Tin(II)apatite: Synthesis, Characterization, and Challenge with Pertechnetate - 16194

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ABSTRACT

We will report on the synthesis of stannous apatite and the subsequent reductive capacity attained, using a cerium (IV) titration method. Also reported will be the distribution coefficients derived using a Hanford tank supernatant simulant of 7.8 M sodium with chrome (VI) as a contaminant of concern, as a potential non-isotopic oxyanion and technetium surrogate for reductive capacity determinations. Pertechnetate will be subjected to reduction using hydroxylamine, glucose and threose. The purpose is to take the first step in laboratory analyses to determine the amount of non-pertechnetate species in Hanford tank waste. A proposed sequestration mechanism will be presented as to why the reacted tin(II)apatite does not release technetium once reacted. SEM and EDS spectra will be presented on the crystalline apatite. Areas of incorporation of the tin(II)apatite will be presented for the Hanford tank waste process.

INTRODUCTION

This study is part of the technetium management initiative to provide data for the safe handling and disposition of technetium in Hanford tank waste treatment.

Technetium (Tc-99) is a major fission product from nuclear reactors, and because it has few applications outside of scientific research, most of the technetium will ultimately be disposed of as nuclear waste. The radioactive decay of Tc-99 to ruthenium 99 (Ru-99) produces a low energy β^- particle (0.1 MeV max). However, due to its fairly long half-life (t1/2 = 2.13E05 years), Tc-99 is a major source of radiation in low-activity waste [1].

Technetium forms the soluble oxy anion pertechnetate (TcO_4^-) under aerobic conditions. This anion, which is very mobile in groundwater, poses a health risk [2]. Several reports have been published on the mobility of the pertechnetate ion in the environment. For example, Tc-99 has been shown to increase in the western Irish Sea as a direct result of the increases in discharge of Tc-99 from the Sellafield reprocessing site. During the period of 1996 to 1998, the mean committed effective doses to Irish typical and heavy seafood consumers due to Tc-99 were 0.061 µSv (0.0061 mrem) to 0.24 µSv (0.024 mrem) respectively. Technetium-99 emanates from the Enhanced Actinide Removal Plant at Sellafield which removes actinides but is ineffective at removing Tc-99 [3]. In a study by the International Atomic Energy Agency, it was reported that very mobile radionuclides such as technetium have a soil to plant transfer factor of 100 or greater. The soil to plant transfer factor (dimensionless) is defined as the ratio of the activity concentration of the radionuclide in the plant (Bq/kg) to that in the soil (Bq/kg). Furthermore, it was reported that technetium is very mobile in the

soil and may be subject to considerable migration to deeper soil layers [4].

Technetium, with a half life of 2.13×10^5 years, has been identified as one of the significant radiological risk drivers in the Tank Closure and Waste Management Final Environmental Impact Statement [5]. The risk is based upon the high mobility through the soil and contamination of the groundwater. The mobility of the technetium species is predicated upon its valence state. In the +7 state, technetium exists as pertechnetate (TcO_4^-), in a lower valence state, +4 it exists as a solid precipitate (TcO_2). Technetium exists in other valence states that have been reported and those valence states are predicated upon the ligand associated with technetium [6]. Researchers have also reported that non pertechnetate species exist in the Hanford tanks [7]. Schroeder, et al., stated that ~70% of the technetium species in the 101-SY and 103-SY samples sent to Los Alamos was not pertechnetate. Furthermore, the authors state that oxidation of these non pertechnetate forms is not readily achieved. The problem is significant because it may affect the feasibility of separating technetium from tank waste. Table I lists tanks known to contain non-pertechnetate.

TABLE I. Tanks Known to Contain Non-Pertechnetate

Tank	Report	Cited Non-pertechnetate (%)	Known Complexants
AN-102	King, et al. [8]	~70	Yes
AN-107	Kurath, et al. [9]	75 - 80	Yes
SY-101	Schroeder, et. al. [7]	63 +/- 16	Yes
SY-103	Schroeder, et. al. [7]	70 +/- 25	Yes
AW-101	Blanchard, et al. [10]	15 - 25	No
AN-103	Hassan, et al. [11]	2.3 to 8	No

The Hanford Waste Treatment Plant (WTP) does not contain technetium removal in the pretreatment flow sheet, indicated that within the WTP immobilization plant, the technetium will partition between both the high level waste (HLW) and low activity waste (LAW) fractions of the tank waste. In both facilities, technetium is incorporated into the glass form, however a significant fraction of the technetium volatilizes at the glass melting temperatures and is captured in the off gas treatment systems at both facilities [12]. Vitreous State University, has indicated that a high per cent of the technetium escaping the melter is captured in the off gas treatment system composed of the submerged bed scrubber and wet electrostatic precipitator. Single pass technetium retention averaged approximately 35%, however recycle of the off gas treatment stream will significantly increase the

technetium retention [13]. There are issues around the recycle of the off gas treatment stream. Specifically, the recycle disproportionately increases the sulfur and halides in the melter feed, which increases both the amount of the glass and either the duration of the vitrification mission or would require supplemental capacity [12].

The RJ Lee Group, Inc., and Sandia National Laboratories have collaborated for several years on the development and evaluation of the efficacy of the apatite radionuclide interactions. Specifically, Sandia National Laboratories has formulated a process to synthesize apatite *in situ* for the interception of strontium-90 at Hanford N-springs [14]. The apatite barrier successfully met and exceeded the treatment target of 90% reduction before reaching the Columbia River [15]. Sandia National Laboratories has met with success in using the apatite for a number of applications, one of which is the addition of stannous (tin II) to the apatite lattice (patent applications filed). The apatite lattice is composed of $Ca_{10}(PO_4)_6(OH)_2$, the addition of the tin(II) atom replaces a portion of the calcium, yielding tin(II)apatite. The role of synthesizing an apatite with tin (II), is that the tin (II) serves to reduce the pertechnetate to a solid non-mobile technetium dioxide as shown in Figure 1 [16]. Simply reducing technetium will not inhibit reoxidation. When waste forms contain ferrous (+2) state, the technetium will be reduced. However, once the iron has been converted to the ferric (+3) state, technetium will begin to leach out of the waste form. The use of apatite minerals, which have been found stable on a geological time scale may well hold the answer to sequestering the nonpertechnetate Tc-99 form the environment [17]. Work carried out by Savannah River National Laboratories showed the efficacy of using tin(II)chloride to reduce pertechnetate and identified the importance of the apatite in the role of sequestering the technetium from being reoxidized [18].

The pertechnetate tin(II)apatite reaction is quite rapid, and we have shown that it appears to be an exchange reaction with the phosphate. The technetium apatite complex does not easily allow the technetium to return to the mobile pertechnetate state. We have washed the technetium apatite complex with 0.01 M nitric acid as well as sparged air in a water column with the apatite complex over six weeks with no release of technetium [19].

Fig. 1. Technetium dioxide (black precipitant) in groundwater brine simulant

Moore, et al., demonstrated a significant effect of the apatite when coupled with a reductant such as tin(II)chloride, as shown in Figure 2 [20]. It appears as if it is a two-step process; 1) reduction and 2) incorporation or formation of an insoluble apatite technetium compound.
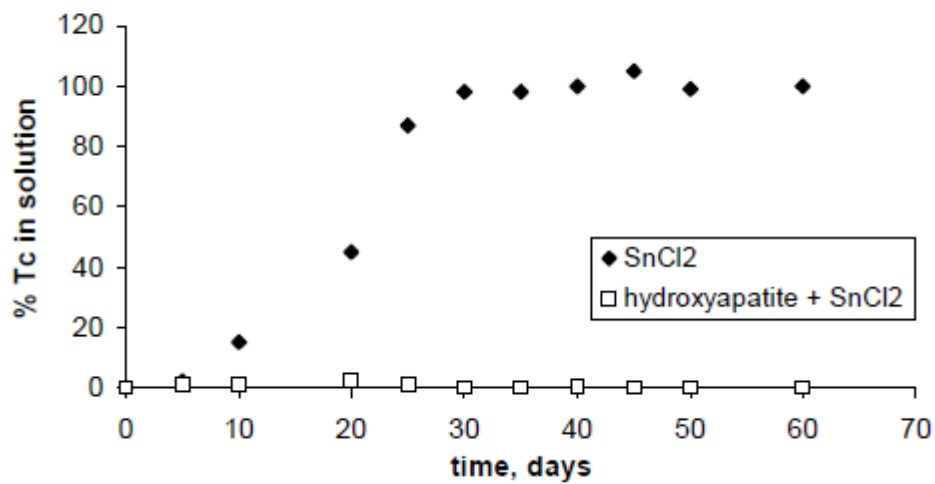

Fig. 2. Effect of tin(II)chloride and tin(II)chloride plus hydroxyapatite on technetium concentration

There are many reductants that will reduce the pertechnetate (+7) to a lesser valence state, however the apatite achieves sequestering the Tc-99 in the lower valence state.

The distribution coefficients of the tin(II)apatite are shown in Table II over a pH range of 1.3 to 11.4 [19].

TABLE II. Distribution Coefficients for Tin(II)apatite Challenged with Pertechnetate

pH	Distribution Coefficient, Kd mL/g
11.4	65,669
10.2	170,900[a]
8.5	170,900[a]
2.5	170,900[a]
1.3	6,059
[a]The results were below the detection limit of the ICP-MS, therefore the lower detection limit was used to calculate the Kd.	

Researchers have identified that redox conditions play an important part in the retardation of mobility of the pertechnetate species [21, 22]. Capitalizing upon the redox conditions and using tin(II)apatite, further work has demonstrated that pertechnetate is reduced to the non-mobile TcO_2 species. It was also demonstrated that technetium-loaded tin(II)apatite achieves a leachability index in Cast Stone of 12.8 [16, 23]. The mechanism appears to be an exchange with the phosphate group in the apatite molecule. It has been reported that the apatite lattice is very tolerant to substitutions [24, 25].

MATERIALS AND METHODS

Characterization of Tin(II)apatite

The tin(II)apatite was synthesized as reported earlier [26]. Figure 3 shows an scanning electron microscope image of a cluster of the tin(II)apatite synthesized lattices. Figure 4 shows an energy dispersive spectroscopy scan of the tin(II)apatite lattice from Figure 3. Figure 5 shows the X-ray diffraction pattern.
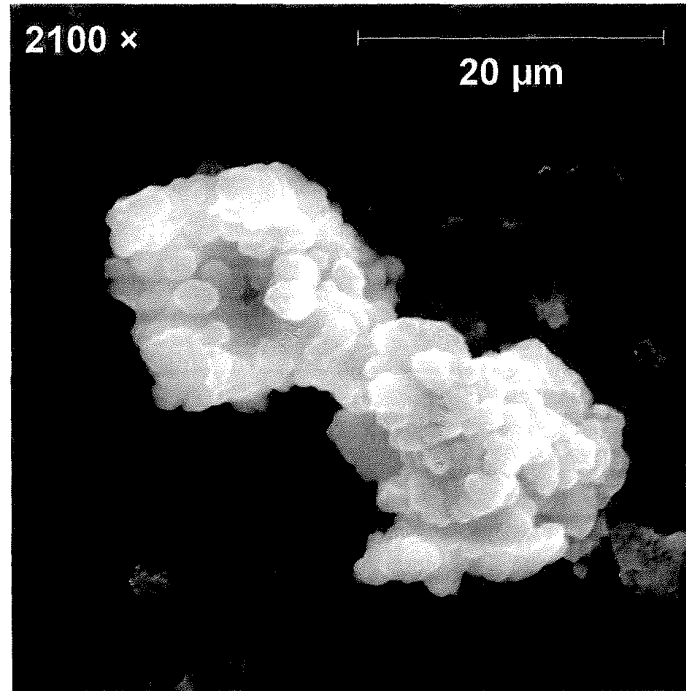
Fig. 3. Scanning Electron Microscope Photo of Synthesized Tin(II)apatite
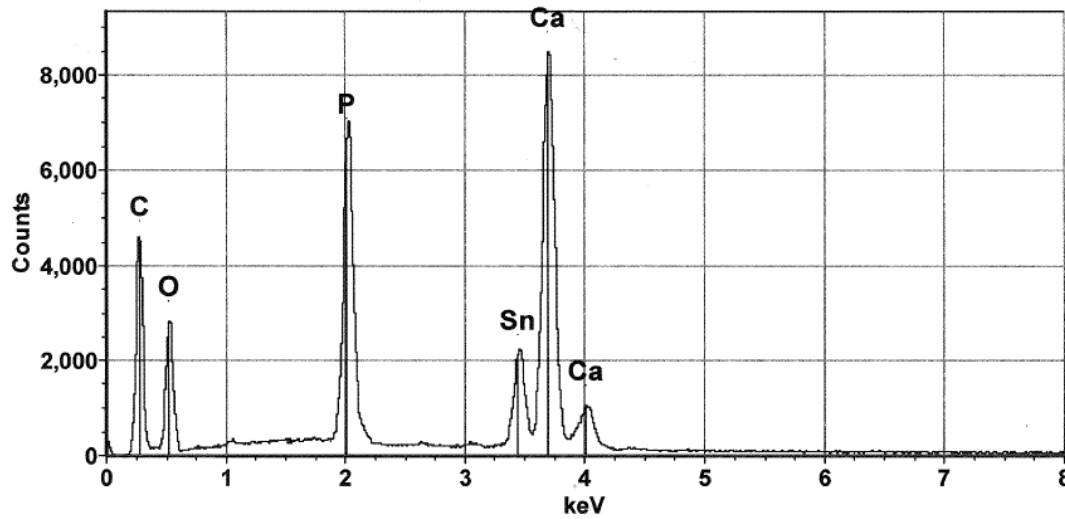

Fig. 4. Energy Dispersive Spectroscopy Scan of the Tin(II)Apatite shown in Fig. 1.

MooreSnII-apatite - File: MooreSnII-apatite.raw - Type: 2Th/Th locked - Start: 10.000 ° - End: 90.000 ° - Step: 0.020 ° - Step time: 10. s - Temp.: 25 ℃
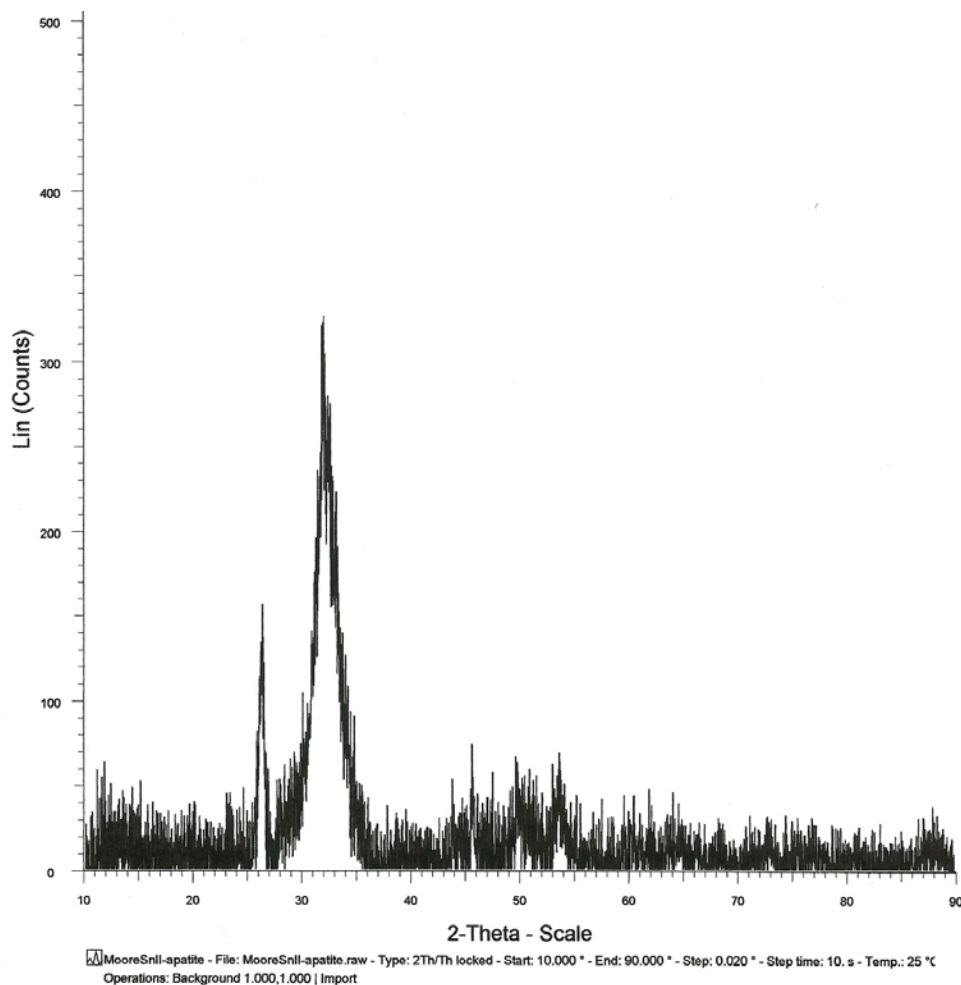Operations: Background 1.000,1.000 | Import

Fig. 5. X-ray Diffraction Pattern of the Tin(II)Apatite Formulation

The tin(II)apatite was digested and submitted for analysis by inductive couple plasma optical emission spectroscopy. The elemental results are shown in Table III.

TABLE III. ICP-OES Analysis of Tin(II)Apatite

Analyte	Result (mg/g)
Ca	211
P (PO4)	68 (214)
Sn	99

Reductive capacity was determined by the method described by Roberts and Kaplan [27]. The determination of reductive capacity was as follows: The tin(II)apatite was sampled and divided, half was titrated the other half was dried in a 110 ^{o}C oven for moisture determination. The tin(II)apatite for titration was weighed and

placed into a 250 mL Erlenmeyer flask, 25.0 mL of 0.05 N Ce(IV) was added using a volumetric pipette. The solution was allowed to mix using a stir bar for 30 minutes, or until well dispersed. The solution was then titrated against 0.05 M ferrous ammonium sulfate. The reducing equivalents were then calculated against the oxidizing equivalents of Ce(IV).

The tin(II)apatite was determined to have a reductive capacity of 5.2E-03 M e^-/g. The sample was split and sent to PNNL and SRNL for further experiments with pertechnetate.

Distribution Coefficient

Table II above, shows the distribution coefficients at various pH levels. One of the questions around the use of Tc-99 and the determination of distribution coefficients: is there a surrogate that is able to be used to determine Kd's without the use of pertechnetate and a radiological use license. To that end, Cr(VI) was used in a single shell tank blend saltcake simulant of 7.8 M sodium formulation [28], Table IV.

To determine the distribution coefficient (on a dry weight basis), the following equation was used:

$$Kd = ((C_o - C_f)/C_f)*(V/M) \qquad\qquad \textbf{Eqn 1}$$

Where:

Kd = distribution coefficient
C_o = initial concentration
C_f = final concentration
V = volume of the liquid (mL)
M = dry weight mass of the tin(II)apatite

TABLE IV. Formula for the 7.8 M Sodium Simulant

Analyte		7.8 M Na Target Mass
KNO_3		5.17
NaCl		3.85
KF^a		5.44
Na_2SO_4		18.95
$Al(NO_3)_3 \cdot 9H_2O$		179.54
$NaNO_3$		88.70
NaOH (50% solution)^b		347.81
$Na_3PO_4 \cdot 12H_2O$		29.18

Analyte		7.8 M Na Target Mass
NaCH3COO•3H2O		8.14
Na2CO3•H2O		53.03
NaNO2		60.80
	COCs	
Na2CrO4•4H2O		5.00
[a] KF was substituted for NaF; 5.44 g was used to maintain the fluoride concentration.		
[b] 50% NaOH is formulated at 174g H_2O to 174 g NaOH		
Specific gravity of the 7.8 M solution was 1.32; pH		

Table V shows the Cr(VI) distribution coefficients on a dry weight basis. The conclusion is that Cr(VI) is not a good surrogate for pertechnetate at high pH using tin(II)apatite. The question remains unanswered at lower pH levels. It is noteworthy that the solution, whether the pH level, or the ionic strength did decrease the Kd for Cr(VI) somewhat substantially.

TABLE V. Chrome(VI) Distribution Coefficients

Tin(II)Apatite				
Condition	Wet Weight	Dry Weight	Kd (Cr(VI))	Kd (TcO4)
7.8M w/Cr	3.7959	3.0026	7,959	703 (pH 12.5)
DI w/Cr(VI)	3.7895	2.9975	13,234	

Conversion of pertechnetate to non pertechnetate

The scope of this task is to delineate a laboratory technique to quantify the partitioning of technetium between the pertechnetate and non-pertechnetate species in the Hanford tanks. It has been known that there are non pertechnetate species in the Hanford tanks (Schroeder, et al.).

The procedure for removing technetium from Hanford tanks is ion exchange of pertechnetate (TcO_4^-), the most thermodynamically stable of the technetium
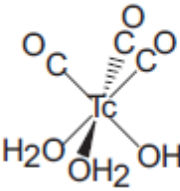
species. While ion exchange is effective for many tanks, it fails for the complexant concentrate (CC) waste tanks and any tanks containing organic complexants such as nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), citrate, and gluconate [29]. Table VI list Hanford tanks known to contain non pertechnetate.
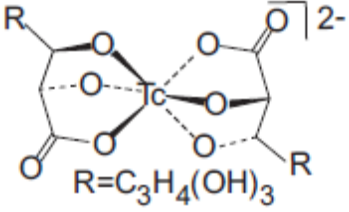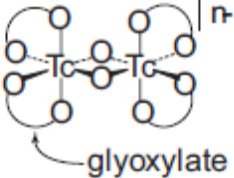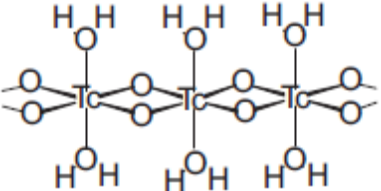
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TABLE VI. Tanks Known to Contain Non-Pertechnetate

Tank	Report	Cited Non-pertechnetate (%)	Known Complexants
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AN-103	Hassan, et al. [11]	2.3 to 8	No

Species that have been identified are shown in Table VII ("Identification of the Non-Pertechnetate Species in Hanford Waste Tanks, Tc(I)-Carbonyl Complexes," [6].

TABLE VII. Non-Pertechnetate Species of Technetium Identified in Hanford Tanks

Structure	Name
	Tc(I) carbonyl complex (stable neutral complex) fac-Tc(CO)$_3$(H$_2$O)$_2$(OH) fac refers to the ligands (CO) being mutually in a cis configuration rather than coplanar.

Structure	Name
	Tc(IV)gluconate (soluble)
	Tc(IV)glyoxylate - 30% present as monomeric species (soluble)
	Non soluble $TcO_2 \cdot 2H_2O$

Once it was established that the technetium was in the Tc(VII) valence state, which is the oxyanion state of pertechnetate, the next step was to reduce the pertechnetate to a lower valence state. Previous work at the 222-S laboratory using Aliquot[1] 336 and TEVA[2] resin (LAB-RPT-13-00009 R0) demonstrated that the TEVA® is a candidate for the uptake of pertechnetate, but it is unknown how non pertechnetate species will behave in this media. It is known that the Purolite® A530E is highly specific to pertechnetate. Therefore, the A530E™ sorbent was chosen to capture pertechnetate.

The matrix used was the 5 M Na Hanford Tank Operator Waste System (Table VIII) with slight modification from PNNL-22352 [28].

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[1] Aliquat 336 is a registered trademark of BASF, Ludwigshafen, Germany.
[2] TEVA is a registered trademark of Eichrom Technologies, Inc., Lisle, Illinois.

TABLE VIII. Hanford Tank Operator Waste System Average 5 M Na Simulant

Compound	5 M Na Simulant, Amount (g/L)
KNO_3	3.31
NaCl	2.47
NaF	1.33
Na_2SO_4	12.15
$Al(NO_3)_3*9H_2O$	115.09
$NaNO_3$	56.86
NaOH (50% solution)	222.96
$Na_3PO_4*12H_2O$	18.70
$NaCH_3COO-3H_2O$	5.22
$Na_2CO_3*H_2O$	33.99
$NaNO_2$	38.97
NaI	0.012
$Na_2Cr_2O_7*2H_2O$	3.20

Berning, et al., reported the auto reduction of pertechnetate using reducing sugars threose and glucose [29]. In addition, hydroxylamine was incorporated as it has been shown to reduce pertechnetate in alkaline conditions [30].

With the exception of threose, the first round used 1 M solutions of the glucose and hydroxylamine. The threose did not solubilize from the container and was not used. A second round was planned using 2 M each of glucose and hydroxylamine. The threose was input at 0.8 mM. This was due to budget constraints, as a mole of threose is quite expensive. However, the glucose and hydroxylamine are known to reduce pertechnetate. Table IX shows the ppm converted from an initial concentration of 824 mg/L pertechnetate, based on a standard curve using counts versus concentration, R^2 = 0.9998.

TABLE IX. Conversion of Pertechnetate to Non Pertechnetate

Reductant	Amount converted (mg/L)	Per Cent Conversion Co = 824 mg/L	Solution Color
Run 1 without threose			
Hydroxylamine, 1 M	333	40	Red
Glucose, 1 M	329	39	Green
Run 2 with threose			
Hydroxylamine, 2M	262	32	Red
Glucose, 2M	247	30	Green
Threose, 0.8 mM	2	0.2	Pink

Although the threose did not return the same conversion as Bering reported, it is not that surprising as the researchers used 1 M ligands.

The solutions were allowed to remain in 250 mL poly bottles in a hood at ambient temperatures.

After approximately eight weeks, the second run was recounted by the Ludlum[3], the results are shown in Table X.

TABLE X. Non Pertechnetate After Eight Weeks

Reductant	Amount converted (mg/L)	Initial Per Cent Conversion	Per Cent Non-Pertechnetate Remaining from C_0 = 824 mg/L
Hydroxylamine, 2M	294	32	36[a]
Glucose, 2M	94	30	11
Threose, 0.8 mM	0	0	0
[a] The hydroxylamine differences are assumed to be within experimental error and therefore essentially the same. That is, the hydroxylamine is the most stable reductant.			

It would appear that the ligands of glucose and possibly threose (which cannot be determined as the molarity was very low and below that of the pertechnetate) allow reoxidation. The hydroxylamine appears to have increased by approximately 12%. This is most probably with in experimental pipetting error.

Since non pertechnetate standards are not available for analytical work, the use of the Purolite® A530E is a definite candidate for a laboratory separation of pertechnetate and from other technetium species and hence an estimate of non pertechnetate species in the Hanford Tanks..

Areas of incorporation into Hanford tank waste treatment

A conceptual schematic for the high level off gas treatment is shown in Figure 6. The off gas condensate will emanate from three unit operations: The submerged bed scrubber, the wet electrostatic precipitator, and the high efficiency mist eliminator. The condensate will be collected in a tank and fed to a unit operation such as a continuous stirred tank reactor (CSTR). At the CSTR tin(II)apatite will be introduced and a filtration step will occur to collect the technetium apatite complex for inclusion into cast stone.

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[3] Ludlum is a trademark of Ludlum Measurements, Inc., Sweetwater, Texas.
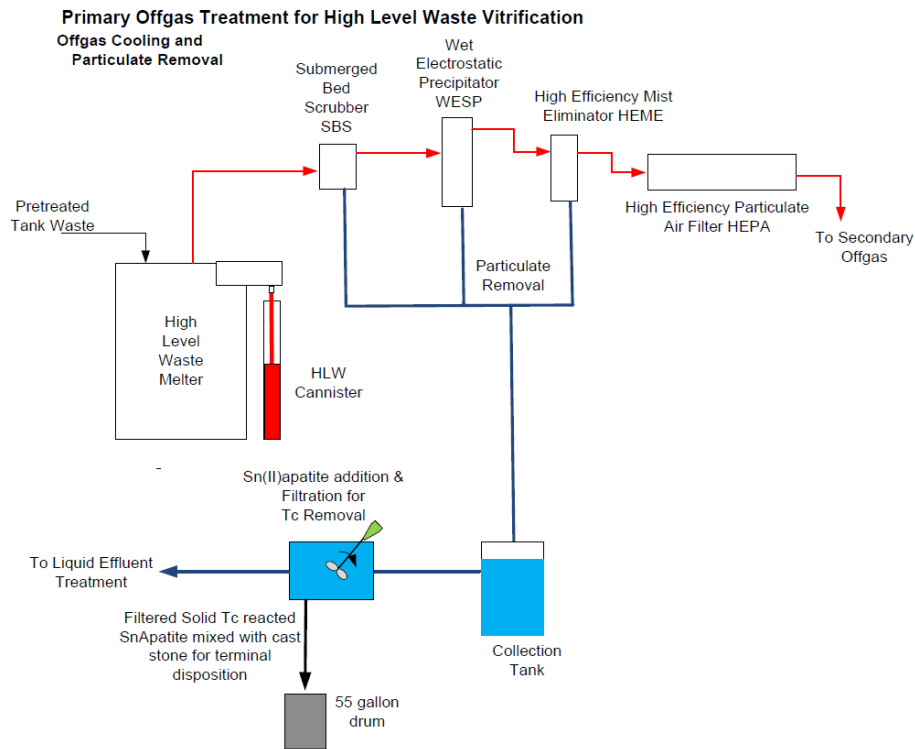
Fig. 6. Primary Off Gas Treatment of High Level Waste Vitrification

For the LAW vitrification process, Figure 7 illustrates two cases where technetium may be intercepted during pretreatment. In both cases, solids removal will be carried out, otherwise the first ion exchange vessel would foul and plug. In Case 1, only the isotopic cesium would be removed and the stream would go directly to LAW vitrification. The technetium, thought to be predominately in the pertechnetate state (TcO_4^-) would be intercepted in a similar manner as in the high level waste vitrification schematic in Figure 6. In Case 2, the pertechnetate would be intercepted using a resin such as SuperLig® 639 before the melter, backwashed and contacted with the tin(II)apatite then sent to terminal disposal. In Case 2, for supplemental (low temperature) LAW processing, by eliminating the isotopic cesium and capturing the technetium with tin(II)apatite, and grouting; the technetium waste form may indeed be better than glass.
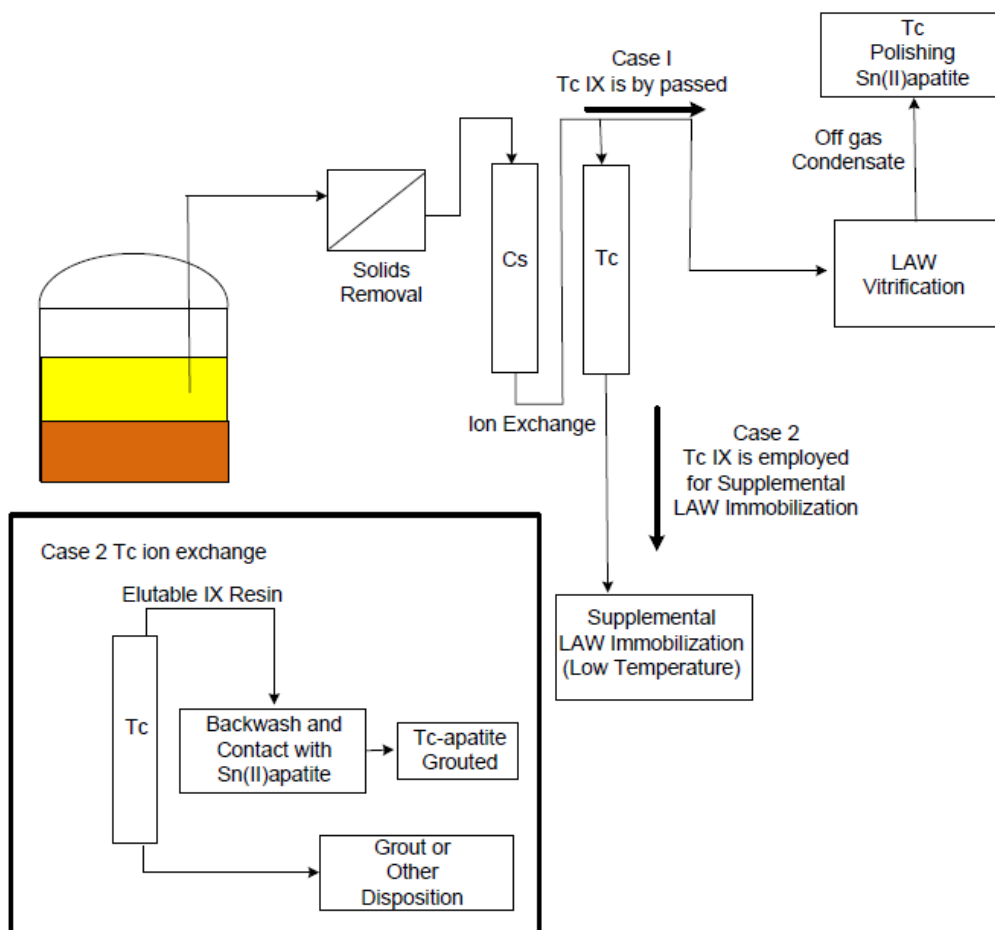
Fig. 7. Technetium Interception for Low Activity Waste Vitrification

By reducing pertechnetate and sequestering the technetium from reoxidation it is possible to immobilize the radioisotope on a geologic time frame and allow enough half lives for technetium-99 to transmute to the stable ruthenium-99 state.

RESULTS

Tin(II)apatite

The formulation and synthesis for the tin(II)apatite has not been optimized, nor have the conditions for storage been investigated – shelf life, anoxic conditions, UV sensitivity, etc. However, the "long term" storage of the material synthesized in

It is apparent that the tin(II)apatite has shown affinity for the reduction of oxyanions such as pertechnetate and chromate. However, to use a surrogate, such as chromate for the reductive capacity of tin(II)apatite does not appear to be feasible without a statistically defensible correlation.

The area of pertechnetate reduction and the subsequent sequesterization has not been fully investigated. For example, due bone scan tests, the Tc-99 metastable is introduced with a reductant and finds its way into the apatite structure of the human bone at a reduced valence state. Taking this concept one step forward, it may be possible to introduce a reductant in line before a static in-line mixer, and expose the reduced Tc to apatite in a continuous stirred tank reactor (CSTR) as indicated in Figure 6. The CSTR effluent would then be filtered and the captured material grouted.

Reduction of pertechnetate

It has been shown that the pertechnetate can be reduced and this was verified by the Purolite® A530E not sorbing the compound into the matrix. It is suggested that the Purolite® A530E be used in the analyses of Tc for Hanford tanks, in that technetium in the effluent that passes the A530E will be of a non pertechnetate species.

Total technetium may be determined by ICP-MS (using a reaction cell). Another analysis by ICP-MS (using a reaction cell) of tank waste passed through A530E would indicate non pertechnetate levels. Then total technetium is equal to non pertechnetate plus pertechnetate.

The question of the non pertechnetate being recalcitrant to oxidation to Tc(VII) has yet to be answered. This is mainly due to the unavailability of non pertechnetate standards. The above reduction method(s) and confirmation by A530E would allow for reoxidation experiments.

DISCUSSION

Tin(II)apatite shows much promise as a terminal waste form for the reduction and sequesterization of technetium from previous work reported in this paper. There are optimization steps which still need to be investigated, for example:

- Optimization of the formulation
- Optimization of drying
- Optimization of storage
- Shelf life determination
- Can a reductant be used separate from tin(II) and achieve the same effects
- Maximizing grout loading before structural integrity is compromised.

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