

Technetium and Iodine Getters to Improve Cast Stone Performance – 15420

R. Matthew Asmussen *, James J. Neeway *, Amanda R. Lawter *, Wayne Lukens # and Nikolla P. Qafoku *

* Pacific Northwest National Laboratory

Lawrence Berkeley National Laboratory

ABSTRACT

Technetium-99 (^{99}Tc) and iodine-129 (^{129}I) have been determined to be tank waste components contributing most to the environmental impacts associated with the cleanup of the Hanford site. Cast Stone, which has the ability to immobilize ^{99}Tc , ^{129}I , and other contaminants of concern, is being considered as a low temperature waste form for solidification of aqueous secondary liquid effluents from the Hanford Tank Waste Treatment and Immobilization Plant (WTP). An environmental assessment of Cast Stone performance, using measured diffusivities of the radionuclides from the Cast Stone product, calculates groundwater at the 100 m down-gradient in excess of the allowable maximum permissible concentrations for both radionuclides. Therefore, an opportunity exists to improve the performance of Cast Stone. One method for improvement is through the addition of immobilizing agents known as “getters” that selectively sequester Tc and I. In the present paper, we report on seven getter materials that have been tested for Tc and five materials that have been tested for I to determine their effectiveness for radionuclide removal in a series of batch sorption tests in 18.2 MΩ DI H₂O and a 7.8 M Na Ave LAW waste simulant. Contact experiments have been carried out in anoxic conditions at room temperature, with varying solid-to-solution ratios, and in the presence and absence of competing species. Results indicate that most materials perform better in the 18.2 MΩ DI H₂O compared to the 7.8 M Na LAW waste simulant for both Tc and I getter. Radionuclide sequestration may be affected by the presence of the redox sensitive Cr(VI) in the simulant. The top performing Tc getter materials, Sn(II)-apatite, BFS-2, KMS-2 and Sn-hydroxyapatite, were examined through various solid-state characterization techniques such as SEM/XEDS, XANES and EXAFS. Tc removal is theorized to occur through reduction of the highly soluble Tc(VII) species to the less soluble Tc(IV). Solution results from the series of I tests show that iodide is effectively removed from solution via, most likely, a precipitation reaction of AgI. A wide range of I getter materials and the silver exchanged zeolite getter performed well in both DI water and the simulant.

INTRODUCTION

Cast Stone is being considered as a low-temperature waste form for the solidification of aqueous secondary liquid effluents from the Hanford Tank Waste Treatment and Immobilization Plant (WTP) [1]. Two radionuclides of concern in these wastes, due to their high environmental mobility and long half-life, are ^{99}Tc ($t_{1/2} = 2.1 \times 10^5$ a) and ^{129}I ($t_{1/2} = 1.57 \times 10^7$ a). In aqueous environments, both radionuclides will dominantly exist as anions (TcO_4^- , I^- , IO_3^-), which are not easily sorbed onto naturally occurring materials and sediments (Tc) or they form strong covalent bonds with organic matter (I) creating a need for their long term immobilization in a stable matrix [2].

Cast Stone is comprised of a baseline dry blend mix of 8 wt% Portland cement Type I/II, 45 wt% Class F fly ash and 47 wt% Grade 100 or 200 blast furnace slag (BFS) [1]. Short term (28 to 91 days) leach studies of Cast Stone monoliths have garnered Tc effective diffusivities in the range of 2×10^{-10} cm²/s to 6×10^{-12} cm²/s and I effective diffusivities of 1×10^{-8} to 2×10^{-9} cm²/s [3]. These short term measurements, while promising, do not account for the potential of long-term release of ^{99}Tc due to its re-oxidation upon exposure to dissolved oxygen in vadose zone pore water nor do they provide a measured range for I release

that is within that required for full protection of ground water below a potential storage site. Therefore, there is a need for improved retention of these radionuclides within the Cast Stone formulations.

One method of improving the performance of Cast Stone for the retention of ^{99}Tc and ^{129}I is through the addition of “getters” which can selectively sequester the radionuclide(s) of concern. The getters can function in one of two modes: 1) addition to the liquid waste, where upon completion of its sequestration of the radionuclide the getter can be removed and placed in a second waste form; 2) the getter is added to the liquid waste or Cast Stone dry blend and becomes a final component of the waste form. A wide range of getters, both naturally occurring and synthetic, have been tested for many radionuclides with varying success rates [4, 5].

In this investigation, the getters for ^{99}Tc can be grouped into three categories: 1) Sn-containing getters, 2) ion exchange compounds, and 3) Cast Stone components. The Sn-containing getters were selected to utilize the favourable oxidation potential of Sn(II) to Sn(IV), which can facilitate the reduction of TcO_4^- (Tc(VII)) to highly insoluble, and thus immobile, TcO_2 (Tc(IV)). Potassium metal sulfides (KMS) have shown previous success in the removal of toxic cations, including Cs^+ , Sr^{2+} , and Ni^{2+} , from solution [6] and were selected to test their performance for TcO_4^- removal. Blast furnace slag (BFS), comprising 47 wt% of the Cast Stone, has long been known to have retentive properties towards ^{99}Tc [7] with its removal properties due to reductive Fe and S species contained within the BFS.

The potential ^{129}I getters were mainly selected to utilize the low solubility of AgI ($K_{sp} = 8 \times 10^{-17}$) to immobilize the ^{129}I that is present in the liquid waste. Several Ag-containing getters were examined along with a layered bismuth hydroxide material which has shown previous affinity for removal of I anions from solution [8].

This study investigated the performance of the Tc and I getters in DI water (18.2 MΩ-cm) and in a 7.8 M Na Ave LAW waste simulant. Batch sorption testing with regular sampling was employed to calculate distribution coefficients (K_d) for individual getter materials. Getters showing strong performance in the removal of the radionuclides were subsequently characterized with a series of analytical techniques including scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (XEDS), and x-ray absorption fine structure spectroscopy (XAFS) with x-ray absorption-near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS).

METHODS

A representative solution of the LAW in the tanks was used in the batch experiments to test the getters, along with DI (18.2 MΩ-cm) water. This simulant, named 7.8 M Na Ave LAW (7.8 M LAW simulant), is identical in composition to the solution used in LAW Cast Stone screening tests [3]. The composition of the simulant and the levels of major ionic species are given in Table I.

Table I – 7.8 M LAW simulant composition for getter tests

Compound	Amount (g/L)		Waste Constituent	Overall Average (mol/L)	Theoretical Concentration (mmol/L)
$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	179.54		Al^{3+}	0.48	
KNO_3	5.17		K^+	0.06	
NaNO_2	60.80		Na^+	7.80	

NaNO ₃	88.70		Cl ⁻	0.06	
Na ₃ PO ₄ · 12 H ₂ O	29.18		CO ₃ ²⁻	0.43	
Na ₂ SO ₄	18.95		F ⁻	0.05	
Na ₂ CO ₃	45.33		NO ₂ ⁻	0.88	
NaF	2.07		NO ₃ ⁻	2.53	
NaCl	3.85		PO ₄ ³⁻	0.08	
NaOH (50% sol'n)	347.81		SO ₄ ²⁻	0.13	
NaC ₂ H ₃ O ₂	4.91		TOC total	0.12	
NaCr ₂ O ₇ · 2 H ₂ O	4.96		Free OH ⁻	2.43	
Pb(NO ₃) ₂	0.13		Cd		0.25
Ni(NO ₃) ₂ · 6 H ₂ O	1.49		Cr		33.3
Cd(NO ₃) ₂ · 4 H ₂ O	0.08		Pb		0.40

The getters selected for the removal of ⁹⁹Tc were BFS-1 (Lafarge North American), BFS-2 (Holcim Inc. (USA)), Sn(II)-apatite (Sn-A) [9], SnCl₂ (Sigma Aldrich), KMS (supplied by [6]) and Sn(II)-hydroxyapatite (Sn-HA) (supplied by outside laboratory). For removal of ¹²⁹I the selected getters were LBH (synthesized in house per [8]), synthetic argentite (Syn-Arg) (synthesized in house per [10]), silver impregnated carbon (Ag-C) (Prominent Systems Inc.), and silver exchanged zeolite (Ag-Z) (Aldrich).

Batch experiments were performed in 250 mL polytetrafluoroethylene bottles at room temperature (~ 22 °C) in an anaerobic chamber containing N₂ and 0.7% H₂ and O₂ levels near 5 ppm. A getter mass of 1.0 g was added to 100 mL of desired test solution, spiked with a set volume (< 1 mL) of a concentrated stock solution (> 10 000 ppm) of NaTcO₄ or NaI to garner radionuclide concentrations which were 1×, 5× and 10× the concentration of those predicted using the Hanford Tank Waste Operations Simulator (5 ppm for ⁹⁹Tc and 0.6 ppm for ¹²⁹I)[11]. Periodic sampling was performed by removing a 2 mL aliquot of solution from the test vessels, which was immediately filtered (0.2 μm). Tc samples were acidified with 20 μL of Optima grade 70% HNO₃ for analysis with inductively coupled plasma mass spectroscopy (ICP-MS). Iodine samples were divided into a 1 mL aliquot which was alkalized with 20 μL of Spectrosol © to prevent volatilization of I₂ at low pH and a 1 mL aliquot acidified with HNO₃ for determination of other species with ICP-MS.

Following exposure, selected getter materials were imaged with SEM on a FEI Helios 600 NanoLab FIB-SEM at 5 keV and elemental compositions determined with XEDS at 20 keV using Oxford INCA software. XANES and EXAFS were performed at the Stanford Synchrotron Radiation Lightsource, and experimental details are listed in a previous report ([12]).

RESULTS

Batch Experiments

Batch experiments were performed to compare the performance of the getters to one another in DI water and 7.8 M LAW simulant. The effectiveness of the getters was quantified using distribution coefficients, K_d (mg/L), which was calculated as follows:

$$K_d = \frac{c_{i,blank} - c_i}{c_i} \times \frac{V_s}{m_g}$$

Where $c_{i,blank}$ is the concentration of the species, i , in the blank solution with no getter present in $\mu\text{g/L}$, c_i is the concentration of the species at a specific interval in $\mu\text{g/L}$, V_s is the volume of solution in mL and m_g is the mass of the getter added to solution in g.

The performance of the Tc getters in DI water with Tc = ~ 53 ppm, are shown in Figure 1 (a). It is clear from the plot that the Sn-A has the best performance over the initial 16 days with K_d values of $\sim 5 \times 10^7$ mL/g achieved after a steady increase in the first 10 days of exposure. The SnCl₂ outperformed the remaining getters, K_d of 1×10^3 mL/g, over the initial exposure period. The SnCl₂ reached this value almost immediately and displayed little change after the initial sampling. The other getters had poor performance, $K_d < 10^2$ mL/g, in the first 16 days. However, at long exposure times some variances in the getter performance were observed. The Sn-HA increased in K_d by four orders of magnitude to 9.6×10^5 mL/g at 29 days. The BFS-2 showed the largest improvement with a near six order of magnitude change to a K_d of 3.5×10^7 mL/g at 35 days, which may have arisen from Tc diffusive transfer from solution into the BFS structure over the duration of the experiment. Overall in DI water, the getters containing Sn(II) had the highest success removing Tc most likely because of their ability to reduce the Tc(VII) to Tc(IV). A similar trend in performance was observed for lower Tc concentrations as well[13]. Upon correction of the data to surface area of the getter, calculated with the BET method, little change was observed with Sn-A still having over an order of magnitude higher K_d than its counterparts. In experiments increasing the amount of the getter solid-to-solution ratio, a 10 \times increase in BFS led to a seven order of magnitude increase in K_d , again confirming surface area is not the sole influence on Tc getter behaviour.

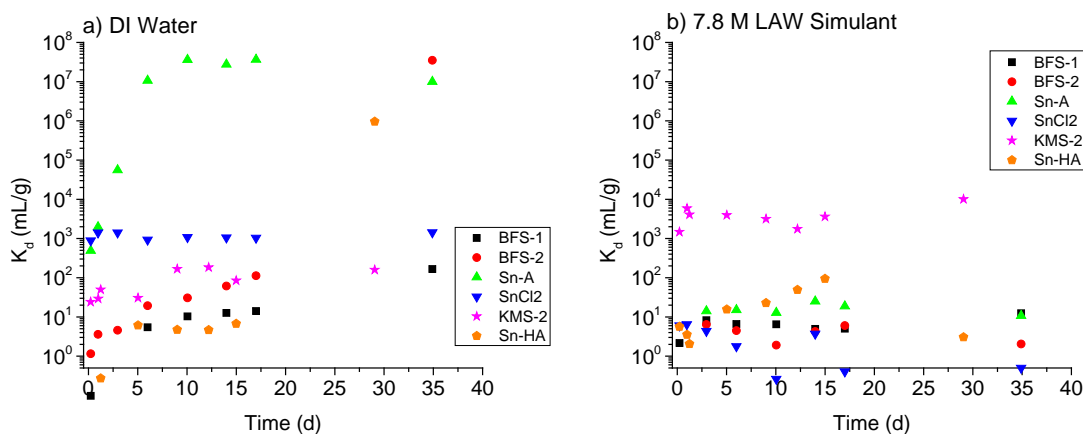


Figure 1 – Distribution coefficients, K_d (mL/g), for various Tc getters in a) DI water and b) 7.8 M LAW simulant with Tc = 53 ppm.

A significant decrease in getter performance was observed in getters experiments in the 7.8 M LAW simulant (Tc = 53 ppm), Figure 1 (b). The KMS-2 displayed the best performance, K_d 1.0×10^4 mL/g, over the duration of the exposure, while all other getters removed very little Tc from the simulant. The KMS-2 is the only getter to have performed much better in the more alkaline, higher ionic strength simulant than in DI water. This result suggests that the mechanism of removal of Tc from solution by KMS-2 depends on the secondary ions in solution. The secondary ions (ex Cr^{3+/6+}, NO₃⁻, OH⁻) interfere with the ability of the other getters to sequester the Tc in the waste simulant. Studies into the performance of the getters in simulant conditions without individual secondary ions showed Cr to be the most likely species impacting

getter performance [12]. Cr(VI), a strong oxidant, was present in a much larger concentration than the Tc in the simulant (Cr = 1700 ppm to Tc = 53 ppm). Many of the getters rely on their ability to reduce Tc(VII) to Tc(IV) for immobilization. The presence of excess amounts of Cr(VI) would directly interfere with the reduction of Tc as the Cr may be preferentially reduced, and the likelihood of a reaction between the getter and Cr was higher than the getter and Tc due to the increased concentration of Cr.

The removal of I (I = 6 ppm) from DI water by the selected getters is shown in Figure 2(a). The Syn-Arg and Ag-C displayed the best performance in removal of I, having attained K_d of 3.6×10^5 mL/g and 6.2×10^5 mL/g, respectively. The Syn-Arg was observed to have a steady increase in K_d within the first 16 days of exposure being a likely result of continuous dissolution of the getter leading to continual release of Ag^+ ions to solution. The effective removal of I by Syn-Arg and Ag-C was followed in order by the Ag-Z (K_d 8.8×10^4 mL/g) and the LBH (2.0×10^3 mL/g). It is not surprising that the Ag-containing getters were successful in the removal of I as AgI could be formed to immobilize the I. Thus the formation of an AgI compound was a more successfully mechanism for I removal than the anion exchange by the LBH.

Figure 2(b) shows a markedly less compromised performance in the 7.8 M Na simulant for the I getters, compared with Tc getters. The Ag-Z displayed very little change in the removal of I between DI water and in the 7.8 M LAW simulant with a K_d of 2.5×10^4 mL/g. It should be noted that this K_d for Ag-Z is a minimum value due to I levels being below the detectable limit. The Syn-Arg decreased in performance by two orders of magnitude to a K_d of 1.8×10^3 mL/g at 16 days, albeit with a steady increase in removal over time, a trend also observed for batch sorption tests performed in DI water. The Ag-C and LBH, on the other hand, displayed a drastic drop in their behaviour in the simulant. The secondary ions in the simulant interfere with the ion exchange of the LBH, and interfere with the ability of the Ag-C to form AgI as the excess Cr may be reducing the Ag^+ supplied from the Ag-C. The Syn-Arg has its getter mechanism interfered with by the simulant constituents, however the Ag-Z was relatively consistent in both solutions. This steady behaviour of the Ag-Z may be attributed to the ion-exchange function of the zeolite between Na^+ and Ag^+ . In DI, there are no secondary ions to interfere with the removal of I, however, in the 7.8 M LAW simulant the high levels of Na^+ can facilitate increased release of Ag^+ from the zeolite structure in an ion exchange process to facilitate a continued removal of I from solution and overcome any interference from the secondary ions.

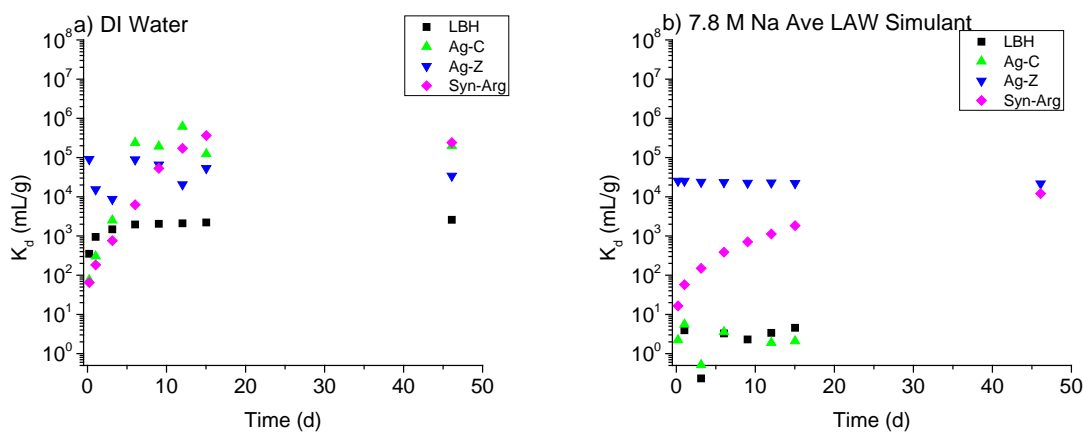


Figure 2 - Distribution coefficients, K_d (mL/g), for various Tc getters in a) DI water and b) 7.8 M LAW simulant with I = 6 ppm.

Solid-State Characterization and Analyses of Getter Materials

To begin elucidating removal mechanism of the successful Tc getters, the successful “loaded” Tc getters were characterized following the batch experiments discussed above. The getters selected were Sn-A and BFS-2 from DI water and Sn-HA and KMS-2 from the 7.8 M LAW simulant. SEM/XEDS were utilized to image the getter materials and determine, qualitatively, the distribution of Tc throughout the getter. Sn-A displayed an evened distribution of Tc across its surface, while Tc-rich regions were identified on the BFS-2. These locations of high Tc in the BFS-2 are likely oldhamite (CaS) phases as identified previously [14]. The KMS-2 was difficult to assign Tc locations due to overlap in the XEDS by the high S content and the Sn-HA experienced interference from the high amount of Na remaining on the getter following removal from solution.

Determination of the oxidation state of the Tc contained within the getter was performed using XANES analysis. The results from the DI water loaded getters showed that in Sn-A the Tc was mainly in its reduced Tc(IV) form, with similar bonding signature to a Tc(IV)EDTA form where it is coordinated by oxygen atoms. On the BFS-2 getter the Tc was found to be in its Tc(VII) state as TcO_4^- , a result of either slow reaction time of the BFS-2 or re-oxidation during the timeframe of the post-treatment sample handling and/or the spectroscopic measurement [15]. In the 7.8 M LAW simulant the Sn-HA had Tc in the Tc(IV)EDTA form while the KMS-2 displayed Tc(IV) as a Tc_2S_7 environment, where it was coordinated by sulfide and disulfide groups.

EXAFS spectra were collected for the Sn-A and KMS-2, but reliable spectra could not be attained for the BFS-2 and Sn-HA. From the EXAFS on the Sn-A sample the Tc was measured to be in a $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ form, expected due to the reduction of Tc by the Sn. There was also no evidence of the Tc incorporation into the apatite structure to replace a Ca or Sn. In the KMS-2, where XANES showed the Tc to be in the Tc(IV) state, the same $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ structure was not observed, confirming the XANES data of a Tc_2S_7 coordination and a different removal mechanism than the Sn-containing getters.

CONCLUSIONS

Cast Stone has been identified as a potential waste form for Hanford low activity wastes which contains ^{99}Tc and ^{129}I . In order to ensure the waste form meets environmental requirements for the long-term management of these radionuclides, the retention properties of Cast Stone need to be improved. One method for improvement can be achieved through the addition of getters to specifically sequester such species.

Studies into various getters for ^{99}Tc showed Sn(II)-containing getters have the highest removal rates of Tc in DI water. Sn(II)-apatite, which was observed spectroscopically to reduce Tc(VII) to Tc(IV), was the strongest getter in this study in DI water. However, the performance of Sn(II)-apatite was lowered significantly in a 7.8 M LAW simulant, likely a result of interference from the Cr(VI) species present in the simulant solution that directly competes with Tc(VII) for reduction. KMS-2, a potassium metal sulfide, had the highest performance in the simulant solution. Tc was found in its reduced state Tc(IV), coordinated by S atoms, in the KMS-2 getter, showing that the Tc is reduced by the KMS-2 but anion exchange in the interstitial layers of the material may also play a role in the ability of the getter as well.

Of the getters for ^{129}I , the synthetic argentite and silver impregnated carbon had the highest levels of removal in DI. Though both getters saw a decrease in performance in the 7.8 M LAW simulant, the origin of the interference is not yet understood, but may be caused by Cr interference as observed with the Tc getters. Silver-exchanged zeolite had strong performance in both DI and the waste simulant. The

presence of secondary ions may be facilitating increased ion exchange and release of Ag^+ from the Ag-Z leading to this strong performance in both solutions. The Ag-Z is thus a strong candidate for the immobilization of ^{129}I . Further tests will incorporate well-performing getters into the Cast Stone formulation to demonstrate their effectiveness in decreasing diffusivities of both Tc and I from the cementitious waste form.

REFERENCES

1. SUNDARAM, S.K., K.E. PARKER, M.M. VALENTA, S.G. PITMAN, J. CHUN, C.W. CHUNG, M.L. KIMURA, C.A. BURNS, W. UM, and J.H. WESTSIK JR., "Secondary Waste Form Development and Optimization - Cast Stone". PNNL-20159. Rev. 1, Pacific Northwest National Laboratory, Richland, Washington 2011.
2. LI, D., D.I. KAPLAN, A.S. KNOX, K.P. CRAPSE, and D.P. DIPRETE, "Aqueous ^{99}Tc , ^{129}I and ^{137}Cs removal from contaminated groundwater and sediments using highly effective low-cost sorbents". *Journal of Environmental Radioactivity*. 136(0) 56-63 2014.
3. WESTSIK, J.H., G.F. PIEPEL, M.J. LINDBERG, P.G. HEASLER, T.M. MERCIER, R.L. RUSSEL, A.D. COZZI, W.E. DANIEL, R.E. EIBLING, E.K. HANSEN, M.R. REIGAL, and D.J. SWANBERG, "Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Screening Tests". PNNL-22747, SRNL-STI-2013-00465. Rev. 0, Pacific Northwest National Laboratory, Richland, Washington and Savannah River National Laboratory, Aiken, South Carolina 2013.
4. MATTIGOD, S.V., R.J. SERNE, and G.E. FRYXELL, "Selection and Testing of "Getters" for Adsorption of Iodine-129 and Technetium-99: A Review". PNNL-14208. Pacific Northwest National Laboratory, Richland, Washington 2003.
5. PIERCE, E.M., S.V. MATTIGOD, R.J. SERNE, J.P. ICENHOWER, R.D. SCHEELE, W. UM, N. QAFOKU, and J.H. WESTSIK, "Review of Potential Candidate Stabilization Technologies for Liquid and Solid Secondary Waste Streams". PNNL-19122. Pacific Northwest National Laboratory, Richland, Washington 2010.
6. MERTZ, J.L., Z.H. FARD, C.D. MALLIAKAS, M.J. MANOS, and M.G. KANATZIDIS, "Selective Removal of Cs^+ , Sr^{2+} , and Ni^{2+} by $\text{K}_2\text{xMg}_x\text{Sn}_3\text{-xS}_6$ ($x = 0.5-1$) (KMS-2) Relevant to Nuclear Waste Remediation". *Chemistry of Materials*. 25(10) 2116-2127 2013.
7. GILLIAM, T.M., R.D. SPENCE, W.D. BOSTICK, and J.L. SHOEMAKER, "Solidification/stabilization of technetium in cement-based grouts". *Journal of Hazardous Materials*. 24(2-3) 189-197 1990.
8. KRUMHANS�, J.L., J.D. PLESS, J.B. CHWIRKA, and K.C. HOLT, "Yucca Mountain Project Getter Program Results (Year 1)". SAND2006-3869. Sandia National Laboratory, Albuquerque, New Mexico 2006.
9. DUNCAN, J.B., G.A. COOKE, and L.L. LOCKREM, "Assessment of Technetium Leachability in Cement Stabilized Basin 43 Groundwater Brine". RPP-RPT-29195, 2009.
10. KAPLAN, D.I., S.V. MATTIGOD, K.E. PARKER, and G. IVERSEN, "Experimental Work in Support of the ^{129}I Disposal Special Analysis". WSRC-TR-2000-00283. Westinghouse Savannah River Company, Aiken, South Carolina 2000.
11. CERTA, P.J. and P.A. EMPEY, "River Protection Project System Plan". ORP-11242. Revision 6, Washington River Protection Solutions, LLC, Richland, Washington 2011.
12. NEEWAY, J.J., N. QAFOKU, R.J. SERNE, A.J. LAWTER, J.R. STEPHENSON, W.W. LUKENS, and J.H. WESTSIK JR., "Evaluation of Technetium Getters to Improve the

- Performance of Cast Stone". PNNL-23667. Pacific Northwest National Laboratory, Richland, Washington 2014.*
13. QAFOKU, N., J.J. NEEWAY, A.R. LAWTER, T.G. LEVITSKAIA, R.J. SERNE, J. WESTSIK, J.H., and M.M. VALENTA SNYDER, "*Technetium and Iodine Getters to Improve Cast Stone Performance". PNNL-23282, 2014.*
 14. UM, W., H.B. JUNG, G. WANG, J.H. WESTSIK JR., and R.A. PETERSON, "*Characterization of Technetium Speciation in Cast Stone". PNNL-22967. Pacific Northwest National Laboratory, Richland, Washington 2013.*
 15. LUKENS, W.W., J.J. BUCHER, D.K. SHUH, and N.M. EDELSTEIN, "*Evolution of Technetium Speciation in Reducing Grout". Environmental Science & Technology. 39(20) 8064-8070 2005.*

ACKNOWLEDGEMENTS

This work was completed as part of the Supplemental Immobilization of Hanford Low-Activity Waste project. Support for this project came from Washington River Protection Solutions. The authors wish to acknowledge the Kanatzdis group at Northwestern University for providing one of the technetium getters, and Dave Swanberg (Washington River Protection Solutions, Supplemental Treatment Waste Form Development Project) for programmatic guidance, direction, and support and for synthesizing and providing the tin apatite material used in this study and Steven Baum and Ian Leavy of the Geosciences Group for help in running the ICP-MS analyses.