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Impact of Cementitious Material Leachate on Iodine Partitioning

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1.0 EXECUTIVE SUMMARY

A series of batch experiments were conducted to evaluate iodine-129 (^{129}I) partitioning to an SRS subsoil typical of materials underlying the Saltstone Disposal Facility (SDF), and Saltwaste Disposal Unit (SDU) construction concrete materials. Iodide partitioning was evaluated under four different background solution chemistries chosen to mimic various stages of saltstone/cement aging throughout the lifetime of the closed facility, from initial cementitious material formation and curing through weathering and eventual far-field leaching in the underlying soil environment. Two alkaline treatment solutions (pH \approx 11-12), termed portlandite and saltwaste leachate solution (SLS), were chosen to mimic the initial stages of cement weathering where leachate composition has the potential to dramatically alter contaminant partitioning to SRS soils and sediments. The remaining two treatment solutions, termed calcite-saturated solution (CSS) and artificial groundwater (AGW), were used to approximate conditions for contaminant partitioning after extensive weathering of the cementitious materials and/or dilution with non-impacted SRS groundwater. Partitioning experiments were conducted under oxic and anoxic (2% H_2 atmosphere) conditions to evaluate the overall impact of redox status on contaminant partitioning to SRS soils and sediments in the absence of direct contact to reactive cementitious material. Additional tests were conducted to evaluate ^{129}I partitioning to ground SDU construction materials under similar redox conditions.

Previously reported SRS soil distribution coefficients for I^- are generally quite low, $< 1 \text{ mL g}^{-1}$, especially under alkaline pH conditions (Seaman and Change, 2014, 2013; Kaplan, 2010). In the current study the initial ^{129}I concentration was 140 pCi mL^{-1} , which is approximately an order of magnitude higher than the average ^{129}I levels ($\approx 14 \text{ pCi mL}^{-1}$) reported for Tank 50 saltwaste (Bannochie, 2012, 2014). While some ^{129}I sorption was observed for the SDF soils under acidic pH conditions ($K_d \approx 0.18$ to 1.0 mL g^{-1}), ^{129}I partitioning levels were quite low for the soil under alkaline conditions ($< 0.18 \text{ mL g}^{-1}$), making it difficult to discriminate between partitioning to the solid-phase from experimental variation and analytical error. Due to the relatively high pH (ranging from 11.5 to 11.9), similar behavior was observed for the SDU construction concrete, regardless of the test atmosphere or background solution. Therefore, the SDU data likely reflect only Stages I/II of the cement weathering sequence.

Table of Contents

1.0	EXECUTIVE SUMMARY	ii
	List of Tables.....	iv
	List of Acronyms and Abbreviations	iv
2.0	INTRODUCTION	1
3.0	MATERIALS AND METHODS	1
	3.1 Characteristics of the SDF Soil	1
	3.2 Oxidic Partitioning Treatments	2
	3.3 Anoxic Partitioning Treatments	3
	3.4 Sample Analysis.....	3
4.0	RESULTS AND DISCUSSION	5
5.0	ACKNOWLEDGEMENTS	6
6.0	REFERENCES	6

List of Tables

Table 1. Characteristics of the SDF soil compared to other SRS soil materials.....	4
Table 2. Composition of the artificial groundwater (AGW) simulant.....	4
Table 3. Summary of ¹²⁹I partitioning results as a function of background solution chemistry.....	6

List of Acronyms and Abbreviations

AGW	Artificial Groundwater
DIW	Deionized Water
LSC	Liquid Scintillation Counting
SDF	Saltstone Disposal Facility
SDU	Saltstone Disposal Unit
SREL	Savannah River Ecology Laboratory
SRR	Savannah River Remediation LLC
SRS	Savannah River Site

2.0 INTRODUCTION

Iodine-129 (^{129}I) is a uranium fission product with a half-life of 1.6×10^7 years. The reduced species, iodide (I^-), is likely to predominate in the presence of saltstone due to the presence of reducing agents within the blast furnace slag (BFS) (Atkins and Glasser, 1992). The objective of the current study was to measure the impact of four cement leachate compositions on the K_d values for ^{129}I partitioning to soil and ground SDU concrete from the Saltstone Disposal Facility (SDF). In previous sorption studies using ^{127}I (i.e., stable iodine), Seaman and Chang (2013 and 2014) reported K_d values of $\leq 1.0 \text{ mL g}^{-1}$ for SDF soils and ground SDU concrete. The current study reflects an effort to further refine I partitioning behavior using the lower detection limits associated with radiological analysis to determine K_d values appropriate for SDF soils and disposal unit construction materials.

Four background test solutions were chosen to mimic various stages in the weathering of cementitious materials (Ochs et al., 2016). Two alkaline solution treatments, referred to as portlandite and the saltstone leachate solution (SLS) were chosen to represent the early stages of cement aging, i.e., Stage I/II. The portlandite treatment, made with $\text{Ca}(\text{OH})_2$, was chosen to mimic the initial high-pH ($\text{pH} \approx 12$) weathering phase of conventional cement where chemical equilibria is controlled by portlandite. The SLS treatment described in greater detail below was chosen to mimic the early weathering stages of reducing grout materials, Stage II. Solution chemistry during Stage III of cement weathering is generally controlled by calcite, CaCO_3 , with a pH of ≈ 9.6 (Kaplan et al., 2010). The Stage IV solution treatment, the artificial groundwater (AGW) simulant, represents more-natural conditions within the subsurface environment following extensive weathering of cementitious materials and dilution with native groundwater.

3.0 MATERIALS AND METHODS

3.1 Characteristics of the SDF Soil

The characteristics of the soil material, termed SDF soil (Table 1), are intermediate in terms of texture and clay mineralogy between the SRS “Clay” and “Sand” materials that have been used extensively to estimate contaminant partitioning on the SRS (Kaplan, 2010; Seaman and Kaplan, 2010; Seaman and Chang, 2013, 2014). The SDF material is a Sandy Clay Loam, with a clay mineralogy dominated by kaolinite and Fe-oxyhydroxides, such as goethite. The material was air dried, homogenized, and passed through a 2-mm sieve before it was used in the current study. All test solutions were prepared with ultrapure de-ionized water (DIW; $18.2 \text{ M}\Omega \text{ cm}^{-1}$ @ 25°C) using reagent-grade chemicals.

Four distinct background solutions, initially chosen to mimic various stages of saltstone and cement weathering, were used in evaluating contaminant partitioning. The two alkaline solutions described below were chosen to reflect the initial weathering (i.e., Stage I/II) of two distinctly different cementitious materials (i.e., portlandite cement and reducing saltstone grout) at a time when their leachates may dramatically impact contaminant partitioning to SRS soils and sediments. A $\text{Ca}(\text{OH})_2$ -saturated leaching solution (referred to as Portlandite) and a solution created using ground up saltstone (referred to as the saltstone leachate solution, labeled SLS) were used to mimic the leachates derived from portlandite cement and saltstone grout, respectively. A calcite (CaCO_3) saturated solution (CSS) and an artificial ground water (AGW) surrogate, the final composition of which is specified in Table 2, were chosen to reflect the contaminant partitioning after significant weathering of the cementitious materials and dilution with non-impacted pore waters (i.e., weathering Stages III and IV) (Ochs et al. 2016).

The “portlandite” test solution was created by adding 1.26 g L^{-1} of $\text{Ca}(\text{OH})_2$ to CO_2 purged DIW. Further contact with the atmosphere was minimized by storing under N_2 until the solution was used. The CSS test solution was created by adding an excess of CaCO_3 to a liter of warm DIW and stirring overnight. After 24 hrs the calcite solution is then passed through a $0.45 \text{ }\mu\text{m}$ pore size filter to remove any residual calcite. The SLS was created by equilibrating ground saltstone with DIW for 24 hrs at a 1/10 (g/g) saltstone to DIW ratio. After equilibration, the solution was vacuum filtered ($0.45 \text{ }\mu\text{m}$ pore size) before use. The composition of the AGW test solution was based on the typical groundwater composition for unimpacted water-table wells on the SRS (Strom and Kaback, 1992).

3.2 Oxidic Partitioning Treatments

Triplicate $3 \pm 0.10\text{-g}$ of air-dried SDF soil samples were suspended in 10 mL of the appropriate background solution in 15-mL polypropylene centrifuge tubes. In addition, three replicate no-sorbent control tubes were included for each of the four test solutions. The suspensions were shaken overnight on a horizontal orbital shaker ($\sim 100 \text{ rpm}$) to equilibrate with the specific test solution. Afterwards, the pre-reaction set was centrifuged using a Sorvall RC 5B plus centrifuge for 15 minutes at 10,000 rpm. Then 7 to 8 mL of the supernatant was removed from each tube and the tubes were re-weighed to obtain residual soil + solution mass.

A $14,000 \text{ pCi mL}^{-1} \text{ }^{129}\text{I}$ (as iodide, I^-) spike solution was created by diluting an aliquot of NIST traceable $20 \text{ }\mu\text{Ci}$ stock solution supplied by Eckert & Ziegler Analytics, Inc. The samples were then refilled with the appropriate background solution to a volume of 10 mL and 0.1 mL of the $14,000 \text{ pCi }^{129}\text{I mL}^{-1}$ spike solution for a total volume of 10.1 mL. The samples were then placed on the horizontal orbital shaker ($\sim 100 \text{ rpm}$) for 5 days. At the end of the equilibration period, the samples were centrifuged as described above, and a 1-mL aliquot was removed for liquid scintillation analysis of ^{129}I (Beckman Coulter LS6500). Then remaining supernatants in the 50-mL Oak Ridge tubes were analyzed for pH.

3.3 Anoxic Partitioning Treatments

As noted for the oxic treatments, three replicate no-sorbent control tubes were included for each of the four test solutions. All background solutions were prepared with N₂-sparged ultrapure DIW using reagent-grade chemicals. The anoxic sample tubes with 3.0 ± 0.10-g of air-dried SDF Soil or test concrete were opened inside of a glove box (Coy Vinyl Anaerobic Chambers, Grass Lake, MI) and allowed to equilibrate in the absence of O₂ for 30 to 60 minutes before filling with 10 ± 0.1-mL of the appropriate background solution and resealing. The anoxic environment in the glove box was maintained by addition of a 95% N₂/5% H₂ gas mixture to establish a consistent 2% H₂ atmosphere. The samples were then secured on an orbital shaker at 100 rpm inside the glove box and reacted overnight. The pre-reaction set was then removed from the glove box and centrifuged as noted previously for 15 minutes at 10,000 rpm. The centrifuged tubes were returned to the glove box and 7 to 8 mL of the supernatant was removed from each tube. The samples were then resealed and removed from the glove box and re-weighed to obtain residual soil + solution mass. The samples were then allowed to equilibrate with the anoxic atmosphere and then filled with the necessary volume of the appropriate background solution to reach 10 mL, and then 0.1 mL of the ¹²⁹I spike solution was added for a total volume of 10.1 mL.

The spiked samples were then placed on the orbital shaker (~100 rpm) and equilibrated for 5 days. At the end of the equilibration period, the samples were centrifuged for 15 minutes at 10,000 rpm, and then returned to the anoxic chamber. Inside the anoxic chamber, a 1-mL aliquot was removed for liquid scintillation analysis of ¹²⁹I. Then remaining supernatants in the 50-mL Oak Ridge tubes for iodine experiments were analyzed for pH.

3.4 Sample Analysis

The concentration of ¹²⁹I remaining in solution after equilibration was determined by Liquid Scintillation Counting (LSC) in accordance with the quality assurance (QA) and quality control (QC) protocols of ASTM D4785-08. The ¹²⁹I K_d values were calculated as given in ASTM D-4646-03, using the following equation:

$$K_d = \frac{(C_i - C_f) \times V}{C_f \times m_{\text{sorbent}}}$$

where C_i and C_f are the initial and final aqueous concentrations of ¹²⁹I in pCi mL⁻¹ after equilibration; V = volume of liquid in the final equilibrated suspension (mL); and m_{sorbent} is the soil (g).

Table 1. Characteristics of the SDF soil compared to other SRS soil materials.

Soil/Sediment	SDF Soil ¹	Subsurface Red Clay ²	Subsurface Yellow Sandy ²
PSD ³			
% Sand	68.3	1.6	97
% Silt	4.1	40.6	2.9
% Clay	27.7	57.9	0.2
Texture Classification ⁴	Sandy Clay Loam	Silty Clay	Sand
pH _{DIW} ⁵	4.56 ± 0.39	4.55	5.1
CEC (cmol/kg) ⁶	1.01 ± 0.17	1.91 ± 0.15	0.091 ± 0.035
CDB ext. Fe (mg/gm) ⁷	12.82 ± 0.28	15.26 (17.43 ± 0.72)	7.06 (9.82 ± 0.21)
Clay Mineralogy ⁸	kaol, goe, ill	kaol, goe, hem	kaol, goe, ill

¹SDF Soil: Soil collected from the Saltstone Disposal Facility.²Soil materials commonly used in SRS PA studies (e.g., Kaplan, 2010; Seaman and Kaplan, 2010).³PSD: Particle Size Distribution (Gee and Bauder, 1986).⁴Textural classification based on USDA classification scheme.⁵pH in DIW, 2/1 solution to soil ratio⁶CEC, Cation exchange capacity determined using Ba saturation method (Rhoades, 1982).⁷CDB ext. Fe: citrate dithionite bicarbonate extractable Fe (Jackson et al., 1986). Values in parentheses reflect additional CDB extractions conducted for the current study.⁸Clay mineralogy of the ≤2 μm fraction; kaol = kaolinite, goe = goethite, ill = illite, and hem = hematite.**Table 2. Composition of the artificial groundwater (AGW) simulant.**

Constituent/Parameter	AGW ^a
pH	5.0
	(mg L ⁻¹)
Na	1.39
K	0.21
Ca	1.00
Mg	0.66
Cl	5.51
SO ₄	0.73

^aArtificial Groundwater: non-impacted groundwater derived from natural infiltration (Strom and Kaback, 1992)

4.0 RESULTS AND DISCUSSION

The current study focused on the reduced I species, iodide (i.e., I^-), rather than the oxidized iodate (IO_3^-) species because I^- tends to persist in cements that contain reductive additives like BFS (Atkins and Glasser, 1992) and Hu et al. (2005) observed that significant IO_3^- reduction occurred in the presence of SRS soils and sediments under oxic conditions, including SRS subsoils and sediments that are rich in Fe oxyhydroxides such as goethite. In previous studies, Seaman and Chang (2013 and 2014) reported K_d values based on stable I^- (i.e., ^{127}I) sorption experiments that were $< 1.0 \text{ mL g}^{-1}$ for SRS soils impacted by cementitious material leachates and SDU concrete. The current study was conducted using ^{129}I in an effort to better constrain K_d estimates.

A summary of the ^{129}I batch results is provided in Table 3 and compared with the earlier values reported in Seaman and Chang (2014). In the current test, the pH for the soil ranged from 4.66 to 6.04 for the AGW and CSS treatment solutions, respectively, illustrating the buffering capacity of the SRS subsoil. The K_d values under oxic conditions were 1.08 and 0.59 mL g^{-1} for the AGW and CSS treatment solutions, respectively. Under anoxic conditions the values were considerably lower, 0.19 and $< 0.18 \text{ mL g}^{-1}$ for the AGW and CSS treatment solutions, respectively. In the presence of the two more-alkaline treatment solutions, the final soil pH values were much higher, 9.7 to 12.2, a bit higher than values reported by Seaman and Chang (2014). The K_d values observed for I^- in the current study ($< 1.0 \text{ mL g}^{-1}$) are consistent with the values reported by Hu et al. (2005), and by Kaplan (2010; SRNL-STI-2009-00473) for Sandy (0.3 mL g^{-1}) and Clayey (0.9 mL g^{-1}) SRS sediments under baseline solution conditions. The ^{129}I $K_d < 0.18 \text{ mL g}^{-1}$ reported for the Saltstone and Portlandite leachate treatments under both atmospheric conditions reflects a 95% ^{129}I recovery in the sorbent-containing treatments, making it difficult to distinguish sorption from experimental variation and simple analytical counting errors.

For the SDU concrete samples, the equilibrium pH was quite high regardless of the initial background solution, indicating that the concrete had a big impact on solution chemistry. In fact all of the observed K_d values for the SDU concrete materials were $< 0.18 \text{ mL g}^{-1}$. Therefore, the SDU data likely reflect only Stages I/II of the cement weathering sequence. Although, some studies have observed higher K_d values with specific cement components, the exact sorption mechanism is unclear. In many instances K_d values decrease with increasing concentration, indicative of limited sorption capacity, and may tend to decrease with extended equilibrations (Ochs et al., 2016). Even so, Ochs et al. (2016) recommend evaluating iodine partitioning using methods that better mimic the solid to solution ratio of repository conditions, like EPA 1315 leaching test for in-tact monoliths or the SREL/SRR DLM method (Seaman, 2016; Seaman et al. 2016; Seaman and Coutelot, 2017).

Table 3. Summary of ^{129}I partitioning results as a function of background solution chemistry.

Treatment Sol.	AGW		Calcite		Saltstone Leachate		Portlandite Leachate	
Cement Weathering Stage	Stage IV		Stage III		Stage I/II		Stage I/II	
Redox State	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
pH	4.66	5.22	5.74	6.04	9.70	10.4	12.1	12.2
SDF Soil (^{129}I)	Kd (mL/g)				Kd (mL/g)		Kd (mL/g)	
I	1.08	0.19	0.59	<0.18	<0.18	<0.18	<0.18	<0.18
Redox State	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
pH	11.7	11.9	11.6	11.8	11.4	11.5	11.8	11.9
SDU Concrete (^{129}I)	Kd (mL/g)				Kd (mL/g)		Kd (mL/g)	
I	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
Redox State	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic	Oxic	Anoxic
pH	4.70	5.30	5.49	5.95	9.11	8.34	10.5	11.1
SDF Soil (Stable Iodine)*	Kd (mL/g)				Kd (mL/g)		Kd (mL/g)	
I	0.23	<<1	0.10	<<1	<<1	<<1	<<1	<<1

*Results from Seaman and Chang (2014): Values of <<1 reflect tests where greater than 95% of the I was recovered after equilibration

A series of batch tests were conducted to determine ^{129}I K_d values for partitioning to SDF soils and SDU concrete. Earlier tests using stable iodine (i.e., ^{127}I) as a surrogate for ^{129}I showed limited sorption to SRS soils and cementitious materials (Seaman and Chang; 2014; Seaman and Chang; 2013), especially under elevated pH conditions. While some ^{129}I sorption was observed for the SDF soils under acidic pH conditions ($K_d \approx 0.1$ to 1.0 mL g^{-1}), ^{129}I partitioning levels were quite low for the soil and the SDU concrete under alkaline conditions, making it difficult to discriminate between partitioning to the solid-phase from experimental variation and analytical error.

5.0 ACKNOWLEDGEMENTS

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