PNNL-26730
RPT-DVZ-AFRI-038 Rev 0.0

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

The Evaluation of Novel Tin Materials for the Removal of Technetium from Groundwater

June 2017

KE Parker
DM Wellman

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract **DE-AC05-76RL01830**

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

PNNL-26730

RPT-DVZ-AFRI-038 Rev 0

The Evaluation of Novel Tin Materials for the Removal of Technetium from Groundwater

KE Parker
DM Wellman

June 2017

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Technetium-99 (^{99}Tc) is present at several U.S. Department of Energy (DOE) facilities, including the Hanford, Oak Ridge, Paducah, Portsmouth, and Savannah River sites.[1] Due to its mobility, persistence, and toxicity in the environment,[2] developing means to immobilize and/or remove technetium from the environment is currently a top priority for DOE. However, there are currently very few approaches that effectively manage the risks of technetium to human health and the environment. The objective of this study is to evaluate novel synthetic materials that could enable direct removal of technetium from groundwater. The following report

- assesses the viability of existing methodologies for synthesis of tin (II) apatite for in situ formation and remediation of ^{99}Tc within the subsurface environment
- discusses the development of alternative methodologies for production of tin (II) apatite
- evaluates nanoporous tin phosphate materials for removal of technetium from groundwater.

---

[1] DOE. 2009. “Groundwater contamination and treatment at Department of Energy Sites. *In* O.o.E.a. Technology (ed.), Washington, D.C.

[2] Wildung RE, KM McFadden, et al. 1979. “Technetium sources and behavior in the environment,” *Journal of Environmental Quality* 8:156-161.

Acknowledgments

This document was prepared by the Deep Vadose Zone-Applied Field Research Initiative at Pacific Northwest National Laboratory. Funding for this work was provided by the U.S. Department of Energy Richland Operations Office. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the Department of Energy (DOE) under Contract DE-AC05-76RL01830.

The authors wish to thank Jarod Crum for the XRD and EDS analysis of the tin (II) apatite.

Acronyms and Abbreviations

CAWSRP	*Conducting Analytical Work in Support of Regulatory Programs*
CERCLA	*Comprehensive Environmental Response Compensation and Liability Act*
DIW	deionized water
DOE	U.S. Department of Energy
DVZ-AFRI	Deep Vadose Zone – Applied Field Research Initiative
EDS	energy dispersive spectroscopy
EPA	U.S. Environmental Protection Agency
ESL	Environmental Sciences Laboratory
HASQARD	*Hanford Analytical Services Quality Assurance Requirements Document*
ICP-MS	inductively coupled plasma mass spectrometer
K_d	distribution coefficient(s)
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
SEM	scanning electron microscope
XRD	X-ray diffraction

Contents

Figures

Tables

1.0 Introduction

Technetium-99 (^{99}Tc) is present at several U.S. Department of Energy (DOE) facilities, including the Hanford, Oak Ridge, Paducah, Portsmouth, and Savannah River sites (DOE 2009). Technetium-99 is of environmental concern due to its long half-life (2.1×10^5 years), toxicity, and mobility in the environment (Wildung et al. 1979). However, there are currently very few approaches to immobilize and/or remove technetium from the environment, and it is currently a top priority for DOE. The objective of this study is to evaluate novel synthetic materials that could enable direct removal of technetium from groundwater.

2.0 Quality Assurance

The Pacific Northwest National Laboratory (PNNL) Quality Assurance (QA) Program is based upon the requirements as defined in DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, E*nergy/Nuclear Safety Management*, Subpart A, Quality Assurance Requirements (a.k.a. the Quality Rule). PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.
- ASME NQA-1-2000, Part II, Subpart 2.7, Quality Assurance Requirements for Computer Software for Nuclear Facility Applications, including problem reporting and corrective action.
- ASME NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The procedures necessary to implement the requirements are documented through PNNL’s “How Do I?” (HDI), a system for managing the delivery of laboratory-level policies, requirements, and procedures.

The DVZ-AFRI Quality Assurance Plan is the minimum applicable QA document for all Deep Vadose Zone – Applied Field Research Initiative (DVZ-AFRI) projects. This QA Plan also conforms to the QA requirements of DOE Order 414.1D and 10 CFR 830, Subpart A. The DVZ-AFRI is subject to the *Price Anderson Amendments Act*.

The implementation of the DVZ-AFRI QA Program is graded in accordance with NQA-1-2000, Part IV, Subpart 4.2.

The following technology levels are defined for this DVZ-AFRI QA Program:

- Basic Research consists of research tasks that are conducted to acquire and disseminate new scientific knowledge. During basic research, maximum flexibility is desired to give the researcher the latitude to conduct the research.
- Applied Research consists of research tasks that acquire data and documentation necessary to ensure satisfactory reproducibility of results. The emphasis during this stage of a research task is on achieving adequate documentation and controls necessary to be able to reproduce results.
- Development Work consists of research tasks moving toward technology commercialization. These tasks still require flexibility and uncertainty still exists in many cases. The role of quality in

development work is to make sure that there are adequate controls to support movement into commercialization.

Research and development support activities are those that are conventional and secondary in nature to the advancement of knowledge or development of technology, but allow the primary purpose of the work to be accomplished in a credible manner. An example of a support activity is controlling and maintaining documents and records. The level of quality for these activities is the same as for developmental work.

Within each technology level, the application process for QA controls is graded such that the level of analysis, extent of documentation, and degree of rigor of process control are applied commensurate with their significance, importance to safety, life-cycle state of a facility or work, or programmatic mission. The work for this report was performed under the technology level of Basic Research.

The project used PNNL's Environmental Sciences Laboratory (ESL) for chemical analyses required as part of laboratory and field experiments and testing. The ESL operates under a dedicated QA plan that complies with the *Hanford Analytical Services Quality Assurance Requirements Document* (HASQARD) (DOE/RL-96-68). ESL implements HASQARD through *Conducting Analytical Work in Support of Regulatory Programs* (CAWSRP). Data quality objectives established in CAWSRP were generated in accordance with HASQARD requirements. Chemical analyses of testing samples and materials were conducted under the ESL QA plan.

3.0 Methods and Materials

Table 3.1 lists the chemicals used in the synthesis of Sn (II) apatite and nanoporous tin phosphate.

Table 3.1. List of Chemicals

Chemicals	Manufacturer
Sodium phosphate, dibasic, anhydrous	Mallinckrodt, Paris, KY
Tin (II) chloride, dihydrate	Alfa Aesar, Ward Hill, MA
Calcium chloride, dihydrate	Fisher, Fairlawn, NJ
Ammonium hydroxide reagent	Acros, NJ
Hydrochloric acid	Fisher, Fairlawn, NJ
Hydroxyapatite	Aldrich, St. Louis, MO
Hydrazine hydrate	Acros, NJ
Cetyltrimethylammonium chloride, 25%	Aldrich, St. Louis, MO
Phosphoric acid	Fisher, Fairlawn, NJ

3.1 Characterization

3.1.1 X-ray Diffraction

X-ray diffraction (XRD) is a commonly used technique for identifying crystalline minerals in a sample. Before mounting, a representative sample of the bulk material was ground, using an agate mortar and pestle, to improve the diffraction patterns. XRD data of the tin (II) apatite were obtained at 40 kV and 40 mA, using a Bruker D8 Advance (Madison, WI) automated powder diffractometer configured with

Brag-Brentano optics and a copper target, Cu $K\alpha = 1.54$ Å. The sample was analyzed over the 2-theta (2θ) range from 5-90°, using a step size of 0.015° 2θ and a 1- to 2-second step time.

3.1.2 Scanning Electron Microscope and Energy Dispersive Spectroscopy

The samples were mounted to an aluminum stub using double-sided carbon tape. The samples were evaluated with a JEOL 7001F field emission gun microscope in low vacuum conditions (27 Pa) to avoid sample charging. Photomicrographs were obtained with a backscattered electron imaging detector. The beam conditions were 8 kV acceleration with a probe size of 10. The images from the scanning electron microscope (SEM) were acquired using JEOL software PC-SEM version 2.1.0.9. Elemental analysis was collected on a Bruker X-Flash 6-60 silicon drift energy dispersive spectrometer, and the data were quantified using Bruker software Quantax version 2.0.3.15222.

3.2 Tin (II) Apatite Synthesis

To synthesize tin (II) apatite, the procedure described by Duncan et al. (2012) was initially used. Interested readers should review the cited reference; but briefly, solutions of Na_2HPO_4 and $CaCl_2$ are prepared and pH adjusted with NH_3OH. After preparing the $SnCl_2$ solution, 1 mL hydrazine is added. The solutions are mixed together in a reactor containing boiled deionized water (DIW) and hydrazine, and sparged with nitrogen. The solution pH and temperature are maintained at 7.4±0.2 and 37°C, respectively. After 3 days of mixing, the solids are filtered and dried at 50°C under nitrogen. The solids are ground under liquid nitrogen using a mortar and pestle.

3.3 Development of Alternate Tin (II) Apatite Synthesis

As discussed in detail below, several technical issues were encountered while trying to replicate the procedure of Duncan et al. (2012). As such, an alternate synthesis approach was developed here. This procedure is referred to as Parker 2017a and is shown below.

Note: The Sn (II) must be kept from oxidizing during synthesis by keeping all oxygen out of the system.

1. Bring 2 L of DIW to a boil for 30 minutes and continuously sparge with 99.99% pure nitrogen. Allow the water to cool and add 1 L to the reactor. Sparge the boiled water in the reactor with nitrogen. Mix the water in the reactor at 100 rpm.

2. While sparging with nitrogen, prepare 250 mL of 1.0 M Na_2HPO_4 in DIW and adjust the pH to 7.3+0.1 with concentrated HCl. Seal the container to prevent the solution from contacting oxygen. If the solution is not used within 12 hours, verify the pH and adjust as necessary. Sparge the solution with nitrogen during the pH adjustment.

3. While sparging with nitrogen, prepare 250 mL of 1.38 M $CaCl_2$ in DIW and adjust the pH to 7.3+0.1 with 0.25 M NH_3OH. Seal the container to prevent the solution from contacting oxygen. If the solution is not used within 12 hours, verify the pH and adjust as necessary. Sparge the solution with nitrogen during the pH adjustment

4. Heat the water in the reactor to 37°C and continue to sparge with nitrogen.
5. While sparging with nitrogen, prepare 250 mL of 0.4 M $SnCl_2$ in DIW. Do not adjust the pH. Seal the container to prevent the solution from contacting oxygen.
6. Verify that the water in the reactor is at 37°C before adding the reagents. Continuously monitor and maintain the temperature of the reactor.
7. Add 4 mL of hydrazine to the reactor.
8. Stir the reactor at 100 rpm and add each reagent simultaneously at a rate of 1 to 2 mL/min (Total flow = 3 to 6 mL/min).
9. The pH of the solution in the reactor must be maintained at 7.3+0.1. During the first 8 hours, adjust the pH continuously with concentrated NH_3OH as required.
10. Continue to sparge the solution with nitrogen, maintain the pH at 7.3 +0.1 and temperature at 37°C, and stir the solution for 3 days.
11. Filter the tin (II) apatite using a Buchner funnel and 1 µm filter paper. Wash the solids with boiled and nitrogen sparged DIW at least three times.
12. Transfer the solids to a beaker and place the tin (II) apatite in a vacuum desiccator at room temperature. After 3 to 4 days, obtain a small sample of the tin (II) apatite and weigh. Return the sample to the desiccator and store under vacuum. After 24 hours, weigh the sample again to verify the solids are dry. Repeat until a constant weight is obtained.
13. When the solids are dry, grind the tin (II) apatite using an agate mortar and pestle in a 99.99% pure nitrogen filled enclosure. Store under nitrogen or in a vacuum desiccator.

A second procedure was developed by increasing the stirring time in Step 10 to 2 weeks. The procedure with the increased stirring time is referred to as Parker 2017b.

3.4 Nanoporous Tin Phosphate Synthesis

Nanoporous tin phosphate was included for consideration as a potential remedial treatment option because it has been previously demonstrated to retain technetium (Wellman et al. 2006). Additionally, the synthesis of nanoporous tin phosphate does not require the use of hydrazine, nor does it require continuous sparging with nitrogen or pH adjustments during synthesis.

Two batches of nanoporous tin phosphate were synthesized using the method described by Wellman et al. (2006). The synthesis method was scaled by a factor of 10 times to increase the synthesis yield such that sufficient material was obtained through a single batch and to minimize any potential variability in the product performance. To assess the potential for oxidation of the material and a resulting decrease in performance, one batch was stored in a glass bottle under a nitrogen atmosphere for 4 months. The second batch was prepared immediately prior to conducting the batch sorption tests.

3.5 Substitution Synthesis of Tin (II) Apatite

It was theorized that under the certain chemical and temperature conditions, tin (II) apatite could be prepared through substitution by reacting calcium apatite with tin (II) chloride at a low pH. To test the theory, nominally 0.5 g of apatite was added to two separate poly bottles, each containing 100 mL of 0.4 M $SnCl_2$ that had been pH adjusted to either 1 or 2, respectively. The poly bottles were placed into an oven set at 65°C for 2 weeks. The bottles were removed from the oven, placed on a benchtop, and allowed to cool to room temperature for 24 hours. The solids were filtered using a 1 µm filter paper and washed three times at room temperature using nitrogen sparged DIW that had been boiled for 30 minutes. Finally, the solids were dried under vacuum to a constant weight.

3.6 Batch Sorption Tests

Batch sorption tests were conducted to quantify the retention of ^{99}Tc. A solution of 2.65 µg/L ^{99}Tc in 18 ΩM distilled DIW was prepared. The ^{99}Tc concentration of 2.65 µg/L was selected highest concentration reported in well 299-W23-10 (DOE/RL-2015-06, Rev. 0).

Table 3.2 lists the nominal solution-to-solid ratios used for batch sorption tests. Actual material masses and solution volumes used in the batch tests are reported with the test results in Section **Error! Reference source not found.**.

Tests were conducted by adding the mass of synthesized material and the respective amount of water into poly bottles for a given solution-to-solid ratio. The poly bottles were sealed and placed on a shaker table at 60 rpm to maintain a well-mixed solution of sorption materials and aqueous media for 24 hours. All sorption tests were conducted at room temperature and in duplicate. After the 24-hour contact time, the poly bottles were removed from the shaker table and the sorption materials were allowed to settle for 30 minutes. A 0.45 µm syringe filter was then used to separate the aqueous matrix from the sorbent. A 5 mL aliquot was analyzed for total technetium by inductively coupled plasma mass spectrometry. See Appendix A for description of analysis procedure.

The ^{99}Tc concentration of 2.65 µg/L was selected based on the highest concentration reported in 299-W23-10 (DOE/RL-2015-06, Rev. 0).

Table 3.2 lists the solution-to-solid ratios used in the batch sorption tests. Actual material masses and solution volumes used in the batch tests are reported with the test results in Section **Error! Reference source not found.**.

Table 3.2. Solution-to-Solid Ratios

Ratio #	Dry Solid Material (g)	Solution Volume (mL)	Solution-to-Solid Ratio
1	0.2	10	50
2	0.1	10	100
3	0.04	10	250
4	0.2	100	500

5	0.1	100	1000
6	0.04	100	2500
7	0.05	250	5000

4.0 Results

4.1 Tin (II) Apatite Synthesis and Characterization

While attempting to synthesize tin (II) apatite using the procedure by Duncan et al., a number of technical issues were discovered. Thus, a new procedure had to be developed. Table 4.1 briefly lists each procedure step and the issue, describes the new step in Parker 2017a, and briefly describes how this change improves the procedure.

Table 4.1. Summary of Procedure Changes for Tin (II) Synthesis

Duncan et al. (2012)	Technical Issue	Parker 2017a	Discussion
1. Bring the water (1 L) in the reactor to a boil and cool to 37°C while sparging with nitrogen. Add 3 mL of hydrazine.	Water will not boil in the reactor using a water bath. Hydrazine may evaporate before the synthesis starts.	1. Bring 2 L of DIW to a boil in a flask and continuously sparge with 99.99% pure nitrogen. Allow the water to cool and add 1 L to the reactor. Sparge the boiled water in the reactor with nitrogen.	Hydrazine is added later.
2. Prepare 250 mL of 1.0 M Na_2HPO_4 in DIW and adjust the pH to 7.4 with NH_3OH. Purge any air from flask.	Solution pH is > 8. Cannot adjust with NH_3OH. Concentration not specified. Water not boiled or sparged.	2. While sparging with nitrogen, prepare 250 mL of 1.0 M Na_2HPO_4 in DIW and adjust the pH to 7.3±0.1 with concentrated HCl. Seal the container to prevent the solution from contacting oxygen.	Adjust pH with concentrated HCl to overcome the buffering of the solution and not change the concentration of the Na_2HPO_4 solution.
3. Prepare 250 mL of 1.38 M $CaCl_2$ in DIW and adjust the pH to 7.4 with NH_3OH. Purge any air from flask.	Concentration of NH_3OH not specified. Water not boiled or sparged.	3. While sparging with nitrogen, prepare 250 mL of 1.38 M $CaCl_2$ in DIW and adjust the pH to 7.3+0.1 with 0.25 M NH_3OH. Seal the container to prevent the solution from contacting oxygen.	Concentration of NH_3OH is specified.
4. Prepare the $SnCl_2$ solution by adding 1 mL of hydrazine to 250 mL of deionized, degassed water, and then add the $SnCl_2$ to make a 0.4 M solution. Do not adjust the pH.	The $SnCl_2$ will precipitate when it contacts the hydrazine.	4. While sparging with nitrogen, prepare 250 mL of 0.4 M $SnCl_2$ in DIW. Do not adjust the pH.	Eliminates the hydrazine from the tin solution.

Duncan et al. (2012)	Technical Issue	Parker 2017a	Discussion
		5. Add the hydrazine to the reactor just prior to starting the synthesis.	Hydrazine is available to remove any oxidizing agent.
6. While maintaining the reactor at 37°C, slowly add the reagents at the flowrate of approximately 1 mL/min, while vigorously stirring and bubbling nitrogen through solution.	Mixing rate not specified and reactant flow rate is not clear.	6. Stir the reactor at 100 rpm and add each reagent simultaneously at a rate of 1 to 2 mL/min (Total flow = 3 to 6 mL/min).	Stir rate is specified and flow rate is now clear.
7. The pH of the solution must be kept at 7.4±0.2 during the first phase, which takes 6 hours to complete.	With a wide pH range, the Sn(II) may change to Sn(IV). The pH changes rapidly during the first 8 hours.	7. The pH of the solution in the reactor must be maintained at 7.3+0.1. During the first 8 hours, continuously adjust the pH with concentrated NH_3OH as required.	Specifies a narrow pH range and monitors the pH for 2 additional hours.
8. Place the product apatite into a Pyrex vial and dry for 24 hours at 50°C under a constant flow of dry, high-purity nitrogen.	The tin will change from the beta allotrope to the alpha allotrope at high temperatures.	8. Transfer the solids to a beaker and place the tin (II) apatite in a vacuum desiccator at room temperature.	Solids are dried at room temperature to prevent the tin from changing allotropic states.
9. Place the tin apatite into liquid nitrogen to minimize the oxidation of the tin (II) and grind to a fine powder.	Extremely cold temperatures thermally shock the agate mortar and pestle and cause them to crack.	9. When the solids are dry, grind the tin (II) apatite using an agate mortar and pestle in a 99.99% pure nitrogen filled enclosure.	Allows the grinding to be performed at room temperature, eliminates the liquid nitrogen, and prevents the oxidation of the tin (II).

Using Parker 2017a, a batch of tin (II) apatite was synthesized. Initially upon adding the three solutions to the reactor, the material was white. However, after being mixed in the reactor for approximately 24 hours, the slurry turned gray when the temperature of the solution dropped below 13.2°C. At this temperature, tin changes from the white beta allotrope to the gray alpha allotrope (*Handbook of Chemistry and Physics*, 53rd Edition). Based on unpublished data,[1] the gray tin (II) apatite has ~25% of the sorption capacity of the white tin (II) apatite.

A batch of tin (II) apatite was synthesized using Parker 2017a. A sample was analyzed using XRD, and the results are shown in Figure 4.1.

---

[1] Duncan JB. Personal communication from JB Duncan (RJ Lee Group) to KE Parker (PNNL), 23/12/2016.

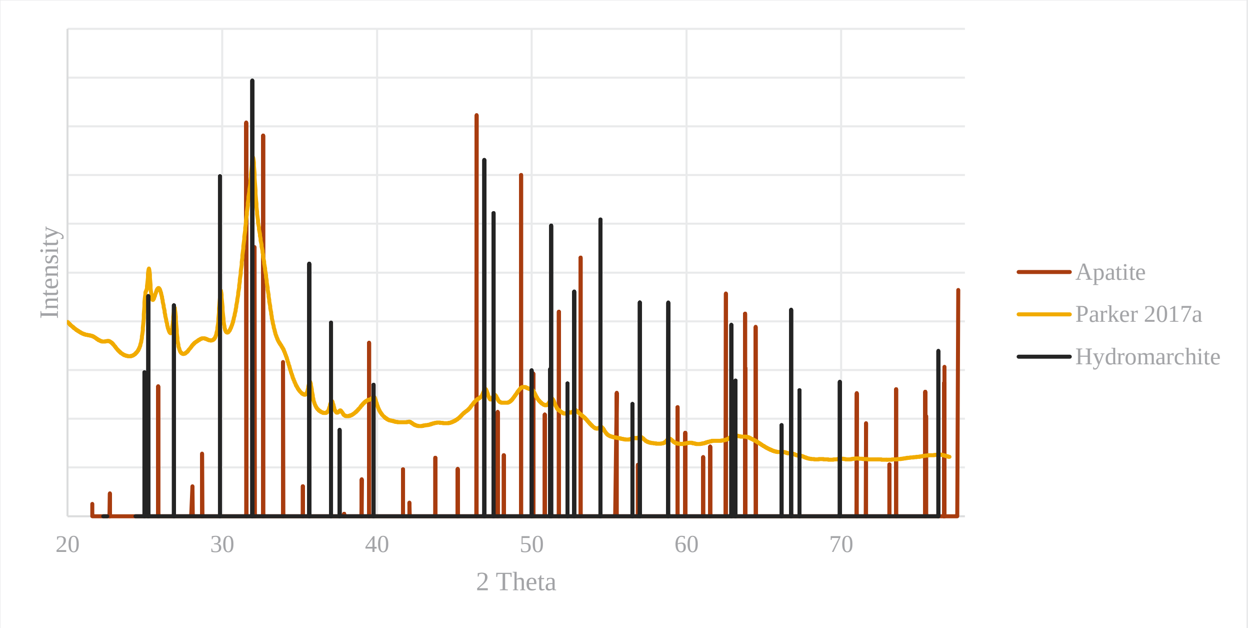

Figure 4.1. XRD Analysis of Tin (II) Apatite Using Parker 2017a.

The diffraction pattern from the tin (II) apatite sample mixed for 3 days cannot be matched directly to a reference pattern because one doesn't exist. The closest match is calcium apatite. The XRD reference patterns of calcium apatite and hydromarchite were plotted along with the pattern from a sample obtained from Parker 2017a. The major peaks of the reference materials align with the peaks from the Parker 2017a sample. Some of the sample peaks are in the shoulders of the sample pattern, such as the apatite reference peak at a 2Θ of 34.5 degrees. Note that two peaks have shifted slightly. The Parker 2017a sample has two peaks at 2Θ values of 26 and 50 degrees. The apatite reference peaks are at 2Θ values of 25.8 and 49.3 degrees, respectively. Additional characterization would be required to determine why these peaks shifted.

The sample was determined to contain 97% calcium apatite and 3% hydromarchite. Hydromarchite is a tin mineral with the chemical formula of $Sn_6O_4(OH)_4$.

The unit cell dimensions obtained from the XRD data for Parker 2017a are a = 9.4938 Å, c = 6.8852 Å, and a unit cell volume = 537.45 $Å^3$. The density was determined to be 3.10 g/cm^3.

Figure 4.2 displays an SEM image of the product, synthesized herein, at 5000 times magnification. The analysis was conducted at 8 KV. The image shows well-formed, discrete particles, as well as some amorphous secondary materials. As evidenced by white "hot spots" in the SEM images, synthetic material is likely of heterogeneous composition and further effort may be needed to refine the synthesis procedure to obtain a product of greater consistency. Nonetheless, energy dispersive spectroscopy (EDS) analysis was conducted to identify the composition of the crystalline material and the white spots. The sample locations are shown in Figure 4.3.

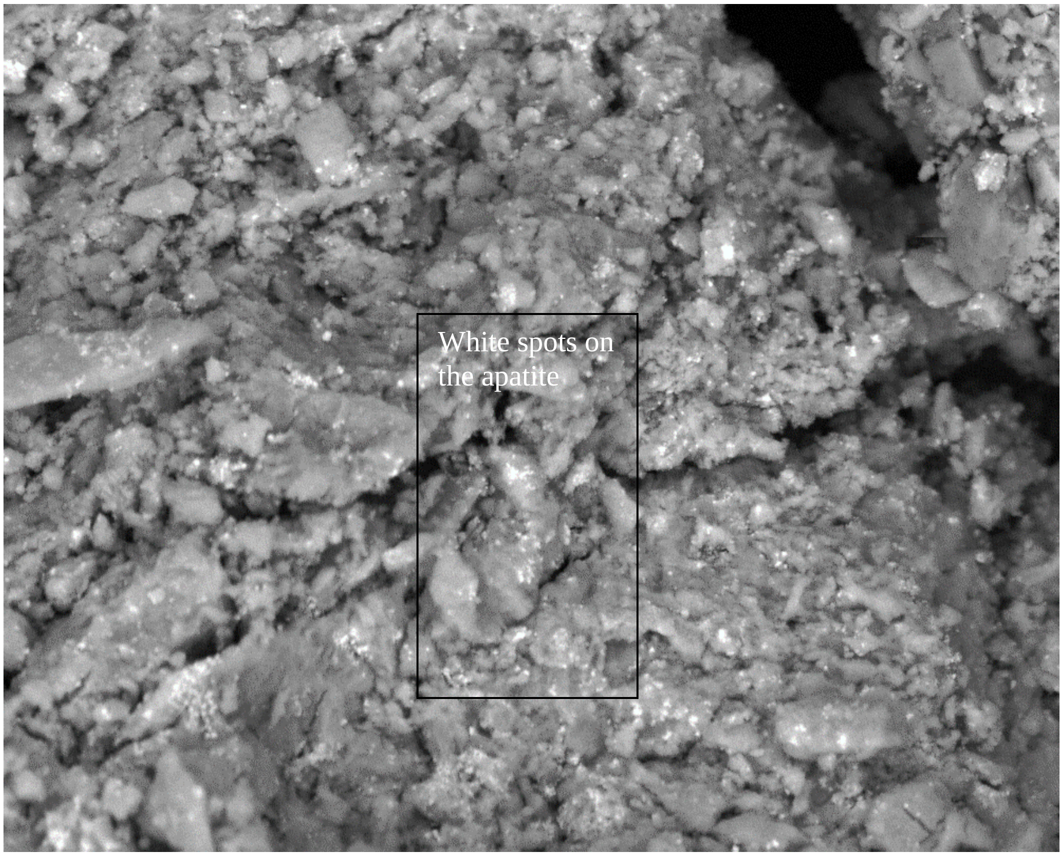

Figure 4.2. Photomicrograph of Tin (II) Apatite

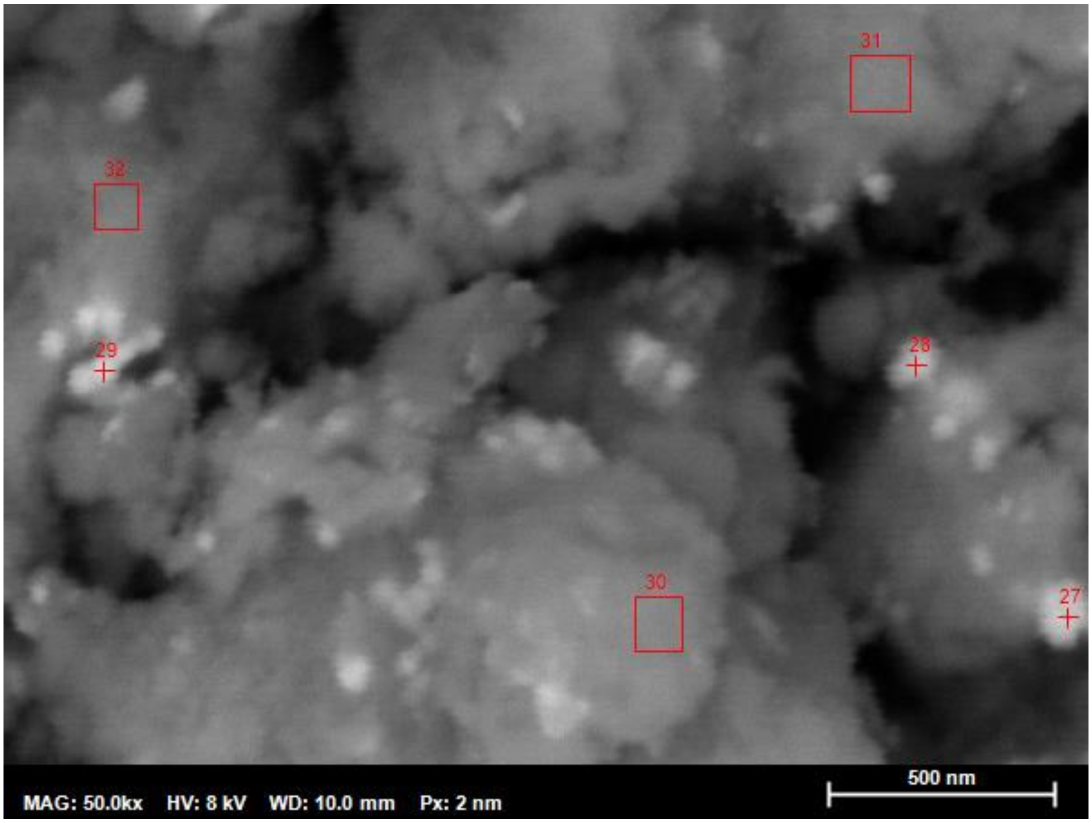

Figure 4.3. EDS Sample Points

The scale identified on the energy dispersive spectroscopy (EDS) image is approximate.

The concentrations determined by EDS are shown in Table 4.2.

Table 4.2. Atomic Concentrations

Spectrum #	Carbon	Oxygen	Sodium	Phosphorous	Chlorine	Calcium	Tin
27	0.0	67.2	0.4	10.2	0.33	16.82	5.07
28	0.0	67.4	0.4	10.2	0.29	16.22	5.59
29	0.0	68.0	0.4	9.5	0.32	15.69	6.15
30	0.0	67.2	0.5	9.4	0.2	17.24	5.45
31	0.0	46.6	0.4	15.3	0.51	28.41	8.69
32	0.0	70.6	0.4	9.5	0.26	15.12	4.14

All values are in percent concentration

The EDS measurements indicate that tin is uniformly distributed throughout the sample. The percentage concentration is 4.14 to 8.69 with an average concentration of 5.85 $\pm$1.54%. Computer modeling by Weck and Kim (2016) calculated the predominant compositions of tin (II) apatite as $Sn_xCa_{10-X}(PO_4)_6(OH)_2$ (x = 4–9), with the most likely formula being $Sn_6Ca_4(PO_4)_6(OH)_2$. Due to the presence of sodium and chloride, which may have substituted into the apatite matrix, a second tin phase and excess amounts of oxygen possibly from hydration, an accurate formula cannot be determined.

Based on these results, it is theorized that a tin-substituted calcium apatite was formed. However, additional characterization is needed to confirm that the tin has substituted for the calcium rather than sorbed onto the surface of the apatite.

To try to purify the product, the procedure was repeated, but the reaction time was increased from 3 days to 14 days. Subsequently, the product was filtered, dried, and analyzed using XRD as previously described.

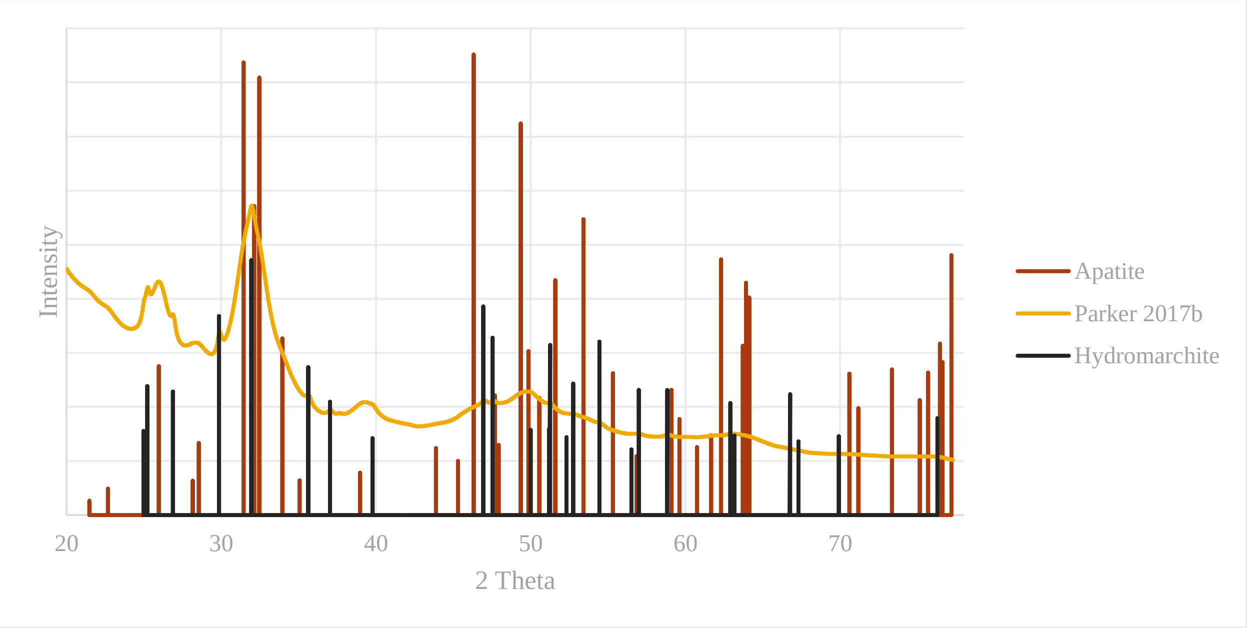

Figure 4.4. XRD Pattern of Tin (II) Apatite Based on Parker 2017b

The diffraction pattern from the tin (II) apatite sample mixed for 14 days cannot be matched directly to a reference pattern; thus, the XRD reference patterns of calcium apatite and hydromarchite were plotted along with the pattern from a sample obtained from Parker 2017b. The major peaks of the reference materials align with the peaks from the Parker 2017b sample. Some of the sample peaks are in the shoulders of the sample pattern, such as the apatite reference peak at a 2Θ of 34.6 degrees.

The unit cell dimensions obtained from the XRD data for Parker 2017b are a = 9.5448 Å, c = 6.8566 Å, and a unit cell volume = 540.96 Å^3. The density was determined to be 3.08 g/cm^3.

The amount of tin (II) apatite increased from 97% to >98%, with a concomitant decrease in the percentage of hydromarchite from 3% to <2%. Due to resource limitations, no additional characterization of this material was performed at this time.

4.2 Sorption Results

4.2.1 Tin (II) Apatite

A limited sorption test was performed on material synthesized by Parker 2017a, using solid-to-solution ratios of 4 to 6. The results are shown in Table 4.3. Technetium loading ranged from of 906 µg/g at ratio #4 to 5709 µg/g at ratio #6. The K_d values were 1195 to 16,358 mL/g over the same range.

Table 4.3. Sorption Results for Tin (II) Apatite Mixed Three Days.

Ratio #	Tc-99 Initial Concentration (µg/L)	Tc-99 Final Concentration (µg/L)	Mass of Material (g)	Soln. Vol. (mL)	Tc-99 Adsorption (µg/g)	K_d (mL/g)
4	2570	758	0.20	100	906	1195
5	2570	656	0.10	100	1915	2920
6	2570	349	0.04	103	5709	16,358

4.2.2 Nanoporous Tin Phosphate

Using the solution-to-solid ratios shown in

Table 3.2, sorption tests were performed using nanoporous tin phosphate aged for 4 months. The results are shown in Table 4.4.

Table 4.4. Sorption Data Using Nanoporous Tin Phosphate Aged for 4 Months

Ratio #	Tc-99 Initial Concentration (µg/L)	Tc-99 Final Concentration (µg/L)	Mass of Material - (g)	Soln. Vol. (mL)	Tc-99 Adsorption (µg/g)	K_d (mL/g)
1	2570	943	0.2	10	82.4	87.4
1	2570	1080	0.2	10	74.6	69.1
2	2570	1070	0.1	10	151.9	142.0
2	2570	1540	0.1	10	103.0	66.9
3	2570	2270	0.04	10	75.2	33.1
3	2570	2380	0.04	10	47.6	20.0
4	2570	2440	0.2	100	65.0	26.7
4	2570	2460	0.2	100	55.0	22.4
5	2570	2510	0.1	100	60.0	23.9
5	2570	2520	0.1	100	50.0	19.8
6	2570	2540	0.04	100	75.0	29.5
6	2570	2530	0.04	101	100.0	39.5
7	2570	2550	0.1	252	100.0	39.2
7	2570	2600	0.1	251	-	-

Data from sorption tests using nanoporous tin phosphate aged for 4 months show that technetium loading ranged from 47.6 µg/g at ratio #3 to 151.9 µg/g at ratio #2. The K_d values were 20.0 to 1420 mL/g over the same range.

Using unaged prepared nanoporous tin phosphate, sorption tests using the ratios in Table 3.2 were conducted, and the results are shown in Table 4.5.

Table 4.5. Sorption Data Using Unaged Nanoporous Tin Phosphate

Ratio #	Tc-99 Initial Concentration (µg/L)	Tc-99 Final Concentration (µg/L)	Mass of Material - (g)	Soln. Vol. (mL)	Tc-99 Adsorption (µg/g)	K_d (mL/g)
1	2570	38	0.2	10	126.6	3359.0
1	2570	63	0.2	10	125.9	2012.5
2	2570	57	0.1	10	252.1	4405.5
2	2570	55	0.1	10	251.4	4598.4
3	2570	832	0.04	10	435.1	529.4
3	2570	680	0.04	10	472.7	695.2
4	2570	1690	0.2	100	440.0	260.4
4	2570	1560	0.2	100	505.0	323.7
5	2570	2040	0.1	102	542.1	266.0
5	2570	1960	0.1	100	610.0	311.5
6	2570	2380	0.04	100	475.0	199.6
6	2570	2350	0.04	100	550.1	234.1
7	2570	2510	0.1	251	300.0	120.3
7	2570	2480	0.1	251	449.7	182.1

Data from sorption tests using unaged nanoporous tin phosphate show that technetium loading ranged from 125.9 µg/g at ratio #1 to 610.0 µg/g at ratio #5. The K_d values were 120.3 to 4598.4 mL/g.

The average loading and sorption values for the nanoporous tin phosphate given in Table 4.4 and Table 4.5 for each ratio are summarized in Table 4.6.

Table 4.6. Average Loading and Sorption Values for Unaged and Aged Nanoporous Tin Phosphate

	Aged Nanoporous Tin Phosphate		Unaged Nanoporous Tin phosphate	
Ratio	Loading-µg Tc/g solid	Kd-µL/g	Loading-µg Tc/g solid2	Kd-µL/gram
1	78.5	78.3	126.2	2685.8
2	127.5	104.4	251.8	4502.0
3	61.4	26.5	453.9	612.3
4	60.0	24.5	472.5	292.0
5	55.0	21.9	576.0	288.8
6	87.5	34.5	512.6	216.8
7	100.0	39.2	374.9	151.2

For all seven ratios, the loading and sorption values for nanoporous tin phosphate stored for 4 months were lower than the values for the freshly prepared material. The largest decrease in loading occurred in ratio #5, where the material that had aged for 4 months did not perform as well as the new material, 55.0 vs. 576.0 ug Tc/g solid, respectively. The largest decrease in K_d values occurred with ratio #2, 104.4 vs. 4502.0 µL/g. It is unlikely this material would be viable for environmental remediation given the rapid oxidation and decrease in loading performance measured after only 4 months of atmospheric exposure.

4.3 Substitution Reaction Results

Due to resource limitations, the materials from the two substitution tests were not characterized and sorption tests were not performed at this time. Additional resources would be necessary to determine if tin (II) apatite could be synthesized using this method.

5.0 Considerations for Groundwater Remediation via Tin (II) Apatite

To synthesize tin (II) apatite in the subsurface, all oxygen has to be removed from the injection point to keep the tin (II) from oxidizing to tin (IV) and the temperature has to be above 13.2°C to maintain the tin in the beta allotrope. As reported by Truex et al. (2013), the temperature in the subsurface ranges from 14°C to 16°C, and with evaporative cooling, temperatures as low as 7°C were measured. Due to the availability of oxygen and temperatures close to the tin allotrope, forming tin (II) apatite in the subsurface of the Hanford Site would require further research. In addition, tests of long-term stability, sorption using groundwater, toxicity, and characterization will need to be conducted.

The environmental impact of discharging chemicals used for the synthesis of tin (II) apatite to groundwater was investigated. The Washington State groundwater standards are included in WAC-173-200, *Water Quality Standards for Groundwaters of the State of Washington.*[1] WAC 173-200-010(3)(c) directs that cleanup actions be approved by Washington State or be approved by the U.S. Environmental Protection Agency (EPA) under the *Comprehensive Environmental Response Compensation and Liability Act* (CERLA), 42 U.S.C. 9601 et seq. Groundwater cleanup standards for such sites must be developed under WAC 173-340-720.[2] Cleanup standards for the various Hanford CERCLA operable units may be variable, as these standards are negotiated with the regulators (EPA) and a determination is formed based on beneficial use and protection of human health and the environment (assessing the risk to protection of sensitive subgroups, food chain contamination, damage to soil/biota, protection of nearby surface waters, etc.).

Per WAC-173-200-040, *Groundwater Quality Criteria (GWQC)*, the amount of hydrazine discharged could not exceed 0.03 µg/L. Hydrazine is a Class C hazard, is extremely corrosive, and reacts with moisture and oxidants. The material safety data sheet (MSDS) states that the eco toxicity of hydrazine is not known, but the products of biodegradation are more toxic than the parent compound. Potentially hazardous short- and long-term degradation products are to be expected.

Chloride is also listed in WAC-173-200-040, and cannot exceed 0.250 g/L. The amount of chloride discharged to the subsurface from 1.4 M calcium chloride and 0.4 M tin (II) chloride would be 127.6 g/L, which would violate this standard.

Per the tin (II) chloride MSDS, the compound is a Class C hazard and is corrosive. Tin is known to be toxic to bacteria and mammals (Barnes and Stoner 1959; Cooney and Wuertz 1989).

---

[1] http://apps.leg.wa.gov/WAC/default.aspx?cite=173-200&full=true

[2] http://app.leg.wa.gov/WAC/default.aspx?cite=173-340-720

6.0 Conclusions

The synthesis and testing of novel synthetic materials tin (II) apatite and nanoporous tin phosphate were evaluated, and the results were as follows:

- The method used to synthesize tin (II) apatite in this evaluation is not practical in the subsurface environment. Oxygen needs to be kept from tin (II) to prevent oxidization to tin (IV). The subsurface temperature (14°C to 16°C) is very close to the temperature where the white tin beta allotrope changes to the gray alpha form (13.2°C).
- Using tin (II) apatite in the subsurface is not practical due to the allotropic change that occurs at 13.2°C. Additional research is required to stabilize the white tin allotrope at lower temperatures.
- The chemicals and their degradation products used to synthesize tin (II) apatite are harmful to the environment, and their use in the subsurface would require approval by the State of Washington or the EPA.
- Nanoporous tin phosphate materials will remove technetium, but additional studies are required to improve the storage of the material and optimize the yield.

7.0 References

10 CFR 830, *Energy/Nuclear Safety Management*. Code of Federal Regulations.

42 U.S.C. 9601 et seq., *Comprehensive Environmental Response Compensation and Liability Act*. United States Code.

ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*. ASME International, New York, NY.

Barnes JM and HB Stoner. 1959. “The Toxicology of Tin Compounds,” *Pharmacological Review* 11:211-231.

Cooney JJ and S Wuertz. 1989. “Toxic effects of tin compounds on microorganisms,” *Journal of Industrial Microbiology* 4(1989):375-402.

DOE. 2009. “Groundwater contamination and treatment at Department of Energy Sites. *In* O.o.E.a. Technology (ed.), Washington, D.C.

DOE Order 414.1D, *Quality Assurance*. U.S. Department of Energy, Washington, D.C.

DOE/RL-2015-06, Rev 0, *Calendar Year 2014 Annual Summary Report for the 200-ZP-1 and 200-UP-1 Operable Unit Pump and Treat Operations*. U.S. Department of Energy, Richland Operations Office, Richland, WA.

DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Document*. U.S. Department of Energy, Richland Operations Office, Richland, WA.

Duncan JB, K Hagerty, WP Moore, RN Rhodes, JM Johnson, and RC Moore. 2012. *Laboratory Report On The Reduction And Stabilization (Immobilization) Of Pertechnetate To Technetium Dioxide Using Tin (II) Apatite*. LAB-RPT-12-00001, Rev. 0, Washington River Protection Solutions, Richland, WA.

Handbook of Chemistry and Physics, Robert C. Weast, Editor, 53rd Edition, CRC Press, 1973.

Truex MJ, M Oostrom, CE Strickland, TC Johnson, CD Johnson, RE Clayton, and GB Chronister. 2013. *Deep Vadose Zone Treatability Test for the Hanford Central Plateau: Interim Post-Desiccation Monitoring Results*. PNNL-22826, Pacific Northwest National Laboratory, Richland, WA.

WAC-173-200, *Water Quality Standards for Groundwaters of the State of Washington*. Washington Administrative Code.

WAC 173-340-720, *Groundwater Cleanup Standards*. Washington Administrative Code.

Weck PF and E Kim. 2016. "Energetics of Sn2+ isomorphic substitution into hydroxylapatite: first-principles predictions." *Royal Society of Chemistry 6*, 107286.

Wellman DM, SV Mattigod, KE Parker, SM Heald, CM Wang, and GE Fryxell. 2006. "Synthesis of organically templated nanoporous tin (II/IV) phosphate for radionuclide and metal sequestration." *Inorganic Chemistry* 45(6):2382-2384.

Wildung RE, KM McFadden, et al. 1979. "Technetium sources and behavior in the environment," *Journal of Environmental Quality* 8:156-161.

Appendix A

Analytical Methods

Appendix A

Analytical Methods

A.1 Technetium Analysis

Technetium analyses were performed using an inductively coupled plasma mass spectrometer (ICP-MS) following procedure PNNL-AGG-415,[1] which is similar to EPA SW-846, Method 6020A (EPA 1996). High-purity single-element standards traceable to the National Institute of Standards and Technology (Ultra Scientific [(Kingston, RI] and Inorganic Ventures [Lakewood, New Jersey]) were used to generate calibration curves and to verify continuing calibration during the analytical run. A serial dilution was made of select samples to investigate and correct for matrix interferences. Instrument detection limits for technetium on the ICP-MS are 0.0033 µg/L.

A.2 References

EPA. 1996. "Method 6020A, Inductively Coupled Plasma – Mass Spectrometry," Rev. 1. In *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. EPA SW-846, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

---

[1] Clayton ET. 2008. *Inductively Coupled Plasma Mass Spectrophotometry (ICP-MS)*. PNNL-AG-415, unpublished PNNL Technical Procedure, Pacific Northwest National Laboratory, Richland, WA.

Distribution

No. of
Copies

OFFSITE

DOE-EM HQ
Rod Rimando
John Lee

Sandia National Laboratory
Robert Moore

No. of
Copies

ONSITE

Pacific Northwest National Laboratory
Kent Parker
Jarod Crum
Dawn Wellman
Vicky Freedman
Mike Truex
Jim Neeway
Nik Qafoku
Tatiana Levitskaia
Matt Asmussen
Carolyn Pearce

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

U.S. DEPARTMENT OF
ENERGY

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnnl.gov