Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste

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Technetium Partitioning

History: ^{99}Tc is a major fission product resulting from the production of Pu at Hanford; ~ 2000 Kg of ^{99}Tc are stored in the Hanford Tanks (Ave [Tc] = 1 x 10^{-4} M).

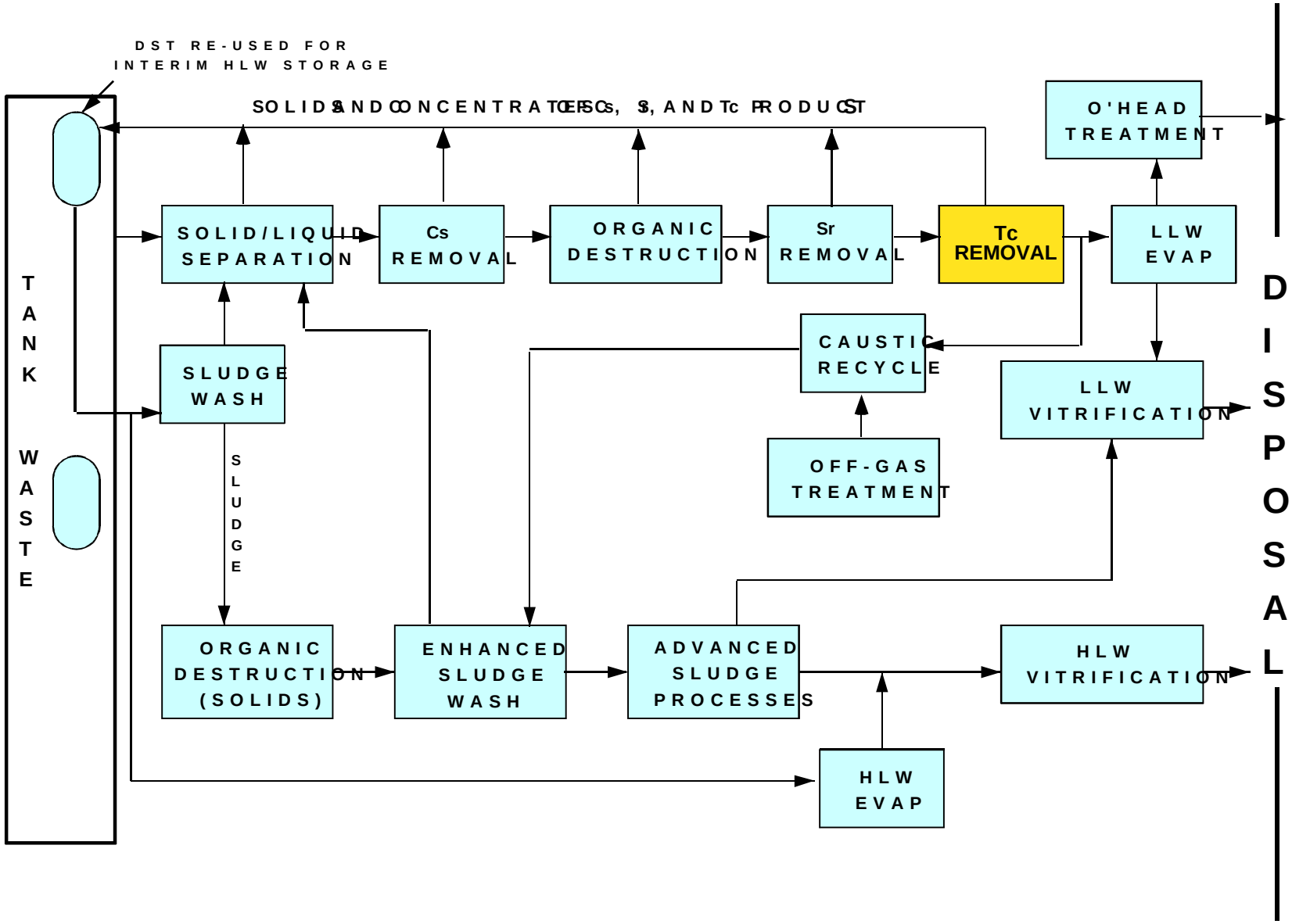
Risk: ^{99}Tc, because of its long half-life (213,000 years) and ability to migrate in the environment, contributes to the long-term risk associated with LLW disposal.

Goal: Remove ^{99}Tc from the Hanford LLW waste streams so that the final waste forms meets their performance assessment criteria. Current criteria for Hanford require a separation factor (SF) of ~ 6.4 to meet the NRC Class "A" waste limit: 0.3 Ci/m^3, 18g Tc/m^3, or 6000 ppb.

Problems: Pertechnetate (TcO_4^-) in the tank waste has been reduced and complexed (by EDTA, oxalate, citrate, etc.) to unknown, stable, non-pertechnetate species. These species will have to be oxidized to pertechnetate (TcO_4^-) in order for separation methods based on this anion to work.

Solution: Understanding the chemistry of the these species could help develop efficient oxidation or separation methods for these species.

Hanford Waste Pretreatment Flow Diagram



Project Goals

The proposed research will develop the complexation chemistry of aqueous pertechnetate under reducing conditions. The four major goals of this research are to:

1. synthesize and characterize the major classes of technetium complexes formed under tank waste conditions

2. study the ligand substitution and redox chemistry of these complexes

3. use the complexes as standards for characterizing the non-pertechnetate species in actual waste using x-ray absorption spectroscopy (EXAFS and XANES) and for developing capillary electrophoresis mass spectrometry as a characterization technique, and

4. use the technetium complexes to develop efficient oxidation or separation methods for the non-pertechnetate species in actual wastes.

Composition of 101-SY, 103-SY, and AN-107 Hanford Tank Waste Samples

Species (M) Dilution	101-SY 1:3.9	103-SY 1:2.9	107A 1:1.9	107B 1:3.8	AN-107 undiluted	107C 1:4
Na	4.6	4.9	4.96	-	8.83	-
K	0.03	0.03	0.027	-	0.046	-
Fe	-	-	0.009	-	0.032	-
Al	0.48	0.49	0.025	-	0.017	-
P	0.03	0.04	0.008	-	0.016	-
Ca	-	-	0.010	-	0.015	-
Ni	-	-	0.005	-	0.010	-
Pb	-	-	0.001	-	0.002	-
W	-	-	0.001	-	0.001	-
NO_2^-	0.69	0.73	1.51[a]	0.76	3.90[a]	0.98
NO_3^-	0.74	0.95	2.92[a]	1.46	3.52[a]	0.88
^{99}Tc (μCi/L)	98	120	76.7	38.1	129	32.5
pH	-	-	12.3	-	11.8	-
TOC (g/L)	4.01	2.67	20.7[c]	10.4[c]	39.0[b]	9.8[c]
OH^- (free)	1.70	2.06	-	0.78		
density (g/mL)[d]	1.22	1.24	1.29	1.18	1.43	1.09

[a]These values were obtained from the analyses of the corresponding more concentrated or dilute sample. [b]Based on the AN-107 grab sample analysis. [c]Concentration are calculated using the dilution factor relative to AN-107. [d]The density of 107D (1:19 dilution) is 1.059 ± 0.007 g/mL.

Concentrations of the Major Organics Measured in a Hanford Complexant Concentrate Waste Sample

(A. P. Toste et al. *J. Radioanal. Nucl. Chem.* **194**, 25-34 (1995).

Organic Compound	Concentration (mM)
Chelating/Complexing Agents	
Citric Acid	64.4
N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid (HEDTA)	37.5
Ethylenediaminetetracetic Acid (EDTA)	31.4
Nitriloacetic Acid (NTA)	7.33
Chelator/Complexor Fragments	
Iminodiacetic Acid (IDA)	188
N-(Methylamine)iminodiacetic Acid (MAIDA)	28.0
Ethylenediaminetriacetic Acid (ED3A)	17.9
N-(Carboxy)ethylenediamine-N’,N’-diacetic Acid	5.32
N-(Carboxy)ethylenediamine-N,N’-diacetic Acid	2.73
N-(Methyl, ethyl)iminocarboxy Acid	2.52
N-(Ethylene)ethylenediaminetriacetic Acid	2.28
N-(2-Hydroxyethyl)iminodiacetic Acid	2.14
N-(2-Hydroxyethyl)-N’-(methyl)ethylenediamine-N,N’-diacetic Acid	1.83
N-(Diethyl)iminocarboxy Acid	1.54
N-(3-Carboxypropyl)iminocarboxyacetic Acid	1.12
N-(Methyliminocarboxy)ethylenediamine-N-acetic Acid	1.09
N-(Ethyl)propylenediaminetriacetic Acid	1.09
Ethylenediaminecarboxytriacetic Acid	1.08
N-(3-carboxypropyl)-N-iminoacetic Acid	1.07
N-(Ethy)ethylenediamine-N-acetic-N’-carboxy Acid	1.02
Propylenediaminecarboxytriacetic Acid	0.91
N-(Methylamine)-N’-(methyl)ethylenediamine-N’,N’-diacetic Acid	0.90
N-(2-Hydroxyethyliminoacetic)ethylenediamine-N’,N’-diacetic Acid	0.89
N-(Hydroxymethyl)ethylenediamine-N’,N’-diacetic Acid	0.83
N-(Ethyl)-N’-(2-hydroxyethyl)ethylenediamine-N-carboxy-N’-acetic Acid	0.77
N-(Methyl, 2-hydroxyethyl)iminocarboxy Acid	0.67
N-(Ethyl)ethylenediamine-N’,N’-carboxyacetic Acid	0.58
N-(Ethylene)iminocarboxyacetic Acid	0.23
Miscellaneous	
C23-C35 Alkanes	7.77
Dibutylphthalate	1.24
Dioctylphthalate•	0.05
Percent Total Organic Carbon Identified	**80.4 %**

The Apparent, True, and Calculated K_d Values for Unoxidized Waste Samples

Sample	$[OH^-]$, M[b]	$[NO_3^-]$, M	K_d, mL/g			
			Cesium[a]	Technetium		
				$^{app}K_d$	$^{True}K_d$[a]	$^{Calc}K_d$
107A	0.02	2.92 ± 0.12	-	8.11 ± 0.42	-	131 ± 12
107B	1.00	1.46 ± 0.06	3009 ± 216	5.20	321 ± 84	318 ± 20
107B	5.20 ± 0.2	1.12 ± 0.05	-	8.91	672 ± 206	746 ± 32
107D	0.89	0.292 ± 0.012	-	-	-	1109 ± 65
	1.45	0.292 ± 0.012	-	-	-	1205 ± 65
	5.08	0.292 ± 0.012	-	-	-	1828 ± 65
AN-107	0.0063	3.52 ± 0.14	-	-	455 ± 94	109 ± 10
107C	0.775 ± 0.040[c]	0.88 ± 0.02	3327 ± 161	7.98	406 ±142	470 ± 12
107C	5.20 ± 0.20	0.68 ± 0.049	-	-	558 ± 127	1090 ± 58
101-SY	1.70 ± 0.08[c]	0.74 ± 0.04	3183 ± 150	3.99 ± 0.19	545 ± 154	591 ± 38
103-SY	2.06 ± 0.10[c]	95 ± 0.04	2590 ± 110	5.16 ± 0.44	543 ± 21	516 ± 32

[a]The uncertainties in these K_d values are due primarily to counting statistics. [b]The hydroxide concentrations are calculated values based on dilutions of added NaOH or pH measurements. [c]Hydroxide concentration are titrated free hydroxide concentrations.

Apparent Technetium K_d Values and True Pertechnetate K_d Values

Based on our previous experience with TcO_4^- in simple $NaOH/NaNO_3$ solutions, the unoxidized waste technetium K_d values ($^{app}K_d$) are lower than expected calculated K_d values ($^{Calc}K_d$) for these waste matrixes. This indicates that a substantial amount of the technetium in these waste is not TcO_4^-. We have measured the "true pertechnetate K_d values" for these waste by first removing a significant amount of the residual cesium with a cation exchanger and then adding $^{95m}TcO_4^-$ to the waste and measuring the pertechnetate distribution coefficient between the waste and Reillex™-HPQ resin. The "true pertechnetate K_d values" are ~100 times higher than the $^{app}K_d$ values. The true pertechnetate K_d and $^{app}K_d$ values can be used to calculate the % non-TcO_4^- species in a waste sample before and after an oxidation procedure.

Percent Non-Pertechnetate in Waste Samples Before Oxidation

Sample		$^{app}K_d$ mL/g	% Non-TcO_4^-
107A	(1:1.9 diluted waste)	8.11 ± 0.42	48
107B	(1:3.8 diluted waste)	5.20	63
107B	(1:3.8 diluted waste)	8.91	51
107C	(1:4 diluted waste)	7.98	53
101-SY	(1:3.9 diluted waste)	3.99 ± 0.19	70
103-SY	(1:2.9 diluted waste)	5.16 ± 0.44	64
103-SY	(supernate from the initial contact subjected to a second batch contact)	< 1	>90
103-SY	(supernate from an initial contact subjected to a warm 25 minute digestion in H_2O_2 and then a second batch contact)	< 1	>90

Oxidation of Non-Pertechnetate Species

The previous slides indicate that >50% of the technetium in the complexant waste is not pertechnetate. The slides below shows that these non-pertechnetate species are not easily oxidized to pertechnetate. Peroxydisulfate, with and without silver, have been successful in oxidizing these species. It has shown some kinetic selectivity for the non-pertechnetate species over the other major reduced species in the waste, nitrite and organic material. However, we have observed that the non-pertechnetate species in 103-SY waste will oxidize slowly if the waste is repeatedly warmed and exposed to air. Without this treatment the 101-SY has been stable for several years.

Selected Standard Potentials in 1.00 M Base[a]

Couple	E°, volts vs. SHE
$VO_4^{3-}/HV_2O_5^-$	2.19
$S_2O_8^{2-}/SO_4^{2-}$	1.96
VO_4^{3-}/V_2O_3	1.37
$(Re(IV)Re(V)/Re(IV)_2$	1.29[b]
O_3/O_2	1.25
OCl^-/Cl^-	0.89
HO_2^-/OH^-	0.87
VO_4^{3-}/VO	0.75
MnO_4^-/MnO_2	0.60
MnO_4^-/MnO_4^{2-}	0.56
$HFeO_4^-/FeO_2^-$	0.55
O_2/OH^-	0.40
PbO_2/PbO	0.25
NO_3^-/NO_2^-	0.01
$NaBiO_3/Bi_2O_3$	---
TcO_4^-/TcO_2	-0.37[c]
TcO_4^-/TcO_4^{2-}	-0.57
$CO_3^{2-}/HCOO^-$	-1.01

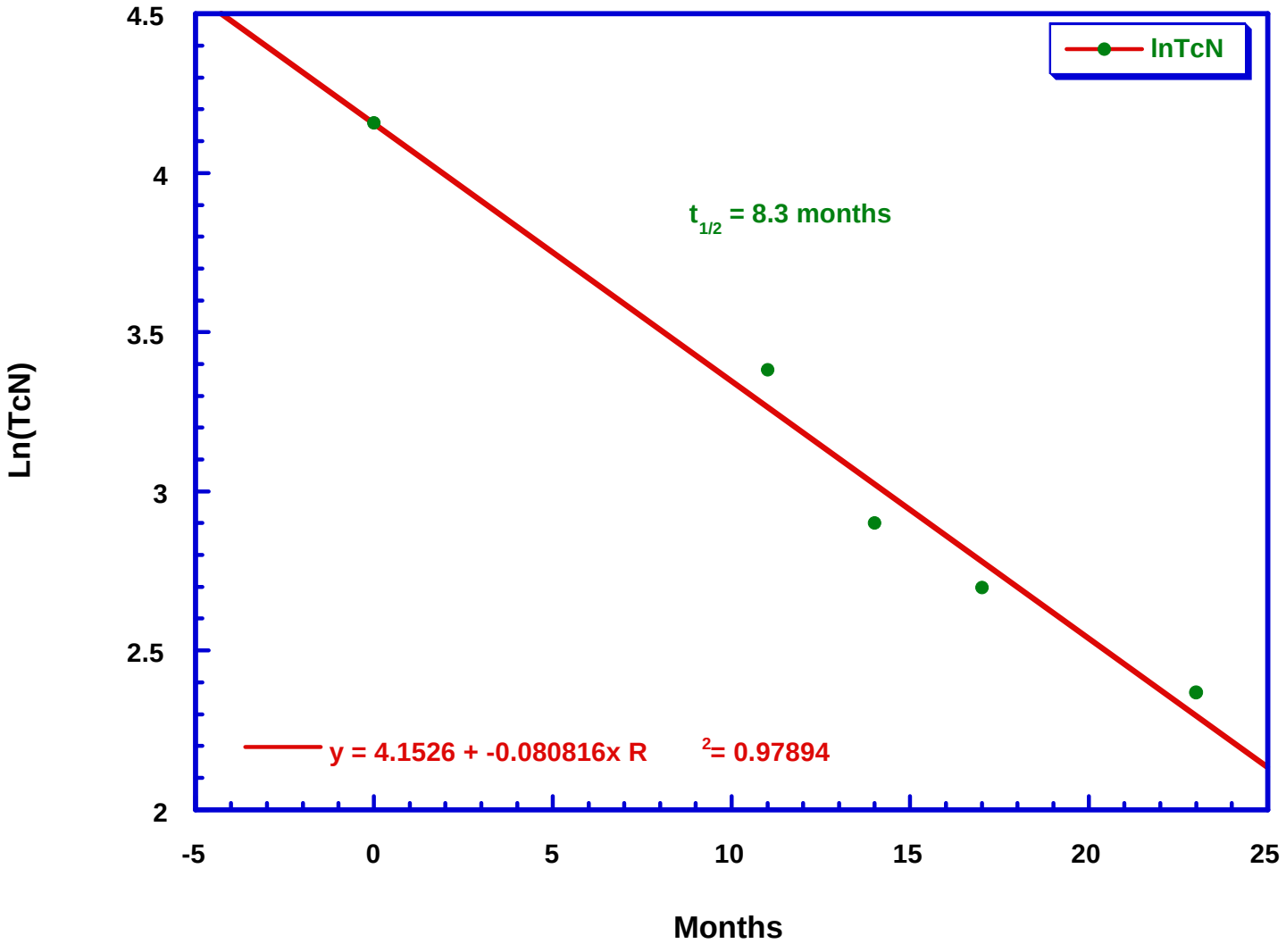
[a]*Standard Potentials in Aqueous Solutions*, Allen J. Bard, Roger Parson, and Joseph Jordan, eds., IUPAC, Marcel Dekker, Inc., New York, 1985. ISBN: 0-8247-7291-1; [b]CV of $[Re(IV)_2(\mu\text{-}O)_2(EDTA)_2]^{4-}$ in phosphate buffer at pH=7.5; [c]Calculated from data for 1.00 M acid.

103-SY Oxidation Results[a]

Oxidant	Ox (meq)	Ox[b] / Tc	Ox[c] / Red	°C	$^{app}K_d$ ± st dev	% not TcO_4^-
NaOCl	9.65	1800	3.0	50/22[d]	165 ± 10	3.9
$NaOCl/H_2O_2$	6.4/18	4500	7.5	50/22[d]	38.1 ± 3.6	19.0
H_2O_2	0.28	100	0.17	40	4.84	68
PbO_2	1.16	198	0.33	50	41.6 ± 7.5	17.6
$NaBiO_3$	1.16	198	0.33	50	37.3 ± 0.6	19.3
NH_4VO_3	1.02	175	0.29	50	18.3 ± 0.4	33.5
$KMnO_4$	1.00	172	0.29	50	64.4 ± 2.9	11.6
$K_2S_2O_8$	11.6	1980	3.3	50	209 ± 3	2.8
$K_2S_2O_8$	1.16	198	0.33	50	188 ± 6	3.2
$K_2S_2O_8/Ag^+$	1.20[e]	205	0.34	60	538 ± 20	0.01
$K_2S_2O_8/Ag^+$	0.12[f]	21	0.034	60	150 ± 15	4.44
$K_2S_2O_8/Ag^+$	1.20[g]	205	0.34	60	516 ± 52	0.09
$K_2S_2O_8/Ag^+$	1.20[g]	205	0.34	25	444 ± 44	0.39
$K_2S_2O_8/Cu^{2+}$	1.20[e]	205	0.34	60	263 ± 26	1.9
$K_2S_2O_8/Ce^{4+}$	1.20[e]	205	0.34	60	69 ± 7	10.8
Ozone	excess	>100	>100	25[h]	440 ± 40	0.4

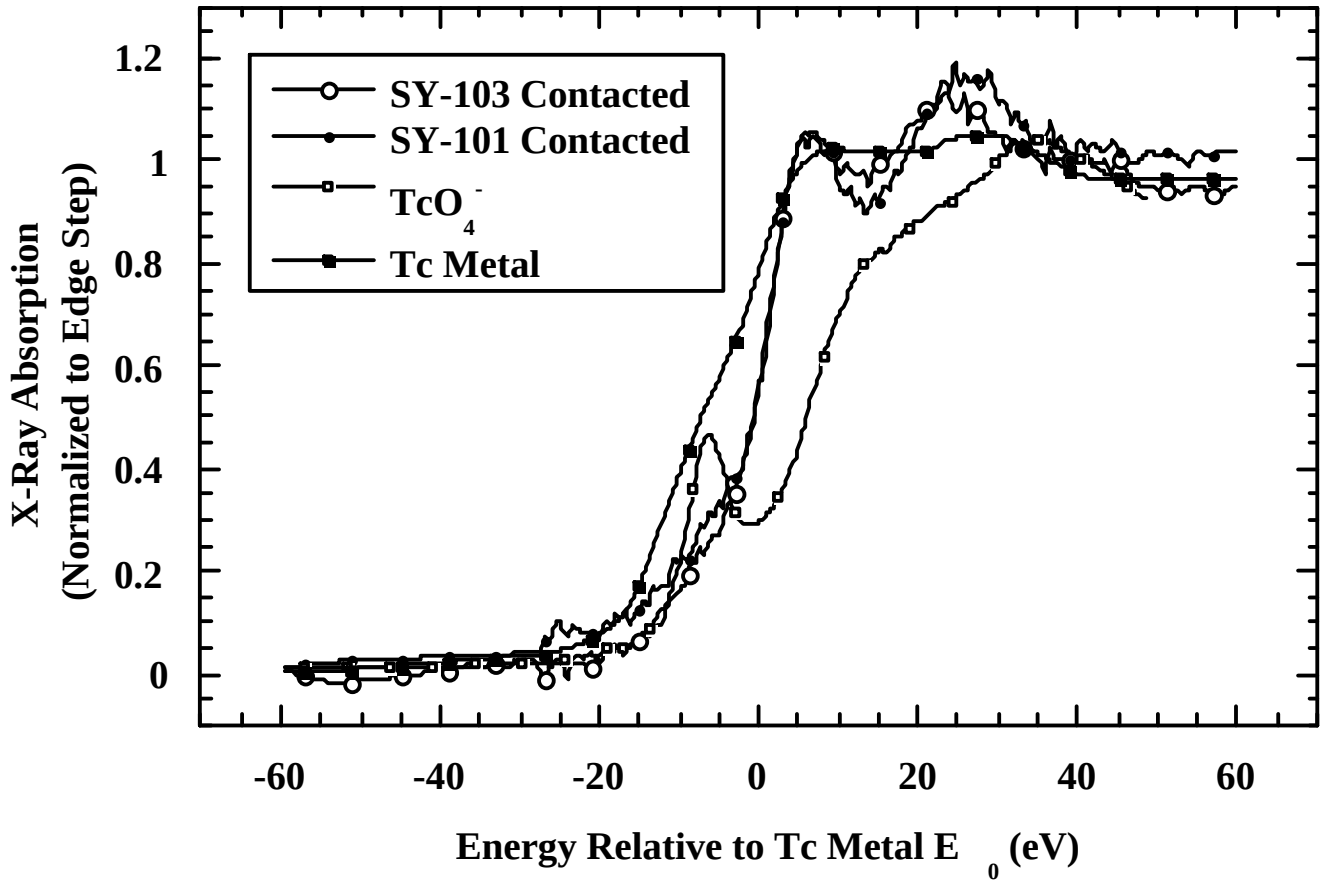
[a]1 hour oxidations; [b]meq ratio of oxidant present relative to the amount of oxidant required to bring a presumed Tc(IV)EDTA species to TcO_4^- per mL of 103-SY waste; [c]meq ratio of oxidant to total reduced species: non-pertechnetate (0.00265 meq) + organic material in 103-SY(0.486 meq) + NO_2^- (1.10 meq); [d]6 hours at 50°C followed by 18 hours at 22°C; [e]$S_2O_8^{2-}$ oxidant with 0.6 mmoles of Ag^+, Cu^{2+}, or Ce^{4+} present; [f]$S_2O_8^{2-}$; oxidant with 0.06 mmoles of Ag^+ present; [g]$S_2O_8^{2-}$ oxidant with 0.06 mmoles of Ag^+ present; [h]8 hours.

Decay of the Non-Pertechnetate Species in 103-SY with Time



XANES Spectra of Hanford Wastes

Dave Blanchard, our collaborator, at PNNL has studied the X-ray Absorption Near Edge Spectroscopy (XANES) analysis of the Tc in samples of waste from Hanford tanks AN-107, AW-101, 101-SY, and 103-SY. Both pertechnetate and non-pertechnetate Tc species are present in all untreated samples. Pertechnetate is almost completely removed by contacting the waste samples with Reillex-HPQ anion exchanger. The highest concentrations of non-pertechnetate species were found in waste with the highest organic complexant concentration, suggesting the presence of a Tc species complexed or bound to complexants or complexant fragments. The XANES of the Tc in these treated samples (which varies from 20% to 80%, depending on the tank) is consistent with a Tc(IV) species bound to complexants or complexant fragments through oxygen linkages. Spectra of one of the wastes (103-SY) before and after aging for approximately 4 months shows an increase in the fraction of pertechnetate present, indicating oxidation of the non-pertechnetate to pertechnetate.



Data from David L. Blanchard (PNNL)

Speculation on the Source of the Technetium Problem

Model System

In aqueous solution:

$$TcO_4^- + Na_2H_2EDTA + \text{reductant} \xrightarrow[\text{70°C, 4 days, pH ~3-4}]{} Tc_2O_2(H_2EDTA)_2$$

- Other examples with oxalate, NTA, TCTA.
- Complexes are quite stable to oxidation.

H. B. Burgi, G. Anderegg, and P. Blauenstein, *Inorg. Chem.*, 1981, 20, 3829.

Waste Tanks

$$TcO_4^- + Na_2H_2EDTA + \text{radiolysis} \xrightarrow[\text{70°C, 30-50 years, pH 14}]{} Tc_2O_2(H_2EDTA)_2$$

Synthesis of Technetium Complexes

Technetium complexes are being prepared by chemical reduction of pertechnetate in the presence of ligands which are known to exist in the aged tank wastes. The ligand set chosen will yield a series of μ-oxo complexes that differ systematically in their potential denticity and combination of four nitrogen and/or oxygen coordinating atoms. This approach will provide a diverse set of complexes that will have important structural differences that may be reflected in their redox and ligand substitution chemistry. The first synthesis will be of the $[(EDTA)Tc(\mu\text{-}O)_2Tc(EDTA)]^{4-}$ complex because a) it is a known preparation under acidic conditions, and b) EDTA has a high concentration in the waste.

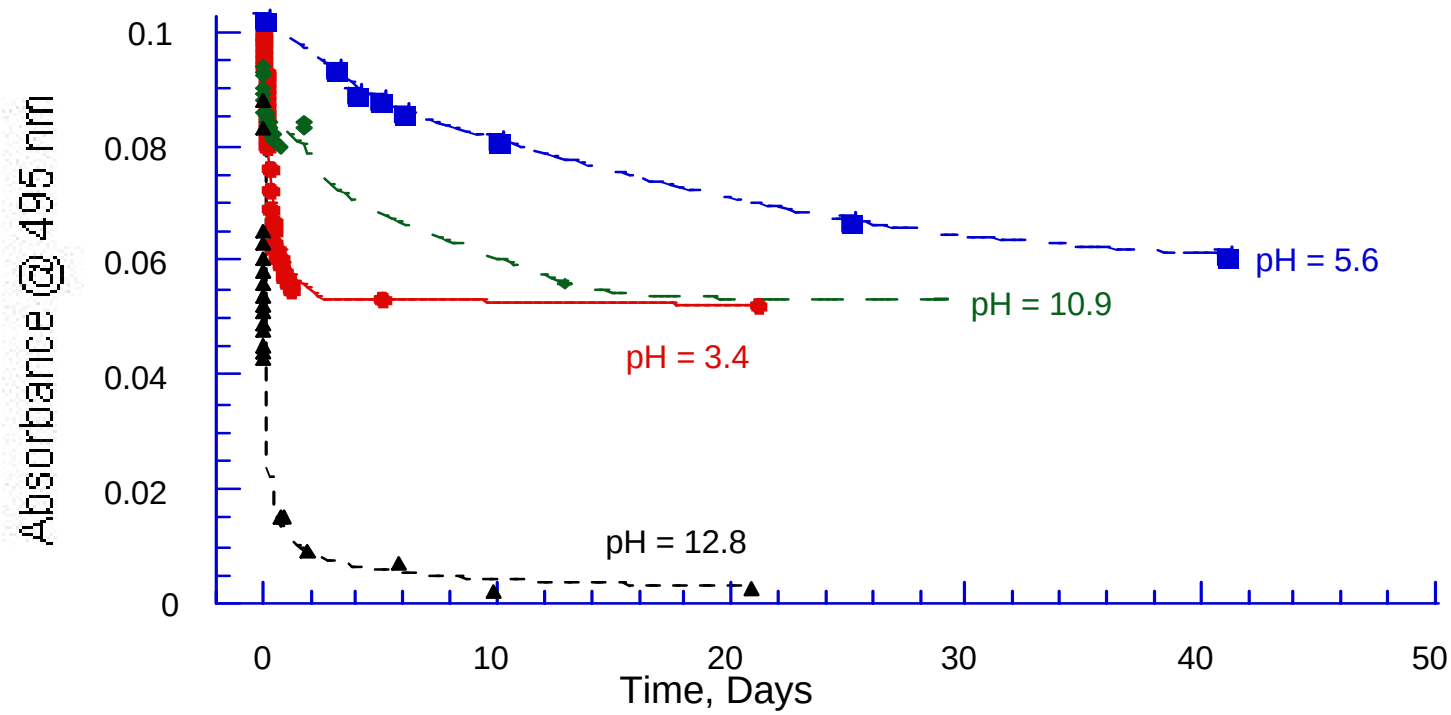
Ligand Set to be Used for Synthesizing Reduced Technetium Complexes

Ligand	Denticity	Coordinating atom set
oxalate *and/or* phthalate	bidentate	O_4
NTA	tetradentate	O_3N
EDTA	tetradentate	O_2N_2
DTPA	tetradentate	ON_3
triethylenetetraamine (tetn)	tetradentate	N_4
ethylenediamine (en)	bidentate	N_4

Stability of the $[Tc_2(\mu\text{-}O)_2(EDTA)_2]^{4-}$

We are using the pink $[Tc_2(\mu\text{-}O)_2(EDTA)_2]^{4-}$ complex. as a surrogate for the non-pertechnetate species in Hanford waste. We are conducting stability studies on 5 x 10^{-5} M solutions of the complex; at concentrations >10^{-3} M it is stable. The UV-Vis spectra of this complex has been followed with time at different pH values (3.4, 5.6, 10.9, and 12.8). All the samples show a decrease in absorbance of the 500 nm peak with time. We speculate that a monomer/dimer equilibrium exits at pH values < 12 and that the monomer is stable. At pH 12.8, the $[Tc_2(\mu\text{-}O)_2(EDTA)_2]^{4-}$ complex decomposes within 2 days to a colorless intermediate that slowly oxidizes to pertechnetate. The conversion to pertechnetate is measured by an increasing technetium K_d value for this solution with time. Over 50 days the K_d value has gone from 40 to ~1000 mL/g. The expected pertechnetate K_d value for this solution matrix is ~3000 mL/g.

Decrease in Absorbance vs. Time



- pertechnetate is the decomposition product at pH 12.8.
- The absorbances at the other pH's converge at an absorbance near 0.06, suggesting the formation of an unknown intermediate which has been shown not to be pertechnetate.

Other Technetium Dimers Recently Prepared

$[(C_2O_4)_2(Tc\text{-}O)_2(C_2O_4)_2]^{4-}$

- red complex (λ_{max} = 512 nm) is formed at room temperature in approximately 4 hours at pH ~ 2.
- solution turned orange (λ_{max} = 487 nm) within 5 days.
- complex does not form at pH = 10.

$[N(CH_3COO)_3(Tc\text{-}O)_2N(CH_3COO)_3]^{2-}$

- pink/red complex (λ_{max} = 506 nm) is formed at room temperature overnight at pH ~ 2.
- color begins to fade over a period of several days.
- complex does not form at pH = 10.

$[tetn(Tc\text{-}O)_2\ tetn]^{4+}$, where tetn = triethylenetetramine

- dark purple complex (λ_{max} = 540 nm) is formed at room temperature within 4 hours at pH ~ 2.
- deep yellow solution (λ_{max} = 445 nm) is formed with gentle heating within 4 hours at pH ~ 10.
- complex formed in acid decomposes to TcO_2 within one week.
- complex formed under basic conditions has been stable for one week.
- these two products may be interconverted by adjustment of the pH with either K_2CO_3 or HCl.

Summary

Pertechnetate in the tank waste has been reduced and complexed to unknown, stable, non-pertechnetate species.

These species are hard to oxidize.

XANES data suggests that Tc(IV) species are present and it is reasonable to presume that these species are complexed with EDTA type ligands.

Technetium EDTA, NTA, ox, and tetn dimer complexes are more stable to oxidation in caustic media than previously prepared Re analogues.

The stability of these complexes in basic media appears is favored by donor-atom sets with higher N/O ratios.

Dilution of $[Tc_2(\mu\text{-}O)_2(EDTA)_2]^{4-}$ solutions appears to produce a monomeric species which decomposes at pH's > 12. The tetn complex may be more stable under waste relevant conditions.

Future Work

- obtain crystals suitable for x-ray crystallography.
- prepare the complete coordination set of Tc complexes.
- continue to study the reactivity of the Tc complexes under waste relevant conditions.
- further characterize the Tc complexes using NMR (^{1}H, ^{99}Tc) and Raman spectroscopy.
- use the prepared complexes as standards for XANES experiments on actual waste and to to help develop capillary electrophoresis mass spectroscopy (CE-MS) as a tool for characterizing the technetium species in the waste
- use the complexes to help develop oxidation and separation methods for the non-pertechnetate species in the waste

Acknowledgment

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