiments. The pathway responsible for loss of large fractions of technetium is oxidation of TcO_2 to volatile Tc_2O_7, most likely prior to formation of the glass melt. In addition, loss of volatile $CsTcO_4$ is also important at high temperatures. Formation of reducing conditions in the melt leads to less technetium volatility and the presence of Tc(IV) homogenously distributed in the melt.

Interestingly, if vitrification is carried out under air, reducing conditions at the beginning stages of vitrification, due to a large excess of organic material, for example, should lead to increased technetium volatility due to oxidation of TcO_2. However, melt conditions that are slightly reducing relative to atmosphere should lead to decreased volatilization due to the formation of nonvolatile, isolated Tc(IV) centers in the melt.

Recommendations

Since the pretreatment requirements for Hanford high-level waste have recently changed and do not include technetium separation at this time, it is not clear what utility recommendations about Hanford high-level waste would have. One note of caution is that if wastes from different tanks is mixed with CC waste, formation of Tc(IV) gluconate is likely. If such a strategy is again proposed, experiments should be carried out using very fresh waste samples since $TcO_2 \bullet 2H_2O$ is air sensitive. Experiments carried out using old samples are probably not representative of the actual environment of the waste tanks and could lead to incorrect conclusions. Even if Tc(IV) gluconate is formed, it may be possible to oxidize it since it is not kinetically inert, unlike the Tc(I) carbonyl species. Of course, if technetium separation is again considered as part of the Hanford waste treatment process, the knowledge provided by this research, especially the identity of the nonpertechnetate species, will be extremely useful for the development of processes to separate or oxidize this species.

One important property of the Tc(I) carbonyl species that has not been investigated is its volatility during vitrification.

The results from the behavior of technetium in grout clearly show that the lower valent technetium species are quickly oxidized by atmospheric oxygen. Exactly what effect this has on an actual waste form depends upon the limiting size of the waste, either the entire waste block or the spacing between cracks. If the monolith does not contain cracks, it should perform as assumed for the reducing waste form since migration of the oxidized zone into the waste form is slow and the size of the waste form is very large. If the waste form contains cracks that are accessible to oxygenated surface water, the situation is very different depending upon the spacing of the cracks. Since the effective size of the waste form is reduced to the spacing between the cracks, a much larger percentage of the technetium could be oxidized to pertechnetate. Since the oxidation occurs at the surface of the cracks, the technetium leach rate should be similar to that for pertechnetate in non-reducing grout. The main recommendation is

to account for oxidation of the technetium in the reducing waste forms in this manner in performance models. From the results here, the simple reaction/diffusion model of Walton and Smith appears to be appropriate to model the rate of oxidation of the waste form.

At present, we have no extensive recommendations concerning vitrification of waste glasses containing technetium. However, it should be noted that reducing conditions are not desirable during the initial stages of vitrification due to the formation of TcO_2, which is readily oxidized to highly volatile Tc_2O_7. Similarly, using $TcO_2 \bullet 2H_2O$ or NH_4TcO_4 as the technetium source for glasses will lead to a high degree of volatilization.

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 complex chemistry of technetium in high-level waste. The problematic soluble, nonpertechnetate species have been identified as Tc(I) carbonyl complexes, and the role of Tc(IV) gluconate in proposed treatment schemes has been discussed

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, but the behavior of actual waste forms likely depends upon the degree of cracking present.

The speciation of technetium in borosilicate glasses has been investigated, and the technetium species present in glasses prepared under conditions analogous to those used to prepare actual waste have been identified. Preliminary investigations of the role of technetium speciation in technetium volatilization agree with previous studies of technetium volatilization.

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Publications.

Lukens, WW, DK Shuh, NC Schroeder, KR Ashley. "Identification of the Non-Pertechnetate Species in Hanford Waste Tanks, Tc(I)-Carbonyl Complexes" *Environ. Sci. Technol.* **2003**, *in press (currently available on the web at pubs.acs.org).*

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Interactions

<u>Presentations</u>

Lukens, WW, DK Shuh, IS Mueller, DA McKeown. **2003**. "X-ray Absorption Fine Structure Studies of Technetium Speciation in Borosilicate Glasses." Materials Research Society National Symposium, Section DD, Boston, MA, December 3-5.

Lukens WW, DK Shuh, NC Schroeder, KR Ashley. **2003**. "Identification of the Non-Pertechnetate Species in Hanford Waste Tanks, Tc(I)-Carbonyl Complexes." American Chemical Society Meeting, New York, NY, September 7-11.

Lukens WW, DK Shuh. **2003**. "XAFS studies of technetium in alkaline solution and cement and glass matrices." American Chemical Society Meeting, New Orleans, LA March 23-27.

Lukens WW, DK Shuh. **2003**. "Behavior of Technetium in Cement and Glass Matrices." Vitreous State Laboratory, The Catholic University of America, Washington, D.C., January 6.

Lukens WW, PG Allen, JJ Bucher, NM Edelstein, DK Shuh. **2002**. "Behavior of Technetium in Alkaline Solution and in Cement and Glass Waste Forms." Stanford Synchrotron Radiation Laboratory Users' Meeting. October 7-9.

Lukens WW, JJ Bucher, NM Edelstein, DK Shuh. "Radiation Chemistry of Technetium in Highly Alkaline Solution." **2001**. 25th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 15-18.

Lukens WW, PG Allen, JJ Bucher, NM Edelstein, DK Shuh. **2001**. "Behavior of Technetium in Alkaline Solution and in Grout Containing Blast Furnace Slag." Stanford Synchrotron Radiation Laboratory Users' Meeting. October 18-19.

Lukens WW, JJ Bucher, NM Edelstein, DK Shuh, CJ Burns, MG Fickes, BL Scott. **2001**. "Fundamental Chemistry of Technetium (in Alkaline Solution)" DOE Tanks Focus Area Workshop, Salt Lake City, UT, March 11-14.

Lukens WW, JJ Bucher, NM Edelstein, DK Shuh. "Radiation Chemistry of Technetium in Alkaline Solution." **2000**. American Chemical Society Western Regional Meeting, San Francisco, CA, October 25-28.

Consultative and Advisory Interactions

R. Jeff Serne, Pacific Northwest National Laboratory. February and March 2003. Provided information about the behavior of technetium in reducing grout.

Dan McCabe, Westinghouse Savannah River Company. BES Contractors' Meeting, April 2003. Discussed recent results from Hanford high-level waste. Send a preprint of the ES&T paper about Tc(I) carbonyl complexes.

Paul Dean, Science Applications International Corp. September 2002. Provided general information about technetium solution chemistry.

Collaborations

Norman Schroeder, Los Alamos National Laboratory and Kenneth Ashley, Texas A&M University, Commerce. Informal collaboration. Several discussions of technetium chemistry in Hanford high-level waste tanks. These discussions were essential for understanding the chemistry presented in Section II.

Isabelle Muller and David McKeown, Vitreous State Laboratory (VSL), The Catholic Univeristy of America. The VSL researchers have provided glass frit and glass compositions used for some of the studies of technetium in glass. We have provided information about the speciation of technetium in specific glass formulations.

Future Work

Future work in this area will be performed under a renewal of this EMSP program. The main focus of this work will be the behavior of technetium in borosilicate glasses in collaboration with researchers at VSL. The primary focus will be to understand the differences between the behavior of technetium and rhenium in borosilicate glasses since rhenium is used as a surrogate in large-scale melter tests. In addition, the basic chemistry of technetium under vitrification conditions, and the effect of technetium speciation on technetium leach rate will be examined. The effect on technetium volatility of adding Tc(I) carbonyl complexes as the technetium source will be examined.

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