Properties of Selected Non-Pertechnetate Species Relevant to Hanford Tank Waste – 15019

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ABSTRACT
Among radioactive constituents present in the Hanford tank waste technetium-99 (Tc) poses a multitude of problems associated with its radiotoxicity, unique and relatively poorly understood chemistry, and high mobility in the environment. Technetium is one of the most difficult contaminants to be addressed at the U.S. Department of Energy (DOE) Hanford Site because of its complex chemical behavior in tank waste and limited incorporation in the glass waste forms during mid- to high-temperature immobilization processes. The majority of Tc exists in the supernatant and salt cake fractions of both single- and double-shell tanks as pertechnetate TcO_4^- (oxidation state +7) and in the reduced forms (oxidation state < +7) collectively known as non-pertechnetate (non-TcO_4^-) species.   Our research program is aimed at gaining understanding of the behavior of non-pertechnetate species in various oxidation states including such phenomena as redox speciation, hydrolysis, oligomerization, coordination of small organic ligands present in the tank supernatant, and solubility of the complex species. This paper describes our current results on the characterization and properties of the non-pertechnetate species.

INTRODUCTION
Technetium is one of the most difficult contaminants to address at the U.S. Department of Energy (DOE) Hanford Site because of its complex chemical behavior in tank waste, limited incorporation in mid- to high-temperature immobilization processes (vitrification, steam reformation, etc.), and high mobility in subsurface environments.   Approximately 30,000 curies of Tc-99 were produced at the Hanford Site.   Of this, a small amount either has been released to cribs or has leaked from the single-shell tanks, while the balance remains in the Hanford tank wastes and must be disposed of in approved waste forms. Technetium in its most common Tc(VII) [pertechnetate] form is problematic in low-activity waste (LAW) due to its long half-life (213,000 years), complex redox chemistry, high solubility, and volatility at high temperatures.   While most of the long-lived radionuclides in tank waste (e.g., plutonium and uranium) are largely insoluble under storage conditions, such as high pH and low temperature, Tc is predominantly in the aqueous phase and is highly mobile in the subsurface environment.   In addition, Tc volatility at LAW vitrification melter temperatures creates the potential for high Tc concentrations in the secondary waste streams.   Furthermore, although Tc most likely exists in the poorly soluble +4 oxidation state in the tank sludges, with pretreatment operations such as contact with permanganate, there exists the possibility of oxidation of Tc(IV) back to its more soluble Tc(VII) oxidation state.

Most of the Tc at the Hanford Site is soluble Tc in the supernatant fraction of both single- and double-shell tanks.   In strongly alkaline environments, Tc exists as TcO_4^- (Scheme 1a) (oxidation state +7) and in the reduced forms (oxidation state < +7) collectively known as non-TcO_4^- species. A significant (2% to 25%) fraction of the Tc in tank waste may be present as a non-TcO_4^- species that has not been identified and, based on experimentation to date, cannot be effectively separated from the wastes.   It remains uncertain whether alkaline tank conditions even support the formation of proposed low-valent Tc species, i.e., Tc(I) carbonyl compounds (Scheme 1b).   There is no definitive information on the origin of the non-TcO_4^- species, nor is there a comprehensive description of their composition and behavior.   The objective of this work is to investigate aspects of the nature and chemistry of the non-TcO_4^- species derived from the

1

$Tc(CO)_3^+$ coordination center, specifically under the conditions typical for the alkaline liquid fraction of the tank waste and to gain better understanding and control over their redox behavior. This includes exploratory tests on technetium behavior in tank-like environments where conditions for TcO_4^- reduction seem favorable and elucidation of the mechanistic pathways for the formation of non-TcO_4^- species. This paper describes our to-date results.
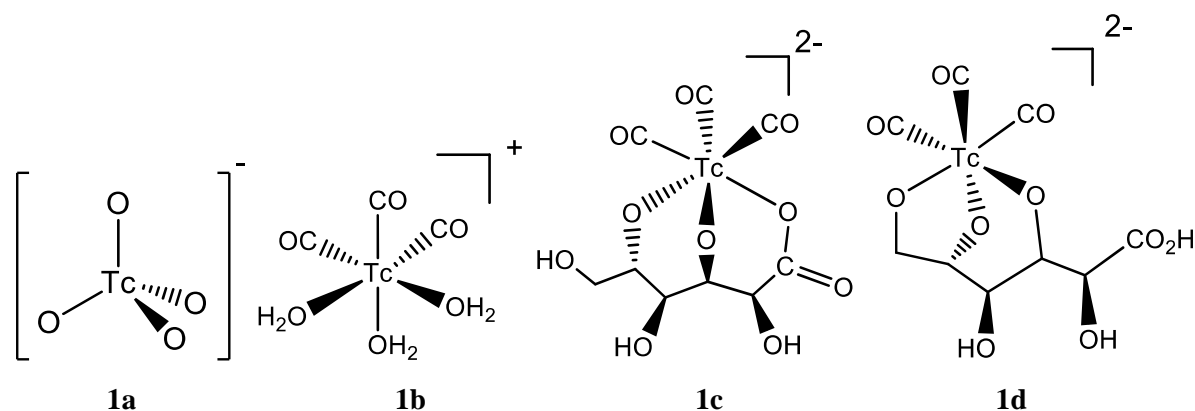
Scheme 1. Structures of **1a**: pertechnetate anion; **1b**: tri-carbonyl-tris-aqua-technetium(I) cation; **1c**: tri-carbonyl-gluconate-technetium(I) anion, structure proposed by Lukens et al. (2004); **1d**: tri-carbonyl-gluconate-technetium(I) anion, alternative structure.

RESULTS

Synthesis of *fac*-$Tc(CO)_3^+$

To prepare Tc(I) compounds containing a *fac*-$[Tc(CO)_3]^+$ (in the following text, the abbreviated notation $[Tc(CO)_3]^+$ is used) center, TcO_4^- was initially reduced to Tc(V) in the form of the stable compound $[Bu_4N][TcOCl_4]$ followed by second step borane reduction using the modified procedure that was originally reported elsewhere (Alberto et al. 1995). Obtained targeted $[Et_4N]_2[Tc(CO)_3Cl_3]$ product is readily dissolved in water, and the Cl$^-$ ligands are exchanged with H_2O, OH$^-$, and/or organic ligands present in the aqueous solution so that $[Et_4N]_2[Tc(CO)_3Cl_3]$ serves as a convenient source of Tc(I)-tricarbonyl species.

^{99}Tc NMR analysis of *fac*-$Tc(CO)_3^+$

Aqueous $[Tc(CO)_3]^+$ species were obtained by dissolving the $[Tc(CO)_3Cl_3]^{2-}$ precursor in either water or 5 M $NaNO_3$ at a pH of 3, 7, or 14 and then were characterized by ^{99}Tc NMR. The pH adjustment was achieved by adding either HNO_3 or NaOH to the test solution. In aqueous solution the chloride ligands coordinated to the Tc(I)-tricarbonyl center are readily exchanged by H_2O, and could likely be exchanged by OH$^-$ as well; the specific products formed depend on the solution composition. The observed ^{99}Tc resonances and corresponding assigned $[Tc(CO)_3]^+$ species are listed in Table 1. The ^{99}Tc resonances assignments were done based on comparison to previously reported chemical shifts and band half-widths (Gorshkov et al. 2000; Alberto et al. 1998). The same aqueous Tc(I) complexes were formed in water and 5 M $NaNO_3$ solutions at the tested pH as evident from the nearly identical positions of the ^{99}Tc NMR resonances. In the acidic and near-neutral solutions, the reaction product was $[Tc(CO)_3(H_2O)_3]^+$, identified by its characteristic resonance at about -866 ppm. In the alkaline solutions examined, the only

product observed was the hydrolyzed $[Tc(CO)_3(OH)(H_2O)_2]$ species, identified by its characteristic resonance at -1062 ppm.

Table 1. Techetium-99–NMR Characterization of the Aqueous Reaction Products

Solution	Solution Acidity	Chemical Shift of [99]Tc Resonance, ppm	Half-width of [99]Tc Resonance, Hz	Assignment of [99]Tc Resonance
Water	pH = 3	-867	100	$[Tc(CO)_3(H_2O)_3]^+$ [a,b]
	pH = 6 - 7	-870	100	$[Tc(CO)_3(H_2O)_3]^+$ [a,b]
	pH = 14	-1062	90	$[Tc(CO)_3(OH)(H_2O)_2]$ [a,b]
5M NaNO$_3$	pH = 3	-869 -902 (very weak)	120	$[Tc(CO)_3(H_2O)_3]^+$ [a,b] $[Tc(CO)_4(H_2O)_2]^+$ [a]
	pH = 6 - 7	-867 -902 (very weak)	100	$[Tc(CO)_3(OH)(H_2O)_2]$ [a,b] $[Tc(CO)_4(H_2O)_2]^+$ [a]
	pH = 14	-1062	100	$[Tc(CO)_3(OH)(H_2O)_2]$ [a,b]

　　a.　Assignment is based on the report by Gorshkov et al. (2000).
　　b.　Assignment is based on the report by Alberto et al. (1998).

The $[Tc(CO)_3]^+$ gluconate complex was obtained by the dissolution of the $[Tc(CO)_3Cl_3]^{2-}$ precursor into 5 M NaNO$_3$ and then adding the resulting solution to a 5 M NaNO$_3$/1 M NaOH/0.5 M sodium gluconate mixture in a 1:1 ratio.   The ^{99}Tc NMR spectrum of the resulting solution showed two bands at -1233 and -1253 ppm with the half-widths of about 300 Hz.   The positions and profiles of these resonances were observed to be very similar for the $[Tc(CO)_3]^+$ gluconate samples previously observed in water (Rapko et al. 2013).

COSMO prediction of the ^{99}Tc NMR spectra for *fac*-Tc(CO)$_3$[+]
Chemical shifts of technetium-99 for the investigated *fac*-Tc(CO)$_3^+$ compounds in water were calculated using the screening continuum solvation model COSMO.   All calculations, geometry optimization, and magnetic response properties were performed at the B3LYP-DFT level of theory with the Def-TZVPP basis set.   Spin-orbit coupling and relativistic effects were included with the zeroth order regular approximation (ZORA).   Solvent effects of an aqueous solution were included with the implicit solvation model Conductor-like Screening Model (COSMO).   The dielectric constant of water, 80.4 at 20 °C, was used for the COSMO model.   The gauge-including atomic orbital (GIAO) approach was used to calculate the NMR-related magnetic response properties.   All chemical shifts are referenced to TcO$_4^-$: d = sref − s where d is the chemical shift of the compound of interest, sref is the reference compound's calculated magnetic shielding, and s is the calculated magnetic shielding of the compound of interest.   The predicted and experimental ^{99}Tc NMR chemical shifts are in excellent agreement for all species except the gluconate complex as is evident from Table 2.

Table 2. Comparison of the Calculated and Experimental ^{99}Tc NMR Chemical Shifts for the $[Tc(CO)_3]^+$ Species in Water

Species	Calculated Chemical Shift (ppm)	Experimental Chemical Shift (ppm)
$[Tc(CO)_3(H_2O)_3]^+$	-834	-868
$[Tc(CO)_3(OH)(H_2O)_2]$	-1053	-1062
$[Tc(CO)_3(OH)_2(H_2O)]^-$	-1129	-1139
$[Tc(CO)_3(OH)_3]^{2-}$	-1308	Not measured
$[Tc(CO)_3(OH)]_4$	-621	-585

$[Tc(CO)_4(H_2O)_2]^+$	-983	-902
$[Tc(CO)_3(gluconate)]^{2-}$	-958	-1232/-1254

In the COSMO calculations, the structure of the Tc(I)-tricarbonyl gluconate complex was assumed to be $[Tc(CO)_3(gluconate)]^{2-}$ where gluconate is bound to Tc(I) via two hydroxyl and one carboxyl oxygen atoms (Scheme 1c) based on the structure proposed by Lukens et al. (2004). Poor agreement between the calculated and experimental chemical shift suggests the presence of a molecule with a different structure, e.g., where gluconate is bound through three hydroxyl oxygen atoms (Scheme 1d). Note that NMR shows two equal intensity signals, which could indicate a gluconate bridging two $[Tc(CO)_3]^+$ groups. Another possible explanation is formation of the mixed hydroxo-gluconate $[Tc(CO)_3(OH)_n(gluconate)]^{n-2}$ complexes. In this mixed hydroxo-gluconate, the hydroxide ion is expected to increase the electron density and shielding of the ^{99}Tc nucleus, causing moving chemical shift of the $[Tc(CO)_3(OH)_n(gluconate)]^{n-2}$ species up-field in comparison with the $[Tc(CO)_3(gluconate)]^{2-}$ complex. This trend is evident for the successive substitution of H_2O of the species $[Tc(CO)_3(H_2O)_3]^+$ by hydroxide upon hydrolysis and formation of $[Tc(CO)_3(OH)(H_2O)_2]$ and $[Tc(CO)_3(OH)_2(H_2O)]^-$, causing the respective chemical shifts to move up-field from -868 ppm to -1062 and -1139 ppm.

Stability of the $[Tc(CO)_3]^+$ Species at High Nitrate Concentrations
The test samples were prepared by the direct dissolution of $[Et_4N]_2[Tc(CO)_3Cl_3]$ solid in aqueous solutions under atmospheric conditions. The stability of aqueous Tc(I) coordination compounds over time with respect to their oxidation to pertechnetate, TcO_4^-, was monitored by ^{99}Tc NMR spectroscopy. Speciation stability for the $[Tc(CO)_3]^+$ compounds was examined in matrices from 2 – 5.7 M $NaNO_3$ and in 5 M $NaNO_3$/0.01 – 2 M NaOH. The results obtained to date are summarized below. Note that the analyses presented assume that Tc mass balance is based on the ^{99}Tc NMR-active species, a method that may be silent with respect to some plausible Tc species such as Tc(IV). The absence of the Tc(IV) species was supported by the observation that no precipitate (e.g., TcO_2) was found in any of the stability samples. However, the formation of soluble Tc(IV) cannot be ruled out and should be investigated in future testing.

Solutions of 2, 5, and 5.7 M $NaNO_3$ concentrations at near neutral pH contained the $[Tc(CO)_3(H_2O)_3]^+$, $[Tc(CO)_3(OH)(H_2O)_2]$ and $[Tc(CO)_3(OH)]_4$ species . Upon dissolution of the $[Tc(CO)_3Cl_3]^{2-}$ in 2 M $NaNO_3$ to form 0.028mM solution generated the $[Tc(CO)_3(H_2O)_3]^+$ species appearing at -869 ppm in the ^{99}Tc NMR spectra. The hydrolyzed tetramer, $[Tc(CO)_3(OH)]_4$, corresponding to the -585 ppm resonance, started to form on day 3 post-solution preparation, and its concentration gradually increased with time. The initial dissolution of the $[Tc(CO)_3Cl_3]^{2-}$ in the 5 and 5.7 M $NaNO_3$ solutions generated nearly equal fractions of the $[Tc(CO)_3(H_2O)_3]^+$ and $[Tc(CO)_3(OH)]_4$ species. It is known that at near-neutral pH, the $[Tc(CO)_3(H_2O)_3]^+$ complex undergoes partial hydrolysis to generate $[Tc(CO)_3(OH)(H_2O)_2]$ species, which in turn readily aggregates and forms a tetrameric hydrolysis product $[Tc(CO)_3(OH)]_4$ (Alberto et al. 1998; Gorshkov et al. 2000). The equilibrium between the parent $[Tc(CO)_3(H_2O)_3]^+$ species and its first hydrolysis product $[Tc(CO)_3(OH)(H_2O)_2]$ is sensitive to even small variations in the solution pH, while the formation of the $[Tc(CO)_3(OH)]_4$ tetramer primarily depends on the Tc(I) concentration. It is likely that most of the changes in the extent of tetramer formation can be attributed to varying amounts of the first hydrolysis product coupled with perhaps slight changes in pH as opposed to ionic strength changes. Monitoring of these solutions by ^{99}Tc NMR for 4 month showed no formation of TcO_4^- indicating high resistance to reoxidation of these $[Tc(CO)_3]^+$ species in the concentrated $NaNO_3$ solutions at near-neutral pH, a stability that is present regardless of the presence of either $[Tc(CO)_3(H_2O)_3]^+$ or its first hydrolysis products.

To monitor stability of the $[Tc(CO)_3]^+$ species in solutions containing high nitrate and variable hydroxide concentrations, a stock solution containing the Tc(I)-tricarbonyl complex in 5 M $NaNO_3$ matrix was

4

prepared. This stock solution was added to the 5 M NaNO$_3$ solutions containing 0.01, 0.1, 0.5, 1, or 2. M NaOH. In all alkaline solutions, formation of the single [Tc(CO)$_3$(OH)(H$_2$O)$_2$] hydrolyzed monomeric species appearing at -1062 ppm in the NMR spectra was observed. No [Tc(CO)$_3$(OH)]$_4$ tetramer was found in these solutions. This finding is consistent with the previous reports (Alberto et al. 1999 and references therein) that tetrameric species exist only in a limited pH range in the vicinity of the first pK$_a$ value of the parent [Tc(CO)$_3$(H$_2$O)$_3$]$^+$ species, which was estimated to be 7.75 in the low-ionic-strength solutions in our previous studies (Rapko et al. 2013). The ^{99}Tc NMR results indicated gradual oxidative decomposition of the [Tc(CO)$_3$(OH)(H$_2$O)$_2$] species and in-growth of TcO$_4^-$ in all samples. The relative concentrations of the [Tc(CO)$_3$(OH)(H$_2$O)$_2$] species and TcO$_4^-$ were determined by integrations of the respective resonances in each spectrum. It was observed that the oxidation of the Tc(I) inversely correlates with the OH. concentration. The 5 M NaNO$_3$/0.01 M NaOH exhibited the greatest stability of the [Tc(CO)$_3$(OH)(H$_2$O)$_2$] species among other alkaline solutions so that about only 11% of Tc(I) was oxidized to Tc(VII) in 74 days. By way of comparison, in 5 M NaNO$_3$/0.1 M NaOH solution, 50% and 100% Tc(I) was oxidized to Tc(VII) in 39 and 74 days, respectively. In 5 M NaNO$_3$ solution containing 0.5, 1, or 2 M NaOH Tc(I) conversion to Tc(VII) was completed in 17, 2, or 1 days, respectively. To compare rates of the [Tc(CO)$_3$(OH)(H$_2$O)$_2$] conversion to TcO$_4^-$, the kinetic plots were constructed for the 5 M NaNO$_3$ solutions containing 0.01, 0.1, 0.5, or 1 M NaOH (Figure 1). Even though the oxidation mechanism has not been elucidated yet, it was found that the initial increase of the TcO$_4^-$ concentration over time can be reasonably fitted by a linear equation. The obtained slope values quantifying the rate of the Tc(I) oxidation with time (fraction per hour) exhibited nearly linear dependence on the OH$^-$ concentration in the solution (Figure 2, left pane) consistent with an oxidation rate that is first-order in hydroxide.
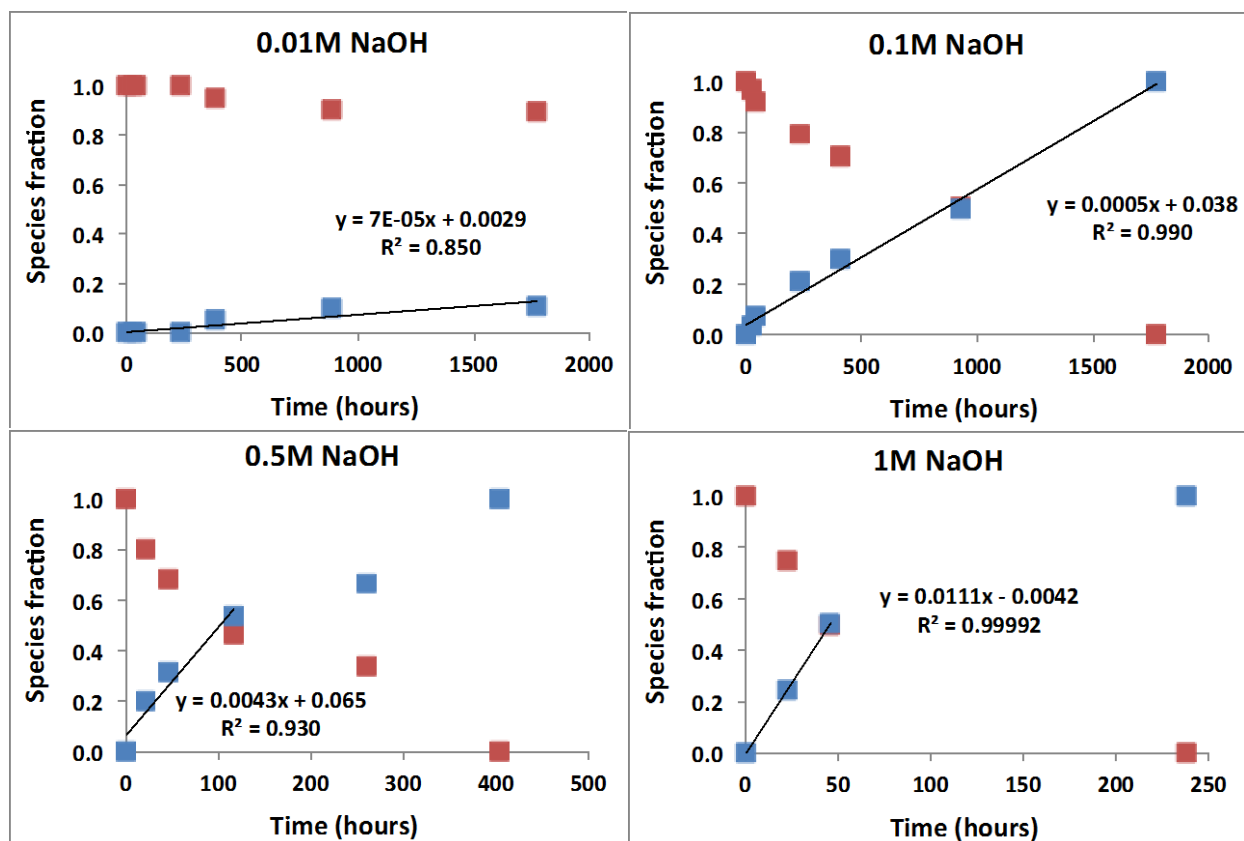
Figure 1. Technetium-99 Time Speciation in 5 M NaNO$_3$/Variable Hydroxide Solutions Containing 0.01 M (top left), 0.1 M (top right), 0.5 M (bottom left) or 1 M (bottom right) NaOH.   Red symbols: [Tc(CO)$_3$(OH)(H$_2$O)$_2$].   Blue symbols: TcO$_4^-$.
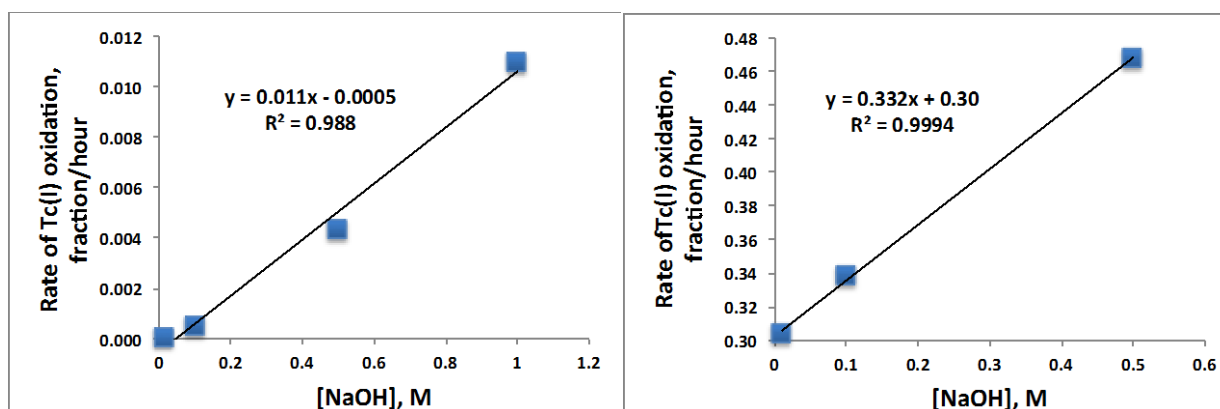

Figure 2. Dependence of the Kinetics of Tc(I) Oxidation to TcO$_4^-$ on the OH$^-$ Concentration in 5 M NaNO$_3$ (left pane) or 5 M NaNO$_3$/0.5 M Sodium Gluconate Solution (right pane).

To evaluate the effect of gluconate on the oxidative stability of Tc(I) species in alkane solutions containing high nitrate concentration, three 5 M NaNO$_3$/0.5 M sodium gluconate solutions with the 0.01, 0.1, or 0.5 M NaOH were prepared.   To each solution, a Tc(I)-tricarbonyl stock solution in 5 M NaNO$_3$ was added. The representative ^{99}Tc NMR spectra are shown in Figure 3.
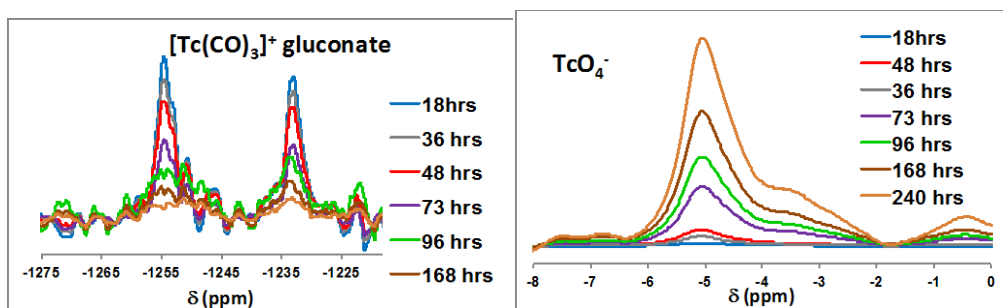

Figure 3. Selected Spectral Regions of Representative Spectra from Monitoring the Stability of [Tc(CO)$_3$]$^+$ Species in 5 M NaNO$_3$/0.1 M NaOH/0.5 M Sodium Gluconate with Time.

Consistent with our previous observations (Rapko et al. 2013), the ^{99}Tc-NMR spectrum of the [Tc(CO)$_3$]$^+$ complex with gluconate is characterized by the presence of two resonances at -1232 and -1253 ppm revealing the presence of two distinct Tc(I) centers (Figure 3, left pane). In about 24 – 36 hours post-solution preparation, about 3 – 5% of Tc(I) had oxidized to TcO$_4^-$ in all tested solutions as was evident from the appearance of the corresponding TcO$_4^-$ resonance (Figure 3, right pane), and the percent-fraction of the [Tc(CO)$_3$]$^+$/gluconate complex continued to decrease with time. Fast oxidation of the [Tc(CO)$_3$]$^+$/gluconate complex species to TcO$_4^-$ was observed so that the conversion was completed in 14, 12, and 9 days for 0.01, 0.1, and 0.5 M NaOH solutions, respectively. It was discovered that the decrease of

Tc(I) concentration and the corresponding increase of Tc(VII) concentration were nearly linear with time as evident from the high values of the observed linear regression R^2 values (Figure 4).   The obtained slope correlates the rate of Tc(I) oxidation with the solution composition; the slope values then were plotted against OH^- concentration, and a linear dependence was observed (Figure 2, midlle pane). Consistent with the results obtained for the $[Tc(CO)_3(OH)(H_2O)_2]$ conversion to TcO_4^- in 5 M $NaNO_3$/0.01 – 2 M NaOH solutions, this finding suggests that the oxidation of the $[Tc(CO)_3]^+$ gluconate complex to Tc(VII) and formation of TcO_4^- is facilitated by the hydroxide ion.

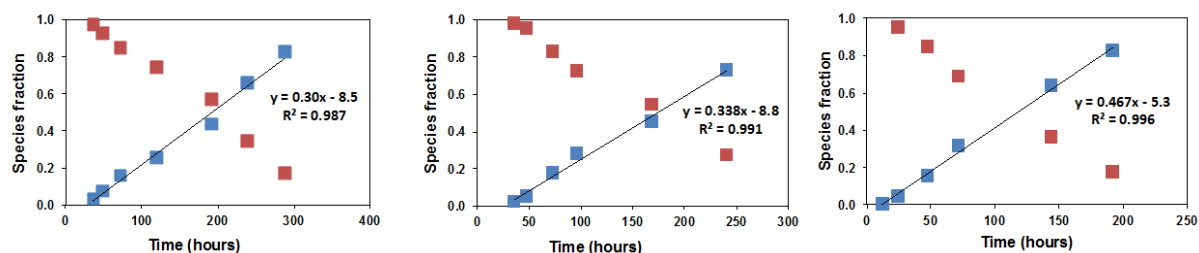**Figure 4**. Technetium-99 Time Speciation in 5 M $NaNO_3$/0.5 M Sodium Gluconate Solutions Containing 0.01 M (left), 0.1 M (middle), or 0.5 M (right) NaOH.   Red symbols: $[Tc(CO)_3]^+$/gluconate complex. Blue symbols: TcO_4^-.

Comparison of the Tc(I) oxidative stability in the 5 M $NaNO_3$/0.01 M NaOH and 5 M $NaNO_3$/0.01 M NaOH/0.5 M NaGluconate clearly indicates that the $[Tc(CO)_3(OH)(H_2O)_2]$ species exhibit significantly greater stability than the $[Tc(CO)_3]^+$ gluconate complex in these high ionic strength solutions.   Only about 11% Tc(I) was oxidized to Tc(VII) in 5 M $NaNO_3$/0.01 M NaOH solution over a 2.5 month time period while the presence of gluconate in this solution results in the complete oxidation of Tc(I) in about 2 weeks.

Reduction of TcO_4^- in a Pseudo-Hanford Tank Supernatant Simulant
The purpose of this test was to evaluate the reductive stability of pertechnetate and the potential of generation of non-pertechnetate species, such as Tc(I)-tricarbonyl, in a pseudo-Hanford tank supernatant simulant considered to be well suited to observe these phenomena. For this test, the average supernatant simulant composition previously developed for the Pretreatment Engineering Platform (PEP) testing (Scheele et al. 2009) was used, albeit with a reduced NaOH concentration.   The composition of the simulant is given in Table 3. To facilitate TcO_4^- reduction, noble metals, including 0.13 mM Pt, 0.57 mM Pd, 0.014 mM Rh, and 1.04 mM Ru, were added to the simulant.   The simulant was also adjusted to contain 0.05 M sodium gluconate.   To the resulting solution, a concentrated stock of NH_4TcO_4 solution was added to achieve a 5 mM Tc concentration

Table 3. A Pseudo-Hanford Tank Simulant Composition

Constituent	Target Concentration	
	µg/mL	M
Al [a]	5,900	0.217
Na [a]	108,700	4.73
C_2O_4 [b, c]	<450	<0.005
NO_2 [b]	25,300	0.55 ± 0.03

NO_3 [b]	104,800	1.69 ± 0.03
PO_4 [a, d]	15,100	0.158
SO_4 [a, d]	19,200	0.200
CO_3 [b]	7,360	0.613 ± 0.006
OH [b]	18,800	0.47

a. Determined by ICP-OES
b. Determined by Raman spectroscopy
c. Based on Raman detection limit for oxalate
d. Based on total P and S and assuming all P and S is present as phosphate and sulfate, respectively.

The solution was placed in an unstirred pressure vessel, flushed with CO, and pressurized with CO gas that contained approximately 75 ppm H_2. The simulant was kept at 80 °C and 1300 psi for 12 days.   Upon conclusion of the test, the solution was returned to room temperature and pressure, unsealed, and sampled soon after exposure to the atmosphere. ^{99}Tc NMR spectroscopy revealed that > 99% TcO_4^- was reduced, this estimate being based on the proportional reduction of the pertechnetate resonance after being normalized to the number of scans. The NMR spectrum of the CO/H_2-reacted simulant containing 0.05 M gluconate exhibited two Tc(I) resonances at -1232 and -1254 ppm corresponding to the Tc(I)-tricarbonyl gluconate species, with an additional resonance at -1094 ppm (Figure 5). The resonance at -1094 ppm was speculatively attributed to also be a species derived from $[Tc(CO)_3]^+$ as it appeared in the frequency range typical for the Tc(I)-tricarbonyl compounds.   However, the exact composition of these species has not been elucidated.   The $[Tc(CO)_3]^+$/gluconate complex resonances at -1232 and -1254 ppm observed in the reacted simulant are nearly identical to those generated by the dissolution of the Tc(I) $[Tc(CO)_3Cl_3]^{2-}$ compound in either the 5 M $NaNO_3$/0.5 M NaOH/0.5 M sodium gluconate (green trace) solution or in the simulant (red trace, Figure 5). The major TcO_4^- reduction product in the CO/H_2-reacted simulants was tentatively assigned to the ^{99}Tc NMR-inactive Tc(IV) species as no additional resonances were found in the NMR spectrum.   This assumption was also supported by the visual inspection of the reacted simulant solution, which contained a significant amount of black precipitate similar to that observed with insoluble TcO_2.   The ^{99}Tc NMR spectrum, collected over a positive chemical shift window characteristic of Tc(V) compounds, did not reveal the presence of any Tc(V) species.
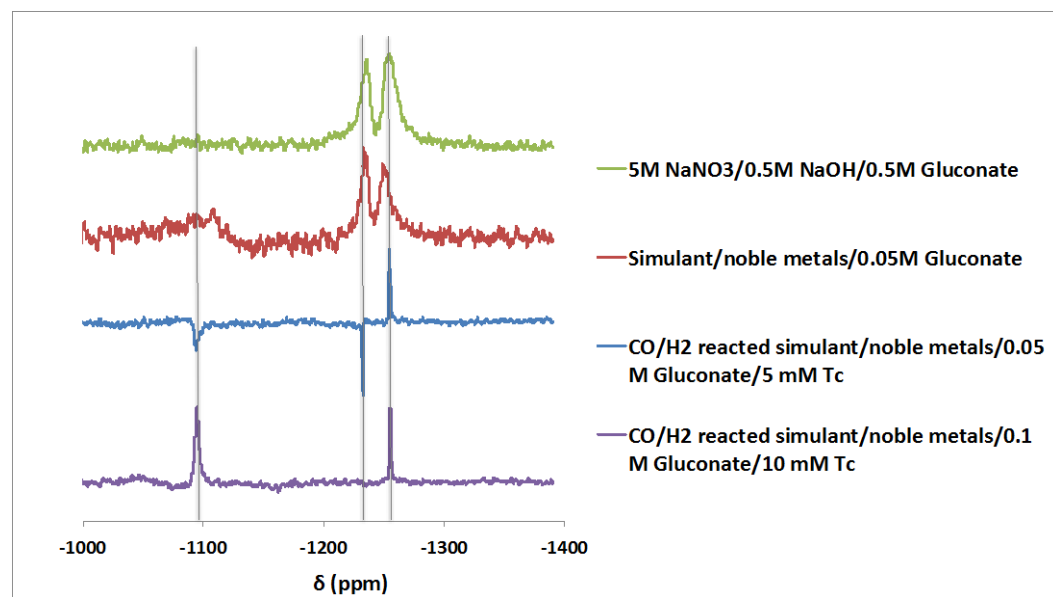
Figure 5. Comparison of the ^{99}Tc NMR Spectra of the [Tc(CO)$_3$]$^+$ Gluconate Complex Generated by the Reduction of TcO$_4^-$ in the CO/H$_2$-reacted Pseudo-Hanford Tank Supernatant Simulant Solutions Containing Noble Metals and 0.05M Gluconate/5 mM Tc (blue trace) or 0.1M Gluconate/10 mM Tc (purple trace) with the Spectra of Tc(I) Solutions Obtained by the Dissolution of the [Et$_4$N]$_2$[Tc(CO)$_3$Cl$_3$] Compound in the 5 M NaNO$_3$/0.5 M NaOH/0.5 M Sodium Gluconate (green trace) and in the Pseudo-Hanford Tank Supernatant Simulant Containing Noble Metals and 0.05M Gluconate (red trace). The phase correction of the CO/H$_2$-reacted simulant spectra was not possible and is believed to be due to the presence of paramagnetic constituents, presumably Tc(IV).

The reaction to reduce TcO$_4^-$ in the supernatant simulant was repeated under slightly modified conditions. In this test, the concentration of gluconate in the simulant was 0.1 M, double the first test. The concentration of TcO$_4^-$ was doubled as well to improve the ^{99}Tc NMR signal-to-noise ratio for the Tc(I) reaction product. The simulant was kept at 80 °C and 1300 psi of CO/H$_2$ mixed gas atmosphere for 12 days. The visual examination of the reaction mixture indicated the presence of a significantly smaller amount of the black solids that have tentatively been attributed to the TcO$_2$ reduction product. Interestingly, in this test 100% TcO$_4^-$ was reduced, as was apparent from the absence of the TcO$_4^-$ resonance in the reacted simulant. The concentration of the Tc(I) products was significantly increased as compared with the first reaction. Only two resonances at -1096 and -1254 were observed in the spectrum (Figure 5) with the [Tc(CO)$_3$]$^+$ compound corresponding to the -1094 ppm resonance being the dominant product.

The solid and liquid fractions of the reacted simulant were analyzed by ^{99}Tc electron paramagnetic resonance spectroscopy (EPR) for the paramagnetic Tc species. Technetium in oxidation states of II, IV, and VI has outer electron configuration of 4d^5, 4d^3, and 4d^1, respectively, and is therefore paramagnetic. The EPR method can provide useful information about oxidation state, symmetry, and bonding properties of the Tc compounds in the even oxidation states. The EPR spectra obtained at 3K are shown in Figure 6. The solid fraction exhibited a half field signal ~800 to 2000 G is unique and speculatively assigned to Tc(IV) or Tc binuclear compound; it is only visible below 10 K. Both solid and liquid fractions exhibited a signal at 2000 – 5000 G originated from an oxidation state with spin of ½ and was preliminary attributed to the Tc(VI) gluconate complex, this spectrumis detectable at much higher temperatures (~180K).
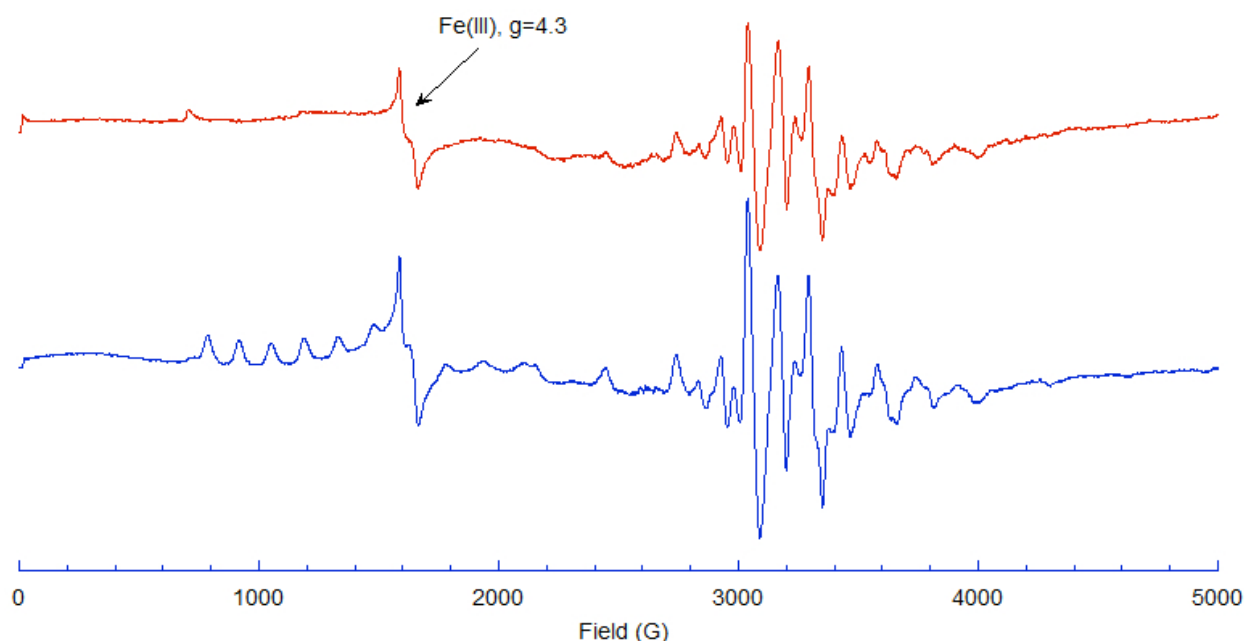
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Figure 6. ^{99}Tc EPR spectra collected at 3K corresponding to the solid (blue trace) and liquid (red trace) fractions of the CO_2/H_2-reacted simulant.

DISCUSSION

The pH speciation of the $[Tc(CO)_3]^+$ aqua complexes was found to be similar in water and in 5 M $NaNO_3$. The triaqua $[Tc(CO)_3(H_2O)_3]^+$ ion exists only in acidic aqueous solutions and undergoes extensive hydrolysis starting at near-neutral pH.   Consistent with literature reports (Gorshkov et al. 2000; Alberto et al. 1998), the mono-hydrolyzed $[Tc(CO)_3(OH)(H_2O)_2]$ species was observed to undergo oligomerization readily and form the neutral, tetrameric $[Tc(CO)_3(OH)]_4$ species.   This oligomerization takes place over the relatively narrow pH range from about 6.5 to about 8.   In more alkaline solutions, the monomeric $[Tc(CO)_3(OH)(H_2O)_2]$ species persists in solution.   Theoretical COSMO calculations resulted in excellent agreement of the predicted and experimental ^{99}Tc NMR chemical shifts of these Tc(I) $[Tc(CO)_3]^+$ aqua complexes.

This work demonstrated that the $[Tc(CO)_3]^+$/gluconate complex is formed in alkaline solutions containing no to high concentrations of nitrate.   The theoretical calculations revealed that this complex is unlikely to have chemical composition of $[Tc(CO)_3(gluconate)]^{2-}$; formation of a mixed hydroxo/gluconate $[Tc(CO)_3(OH)_n(gluconate)]^{n-2}$ species is feasible but is by no means the only alternative.   This conclusion is supported by the appearance of two resonances in the NMR spectrum suggesting the existence of two non-equivalent Tc(I) centers.   The positions of these resonances are shifted up-field from the calculated position of the single resonance predicted by the theory due to the shielding effect of OH^- ligand. Additional studies are warranted to elucidate the structure of the $[Tc(CO)_3]^+$/gluconate complex.

Extensive testing has been conducted in monitoring the oxidative stability of aqueous $[Tc(CO)_3]^+$ species in different matrices.   Our initial studies indicate that both $[Tc(CO)_3(H_2O)_3]^+$ and its oligomerized first

10

hydrolysis product $[Tc(CO)_3(OH)]_4$ are stable to oxidation in strong $NaNO_3$ solutions at near-neutral pH for months.   This stands in marked contrast to the results of our previous testing, which indicated poor oxidative stability of the $[Tc(CO)_3]^+$ species in aqueous solutions of low ionic strength regardless of the solution's pH (Rapko et al. 2013).   One possible explanation for the increased stability of the aqueous $[Tc(CO)_3]^+$ species in the concentrated $NaNO_3$ solutions could be the lower levels of the dissolved oxygen in these solutions as compared with water.   The solubility of oxygen significantly decreases as an electrolyte concentration in solution increases so that the concentration of the dissolved oxygen in the 5 M $NaNO_3$ solution is about half of that in water (Tromans 2000). The 5 M $NaNO_3$/0.01M NaOH solution also exhibited high stability for the aqueous $[Tc(CO)_3]^+$ species so that only about 11% $[Tc(CO)_3(OH)(H_2O)_2]$ was oxidized to TcO_4^- in 74 days.   Moreover, the rate of oxidation of this species reduced with time, and its concentration remained nearly constant after 34 days from the time of solution preparation.   This finding suggests similar stability for any simple $[Tc(CO)_3]^+$ species in the low-alkalinity, high-ionic-strength, Hanford liquid waste. Higher NaOH concentrations significantly reduce the oxidative stability of the $[Tc(CO)_3]^+$ species, even in highly concentrated sodium nitrate solutions. The oxidative stability of the $[Tc(CO)_3]^+$ gluconate complex species in alkaline solutions containing 5 M $NaNO_3$ was diminished as compared to the Tc-tricarbonyl species present in analogous solutions that lacked gluconate.   The same trend was observed with the supernatant simulant with and without gluconate.

Initial investigations were undertaken to determine whether TcO_4^- reduction and formation of the $[Tc(CO)_3]^+$ species in the alkaline supernatant simulant under a CO gas containing 75 ppm H_2 is plausible. Previous studies have documented radiolytic (Lukens et al. 2001) and hydrogen-induced (Bernard et al. 2001) reduction of TcO_4^- in the alkaline simulated waste solutions containing organic complexants.   In these instances, technetium(IV) was proposed as the TcO_4^- reduction product.   The latter study was conducted in the presence of organic complexants and the noble metals Ru, Rh, and Pd, which are byproducts of uranium fission and often catalysts for reduction reactions involving hydrogen.   Under selected conditions of noble metals and complexants, quantitative reduction of Tc(VII) was observed (Bernard et al. 2001).   Since radiolytic decomposition of the organic complexants in the tank's waste involves generation of CO in addition to H_2, we sought to investigate the feasibility of formation of Tc-tricarbonyl species from pertechnetate.   Our TcO_4^- reduction was conducted under high CO/H_2 pressure and at an elevated temperature to accelerate the reductive processes potentially occurring in the tank waste over prolonged time.   In this report, two tests using the pseudo-Hanford supernatant simulant containing noble metals and 0.05 or 0.1 M gluconate are described.   In both experiments, nearly quantitative Tc(VII) reduction and formation of Tc(IV) and $[Tc(CO)_3]^+$ products was observed.   The simulant containing the greater, 0.1 M, gluconate concentration qualitatively generated a greater amount of the $[Tc(CO)_3]^+$ products.   Two Tc-tricarbonyl compounds were identified, including both the $[Tc(CO)_3]^+$ gluconate complex and an additional $[Tc(CO)_3]^+$ species.   The composition of the latter is currently being investigated.   Nonetheless, the identification of soluble Tc(I)-tricarbonyl species in a tank waste supernatant simulant provides significant support to the hypothesis that a Tc-tricarbonyl species of some sort is the source of "soluble, non-pertechnetate Tc".   Further multiparametric reduction studies are warranted to identify the TcO_4^- reduction mechanism and the exact composition of Tc(I) species.   Such elucidation of the Tc(VII) reduction mechanism will necessitate the further development of an EPR characterization method, as this will allow characterization of the Tc intermediates in the even oxidation states invisible to our characterization method of choice, ^{99}Tc NMR spectroscopy.

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