

Development of Tc(IV)-Incorporated Fe Minerals to Enhance ⁹⁹Tc Retention in Glass Waste Form – 15239

Wooyong Um *, Steven A. Luksic *, Guohui Wang *, Dong-Sang Kim *, Michael J. Schweiger *, Pavel Hрма *, and Albert A. Kruger **

* Pacific Northwest National Laboratory

** US DOE ORP

ABSTRACT

Iron minerals have been considered to be good hosts for Tc immobilization because the Tc(IV) ion substitutes for Fe(III) in the crystal structure of the Fe oxide due to similarities in (1) cation size [Tc(IV) = 78.5 pm ; Fe(III) = 69 or 78.5 pm], (2) metal-oxygen interatomic distance (Tc—O = 0.199 nm, Fe—O = 0.203 nm), (3) number of coordinating oxygen atoms (both 6-fold coordinated), and (4) the redox potential (Eh=ca. +20 mV at pH = 7) for a redox couple between Tc(VII)/Tc(IV) and Fe(III)/Fe(II). Magnetite, maghemite, and Trevorite are iron oxide minerals and all belong to spinel mineral group. Laboratory testing shows that Tc can be removed from aqueous waste solutions by a process of Tc reduction from Tc(VII) to Tc(IV) followed by co-precipitation with iron oxide minerals during recrystallization of Fe(OH)₂(s) used as an initial solid precursor. X-ray absorption near edge structure (XANES) spectroscopy confirmed that Tc was in the +4 oxidation state in final Tc-Fe minerals. The Tc-incorporated Fe minerals (Tc-goethite and Tc-magnetite/maghemite) were also tested for Tc retention in glass melts at different temperatures between 600 – 1,000 °C in a furnace. After being cooled in air, the solid glass specimens collected at different temperatures were analyzed for Tc oxidation state using XANES and Tc retention using liquid scintillation counting (LSC). Although Tc(IV) started to reoxidize at 600 °C, Tc retention in the final glass specimen prepared with Tc-incorporated Fe mineral at high temperatures was at least two times higher than glass prepared with K₂TcO₄ salt. Higher Tc retention in glass is considered to result from limited and delayed Tc volatilization process due to Fe mineral encapsulation for Tc. Therefore, the results showing the presence of Tc(IV) in the Fe mineral structure indicate strong possibility to enhance Tc retention in borosilicate glass as well as to reduce the remediation costs at the Hanford Site.

INTRODUCTION

A long-lived fission product, technetium-99 (Tc-99), presents a challenge in managing legacy wastes from the production of nuclear materials at Hanford and other DOE sites. Because of the extremely complex chemical behavior of technetium, a novel method for managing Tc in waste treatment systems is needed for the safe and cost-effective treatment of Tc-containing nuclear waste. In the high temperatures (~1,000–1,200°C) of the melters typically used in vitrification, a significant fraction of the Tc is expected to volatilize and be collected in off-gas scrubber systems. Two major Tc species, Tc(VII) and Tc(IV) show different volatilization rates, because Tc₂O₇ melts at 119.5 °C, while TcO₂ sublimates at 900 °C. Therefore, reducing conditions are likely to increase Tc immobilization and increase Tc retention in various waste forms such as glass and grout prepared at various temperature conditions. Although the off-gas scrubber solutions containing Tc are recycled back to the melters, some Tc ultimately is expected to be lost and become part of the secondary waste stream requiring additional treatment and immobilization processes. In addition, the off-gas scrubber solutions capture other ions like S, Cl, F, and Cr when recycled to the melter, which reduces the waste loading in the final glass waste form. Recent tests have shown that iron minerals have been considered to be good hosts for Tc immobilization. Tc(IV)-

incorporation within Fe mineral structures such as spinel is proposed as a novel method to increase Tc retention even at high temperature process conditions used for making glass waste forms [1,2]. Because of its physical and chemical stability, spinel can be present in a final borosilicate glass prepared with glass feed containing Fe_2O_3 , and is considered an effective sink for Tc in glass [2-4].

MATERIALS AND METHODS

Synthesis of Tc-Incorporated Iron Minerals

Tc-incorporated iron minerals (Tc-goethite and Tc-magnetite/maghemite) were prepared and used for Tc retention in simplified glass melts tests. Details of the synthesis procedures and the strategy for incorporating reduced Tc(IV) into goethite can be found in a previous paper by Um et al. (similar to Sample 2-5 preparation) [5]. In brief, synthesized goethite powder was re-suspended in de-ionized (DI) water and the pH was adjusted to ≤ 2.0 by adding 2M nitric acid. Powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.48 g) was directly added to the goethite slurry as the Fe(II) source and reacted for 1 day in an anoxic chamber. Following this, Tc(VII) from a NaTcO_4 solution was added to make a target concentration of Tc in the Fe(II)-goethite slurry and homogenized for 1–2 days on a platform shaker. After mixing, sodium hydroxide was added to facilitate Tc-goethite precipitates. The Tc-goethite solids were further modified to armor the Tc-goethite solids with additional goethite precipitates using separately prepared $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution. After 1 to 2 days of reaction with added ferric nitrate and sodium hydroxide solutions, the bottle containing the final Tc-goethite slurry was removed and placed inside an oven at 80°C for 7 days. The final Tc-goethite solid products were separated by filtration, dried in air, and used for additional analysis. For Tc-incorporated magnetite/maghemite mixture, the mineral transformation reaction was used, because $\text{Fe}(\text{OH})_2(\text{s})$ could be successfully transformed into magnetite and maghemite mixture. Therefore, Tc removal experiment was prepared using $\text{Fe}(\text{OH})_2(\text{s})$ as the initial Fe mineral substrate under different temperatures (room vs. 80°C) and high pH (~ 12) conditions at a solution-to-solid ratio of 1000. All the solution pHs in this test sequence were initially adjusted to ~ 3.3 pH using 2 M HNO_3 to avoid any Fe precipitating from the solution at higher pH conditions. Then 0.05 g of the synthesized $\text{Fe}(\text{OH})_2(\text{s})$ was re-suspended in 25 mL of Tc-spiked DI solution in 50 mL-size centrifuge tubes. The solution with a Tc spike was prepared independently with DI water in which the solution pH was adjusted to pH ~ 12 using 1 M NaOH. The reaction tubes were immediately sealed after mixing the two solutions and the reaction lasted for 7 days at either room or 80°C temperatures with hand shaking at least once per day. After the reaction, about 4 mL of supernatant was collected and filtered using a $0.02\text{-}\mu\text{m}$ syringe filter before use. The supernatant concentrations of Tc and total Fe were determined using inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, respectively.

Characterizations of Tc-Incorporated Iron Minerals

The final solid products were first characterized using x-ray diffraction (XRD) unit equipped with a Cu K-alpha radiation (40 kV, 35 mA) source. The bulk samples were homogenized by grinding in an agate mortar and pestle and mounted onto a small circular sample holder before scanning from 2 to 75 degrees 2-theta. Data reduction and mineral identification were done by Jade software with PDF XRD database. Strong microwave-assisted digestion with a solution consisting of 16 M HNO_3 (17%), 12 M HCl (7%), 32 M HF (3.3%), 0.5 g of H_3BO_3 (1.5%), and DI water (71.2%) on a volume basis was used to determine the total Tc concentration in the final Tc-goethite or Tc-magnetite/maghemite solid. In addition, the XAFS spectra were collected on Beamline 4-1 at the Stanford Synchrotron Radiation Laboratory. The Tc-goethite solid samples were mounted on Teflon® sample holders and sealed with Kapton tape. A Si(220) double-flat crystal monochromator was used and the energy was calibrated by using the first inflection

point of the Tc K edge spectrum of the Tc(VII) standard (KTcO₄) defined as 21.044 keV. The XAFS spectra of Tc-standards and Tc-iron mineral samples were collected in transmission and fluorescence mode, respectively, at RT using a 13-element germanium detector. Data reduction and analysis were performed using the software IFEFFIT and Athena/Artemis [6] after correction for detector dead-time. The x-ray absorption near-edge structure (XANES) spectra for the Tc-iron mineral samples were fit using a linear combination of the XANES spectra of KTcO₄ as the Tc(VII) standard spectrum and TcO₂•2H₂O as the Tc(IV) standard spectrum, respectively [7].

Tc-Retention in Simulated Glass Melter Test

An individual batch of the final Tc-iron mineral containing a constant Tc concentration was prepared and heated for a few hours in a furnace. Three different samples (Tc-goethite, Tc-magnetite/maghemite, and KTcO₄ salt) were tested. About 5 g of Tc-iron mineral was mixed with other basic glass feeds in a Pt crucible and heated up to 1,000 °C at 5°C increase per minute in a furnace. Target Tc concentration in a final glass was roughly 10 ppm. The baseline glass for Tc-retention testing was AN-102 glass, which is one of the formulations used for the DOE-ORP small-scale melter tests for Tc retention [8] and for the Re/Tc incorporation mechanism study [9]. The compositions of simulated AN-102 waste, additives, and AN-102 glass are shown in Table 1.

Table 1. Target compositions of simulated AN-102 waste, additives, and resulting AN-102 glass.

Target glass compositions (mass%)			
	AN-102 waste	Additives *	AN-102 glass
Loading	16.22	83.78	100.00
Al ₂ O ₃	6.29	5.97	6.02
B ₂ O ₃	0.06	11.77	9.87
CaO	0.18	7.50	6.31
Cr ₂ O ₃	0.49		0.08
Fe ₂ O ₃		6.48	5.43
K ₂ O	3.33		0.54
Li ₂ O		3.78	3.17
MgO		1.78	1.49
Na ₂ O	83.42		13.53
NiO	0.06		0.01
PbO	0.06		0.01
SiO ₂	0.06	53.41	44.75
TiO ₂		1.65	1.38
ZnO		4.13	3.46
ZrO ₂		3.53	2.96
Cl	1.23		0.20
F	0.49		0.08
P ₂ O ₅	0.74		0.12
SO ₃	3.64		0.59
Sum	100.00	100.00	100.00
* Additives contain both glass formers and glass modifiers necessary for making the glass waste form.			

After air-quenching, the final glass was pulverized and the activity of Tc in glass was analyzed using LSC to compare with initial Tc activity measured in glass feeds. An aliquot of the same glass sample was analyzed using SEM/EDS for Tc distribution and location in the glass, and XAFS for Tc oxidation state and coordination environment in a final glass feeds. Preparation of glass feed and melted glass are shown in Fig.1.

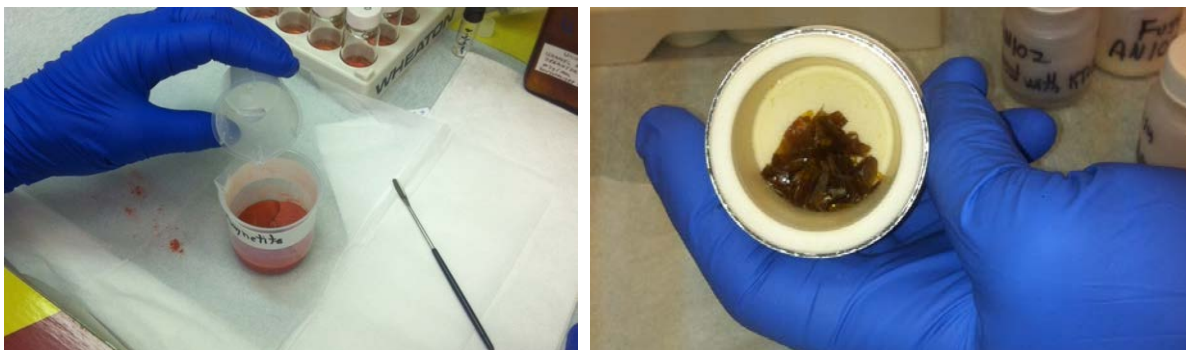


Fig. 1. Glass feed preparation (Left) and final glass before grinding (Right).

RESULTS AND DISCUSSION

Final Tc concentration on different iron mineral products was 5.02 mg-Tc/g and 25.0 mg-Tc/g for Tc-goethite and Tc-magnetite/maghemite, respectively. XRD analysis also showed that the measured XRD pattern of the Tc-goethite powder was found to be solely goethite, which is the same as Sample 2-5 in Um et al. [5] based on the exact match to the XRD-JADE program. The mineral transformation from $\text{Fe}(\text{OH})_2(\text{s})$ to a mixture of maghemite/magnetite was also confirmed by XRD analysis (Fig. 2).

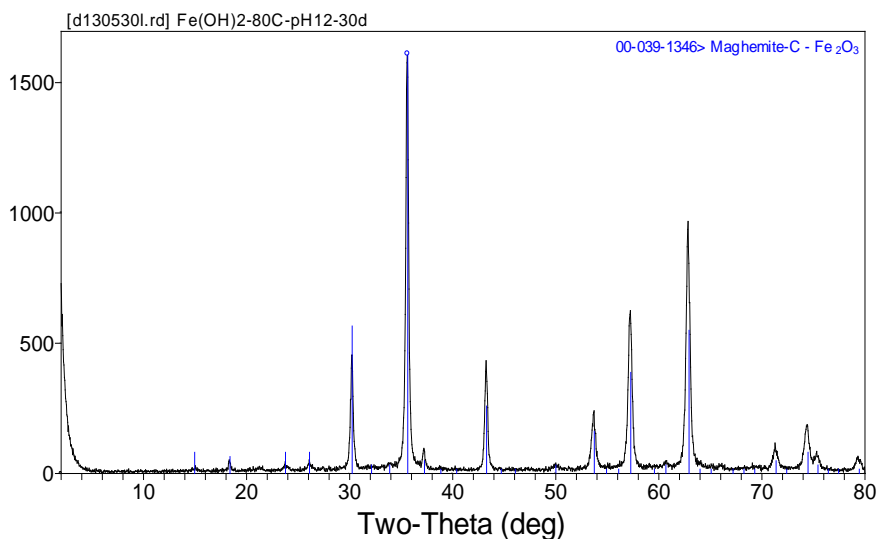


Fig. 2. XRD Pattern of maghemite/magnetite mixture transformed from $\text{Fe}(\text{OH})_2(\text{s})$ reacted under pH 12 at 75°C with a solution-to-solid ratio of 1000.

Compared with the XRD patterns of pure synthesized magnetite and goethite, the XRD intensity peak in the region of about 35.60 2-theta degrees can be identified as magnetite/maghemite. The well-crystallized magnetite and maghemite are thermodynamically more stable than the ferrous hydroxide, Fe(OH)₂(s) starting substrate.

X-ray absorption fine structure (XAFS) spectroscopy was used to characterize the Tc oxidation state in the Tc-iron minerals and to determine the local atomic environment for the Tc within the iron oxide matrix, respectively. The XANES spectrum for the Tc(VII) standard of NaTcO₄ is characterized by a strong pre-edge feature due to the 1s to 4d transition for the tetrahedral TcO₄⁻ anion. The XANES spectrum of the TcO₂•2H₂O standard for Tc(IV) is very distinctive and characteristic for Tc(IV) coordinated by six oxygen atoms in an octahedral geometry. The oxidation state of Tc in the Tc-goethite powder sample was determined by fitting their collected XANES spectra by a linear combination fit using the spectra for the Tc(VII) and Tc(IV) standards, and showed that only Tc(IV) was present in Tc-goethite sample like Sample 2-5 found in Um et al. [5]. In addition, XANES analysis for Tc-magnetite/maghemite confirmed that the Tc speciation in the final Tc-magnetite/maghemite transformed product at high temperature consisted of Tc(IV) (96%) with at most 4% Tc(VII) (Fig. 3). At room temperature, the Tc speciation in the final Tc-magnetite/maghemite transformed product consisted of 78% Tc(IV) and 22% Tc(VII). The Tc-magnetite/maghemite sample prepared at high temperature and high pH conditions was used for the glass melt test. The EXAFS fit also showed that both room and high temperature conditions have Tc(IV) in the octahedral site of magnetite (or maghemite). Due to the similarity in mineralogy between magnetite and maghemite, it is not easy to distinguish Tc site location correctly. However, the EXAFS fit for both cases of room and high temperature was not consistent with the presence of TcO₂•2H₂O or Tc(IV) adsorbed on the surface of iron oxide particles. In addition, because the final pH of a slurry of mixed Fe(OH)₂(s)-Tc(VII) is fairly neutral to alkaline (pH = 7–11.5), Tc removal is not considered to be from Tc adsorption on mineral surfaces but rather Tc incorporation into the final transformed iron mineral product, a mixture of magnetite and maghemite.

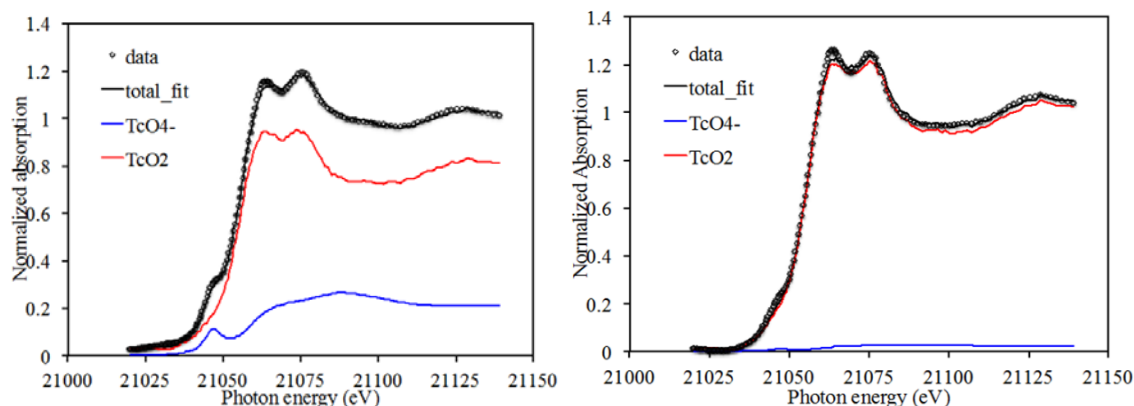


Fig. 3. XANES spectrum and fit for Tc-magnetite/maghemite samples at room (Left) and 75°C (Right). The contribution of each component to the total fit is shown in different colors.

The XANES analysis of the final glass samples showed that Tc(IV) in Fe minerals started to reoxidize at 600 °C due to a partial breakdown of the Fe mineral structure and oxidation of magnetite to maghemite or hematite. Initial Tc(IV) contribution to glass feeds with Tc-magnetite/maghemite showed 100% of Tc(IV), but Tc(IV) contribution reduced to 46%, 3%, and 0% as melting temperature increased from 600°C, 800°C, and 1000°C, respectively (Table 2). The glass sample prepared with Tc-goethite could hold

Tc(IV) slightly longer than Tc-magnetite/maghemite glass at 600°C, but it also showed significant decrease of the Tc(IV) contribution at melting temperatures higher than 800°C.

Table 2. The XANES results of Tc species contribution in glass samples for different Tc-iron minerals and KTcO_4 salt with different melting temperatures.

Glass specimens	Tc species	Feed at 25°C	600°C	800°C	1000°C
KTcO_4 salt	Tc(VII)	100%	100%	100%	100%
	Tc(IV)	0%	0%	0%	0%
Tc-magnetite/maghemite	Tc(VII)	0%	54%	97%	100%
	Tc(IV)	100%	46%	3%	0%
Tc-goethite	Tc(VII)	0%	0%	95%	99%
	Tc(IV)	100%	100%	5%	1%

However, Tc retention in the final glass specimen prepared with Tc-incorporated iron minerals at different temperatures showed higher Tc retention compared to the glass prepared with KTcO_4 salt. The enhanced Tc retention in the glass prepared with Tc-iron minerals was at least two times higher than glass prepared without Tc-iron minerals. Higher Tc retention in glass prepared with Tc-incorporated iron minerals is considered to result from limited Tc volatilization due to the encapsulated Tc in Fe mineral and delayed Tc volatilization at high melting temperatures (Fig. 4).

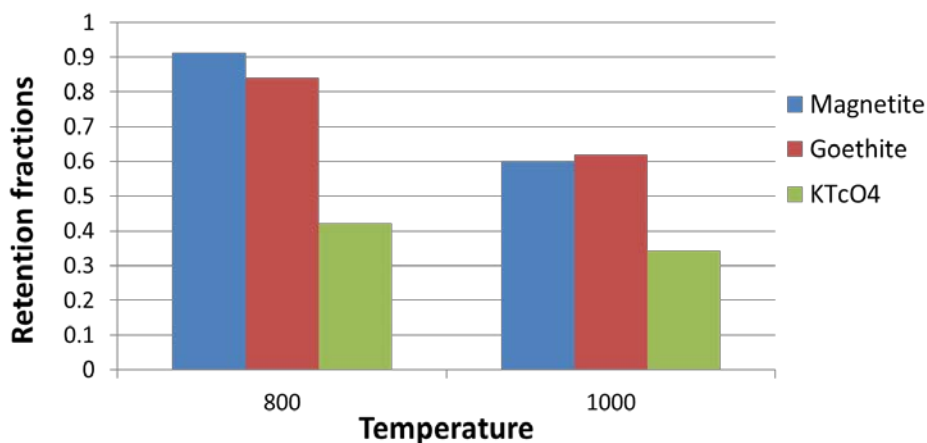


Fig. 4. Tc retention in crucible melts for three different glass samples at two different temperatures.

CONCLUSIONS

This study shows the possible innovative radioactive waste treatment process for enhancing Tc retention in glass waste forms using Tc-incorporated Fe minerals. This process can remove Tc from numerous Hanford waste streams through Tc reduction and incorporation into stable Fe minerals. Analysis of Tc speciation in the final product confirmed Tc incorporation within the Fe mineral structure which can limit Tc volatilization in glass. Because magnetite, maghemite, and trevorite all exhibit a spinel crystal structure, our results show the possibility that spinel minerals can increase Tc retention in a final glass for Hanford radioactive waste streams.

REFERENCES

1. O. MULLER, W.B. WHITE, AND R. ROY. "Crystal chemistry of some technetium-containing oxides", *J. Inorg. Nucl. Chem.*, **26**, 2075-2086 (1964).
2. M.Y. KHALIL AND W.B. WHITE. "Magnesium titanate spinel: A ceramic phase for immobilization for Technetium-99 from radioactive wastes", *Communication of the American Ceramic Society*, C-197-198 (1983).
3. K. RIGHTER, J. T. CHESLEY, D. GEIST, AND J. RUIZ. "Behavior of Re during Magma Fractionation: an Example from Volcán Alcedo, Galápagos," *J. Petrology*, **39**, 785-795 (1998).
4. P. IZAK, P. HRMA, B.W. AREY, AND T.J. PLAISTED. "Effect of feed melting, temperature history, and minor component addition on spinel crystallization in high-level waste glass." *J. Non-Crystalline Solids*, **289**, 17-29 (2001).
5. W. UM, H.-S. CHANG, J.P. ICENHOWER, W.W. LUKENS, R.J. SERNE, N.P. QAFOKU, J.H. WESTSIK, E.C. BUCK, AND S.C. SMITH. "Immobilization of 99-Technetium (VII) by Fe(II)-Goethite and Limited Reoxidation", *Environmental Science & Technology*, **45**, 4904-4913 (2011).
6. B. RAVEL, AND M. NEWVILLE. "ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT", *J. Synchrotron Radiat.*, **12**, 537-541 (2005).
7. W.W. LUKENS, J.J. BUCHER, N.M. EDELSTEIN, AND D.K. SHUH. "Products of pertechnetate radiolysis in highly alkaline solution: Structure of $TcO_2 \cdot xH_2O$ ", *Environ. Sci. Technol.* **36**, 1124-1129 (2002).
8. K.S. MATLACK, H. ABRAMOWITZ, M. BRANDYS, I.S. MULLER, R.A. CALLOW, N. D'ANGELO, R. CECIL, I. JOSEPH, AND I.L. PEGG. "Technetium Retention in Hanford LAW Glass with Recycle Flow-Sheet: DM10 Melter Testing," VSL-12R2640-1, Vitreous State Laboratory, The Catholic University of America: Washington, DC (2012).
9. T. JIN, D. KIM, AND M.J. SCHWEIGER. "Effect of Sulfate on Rhenium Partitioning during Melting of Low-Activity-Waste Glass Feeds - 14116" to be published in the Proceedings of the WM2014 Conference, March 2 - 6, 2014, Phoenix, AZ (2014).

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy's (DOE) Waste Treatment and Immobilization Plant Project of the Office of River Protection. The authors thank Wayne W. Lukens for XAFS sample collection and data analysis at the Stanford Synchrotron Radiation Lightsource (SSRL), a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for DOE's Office of Science by Stanford University. We also appreciate Chuck Z. Soderquist in PNNL for radiochemical analysis. Pacific Northwest National Laboratory (PNNL) is operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.