Silver-iodine Secondary Waste Stabilization: Multi-scale Evaluation

Iodine-129 is a key risk driver in most low-level waste cementitious waste repositories. The objectives of this study were to determine iodine speciation in cementitious materials with slag (Grout$_{+slag}$) and without slag (Grout$_{-slag}$) and its impact on iodine immobilization. Additional studies were conducted to

determine if grout was compatibility as a waste form for the most common adsorbent used to remove aqueous and gaseous radioiodine, silver-impregnated granular activated carbon (Ag-GAC). Rankings of iodine species by their tendency to bind to grout were: iodide << organo-iodine ≤ iodate. Similarly, ranking of grout formulations by their tendency to immobilize iodine were: Grout$_{+slag}$ < Grout$_{-slag}$. Organo-iodine comprised >40% of the leachate solution from grout samples initially hydrated (cured) with iodide. The origin of the organic ligand
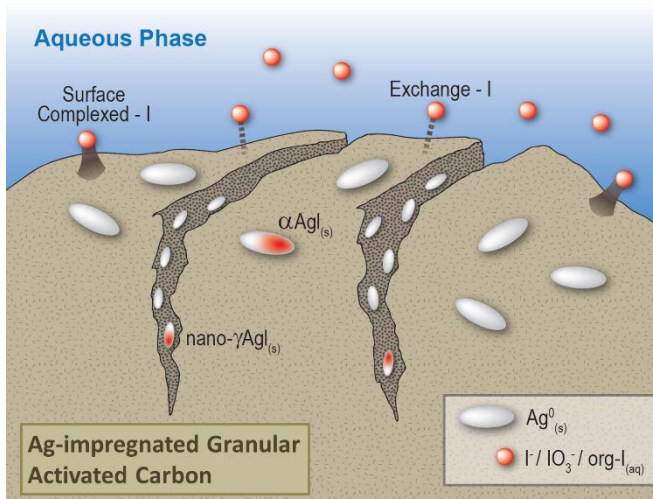
comprising the organo-iodine was organic carbon in the grout material (~1200 mg/kg). Iodine in the solid phase, as determined by K-edge X-ray Absorption Near-Edge Spectroscopy, and aqueous phases were not in equilibrium and essentially no iodine speciation transformations occurred within the grout after one month of curing, irrespective of which iodine species was initially added to the mix. For the first time, these studies demonstrate that multiple iodine species can co-exist simultaneously in grout porewater, the iodine species initially added to the grout can greatly affect immobilization, and that Ag-GAC can be safely disposed in grout formulation, but not in the presence of slag. These results help explain previous data and reduce uncertainty associated with the disposal of nuclear waste.

Awards and Recognition

None

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature	**Date**

Silver-iodine Secondary Waste Stabilization: Multi-scale Evaluation

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Thrust Area: ES

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Iodine-129 is a key risk driver in most low-level waste cementitious waste repositories. Rankings of iodine species by their tendency to bind to grout were: iodide << organo-iodine ≤ iodate. Similarly, ranking of grout formulations by their tendency to immobilize iodine were: Grout$_{+slag}$ < Grout$_{−slag}$. A significant fraction of the iodide hydrated (cured) with the grout had converted to organo-iodine in the leachate. For the first time, these studies demonstrate that multiple iodine species can co-exist simultaneously in grout porewater, the iodine species initially added to the grout can greatly affect immobilization, a large fraction of the hydrated iodine was strongly bound into the structure of the grout, and that Ag-GAC can be safely disposed in grout formulation, but not in the presence of slag. These results help explain previous data and reduce uncertainty associated with the disposal of nuclear waste.

FY2018 Objectives

- *Determine iodine speciation in cementitious materials with slag (Grout$_{+slag}$) and without slag (Grout$_{−slag}$)*
- *Determine the impact of iodine speciation on immobilization by grout*
- *Determine if grout is compatibility as a waste form for the most common adsorbent used to remove aqueous and gaseous radioiodine, silver-impregnated granular activated carbon (Ag-GAC)*

Introduction

Iodine-129 (^{129}I) is commonly the single greatest risk driver in high-level and low-level nuclear repositories.[1] This risk stems from several basic properties of ^{129}I, including that under many geochemical conditions, it can move as an anion at nearly the rate of water through the subsurface environment. ^{129}I is also extremely radiologically toxic because over 90% of body burden accumulates in the thyroid, which weighs only about 14g in an adult.[2] To illustrate how the properties of ^{129}I magnify its risk, ^{129}I accounts for only 0.00002% of the radiation released from the Savannah River Site in Aiken, South Carolina, but contributes 13% of the population dose, a six orders of magnitude magnification of risk with respect to its radioactivity.[3] There is also a large worldwide inventory of radioiodine as a result of its high fission yield and this inventory is rapidly increasing as a result of nuclear energy production.[1] Radioiodine is produced at a rate of 1 Ci per gigawatt of electricity produced by nuclear power.[4]

Low-level aqueous radionuclide waste is presently being disposed as a cementitious waste form in the vadose zone of Savannah River Site[5] and is being evaluated at several other locations around the world.[6,7,8] The radioactive liquid waste is blended into the cementitious dry mix and then disposed in the vadose zone. The resulting waste form binds the radionuclide through a wide range of mechanisms, while at the same time reducing water flux.[7, 9] Slag is a common ingredient in cementitious waste forms because it reduces porosity, alters set time, and creates a strongly reducing environment that promotes the immobilization of several redox sensitive radionuclides, including Np, Pu, Se, Tc, and U. Slag is a glass-like by-product from smelting raw ore. Upon activation of the slag by the high pH of cement porewater, the redox condition decreases and is poised by sulfide species, mainly S^{2-}.[10,11] The reductive capacity of slag varies depending on its source, but is quite high and comparable to that of pyrite, in the

range of 799 and 820 meq/kg.[12,13] The impact of the strongly reducing conditions created by slag-based cementitious waste forms on iodine immobilization has not been evaluated.

To the best of our knowledge, there have been no measurements of aqueous iodine speciation in cementitious systems. This can be in part attributed to the fact that the analytical methods of choice for speciation measurements, such as XANES/EXAFS and ion chromatography, require much higher iodine concentrations than commonly exists in these systems. Thermodynamic calculations predict that iodide (I^-) should be the dominant species, especially under subsurface repository conditions. Atkins and Glass[10] concluded that iodine in cementitious systems will likely exist as I^- because I^- oxidation to iodate (IO_3^-) by molecular oxygen is extremely slow. In slag-containing cement blends, the strongly reducing environment would favor the I^- species.[11]

Approach

A series of batch adsorption and desorption experiments were conducted utilizing grout samples with slag (Grout$_{+slag}$) and without slag (Grout$_{-slag}$) and with and without silver impregnated granular activated carbon (Ag-GAC) that had been equilibrated with dissolved I^- (AgI-GAC) (**TABLE 1**). Solutions used in the batch experiments were created to simulate grout porewater. These solutions were created by equilibrating a 1:10 grout:water suspension for 2 weeks, then pass the suspension through a 0.1-µm filter (**TABLE 2**). All experiments involving the slag-free grout samples were conducted on the benchtop, whereas all the slag-containing grout samples were conducted in an inert glovebag (5%H_2/95% N_2).

Iodine speciation was conducted by the derivitization method described by Zhang et al.[14] The hydrated grout samples were characterized by standard methods, including XRF, XRD, and CHN analyses (to quantify organic and inorganic carbon). All measurements were conducted in duplicate.

K-edge XANES spectra of grout samples, together with several reference materials (i.e., KI, KIO_3 and 4-iodoaniline), were collected using the Materials Research Collaborative Access Team Sector 10-BM beamline at the Advanced Photon Source (Argonne National Lab, Argonne, IL). Statistical analyses were performed in the software R version 3.5.0 (2018-04-23),[15] using the Student's t-test or Tukey's Range Test in the STATS package (version 3.6.0).[16]

TABLE 1. Grout Samples Formulations.

	Wt-% Dry Blend				
	Slag	Cement	Fly Ash	AgI-GAC[a]	Liquid:Dry Blend
Grout$_{-slag}$	0	25	75	0	0.29
Grout$_{+slag}$	45	8	47	0	0.45
Grout$_{-slag/AgI-GAC}$	0	25	55	20	0.29
Grout$_{+slag/AgI-GAC}$	45	8	27	20	0.49

[a] AgI-GAC = 10 wt% Ag impregnated on granular activated carbon. The Ag-GAC was loaded with ~9 mg/kg iodide.

TABLE 2. Grout and Grout Leachate Characterization[a]

		Grout$_{-slag}$	Grout$_{+slag}$
Solid Phase[b]	Total I (mg/kg)	0.083	0.177
	Organic C (mg/kg)	1,200	1,300
	Inorg. C (mg/kg)	16,400	14,500
	Fe_2O_3 (wt-%)	4.47	3.04
	SO_3 (wt-%)	0.81	1.06
	LOI	12.79	11.43
Grout Leachate	Total I (µg/L)[c]	1.80	20.08
	pH	12.21	12.37
	Eh (mV)	+423	-307
	DOC (mg/L)	4.28	4.98
	Ca (mg/L)	8.31	38.48
	Fe (mg/L)	0.10	0.48
	K (mg/L)	314.7	235.0
	Na (mg/L)	1135	512
	Si (mg/L)	13.60	9.41
	Cl^- (mg/L)	5.44	23.60
	NO_3^- (mg/L)	7.87	5.02
	SO_4^- (mg/L)	323.4	41.67

[a] Average of duplicate analyses; Grout leachate data from a 1:10 grout-to-water suspension; Grout$_{-slag}$ suspension equilibrated for 14 days on a benchtop and Grout$_{+slag}$ suspension equilibrated for 14 days in an inert glovebox.

Results/Discussion

Kinetic Desorption Experiment with Iodide, Iodate, and 4-Iodoaniline Hydrated in Grout.

A ranking of the iodine amendments based on their tendency to release iodine into the aqueous phase was: I^- >> 4-iodoaniline (representative of an organo-iodine species) ≥ IO_3^-

(**FIGURE 1**). For the I⁻ or 4-iodoaniline amended grout samples, there were no significant difference between the amount of total iodine released from the Grout−slag and Grout+slag suspensions. For the IO_3^- amended samples, total iodine concentrations leached from the Grout−slag were about twice that of the Grout+slag.

Apparent (non-steady state) desorption distribution coefficients (K_d; solid:liquid iodine concentration ratio) (**TABLE 3**) were between 3 and 40 times greater than the adsorption K_d values (on average ~ 3 L/kg). Furthermore, the I⁻, IO_3^-, and 4-iodoanaline apparent desorption K_d values for Grout-slag were significantly less than corresponding K_d values for the Grout+slag suspensions (Student's t-test at $p \le 0.05$) (**TABLE 3**). Furthermore, I⁻ K_d values were less than IO_3^- or 4-iodoaniline K_d values. 4-iodoaniline K_d values were less than or equal to IO_3^- K_d values (Tukey's Range Test at $p \le 0.05$).

Iodine K-edge XANES Analysis. Iodine K-edge XANES analysis was conducted on Grout−slag and Grout+slag samples that had been hydrated with I⁻, IO_3^-, or 4-iodoaniline (**FIGURE 2**). Potassium iodide (KI), potassium iodate (KIO₃), and 4-iodoaniline were included in the analyzes as reference materials. Irrespective of whether slag was or was not
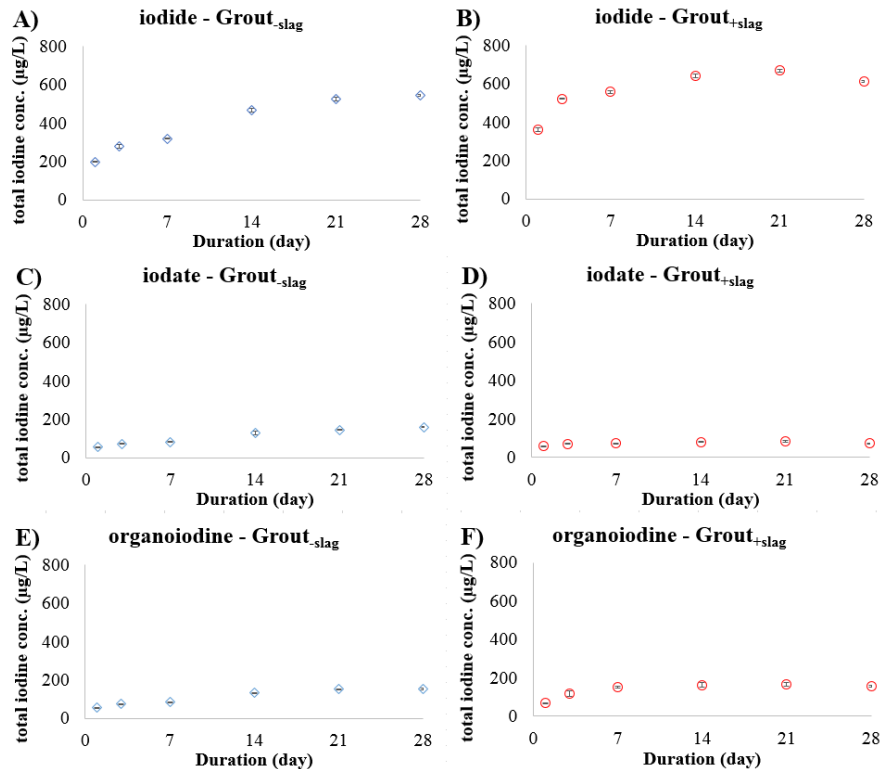

FIGURE 1. Total aqueous iodine concentrations desorbed from 6 grout treatments: (a) Grout−slag amended with I⁻, (b) Grout+slag amended with I⁻, (c) Grout−slag amended with IO_3^-, (d) Grout+slag amended with IO_3^-, (e) Grout−slag amended with 4-iodoanaline, and (f) Grout+slag amended with 4-iodoanaline. Error bars were calculated from duplicate samples and propagated error and may be hidden by symbol. Grout samples were hydrated with 190 µmol/L iodine as I⁻, IO_3^- and 4-iodoaniline, cured for >3 months, and the solid:liquid ratio during the 28 day desorption period was 1:20. The aqueous phase was the grout leachate described in Table 1.

TABLE 3. Desorption K_d values (L/kg) as a function of grout formulation and iodine species added to mix prior to curing.

	iodide amended	iodate amended	4-iodoaniline amended
Grout−slag	6.14 ± 0.07^a bB^b	30.62 ± 0.17 aB	32.28 ± 1.15 aB
Grout+slag	7.50 ± 0.10 cA	121.78 ± 9.54 aA	42.07 ± 2.47 bA

^{a} K_d values (C_{grout}/C_{aq}) were calculated using the 28-day data from Fig. 1 (C_{aq}) and the solid concentration at the end of the 28-day equilibration period (C_{grout}). Initially, the total iodine in Grout−slag was 9.077 ± 1.030 µg/g and in Grout+slag was 9.469 ± 1.981 µg/g.

^{b} Different lowercase letters within a row represent significantly ($p \le 0.05$, $n = 2$) different values according to Tukey's HSD Range Test. Different uppercase letters within a column represent significantly ($p \le 0.05$, $n = 2$) different values according to Student's t-test.

present, iodine speciation in the grout samples did not change between the time it was added and the time it was analyzed by XANES (about 1 month later). This lack of iodine transformations noted in the aqueous

phase (TABLE 2 and FIGURE 2). Clearly, the solid and aqueous phases were not in equilibrium. Under these experimental conditions, measurement of the solid phase iodine speciation provided little insight into the aqueous iodine speciation.

Kinetic Desorption of Iodine from Ag-GAC imbedded in Grout. Much more iodine was released from the Grout$_{+slag/AgI-GAC}$ samples than from the Grout$_{-slag/AgI-GAC}$ sample (**FIGURE 3** and **TABLE 4**). Geochemical modeling (Geochemist's Workbench) suggested that the release of iodine may be attributed to the strongly reducing conditions created by the slag (**TABLE 4**), which promoted the reduction of the Ag$^+$ in the AgI to Ag^0. This reduction process resulted in the dissolution of the AgI solid, thereby releasing the iodide. Furthermore, in the presence of slag, the concentration of Ag in the aqueous phase was <2 µg/L, XRD and geochemical modeling indicated the Ag had precipitated as nano-Ag^0 particles.
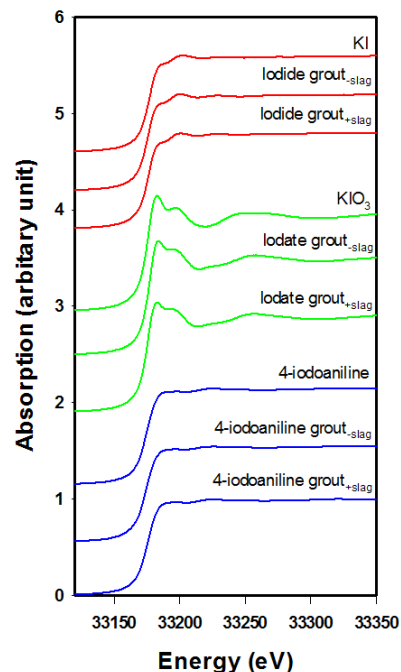

FIGURE 2. Iodine K-edge XANES spectra of grout with and without slag, that were hydrated with iodide, iodate, or 4-iodoaniline. Also presented are reference standards of KI, KIO$_3$, and 4-iodoaniline.

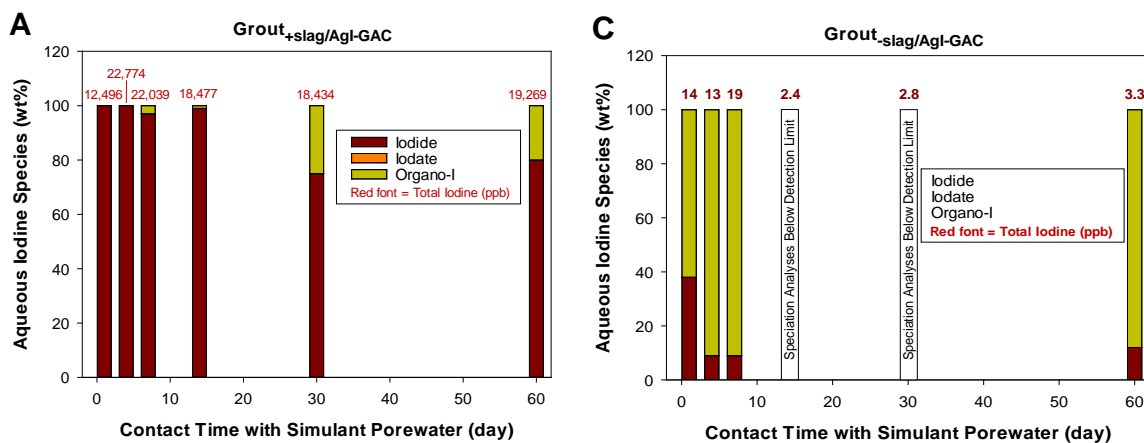**FIGURE 3.** Percent aqueous iodine speciation in suspensions of grout with slag, Grout$_{+slag\ AgI-GAC}$, and without slag, Grout$_{-slag\ AgI-GAC}$. The Grout$_{+slag\ AgIGAC}$ experiments were conducted in an inert atmosphere, whereas the Grout$_{-slag\ AgIGAC}$ experiments were conducted on a benchtop. Total aqueous iodine (µg/L) is noted above histogram. Results are averages of duplicate measurements.

TABLE 4: Comparison of Aqueous Chemistry after 60 days of the Suspensions Containing Grout with and without Slag that were Amended with AgI-GAC.

Variable	Grout$_{+Slag/AgI-GAC}$	Grout$_{-Slag/AgI-GAC}$
Eh (mV)	-392 ± 37	439 ± 1*
pH	12.41 ± 0.04*	9.34 ± 0.08.
Ag (µg/L)	0.82 ± 0.96	92.11 ± 11.37*
DOC (mg/L)	7.66 ± 0.53	13.60 ± 1.56*
Tot I (µg/L)	19,269 ± 26263*	3.3 ± 1.1
I- (wt%)	80*	12
IO_3^- (wt%)	0	0
Org-I (wt%)	20	88*

* Indicates a significant greater value according to the Student t-test (p ≤ 0.05, n = 2).

FY2018 Accomplishments

- Developed a new analytical protocol that permits identifying iodine speciation in high salt environments.
- Demonstrated that multiple iodine species exist at the same time in grout leachate.
- Demonstrated that the iodine speciation of waste may influence cementitious waste form effectiveness.
- A fraction of iodine that is hydrated in grout cannot be readily released from the grout (data not shown here), suggesting that the single low distribution coefficient (K_d) approach to describing radioiodine release may not be appropriate for all cementitious iodine.

Future Directions

Two Proposals Stemming from Seed Data Generated from this Study:

1. Kaplan, D. I., and D. Li. 2018. Iodine and Ruthenium Removal from the Advanced Liquid Processing System (ALPS) Multi-nuclide Removal Facility. TEPCO. $270k for FY19
2. Nichols, R., and D. I. Kaplan. Solid Secondary Waste, C. A. Langton. 2018. Response to Request for Information on HEPA Filter Waste Form Development and Testing Related to Radioiodine Immobilization to Support the IDF PA. Washington River Protection Services, Hanford. $700k for FY19.

FY 2018 Publications/Presentations

Publications

1. Kaplan, D. I., Xu, C., Li, D., Lin, P., Xing, W., Nichols, R., Schwehr, K., and Santschi, P. H. (2018). Radioiodine Speciation in Cementitious Environments. *Environmental Science & Technology* (Submitted).
2. Kaplan, D. I., K. Price, C. Xu, D. Li, P. Liu, W. Xing, R. Nichols, K. Schwehr, J. C. Seaman, P. H. Santschi. (2018). Radioiodine Speciation in a Silver-Amended Cementitious Environments. *Environmental Science & Technology* (In Review).
3. Tanaka, K., Kaplan, D. I., and Ohnuki, T. (2017). Radionuclides in the Environment. Applied Geochemistry 85: 119-120.
4. Arai, Y.; Powell, B. A.; Kaplan, D. I., (2017) Sulfur Speciation in Untreated and Alkali Treated Ground-granulated Blast Furnace Slag. *Sci. Total Environ.* 589, 117-121.

Presentations

1. Kaplan, D. I.; Santschi, P. H.; Ohnuki, T.; Li, D.; Nichols, R.; Price, K.; Xu, C.; Lin, P.; Xing, W.; Schwehr, K.; Tanaka, K.; Seaman, J. (2018) Radioiodine Speciation in Cementitious Environments. In *International Conference on Heavy Metals in the Environment*, Athens, GA, 2018.
2. Kaplan, D. I., Xu, C., Lin, P., Li, D., Schwehr, K., Tanaka, K., Ohnuki, T., and Santschi, P. H. (2018). Radioiodine Speciation in Cementitious Environments. *In* "Goldschmidt 2018". Geochemistry Society, Boston, MA.
3. Kaplan, D. I., Price, K. A., Seaman, J. C., Li, D., Lin, P., Xu, C., Schwehr, K., Tanaka, K., Ohnuki, T., and Santschi, P. H. (2018). Iodioiodine Speciation Impact on Ag-Activated Carbon Immobilization in Cementitious Environments. *In* "Goldschmidt 2018". Geochemistry Society, Boston, MA.
4. Qafoku, N. P., Kaplan, D. I., Lawter, A. R., Neeway, J. J., Szecsody, J. E., Bagwell, C. E., and Truex, M. J. (2018). Iodine conceptual models at the Hanford and Savannah River sites: Similarities and differences *In* "Goldschmidt 2018". Geochemistry Society, Boston, MA.
5. Ohnuki, T., Kozai, N., Tanaka, K., Tokunaga, K., Utsunomiya, S., Ikehara, R., Komiya, T., Takeda, A., Kaplan, D. I., and Santschi, P. H. (2018). Alkaline-activated metakaolin solidification of iodine sorbed by layered double hydroxides. *In* "Goldschmidt 2018". Geochemical Society, Boston, MA.
6. Kaplan, D. I., P. Santschi, T. Ohnuki, K. Roberts, D. Li, K. Price, C. Xu, P. Lin, K. Tanaka, J. Seaman. (2018). Influence of Aqueous Radioiodine Speciation on Uptake by Silver-Granulated Activated Carbon. 19th International Conference on Heavy Metals in the Environment – 2018, Athens, GA, July 21 – 25, 2018.
7. Ohnuki, T., N. Kozai, K. Tanaka, K. Tokunaga, S. Utsunomiya, D. I. Kaplan, P. Santschi. (2018) Sorption and Solidification of Iodate. RadChem 2018. Marianske Lazne, Czech Republic, May 13 – 18, 2018.
8. Kaplan, D. I.; Powell, B. A.; Um, W.; Seaman, J. M.; Kukkadapu, R.; Qafoku, O.; Du, Y.; Bowden, M. E.; Li, D.; Arai, Y. (2017) *Radionuclide Leaching and Mineral Characterization of Core Samples Recovered from the Saltstone Disposal Facility, Aiken, SC USA*, Migration 2017 - 16th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Barcelona, Spain, September 10-15, 2017, 2017; Barcelona, Spain, 2017.

Acronyms

Ag	Silver
Ag^0	Zero valent silver
AgI	Silver iodide
APS	Advanced Photon Source
CHN Analyzer	Carbon, Hydrogen, Nitrogen Analyzer
GAC	Granular activated carbon
$Grout_{+slag}$	Grout containing slag
$Grout_{-slag}$	Grout without slag
$Grout_{+slag/AgI-GAC}$	Grout with slag and silver impregnated activated carbon
$Grout_{-slag/AgI-GAC}$	Grout with slag and silver impregnated activated carbon
I^-	Iodide
IO_3^-	Iodate
K_d	Distribution coefficient
KI	Potassium iodide
KIO_3	Potassium iodate
XANES	X-ray Absorption Near-Edge Spectroscopy
XRF	X-ray Florescence
XRD	X-ray Diffraction

Intellectual Property
None

Total Number of Post-Doctoral Researchers
2 Post-Doctoral Researchers were funded under this project: Dr. Chen Xu and Dr. Peng Liu from Texas A&M University

References

1. Kaplan, D. I.; Denham, M. E.; Zhang, S.; Yeager, C.; Xu, C.; Schwehr, K. A.; Li, H. P.; Ho, Y. F.; Wellman, D.; Santschi, P. H., Radioiodine biogeochemistry and prevalence in groundwater *Critical Reviews of Environmental Science and Technology* **2014,** *44*, (20), 2287-2337.
2. ICRP, *Report of the Task Group on Reference Man*. Pergamon Press: Oxford, 1975.
3. Kantelo, M. V.; Bauer, L. R.; Marter, W. L.; Murphy, C. E., Jr.; Zeigler, C. C. *Radioiodine in the Savannah River Site Environment*; WSRC-RP-90-424-2; Westinghouse Savannah River Company, Aiken, SC, 1990.
4. McKay, A., The Making of the Atomic Age. *Oxford University Press* 1984.
5. SRR *FY2016 Special Analysis for the Saltstone Disposal Facility at the Savanah River Site*; Savannah River Remediations: Aiken, SC, 2016.
6. Mann, F. M.; Puigh, R. J.; Finfrock, S. H.; Khaleel, R.; Wood, M. I. *Integrated Disposal Facility Risk Assessment*; RPP-15834; CH2M Hill Hanford Group, Inc., Richland, WA, 2003.
7. Ochs, M.; Mallants, D.; Wang, L., *Radionuclide and Metal Sorption on Cement and Concrete*. Springer: Heidelberg, 2016.

8. Li, J.; Wang, J., Advances in cement solidification technology for waste radioactive ion exchange resins: A review. *Journal of hazardous materials* **2006,** *135*, (1-3), 443-448.

9. Evans, N., Binding mechanisms of radionuclides to cement. *Cem. Concr. Res.* **2008,** *38*, (4), 543-553.

10. Atkins, M.; Glasser, F. P., Application of portland cement-based materials to radioactive waste immobilization. *Waste Management* **1992,** *12*, 105-131.

11. Angus, M. J.; Glasser, F. P., The Chemical Environment in Cement Matrices. *Mat. Res. Soc. Symp. Proc.* **1985,** *50*, 547-556.

12. Um, W.; Yang, J.-S.; Serne, R. J.; Westsik, J. H., Reductive Capacity Measurement of Waste Forms for Secondary Radioactive Wastes. *J. Nucl. Mater.* **2015,** *467*, 251-259.

13. Roberts, K. A.; Kaplan, D. I. *Reduction Capacity of Saltstone and Saltstone Components*; SRNL-STI-2009-00637, Rev 0; Savannah River National Laboratory, Aiken, SC, 2009.

14. Zhang, S.; Schwehr, K. A.; Ho, Y. F.; Xu, C.; Roberts, K. A.; Kaplan, D. I.; Brinkmeyer, R.; Yeager, C. M.; Santschi, P. H., A Novel Approach for the Simultaneous Determination of Iodide, Iodate and Organo-Iodide for I-127 and I-129 in Environmental Samples Using Gas Chromatography-Mass Spectrometry. *Environmental Science & Technology* **2010,** *44*, (23), 9042-9048.

15. R Core Team R: A Language and Environment for Statistical Computing. www.R-project.org/ (2Jun2018),

16. R Core Team and Contributors Worldwide The R Stats Package, Version 3.6.0. (2Jun2018),