Assessment of Technetium Leachability in Cement-Stabilized Basin 43 Groundwater Brine

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U.S. Department of Energy Contract DE-AC27-08RV14800

EDT/ECN: DRF

UC:

Cost Center: 2EK00

Charge Code:

B&R Code:

Total Pages: 29 ^{mw} 7/24/09

Key Words: pertechnetate, technetium, leachability, groundwater brine, cementitious waste, AMSI Leach Index, TCLP Leach, Tin Appetite, solid waste form.

Abstract: This report documents the effort to sequester technetium by the use of getters, reductants (tin(II)apatite and ferrous sulfate), sorbents (A530E and A532E ion exchange resins), and cementitious waste form. The pertechnetate form of technetium is highly soluble and mobile in aerobic (oxidizing) environments.

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Release Approval

7/20/2009
Date

Release Stamp

Approved For Public Release

Tank Operations Contractor (TOC) RECORD OF REVISION		(1) Document Number: RPP-RPT-39195		Page 1
(2) Title: Assessment of Technetium Leachability in Cement Stabilized Basin 43 Groundwater Brine				
Change Control Record				
(1) Revision	(4) Description of Change – Replace, Add, and Delete Pages	Authorized for Release		
		(5) Resp. Engr. (print/sign/date)	(6) Resp. Mgr. (print/sign/date)	
1 RS	This revision incorporates new data obtained under subcontract 21065, release 30 from the RJ Lee Group, Inc., Center for Laboratory Sciences (CLS). The data has been analyzed, subjected to quality control and quality assurance by WRPS scientists. The new data has been accepted and is incorporated in this revision.	James Duncan- 7/21/09	Cary Seidel- 7/21/09	

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Date Published
July 2009

Prepared for the U.S. Department of Energy
Office of River Protection

Contract No. DE-AC27-^{08RD14800}~~99RL14047~~ mw
7/20/09

EXECUTIVE SUMMARY

The pertechnetate form of technetium is highly soluble and mobile in aerobic (oxidizing) environments. When pertechnetate is reduced from the TcO_4^- valence state (+7) to the form TcO_2 valence state (+4), it becomes non-mobile and desirable for cementitious waste forms.

This report documents the effort to sequester technetium by the use of getters, reductants (tin(II)apatite and ferrous sulfate), sorbents (A530E and A532E ion exchange resins), and cementitious waste form.

The test matrix was a brine solution of approximately 25 weight percent mimicking the anticipated Basin 43 waste from the Effluent Treatment Facility, and is based on data obtained from wells 299-W11-45 and 299-W11-46.

Conclusions from this effort and supported in this document are the following:

- a. Calcium-phosphate-based getters are not effective in reducing the mobile pertechnetate in matrices of high salt concentration.
- b. Adjusting the oxidation-reduction potential to reduce pertechnetate is effective in reducing the pertechnetate species to the technetium dioxide species.
- c. Encapsulation in a reducing cementitious waste form provides good retention of technetium.
- d. Tin(II)apatite and sorbents (ion exchange resins) are effective in substantially decreasing the mobility of pertechnetate in high salt and alkaline matrices.
- e. Leachability indices greater than 12 are attainable with a combination of tin(II)apatite and cementitious monoliths.

It was beyond the scope of this effort to investigate the effect oxidizing materials in cementitious waste forms exposure to the atmosphere through cracks and fissures has on the re-oxidation of technetium dioxide to pertechnetate with and without an added reductant such as tin(II)apatite.

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Acronyms

ANSI	American National Standards Institute
CLS	RJ Lee Group, Inc., Center for Laboratory Sciences
EPA	U.S. Environmental Protection Agency
GWBS	groundwater brine simulant
ICP-MS	inductively coupled plasma-mass spectrometry
LOQ	limit of quantification
ORP	oxidation-reduction potential
TCLP	Toxicity Characteristic Leaching Procedure

1. INTRODUCTION

This report presents the final group of data subjected to quality control and quality assurance collected from the laboratory effort executed under RPP-PLAN-33338, Rev. 1A, *Test Plan for the Assessment of Technetium Leachability in Cement-Stabilized Basin 43 Groundwater Brine*. This report delineates data obtained under subcontract 21065, release 30 from the RJ Lee Group, Inc., Center for Laboratory Sciences (CLS), which has been analyzed and accepted. The report is predicated on the data generated by CLS and contained in the CLS report in Appendix A.

2. MATERIALS AND METHODS

This section describes the activities around the Basin 43 Groundwater simulant (referred hereafter as simulant), testing of technetium getters, cement matrix, U.S. Environmental Protection Agency (EPA) SW-846 Method 1311, "Toxicity Characteristic Leaching Procedure" (TCLP), and ANSI/ANS-16.1, *Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-term Test Procedure*. The results are reported in Section 3.

2.1 SIMULANT FORMULATION

The simulant used is shown in Table 1. The simulant is concentrated brine consisting of approximately 25 weight percent salts.

**Table 1. Simulant Formulation for
Basin 43 Evaporated Groundwater**

Reagent	Gram/Liter
NaNO ₃	140.7948
MgSO ₄	19.6177
AlCl ₃	0.1337
KCl	2.7886
BaCl ₂	0.0235
NaF	1.4126
CaCl ₂	7.9349
Na ₂ CrO ₄	0.1424
Ca(OH) ₂	5.5384
Ca(NO ₃) ₂	42.3001
NaHCO ₃	37.8555
Total	258.5422

The simulant used was formulated to match the anticipated Basin 43 waste from the Effluent Treatment Facility and is based on data obtained from wells 299-W11-45 and 299-W11-46.

2.2 TECHNETIUM GETTERS/REDUCTANTS

The technetium getters initially chosen for the effort were identified in RPP-RPT-26742, *Hanford Containerized Cast Stone Facility Task 1 – Process Testing and Development Final Test Report*. The initial technetium getters are presented in Table 2.

Table 2. Candidate Technetium Stabilizers

Material	Source
Getters	
Bone black	Ebonex
PIIM ¹ S (fish bone fines)	UFA Ventures
Reductants	
Ferrous sulphate 1M	Fisher Scientific ¹
Iron powder (Fe ⁰), ~325 mesh	Fisher Scientific ¹
Sodium metabisulfite	Effluent Treatment Facility
Tin(II)apatite	Moore 2003 ²
Iron(III) phosphate	Alfa Aesar ³
Ion Exchange	
A530-E	Purolite ⁴
A532-E	Purolite ⁴

The sodium metabisulfite was discarded due to the deleterious effect on the chrome passivating layer in 304 and 316L stainless steel leaving it vulnerable to corrosion processes.

2.3 EXPERIMENTAL DESIGN AND RESULTS

Figure 1 shows the Pourbaix diagram indicating that the TcO₂ species is attainable at a potential of approximately -400 mV (SHE) and a pH of approximately 12.

Table 3 shows the experimental matrix used during the experiment

Table 4 shows the results from the inductively coupled plasma mass spectrometry (ICP-MS) analyses of the test solutions in conditions outlined in Table 3.

¹ Fisher Scientific is a trademark of the Fisher Scientific Company, Pittsburgh, Pennsylvania.

² "Sorption of Tc by Sn(II) Treated Apatite Draft Letter Report, Sandia National Laboratories."

³ Alfa Aesar is a trademark of Johnson Matthey Public Limited Company, London, United Kingdom.

⁴ Purolite is a trademark of the Brotech Corporation, Cynwyd, Pennsylvania.

Figure 1. Potential-pH Diagram for the System Technetium-Water at 25 °C from Pourbaix **Table 3. Experimental Design Matrix**

Getters (0.25 gm in 25-mL Basin 43 simulant; 0.293 mg ⁹⁹ Tc)	Sn(II)Apatite (0.01, 0.1, 1.0 g each in 25-mL Basin 43 simulant; 0.293 mg ⁹⁹ Tc)	Resin (0.01, 0.1, 1.0 g each in 25-mL Basin 43 simulant; 0.293 mg ⁹⁹ Tc)
Challenged at pH 5-6 with 0.29 mg ⁹⁹ Tc	Challenged at pH 5-6	Challenged at pH 5-6
Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis
Adjust to pH 12, adjust oxidation reduction potential (ORP) to -400 mV challenge	Adjusted to pH 12, no ORP adjustment	Adjusted to pH 12, no ORP adjustment
Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis	Rotomixed for ~12 hours; aliquot withdrawn for analysis

**Table 4. Inductively Coupled Plasma-Mass Spectrometer Analyses,
Technetium Reductant/Absorbent Efficiency
Study Solutions for Technetium**

Sample ID	pH	⁹⁹ Tc $\mu\text{Ci/L}$	Result	Conc. in GWBS	Percent ⁹⁹ Tc ⁷⁺
			[⁹⁹ Tc ⁷⁺] ppm*	⁹⁹ Tc ⁷⁺ ppm	Mobile
⁹⁹ Tc control average	5-6	151	8.9	10.6	84
⁹⁹ Tc control average	12	133	7.8	10.6	74
FeSO ₄ (1M solution), ORP adjusted	12	3	0.17	10.6	2
Bone black	5-6	145	8.5	10.6	80
Bone black	12	156	9.2	10.6	87
Bone black, ORP adjusted	12	2	0.13	10.6	1
Fishbone	5-6	146	8.6	10.6	81
Fishbone	12	150	8.8	10.6	83
Fishbone, ORP adjusted	12	2	0.12	10.6	1
Fe ⁰ powder	5-6	136	8	10.6	75
Fe ⁰ powder	12	150	8.8	10.6	83
Fe ⁰ powder, ORP adjusted	12	1	0.086	10.6	1
Iron III phosphate	5-6	151	8.9	10.6	84
Iron III phosphate	12	116	6.8	10.6	64
Iron III phosphate, ORP adjusted	12	7	0.42	10.6	4
⁹⁹ Tc control average	5-6	204	12	12.0	100
⁹⁹ Tc control average	12	204	12	12.0	100
Sn(II)apatite, 0.01g	5-6	145	8.5	12.0	71
Sn(II)apatite, 0.1g	5-6	111	6.5	12.0	54
Sn(II)apatite, 1.0g	5-6	44	2.6	12.0	22
Sn(II)apatite, 0.01g	12	112	6.6	12.0	55
Sn(II)apatite, 0.1g	12	65	3.8	12.0	32
Sn(II)apatite, 1.0g	12	9.2	0.54	12.0	5
A530-E, 0.01g	5-6	187	11	12.0	92
A530-E, 0.1g	5-6	65	3.8	12.0	32
A530-E, 1.0g	5-6	7.3	0.43	12.0	4
A530-E, 0.01g	12	158	9.1	12.0	76
A530-E, 0.1g	12	49	2.9	12.0	24
A530-E, 1.0g	12	5.8	0.34	12.0	2.8
A532-E, 0.01g	5-6	155	9.1	12.0	78
A532-E, 0.1g	5-6	36	2.1	12.0	18
A532-E, 1.0g	5-6	3.9	0.23	12.0	1.9
A532-E, 0.01g	12	107	6.3	12.0	53
A532-E, 0.1g	12	24	1.4	12.0	12
A532-E, 1.0g	12	2.6	0.15	12.0	1.3

* Specific activity value of 0.017 Ci/g was obtained from Idaho Department of Environmental Quality fact sheet on technetium (IDEQ 2001).

GWBS = groundwater brine simulant

Since the groundwater brine simulant (GWBS) contained hexavalent chromium, an analyses of the reduction by Sn(II)apatite and adsorption by the ion exchange resins was carried out. The results are presented in Table 5.

Table 5. Inductively Coupled Plasma-Mass Spectrometer Analyses of the Sn(II)Apatite and Ion Exchange Resin Efficiency Study for Chromium

Sample ID	pH	ICP-MS Result [Cr] ppm	ICP-MS Expected [Cr] ppm	Percent Cr Mobile
Sn(II)apatite, 0.01 g	5-6	22	37	59
Sn(II)apatite, 0.1 g	5-6	15	37	41
Sn(II)apatite, 1.0 g	5-6	5.3	37	2.7
Sn(II)apatite, 0.01 g	12	18	37	49
Sn(II)apatite, 0.1 g	12	10	37	27
Sn(II)apatite, 1.0 g	12	1.4	37	3.8
A530-E, 0.01g	5-6	36	37	97
A530-E, 0.1 g	5-6	32	37	86
A530-E, 1.0 g	5-6	20	37	54
A530-E, 0.01g	12	31	37	84
A530-E, 0.1 g	12	32	37	86
A530-E, 1.0 g	12	23	37	62
A532-E, 0.01g	5-6	36	37	97
A532-E, 0.1 g	5-6	26	37	70
A532-E, 1.0 g	5-6	32	37	86
A532-E, 0.01g	12	27	37	73
A532-E, 0.1 g	12	29	37	78
A532-E, 1.0 g	12	30	37	81

2.4 CEMENTITIOUS MATRIX

The samples containing getters, reductant, and resin were cast in the grout formulation 8A, specified in RPP-PLAN-33338. However, the presence of excess bleedwater and poor setting strengths led to modifications of the formula. Table 6 presents the original proposed formula and the modification that allowed for less bleedwater and a firmer set. The modified formula was employed for monolith casing. The cement samples were cured for a 28-day period before final leach testing.

Table 6. Grout Formulation for Monoliths

Material	RPP-RPT-33338, Rev. 1A	Monolith Casting
Brine:solids ratio	1.3:1	1.1:1
Basin 43 waste	100 g	110 g
Portland cement	38.5 g	66.64 g
Blast furnace slag	38.5 g	33.36 g

The monoliths were cured in a drying oven set at 54 °C for the first 3-4 days and then removed and allowed to cure adiabatically for the remainder of the 28 days. At the conclusion of the cure period, the monoliths were removed from the casting vessels.

Tables 7, 8, and 9 show the casting conditions of the reductants, absorbents, and getters with and without oxidation-reduction potential (ORP) adjustment.

Table 7. Monolith Formulation: Technetium-99 Reductants/Absorbents, without Oxidation-Reduction Potential Adjustment

Material	Cold Blank (g)	⁹⁹ Tc Control (g)	Fish Bone (g)	Iron ⁰ Powder (g)	Bone Black (g)	Iron ³⁺ Phosphate (g)	Hydrotalcite (g)
Basin 43 Groundwater brine Batch 1 (1.16 ppm ⁹⁹ Tc)	NR	109.71	110.00	110.09	110.02	110.00	66.0065
Portland cement	33.34	66.612	66.63	66.60	66.60	66.675	39.99
Blast furnace slag	16.7047	33.37	33.29	33.34	33.31	33.33	19.99
Reactant	0	0	10.01	10.00	10.01	10.00	6.05
Total grams	NR	209.692	219.93	220.03	219.94	220.01	132.0365
Final concentration ⁹⁹ Tc ppm	NA	0.61	0.58	0.58	0.58	0.58	0.58
Number of TCLP casts (6/24/08)	2	2	2	2	2	2	2
Number of ANSI/ANS-16.1 casts (6/24/08)	2	2	2	2	2	2	2

NR = Not Recorded

NA = Not Applicable

Table 8. Monolith Formulation: Technetium-99 Reductants/Absorbents with Oxidation-Reduction Potential Adjustment

Material	Cold Blank (g)	⁹⁹Tc Control (g)	Fish Bone (g)	Iron⁰ Powder (g)	Bone Black (g)	Iron³⁺ Phosphate (g)	Hydrotalcite (g)
Basin 43 Groundwater brine Batch 2 (1.23 ppm ⁹⁹ Tc)	NR	110.01	110.05	110.02	110.01	110.01	NA
Portland cement	NR	66.62	66.62	66.6	66.61	66.63	NA
Blast furnace slag	NR	33.31	33.32	33.3	33.3	33.03	NA
Reactant	NR	0	10.02	10.01	10.02	10.04	NA
Total grams	NR	209.94	220.01	219.93	219.94	219.71	NA
Final concentration ⁹⁹ Tc ppm	NA	0.64	0.62	0.62	0.62	0.62	NA
Number of TCLP casts (6/24/08)	2	2	2	2	2	2	NA
Number of ANSI/ANS-16.1 Casts (6/24/08)	2	2	2	2	2	2	NA

Table 9. Monolith Formulation: Sn(II)Apatite and Resin Technetium-99 Reductants/Absorbents

Material	Cold Blank (g)	⁹⁹Tc Control (g)	Sn(II) Apatite (g)	Sn(II)Apatite Duplicate (g)	Resin A530-E (g)	Resin A532-E (g)
Basin 43 Groundwater brine Batch 1 (1.34 ⁹⁹ Tc ppm)	110.16	109.99	110.07	110.28	110.66	110.12
Portland Cement	66.64	66.65	66.63	66.6	66.60	66.61
Blast furnace slag	33.41	33.4	33.41	33.4	33.41	33.41
Reductant/absorbent	0	0	3.278	3.274	2.162	1.71
Total grams	210.21	210.04	213.388	213.55	212.832	211.85
Final concentration ⁹⁹ Tc ppm	0	0.71	0.70	0.70	0.70	0.70
Number of TCLP casts (9/02/08)	2	2	2	2	2	2
Number of ANSI/ANS-16.1 Casts (9/02/08)	2	2	2	2	2	2

2.4 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

Method 1311 was carried out on the cured samples. At the conclusion of the 28-day cure period, the monoliths identified for TCLP analysis were crushed in their casting vessels to <3/8-inch grain size in accordance with Method 1311. Each monolith yielded ~ 40-50 g of sample, which was added to 800-1000 g of TCLP extraction fluid 2 (glacial acetic acid at pH of 2.88), and then subjected to continuous rotation at 30 ± 2 rpm for 18 ± 2 hours. The leached portions continued to be subjected to the acetic acid environment for an additional 24 hours prior to the removal of aliquots for ICP-MS preparation and analysis via EPA Method 3005A, "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy," and EPA Method 200.8, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry."

The resultant leachate was analyzed for technetium using an ICP mass spectrometer. Tables 10 and 11 present the TCLP data from the candidate getters, reductants, and ion exchange resins.

**Table 10. Method 1311, Toxicity Characteristic Leaching Procedure
Inductively Coupled Plasma-Mass Spectrometry Data**

⁹⁹ Tc Reductants/Absorbents in Leached Monolith	Average ⁹⁹ Tc Concentration (ppm)	⁹⁹ Tc Spiked Concentration (ppm)	Average ⁹⁹ Tc (ppm) ⁷	Percent ⁹⁹ Tc Leached ⁸
⁹⁹ Tc control	0.0070	0.65	0.0083	22
ORP adjusted (1M FeSO ₄)	0.012	0.64	0.012	36
Fishbone	0.009	0.58	0.0091	31
Fishbone, ORP adjusted	0.012	0.61	0.012	38
Iron ⁰ powder	0.004	0.58	0.0037	12
Iron ⁰ powder, ORP adjusted	0.010	0.61	0.013	33
Bone black	0.011	0.58	0.011	38
Bone black, ORP adjusted	0.012	0.61	0.012	40
Iron ³⁺ phosphate	0.012	0.57	0.012	42
Iron ³⁺ phosphate, ORP adjusted	0.011	0.62	0.011	35
Hydrotalcite	0.017	0.57	0.017	59

Notes:

Average ⁹⁹Tc activity is determined by the ICP-MS concentration (mg/L) multiplied by the ⁹⁹Tc specific activity (0.017 Ci/gm).

Monoliths were not spiked with additional chromium. The monolith chromium concentration is a byproduct of the GWBS 35 ppm chromium concentration.

Table 11. Method 1311, Toxicity Characteristic Leaching Procedure Inductively Coupled Plasma-Mass Spectrometry Data

⁹⁹ Tc Reductant or Absorbent in Leached Monolith	Average Total Cr Concentration (ppm)	⁹⁹ Tc Spiked Conc. (ppm)	Initial Cr Conc. (ppm)	Average ⁹⁹ Tc Conc. (ppm)	Average ⁹⁹ Tc Activity μ Ci/L	Percent ⁹⁹ Tc Leached	Percent Cr Leached
Sn(II)apatite, 1.0 g	0.012	0.69	18	0.0029	0.05	8.4	1.2
A530-E	0.020	0.69	18	0.0025	0.043	7.3	2.2
A532-E	0.021	0.70	18	0.0021	0.036	6.0	2.4

Note:

Average ⁹⁹Tc activity is determined by the ICP-MS concentration (mg/L) multiplied by the ⁹⁹Tc specific activity (0.017 Ci/gm).

2.5 AMERICAN NATIONAL STANDARDS INSTITUTE LEACH PROCEDURE

The ANSI leaching process was conducted according to the method ANSI/ANS-16.1-2003.

The monoliths produced for the ANSI/ANS-16.1 leach test are cylindrical and on average 3.5 cm in height with a diameter of 2.9 cm. The surface area (S) is 45.1 cm². The volume of deionized water necessary for leaching the monoliths as described in the method is 451 $\pm$ 90.2 ml as determined by

$$VL \text{ (cm}^3\text{)}/S \text{ (cm}^2\text{)} = 10 \pm 0.2 \text{ (cm)}.$$

A clean 500-ml Teflon^{®5} jar fitted with a screened dipper and lid was used for each leaching test. These vessels permitted the monolith to be submerged and suspended in the water column with minimal surface occlusion. To control for potential evaporation, the vessels were securely capped during each leaching interval.

At the conclusion of the 28-day cure period, the monoliths selected for ANSI/ANS-16.1 testing were removed from the cure vessels as a solid cylinder. Every effort was made to ensure the integrity of the entire monolith. The leaching procedure as described by ANSI/ANS-16.1 requires use of deionized water as the extraction medium. A sample of each leaching solution was drawn off immediately following the leach interval end time. The monolith was then resubmerged in a fresh deionized water bath.

All ANSI-16.1 leachates were analyzed by ICP-MS for ⁹⁹Tc. The Sn(II)apatite and resin bead agent leachates were also analyzed for chromium content. The results for each reductant/absorbent at each leaching interval are presented in Table 12 for ⁹⁹Tc. The leachability index was calculated based on the average of the two sample analyses for each reductant/absorbent at each leaching interval for ⁹⁹Tc. The leachability index spreadsheets for each reductant/absorbent are compiled in the CLS report in Appendix A. All data points

⁵ Teflon[®] is a registered trademark of I. E. du Pont de Nemours and Company, Wilmington, Delaware.

less than the analytical limit of quantification (LOQ) were entered into the leachability index calculations as equal to the LOQ. The LOQ for ^{99}Tc was 5×10^{-5} ppm and for chromium was 1×10^{-2} ppm. The resulting indices are therefore conservative in nature.

Table 12. ANSI/ANS-16.1 Technetium-99⁷⁺ Concentrations for the Seven Leaching Periods for all Reductants/Absorbents

Monolith Description	Rinse	2 Hr (ppm)	5 Hr (ppm)	17 Hr (ppm)	24 Hr (1) (ppm)	24 Hr (2) (ppm)	24 Hr (3) (ppm)	24 Hr (4) (ppm)
^{99}Tc control #1 average	Not analyzed	1.3E-03	8.0 E-05	2.3 E-04	2.2 E-04	6.0 E-05	4.4 E-04	1.5 E-04
Fishbone average	Not analyzed	7.9E-04	2.2 E-04	6.0 E-04	5.5 E-04	3.7 E-04	4.0 E-04	3.3 E-04
Iron ⁰ powder average	Not analyzed	3.7E-04	2.4 E-04	4.8 E-04	3.6 E-04	1.8 E-04	2.7 E-04	2.1 E-04
Bone black average	Not analyzed	2.3 E-04	7.1 E-05	1.1 E-04	1.1 E-04	6.3 E-05	1.3 E-04	9.8 E-05
Iron III phosphate average	Not analyzed	2.1 E-04	1.0 E-04	2.1 E-04	1.9 E-04	6.3 E-05	1.5 E-04	1.0 E-04
Hydrotalcite	Not analyzed	1.9 E-04	1.1 E-04	4.4 E-04	4.5 E-04	2.3 E-04	3.2 E-04	2.8 E-04
Fishbone, ORP adjusted average	Not analyzed	2.0 E-04	1.2 E-04	2.6 E-04	2.7 E-04	8.5 E-05	2.0 E-04	1.3 E-04
Bone black, ORP adjusted average	Not analyzed	1.2 E-04	8.2 E-05	1.6 E-04	1.6 E-04	6.3 E-05	1.3 E-04	6.5 E-05
Iron ⁰ powder, ORP adjusted average	Not analyzed	9.7 E-05	7.2 E-05	1.5 E-04	1.4 E-04	6.3 E-05	1.3 E-04	5.3 E-04
Iron III Phosphate, ORP adjusted average	Not analyzed	1.1 E-04	7.4 E-05	1.3 E-04	1.3 E-04	6.3 E-05	9.5 E-05	1.3 E-04
^{99}Tc ORP adjusted average	Not analyzed	9.2 E-05	8.2E-05	1.6 E-04	1.5 E-04	6.3 E-05	8.5 E-05	6.3 E-05
^{99}Tc control #2 average	6.1E-05	6.3 E-04	4.2 E-04	7.3 E-04	5.6 E-04	3.2 E-04	2.1 E-04	1.9 E-04
Sn II apatite	5.0E-05	5.0 E-05	5.0 E-05	5.0 E-04	8.6 E-04	6.0 E-05	5.0 E-05	7.8 E-05
Purolite® resin A530-E	5.0E-05	8.5E-05	6.4 E-05	1.5 E-04	1.4 E-04	6.9 E-05	5.0 E-05	7.3 E-05
Purolite® resin A532-E	6.9E-05	7.1 E-05	5.8 E-05	1.1 E-04	1.1 E-04	5.0 E-05	5.0 E-05	5.8 E-05

The chromium concentration in the Sn(II)apatite and resin ^{99}Tc reductant/absorbent leachates exhibited little variation between the individual agents and leaching periods. The concentrations of chromium are less than the LOQ (0.001 ppm). For this reason, the leachability index for each individual reductant/absorbent was not calculated. A leachability index of 10.6 is obtained by using 0.001 ppm as the leaching concentration (based on the

chromium LOQ). Given that most concentrations were less than the LOQ, the leachability index may be higher with an increased analytical sensitivity.

The initial monolith rinses were conserved and analyzed for the Sn(II)apatite and resin ^{99}Tc reductant/absorbent monoliths only. The leachability indices for the samples without rinsate analysis are therefore not adjusted for the potential reduction in the source term that these rinses would have been used to calculate. The amount of reduction in the source term for these conserved and analyzed rinses was observed to be negligible. Figure 2 shows that less than 0.1% by weight technetium is removed by the rinse. The full analytical reports from each leaching period are available in Appendix A.

Figure 2. Percent of Total Technetium-99 Removed by the ANSI-16.1 Rinse Step

3. RESULTS

Due to the experimental protocols carried out by the CLS, it was not possible to delineate a distribution coefficient for tin(II)apatite. Although distribution coefficients were not carried out in the present study, "Sorption of Tc by Sn(II) Treated Apatite Draft Letter Report, Sandia National Laboratories" (Moore 2003), reported distribution coefficients with tin(II)apatite of 475,000 to 3,202,100 ml/g in a groundwater matrix and 5140 to 4890 ml/g in a concentrated sodium salt solution (2003). The tin(II)apatite was successful in reducing the pertechnetate to technetium dioxide as evidenced by the black precipitant (Figure 3) and substantially decreasing the mobile technetium species.

As indicated in Table 4, the ORP adjusted samples reduced the mobile technetium substantially, approaching two orders of magnitude. In a mixture of hexavalent chromium the tin(II)apatite was effective in reducing the mobile hexavalent chromium (see Table 5).

Although there are no regulatory drivers for the determination of technetium using the TCLP, a TCLP was carried out to provide an indication of the percent of technetium that would be leached in the procedure. Tables 10 and 11 show the values obtained with the TCLP. Both the tin(II)apatite and the ion exchange resins were most successful in retarding the movement of technetium (see Figure 4).

**Figure 3. Technetium Dioxide (black precipitant)
in Groundwater Brine Simulant**

**Figure 4. Percent Technetium Leached During
Toxicity Characteristic Leaching Procedure**

The most important test carried out in the course of this study is the ANSI/ANS-16.1 leach test. As indicated in Figure 5, the highest leach index (LI = 12.7) was obtained using tin(II)apatite reacting with the pertechnetate then incorporating into the cementitious waste form. The calculated index is the negative logarithm of the measured effective diffusivity of the radioisotope; therefore, a larger LI indicated less of the isotope has leached during the procedure.

Figure 5. Leachability Index of Non-Oxidation-Reduction Potential Adjusted Cementitious Waste Forms

If future studies are to be carried out, at a minimum the following should be incorporated:

- Understanding of the fundamental of the Tc (VII) reduction and association with tin(II)apatite; chemisorption or physisorption.
- Determine distribution and selectivity coefficients in matrices of concern.
- Formulate cement and determine leaching for addition waste brine compositions.
- Extend ANSI/ANS-16.1 leach index determinations to longer time periods.
- Examine the effect of aging, curing, cracking, and fissuring of cementitious waste forms on the re-oxidation of technetium dioxide.
- Examine initial and leached cementitious waste forms using scanning electron microscopy to determine failure modes.

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