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Literature Review of the Potential Impact of Glycolic Acid on the Technetium Chemistry of SRS Tank Waste

Charles A. Nash

Daniel J. McCabe

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REVIEWS AND APPROVALS

AUTHORS:

Charles A. Nash, Advanced Characterization and Processing Date

Daniel J. McCabe, Waste Form Processing Technologies Date

TECHNICAL REVIEW:

Kathryn Taylor-Pashow, Advanced Characterization and Processing, Reviewed per E7 2.60 Date

Daniel I. Kaplan, Environmental Sciences & Biotechnology Date

APPROVAL:

Frank M. Pennebaker, Manager Date
Chemical Process Technology

Eric J. Freed, Manager Date
Manager, Defense Waste Processing Facility and Saltstone Facility Engineering

EXECUTIVE SUMMARY

This document presents a literature study of the impact of glycolate on technetium chemistry in the Savannah River Site (SRS) waste system and specifically Saltstone. A predominant portion of the Tc at SRS will be sent to the Saltstone Facility where it will be immobilized. The Tc in the tank waste is in the highly soluble chemical form of pertechnetate ion (TcO_4^-) which is reduced by blast furnace slag (BFS) in Saltstone, rendering it highly insoluble and resistant to leaching.

Currently, the Defense Waste Processing Facility (DWPF) uses formic acid as a reducing agent. DWPF is investigating the use of glycolic acid in lieu of formic acid for various reasons, including the fact that the byproduct generation of hydrogen gas during decomposition of formic acid is minimized. Although most of the glycolic acid would be destroyed in DWPF, some of it could be returned to the Tank Farm where it would be mixed with other tank waste. Glycolic acid is a chemical reductant and can be a complexant for metal ions. It is thus important to investigate if it reacts in the tank waste to form soluble species that are not pertechnetate and that may not undergo the reduction reaction with BFS.

The literature shows several experiments and analyses with SRS tank waste that likely would have indicated if soluble non-pertechnetate forms of Tc were already present in SRS waste. The experiments with SRS tank waste used ion exchange resin that selectively absorbs only pertechnetate. The methods with anion exchange had already been used at Hanford to detect non-pertechnetate. Such analyses with SRS waste were consistent with the presence of only pertechnetate. Secondly, the tank sample analyses that have been done used sample preparation methods that separated pertechnetate and would have shown a difference if non-pertechnetate was present. The results gave no indication that any soluble non-pertechnetate species is currently present in SRS tank waste.

The impact of glycolate on technetium was examined by (1) testing which showed that glycolate did not complex with Tc(I) tricarbonyl, which is believed to be the form of non-pertechnetate present in Hanford, (2) testing that showed that glycolate did not interfere with technetium immobilization as Tc_2S_7, (3) testing that showed that glycolate in the presence of noble metals caused the reduction of pertechnetate to insoluble Tc dioxide but no soluble complexed species, (4) real waste testing that showed the absence of non-pertechnetate in Hanford tanks (241-AW-101 and 241-AZ-101) that are known to contain glycolate, and (5) testing that showed for a tank 241-AN-105 simulant spiked with both pertechnetate and glycolate at room temperature, the Tc adsorption using the ion exchange resin Purolite® A530E[a] is not affected by the presence of glycolate. The literature review of glycolate-pertechnetate interactions relevant to SRS did not reveal indications that glycolate would impact the chemistry of Tc in alkaline tank waste or the behavior of Tc during reduction to Tc dioxide in Saltstone.

However, SRS would benefit from development of a robust analytical technique for periodically measuring tanks for the presence of non-pertechnetate as an early indicator if any Tank Farm activities adversely impact Tc chemistry. This recommendation is independent of whether or not the glycolic acid flowsheet is implemented at SRS. This analytical method is recommended for periodic use to identify if any processing activities and especially those using organic chemicals like caustic side solvent extraction or tank chemical cleaning, impact the waste Tc chemistry.

In summary, literature indicates that adding glycolate to SRS tanks in the concentrations planned with the implementation of the Nitric-Glycolic Acid flowsheet will not impact the behavior of pertechnetate in processing Saltstone or in the Saltstone Performance Assessment (PA) through chemical reaction with Tc in tank waste.

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[a] Purolite is a registered trademark of Purolite corporation, Bala Cynwyd, PA, USA

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LIST OF ABBREVIATIONS

B2EHP	Bis(2-ethylhexyl)phosphoric acid
BFS	Blast Furnace Slag
C	Celsius
DLM	Dynamic Leaching Method
DOE	Department of Energy
DTPA	Diethylenetriamine-N,N,N,N’’,N’’-pentaacetic acid
DWPF	Defense Waste Processing Facility
EDDA	Ethylenediamine-N,N-diacetic acid
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
EPR	Electron Paramagnetic Resonance
HEDTA	(Hydroxyethyl) ethylenediaminetriacetic acid
HEIDA	Hydroxyethyliminodiacetic acid
HLW	High Level Waste
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
IDA	Iminodiacetic acid
L	Liter
LAW	Low Activity Waste
M	Molar
mg	milligram
mL	milliliter
MT	Metric Ton
NMR	Nuclear Magnetic Resonance
NTA	Nitrilotriacetic acid
PA	Performance Assessment
pCi	Picocuries
PNNL	Pacific Northwest National Laboratory
ppb	Parts per billion
psi	Pounds per square inch (pressure)
redox	Reduction-oxidation (chemical reaction)
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TBP	Tributyl Phosphate
TOC	Total Organic Carbon
WTP	Waste Treatment and Immobilization Plant
XANES	X-ray Absorption Near Edge Structure

1. Introduction

1.1 Background

Nuclear materials production at the Savannah River Site (SRS) has generated High Level Waste (HLW) contained in underground storage tanks. One isotope in the tank waste is Technetium-99 (^{99}Tc), which is a long-lived radionuclide with a half-life of 211,000 years[1] and is a significant fission product from nuclear reactors. The Tc is predominantly soluble in the salt solution, which is disposed in the Saltstone Disposal Facility (SDF) as a cementitious waste form.

1.2 Technetium in the SRS Flowsheet

The primary chemical form of ^{99}Tc found in tank waste is pertechnetate anion (TcO_4^-) with a +7 oxidation state and is a moderately strong oxidizer. Pertechnetate is highly soluble in water, and is mobile if released to the environment. Because ^{99}Tc has a very long half-life and is highly mobile, it is a significant potential dose contributor to the long-term SDF environmental transport modeling that was done for the Saltstone Disposal Units (SDUs).[2] Depending on the chemistry and reduction-oxidation (redox) state of a particular waste, some of the Tc in tank waste can also be present as TcO_2 in the +4 oxidation state. This Tc dioxide is highly insoluble and would remain with the HLW sludge. However, as the sludge is melted into glass in the Defense Waste Processing Facility (DWPF), the Tc is expected to convert to the +7 oxidation state, with some portion remaining in the glass and some portion vaporizing. The vaporized portion is captured by the offgas system[3], returning to the Tank Farm in the form of pertechnetate (although this speciation has not been specifically measured). The fraction that vaporizes from the melter and returns to the Tank Farm is dependent on several factors, such as the redox state of the glass and the operating environment of the melter. Overall, however, this is inconsequential because only a small fraction of the total Tc inventory in the Tank Farms is in the waste sludge sent to DWPF.

Saltstone at SRS is formed by mixing the decontaminated aqueous tank waste with a blend of grout-forming additives. The additives are 10% Ordinary Portland Cement, 45% Fly Ash, and 45% Blast Furnace Slag (BFS). The BFS contains inorganic reducing agents, primarily Fe(II), Mn(II), and reduced forms of sulfur in a glassy matrix.[4] During production of saltstone at SRS, the pertechnetate ion reacts with these electron donors, causing it to be chemically reduced from Tc(VII) to Tc(IV),[5,6] dramatically lowering its solubility and thereby immobilizing it. Once completely reacted, it is present as either an oxide or sulfide species that is part of the grout matrix.[7,8,9] That redox reaction is key to sequestering the ^{99}Tc in the matrix, thus it is not easily leached with water.[10,11]

Sequestration and immobilization to reduce leachability of Tc to the solubility limit of $TcO_2 \cdot xH_2O$ is fundamental to the basis for SDF Performance Assessment (PA) transport modeling.[2] If the Tc in the tank waste were in another chemical form that is not pertechnetate, it is not known if a reaction would occur that would generate the same insoluble $TcO_2 \cdot xH_2O$ species. Another possible reaction with BFS is formation of a sulfide species, resulting in formation of TcS_x. Under laboratory conditions, Lukens et al., showed that reaction with sodium sulfide in a grout matrix forms this species and extended X-ray absorption fine structure (EXAFS) spectroscopy indicates it is Tc(IV) containing bridging sulfide and S_2^{2-} moieties.[7] The TcS_x has stoichiometry comparable to Tc_2S_7, but may actually be Tc_3S_{10}. However recently, Arai et al. used XANES and EXAFS analysis of 29- to 433-day aged saltstone samples to show that Tc(IV)-S phases form even when no extra sulfur-containing species was added to the mixture.[12] They proposed that Tc(VII) initially underwent reduction to form $Tc(IV)O(OH)_2(H_2O)_3$, followed by partial sulfidation to form $Tc(IV)O(H_2O)_{5-x}S_x^{2-}$, and finally formed a polymerized species of $Tc(IV)O(H_2O)_{5-x}S_x^{2-}$. They concluded that variable sulfur species contribute to stabilize the partially sulfidized Tc(IV) species in aged saltstone. Regardless, since the sulfide is less soluble, the oxide can be used to bound the maximum solubility in modeling calculations.[13] It is that reduced Tc(IV) species that is relied upon to minimize its leachability. Specifically, if Tc was already reduced to less than the +7 oxidation state and was still soluble, it would not be expected to undergo the same reaction with BFS that makes Tc insoluble because it would not have the same oxidation potential. To maintain the basis of Tc leachability used for the SDF PA then, it is vital that all of the Tc sent to SDF is in the form of the pertechnetate ion.

The DWPF converts HLW from SRS tanks into a glass waste form by mixing it with frit and melting it at high temperature. One of the preparation steps prior to melting the sludge waste in DWPF is to add nitric acid and a reducing agent to reduce pH, destroy nitrite and carbonate, reduce mercury to its metallic form, and reduce the slurry yield stress. Currently, the DWPF uses formic acid as the reducing agent, but is investigating using glycolic acid instead.[14] Using formic acid has the disadvantage of generating hydrogen gas during its decomposition in the Chemical Process Cell in DWPF, which limits facility throughput. If glycolic acid is used instead, although most of it would be destroyed in the sludge processing or the melter, some of it could be returned to the Tank Farm where it would be mixed with other tank waste containing pertechnetate. Since glycolic acid is both a reductant and a possible complexant, it is important to investigate if it reacts in the tank waste to form a soluble species that is not pertechnetate, which may impact the redox chemistry at the SDF.

Although this paper focuses predominantly on saltstone, it is also important that the Tc be present as pertechnetate in the residual waste after the tanks have been chemically cleaned and emptied in preparation for closure. These same reduction-oxidation (redox) reactions are also important to sequestering Tc in grouts used to backfill tanks, since this chemistry is also a basis for the PA for tank closure.[15]

1.3 Task Objective

Since the SDF transport modeling relies on the chemically reduced form of Tc in grout, it is vital that the Tc in SRS tank waste be in the form of pertechnetate so that it can react with BFS during formation of saltstone to form the Tc(IV) species. It is important to know if adding glycolate, which is both a chemical reductant and possible complexant, to the SRS tanks will react with Tc to form any species that is soluble and is not pertechnetate. As discussed in Section 1.2, if Tc forms an insoluble non-pertechnetate, i.e., TcO_2, it is not expected to be problematic to saltstone since that species would partition with sludge to DWPF and be converted to Tc(VII) in the melter and incorporated into glass or vaporized and returned to the Tank Farm as pertechnetate. To determine if glycolate is likely to form a soluble non-pertechnetate in tank waste, Savannah River Remediation (SRR) requested Savannah River National Laboratory (SRNL) to perform a literature search (Technical Task Request HLW-DWPF-TTR-2011-0025, Rev. 4, Task 2 clarification). The results of that literature search are discussed in this report.

1.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in SRS Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Information in this literature review is not RW-0333P (enhanced quality assurance requirements).

2. Non-pertechnetate in Hanford Tank Waste

Unlike SRS, the Hanford tank waste is known to contain a soluble form of Tc that is not pertechnetate, and is generically referred to as "non-pertechnetate". A significant body of literature examines Hanford non-pertechnetate, and this is contained in the appendix to this paper, with introductory discussion given in this section.

Non-pertechnetate was first observed by Schroeder, et al., when the waste was being tested using an anion exchange resin that removes pertechnetate.[16] In those tests using Tank 241-SY-101 and Tank 241-SY-103 samples, more than 50% of ^{99}Tc was observed to pass through the resin. The resin removes only pertechnetate forms of Tc and this species passed through the column uninterrupted. This phenomenon was not expected. Since then, additional testing has shown other tanks to contain substantial fractions of ^{99}Tc that is not removed by anion exchange resins, primarily Tank 241-AN-102 and Tank 241-AN-107. Only eleven of the 177 Hanford tanks have ever been tested for the presence of non-pertechnetate, and it is the predominant form (>60%) in five of those, with 0-~10% in others.[17] The fifth tank is Tank 241-AP-104 and it was found to contain a large fraction of non-pertechnetate while developing an analytical analysis method, not during an ion exchange column test.[18] There has never been a systematic examination of non-pertechnetate inventory at Hanford, and most of the testing that quantified it was associated with the initial contract for development and construction of the Waste Treatment and Immobilization Plant (WTP). That contract required removal of most of the Tc from the tank waste, so an ion exchange removal method was developed and tested on several Hanford tank samples and one SRS tank sample (since SRS waste is similar to some wastes at Hanford). Although the Hanford tanks with a high proportion of non-pertechnetate (>60% of total Tc) are associated with high concentrations of organic carbon, it is also present in tanks with relatively low organic carbon, and no correlation was found when comparing non-pertechnetate content with Total Organic Carbon (TOC) measurements.[17] It is important to recognize that Hanford tanks that contain wastes with relatively low organic, such as Tank 241-AW-101 which has 2.9 g/L TOC[17,19], have measurable concentrations of non-pertechnetate, albeit the Tc data are inconsistent. Although note that low organic content tanks at Hanford are much higher than typically present in SRS tanks. Conversely, total soluble Tc concentrations in the supernate at the two sites are comparable, at around 2-20 mg/L.

Since no samples of Hanford tank waste have been measured for about fifteen years, it is not known if non-pertechnetate still exists in the tanks. However, relatively fresh samples have recently been obtained by Pacific Northwest National Laboratory (PNNL) and will be analyzed for non-pertechnetate this year. There is no specific analytical method that selectively measures non-pertechnetate, although work has recently been done in this area by Bryan et al. at PNNL and Diprete and McCabe at SRNL.[20,21] All of the original determinations of the fraction of non-pertechnetate have been done by measuring the amount of mass 99 species that passes through an anion exchange resin or sorbent, even though this method can also be convoluted by the presence of ^{99}Ru. If any ^{99}Ru was present it would artificially inflate the mass 99 measurement, and this may account for some of the fraction of material that is reported as "non-pertechnetate". This is further discussed in the first section of the appendix to this report.

An X-ray Absorption Near Edge Structure (XANES) analysis of two samples of Hanford tank waste performed by Lukens et al., indicated that non-pertechnetate is a Tc(I) species, believed to be predominantly a tricarbonyl, $Tc(CO)_3^+$, probably stabilized by an organic ligand such as gluconate $[Tc(CO)_3(gluconate)^{2-}]$,[22,23] although this has not been definitively proven. The presence of a Tc(I) species as an organometallic carbonyl compound was unexpected, since this is a highly reduced species. It is surprising that some of the Tc at Hanford became reduced to Tc(I) and remained soluble in the tank waste, but how and where that multi-electron reduction occurred and how and where it bonded with the carbon monoxide from solution is not known. The reductant that reduces the Tc is not known for certain either, but the high dose rates in the aqueous phase can generate reducing free radicals, and note that the aqueous waste at SRS has higher dose than Hanford. The key difference at Hanford evidently lies in the presence of the organic complexants which are largely absent at SRS. Since the soluble Tc(I) species is already reduced, if it was made into a grout waste form it would not be expected to convert to the insoluble Tc(IV) species with BFS and would therefore not be sequestered by the waste form. More information about this can be found in the first section of the appendix to this report.

The presence of high concentrations of non-pertechnetate is primarily, but not exclusively, in the Hanford tanks with high soluble organic content. The high organic tanks, such as 241-AN-107 and 241-AN-102, contain a substantial amount of a species at mass 99 that is not removed by anion exchange. However, much of the data on non-pertechnetate is conflicting, particularly for tanks that exhibit low concentrations (<10%) of non-pertechnetate.[17,24] It has not been an area of intense study, since it is assumed that the melter in the Hanford WTP will readily destroy the non-pertechnetate, rendering it intimately mixed into the glass matrix as Tc(VII) and thereby minimizing its environmental availability. Waste from WTP will not get returned to the Hanford Tank Farms, so any forms of Tc or chemicals introduced in WTP cannot impact tank waste chemistry. Since the Tc will be incorporated into the Low Activity Waste (LAW) glass and any non-pertechnetate destroyed by the melter, the current inventory of non-pertechnetate in tank waste is not pertinent to the Hanford baseline disposal path. The mechanism and location where non-pertechnetate formed in Hanford tank waste is not known. Although it has not been verified, it is logical that non-pertechnetate would be highest in wastes that originated in Hanford's B-plant. The B-plant process added large amounts of organic complexants, including glycolic acid, as part of their strontium recovery system.[25] B-plant removed both ^{90}Sr and ^{137}Cs. It was found by Rapko et al. that non-pertechnetate concentration in tank waste has a weak inverse correlation with ^{137}Cs concentration.[17] Although not discussed by Rapko et al., presumably this is because non-pertechnetate, or a predecessor species, either formed in B-plant or was formed in B-plant waste after being stored in the waste tanks. Since ^{137}Cs had been removed, and those B-plant wastes generated the non-pertechnetate, it would be expected that there would be an inverse correlation between ^{137}Cs and non-pertechnetate concentrations (i.e., the B-plant waste stream was depleted in ^{137}Cs because it was removed, but became enriched in non-pertechnetate because the addition of organics and the processing and storage conditions evidently produced it).

The eight major soluble organics discharged to the tanks from B-plant were (hydroxyethyl) ethylenediaminetriacetic acid (HEDTA) (1386 Metric Tons (MT)), Ethylenediaminetetraacetic acid (EDTA) (758 MT), Glycolate (446 MT), Citrate (318 MT), Bis(2-ethylhexyl) phosphoric acid (B2EHP) (44 MT), Tartrate (42 MT), Tributyl Phosphate (TBP) (23 MT), and Gluconate (21 MT).[25] In addition, 1,100 MT of sucrose was used in Hanford as a denitration agent (i.e., reductant for nitric acid), but would have been largely consumed in that reaction and so should be in relatively low concentrations as sucrose in the tanks. Because the denitration process was only 95% efficient, it left a residual byproduct of oxalic acid, estimated at 22 MT.[25] Wastes containing high concentrations of organic complexants are associated with non-pertechnetate, but a direct correlation of non-pertechnetate to organic carbon concentration has not been found. Any of these organics presumably could serve as a reductant for Tc, as could hydrogen or e^-_{aq} from radiolysis. Unless stabilized somehow, it would be expected that if pertechnetate in a waste tank encountered a reducing environment, it would eventually lead to Tc(IV) which would precipitate as TcO_2, minimizing its further reaction with soluble organics and minimizing further reduction to lower oxidation states.

It was observed by Schroeder et al., that samples of Hanford tank waste containing high concentrations of non-pertechnetate slowly decompose to pertechnetate.[26] During storage of samples at ~33 °C, with occasional heating to 80 °C and opening of the bottle, the conversion took about three years. Whether this was due to heating, introduction of oxygen, or the reduced dose rate is unknown. This is also consistent with more recent work showing that in alkaline aqueous solution and without a stabilizing organic ligand, a synthetic sample of the $[Tc(CO)_3]^+$ moiety is unstable with time and eventually converts to pertechnetate.[27]

3. Technetium Chemistry at SRS

3.1 Measurement of Pertechnetate at SRS

Tests have been performed with SRS tank waste that would have revealed if non-pertechnetate was already present. These have included both measurements of the leaching behavior of Tc from saltstone samples and experiments that separated pertechnetate. If non-pertechnetate was present in SRS tank waste, it would not be expected that the low leach rates of cured saltstone samples would have been observed. Using simulants containing pertechnetate, Tc leaching has been shown by Arai and Powell and by Cantrell and Williams to be controlled by the solubility of TcO_2 hydrates,[9, 28] and this is consistent with the leach rates of actual waste samples observed by Reigel and Hill.[29] Those tests showed that the soluble Tc in actual saltstone leachates was ~2E-8 Molar (M), which is similar to the soluble concentration of $TcO_2 \cdot 1.6H_2O$ in dilute sodium chloride solution at slightly alkaline pH.[30] If a complexed, soluble form of Tc was present that did not get converted to the oxide or sulfide, the leach rates would be higher.

Another example of the behavior of Tc in saltstone by Seaman et al. utilized two different leaching methods; the Environmental Protection Agency (EPA) 1315 method, and a Dynamic Leaching Method (DLM).[13] Using the EPA 1315 static leaching method, the Tc concentrations were similar in leachates from a saltstone waste form produced using a spiked simulant and from actual core samples from an SDU. The leaching results (6.8E-10 to 4.3E-9 M ^{99}Tc) were lower than that measured in other work which had attributed the Tc speciation to $TcO_2 \cdot 1.6H_2O$. They attributed the lower Tc level to a slightly lower pH. The measured value is lower than the solubility of hydrates of TcO_2 at pH 10-11, and is supporting evidence that there is no non-pertechnetate present in the SDU core grout samples. Conversely, the DLM test was performed using a de-gassed liquid to preclude oxidation from air. This test indicated the Tc leachate (up to ~5E-7 M ^{99}Tc) exceeded the $TcO_2 \cdot 1.6H_2O$ solubility limit, which contrasted with the leachate from grout samples produced with pertechnetate in simulated waste. The report attributes the difference between the samples to complex chemical and physical processes controlling behavior during the immobilization and leaching steps, perhaps related to pore water residence time. It is pointed out, however, the cumulative amount of leachate was only 2% of the total Tc in the grout sample, which is a lower percentage than the percentage of ^{137}Cs that leached in the same experiment. These observations are consistent with the Tc being present predominantly as pertechnetate in the tank waste and converting to Tc(IV) in grout, but is not quantitative. It is stated in the report by Seaman et al. that further work is needed to continue this study using a modified DLM and to perform additional testing to fully understand the solubility and leaching behavior.[13]

Likewise, experiments have been performed using SRS tank waste that would have revealed if non-pertechnetate was present. These tests were conducted to support Hanford objectives but used SRS waste, since the chemical matrix and radionuclide characteristics are similar for the Hanford Purex waste stream, which is a large portion of their salt waste type. In one test by King et al., the Tc was removed from a 30-L sample of Tank 44F waste using a pertechnetate-selective ion exchange resin.[31] The first sample of effluent from the ion exchange column contained 1.4% of the feed concentration of Tc, so at least 98.6% of the Tc was present as pertechnetate. There are several possible reasons why 1.4% of the mass 99 species was not captured, including that the first sample was not collected until 54 Bed Volumes of liquid had passed through the column (potentially missing the lowest concentration sample), poor packing of the resin, wall effects of the column, or the presence of ^{99}Ru. Another test was performed by Nash et al. using Tank 50H and a pertechnetate-selective ion exchange resin but as a batch distribution coefficient measurement instead of a column.[32] The extraction of ^{99}Tc agreed reasonably well with the expected result, consistent with the ^{99}Tc being present entirely as pertechnetate, but did not quantify it specifically. Finally, preliminary work was performed by Diprete and McCabe to develop a non-pertechnetate analysis method for Hanford but using a sample of SRS Salt Batch 7 waste (for the Modular Caustic Side Solvent Extraction Unit) extracted using Aliquat 336®[b] sorbed onto a TEVA®[c] resin.[21] This method indicated that >99.9% of the ^{99}Tc in the Salt Batch 7 sample was present as pertechnetate.

There have also been several measurements of ^{99}Tc in SRS tank waste that utilized both separation and beta counting ("Rad Chem" method) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) as reported by Stallings et al.[33] See Table 3-1. The separation method involves acidification of the sample with nitric acid, followed by extraction with Aliquat 336®. That Rad Chem method probably would not have extracted any non-pertechnetate form into the Aliquat 336® and therefore would not have counted its beta emissions. This has not been verified experimentally. Peroxydisulfate or comparably powerful oxidant is typically needed to fully oxidize non-pertechnetate in Hanford waste.[17] Conversely, the ICP-MS measures the total mass 99 directly, and if any non-pertechnetate was present, it would have been included. Since the two methods yielded the same concentration of Tc within analysis uncertainty, this also indicates that there is no non-pertechnetate present. Although the Tank 39H sample indicates a ~10X higher result by Rad Chem than by ICP-MS, that is the opposite of what would have been observed if there was non-pertechnetate present, and suggests an inhomogeneity, analysis, or dilution problem with the sample.

Table 3-1. Tc concentrations in SRS tank wastes (0.45-μm filtered samples)[33]

Tank	**Rad Chem (pCi/mL)**	**Standard Deviation**	**ICP-MS (pCi/mL)**	**Standard Deviation**
13H	2.74E5	1.64E4*	3.17E5	4.13E3
30H	1.86E5	1.28E6*	2.02E5	5.50E2
37H	3.38E5	2.04E4*	3.76E5	1.41E4
39H	1.42E6**	3.55E5*	1.25E5***	4.53E4
46F	8.35E4	5.85E3*	8.43E4	3.20E3
49H	1.28E5	7.64E3*	1.87E5	6.31E4

*method uncertainty from single analysis; **unfiltered sample; ***0.1 μm filtered sample

3.2 Organic Chemicals in SRS Waste

Many organic chemicals have been introduced into SRS tank waste, as summarized by Walker,[34] but in significantly lower concentrations than at Hanford. The predominant species are *n*-paraffin and TBP (395 MT), breakdown products, and formate. Radiolytic decomposition of n-paraffin yields carboxylic acids, and TBP would yield *n*-butanol. Neither of these would be expected to impact Tc chemistry, as evidenced by the lack of non-pertechnetate in SRS tank waste. Ion exchange resins are also sent to the tanks. These generally contain quaternary amine functionalities, which would be expected to bond with pertechnetate (quaternary amine resins are used to remove pertechnetate from groundwater), but that bonding would not be expected to cause reduction to a lower oxidation state. The resins are largely digested using permanganate prior to disposal into the tanks, so the residual organic chemicals are not characterized, but some resin is also sent without decomposition. The total amount is 36 MT of decomposed resin and 20 MT of resin that was not decomposed. A few campaigns in the canyons in the 1950s introduced gluconic acid to the tanks, but this radiolytically decomposes to carbon dioxide and the report states that it is unlikely that any remains in the waste today. Tank 48H contains the organic chemicals and breakdown products from the In-Tank Precipitation process, which utilized tetraphenylborate to precipitate Cs. It is unknown how the tetraphenylborate or decomposition products interact with Tc, but they are not acid-type donor complexants like gluconate, thought to be critical to formation and stabilization of the non-pertechnetate species at Hanford. However, that waste would be expected to have high quantities of carbon monoxide due to radiolytic degradation of the organics, and carbon monoxide is implicated in non-pertechnetate

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[b] Aliquat® 336 is a trademark of BASF, Germany.

[c] TEVA® is a registered trademark of Eichrom Technologies, LLC, Lisle, Illinois, U.S.A.

chemistry. But note that since the contents of Tank 48H are isolated from the rest of the Tank Farms, its chemistry would not impact the vast majority of liquid waste.

Antifoam (a.k.a. defoamer) used in DWPF is another source of organic compounds in SRS tank waste.[34] Antifoams are not known to be involved in Tc chemistry, but are a source of reductant potential and carbon monoxide. There are also small amounts of EDTA that have been added to the waste tanks originating from decontamination processes in 299-H. Although EDTA is a good complexant, it is expected that the concentrations present are not sufficient to impact the Tc chemistry, and EDTA is not the complexant that has been suspected to be involved in the non-pertechnetate chemistry at Hanford. Formic acid has been used in DWPF since start-up, and it is expected that formate ion is spread throughout the Tank Farm. Formate ion is a reductant, and source of carbon monoxide from radiolysis, but is not a good complexant. Oxalate ion is also present throughout the Tank Farm from tank cleaning, and although it is a good complexant for transition metals in acidic solution, it converts to the predominantly insoluble sodium oxalate in the alkaline tank waste. Overall then, there is no indication that the organics currently present in the tanks are sufficient to stabilize a reduced Tc, but conversely much of the chemistry of Tc and its reaction chemistry with organics is poorly understood. Although there is no direct evidence of organic complexants in SRS tank waste, the chemistry of Tc has not been explored under some process or storage conditions, such as during tank cleaning with oxalic acid or in Tank 48H.

Since the redox chemistry of Tc and grouts is important to the basis used for leaching of Tc from saltstone at SRS, the SRS would benefit from development of a robust analytical technique for periodically measuring the presence of non-pertechnetate and to implement it for use as an early indicator if any Tank Farm activities adversely impact Tc chemistry. A better understanding of Tc redox chemistry is important to tank closure at both SRS and Hanford, and the technique would be useful for examining the chemical environments in preparation for tank closure as well, regardless of the implementation of the glycolic acid flowsheet at DWPF.

3.3 Potential Use of Gycolic Acid at SRS

SRR is evaluating changes to its current DWPF flowsheet to improve processing cycle times that will enable the process to support higher canister production while maximizing waste loading.[14] Catalytic decomposition of formic acid in the Chemical Process Cell has the potential for producing flammable quantities of hydrogen and controlling it can limit facility throughput, requires significant instrumentation maintenance, and causes high vapor space purge rates. To improve canister production, reducing the amount of formic acid used in the Chemical Process Cell is one of the options being considered. Earlier work at SRNL has shown that replacing formic acid in the existing nitric/formic acid flowsheet with glycolic acid has the potential to perform the necessary chemical reactions in the Sludge Receipt and Adjustment Tank without any significant catalytic hydrogen generation.[35] This change is being pursued, so impacts to the remainder of the SRS tank waste flowsheet must be evaluated.

4. Chemistry of Technetium and Glycolate

4.1 Literature on Technetium Complexation Chemistry

The primary goal of this report is to examine impacts of glycolate on the ability of saltstone to retain Tc. If water-soluble glycolate complexes of Tc were produced, they would be expected to increase Tc leaching. As discussed above, saltstone retention of Tc (as the solid dioxide or sulfides) would be adversely impacted. Thus, it is of interest to determine if stable, soluble, reduced Tc species with glycolate are known to exist, or if glycolate interferes with precipitation and reduction reactions that occur during grout formation. Table

4-1 below summarizes literature that addressed the existence of Tc complexes including glycolate. The works also considered other organic complexants, which serve here as comparisons. The works listed in Table 4-1 are discussed in more detail below.

Steigman and Eckelman reduced pertechnetate in alkaline solution using stannous chloride and found that glucoheptonic, ethylene glycol, and glyceric ion formed stable complexes.[36] In contrast, mannitol, and glycolic and lactic ion tests caused a brown precipitate to form, with the precipitate assumed to be Tc dioxide. The glycol and glyceric complexes were found to rapidly disproportionate when those solutions were acidified.

Levitskaia et al. started their tests on Tc complexation by first creating the Tc(I) tricarbonyl complex.[37] After forming the initial tricarbonyl species as the trichloride, Levitskaia et al. dissolved the complex in a 5 M $NaNO_3$, 0.1 M NaOH solution and tested candidate complexing reagents including formate, acetate, citrate, glycolate, gluconate, IDA, nitrilotriacetic acid (NTA), EDTA, HEDTA, and diethylenetriamine-N,N,N,N'',N''-pentaacetic acid (DTPA).[37] Nuclear Magnetic Resonance (NMR) spectroscopy indicated that no complexation was caused by glycolate. In contrast, DTPA, IDA, EDTA, and gluconate did form complexes with the Tc tricarbonyl as determined by NMR.

Liu et al. specifically examined the effect of various candidate complexants on the chemistry of the pertechnetate-sulfide immobilization reaction.[38] As discussed above, sulfide can complex and precipitate Tc(VII) by converting it from pertechnetate to TcS_x, which has been shown to be a Tc(IV) species.[7] Liu et al. indicated that Tc mobility in soil could thus be slowed by the hydrogen sulfide gas treatment. They did also acknowledge that reduction of Tc can also occur to form products other than Tc_2S_7. Liu et al. found that potential complexants including EDTA, IDA, HEDTA, and gluconate did not interfere with the immobilization reaction using hydrogen sulfide at pH 9. Liu found that glycolate did not impact the chemistry, along with acetic, oxalic, and lactic species. Liu et al. did find that maleic and fumaric acids at pH 9 did interfere, causing some Tc to remain soluble.

Chamberlin and Arterburn studied the use of organic complexants and metal catalysts to reduce pertechnetate.[39] The organic reagents included glycolate, EDTA, NTA, oxalate, citrate, HEDTA, and formate. The general method was to mix 0.05 M of the organic chemicals into 2.5 M sodium hydroxide solution along with 1 mM of Pd, Rh, and Ru salts (assumed to help with reduction by catalysis), and 0.1 mM of pertechnetate. Any combination of all of the complexants and two of the catalysts (or Ru only) exhibited >98% reduction after 4 days of temperature held to 65 °C. Further, mixtures of the three catalytic metals and individual complexants EDTA, HEDTA, glycolate, hydroxyethyliminodiacetic acid (HEIDA), formate, and glyoxylate all produced >99% reduction of pertechnetate. Only the citrate, oxalate, and NTA (along with the catalytic metals), failed to cause the reduction of pertechnetate. However, despite very high concentrations of the complexants, which greatly exceeded the pertechnetate concentration, Chamberlin and Arterburn's work found that only insoluble Tc dioxide was observed, not a soluble complexed Tc species. Later, additional preliminary tests indicating that heating the catalytic metals and gluconate with pertechnetate resulted in a soluble Tc species that was not extracted by pertechnetate-selective ion exchange resin. Chamberlin and Arterburn speculated that it was a complex of the type $[TcO(gluconate)_2]^{n-}$. However, it is not stated if this test was also performed in an alkaline aqueous solution. Regardless, the initial tests using glycolate did not indicate formation of any soluble non-pertechnetate species.

Schroeder et al. issued a project report on their work producing aqueous-soluble reduced Tc complexes of IDA, EDDA, citrate, and glycolate under mildly alkaline conditions using sulfite as a reductant.[40] The products were isolated by precipitation using ethanol to reduce their solubility in aqueous solution. Of the complexants listed, the glycolate complex was most stable, but decomposed in 1 to 3 days when exposed to 2 M sodium hydroxide solution.

Table 4-1. Summary of Documented Tests on Technetium and Glycolate

All works in the table tested glycolate and found no soluble non-pertechnetate species.

Reference	Aqueous Solution	Active Ligands Found
Steigman, J, and Eckelman, W. C., The Chemistry of Technetium in Medicine, pp. 40-43, National Academy Press, Washington, DC, (1992).[36]	pH 11 to 12, stannous reductant	Glyceric, gluconate, glucoheptanate, ethylene glycol
Levitskaia, T.G., Andersen, A., Chatterjee, S.D., Hall, G.B., Walter, E.D., and Washtin, N.M., Spectroscopic Properties of Tc(I) Tricarbonyl Species Relevant to the Hanford Tank Waste, Pacific Northwest National Laboratory, PNNL-25000, 2015[37]	5 M $NaNO_3$, 0.1 M NaOH. Tc(I) tricarbonyl was the input species after being synthesized in the laboratory. Other works shown in this table started with pertechnetate.	DTPA, EDTA, IDA, NTA, gluconate
Liu, Y., Terry, J., and Jurisson, S.S., Potential interferences on the pertechnetate-sulfide immobilization Reaction, *Radiochim.Acta*, vol. 97, pp.33-41 (2009).[38]	pH 9, zinc, iron sulfide reductants, phosphate buffer, anaerobic conditions, potential complexants are up to 9.4 mM.	Interference found: fumaric acid and maleic acid inhibit Tc immobilization. No interference with immobilization found: acetic acid, glycolic acid, oxalic acid, lactic acid.
Chamberlin, R.M., Arterburn, J.B., Final Report: Dynamic Effects of Tank Waste Aging on Radionuclide Complexant Interactions , LA-UR-00-5998, Los Alamos National Laboratory, Project 59993, 2000.[39]	Noble metals, pertechnetate, glycolate in 2.5 M NaOH, 65 °C for 4 days caused formation of only insoluble Tc species	NTA, Citrate, oxalate did not cause reduction of pertechnetate
Schroeder, N.C., Ashley, K.R., and Blanchard, D.L., Final Report : Fundamental Chemistry, Characterization, and Separation of Technetium Complexes in Hanford Waste, US DOE Project report 59990, 09/01/1997 to 09/30/2000.[40]	2 M NaOH after reduced Tc complexes were made using a sulfite reductant under mild conditions.	IDA, EDDA (ethylenediamine-N,N-diacetic acid), citrate, and glycolate. The glycolate complex decomposed in 1 to 3 days in the 2 M NaOH.

Hallam performed Tc chemistry studies that aimed at determining the chemistry of Tc retention in alkaline grout when organic complexants were present.[41] As discussed above, the main mechanism recognized for retention was the reduction of pertechnetate to Tc dioxide, which has very low solubility in water. Sorption of Tc(VII) on rock minerals (examples: granite, gypsum, shale) was also examined as a function of pH. The organic complexants gluconate, picolinate, EDTA, NTA, and α-Isosaccharinic acid were tested. The studies with organic complexants started with the electrochemical reduction of pertechnetate in solutions of pH about 13.3. Tc solubilities were then measured as a function of complexant molarity up to 0.4 M. NTA data were inconclusive; the other four complexants increased the solubility of reduced Tc as a function of their concentration. Gluconate was noted to be especially strong as a complexant, but glycolate was not tested.

4.2 Glycolate Bearing Waste and Evidence of Non-Pertechnetate

Another approach to gauge the potential impacts of glycolate on the soluble form(s) of Tc in caustic liquid waste is to review what has been found in studies of Hanford wastes. The logical goal here is to find the wastes that are considered “non-complexant”, yet that are known to contain glycolate, and that apparently contain Tc only in the pertechnetate form. First of all, then, complexant bearing wastes such as Hanford Tank 241-SY-101, 241-SY-103, 241-AN-107, and 241-AN-102 materials are excluded because they are known to contain non-pertechnetate as well as mixtures of organic complexants. Effects of glycolate on Tc chemistry would be confounded by the mix of various organic complexing agents in those cases.

In order to find examples of tanks that are known to contain glycolate but are also known to contain Tc predominantly in the pertechnetate form, the data compiled by Hamm et al. in their review of Hanford tank sample testing can be used.[24] Table 4-3 of Hamm et al. identifies Hanford Tanks 241-AW-101, 241-AN-103, and 241-AN-105 as having less than 2% of their soluble Tc in the non-pertechentate form. Ion exchange work had often been used to assess the relative abundance of pertechnetate and non-pertechnetate. In addition, reports published after the report by Hamm et al. later indicated that Tank 241-AP-101, 241-AZ-101, and 241-AZ-102 are additional candidate wastes for the same evaluation.[42,43,44] The next logical step here is to find reports of measurable glycolate content in these tank wastes. Finding tanks that contain both measured amounts of glycolate and less than the detectable amount of non-pertechnetate together would support the premise that glycolate alone does not impact pertechnetate chemistry in caustic high sodium waste.

Hanford Tank 241-AW-101 was confirmed to contain glycolate during characterization by Hay et al. at SRNL, which included the use of a method that was specific for measuring glycolate.[45] Their reported average value for glycolate was 306 mg/L for a sample diluted to 5.0 M sodium. They also detected EDTA at 94 mg/L and acetate at 2330 mg/L. Analysis of TOC revealed that all of the organic carbon was accounted for by acetate, glycolate, and EDTA, within analytical uncertainty. Complexants HEDTA, NTA, and IDA were below detection concentrations of 94 mg/L. Klinger et al. possibly detected glycolate from Tank 241-AW-101 supernate, but Klinger et al. stated that their method was not able to distinguish between acetate and glycolate.[46]

It is uncertain if Hanford Tank 241-AP-101 contains glycolate. Fiskum et al. reported 1640 mg/L for the total of acetate and glycolate in a 5.6 M sodium composite liquid sample.[47] The report makes it clear that the applied analytical method could not separate acetate and glycolate but would report the total of the two. Esch performed extensive analyses of Tank 241-AP-101 but did not measure glycolate or acetate.[48] Russell reports characterizations of Tank 241-AP-101 along with the follow-on work to create a detailed simulant recipe.[49] Russell assigned the acetate value of 1460 mg/L to a 5 M sodium simulant, but noted that acetate, formate, and fluoride interfere in the analytical method. It is thus not known how much of that 1460 mg/L might be glycolate.

Hanford Tank 241-AZ-101 was confirmed to contain substantial glycolate concentrations. Steen found measurable glycolate in drainable liquid from tank core samples.[50] This work resolved the differences between glycolate, acetate, and formate, and found that glycolate was in nearly the same concentration as the other two. Separately, Duncan and Huber made a composite of Tank 241-AZ-101 and 241-AZ-102 materials and found 57 mg/L glycolate at 4.1 M sodium dilution.[51] In a later test, they measured 58 mg/L glycolate in the liquid after decontamination with a cesium ion exchange media (UOP Ionsiv® IE-911). Separately, Tc-removal ion exchange tests have been performed with Tank 241-AZ-101 by Burgeson et al. and the breakthrough profile indicated that it contains less than 0.1% of non-pertechnetate.[43]

It is unknown if Hanford Tank 241-AZ-102 contains glycolate. No analyses providing glycolate results were found for this tank alone.

Hanford Tank 241-AN-103 does not appear to contain detectable glycolate. Duncan and Huber reported that Tank 241-AN-103 at 5.7 M [Na^+] contained less than 104 mg/L glycolate.[51]

Hanford Tank 241-AN-105 does not appear to contain detectable glycolate. Eibling included glycolate in the final simulant recipe for Tank 241-AN-105, but the logic was that this Envelope A (non-complexant) was thought to be similar to Tank 241-AW-101 organic profile.[52] Jo performed extensive analyses of Tank 241-AN-105 but does not show analyses for glycolate.[53]

Other work examined adding pertechnetate to glycolate-containing simulant. That work, led by Duncan, used a glycolate-bearing version of the simulant of Tank 241-AN-105 (considered non-complexing) with pertechnetate spikes. Note that for this study, whether the actual tank contents contain glycolate is not relevant here because the simulant followed the step suggested by Eibling to add glycolate to Tank 241-AN-105 simulant as representative of organics for some of the unknown organics in the actual waste. In order to justify excluding glycolate in subsequent tests, Duncan et.al. performed a comparison that included batch contact testing using Tank 241-AN-105 simulant with and without glycolate. Since it was not discussed, it is assumed that the simulant was spiked at room temperature. It was reported that including or omitting glycolate did not affect Tc adsorption results when using anion exchange resin Purolite® A530E[54] (although this detail was omitted in Revision 1 of that document for unknown reasons). Sodium was in the range of 5.5 to 6.5 M. Duncan et al. also saw high Tc decontamination using the pertechnetate-spiked simulant and a reductive tin apatite adsorbent up to pH 12.[55] From these works it is seen that glycolate in the simulant did not confound the efforts to remove added pertechnetate from caustic simulant liquids by ion exchange or reductive precipitation.

In summary, of the non-complexant Hanford tanks examined, 241-AW-101 and 241-AZ-101, appear to contain pertechnetate and glycolate co-existing, with the Tc being at least 98% in the form of pertechnetate.

5. Conclusions and Recommendations

The following key points were identified during this literature review:

1. The chemical form of Tc that is used as the basis for transport modeling of leaching from Saltstone is a Tc(IV) dioxide species.
2. Generation of the Tc(IV) species during saltstone curing is based on reduction of pertechnetate in tank waste by reaction with BFS.
3. If a Tc species other than pertechnetate was present in SRS tank waste, it is not known if it would generate an equally insoluble Tc(IV) species during saltstone curing and so its leaching behavior would be unknown.

4. Experimental evidence indicates that all soluble Tc is in the form of pertechnetate in SRS tank samples.
5. A soluble form of Tc that is not pertechnetate is present in Hanford tanks and the characterization of it is most consistent with a tricarbonyl species, $[Tc(CO)_3]^+$, probably stabilized by an organic ligand.
6. There is no routine analytical method available to quantify any non-pertechnetate species.
7. The Tc tricarbonyl species was found by NMR spectroscopy to not form a complex with glycolate ion
8. The origin and formation of non-pertechnetate in Hanford tank waste is not known.
9. The chemistry of Tc with organic complexants, carbon monoxide, and reductive radiolysis products is poorly understood.
10. Radiolysis of formate in SRS tank waste would provide a source of carbon monoxide that would be needed for formation of tricarbonyl, $[Tc(CO)_3]^+$ (although there is no indication this species is currently present)
11. No testing has been done to generate grout waste forms using actual Hanford tank waste samples known to contain non-pertechnetate.
12. Organic complexants thought to be vital to stabilizing non-pertechnetate are not known to be present in appreciable concentrations in SRS tank waste.
13. Glycolate was found to not interfere with forming insoluble Tc sulfides when reacting pertechnetate with hydrogen sulfide at slightly alkaline pH.
14. Combining and heating glycolate, pertechnetate, and catalytic metals in alkaline solution did not yield any soluble non-pertechnetate Tc species.
15. Two Hanford tanks have been identified that are known to contain glycolate but have at least 98% of the Tc in the form of pertechnetate.

This information indicates that there is no indication in the literature that addition of glycolate as the reductant in DWPF would be expected to have any impact on the Tc chemistry in SRS tank waste.

The impact of glycolate on technetium was examined by (1) testing which showed that glycolate did not complex with Tc(I) tricarbonyl, which is believed to be the form of non-pertechnetate present in Hanford, (2) testing that showed that glycolate did not interfere with technetium immobilization as Tc_2S_7, (3) testing that showed that glycolate in the presence of noble metals caused the reduction of pertechnetate to insoluble Tc dioxide but no soluble complexed species, (4) real waste testing that showed the absence of non-pertechnetate in Hanford tanks (241-AW-101 and 241-AZ-101) that are known to contain glycolate, and (5) testing that showed for a tank 241-AN-105 simulant spiked with both pertechnetate and glycolate at room temperature, the Tc adsorption using the ion exchange resin Purolite® A530E is not affected by the presence of glycolate. The literature review of glycolate-pertechnetate interactions relevant to SRS did not reveal indications that glycolate would impact the chemistry of Tc in alkaline tank waste or the behavior of Tc during reduction to Tc dioxide in Saltstone.

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Appendix A

Non-Pertechnetate at Hanford

A1. Non-Pertechnetate Characterization

An X-ray Absorption Near Edge Structure (XANES) analysis of two samples of Hanford tank waste performed by Lukens et al., indicated that non-pertechnetate is a Tc(I) species, believed to be predominantly the tricarbonyl, $[Tc(CO)_3]^+$, probably stabilized by an organic ligand such as gluconate to form $[Tc(CO)_3(gluconate)]^{2-}$,[i,ii] although this has not been definitively proven. Lukens also stated that the non-pertechnetate species could be a nitrosyl compound, $[Tc(CO)_2(NO)(H_2O)_3]^{2+}$ which could be formed under the conditions in the Hanford tank waste. This compound is more stable than the tricarbonyl and the NO could be generated from radiolysis of nitrite/nitrate. The authors also point out that although Tc(I) is not thermodynamically stable in alkaline solution, its low-spin d^6 electron configuration makes it kinetically inert. Note that $[Tc(I)(CO)_3]^+$ is an octahedral complex; with three coordination sites occupied by carbon monoxide and three other coordinated positions around the Tc atom occupied by other ligands like hydroxide (OH^-), nitrosyl (NO), chloride (Cl^-), aqua (H_2O) or multidentate ligands like gluconate. It is not known if there are additional forms of soluble non-pertechnetate species, but there is no confirmed evidence in the current literature that there are multiple species in actual tank waste. The identity of a Tc(I) species as an organometallic carbonyl compound was unexpected, since this is a highly reduced species that would require a 6-electron reduction to form from pertechnetate. It is not surprising that carbon monoxide would be present in tank waste because it forms during radiolysis of organics and is known to be present in Hanford tank vapor space.[iii] Carbon monoxide has also been shown by Crawford and Bibler to form during radiolysis of simulants containing formate ions,[iv] so even though there are no appreciable complexants in SRS waste, carbon monoxide would be present since DWPF has recycled formate to the Tank Farm for years. Initially, the Tc would have been present as pertechnetate during acid dissolution of fuel or targets at Hanford and SRS. Some of the Tc became reduced to Tc(I) and remained soluble in the Hanford tank waste, but how and where that multi-electron reduction occurred and how and where it bonded with the carbon monoxide from solution is not known. The reductant that reduces the Tc is not known for certain either, but hydrogen generated from radiolysis, or the reductive intermediates formed during radiolysis, could be involved (see Appendix section A.2 discussion). Although the waste at SRS contains carbon monoxide and hydrogen and generally has higher dose rates in the aqueous phase (because Sr and Cs were removed in B-plant at Hanford) that can generate reducing free radicals, the key difference evidently lies in the absence of the organic complexants at SRS.

Measuring the presence of non-pertechnetate is complicated, particularly for samples with low fractions (<10% of total Tc). Typical analysis methods for Tc are either Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), which measures the quantity of mass 99 species, or selective chemical extraction of the sample using Aliquat® 336,[a] followed by liquid scintillation counting for beta emissions. The ICP-MS method measures the entire mass 99 concentration, but this can also include ^{99}Ru, a non-radioactive natural isotope of Ru, complicating the analysis for Tc. Lawrence, et al. showed that a Hanford tank waste testing indicated that ~1.3% of the mass 99 species in Tank 241-AW-101 could not be removed by ion exchange, even after extensive electrochemical oxidation.[v] In that testing, about 50% of the original non-extractable mass 99 [80 parts per billion (ppb)] species was quickly oxidized, but the remainder (40 ppb) could not be oxidized and removed. Similarly, in a Tank 241-AN-107 sample, about 50% of the original Tc was non-pertechnetate, based on the ion exchange removal testing. After less than half of the oxidation period, about 12% of the Tc remained non-extractable and this continued throughout the remainder of the

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[a] Aliquat® 336 is a trademark of BASF, Germany

experiment. The electro-oxidation should have oxidized all of the Tc to pertechnetate, so it would have all been extracted by the resin. One explanation is that there is an interfering species at mass 99 that may not be Tc at all, such as ^{99}Ru, which convolutes the interpretation of test results when using ICP-MS analysis alone and must be considered when examining test results.

Conversely, the preparation of samples for radiochemical counting analysis uses Aliquat® 336 (a quaternary ammonium salt that selectively extracts pertechnetate) to separate and concentrate pertechnetate so that it can then be mixed with scintillation cocktail and beta emissions counted. The complication with this method is that non-pertechnetate is not extracted and would therefore not be included in the beta counting. The Aliquat® 336 can be used in either liquid-liquid extraction or sorbed into an organic resin and used to extract the pertechnetate, but both suffer from the same drawback of not removing non-pertechnetate so that it can be counted. A laboratory method is being investigated by Bryan et al., where a different ligand is added to the sample to complex the Tc(I) carbonyl, which can then be illuminated to fluoresce.[vi] To increase sensitivity of the method, an ion exchange film can be added to the surface of the sensor. This method is not yet ready for deployment, and would not measure any non-pertechnetate species that is not the Tc(I) carbonyl species, if any exist. Similarly, a method was partially developed by Diprete and McCabe that uses a series of TEVA®[a] /Aliquat® 336 extraction and oxidation steps followed by liquid scintillation counting,[vii] but this method is also not ready for deployment.

A2. Synthesis of Non-Pertechnetate

Berning et al. showed that pertechnetate in a 2 M sodium hydroxide solution can be reduced by a number of organic compounds.[viii] However, a complete characterization of the products was not performed, although Ultraviolet/Visible spectroscopy indicated that the species were Tc(IV) or Tc(V). The reaction products were reported as a reduced, water-soluble complex. In general, Berning et al. reported that the ligands that showed the greatest reactivity were the mono- and disaccharides. Sugars like glucose and ribose had over 80% conversion to a soluble reduced Tc species. Gluconate and sucrose caused roughly 20% to be converted. Glycolate was not tested. Polyaminocarboxylates showed slight reactivity and the products were unstable in air. Simple alcohols and some polyaminocarboxylates showed no reduction of pertechnetate. Oxalate and EDTA both had 7% conversion to a soluble reduced Tc species, but ethanol, ethylene glycol, formaldehyde, and glycerol had no conversion. Control experiments showed that the reactions did not proceed in neutral water, only in the 2 M sodium hydroxide solution. To gain insight into the functional group necessary to cause the formation of the reduced Tc, they found that mannitol is nearly as reactive as gluconate, but no reaction was observed for acetate. This suggests that the hydroxyl groups or the breakdown of the monosaccharides play a critical role in the reaction. These results indicate that reduction of pertechnetate can be caused by a number of organic compounds. The only one tested that is present in significant quantities in SRS tank waste is the oxalate ion, which had a 7% conversion. However, the analysis method used was unconventional and did not provide much information about the characterization of the resulting species, and there was minimal examination of stability. The principle characterization method used was thin-layer chromatography or paper chromatography followed by beta counting and utilized the difference in Tc mobility behavior between using water and acetone as the mobile phase to discriminate if a soluble species was formed. If the reaction product was mobile with water but not with acetone, it was concluded that a water-soluble Tc(IV) or (V) species was formed. Further verification of the product was not performed.

The $[Tc(CO)_3(OH)(H_2O)_2]$ has been synthesized by Levitskaia et al. in the laboratory by reduction of pertechnetate with tetrabutylammonium chloride to Tc(V), and subsequent reaction with borane and carbon monoxide to form $[Tc(CO)_3Cl_3]^{2-}$.[ix] Dissolving this compound in water forms the aqueous $[Tc(CO)_3]^+$ species. This species was shown to be stable in sodium nitrate solutions at neutral pH, even without an organic complexant, but decomposes in alkaline solutions of 5 M sodium nitrate. At 0.1 M hydroxide, the

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[a] TEVA® is a registered trademark of Eichrom Technologies, LLC, Lisle, Illinois, U.S.A.

Tc tricarbonyl chloride compound decomposed to pertechnetate in 2-3 months, at 0.5 M hydroxide, it decomposed in a little over two weeks, and at 1 M hydroxide, it decomposed in ten days. Unexpectedly, adding gluconate as a complexant sped the decomposition. With sodium gluconate, the decomposition occurred in 12 days with 0.1 M hydroxide and nine days at 0.5 M hydroxide. In a tank simulant, similar results were observed, but adding gluconate and noble metals exhibited an initial fast decomposition which then slowed to a lower rate than in the sodium nitrate solution, and adding an atmosphere of carbon monoxide slowed it further. It was also shown that the $[Tc(CO)_3]^+$ species in a tank waste simulant could be generated by adding catalytic metals and gluconate to a tank waste simulant containing pertechnetate, pressurizing it with 1,300 psi of carbon monoxide containing a small amount of hydrogen, and heating it to 80 °C for twelve days. Hydrogen had been included because of its reductive action on Tc(VII) in previous work cited by Levitskaia et al., along with its known presence in radioactive waste. The resulting Tc(I) species slowly decomposed to pertechnetate in the tank simulant, with 20% converted to pertechnetate in eight days. These results indicate that if the $[Tc(CO)_3]^+$ species was produced in tank waste in the absence of a stabilizer, it would decompose over time, depending on the pH of the solution. Since SRS tank supernate is typically at least 0.1 M hydroxide and there is no known complexant to stabilize it, if this species formed it would be expected to decompose in 2-3 months at ambient temperature, and probably faster at elevated tank temperatures. If complexants are available to stabilize it and other conditions are favorable, it can evidently remain stable for extended periods.

Subsequent work by Levitskaia et al. examined hydrolysis products, stability, spectroscopic characterization, complexation chemistry, and further speciation.[x,xi,xii] It was shown that the $[Tc(CO)_3]^+$ species forms a tetramer $[Tc(CO)_3(OH)]_4$ in solution at high concentrations and within a pH range of 7-11 and $[Tc(CO)_3(H_2O)_2(OH)]$ in Hanford tank waste simulant.[ix] The $[Tc(CO)_3(H_2O)_3]^+$ species was isolated and mixed with chelators in 5 M $NaNO_3$/0.1 M NaOH solution and the mixtures were characterized by Nuclear Magnetic Resonance (NMR) spectroscopy. The NMR shifts indicated that a strong complex was formed with iminodiacetic acid (IDA), an intermediate strength complex was formed with gluconate, and weak complexes were formed with EDTA, nitrilotriacetic acid (NTA), and diethylenetriamine-N,N,N,N'',N''-pentaacetic acid (DTPA). No interaction was evidenced by the NMR when citrate, formate, acetate, or glycolate were added, indicating no complex formed.

Further studies examined the $Tc(CO)_3^+$ stability.[xii] These were done by dissolving the $[Tc(CO)_3Cl_3]^{2-}$ precursor in the aqueous solution. As noted above, it converts to the tetramer slowly, which is stable in 5 M $NaNO_3$ solution at neutral pH. When mixed with Hanford tank waste simulant containing 0.47 M hydroxide, and a mixture of noble metals (Pt, Pd, Rh, Ru), without organic complexants, it decomposed in 50 days. Higher hydroxide concentrations caused faster decomposition. Adding gluconate into the simulant with 0.47 M hydroxide and the noble metals slowed the decomposition to 78 days. Complexing the $Tc(CO)_3^+$ with IDA in a 5 M $NaNO_3$ solution and 0.1 M hydroxide exhibited 25% decomposition in 4 months. Substituting gluconate instead of IDA in this matrix exhibited 100% decomposition in 72 days. Substituting NTA, EDTA, or DTPA caused more rapid decomposition. This indicates that of those complexants tested, IDA is the best at stabilizing the Tc(I) carbonyl.

Additional testing was done by Hall et al., to examine the stability of the $Tc(CO)_3^+$ that was formed by mixing pertechnetate with a tank waste simulant and reacted using the 1,300 psi carbon monoxide/75 ppm hydrogen mixture and catalytic noble metals.[xi] Four tests listed below varied these reaction conditions:

(1) When gluconate was added to this mixture during the reaction at 1,300 psi, > 90% of the Tc was reduced to a variety of reduced Tc species, including the Tc(I)-tricarbonyl gluconate species as well as paramagnetic (NMR silent) species which could be Tc (II, IV, and/or VI). Electron Paramagnetic Resonance (EPR) spectra support a Tc(II) or Tc(VI) species, with the Tc(IV) being less likely. NMR measurements over time found that 62% of these compounds decomposed to pertechnetate in one year.

(2) When the reaction was performed with gluconate but without the catalytic metals, no Tc(I) was formed, but the solution was 100% soluble and pink in color. The NMR/EPR results indicated that the product was either Tc(II) or Tc(VI), and 25% remained as pertechnetate. NMR in-growth indicated that only ~20% of this mixture decomposed to pertechnetate in one year.

(3) When the gluconate was excluded, 72% of the pertechnetate converted to Tc(I) carbonyl, 16% formed an unknown species that was inactive to the NMR instrument that was either in the liquid or solid phase, and 12% remained as pertechnetate. Ninety percent of the Tc in the mixture decomposed to pertechnetate in one year.

(4) When no gluconate and no noble metals were added during the carbon monoxide/hydrogen reaction, 7% remained as pertechnetate, 11% converted to Tc(I), and 82% converted to an NMR inactive liquid or solid phase. In 49 days, NMR indicated that 100% of the Tc(I) decomposed to pertechnetate, but 55% of the total remained as the NMR inactive species after 200 days.

Overall, these results indicate that under these extreme conditions of 1,300 psi of carbon monoxide/75 ppm of hydrogen, even without organic complexants, pertechnetate can form a range of reduced Tc species that are surprisingly resistant toward re-oxidation to pertechnetate.

Medical research has developed synthetic routes to create Tc-tricarbonyl species with the application of gas at atmospheric pressure. Alberto et al. first accomplished this in 0.9 wt% NaCl (isotonic) solution using pertechnetate, sodium borohydride (a strong reducing agent), pH 11, atmospheric pressure carbon monoxide, and a temperature of 75 °C for half an hour.[xiii] Using the rhenium analog, this chemistry also rapidly produced rhenium tricarbonyl species from perrhenate at pH 7.4 in less than 10 minutes. In later work, Alberto et al. found that crystalline potassium boranocarbonate can be added to directly convert pertechnetate to Tc(I) tricarbonyl.[xiv] The later work also discusses various means to synthesize the boranocarbonate salt reagent. The work suggests applying it with borax as a suitable pH buffer and also with tartarate as a stabilizing complexant. While these conditions are not comparable to tank wastes, it does indicate that production of the Tc-tricarbonyl species is relatively easy when specific boron-bearing reagents are applied under simple and controlled conditions.

In strongly alkaline solution, the thermodynamically favored Tc species is pertechnetate.[xv] The presence of low valent Tc species in tanks indicates that there is a reductive chemical environment at some state of the waste processing and/or storage as experienced at Hanford. One possible mechanism for reducing conditions is due to radiolysis, which generates e_{aq}^-. However, Shuh et al. states that the presence of high concentrations of nitrate ion consume the e_{aq}^-, preventing it from reducing Tc(VII).[xvi] Similarly, the report states that the Tc(VII) cannot be reduced at a reasonable rate by organic radicals due to their high reactivity with nitrite ion. The report further indicated that it is unlikely that the primary radiolysis products directly reduce Tc(VII). Also, in alkaline solution in the absence of stabilizing ligands, such as diolates, the primary radiolysis product is insoluble $TcO_2 \cdot xH_2O$. Depending on what other organic chemicals were present, the ligands can scavenge oxidizing radicals and thereby prevent them from re-oxidizing Tc, or they can become oxidizing themselves and oxidize the reduced Tc. It is not plausible to predict the outcomes without detailed mechanistic studies. Methanol and ethanol had high yields of Tc reduction, but acetate had very low yields. These observations indicate acetate had produced an oxidizing radical, but these were in the absence of other quenching species, such as nitrite. Tests of Tc reduction during radiolysis with complexants (NTA and IDA) and sodium nitrate in alkaline solution was much higher than in the absence of nitrate, indicating a possible mechanism where TcO_4^- is reduced by the radiolysis product NO_3^{2-}.[xvi] High concentrations of nitrate caused the highest rate of reduction of TcO_4^-, but how this would translate into the overall reactivity in actual tank waste, where other redox-active species are present and oxidizing species would re-oxidize the reduced Tc, is not known.

A3. Non-Pertechnetate and Grout

Testing has been performed by Serne et al. that examines the leaching performance of a grout waste form containing BFS and a simulant of Hanford tank waste containing a synthesized Tc(I) tricarbonyl gluconate species.[xvii] The cured waste form was subjected to leaching tests. Results indicated that the samples that contained the Tc(I) had ~10X higher Tc leaching than those prepared using pertechnetate. The report states that the results indicate that some reaction chemistry is occurring, i.e., the Tc(I) is not just completely unaffected by the grouting process and remaining entirely soluble. However, it is not known what Tc species is actually leaching or exactly what is happening at the molecular level. It was acknowledged that other impurities and precursor reagents were present in the synthesized Tc(I) tricarbonyl gluconate spike that was used in the test, which may have affected the outcome. Overall, results are consistent with the expectation that reduced, complexed forms of Tc would have different sequestration behavior compared to pertechnetate. The authors describe further work that is needed to improve understanding of the release of contaminants from grout waste forms. Although not identified by the authors, preparation of the simulant in these experiments yielded a composition that is not directly comparable to other tests, but would have been self-consistent within the test matrix in those tests that compared the non-pertechnetate to pertechnetate leaching behavior. Therefore, it is also advisable that the work be repeated using a simulant prepared using standard protocols to generate a known composition so that it can be compared to other work.

No testing results have been found that used actual Hanford tank waste samples with measured amounts of non-pertechnetate made into grout waste forms. Only one report of a grouted waste form produced with Hanford tank waste (Tank 241-AP-102) was found,[xviii] and this preceded identification of non-pertechnetate so it was not measured. The grout formulation did not include BFS, containing only Portland cement, attapulgite clay, and fly ash. Results indicate the leachable Tc was ~1E-7 M, which is slightly higher than the typical range of solubility of $TcO_2 \cdot 1.6H_2O$, for the measured pH range of 9 - 11. However, this would be expected given the absence of BFS and the use of aerobic test conditions.

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