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Technetium in Alkaline, High-Salt, Radioactive Tank Waste Supernate: Preliminary Characterization and Removal

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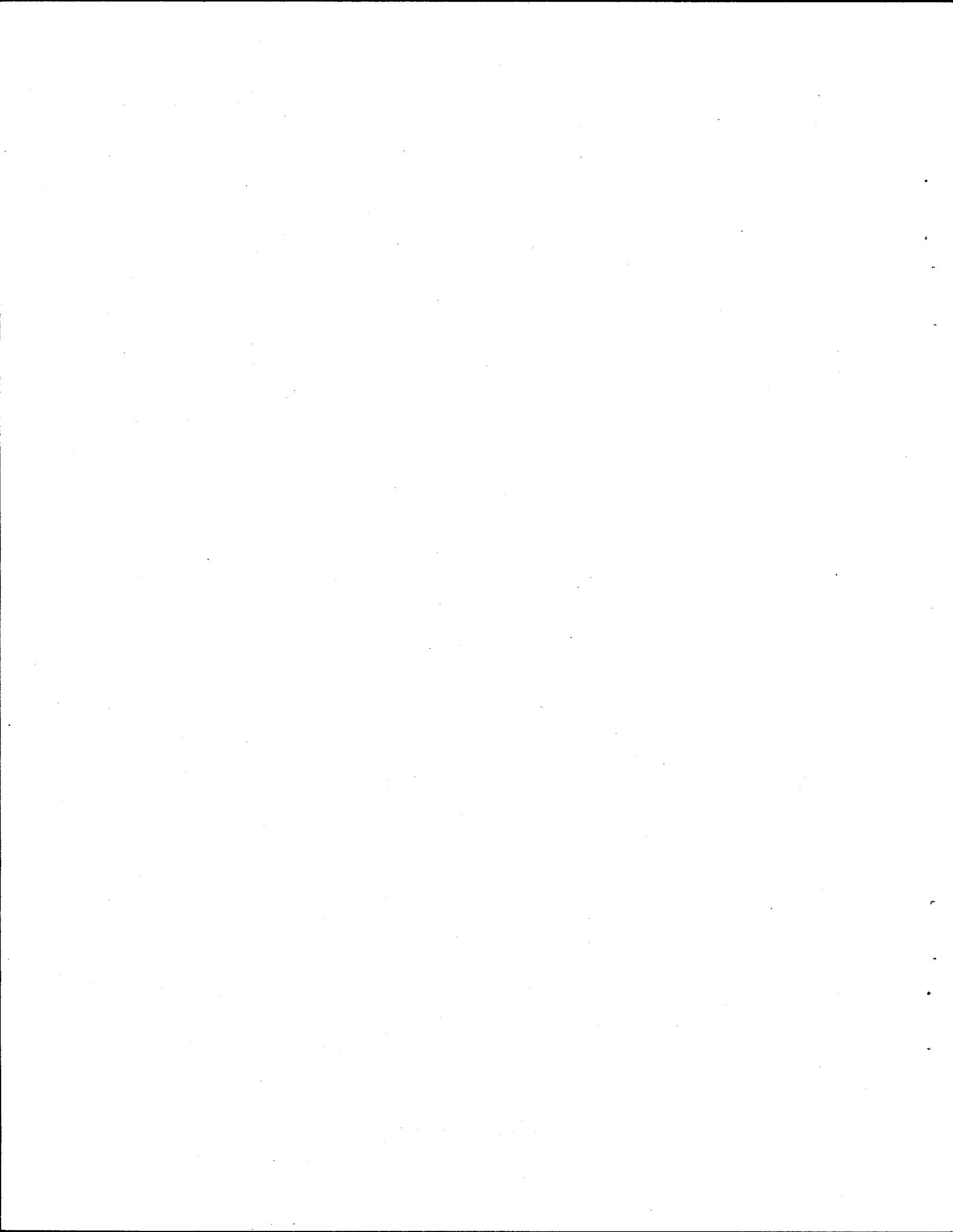
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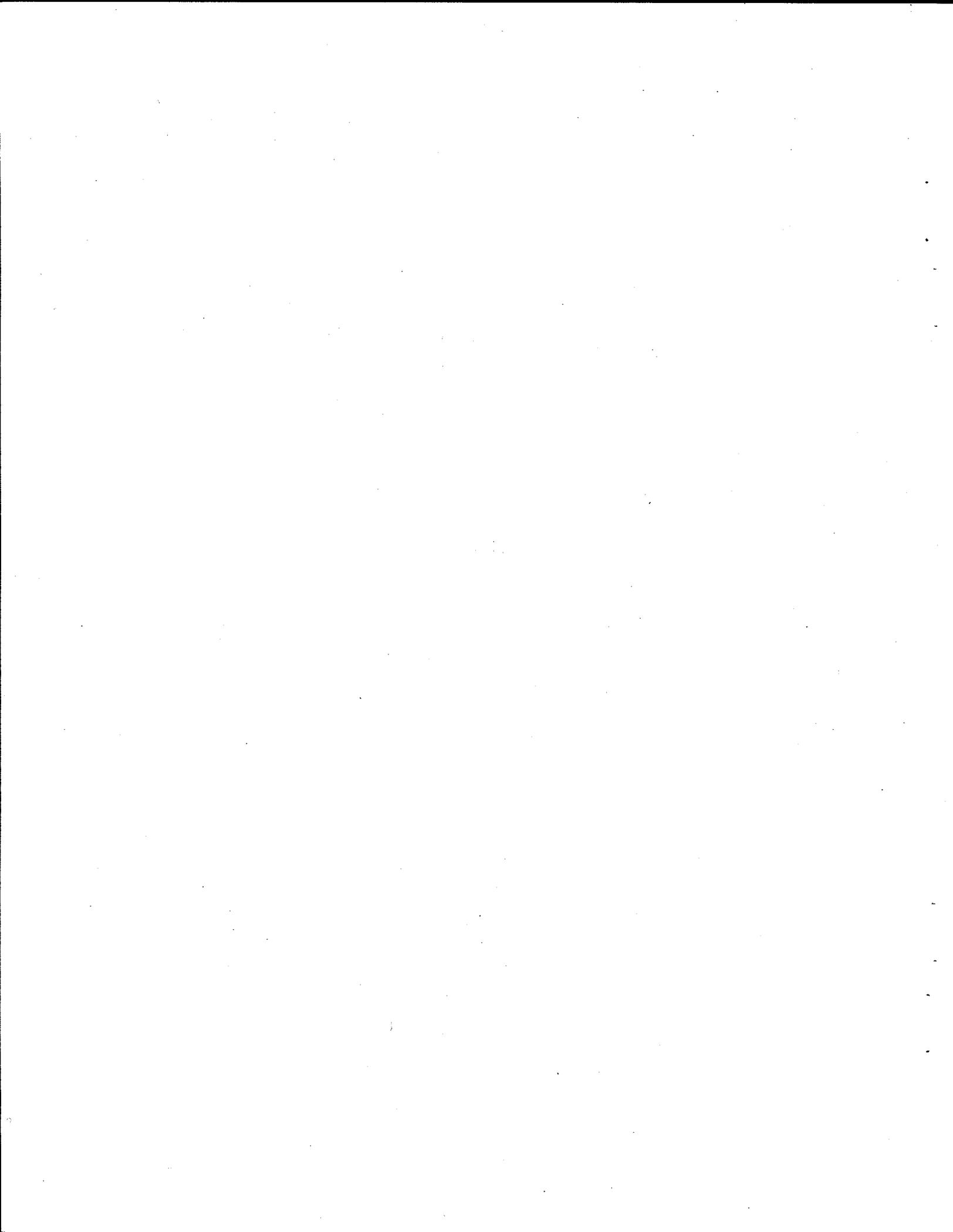


Summary

This report describes the initial work conducted at Pacific Northwest National Laboratory to study technetium (Tc) removal from Hanford tank waste supernates and Tc oxidation state in the supernates. Filtered supernate samples from four tanks were studied: a composite double shell slurry feed (DSSF) consisting of 70% from Tank AW-101, 20% from AP-106, and 10% from AP-102; and three complexant concentrate (CC) wastes (Tanks AN-107, SY-101, ANS SY-103) that are distinguished by having a high concentration of organic complexants. The work included batch contacts of these waste samples with Reillex™-HPQ (anion exchanger from Reilly Industries) and ABEC 5000 (a sorbent from Eichrom Industries), materials designed to effectively remove Tc as pertechnetate from tank wastes. A short study of Tc analysis methods was completed. A preliminary identification of the oxidation state of non-pertechnetate species in the supernates was made by analyzing the technetium x-ray absorption spectra of four CC waste samples. Molybdenum (Mo) and rhenium (Re) spiked test solutions and simulants were tested with electrospray ionization-mass spectrometry to evaluate the feasibility of the technique for identifying Tc species in waste samples.

The highlights from the work are as follows:

- Both Reillex™-HPQ and ABEC 5000 are effective for Tc removal from the composite DSSF waste (70% AW-101), exhibiting 93% and 91% removal, respectively, on the first contact.
- Neither Reillex™-HPQ nor ABEC 5000 are effective for Tc removal from the three CC wastes studied. Technetium removal from the CC wastes was in all cases less than 50%. Removal of Tc from these wastes will require either an alternative process such as electrochemical deposition or addition of a feed adjustment step to oxidize the Tc species to pertechnetate.
- The Tc in CC waste is very resistant to oxidation to pertechnetate in acidified samples generally required for Tc analysis. A vigorous oxidation with Ce(IV) was found effective for this purpose, but is time consuming.
- X-ray absorption near edge spectroscopy indicates that the dominant species in CC waste is not pertechnetate. It also shows that the non-pertechnetate specie(s) in the CC wastes probably has an oxidation state of +IV.
- The batch contacts, oxidation study, and XANES data all indicate that for the tested wastes containing relatively large (> 10 g total organic carbon per liter), amounts of organic complexants, more than half of the total Tc is *not* pertechnetate.
- Inductively coupled plasma-mass spectrometry identified Re species, including polyoxyanions, in simulants and test solutions and was useful for following the Re species through various changes in solution chemistry. Perrhenate, a good surrogate for TcO_4^- , was easily detectable in a CC waste simulant at 200 mg/L, somewhat higher than the concentration of Tc in CC wastes.



Glossary

ALARA	as low as reasonably achievable
CC	complexant concentrate
DDI	distilled deionized (water)
DF	decontamination factor
DI	deionized (water)
DOE	U.S. Department of Energy
DSSF	double shell slurry feed
EXAFS	extended x-ray absorption fine structure
ESI-MS	electrospray ionization-mass spectrometry
HP	Hewlett-Packard
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
LANL	Los Alamos National Laboratory
LAW	low activity waste
LSC	liquid scintillation counting
MIBK	methyl isobutyl ketone
PC	personal computer
NMR	nuclear magnetic resonance
PPG	polypropylene glycol
PEG	polyethylene glycol
PNNL	Pacific Northwest National Laboratory
PR	phase ratio
PRFP	privatization request for proposal
QC	quality control
SSRL	Stanford Synchrotron Radiation Laboratory
RPD	relative percent difference
SAL	Shielded Analytical Laboratory
TOC	total organic carbon
TRU	transuranic
TWRS	Tank Waste Remediation System
UST	underground storage tanks
XANES	x-ray absorption near edge structure
XRD	x-ray diffraction

WHC
XAS

Westinghouse Hanford Company
x-ray absorption spectroscopy

Acknowledgements

The authors thank N.C. Schroeder (Los Alamos National Laboratory) for providing the Reillex™-HPQ resin and for many valuable discussions, and E.P. Horwitz (Argonne National Laboratory and Eichrom Industries, Inc.) and R.D. Rogers (University of Alabama) for providing the ABEC 5000 resin and for discussions on its use. We also thank J.L. Swanson for valuable contributions regarding Tc removal requirements. The authors gratefully acknowledge D.K. Shuh (Lawrence Berkeley National Laboratory) for very valuable discussions regarding the XAS spectra. The authors are grateful to P.R. Bredt for providing the SY-101 and SY-103 samples, and to F.V. Hoopes, R.T. Steele, and S.M. Tingey for hot cell technical assistance. We also thank J.L. Swanson and B.M. Rapko for technical reviews, and W.C. Cosby for editorial review.

This work was prepared with the support of the following contributors:

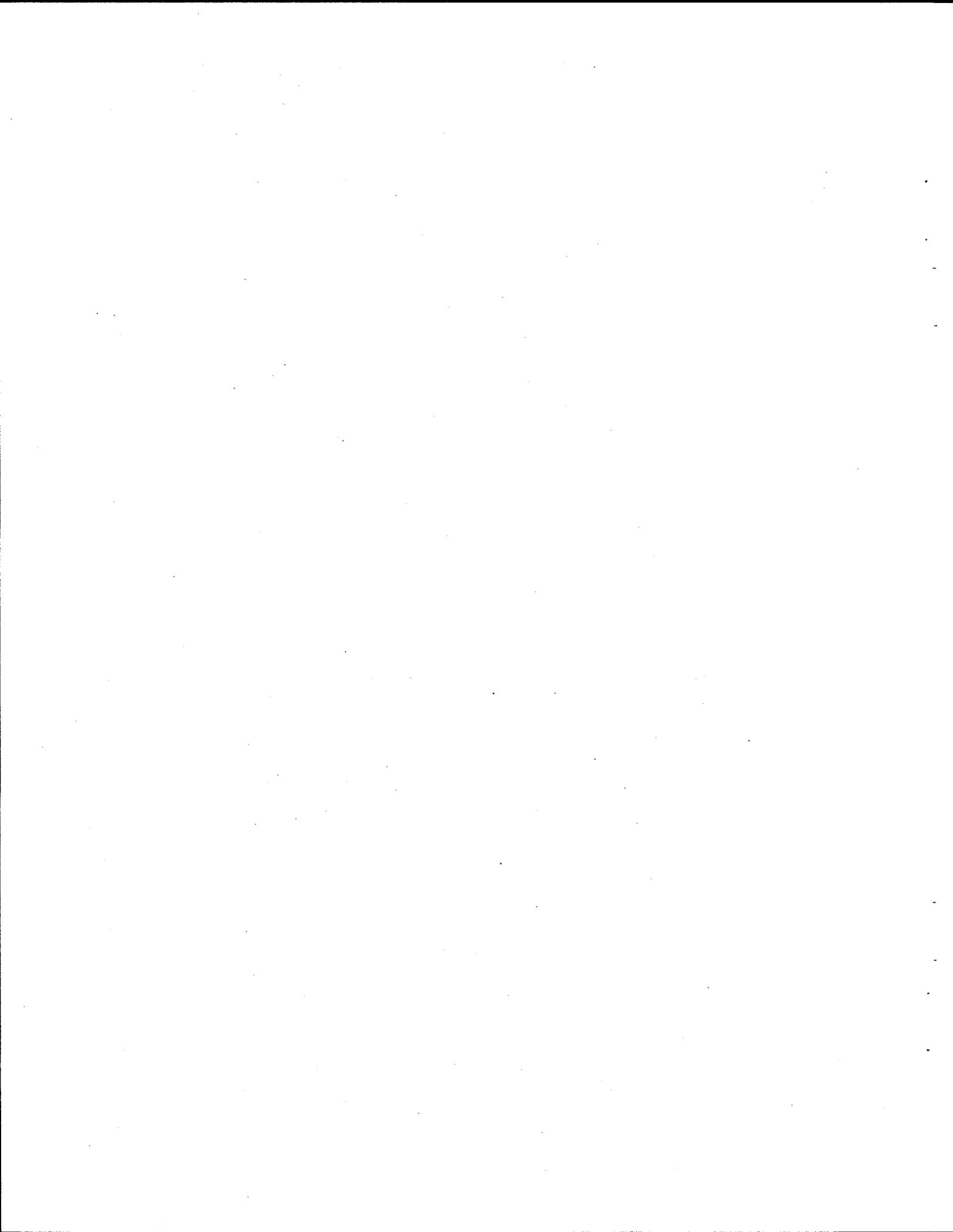
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Focus Area/Program: Tank Waste Remediation System
 Tanks Focus Area
 Phil McGinnis, Pretreatment Technical Integration Manager

Operations Office: Richland Operations Office
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Contractor: Pacific Northwest National Laboratory
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 Technology Development Program
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Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.



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1.0 Introduction

Hanford's 177 underground storage tanks (USTs) contain a mixture of sludge, salt cake, and alkaline supernatant liquid (Van Vleet, 1993). The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains the bulk of the strontium-90 (^{90}Sr) and the transuranic (TRU) radionuclides. The salt cake, generated by extensive evaporation of aqueous solution, consists primarily of dried sodium salts. The supernate consists of concentrated aqueous solutions of sodium nitrate/nitrite salts with smaller quantities of hydroxide, aluminum, potassium, carbonate, sulfate, and phosphate. The supernatant solution fractions and the interstitial liquid in the salt cake contain the bulk of the water soluble radionuclides, such as cesium-137 (^{137}Cs) and technetium-99 (^{99}Tc).

1.1 ^{99}Tc Inventory and Removal Requirements

Although the Hanford tank waste pretreatment and disposal requirements are still being defined, one of the first steps in most pretreatment scenarios will be a solids/liquid separation of the pumpable waste liquor, followed by ion exchange removal of water soluble radionuclides (^{137}Cs , ^{99}Tc , etc.) from the resulting supernatant liquid. Next, a salt cake dissolution and sludge wash step will be initiated followed by another solids/liquid separation. Most of the ^{99}Tc is expected to be in the aqueous liquids from these processes, and these solutions are the focus of the Tc removal processes.

A significant amount of ^{99}Tc is stored in the underground waste tanks. Estimates of the total inventory range from 1300 kg to 1900 kg (22.2 kCi to 32.5 kCi [Eager 1995]). Most analyses of actual double-shell tank waste samples indicate that the highest concentrations of ^{99}Tc are several hundred $\mu\text{Ci/L}$ (Van Vleet 1993; Schmittroth et al. 1995). Estimates based on models are in reasonable agreement with these numbers.^(a) Technetium-99, with a half life of 2.12×10^5 years, is the only Tc isotope found in significant quantities in the waste. All others are either not significant fission products, or have short half lives of seconds to minutes (Anders 1960).

The Tank Waste Remediation System (TWRS) Privatization Request for Proposal (Sol. No. DE-RP06-96RL13308, abbreviated PRFP) specifies a Tc activity in the immobilized low-activity waste (LAW) of $< 0.3 \text{ Ci/m}^3$. The PRFP also specifies that the feed delivered to the privateer for processing will contain a maximum of $7.1 \times 10^6 \text{ Bq Tc per mole of Na}$. Since the minimum Na loading in the waste package from envelopes A and C is specified as 10 moles of feed Na per liter of waste, as much as 1.92 Ci Tc per cubic meter could end up in the LAW unless Tc is removed. In this case a decontamination factor of 6.4 (1.92/0.3) would be required to reach the specified maximum Tc loading. It is highly probable that the actual DF required will be lower than this, since the Tc concentrations in tank samples tested to date are considerably lower than $7.1 \times 10^6 \text{ Bq Tc per mole of Na}$. For example, the activity of ^{99}Tc in AZ-101 supernate, a neutralized current acid (NCAW) waste, is 3.1 Bq per mole of Na (Peterson et al, 1989). This is expected to be the highest Tc activity in the double shell tank supernates (Van Vleet, 1993; Schmittroth et al., 1995).

The PRFP also specifies a maximum average fractional release rate of ^{99}Tc from the LAW of $2.8 \times 10^{-14} \text{ (s}^{-1}\text{)}$. This requirement ties Tc removal requirements to the quality of the LAW. The

(a) "Revised Inventory Estimates of Chemicals and Radionuclides in Single and Double-Shell Tanks," WHC Internal Memo 71320-94.016, Westinghouse Hanford Company, Richland, Washington, by LW Shelton (1994).

higher the quality of the LAW, the less Tc will be released over its lifetime, and the less Tc removal will be necessary.

The latest performance assessment, completed before the PRFP was issued, estimated that 80% average removal of ^{99}Tc will be required to meet DOE drinking water dose standards.^(a) This corresponds to a decontamination factor of 5, close to the maximum DF of 6.4 determined above, and is used in this report as a benchmark to evaluate process performance.

1.2 Need

Historically, much of the work on removing ^{99}Tc from alkaline waste has been directed at recovering ^{99}Tc as Tc(VII) in pertechnetate (TcO_4^-) rather than Tc decontamination of waste (Roberts et al. 1962, Beard and Caudill, 1964). Technetium is expected to be present as pertechnetate in most tank wastes, because this is the most stable form in oxygen-saturated solutions of any pH in the absence of complexants or ligands that stabilize other oxidation states (Pourbaix 1966). Technetium removal from West Valley alkaline supernate simulants by a number of different ion exchangers was investigated in FY 1983 at Pacific Northwest National Laboratory (PNNL) (Bray et al. 1984). Only charcoal and two organic anion exchange resins removed Tc effectively from the simulants. Technetium removal by ion exchange has also been investigated by several researchers at Los Alamos National Laboratory (LANL). Various ion exchange materials removed technetium as pertechnetate from various simulated solutions (Marsh et al. 1994a; Marsh et al. 1994b; Marsh et al. 1994c; Marsh et al. 1995). Much of the recent research concerning technetium removal has focused on the ReillexTM-HPQ resin (Schroeder et al. 1993; Schroeder et al. 1994; Schroeder et al. 1995a; Schroeder et al. 1995b) and ABEC 5000 sorbent (Rogers et al., 1996). These materials are selective for pertechnetate.

In FY 1995, samples of cesium-decontaminated complexant concentrate (CC) waste from tanks SY-101 and SY-103 were shipped from Hanford to LANL for Tc removal experiments with ReillexTM-HPQ. These wastes contain relatively high concentrations of organic complexants (Campbell et al. 1993). Ion exchange column experiments on CC simulants and batch contact experiments on the actual CC waste samples were performed at LANL to determine the equilibrium and kinetic parameters for Tc removal using the ReillexTM-HPQ material. The results of the batch contacts, radiochemical analyses, and ^{99}Tc nuclear magnetic resonance (NMR) analyses indicated that approximately 70% of the Tc in the waste samples was not removed via anion exchange and was probably not present as pertechnetate.

1.3 Approach

Several hypotheses were generated to explain the unexpectedly poor removal of Tc from the SY-101 and SY-103 samples:

- The organic complexants in the waste are probably present as anions and therefore might compete with pertechnetate for the anion exchange sites.

(a) From an internal report by C.T. Kincaid and M.D. White, Pacific Northwest National Laboratory, 1995.

- The organic complexants in the waste could be complexing pertechnetate or another form of Tc(VII), disrupting the anion exchange process.
- The Tc is reduced relative to Tc(VII). The organic complexants in the waste, the organic resin (CS-100) used for the cesium ion exchange process, or reactions during the trip to LANL might have reduced the Tc.
- Analytical error.
- Experimental error.

To address as many of these hypotheses as possible, a combination of experimental and analytical methods were pursued. Batch contacts between small waste samples and pertechnetate separations materials have been conducted at PNNL. Fresh samples from tanks SY-101 and SY-103 have been retested along with another complexant-containing waste (tank AN-107) and a double shell slurry feed (DSSF) composite. There is a wide range of organic complexant concentrations in these wastes (described in Sections 2 and 3), so differences in the batch contact results that correlate with the complexant concentrations will indicate that one of the first three hypotheses is correct. None of these wastes have been subjected to cesium ion exchange or to transportation over long distances, so results that are significantly different than the LANL results would suggest that reactions during the trip to LANL significantly affected the Tc chemical form. The existing analytical methods for ^{99}Tc were evaluated to determine the best methods for analyzing the experimental samples, to minimize analytical and experimental error. X-ray absorption spectroscopy (XAS) was used to study the chemical state of Tc in actual waste samples. An investigation into the efficacy of electrospray ionization-mass spectrometry (ESI-MS) for determining the chemical form of the Tc was initiated. The results of these studies are presented here.

2.0 Batch Contacts

Batch-contact experiments were performed on actual Hanford tank waste supernates at PNNL's Shielded Analytical Laboratory (SAL) remote handling facility in the 325 building. Waste supernate samples from tanks AN-107, SY-101, and SY-103 (CC wastes), and a DSSF waste composite were contacted with Reillex™-HPQ resin and ABEC-5000 sorbent to determine the effectiveness of technetium removal by these materials from these supernate waste streams.

2.1 Experimental

Batch Distribution Coefficient

The batch distribution coefficient (K_d) is an equilibrium measure of the distribution of a chemical species between a solution and a solid sorbent material. It is analogous to the distribution coefficient for partitioning a chemical species between an aqueous and an organic phase:

$$K_{\text{dist}} = C_{\text{org}} / C_{\text{aq}} \quad (2.1)$$

where C_{org} is the concentration of the chemical species in the organic phase, and C_{aq} is its concentration in the aqueous phase, at equilibrium.

However, the concentration of a sorbed species is difficult to define and to determine. Therefore, the batch distribution coefficient is defined by the following equation:

$$K_d = [(C_0 - C_1)/C_1] \cdot (V/M) \cdot (1/F) \quad (2.2)$$

where C_0 is the concentration of the species in solution before contact, C_1 is the concentration in solution after the contact (i.e., at equilibrium), V is the solution volume, M is the sorbent mass and F is the mass of dry ion exchanger divided by the mass of undried ion exchanger (F factor). C_0 and C_1 may be expressed in any convenient concentration or activity unit. V and M are typically expressed in milliliters (mL) and grams (g), respectively.

In comparing K_d values, care must be taken to compare results for identical experimental conditions. Changes in temperature, speciation, concentration of competing ions, and concentration of ligands and complexants will all affect the K_d , in some cases quite dramatically.

The batch distribution coefficient gives the distribution ratio on a "per gram of sorbent" basis. This can be converted to a "per mL of sorbent" basis by multiplication with the suitable sorbent density. Thus lambda, the column distribution ratio, is defined by

$$\lambda = K_d \cdot \rho_B \quad (2.3)$$

where ρ_B is the bed density, the dry mass per unit volume that a settled bed of resin fills in a column when equilibrated with the solution being ion exchanged. In practice, a solution that simulates the pH and ionic strength is often used for the measurement. Lambda is the volume of solution that can be processed per mL of sorbent bed; multiplication by the sorbent bed volume gives the volume of solution that can be processed to 50% breakthrough.

Sample Choice and Description

Tank waste samples were chosen based on high ^{99}Tc content, availability, and expected difficulty of Tc removal. Removing Tc by Reillex™-HPQ anion exchange resin from Cs ion exchanged supernate samples from tanks SY-101 and SY-103 was shown to be much less effective than expected at LANL (Schroeder et al. 1995b). Similar tests were performed at PNNL to corroborate the LANL data, to determine the reason for the poor Tc removal, and to propose methods to improve Tc removal from CC waste supernates.

The AN-107 waste contains a higher concentration of organic complexants than either SY-101 or SY-103. If organic complexants make Tc removal difficult, as the initial LANL results suggest, this waste may be expected to show similar (or greater) resistance to Tc removal.

The DSSF sample is a composite of 70% AW-101, 20% AP-106, and 10% AP-102 (by volume, all DSSF wastes). The DSSF waste is expected to be treated in Phase I of the tank waste remediation completed by private vendors. Given the poor removal of Tc observed for the SY-101 and SY-103 wastes, testing of this waste is urgently needed to determine if Tc removal by the baseline method of ion exchange will be feasible for this type of waste. Experiments in parallel with the CC wastes permit comparison of Tc removal effectiveness for CC and DSSF wastes under identical conditions. The results reported here will be used to plan more extensive column flow testing of AW-101.

Sample Preparation

The DSSF composite sample was received from the Westinghouse Hanford Company (WHC) 222-S laboratory in March 1994, diluted with distilled deionized water (DDI) to 5 M Na, and filtered, as described by Brown et al. (1996). The nitrate (NO_3^-) and hydroxide (OH^-) concentrations in the diluted sample are reported in that study to be 1.34 M and 2.01 M, respectively. Van Vleet (1993) reports a Tc concentration of 118 $\mu\text{Ci/L}$, and a total organic carbon (TOC) concentration of 2.5 g/L in an undiluted AW-101 sample. The sample is a clear light yellow liquid, as observed when samples were removed from the hot cell for XAS experiments. No precipitates were observed in the sample.

The AN-107 sample originated as a grab sample of liquid from the top section of the tank taken during the week of February 12, 1996. The Tc concentration in AN-107 has not been reported. The NO_3^- , OH^- , and TOC concentrations were reported to be 2.7 M, 0.05 M, and 39 g/L, respectively, in a sample taken in December 1986 (Van Vleet 1993). The CC waste in this tank has the highest organic content of any of the tanks tested in this study.

The OH^- concentration of a portion of the AN-107 waste sample was raised to approximately 0.5 M by adding 5 M NaOH. (This was done to simulate a planned caustic addition to tank AN-107 to ensure that the free hydroxide is maintained within specifications.) DDI was then added to this portion of the waste to achieve a final Na concentration of 5 M, the Cs removal baseline.

Following dilution in this manner, filtration of the AN-107 sample through a 0.45- μm filter was attempted. The filter quickly clogged with a fine dark cake of solids. The unfiltered solution was transferred to centrifuge tubes and spun in a small clinical centrifuge for approximately 30 min. The centrifugal force on the samples is unknown, but estimated to be approximately 150 G. Roughly 0.25 mL of solids had settled to the bottom of each tube, each of which held approximately 30 mL of solution. The decantate filtered from the centrifuged solution faster than previously, but still quite slow. Additional centrifugation for 1 hour at approximately 200 G resulted in a decantate that

filtered in approximately 60 minutes and required four filter changes. The filtered solution, still dark, reddish-brown in color, was used for the AN-107 batch-contact experiments.

Samples from Tank SY-101, windows C and E, were composited and diluted 1:1 with 2 M NaOH as described by Brecht et al. (1995). The sample was filtered through a 0.2- μm filter, and a portion of this sample was stored for ^{99}Tc batch-contact experiments. A sample from core 62 of Tank SY-103 was prepared in the same manner (Brecht and Tingey 1996). These CC waste supernate liquid samples were clear yellow (slightly darker than the DSSF sample). The Tc, NO_3^- , OH^- , and TOC concentrations in these samples were not reported. Previous analyses of undiluted samples from these tanks indicated concentrations of approximately 100 $\mu\text{Ci/L}$, 1 M, and 15 g/L for Tc, OH^- , and TOC, respectively (Van Vleet 1993). The Na concentration of both the samples was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) to be approximately 6.8 M. Many randomly oriented white crystalline needles formed at the bottom of the SY-101 sample jar, with many rising as high as 0.25 in from the bottom of the jar. Samples for the contacts were taken from the top of the bottle without stirring. A precipitate was also observed at the bottom of the SY-103 sample jar. The crystals were fine and very sparse, giving the precipitate bed a fuzzy appearance.

Description and Preparation of Separation Materials

The ReillexTM-HPQ resin is a co-polymer of divinylbenzene and 4-vinylpyridine that is subsequently methylated at the pyridine nitrogen. This methylation converts the pyridinium into a strong base anionic site found to be selective for pertechnetate. The resin is approximately 25% cross linked and 70% methylated at the pyridine nitrogen site. Researchers at LANL, in collaboration with Reilly Industries, originally developed ReillexTM-HPQ resin to separate plutonium nitrate complexes from other components in concentrated nitric acid solution. The resin used in the current investigation is macroporous and highly stable to radiolysis. Before batch-contact experiments, the resin was contacted with nitric acid to convert the resin from the chloride form to the nitrate form, then washed with DDI and dried by vacuum filtration. (Chloride removal was monitored by precipitation of AgCl .) The resin was stored dry between experiments. Sieving the material shows that 80% of the resin particles are 250 μm to 450 μm in diameter; approximately 95% are 175 μm to 650 μm .

ABEC 5000 is a sorbent material designed to remove pertechnetate from high salt solutions. The pertechnetate preferentially distributes into a polyethylene glycol (PEG) phase on the surface of the resin beads. The material is engineered by chemical attachment of PEG molecules to the resin beads. A distinct advantage of the ABEC 5000 resin is the eluting "solution" for pertechnetate: distilled de-ionized water (Rogers et al. 1996). The material was received in a 50% methanol-water solution. It was washed three times with distilled de-ionized water (100 mL to 10 g), then dried overnight by vacuum filtration before weighing the material for use.

Contacting Procedure

The experiments were performed in the SAL facilities, allowing remote handling of the materials. An orbital shaker and an analytical balance accurate to ± 0.00001 g were available in-cell. A known mass of exchanger (0.5, 0.1, or 0.05 g) was placed in a vial in the cell, then contacted with the specified volume of sample. The samples were placed on the shaker for 16 to 20 hours. The resin was removed from the sample by filtering through a 0.2- μm syringe filter.

For the first batch contact set (DSSF, SY-101, and SY-103 contacts with ReillexTM-HPQ), the samples were analyzed by inductively coupled mass spectrometry (ICP-MS) following a 100 X

dilution in 0.5 M HNO₃. Further dilutions were made as necessary using 1% HNO₃. Precipitates were observed in 20 X dilutions of the same samples. These were dissolved when the total concentration of HNO₃ was raised to approximately 2 M. Although no precipitates were observed in the 100 X dilutions, it was deemed appropriate to use more concentrated acid for further sample dilutions. Accordingly, for the second batch contact set, a 0.1-mL aliquot of each sample was added to 9.9 mL of 2 M nitric acid, then analyzed by ICP-MS. (The second set included AN-107 contact with Reillex™-HPQ, recontact of the DSSF and SY-101 with Reillex™-HPQ, and contact of AN-107, DSSF, SY-101 and SY-103 with ABEC 5000.)

2.2 Results

The ⁹⁹Tc batch distribution coefficients (K_d) and percent removal (% Rvl) of Tc are shown in Table 2.1. (Precision in the K_d and % Rvl are both approximately ± 15%.) The phase ratio (PR, volume of supernate per gram of dry resin or sorbent) for each test is also shown. The bed densities for Reillex™-HPQ and ABEC-5000 in 4.5 M NaNO₃ / 0.5 M NaOH were 0.38 g/mL and 0.24 g/mL, respectively. The F factors varied from 0.996 to 0.982 for the washed and air-dried materials. Tables 2.2 and 2.3 give a more complete presentation of the data for the Reillex™-HPQ and ABEC-5000 contacts, respectively. (Precision for the Tc concentrations is approximately ± 10%, and for K_d and percent removal, ± 15%.)

Table 2.1. ⁹⁹Tc Distribution Coefficients (K_d, mL/g) and Percent Removal (% Rvl) for Four Hanford Tank Supernate Samples Using Reillex™-HPQ and ABEC-5000. (Only percent removal shown for controls.)

PR ^(a)	K _d (% Rvl), Reillex™-HPQ					K _d (% Rvl), ABEC-5000		
	Control	100	10	Control ^(b)	10 ^(b)	Control	100	10
Waste								
DSSF	(-12)	380 (79)	130 (93)	(8)	6 (43)	(21)	160 (63)	100 (91)
SY-101	(19)	22 (19)	9 (47)	(5)	6 (38)	(10)	22 (19)	2 (18)
SY-103	(22)	73 (43)	9 (46)	(C)	(C)	(14)	32 (24)	6 (35)
AN-107	(1)	35 (26)	3 (23)	(C)	(C)	(3)	8 (7)	3 (22)

(a) Phase ratio, in milliliters of waste sample per gram of resin or sorbent.

(b) Data for recontact of PR=10, Reillex™-HPQ contacted waste sample, 30 days after initial contact.

(c) Not performed.

Table 2.2. Batch Contact Data: Reillex™-HPQ Ion Exchange Resin

Sample ID	Waste	Resin Mass (g)	Phase Ratio ^(a)	Initial [Tc] (μCi/L)	Final [Tc] (μCi/L)	% Tc Rmv'd	Date of Contact
WA-4	DSSF	-	Control	88	99	-12	3/6/96
WB-4	DSSF	0.05	100	88	19	79	3/6/96
WD-4	DSSF	0.5	10	88	6.3	93	3/6/96
WA-3D	DSSF	-	Control	6.3	5.8	8	4/12/96
WD-3D ^(b)	DSSF	0.1	10	6.3	3.6	43 ^(b)	4/12/96
XA-4	SY-101	-	Control	240	190	19	3/6/96
XB-4	SY-101	0.05	100	240	190	19	3/6/96
XD-4	SY-101	0.5	10	240	120	47	3/6/96
XA-3D	SY-101	-	Control	120	120	5	4/12/96
XD-3D ^(c)	SY-101	0.1	10	120	78	38 ^(c)	4/12/96
YA-4	SY-103	-	Control	240	190	22	3/6/96
YB-4	SY-103	0.05	100	240	140	43	3/6/96
YD-4	SY-103	0.5	10	240	130	46	3/6/96
ZA-3	AN-107	-	Control	55	55	1	4/12/96
ZB-3	AN-107	0.05	100	55	41	26	4/12/96
ZD-3	AN-107	0.5	10	55	42	23	4/12/96

(a) Milliliters of waste sample per gram of resin.

(b) Recontact of waste sample WD-4, 30 days after initial contact.

(c) Recontact of waste sample XD-4, 30 days after initial contact.

Technetium removal from the DSSF composite by Reillex™-HPQ and by ABEC 5000 is greater than 90% for the 10:1 contacts, and for the Reillex™-HPQ, a recontact after a month removes another 40% of the remaining Tc. Based on these results, 80% Tc removal appears feasible.

The batch K_d values for Tc partitioning between DSSF and Reillex™-HPQ are about half the 250 mL/g observed for DSSF simulant contacts for approximately 2 hours at a phase ratio of 10 mL/g (Schroeder et al. 1995b). In addition, the removal observed on recontact with fresh resin is about half that observed for the first contact. These observations may reflect the quality of the DSSF simulant, or they may indicate the presence of a small percentage of non-pertechnetate Tc. Flow studies and/or characterization data are required to make this distinction.

Technetium removal from all three CC wastes by both Reillex™-HPQ and ABEC 5000 is much less than from the DSSF waste. The Tc K_d for Reillex™-HPQ are far below the values of approximately 1050 and 850 observed for SY-101 and SY-103 simulant contacts, respectively (Schroeder et al. 1995b). This is consistent with previous results for Cs-decontaminated SY-101 and SY-103 actual waste samples (Schroeder et al. 1995b) and indicates that Cs removal at Hanford, and subsequent sample transport (from Hanford to LANL) did not cause the low Tc removal observed in that study. The striking difference between the Tc K_d results for DSSF and CC wastes is more likely caused by the presence of a large fraction of Tc as a non-pertechnetate species in the CC waste, as shown in the following sections.

Table 2.3. Batch Contact Data: ABEC 5000 Sorbent

Sample ID	Waste	Sorbent Mass (g)	Phase Ratio ^(a)	Initial [Tc] (μCi/L)	Final [Tc] (μCi/L)	%Tc Rmv'd	Date of Contact
WA-3A	DSSF	-	Control	88	70	21	4/12/96
WB-3A	DSSF	0.05	100	88	33	63	4/12/96
WD-3A	DSSF	0.5	10	88	7.9	91	4/12/96
XA-3A	SY-101	-	Control	240	210	10	4/12/96
XB-3A	SY-101	0.05	100	240	180	19	4/12/96
XD-3A	SY-101	0.5	10	240	180	18	4/12/96
YA-3A	SY-103	-	Control	240	210	14	4/12/96
YB-3A	SY-103	0.05	100	240	180	24	4/12/96
YD-3A	SY-103	0.5	10	240	160	35	4/12/96
ZA-3A	AN-107	-	Control	55	53	3	4/12/96
ZB-3A	AN-107	0.05	100	55	51	7	4/12/96
ZD-3A	AN-107	0.5	10	55	43	22	4/12/96

(a) Milliliters of waste sample solution per gram of sorbent.

Recovery of Tc from the controls is generally within the expected precision. This is not the case for the SY-101 and SY-103 contacts with Reillex™-HPQ, and the DSSF contact with ABEC 5000, all of which appear to lose Tc in the control. Re-analyses of the samples showed reproducibility. If it is assumed that Tc is actually removed during the agitation (by some unknown process), the final Tc concentration for the control should be used as the initial concentration for determining the percent Tc removal and the K_d for the sorbent contacts. This reduces the amount of Tc actually removed by the sorbent, and for the SY-101 and SY-103 contacts, does not significantly change the conclusions based on these results. For the DSSF contact with ABEC 5000, the percent removal changes by 2 and 10 % for the 10- and 100-phase ratio contacts, respectively. Again, the conclusions based on these results remain the same.

Recontact of the SY-101 sample with fresh Reillex™-HPQ, 30 days after the initial contact, removed a small but significant amount of Tc. Schroeder et al. (1995b) report no new Tc sorbed from the supernate by a recontact with fresh resin. The time between the initial contact and the recontact at LANL was less than a week.^(a) One possible explanation for these results is that inextractable technetium is oxidized by nitrate, for example, to extractable pertechnetate, but a kinetic barrier makes this a slow process.

2.3 Conclusions

The contact data presented here indicate that Tc removal to the estimated requirement of 80% (Kincaid and White 1995) from the DSSF composite tested is feasible, and flow tests should be conducted to collect data for further scale up. However, the distribution coefficient for Reillex™-

(a) N.C. Schroeder, personal communication.

HPQ is about half the expected value, and additional batch and/or flow tests with other double shell tank wastes are recommended to determine if this is the case for other DSSF wastes.

In contrast, Tc removal for the CC wastes is quite poor for the two materials tested. This corroborates previous data collected on CC wastes by Schroeder (1995b), and adds urgency to the need for testing alternate removal processes and vigorous feed adjustments. Also, more data on the speciation of Tc in the waste, such as that presented in Section 6, should be collected. Identifying the intractable Tc species will provide a basis for developing removal schemes.

3.0 Comparison of Tc Analysis Methods

Samples of SY-101 and SY-103 supernate were shipped in July 1995 from the WHC 222-S laboratory to LANL for a Tc removal study, as previously noted (Schroeder et al. 1995b). These wastes contain relatively high concentrations of organic complexants. Tc concentrations in the samples were determined upon arrival at LANL. The values were significantly higher than those reported by 222-S for essentially the same samples before shipment. The LANL report suggests that the oxidation of non-pertechnetate species to pertechnetate, if required for Tc analysis, must be performed under extremely vigorous conditions. The following study was undertaken to 1) determine if the standard PNNL sample preparation procedure, PNL-ALO-432, is sufficient to oxidize the Tc species in CC waste to pertechnetate, 2) compare the oxidation method used in this procedure with the oxidation used in the LANL and standard WHC procedures, and 3) compare all to analysis by ICP-MS with no front end oxidation or separation.

3.1 Experimental

Table 3.1 identifies and describes the four tank samples studied. A 0.1-mL aliquot of each sample was diluted 100 X in 2 M HNO₃ in the SAL facility. The diluted samples were then transferred to the analytical laboratory for the study.

Table 3.1. Samples Used in the Oxidation Studies

Sample ID	ALO ID	Radchem ID	Sample Description
107AN	96-3655	AN107	Undiluted AN-107 supernate
AWS-0	96-3653	AW101	70% AW-101, 20% AP-106, 10% AP-102 (by vol); diluted to 5 M Na
101SY	96-3654	SY101	SY-101 supernate diluted to 5 M Na
103SY	96-3656	SY103	SY-103 supernate diluted to 5 M Na

A 1-mL aliquot of each diluted sample was prepared for several different oxidation techniques and for a direct ICP-MS analysis. The different oxidation techniques evaluated were 1) PNNL's procedure PNL-ALO-432, using sodium dichromate, 2) a method reported by Schroeder et al. (1995b) that uses the strong oxidant ceric ammonium nitrate with repeated evaporations in 16 M HNO₃ {"Ce(IV) method"}, 3) the oxidation step in the WHC procedure LA-438-101 using 4 M HNO₃ and hydrogen peroxide, and 4) a reduction/oxidation cycling method using hydroxylamine hydrochloride reductant followed by nitric acid-hydrogen peroxide oxidation. To minimize the number of different variables in the study, only the oxidation method was varied. After this step, the separation chemistry and counting methods were identical for all samples.

Quality control (QC) included one duplicate (AN107D), one reagent blank ("BL" in Table 3.2), one blank spike ("BS" in Table 3.2), and a ^{95m}Tc tracer added, as pertechnetate, to each tank sample. A QC sample was also run to evaluate and correct radiochemical yield. This QC was run for each of the radiochemical methods tested. A background correction was made for significant ⁹⁷Tc activity in the ^{95m}Tc tracer. Two 100%-yield comparator samples were also prepared in each of two

counting geometries (glass liquid scintillation counting [LSC] vials and 2-inch aluminum flat counting planchets [on which the ^{95m}Tc was dried under a heat lamp]) at the time the samples were spiked. The amount of ^{95m}Tc tracer added to each sample was 74 pCi, which resulted in 191 cpm by LSC on a Packard 2550 Tricarb and 56 cpm on the LB5100 low-background gas-flow proportional counter.

Oxidation Techniques

1. PNL-ALO-432 (Dichromate)

The 1-mL aliquots were pipetted into a glass vial. After adding 0.1 mL of 0.1 M sodium dichromate at room temperature with mixing, the solution was immediately loaded onto the ion exchange column for separation (see below).

2. Ceric Oxidation [Ce(IV)]

The 1-mL aliquots were pipetted into glass vials, and 3 mL of 16 M HNO_3 and 5 mL water were added. Then 0.1 mL of 0.1 M ceric ammonium nitrate {Ce(IV)} in 0.15 M HNO_3 was added, and the samples were heated with a heat lamp. More Ce(IV) was added in 0.1-mL aliquots as the yellow color, characteristic of Ce(IV), disappeared. When the yellow color no longer faded, the samples were evaporated to incipient dryness, and 1-2 mL 16 M HNO_3 were added; this was repeated twice more. Finally, 5 mL 16 M HNO_3 were added, and the samples were evaporated to incipient dryness. Three milliliters of water were added to the samples. A summary of the amount of Ce(IV) added to maintain color, and the reported TOC in undiluted tank samples (Van Vleet 1993) is indicated in Table 3.2. The blank sample went dry twice under the heat lamp. This oxidation procedure took approximately one 8-hour shift.

Table 3.2. Amount of Ce Required for Complete Oxidation

Radchem ID	Volume of 0.1 M Ce(IV) added	TOC (g/L) ^(a)
AN107	0.5 mL	39
AN107D	0.5 mL	39
AW101	0.1 mL	2
SY101	0.2 mL	14
SY103	0.2 mL	20
BL	0.1 mL	0
BS	0.1 mL	0

(a) From Van Vleet (1993)

3. Peroxide

As per the oxidation step specified in WHC procedure LA-438-101, 10 mL of 4 M HNO_3 were added to the 1-mL aliquots, followed by 1 mL 30% hydrogen peroxide. After storage overnight, the sample volumes were reduced to approximately 0.5 to 1 mL under a heat lamp. Two milliliters of deionized (DI) water were added, bringing the acid to approximately

3 M HNO₃. The volume reduction and DI water addition are at variance to the WHC procedure and were implemented to reduce the acidity of the sample to an appropriate acid concentration for the separation steps.

4. Reduction/Oxidation (Cycling)

A 0.2096-g amount of hydroxylamine hydrochloride was diluted to 1 mL with DI water; 0.1 mL of this solution was added to the 1-mL aliquots. The samples were then heated about 45 minutes under a heat lamp. Then 1 mL 16 M HNO₃ followed by 1 mL hydrogen peroxide were added to each sample, and the samples were heated under the heat lamp. Each was diluted with 3 mL of DI water to approximately 3 M HNO₃.

Separation Chemistry

After the front-end oxidation chemistry described above, all samples were separated according to PNL-ALO-432, in which the sample is passed through a 0.50-mL AG50x8 cation exchange resin bed in a 7-mL plastic dropper. To the column eluent, 100 μ L 0.1 M sodium dichromate, 100 μ L 1 M tartaric acid, 200 μ L 0.01 M tetraphenylarsonium chloride, and 1.0 mL 10 M NaOH were added. After mixing, 5 mL methylisobutyl ketone (MIBK) was added, and the samples were mixed on a vortex mixer for approximately 3 minutes. The samples were centrifuged to separate the phases, and the organic phase was removed and washed with a mixture of 1 mL DI water, 0.5 mL 10 M NaOH, 100 μ L 1 M tartaric acid, and 100 μ L 0.1 M sodium dichromate. The samples were vortexed again for 3 minutes and washed again with the same solution just described. A 2-mL fraction of the final organic phase was plated on a 2-inch planchet and dried under a heat lamp, and 2-mL fractions were placed in LSC vials to which 10 mL Ultima Gold™ LSC cocktail were added.

Counting

Each sample was counted for 30 minutes on both the LB5100 low-background beta counter and the Packard 2550 Tricarb along with the 100% ^{95m}Tc comparator standards. The LSC was calibrated with freshly prepared ⁹⁹Tc standard in 2 mL MIBK. Counting efficiencies were 32% for the LB5100 and about 98% for the LSC. The plated samples were counted for ^{95m}Tc yield on 60% germanium detectors for 2 hours each, resulting in nominally 10% uncertainty in counting statistics. The yield determined for the plated samples was also applied to the corresponding LSC sample because the same volumes were taken for each.

ICP-MS

The 1-mL splits of the starting 98.8X diluted samples were analyzed by ICP-MS after an additional fourfold dilution. No corrections for possible mass interferences were made (e.g., ⁹⁹Ru).

Calculations

The average count rate from the 100% comparator standards was multiplied by the radiochemical yield to determine the contribution to the sample count rate from the ^{95m}Tc. Once this "background" was subtracted, the net count rate was divided by radiochemical yield, detector efficiency, and sample volume and dilutions.

3.2 Results

Tables 3.3 and 3.4 summarize the results. Liquid scintillation counting and gas-flow proportional beta counting (beta counting) techniques were used for ^{99}Tc determination in all samples processed radiochemically. The relative percent difference (RPD, the difference divided by the average) between the samples split for LSC and beta counting is generally less than 10% for the dichromate, peroxide, and cycling methods. For the Ce(IV) method, beta counting gave significantly higher ^{99}Tc values. This was reflected in the RPDs for the method, which were all greater than 10%. Reasons for this bias are not clear. The propagated 1- σ error ("Error") is generally driven by the $^{95\text{m}}\text{Tc}$ yield determinations because a smaller than optimum $^{95\text{m}}\text{Tc}$ spike was used. The errors are nominally 10%, but much worse (greater than 20%, and up to 71%) for the peroxide and cycling methods (due to poor yields). The blank spike recoveries for the various methods are acceptable given the error associated with the methods.

The radiochemical yields for the dichromate and Ce(IV) methods were high. Before the sample split, yields were nominally 70% or better, even on the blank that went dry twice. Yields on the other two methods were very poor, nominally 20% or less. The cause is not clear, but is probably loss due to heating with hydrogen peroxide present. Note that the WHC procedure does not call for heating in the presence of the hydrogen peroxide. This was done to reduce acid concentration and sample volume before loading onto the cation exchange column.

Table 3.3. Contd.

ICP-MS (No Oxidation)		
ID	ICP/MS	Error
AN107	1.16E+05	10%
AW101	9.41E+04	10%
SY101	2.54E+05	10%
SY103	2.77E+05	10%

Table 3.4 compares all method results with the Ce(IV) oxidation method results. All ICP-MS values agree with the Ce(IV) oxidation results within 20%; three of four are within 10%. The ^{99}Tc concentrations found for the CC waste samples by the dichromate method are definitely biased low (by about 40%) relative to the Ce(IV) and ICP-MS results. In contrast, the dichromate results for the DSSF sample, AW-101, are in excellent agreement with the Ce(IV) method and ICP-MS. Evidently the dichromate method does not completely oxidize all technetium to pertechnetate {Tc(VII)} in the high organic waste samples. The errors observed for the peroxide and cycling methods are so high (due to poor radio-chemical recoveries) that meaningful comparisons can not be made.

The dichromate and peroxide oxidations may yield good results on the CC waste samples, provided they are monitored in some way to ensure that sufficient reagent has been added for complete oxidation, as is done for the Ce(IV) oxidation. This is easily seen by the color indicator for the Ce(IV) method, and probably would also be the case for dichromate oxidation. (Dichromate, $\text{Cr}_2\text{O}_7^{2-}$, gives yellow colored solutions, while the reduced form, Cr(III), is colorless at low concentrations.) The toxicity of Cr(VI) and regulations regarding Cr waste may also be considerations in choosing an oxidation technique.

For this study, all $m/z = 99$ signal detected by ICP-MS was assumed to be due to Tc. (All other unstable mass 99 fission product isotopes should have decayed long ago, and the direct fission production of stable ^{99}Ru from any reasonable parent nucleus is more than 3 orders of magnitude lower than the production of ^{99}Tc .) If Ru peaks corresponding to natural Ru are present, correction for the contribution of natural ^{99}Ru is possible. However, because this region of the mass spectra of the tank wastes tested has several mass peaks due to fission products in this region, using the natural abundance of Ru for correction may not be advisable. A more reliable method to correct for the presence of other $m/z=99$ isotopes is to perform the Ce(IV) oxidation, followed by a separation, before ICP-MS analysis. Because the Ce(IV) oxidation is a fairly lengthy process, this would be most effective for spot checking a subset of a large batch of samples.

Table 3.4. Comparison of all Techniques to Ce(IV) Oxidation

ID	Dichrome Oxid/Ce(IV) Oxid		Perox Oxid/Ce(IV) Oxid		Cycle Oxid/Ce(IV) Oxid		ICP-MS/Ce(IV) Oxid	
	Avg's	Error (%)	Avg's	Error (%)	Avg's	Error (%)	Avg's	Error (%)
AN107	0.629	17	0.822	37	1.262	52	0.816	17
AN107D	0.560	13	1.110	52	1.131	29	-	-
AW101	1.009	17	0.765	42	0.966	31	0.957	17
SY101	0.595	13	NA	NA	0.654	24	1.048	14
SY103	0.656	16	1.569	72	1.935	62	1.075	16
BS	0.845	14	0.677	39	0.658	36	-	-

3.3 Conclusions

The Ce(IV) and the ICP-MS results are in good agreement, and recover more (presumably all) Tc from the CC waste samples than the dichromate method. Much less sample preparation is required for the ICP-MS analysis than for the Ce(IV) oxidation/separation/counting method, so the ICP-MS is recommended for Tc analysis for large batches (greater than 10 samples). Because it is possible (although unlikely) that other $m/z=99$ isotopes are present, it is also recommended that sample batches be spot checked by running ICP-MS of some samples following the Ce(IV) oxidation and a chemical separation.

Also, because chemical yields vary from one sample to the next, it is recommended that the ^{95m}Tc tracer be used as standard practice for Tc radiochemical analysis sample preparation. Technetium-95m is satisfactory for high-level samples as the increased beta count rate due to the spike is small relative to the sample itself. (This recommendation does not apply to low-level samples; ^{99m}Tc would probably be a better tracer for low-level samples because the ^{99m}Tc has a short (6-h) half-life, and its presence would be undetectable in about a week.)

The observation that vigorous oxidation is required to completely recover Tc from CC wastes, but not from DSSF waste, suggests that the CC wastes (but not the DSSF wastes) contain a non-pertechnetate species that is difficult to oxidize.

4.0 Technetium Characterization by X-Ray Absorption Spectroscopy

A preliminary investigation of the chemical state of Tc in the tank waste supernate samples was performed. XAS data of the Tc K edge of the samples were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) in Stanford, California, to determine if Tc in CC wastes is present as Tc(VII) or in a different oxidation state.

An atom will absorb an x-ray if the x-ray has an energy equal to the energy binding an electron to the atom's nucleus. When the x-ray is absorbed, the electron is ejected (the photoelectric effect). By sweeping the energy of an intense monochromatic beam of x-rays through an absorption energy for an element in a sample, an absorption spectrum for the element may be collected as a function of x-ray energy. A step function is observed due to the absorption. Additional structure is also apparent if the element is part of a compound, solid, or solution (i.e., if the element is not a monatomic gas).

Near an absorption edge, this structure gives fingerprint-type information that may be used to identify the oxidation state of the element. This is called x-ray absorption near edge structure (XANES). The XANES is found in a range from about 60 eV below the edge to 60 eV above the edge. The structure above the edge is called the extended x-ray absorption fine structure (EXAFS); a relatively straightforward analysis of the EXAFS gives the local structure (geometry of neighboring atom positions and atom identities). Unlike x-ray diffraction (XRD), no long range structure (i.e., crystallinity) is required for obtaining this structural information from the EXAFS. However, an XAS spectrum is the sum of the XAS spectra from all the different species of a given element that are present in a sample. If more than one species is present, care must be taken to account for this in analyzing the data.

The amount and reliability of information obtained by XAS analyses depends on the quality of the data (as measured by the signal-to-noise ratio, s/n). The data quality is largely determined by the concentration of the element in the sample. For most elements, a minimum concentration of 10 mg/L is required to analyze the XANES; 100 mg/L or more is generally required to extract meaningful information from the EXAFS. For confidence in the data interpretation, it is also important to compare the spectra of unknown compounds with those of similar known compounds.

The absorption energies for an element are unique to that element, so the technique may be used to probe only one element in a complex multi-component sample. Spectra from different elements usually overlap very little, so spectral interferences are not usually a problem. The high x-ray energies required (5000 to 40,000 eV) penetrate solids and liquids effectively, so multiphase systems (e.g., suspended solids, slurries, inhomogeneous solid samples) do not present a problem. Also, as stated, the target element does not need to be in a crystal or crystallite. For these reasons, XAS has been very useful in determining oxidation state information and local structural details in complex systems (Konigsberger and Prins 1988). This is particularly true for systems in which the element of interest is not part of an ordered, crystalline array, such as sorbates, solutions and slurries, and amorphous solids.

Oxidation state and speciation information on very dilute samples can be collected because of the technique's high sensitivity. This makes it ideal for investigating radionuclide speciation in U.S. Department of Energy-related waste solutions and solids, since the molar concentration of these components is often quite low (below 100 mg/L). We have previously used the technique successfully for investigating the chemical states of Sr, U, Pu, Cr, and other elements in waste solids and

solutions.^(a) However, the intense monochromatic x-ray beam required can only be found at large synchrotron radiation source user facilities, such as SSRL.

4.1 Experimental

Four samples were analyzed: AN-107 as received from WHC's 222-S laboratory; prepared SY-103; contacted SY-103; and contacted SY-101. Insufficient beam time was available to analyze the DSSF sample. The SY-103 sample was prepared by diluting to 6.7 M Na followed by filtration, as described in Section 2. The contacted SY-101 and SY-103 samples were prepared samples of tank supernate that were contacted with Reillex™-HPQ for 16 hours (samples XD-4 and YD-4, respectively, Table 2.2) to remove pertechnetate (TcO_4^-). All samples analyzed are CC waste type, as described in Section 2. The concentrations of Tc in the AN-107 and the prepared SY-103 samples were approximately 3 mg/L (50 μ Ci/L) and 12 mg/L (200 μ Ci/L), respectively. The concentration of Tc in both the SY-101 and SY-103 contacted samples was approximately 7 mg/L (125 μ Ci/L). The SY-101 and SY-103 samples were clear yellow. The AN-107 sample was dark reddish brown and had a significant fraction of suspended solids, as described in Section 2. If Tc is present in both the AN-107 solids and liquids, the XANES spectra will be a sum of the XANES from the two (or more) species.

The samples were triply contained in holders made of radiation- and chemical-resistant plastics and stainless steel. A thin film plastic window in each containment cell allowed visual inspection of the liquid sample, irradiation with the monochromatic synchrotron x-ray beam, and escape of the transmitted and fluorescent x-rays used for XAS analysis. A sample of powdered Tc metal was run with each spectrum as an energy reference. A sample of approximately 200 mg/L (3.4 mCi/L) ammonium pertechnetate (NH_4TcO_4) was also run for comparison and for use in fitting the spectra.

Sample handling was minimized to maintain doses as low as reasonably achievable (ALARA). The highest contact dose rate was 800 mRem/h for an unshielded assembly, corrected for small source size. All spectra were collected with the samples at ambient temperature. Data were collected on end station 4-2 at SSRL under dedicated operating conditions (3.0 GeV, 40 to 90 mA current). Theta, the angle between the two crystals of the monochromator, was maintained at 0 (fully tuned) with harmonic rejection accomplished by critical angle reflection off a rhodium coated mirror. All measurements on the waste samples were performed in the fluorescence mode using a 13 element Ge detector. Intrinsic radiation emitted by the samples had only minimal effects on these data. The number of scans varied with the concentration, preferred data range, and beam quality.

The XANES data were analyzed using commercially available data analysis and plotting software packages on both Macintosh® and PC compatible computers. Only XANES data were collected and analyzed. Collecting and analyzing EXAFS data were outside the scope of this preliminary study.

(a) *Solution Ion Exchange/Separations Studies: Final Report for Fiscal Year 1994.* TWRSP-94-100, a letter report to Westinghouse Hanford Company from Pacific Northwest Laboratory, Richland, Washington, by DL Blanchard Jr., JA Campbell, S Conradson, RL Gordon, NJ Hess, JC Hutton, MM Lamoureux, RW Stromatt, DL Styris, and KL Wahl (1994).

Sludge Component Speciation: Summary Final Report. TWRSP-95-048, a letter report to Westinghouse Hanford Company from Pacific Northwest Laboratory, Richland, Washington, by DL Blanchard Jr., SD Conradson, NJ Hess, and PK Melethil (1995).

4.2 Results

The x-ray absorption structure near the Tc K edge is shown in Figure 4.1 for the four tank samples and the TcO_4^- reference. All have been normalized to the edge step. This effectively converts absolute absorption to absorption per mole of Tc, including the edge step and all absorption features. The energy scale has been referenced to the first inflection point in the edge for Tc metal, which is denoted E_0 . The prominent pre-edge peak in the TcO_4^- edge arises from transitions allowed because of the tetrahedral geometry of TcO_4^- . The TcO_4^- XANES is consistent with that previously published (Almahamid et al. 1995).

The coincidence of the tank supernate sample edges (the region near 0 eV) indicates that the predominant Tc species is the same for all the samples. The large shift relative to the TcO_4^- standard (almost 10 eV) indicates that this predominant species is not TcO_4^- . This is consistent with the observation that contact with Reillex™-HPQ removed less than 50% of the Tc in the samples.

The Tc XANES for two tank samples (SY-103 and SY-101) contacted with Reillex™-HPQ are compared with the TcO_4^- and Tc metal reference XANES in Figure 4.2. The XANES for the two contacted samples is nearly identical over the range. This indicates that the specie(s) left in solution after removal of the TcO_4^- is the same for the two different tank samples.

The energy of a particular absorption edge for an element generally decreases with decreasing oxidation state (Konigsberger and Prins 1988). The location and appearance of the edges strongly suggests that the oxidation state of Tc in these samples is +IV (Almahamid et al. 1995). Because the edges of all four tank samples are aligned, this is also true for the other two samples, uncontacted AN-107 and SY-103. Unequivocal identification of the oxidation state will require comparison to other standards.

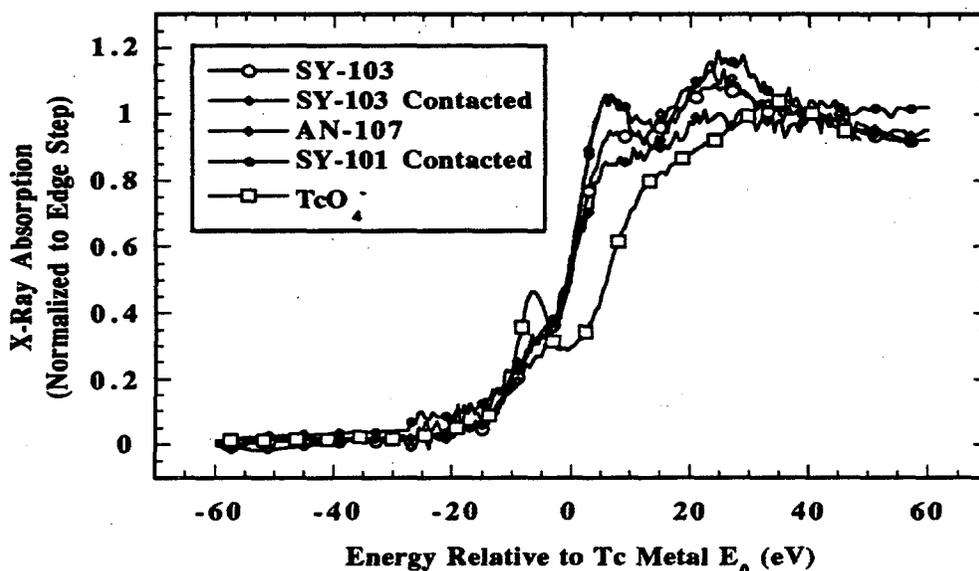


Figure 4.1. XANES for the Four Tank Samples and for TcO_4^-

The Tc XANES for the “as received” AN-107 sample and the prepared SY-103 sample (Figure 4.3) are very similar. The appearance of small shoulders on the edges for these uncontacted samples at the location of the TcO_4^- pre-edge peak indicates the presence of TcO_4^- .

This shoulder is even more prominent when comparing the prepared SY-103 sample with the contacted SY-103 sample (Figure 4.4). The reduced shoulder for the contacted sample indicates that a significant fraction of the TcO_4^- was removed by Reillex™-HPQ.

If, following removal, TcO_4^- is reformed very slowly (i.e., re-establishment of equilibrium is kinetically limited), a linear combination of the contacted SY-103 XANES and the TcO_4^- XANES should fit the uncontacted SY-103 XANES well and would indicate the difference in the amount of TcO_4^- between the two samples. Figure 4.5 shows this fit, indicating 22% TcO_4^- in the uncontacted SY-103 sample. A similar fit of the “as received” AN-107 Tc XANES using the contacted SY-103 XANES and the TcO_4^- XANES indicates 38% TcO_4^- (Figure 4.6). The fit is not as good, suggesting that, although very similar, the specie (or distribution of species) is not identical to that in the prepared SY-103 sample. This is not surprising, given that the conditions in the tanks are quite different even though they are both CC wastes. For example, the TOC, which is a reflection of the concentration of organic complexants, is approximately 40 g/L in AN-107, but only about 20 g/L in SY-103 (Van Vleet 1993).

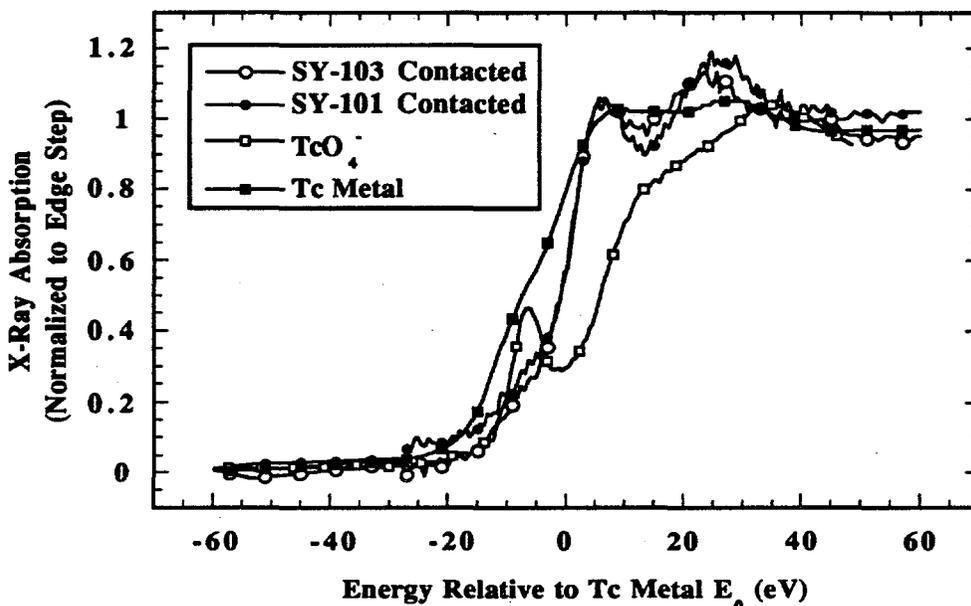


Figure 4.2. Comparison of the Contacted Samples with TcO_4^- and Tc Metal

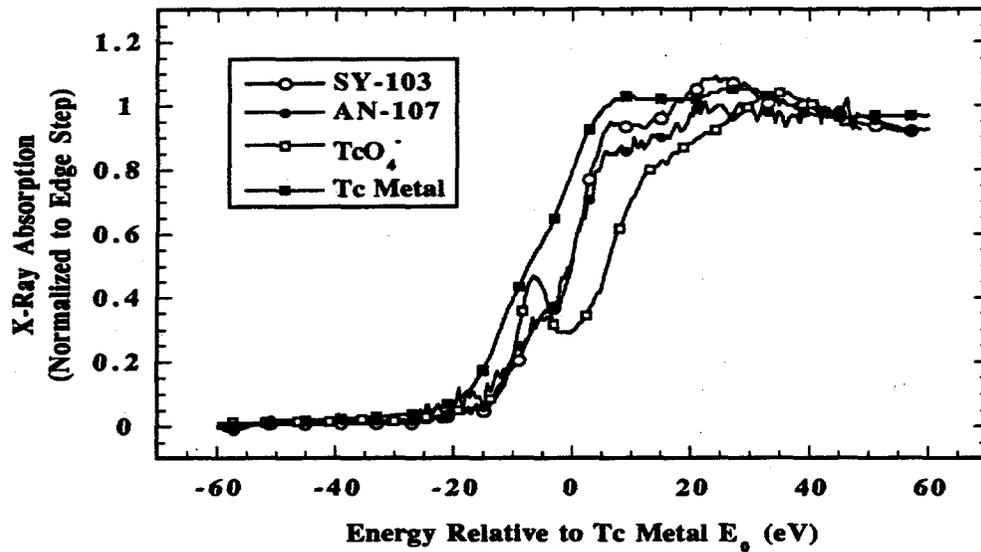


Figure 4.3. Comparison of the Uncontacted Samples with TcO_4^- and Tc Metal

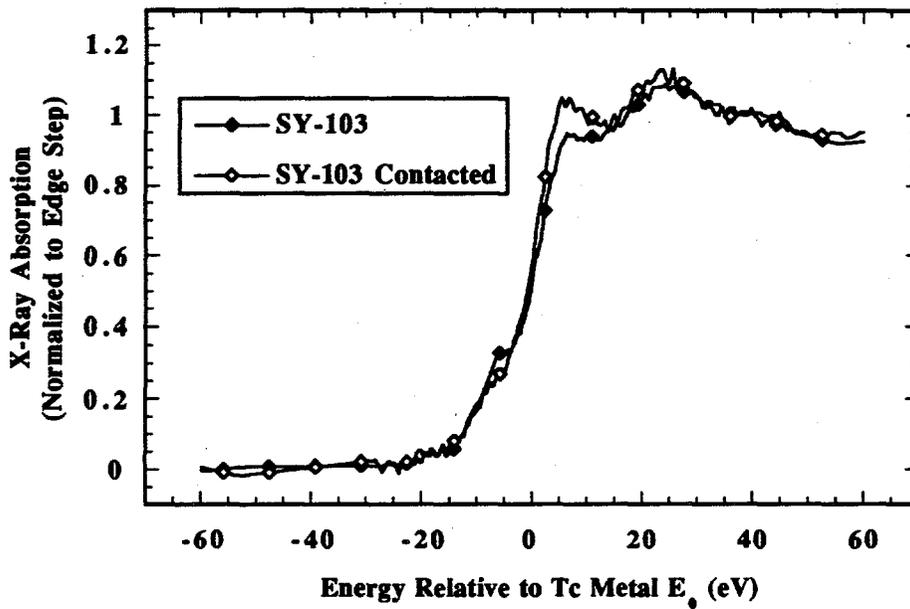


Figure 4.4. Comparison of the Uncontacted and Contacted SY-103 Samples

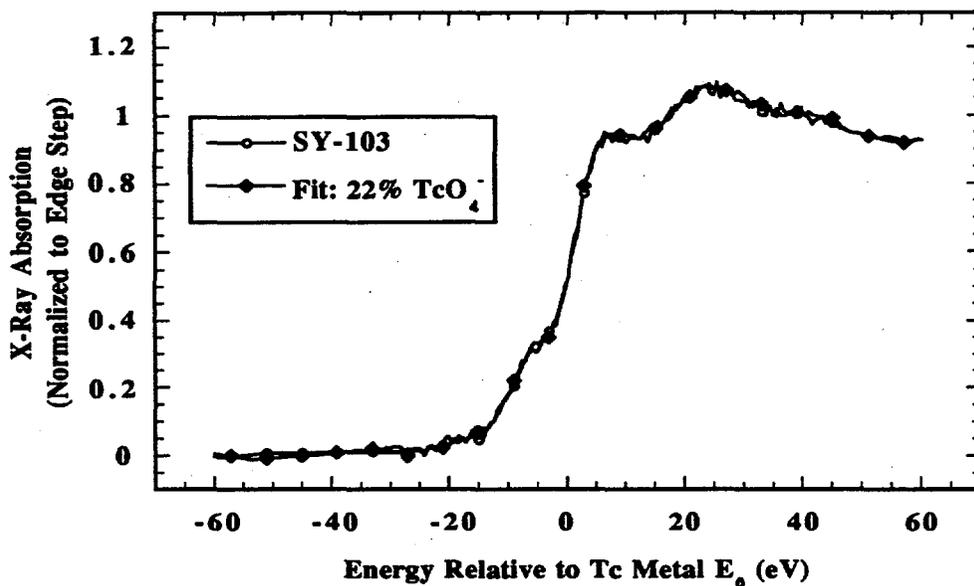


Figure 4.5. SY-103 and a Fit Using a Linear Combination of the Contacted SY-103 and the TcO₄⁻

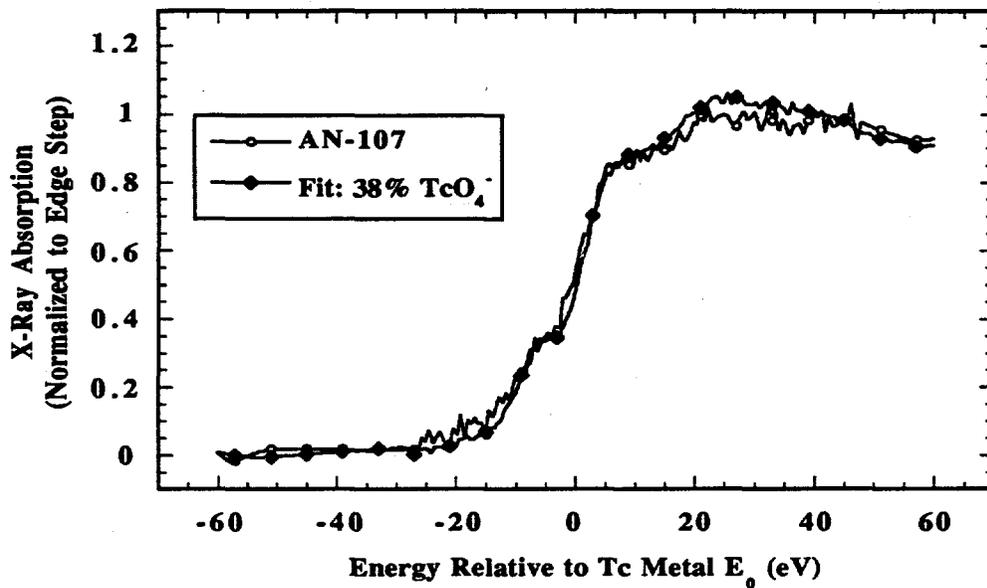


Figure 4.6. AN-107 and a Fit Using a Linear Combination of the Contacted SY-103 and the TcO₄⁻ XANES. The best fit required 38% TcO₄⁻.

Analyzing the solutions by ICP-MS before and after contact with the Reillex™-HPQ resin indicated 46% Tc removal from the SY-103 sample. This is much more Tc than the amount of TcO_4^- the XANES fit indicates. The error in the fit results can be roughly estimated by varying the TcO_4^- contribution and visually inspecting the resulting plot. This method indicates that the error in the TcO_4^- contribution to the prepared SY-103 sample is ± 5 percentage points (i.e., may be 17% to 27%). This error estimate does not take into account systematic errors in the data collection and/or analysis, however, which could be significantly larger.

Another possible cause of the difference is that some of the non-pertechnetate species was removed by the resin (so the amount of Tc removed was actually greater than the amount of TcO_4^- present). The good fit observed suggests that the only difference between the spectra is due to a TcO_4^- component, so this seems unlikely.

Finally, the discrepancy may also be due to the formation of TcO_4^- during the time between the contact (when the original TcO_4^- present was removed) and the time the samples were analyzed. Evidence for such a re-establishment of the Tc species equilibrium was presented in Section 2. The time between the contact and the XAS analysis was approximately 36 days. Formation of new TcO_4^- in this manner is somewhat difficult to reconcile with the observed difficulty in oxidizing the non-pertechnetate species to pertechnetate demonstrated in Section 3. Further experiments are required to resolve this question.

4.3 Conclusions

In conclusion, the XANES spectra presented here indicate that most (greater than 60%) of the Tc in the samples is not TcO_4^- . Removal of TcO_4^- (by contacting with Reillex™-HPQ) is reflected by changes in the XANES spectra that are consistent with removal of a TcO_4^- XANES contribution. The predominant Tc oxidation state appears to be +IV. More standards are needed to definitively identify the oxidation state. Collecting XANES data from other DSSF and NCAW wastes would be useful for determining if non-pertechnetate species are in these wastes as well. Although probably acceptable, TcO_4^- removal was not as complete as expected for the DSSF batch tests reported in Section 2. Determining if this is caused simply by matrix effects or if it is caused by a non-pertechnetate species may be important for predicting the effectiveness of ion exchange for Tc removal from the DSSF waste inventory.

5.0 Electrospray Ionization Mass Spectrometry of Simulants

Electrospray ionization-mass spectrometry was investigated as a technique for the speciation of Tc in CC waste. The strength of ESI-MS for this work is its ability to provide molecular weight information on metal-organic complexes or metal oxides of Tc in solution with minimal sample handling and analysis time. Thus, ESI-MS has the potential to provide direct evidence of Tc speciation, both organic and inorganic, in CC waste.

Dilute samples are usually analyzed with ESI-MS. The tank samples are high in nitrate and nitrite salts and hydroxide, and it was unknown if this would prevent analysis by this technique. Therefore non-radioactive simulants were tested first, before investing the time and money to modify the system for analysis of radioactive samples. For this phase of the work, Mo and Re were selected as non-radioactive surrogates for Tc.

The ultimate objective of this study was to identify Tc species in actual waste solutions using ESI-MS. Budget cutbacks necessitated a reduction in scope. The objective was reduced to speciation of Mo and Re in simulants by ESI-MS as a demonstration of the feasibility of ESI-MS for speciation of Tc in actual waste solutions and to provide insight into Tc chemistry in the waste and waste-related solutions.

The specific experimental goals were to 1) identify molybdate (MoO_4^{2-}) in a reference solution, 2) identify perrhenate (ReO_4^-) in a reference solution, 3) identify the Re species formed (ReO_4^- and any others present) under solution conditions relevant to analytical sample preparation and waste feed stream adjustment, and 4) identify Re species in a CC supernate waste simulant.

5.1 Experimental

The Re used in this study was an ICP calibration reference standard stock solution (Inorganic Ventures, Ventura, CA). This solution contains 10,000 mg/L Re in 2% nitric acid. A Mo calibration reference standard stock solution from the same source was also used. Water used to prepare solutions was 17 M-ohm water (Millipore, Bedford, Massachusetts). Sodium hypochlorite was in the form of ChloroxTM. Sodium hydroxide, ammonium hydroxide, 40% hydrogen peroxide, ceric ammonium nitrate, and all other reagents were reagent grade or higher.

The instrumentation consisted of a Hewlett-Packard (HP) 59987A API-Electrospray Interface, HP 5989B MS Engine, HP Chemstation data system with HP G1047A liquid chromatography/mass spectrometry (LC/MS) software, and a Harvard syringe pump for direct sample infusion. The instrument mass axis was calibrated, and ion source parameters were optimized (tuned) in the positive ionization mode using a 40- $\mu\text{L}/\text{min}$ infusion of a 25-mg/L polypropylene glycol (PPG) solution in 0.1% ammonium acetate. Nitrogen was used to nebulize the sample and as a drying gas.

The mass axis was calibrated using PPG m/z of 251.21, 442.24 and 848.61. The mass spectrometer was scanned in the range spanning 100 to 1000 m/z. In negative ionization mode, the PPG m/z used for mass axis calibration were 376.21, 483.31 and 889.63. Nitrogen was used as the nebulizing gas and an oxygen/nitrogen mixture was used as the drying gas.

5.2 Results

Molybdenum

A 100-mg/L Mo solution was prepared by diluting the Mo standard in ammonium hydroxide. The sample was infused at 40 $\mu\text{L}/\text{min}$ and analyzed in both positive and negative ion modes. Positive ion mode gave no evidence of Mo. In negative ion mode, Mo was observed as a singly charged molybdate ion (MoO_4^-) in the ESI-MS spectrum of this weakly basic solution. Negative ion ESI-MS data obtained for molybdate (Figures 5.1 and 5.2) match the naturally occurring isotopic abundances shown in Table 5.1. Figure 5.1 also shows MoO_4^- clustered with other species as well as more complex polyoxyanions. These polyoxyanions are described in the literature (Lau et al. 1995; Summerfield et al. 1995). While the exact identity of other ions in Figures 5.1 and 5.2 have not been identified, it can be determined, because of the unique isotopic distribution of this metal, that they contain Mo (Table 5.1).

Table 5.1. Isotopic Abundances for Mo (naturally occurring)

Mass	Relative Abundance
92	61.4
93	0
94	38.6
95	66
96	69.3
97	39.8
98	100
99	0
100	39.8

Rhenium

A solution containing 10,000 mg/L Re in 2% nitric acid was diluted to a concentration of 10 mg/L with de-ionized water and analyzed in both positive and negative ion modes. No evidence of Re species was found in positive ion mode, and the ions observed are most likely due to solvent clustering and other impurities in the sample.

Figure 5.3 shows the ESI-MS negative ion data for the 10 mg/L ReO_4^- solution. Table 5.2 shows the expected naturally occurring isotopic ratios for Re at the perrhenate masses and makes it clear that the strong peaks near $m/z = 250$ are due to ReO_4^- .

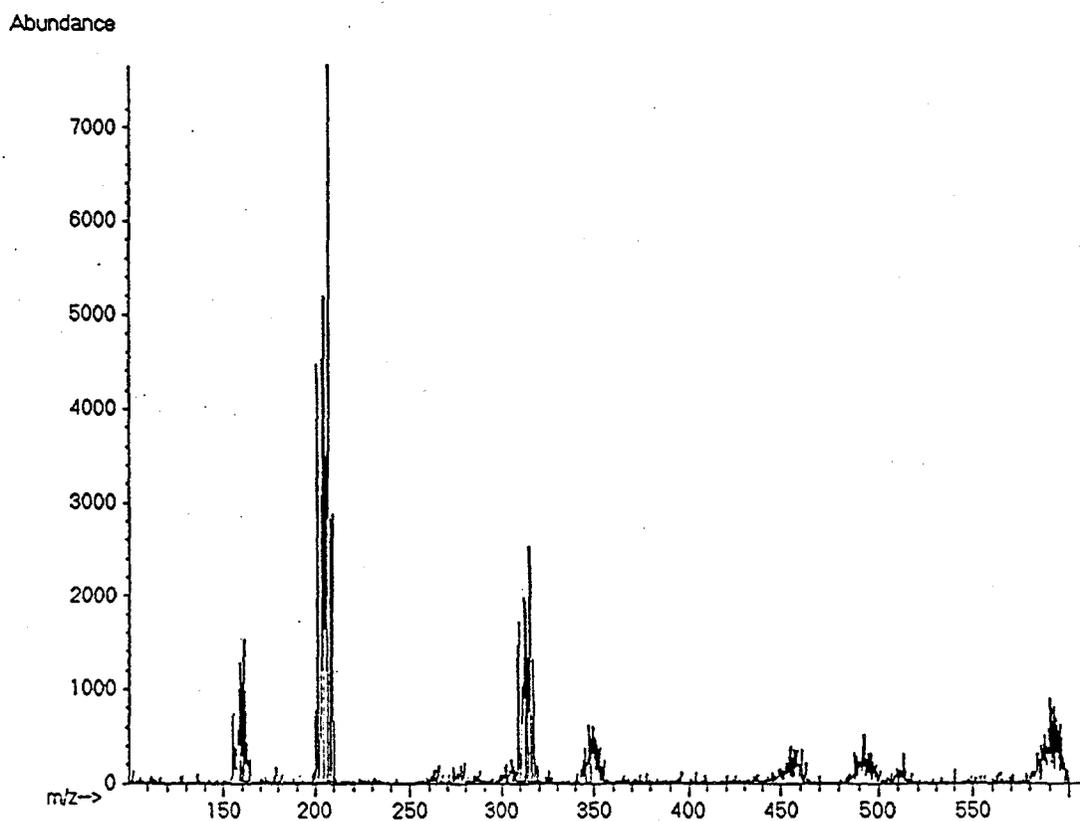


Figure 5.1. Molybdenum ICP Standard, ESI Negative Ion Mode. Molybdate clusters are indicated near m/z 160, 205, and 315. Other peaks also indicate multiple molybdate clusters.

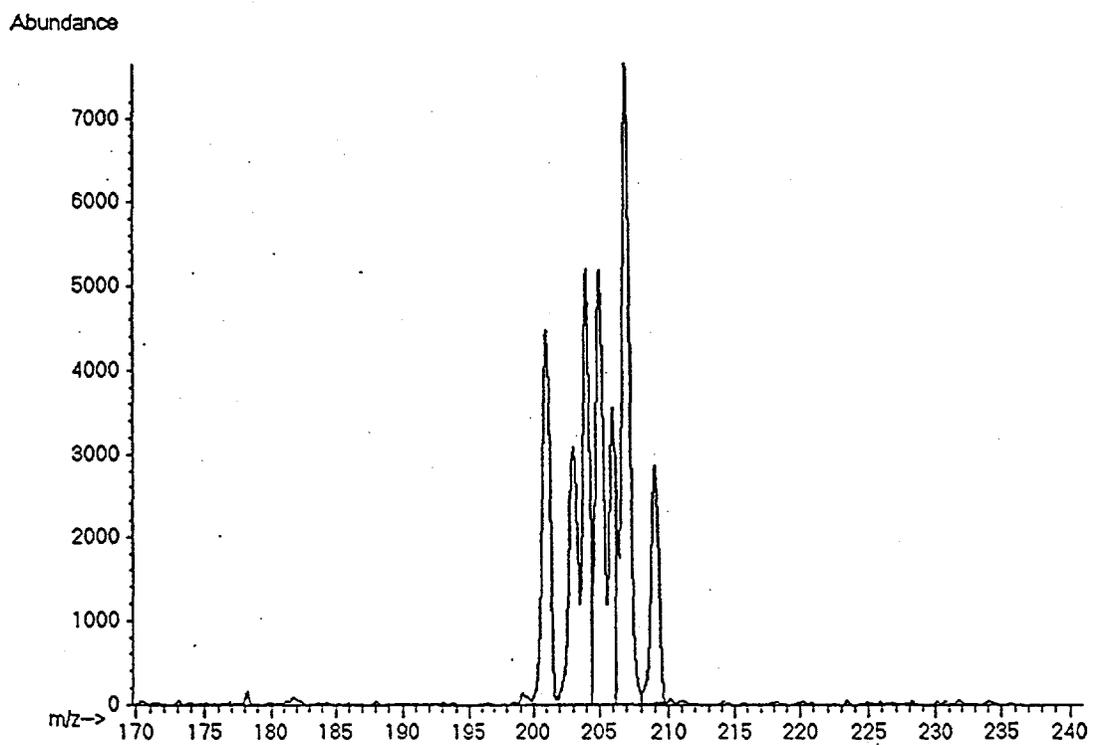


Figure 5.2. Molybdenum Containing Cluster, ESI Negative Ion Mode, Showing Elemental Isotopic Ratios

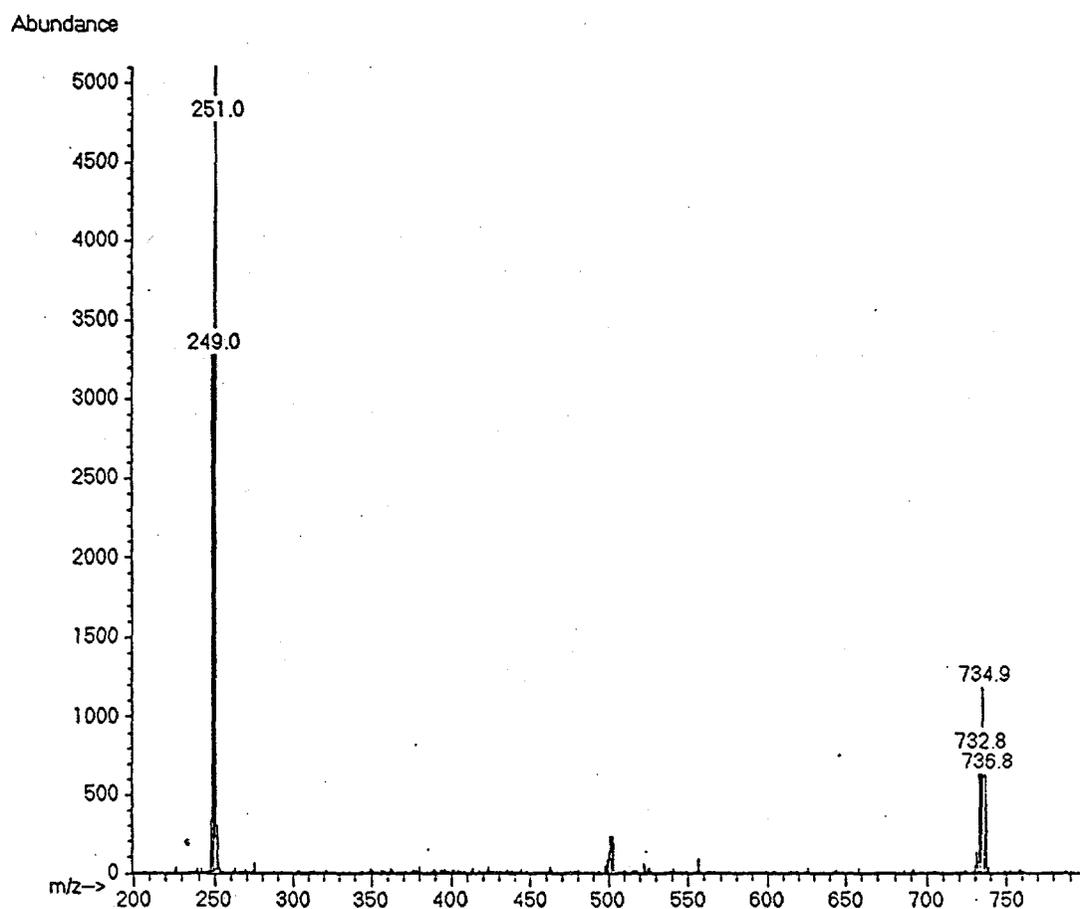


Figure 5.3. Acidic ReO_4^- Solution, ESI Negative Ion Mode. Perrehnate is evident at m/z 249 and 251. The cluster of peaks near m/z 500 is probably due to perrehnate dimer. The peaks near m/z 735 are consistent with $\text{Re}_3\text{O}_{11}^-$ polyoxyanion.

Table 5.2. Isotopic Abundances for ReO_4^-

Mass	Relative Abundance
249	59.5
250	0.1
251	100
252	0.2

The peaks near $m/z=735$ in Figure 5.3 appear to be due to the presence of $\text{Re}_3\text{O}_{11}^-$, as shown by the masses and abundances given in Table 5.3. No reference to this anion of Re could be found in a brief search of the literature.

Table 5.3. Isotopic Abundances for $\text{Re}_3\text{O}_{11}^-$

Mass	Relative Abundance
731	11.8
732	0.1
733	59.2
734	0.3
735	100
736	0.4
737	57.3
738	0.2
739	1.2

Ion source and solution parameters were varied to determine if the $\text{Re}_3\text{O}_{11}^-$ ion is an artifact of the electrospray process (a cluster) or a true polyoxyanion in solution. Ion source parameters (ionization and ion focusing voltages) that generally exhibit effects on clusters had little effect on the $\text{Re}_3\text{O}_{11}^-$ ion.

Solution parameters were then varied. According to the literature (Summerfield et al. 1995; Howarth and Hastings 1992), tungsten and Mo polyoxyanions are formed when hydrogen peroxide is added to aqueous solutions of these metals. It has been speculated (Howarth and Hastings 1992) that

O_2^{-2} replaces O^{-2} in Mo and W oxyanions. Observing analogous changes in the ESI-MS spectrum of the Re solution after adding peroxide would be strong evidence that such polyoxyanions truly exist in solution.

To test this hypothesis, 1 mL of 40% hydrogen peroxide was added to 1 mL of the Re ICP standard stock solution. This was heated on a hotplate to near boiling. This solution was then diluted with deionized water and analyzed. Figure 5.4 shows the region of the spectrum where the $Re_3O_{11}^-$ appears, and it is clear from the peaks near $m/z=751$ and 767 that $Re_3O_{12}^-$ and $Re_3O_{13}^-$ have been formed. From the insensitivity of the $m/z = 767$ amu peak to changes in ionization parameters, and the clear and explainable changes with addition of peroxide, it is evident that $Re_3O_{11}^-$ is a true polyoxyanion in solution and that it undergoes replacement of O^{-2} by O_2^{-2} .

These results also suggest that Tc clusters may form when peroxide is added to acidic Tc-containing solutions, as during sample preparation for analysis. Such formation may result in less Tc detected than actually present because the polyoxyanion probably behaves quite differently than pertechnetate in subsequent separation steps. Detection of Tc polyanions in analytical and actual waste samples certainly appears feasible if they are present.

When this test was repeated under alkaline conditions, no $Re_3O_{11}^-$ or other Re_3 species were observed. (To make the solution alkaline, 1 M NaOH was added until the hydroxide concentration was between 0.1 M and 1.0 M.) The spectrum of an alkaline ReO_4^- solution after adding H_2O_2 displays only perrhenate peaks and a series of sodium nitrate clusters {e.g., $(NaNO_3)NO_3^-$, $(NaNO_3)_2NO_3^-$, $(NaNO_3)_3NO_3^-$, etc.}. Several other oxidizing agents were also tested under both acidic and alkaline conditions. One milliliter of 5.25% NaOCl (ChloroxTM) was added to 1 mL of the Re standard and heated to near boiling. The resultant spectra did not exhibit the m/z for perrhenate ion in either acidic or alkaline solutions. This is probably because the high ionic concentration due to the NaOCl masked the perrhenate signal.

Ceric ammonium nitrate $\{(NH_4)_2Ce(NO_3)_6\}$ was also tested. A 0.1-mL aliquot of 0.1 M ceric ammonium nitrate in 0.15 M HNO_3 was added to the Re solution. The solution turned yellow, indicating the presence of Ce(IV). For both acidic and alkaline Re solutions, the only Re species observed was perrhenate. Peaks consistent with Ce(III) and Ce(IV) nitrate ions $\{Ce(NO_3)_4^-$ and $Ce(NO_3)_5^-\}$ were observed in the acidic test solution spectra, and a series of $(NaNO_3)_nNO_3^-$ peaks were observed in the alkaline solution spectra. It seems reasonable that the Ce species are stable in solution. However, the prevalence of the sodium nitrate peaks, and the observation of very large numbers of $(NaNO_3)_nNO_3^-$ (i.e., large n), suggests that these clusters are formed during the electrospray process.

Spectra of the alkaline solutions were, in general, more complex than the analogous acidic solutions. A number of NaOH clusters were observed, as well as adducts formed by the association of NaOH molecules with other ions.

PNL-ALO-432 Technetium Preparation Procedure

ESI-MS was employed to evaluate PNNL's Tc counting preparation procedure and to determine the effect of dichromate on the Re solution. Samples spiked with the Re solution were put through the PNL-ALO-432 Tc preparation procedure, and solutions were collected at various points and analyzed by ESI-MS in the negative ion mode.

The first step is to pass the sample through an AG50x8 cation exchange resin to replace the bulk of the metal cations with protons. Sodium dichromate then is added to oxidize all Tc species to pertechnetate (TcO_4^-). Tartrate is added next to complex metal cations. Tetraphenylarsonium chloride is next added to precipitate ReO_4^- , but leave the soluble tetraphenylarsonium pertechnetate salt in solution. Perrhenate is observed in the ESI-MS spectra of all these solutions until the tetraphenylarsonium addition, as expected. No clusters were observed.

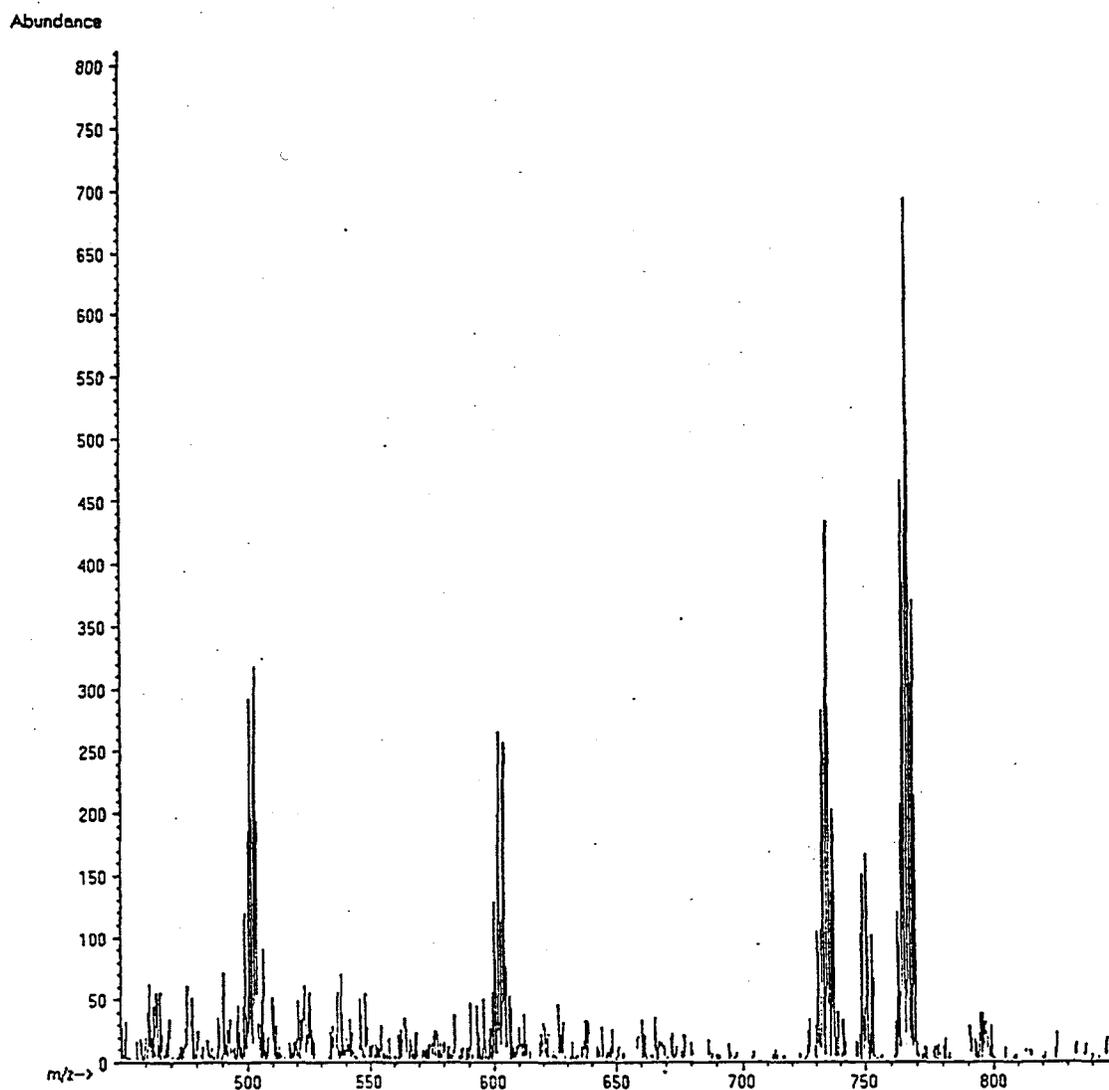


Figure 5.4. ESI Negative Mode of Acidic Re Solution with H_2O_2 . The peak clusters at m/z 735, 750, and 767 indicate $\text{Re}_3\text{O}_{11}^-$, $\text{Re}_3\text{O}_{12}^-$, and $\text{Re}_3\text{O}_{13}^-$.

CC Waste Simulant

The next step in developing ESI-MS for use in determining Tc speciation in tank waste samples was to work with simulant solutions high in salt and alkaline content. The presence of these high salt solutions could potentially interfere with detecting the metal species of interest. Therefore, the next test of this ESI-MS technique was to detect Re spiked into a CC waste simulant.

Figure 5.5 shows the ESI-MS spectrum of 200 mg/L Re (as ReO_4^-) in a CC waste simulant.^(a) The peaks at 249 and 251 indicate that detecting ReO_4^- in the presence of other salts in the complex matrix of the CC waste simulant is not a problem at this concentration. No Re species other than ReO_4^- were observed.

The concentration of Tc in actual CC wastes is about 10 mg/L. Detection of this level of Tc is very likely, considering that the spectrum in Figure 5.5 was collected at a fairly short counting time. Longer counting times of the area around suspected Tc peaks would result in better signal to noise.

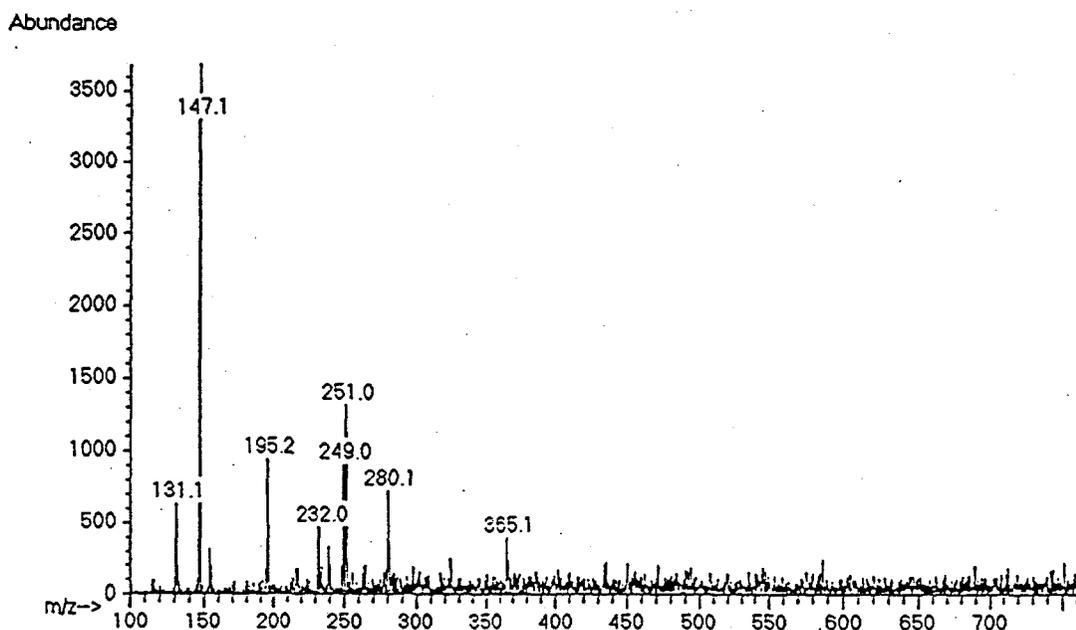


Figure 5.5. Negative Ion ESI-MS Spectrum of Rhenium Spiked into CC Waste Simulant and Diluted 10x with Deionized Water. Concentration of rhenium is 200 mg/L.

- (a) *Equilibrium Data for Cesium Ion Exchange of Hanford CC and NCAW Tank Waste.* TWRSP-92-020, a letter report to Westinghouse Hanford Company from Pacific Northwest Laboratory, Richland, Washington by LA Bray, KJ Carson, RJ Elovich, and DE Kurath (1992).

Technetium

The predicted m/z 's expected in negative ion ESI-MS for ^{99}Tc (based on naturally occurring oxygen isotope ratios) are shown in Table 5.4. It is expected that Tc will form $\text{Tc}_3\text{O}_{11}^-$, $\text{Tc}_3\text{O}_{12}^-$ and $\text{Tc}_3\text{O}_{13}^-$ anions under conditions similar to those that caused formation of rhenium polyoxyanions. The results obtained in this study for Re are expected to be very similar to those seen for Tc under similar solution conditions.

Table 5.4. Relative Abundances for TcO_4^- , Tc_2O_7^- , and $\text{Tc}_3\text{O}_{11}^-$

TcO_4^-		Tc_2O_7^-		$\text{Tc}_3\text{O}_{11}^-$	
Mass	Relative Abundance	Mass	Relative Abundance	Mass	Relative Abundance
163	100	310	100	47	100
164	0.2	311	0.3	474	0.5
165	0.8	312	1.4	475	2.2

5.3 Conclusions

The results obtained in these preliminary experiments are very encouraging. Molybdenum and rhenium species were easily detected at concentrations of 100 mg/L and 10 mg/L, respectively, in reference solutions. Several different species of Re, which is a good non-radioactive surrogate for Tc, were detected by negative ion ESI-MS. Changes in the type and abundance of these species with solution conditions strongly suggests that they are present in solution and not formed during the ESI process. In addition, it was shown that Re species (and presumably Tc species) can be tracked through the standard Tc preparation procedure, PNL-ALO-432, by monitoring aliquots from each step by ESI-MS. Most importantly, however, was the demonstration that Re species could be detected in CC simulant solutions with minimal (10 fold) dilution. This suggests that the high salt matrix typical of tank waste samples will not prevent successful ESI-MS analysis.

These preliminary results indicate that ESI-MS is capable of directly probing Tc speciation and chemistry in tank waste samples. Because converting the non-pertechnetate species to pertechnetate appears difficult (as discussed in Section 3), dilution is not expected to significantly affect the Tc species present. In conclusion, ESI-MS is expected to provide valuable speciation information on Tc in tank waste samples.

6.0 Discussion and Conclusions

The results of the batch contact experiments with both Reillex-HPQ and ABEC 5000 indicate that Tc can be effectively removed from a composite double shell slurry feed sample (70% AW-101, 20% AP-106, 10% AP-102). As much as 96% of the Tc was removed, which corresponds to a DF of 25. Decreasing K_d at the higher percent removal indicate that a small fraction of the Tc may be in an inextractable form.

The results of the batch contacts and the XANES indicate that the dominant form of the Tc in wastes containing high concentrations of organic complexants (SY-101, SY-103, AN-107) is not pertechnetate. This is indicated by the poor Tc removal observed for the batch contact experiments, which was a maximum of 30 to 50%. A successive contact removed only a small additional fraction. Analysis of the XANES indicates that most of the Tc is a non-pertechnetate species. These results are consistent with previous investigations (Schroeder et al. 1995b), which show that only 30 to 35% of the Tc in waste from tanks SY-101 and SY-103 is pertechnetate.

The XANES data strongly suggest that the oxidation state of the non-pertechnetate species is +IV. The oxidation state of Tc in pertechnetate is +VII. Technetium (IV) standards are needed to unequivocally identify the oxidation state, and EXAFS of the non-pertechnetate species would be invaluable for identifying the presence (or absence) of multinuclear complexes and ions, such as the Re species observed in the ESI-MS study.

Alternative processes or adjustment of the feed chemistry will be required to remove Tc from wastes with high concentrations of organic complexants. One alternative process is electrolytic reduction in which Tc may be plated out on the cathode. Adjustment of the feed chemistry would be directed at either destroying the organic materials and/or oxidizing the Tc to pertechnetate using any of a number of oxidizing techniques (i.e., hydrothermal processing, wet air oxidation, ozone, permanganate). However, the resistance of the non-pertechnetate species to oxidation (Section 3) suggests that very vigorous chemical and/or physical processing will be necessary for feed adjustment, unless the non-pertechnetate species is identified and such knowledge allows it to be specifically targeted for oxidation.

An investigation of analytical techniques for ^{99}Tc indicates that vigorous oxidation of analytical samples is required for high organic containing wastes to ensure that all Tc is extractable pertechnetate, as suggested by Schroeder (1995b). The separation of ^{99}Tc from other radioisotopes in the waste matrix is required to obtain an accurate liquid scintillation and/or proportional beta count of the ^{99}Tc present. Tests indicate that several cycles of Ce(IV)/ HNO_3 oxidation and evaporation to near dryness are required to oxidize all Tc in the CC waste samples to pertechnetate. This process is effective, but also time consuming.

The use of ICP-MS was found to be a fast and reasonably accurate method for Tc analyses, although spot checks are recommended to ensure that ^{99}Tc is the only m/z isotope. The method appears to be independent of the chemical form of the Tc. Since sample preparation is minimized, it is also relatively inexpensive.

The ESI-MS method shows promise as an analytical tool for identifying the chemical form of Tc in actual tank wastes. This method identified Re species, including polyoxyanions, in simulants and test solutions, and was useful for following the Re species through various changes in solution chemistry. Perrhenate, a good surrogate for TcO_4^- , was easily detectable in a CC waste simulant at 200 ppm, somewhat higher than the concentration of Tc in CC wastes.

Conclusions

- Both Reillex™-HPQ and ABEC 5000 are effective for Tc removal from a composite DSSF waste (70% AW-101), exhibiting 93% and 91% Tc removal, respectively, on the first contact.
- Neither Reillex™-HPQ nor ABEC 5000 are effective for Tc removal from the three CC wastes studied. Tc removal from the CC wastes was in all cases less than 50%.
- The technetium in CC waste is very resistant to oxidation to pertechnetate in acidified samples generally required for Tc analysis. A vigorous oxidation with Ce(IV) was found effective for this purpose, but is time consuming.
- XANES indicates that the dominant species in CC waste is not pertechnetate. It also shows that the non-pertechnetate specie(s) in the CC wastes probably has a +IV oxidation state. Technetium (IV) standards are needed for definitive identification of the oxidation state.
- The batch contacts, oxidation study, and XANES data all indicate that large amounts of non-pertechnetate species are associated with Hanford tank wastes containing relatively large (i.e., >10 g TOC/L) amounts of organic complexants.
- ICP-MS is the preferred method for determining the Tc content of waste and process samples, although checks are needed to ensure that ⁹⁹Tc is the only component with m/z = 99.

7.0 References

- Almahamid I, JC Bryan, JJ Bucher, AK Burrell, NM Edelstein, EA Hudson, N Kaltsoyannis, WW Lukens, H Nietsche, T Reibh, and DK Shuh. 1995. "Electronic and Structural Investigations of Technetium Compounds by X-ray Absorption Spectroscopy." *Inorg. Chem.*, **34**, 193.
- Anders E. 1960. *The Radiochemistry of Technetium*, NAS-NS-3021, a National Academy of Sciences-National Research Council monograph.
- Beard BJ and HL Caudill. 1964. *Technetium Recovery and Storage at B-Plant*. HW-83348, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.
- Bray LA, LK Holton, TR Myers, GM Richardson, and B Wise. 1984. *Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant*. PNL-4969, Pacific Northwest Laboratory, Richland, Washington.
- Bredt PR, SM Tinger, and EH Shade. 1995. *The Effect of Dilution on the Gas-Retention Behavior of Tank 241-SY-101 Waste*. PNL-10781, Pacific Northwest Laboratory, Richland, Washington.
- Brown GN, LA Bray, CD Carlson, KJ Carson, JR DesChane, RJ Elovich, FV Elovich, FV Hoopes DE Kurath, LL Nenner, and PK Tanaka. 1996. *Comparison of Organic and Inorganic Ion Exchangers for Removal of Cesium and Strontium from Simulated and Actual Hanford 241-AW-101 DSSF Tank Waste*. PNL-10920, Pacific Northwest National Laboratory, Richland, Washington.
- Campbell JA, S Clauss, K Grant, V Hoopes, B Lerner, R Lucke, G Mong, J Rau, and R Steele. 1993. *Flammable Gas Safety Program, Analytical Methods Development: FY 1993 Progress Report*. PNL-9062, Pacific Northwest National Laboratory, Richland, Washington.
- Eager KM. 1995. *Technetium Removal: Preliminary Flowsheet Options*, WHC-SD-WM-TI-718. Westinghouse Hanford Company, Richland, Washington.
- Hastings JJ and OW Howarth. 1992. "A ^{183}W , ^1H , and ^{17}O Nuclear Magnetic Resonance Study of Isopolytungstates." *J. Chem. Soc., Dalton Trans.*, p. 209.
- Konigsberger DC and R Prins, Eds. 1988. *X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*. John Wiley and Sons Inc., New York.
- Lau T-C, J Wang, R Guevremont, and KWM Siu. 1995. "Electrospray Tandem Mass Spectrometry of Polyoxoanions." *J. Chem. Soc., Chem. Commun.*, p. 877.
- Marsh SF, ZV Svitra, and SM Bowen. 1994a. *Distributions of 14 Elements on 63 Absorbers from Three Simulant Solutions (Acid-Dissolved Sludge, Acidified Supernate, and Alkaline Supernate) for Hanford HLW Tank 102-SY*. LA-12654, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Marsh SF, ZV Svitra, and SM Bowen. 1994b. *Distributions of 15 Elements on 58 Absorbers from Simulated Hanford Double-Shell Slurry Feed (DSSF)*. LA-12863, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Marsh SF, ZV Svitra, and SM Bowen. 1994c. *Distributions of 12 Elements on 64 Absorbers from Simulated Hanford Neutralized Current Acid Waste (NCAW)*. LA-12889, Los Alamos National Laboratory, Los Alamos, New Mexico.

- Marsh SF, ZV Svitra, and SM Bowen. 1995. *Effects of Aqueous-Soluble Organic Compounds on the Removal of Selected Radionuclides from High-Level Waste*. LA-12863, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Pourbaix M. 1966. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Pergamon Press, New York.
- Roberts FP, FM Smith, and EJ Wheelwright. 1962. *Recovery and Purification of Technetium 99 from Neutralized PUREX Wastes*. HW-73121, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.
- Rogers RD, AH Bond, ST Griffin, and EP Horwitz. 1996. *New Technologies for Metal Ion Separations: Aqueous Biphasic Extraction Chromatography (ABEC). Part I. Uptake of Pertechnetate. Solv. Ext. Ion Exch.*, 14, p. 919.
- Schmittroth FA, TH DeLorenzo, DW Wootan, and DY Garbrick. 1995. *Inventories for Low-Level Waste Tank Waste*. WHC-SD-WM-RPT-164, Rev. 0, Westinghouse Hanford Company, Richland, Washington.
- Schroeder NC, KD Abney, M Attrep, Jr., S Radzinski, J Brewer, KR Ashley, J Ball, F Stanmore, N LaBebre, A Pinkerton, and R Turner. 1993. *Technetium Partitioning for the Hanford Tank Waste Remediation System: Adsorption and Extraction of Technetium from Double Waste Simulant*. LA-UR-93-4092, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Schroeder NC, KD Abney, M Attrep, Jr., S Radzinski, J Brewer, KR Ashley, J Ball, F Stanmore, N LaBebre, A Pinkerton, and R Turner. 1994. *Technetium Partitioning for the Hanford Tank Waste Remediation System: Sorption and Extraction of Technetium from Simple Caustic Solutions*. LA-UR-94-62, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Schroeder NC, S Radzinski, KR Ashley, J Ball, F Stanmore, and G Whitener. 1995a. *Technetium Partitioning for the Hanford Tank Waste Remediation System: Sorption of Technetium from DSS and DSSF-7 Waste Simulant Using Reillex™-HPQ Resin*. LA-UR-95-40, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Schroeder NC, SD Radzinski, JR Ball, KR Ashley, SL Cobb, B Cutrell, and G Whitener. 1995b. *Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Waste (101-SY and 103-SY) Using Reillex™-HPQ Resin*. LA-UR-95-4440, Los Alamos National Laboratory, Los Alamos, New Mexico.
- Summerfield SG, OW Howarth, and KR Jennings. 1995. "Electrospray Ionization of Polyoxoanions of W, Mo, and Si in Aqueous Solution." In: *Proceedings of the 43rd ASMS Conference on Mass Spectrometry and Allied Topics*. Atlanta, Georgia. Published by ASMS, East Lansing, Michigan.
- Van Vleet RJ. 1993. *Radionuclide and Chemical Inventories for the Double Shell Tanks*. WHC-SD-WM-TI-543, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

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