Iodine Speciation in Cementitious Environments

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Keywords: Iodine speciation, cement, slag, immobilization, redox

ABSTRACT: Iodine-129 is a key risk driver in most low-level waste cementitious waste repositories. 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. Irrespective of which iodine species was amended to the aqueous phase, there were no significant differences in uptake-K_d values (~3 L/kg). However, when the various iodine species were hydrated with the grout, the release-K_d values (6.1 to 121.8 L/kg) were significantly greater than the uptake-K_d values, and the amended iodine speciation ($I^- <<$ org-I $\leqslant IO_3^-$) and grout formulation (Grout$_{–slag}$<Grout$_{+slag}$) had a significant impact on release-K_d values. In grout samples amended with I^- and IO_3^-, org-I was formed and comprised a majority of the iodine in the leachate after 28 days of equilibration. The formed org-I originated from organic carbon (C) in the grout material (~1200 mg/kg C). 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 iodine immobilization, and the addition of slag to the grout formulation increased iodine immobilization. These results may have important implications on radioiodine waste disposal.

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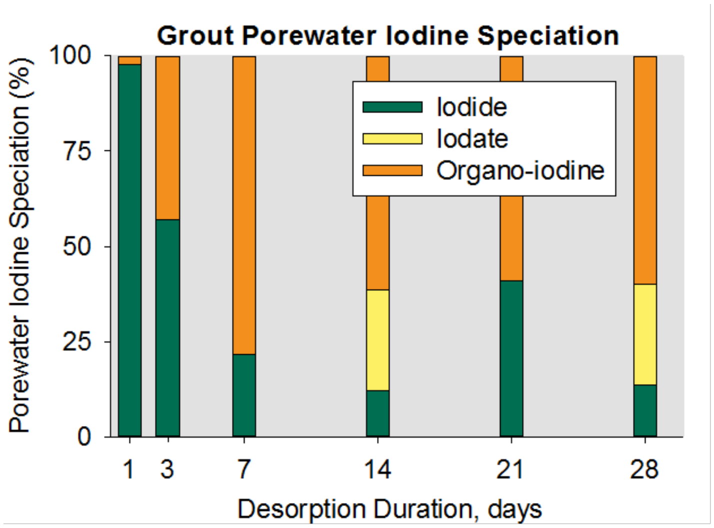

1. INTRODUCTION

Iodine-129 (^{129}I) is commonly the single greatest risk driver in high-level and low-level nuclear repositories (Kaplan et al., 2014). 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 14 g in an adult (ICRP, 1975). 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 (Kaplan et al., 2014). Radioiodine is produced at a rate of 40 GBq (1 Ci) per gigawatt of electricity produced by nuclear power (McKay, 1984). 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 (Kantelo et al., 1990).

Low-level aqueous radionuclide waste is presently being disposed as a cementitious waste form in the vadose zone of Savannah River Site (SRR, 2016) and is being evaluated at several other locations around the world (Li and Wang, 2006; Mann et al., 2003; Ochs et al., 2016). The radioactive liquid waste is blended into the cementitious dry mix and then disposed of 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 (Evans, 2008; Ochs et al., 2016). In thorough reviews of radioiodine interactions in grout, Evans (2008) and Ochs et al. (2016) describe I^- uptake in cement hydrate phases as sorption and/or incorporation in mineral phases. Precipitation as a simple iodide salt is most unlikely, because its salts are either too soluble with the cations commonly in grout. The calcium-silicate-hydrate phases has a much stronger affinity for IO_3^- than for I^-. This has been attributed to the water associated with the IO_3^- anion forming bridges with the complex calcium-silicate hydrate phases (Ochs et al., 2016). 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 becomes more reducing and is poised by sulfide species, mainly S^{2-} (Angus and Glasser, 1985; Atkins and Glasser, 1992). 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 (Roberts and Kaplan, 2009; Um et al., 2015). 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 IC requiring much higher iodine concentrations than commonly exists in these systems. Thermodynamic calculations predict that I^- should be the dominant species, especially under subsurface repository conditions. I^- may prevail if the O_2 partial pressure decreases (Ochs et al., 2016). Atkins and Glasser (1992) concluded that iodine in cementitious systems will likely exist as I^- because I^- oxidation to IO_3^- by molecular oxygen is extremely slow. In slag-containing cement blends, the strongly reducing environment would favor the I^- species (Angus and Glasser, 1985).

Reviews by Evans (2008) and Ochs et al. (2016) concluded that I^- retention on cement can be by sorption through surface processes or incorporation of I^- in the cement structure. Possible sorption sinks in cement include (ranked in decreasing order of sorption potential): aluminoferrite monosulfate, aluminoferrite trisulfate (ettringite-type phases), and calcium-silicate-hydrate phases (with low calcium:silicate ratio). For sorption onto aluminoferrite monosulfate and aluminoferrite trisulfate, substitution of I^- for SO_4^{2-} is considered to be the predominant process (Aimoz et al., 2012a; Aimoz et al., 2012b; Atkins and Glasser, 1992; Reigel and Hill, 2016). X-ray absorption spectroscopy indicate that calcium-silicate-hydrate phases is not the uptake-controlling phase for IO_3^- (Bonhoure et al., 2002). This supports earlier finding that the aluminoferrite monosulfate is a much more efficient scavenger for I^- than calcium-silicate-hydrate phases (Atkins and Glasser, 1992). The uptake process for IO_3^- is immobilization into a solid similar to $Ca(IO_3)_2$ (Bonhoure et al., 2002). Once either I^- and IO_3^- is taken by cement and calcium-silicate-hydrate phases, the iodine speciation does not change during the sorption processes, demonstrating that no iodine redox transformation is required during the uptake process (Bonhoure et al., 2002).

The objectives of this study were to: 1) evaluate the impact of curing I^-, IO_3^-, or org-I with grout on the total amount of iodine leached into the aqueous phase, 2) compare total amount of iodine leached from grout mixes with slag ($\text{Grout}_{+\text{slag}}$) and without slag ($\text{Grout}_{-\text{slag}}$), and 3) compare iodine speciation in the aqueous and solid phases. Batch uptake (adsorption) experiments were conducted and aqueous iodine speciation was monitored to quantify the extent that aqueous iodine (as I^-, IO_3^- or 4-iodoaniline (a proxy for org-I)) partitioned to freshly ground grout surfaces. Batch kinetic desorption experiments were conducted and aqueous iodine speciation was monitored in suspensions containing six grouts amended with different iodine species (I^--$\text{Grout}_{-\text{slag}}$, I^--$\text{Grout}_{+\text{slag}}$, IO_3^--$\text{Grout}_{-\text{slag}}$, IO_3^--$\text{Grout}_{+\text{slag}}$, 4-iodoaniline-$\text{Grout}_{-\text{slag}}$, 4-iodoaniline-$\text{Grout}_{+\text{slag}}$).

2. MATERIALS AND METHODS

2.1. Materials

The ingredients used to make the cementitious materials were Class-F fly ash (FA; LaFarge North America Inc., Pasco, WA), Grade-120 blast furnace slag (BFS; LaFarge North America Inc., Pasco, WA), and type-I/II Portland cement (OPC; Ash Grove Cement West Inc., Durkee, OR). For the $\text{Grout}_{-\text{slag}}$, the dry-mix was composed of 25% cement, 0% slag and 75% fly ash and the water to dry-blend ratio was 0.29 (or cement / slag / fly ash / liquid = 19.4 / 0 / 58.1 / 22.5 wt%). For the $\text{Grout}_{+\text{slag}}$, the dry blend was composed of 8% cement, 45% slag, and 47% fly ash, and the water to dry-blend ratio was 0.45 (or cement / slag / fly ash / liquid = 5.5 / 31.0 / 32.4 / 31.0 wt%). These formulations were selected to reflect existing formulations in use or under consideration at the low-level waste disposal sites at the Savannah River Site and the Hanford Site (Serne and Westsik, 2011; SRR, 2016). Grout samples hydrated (cured) with iodine were prepared in a similar manner except varying iodine concentrations and iodine species were dissolved in the water used to make the hydrated grout sample. Additional details about the iodine spikes are provided below. Generally, the grout formulations containing slag were permitted to hydrate for >3 months in an inert (95% N_2/5% H_2) glovebox at 100% humidity. Similarly, the grout formulations with slag were permitted to hydrate for >3 months on the bench top. After about 3 months, the samples were ground to pass through a 0.1-mm sieve.

Porewater simulants were prepared for the uptake and desorption resuspension experiments. 1:10 grout:water suspensions were permitted to equilibrate for >3 days and then the porewater stimulants were separated with a 0.1–µm filter. The Grout$_{\text{–slag}}$ suspensions were equilibrated on the benchtop and the Grout$_{\text{+slag}}$ suspension was equilibrated in an inert (95% N_2/5% H_2) glovebox.

2.2. Aqueous iodine uptake experiment

Uptake (adsorption) experiments were conducted in duplicate with the ground Grout$_{\text{+slag}}$ samples in an inert glovebox and the Grout$_{\text{–slag}}$ samples on the benchtop. The solid to aqueous phase ratio was 5 g to 20 mL and the initial amended aqueous iodine concentration was 20 µM (2.54 mg/L; 8000 cpm) of iodine made from $^{125}I/^{127}I$ as either I^- or IO_3^-. The ^{125}I was added after converting to the appropriate $^{125}I^-$ or $^{125}IO_3^-$ species as a yield tracer to improve detection limits following the procedure described in Xu et al. (2011). Carrier free $^{125}I^-$ was purchased in the form of NaI from MP Biomedical, USA. $^{125}IO_3^-$ was prepared from $^{125}I^-$ by combustion and oxidation of $Na^{125}I$. Briefly, $Na^{125}I$ solution (total activity (~50 µCi) was mixed with 100 mg V_2O_5 and combusted under an oxygen flow of 100 mL/min with a programmed procedure (Xu et al., 2011). In order to separate ^{125}I from $^{125}IO_3^-$, a Strata X-A 33µ polymeric strong anion exchange column (Phenomenex, USA) was used. $^{125}I^-$ was bound to the resin almost irreversibly and $^{125}IO_3^-$ was rinsed off by 20 mM ammonium acetate. The solids were ground to pass a 0.1–mm sieve and mixed with the porewaster simulant (see above) at a solid-to-liquid ratio of 1: 4. The suspensions were placed on a platform shaker for 7 days, pH was measured, the grout leachate (aqueous phase) was recovered by centrifugation and filtration (0.45µm), and then the aqueous phase was analyzed for iodine speciation (described below). The amounts of I^- or IO_3^- incorporated into the grout samples were determined by measuring the activity of the aqueous phase with a LS 6500 multipurpose scintillation counter (Beckman Coulter). A control porewater simulant (i.e., grout leachate) without the addition of any grout, to which the same I^- or IO_3^- tracer was added, was included in the whole process. Both the quenching effect and radioiodine decay was automatically corrected by using the activity in this grout leachate control as the total queous concentration. The results were presented as uptake distribution coefficients (K_d values; L/kg):

$$Uptake\ K_d = \frac{I_{solid}}{I_{aq}} = \frac{(I_{initial} - I_{eq})V_{aq}}{I_{eq} \times m_{solid}}, \qquad (1)$$

where I_{solid} is the solid phase iodine concentration (µg/kg), I_{aq} is the total aqueous I concentration (µg/L), $I_{initial}$ is the initial total aqueous iodine concentration (µg/L), I_{eq} is the total aqueous iodine concentration at the end of the contact period (µg/L), V_{aq} is the aqueous volume (L), and m_{solid} is the mass solid (kg).

2.3 Kinetic desorption experiment with iodide, iodate, and 4-iodoaniline hydrated in grout

Grout samples used in this experiment were prepared with stable ^{127}I as I^- (from KI), IO_3^- (from KIO_3), or 4-iodoanaline in water. The 4-iodoanaline was selected as an analogue of one of many possible organic forms of iodine originating from liquid and solid radioactive waste, or from organic compounds originating from the various grout ingredients that may complex disposed iodine, including graphitic carbon and aromatic tars associated with fly ash. Non-aromatic organic compounds are expected to be especially important when cellulose degradation products are included in the waste. The 4-iodoaniline solution was prepared by first dissolving the compound in methanol and then diluting 100x with water. The final iodine concentrations were measured to be approximately 9 mg/kg grout, varying slightly between grout samples. The range of total iodine concentrations in actual waste grout, including stable and radioactive isotopes, is expected to vary greatly depending on the source of the feed waste solutions and between facilities around the world. As a point of reference, the total iodine in Savannah River Site grout was estimated to be as high as 10.1 mg/kg (0.30 mg/kg ^{129}I + 9.75 mg/kg ^{127}I) (see Supplemental Material). Monoliths were cured for three months at room temperature and 100% humidity. The Grout$_{+slag}$ monoliths were cured in an inert glovebox (5% H_2/95% N_2) and the Grout$_{-slag}$ monoliths were cured on the bench top. After curing, the samples were ground in their respective climates to pass a 0.1-mm sieve and then used to create suspensions of 5 g grout and 20 mL grout porewater stimulant suspension. The Grout$_{-slag}$ suspensions equilibrated for 14 days on the benchtop, while the Grout$_{+slag}$ suspensions equilibrated for 14 days in an inert glovebox. Aqueous samples were collected after 1, 3, 7, 14, 21, and 28 days of contact with the solid phase, passed through 0.45-μm membranes, and then analysed for iodine speciation as described below. All tests were conducted in duplicate.

2.4. Chemical and mineralogical analyses

Iodine speciation was determined by the procedure reported by Zhang et al. (2010) Briefly, iodide concentrations were quantified using gas GC-MS after derivatization to 4-iodo-N,N-dimethylaniline followed by solvent extraction with cyclohexane. Iodate concentrations were quantified by measuring the difference of iodide concentrations in the solution before and after reduction by sodium metabisulfite, $Na_2S_2O_5$. Total iodine, including inorganic and organic iodine, was measured by converting organic iodine to iodate by combustion at 900 °C with a catalysis, vanadium pentoxide, and then reducing the iodate to iodide as described above. The resulting total iodine recovered in this manner was detected by ICP-MS. Organo-iodine was calculated as the difference between the total iodine and total inorganic iodine (iodide and iodate). All analyses were conducted in glass vials, and if samples had to be stored prior to analysis (<1 week), they were placed in the freezer in light proof containers. Fresh standard solutions and blanks were prepared each day. Total grout iodine concentrations were determined by combining the sample with the catalysis, vanadium pentoxide, in a ceramic boat and then combusting at 850 °C. Using O_2 gas as a carrier, the iodine was trapped in ultrapure water and then analyzed by the 4-iodo-N,N-dimethylaniline derivitization method using a GC-MS, as described above. In some samples, ^{125}I was added after converting to the appropriate $^{125}I^-$ or $^{125}IO_3^-$ species as a yield tracer to improve detection limits. The ^{125}I was detected by liquid scintillation counting (LSC). The detection limit for $^{127}I^-$ was 0.043 μg/L (0.34 nM) and for $^{127}IO_3^-$ was 0.20 μg/L (1.11 nM), respectively.

The aqueous phase of the Grout$_{-slag}$ and Grout$_{+slag}$ leachates used to simulate background grout porewater were analyzed for several parameters, including total iodine, pH, dissolved organic carbon (DOC) and different anions and cations (Table 1). DOC concentrations were measured on a Shimadzu TOC-L analyzer using the high temperature combustion method, while the concentrations of anions and cations were determined by ion chromatography (IC), inductively coupled plasma atomic emission (ICP-AES), and inductively coupled plasma mass spectroscopy

(ICP-MS). Oxidation-reduction potential was measured using a platinum electrode (Ag/AgCl reference electrode) and the results were corrected to standard hydrogen electrode (S.H.E.) values.

The solid phase was characterized by standard methods by x-ray fluorescence (XRF) for elemental composition, by x-ray diffraction (XRD) for mineralogy, and by a CHN analyzer for organic and inorganic carbon content. All measurements were conducted in duplicates.

2.5. Statistical analyses

Statistical analyses were performed in R version 3.5.0 (2018-04-23) (R Core Team, 2018), using the Student's t-test or Tukey's HSD Range Test in the STATS package (version 3.6.0) (R Core Team and Contributors Worldwide, 2018).

3. Results and discussion

3.1. Grout and grout leachate characterization

The leachates (i.e., porewater stimulant) from both grouts had similar pH values of about 12.3 and background total iodine concentrations of between 1.80 and 20.08 µg/L (Table 1). The Grout$_{-\text{slag}}$ leachate had a significantly greater Eh, +423 mV, than the Grout$_{+\text{slag}}$, -307 mV. This difference can be attributed to the presence of sulfides in the slag that promotes reducing conditions (Arai et al., 2017; Um et al., 2015) and to preparing the leachate in an inert atmosphere. The Grout$_{-\text{slag}}$ leachate also had greater dissolved K and Na concentrations than the Grout$_{+\text{slag}}$ leachate, which is likely the result of the greater composition of cement in the Grout$_{-\text{slag}}$. The lower sulfate concentration in the Grout$_{+\text{slag}}$ leachate may be attributed to the formation of insoluble metal sulfides under the strongly reducing conditions. Also, of interest is that both leachate solutions contained significant levels of DOC, >4 mg/L.

The hydrated grout samples had low concentrations of background iodine: 0.083 mg/kg in the Grout$_{-\text{slag}}$ and 0.177 mg/kg in the Grout$_{+\text{slag}}$ (Table 1). XRF analyses indicated that only slightly higher concentration of SO_3 were present in the Grout$_{+\text{slag}}$ than in the Grout$_{-\text{slag}}$. While the two grout samples had similar concentrations of organic carbon (630 to 900 mg/kg), there were much greater inorganic C concentration in the Grout$_{-\text{slag}}$ (11,270 mg/kg) than in the Grout$_{+\text{slag}}$ (847 mg/kg). Each of the ingredients of the dry blend contributed to the organic C in the grout: cement, flyash, and slag contained 0.54 ± 0.14, 0.09 ± 0.04, and 0.06 ± 0.01 mg/kg organic C, respectively. As will be discussed below, both organic and inorganic C can have a significant effect on iodine solid phase and aqueous phase geochemistry. Additional XRF and XRD characterization data about these materials is presented in the Supplemental Material.

Table 1

Background grout and grout leachate characterization without iodine additions.[a]

		$\text{Grout}_{-\text{slag}}$	$\text{Grout}_{+\text{slag}}$	Measurement method
Solid phase[b]	Total I (mg/kg)	0.083	0.177	Zhang et al. 2014
	Organic C (mg/kg)	900	630	CHN Analyzer
	Inorganic C (mg/kg)	11270	8470	CHN Analyzer
	Fe_2O_3 (wt-%)	4.47	3.04	XRF
	SO_3 (wt-%)	0.81	1.06	XRF
	LOI	12.79	11.43	Loss on Ignition (1000 °C)
Grout leachate	Total I (µg/L)[c]	1.80	20.08	Zhang et al. 2014
	pH	12.21	12.37	Single junction combination electrode
	Eh (mV)	+423	-307	Pt; Ag/AgCl; corrected to S.H.E.
	DOC (mg/L)	4.28	4.98	Shimadzu TOC-L Analyzer
	Ca (mg/L)	8.31	38.48	ICP-AES
	Fe (mg/L)	0.10	0.48	ICP-AES
	K (mg/L)	314.7	235.0	ICP-AES
	Na (mg/L)	1135	512	ICP-AES
	Si (mg/L)	13.60	9.41	ICP-AES
	Cl^- (mg/L)	5.44	23.60	IC
	NO_2^- (mg/L)	<1.00	<1.00	IC
	NO_3^- (mg/L)	7.87	5.02	IC
	SO_4^- (mg/L)	323.4	41.67	IC

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

[b] Additional solid phase characterization of the grout samples, and the cement, fly ash, and slag used to make the grout samples are presented in Supplemental Materials Table S1 and Table S2.

[c] Total iodine was measured in the aqueous phase of a 5-g solid into 20 mL grout leachate (as made following the procedure in footnote a above) suspension after a 1-day equilibration.

3.2. Aqueous iodine uptake experiments

Irrespective of whether aqueous I^- or IO_3^- was added, the K_d values were not significantly different (Student's t-test, $p \leq 0.05$) and had an average overall K_d value of 2.81 ± 0.34 L/kg (n = 8; Table 2; Equation 1). For a given grout formulation, the aqueous iodine speciation in the suspension (Table 2; top three rows of data) did not differ significantly between the I^- and IO_3^- amendments (Student's t-test, $p \leq 0.05$; Table 2), which explains in part why there were no significant differences in the corresponding K_d values. This similarity in aqueous speciation between the I^- and IO_3^- amended suspensions suggests that the iodine had reached steady state after one week. However, the grout formulation, i.e., the difference between $\text{Grout}_{+\text{slag}}$ and $\text{Grout}_{-\text{slag}}$, greatly affected the steady state iodine speciation. For $\text{Grout}_{-\text{slag}}$ the percentages of I^-, IO_3^-, and org-I in the suspension were 40.37, 14.97, and 44.67 wt-%, respectively. For $\text{Grout}_{+\text{slag}}$, the percentages of I^-, IO_3^-, org-I in the suspensions were 61.94, 38.06, and 0 wt-%, respectively. It is likely that org-I did not form in the $\text{Grout}_{+\text{slag}}$ suspension because of the prevailing reducing conditions. For iodine to form covalent bonds with organic molecules, it must be in the I(0) oxidation state (such as HOI, I_2, or I(0)) (Kaplan et al., 2014). At steady state, the strongly reducing conditions of this system at pH 12.37 and an Eh of -307 mV, would be expected to convert all iodine into I^-, and as such, no IO_3^- or I(0) would be present.

Table 2

Iodine uptake by grout with and without slag: Iodine aqueous speciation and K_d values after 7-day equilibration period.[a]

	$\text{Grout}_{-\text{slag}}$		$\text{Grout}_{+\text{slag}}$	
	$I^-_{(aq)}$ amended to grout	$IO_3^-{}_{(aq)}$ amended to grout	$I^-_{(aq)}$ amended to grout	$IO_3^-{}_{(aq)}$ amended to grout
$I^-_{(aq)}$ (wt%)	38.88 ± 0.12[b]	41.86 ± 3.17	60.21 ± 0.15	63.67 ± 3.16
$IO_3^-{}_{(aq)}$ (wt%)	16.43 ± 0.25	13.50 ± 3.17	39.79 ± 0.80	36.33 ± 2.20
Org-$I_{(aq)}$ (wt%)	44.69 ± 2.27	44.64 ± 3.44	0	0
Iodine K_d (L/kg)	3.03 ± 0.23	3.06 ± 0.16	2.33 ± 0.10	2.80 ± 0.30

[a] Experimental conditions: 5g grout/20 mL liquid (liquid = grout leachate; Table 1), 7-day equilibration in inert glovebox ($\text{Grout}_{+\text{slag}}$) or on benchtop ($\text{Grout}_{-\text{slag}}$); grout-leachate solutions (Table 1) were amended with 20 µM (2.58 mg/L) of iodine made from $^{125}I/^{127}I$ as either I^- or IO_3^-. K_d values calculated using Equation 1.

[b] All measurements conducted in duplicate and error was calculated by taking into consideration propagation of error.

The equilibrium solution contained 4.28 and 4.98 mg/L DOC in the $\text{Grout}_{-\text{slag}}$ and $\text{Grout}_{+\text{slag}}$, respectively (Table 1). The $\text{Grout}_{-\text{slag}}$ contained 900 mg/kg organic C and $\text{Grout}_{+\text{slag}}$ contained 630 mg/kg organic C (Table 1). The source of DOC is not known, however, the organic C concentrations in the cement, flyash, and slag were 5400, 900, and 600 mg/kg, respectively (Supplemental Materials, Table S2). Paya et al. (1998) used thermogravimetric analysis of fly ash to demonstrate the presence of several aromatic hydrocarbons, such as indene, coumarone, dicyclopentadiene, benzene, toluene and xylene. Fan and Brown (2001) reported from a survey of U.S. fly ash samples that volatile organic compounds, described primarily as aromatic in nature, accounted for 1.14 to 6.43 wt% of the total organic C present in the fly ash. Organic C also exists in Portland cement and is regulated for use in construction to be <0.5% (Dhir and Jones, 2014). Naturally occurring aromatic organic compounds are especially reactive with iodine and can form covalent bonds with iodine (Xu et al., 2013; Xu et al., 2011; Xu et al., 2012). Using ^{13}C DPMAS NMR and ^{1}H NMR, Xu et al. (2012) showed that iodine preferentially associated with aromatic regions of natural organic matter containing esterified products of phenolic and formic acids or other aliphatic carboxylic acids, amide functionalities, quinone-like structures activated by electron-donating groups (e.g., NH_2), or a hemicellulose–lignin-like complex with phenyl-glycosidic linkages. These reports of strong bonds being formed between iodine with organic C, together with our observation of high DOC concentrations support the existence of organic iodine found in the $\text{Grout}_{-\text{slag}}$ equilibrium solutions (44.67 wt%).

3.3. Kinetic desorption experiment with iodide, iodate, and 4-iodoaniline hydrated in grout

A simulated cementitious porewater (Table 1) was used in these desorption experiments to approximate conditions in a disposal repository. The small particles and the vigorously stirred system minimized the impact of diffusional processes and emphasizing surface-aqueous chemical reactions. A ranking of the iodine amendments based on their tendency to release iodine were: I^- >> 4-iodoaniline ≥ IO_3^- (Fig. 1). For the I^- or 4-iodoaniline treatments, there were no significant differences between the amount of total iodine released from the $Grout_{-slag}$ and $Grout_{+slag}$ suspensions. For the IO_3^- treatments, total iodine concentrations leached from the $Grout_{-slag}$ suspensions were about twice that of the $Grout_{+slag}$ suspensions. This observation may be due to the IO_3^- being immobilized by different phases in the $Grout_{+slag}$ than in the $Grout_{-slag.}$ Generally, the iodine concentration in the $Grout_{-slag}$ samples did not achieve steady state within 28 days, whereas the iodine concentrations in the $Grout_{+slag}$ samples achieve steady state within 14 days or less.

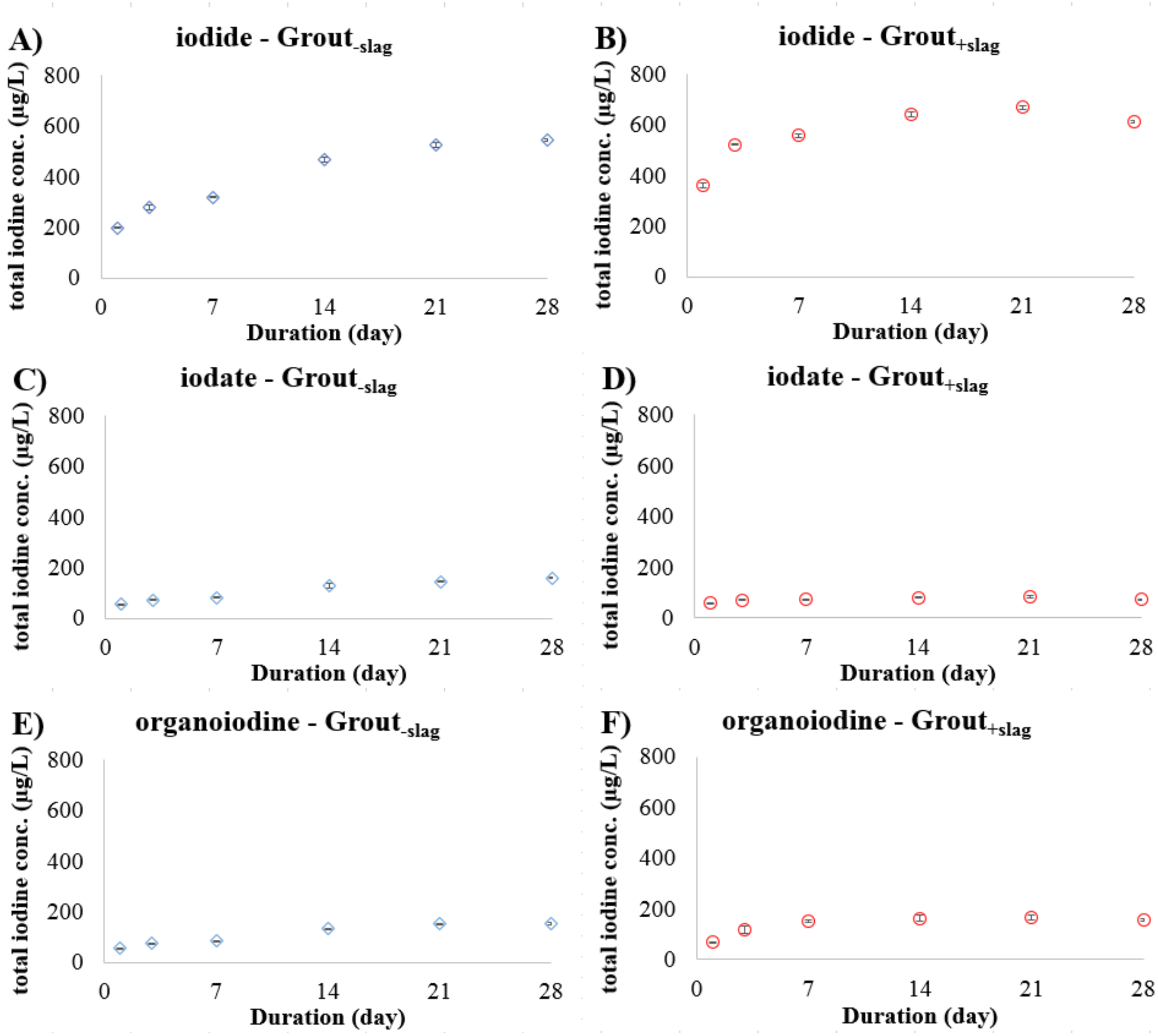

Fig. 1. Total aqueous iodine concentrations desorbed from 6 grout treatments: (A) Grout$_{-slag}$ hydrated with I$^-$, (B) Grout$_{+slag}$ hydrated with I$^-$, (C) Grout$_{-slag}$ hydrated with IO$_3^-$, (D) Grout$_{+slag}$ containing IO$_3^-$, (E) Grout$_{-slag}$ hydrated with 4-iodoaniline, and (F) Grout$_{+slag}$ hydrated with 4-iodoaniline. Error bars were calculated from duplicate samples and the propagated error bars may be hidden by symbol. Grout samples were hydrated with I$^-$, IO$_3^-$ and 4-iodoaniline for >3 months. Suspensions contained 5 g grout and 20 mL grout-leachate (Table 1).

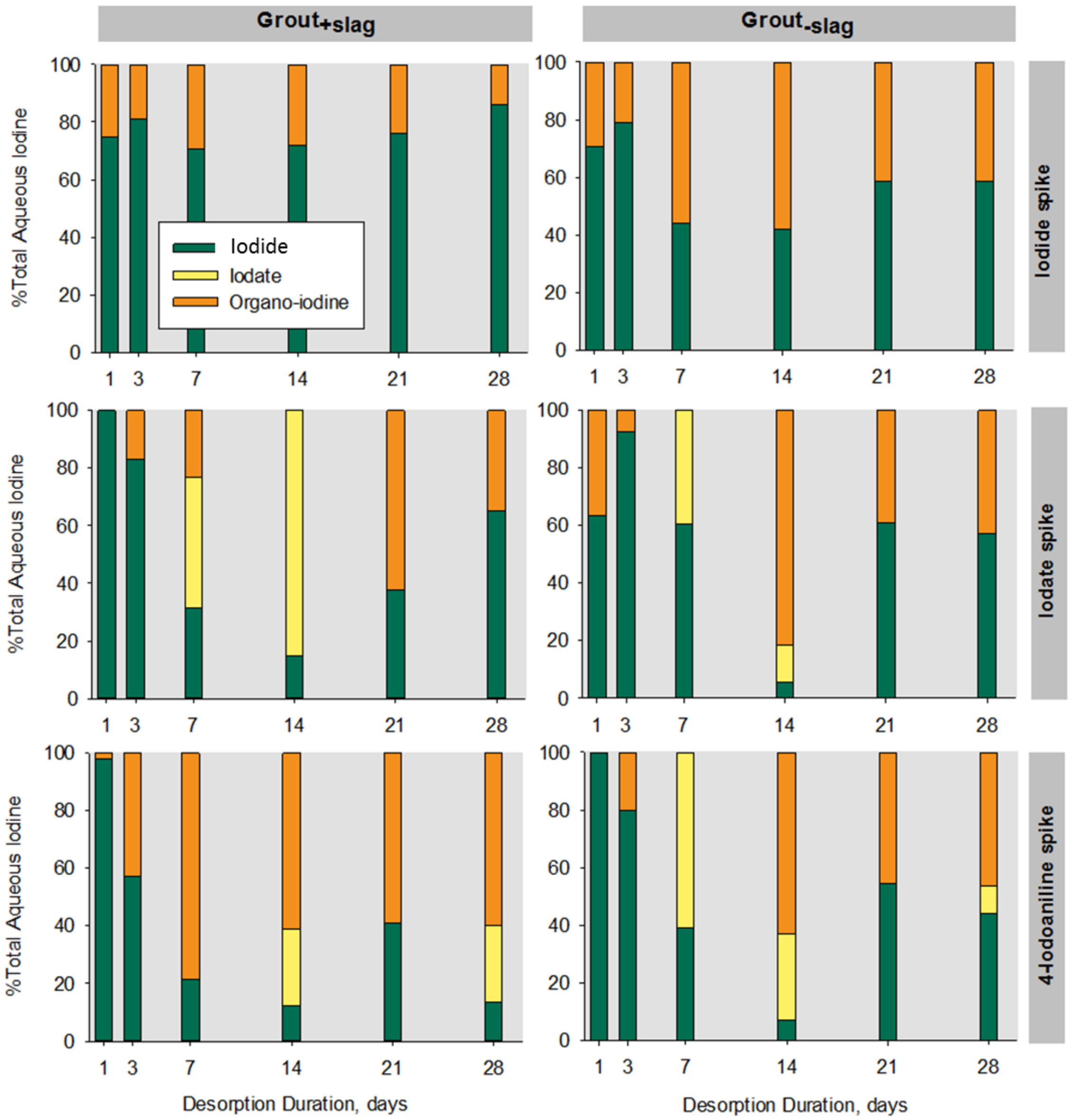

Fig. 2. Aqueous iodine speciation from suspensions containing Grout$_{+slag}$ (left) and Grout$_{-slag}$ (right) hydrated with I$^-$, IO_3^-, or 4-iodoaniline. Suspensions contained 5 g grout and 20 mL grout-leachate (Table 1).

Apparent (non-steady state) release-K_d values (Table 3) using the 28-day leachate concentrations from Figure 1 and the concentrations measured in the solid phase at the end of the equilibration period, were between 3 and 40 times greater than the uptake-K_d values (Table 2). These data indicate that the sorption process is not reversible, and that the leaching process is the rate-limiting reaction and therefore the process controlling iodine transport. Furthermore, while iodine speciation or grout formulation did not have a significant effect on uptake-K_d values (Table 2), both parameters had significant effects on the apparent release-K_d values (Table 3). This difference may be attributed to the fact that the release process, but not the uptake process, requires that the iodine must first break solid-phase bonds before entering the aqueous phase. The strength of these bonds is expected to differ between the three iodine species. In the

The I^-, IO_3^-, and 4-iodoanaline apparent release-K_d values of Grout$_{\text{-slag}}$ were significantly less than corresponding K_d values from the Grout$_{\text{+slag}}$ suspensions (Student's t-test at $p \leq 0.05$). This may in part be attributed to the possible differences in mineralogy between the two grout samples (Table 1, and Table S1 and Fig. S1 in Supplemental Materials). The Grout$_{\text{-slag}}$ contained more carbonate than the Grout$_{\text{+slag}}$, suggesting the presence of mono-carbonate instead of mono-sulphate as the alumina, ferric oxide, monosulfate phase (AFm). This AFm phase would be expected to have a lower anion-exchange capacity than a grout with a lower amount of carbonate. However, an inconsistency with this explanation is the observation that a similar increase in the uptake-K_d values was not observed (Table 2). As noted above, this difference may be due to the fact that the adsorption process is very different from the desorption process where bonds of varying strength, dependent on the iodine species, must be broken. Also noted in Table 3 is that the I^- release-K_d values were less than those for IO_3^- or 4-iodoaniline K_d values. The 4-iodoaniline release-K_d values were less than or equal to IO_3^- release-K_d values (Tukey's HSD Range Test at $p \leq 0.05$).

Table 3

Release-K_d values (L/kg) as a function of grout formulation and iodine species added to mix prior to hydration.

	I^- amended	IO_3^- amended	4-iodoaniline amended
Grout$_{\text{-slag}}$	6.14 ± 0.07[a] b*[b]	30.62 ± 0.17 a*	32.28 ± 1.15 a*
Grout$_{\text{+slag}}$	7.50 ± 0.10 c	121.78 ± 9.54 a	42.07 ± 2.47 b

[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$_{\text{-slag}}$ was 9.077 ± 1.030 mg/kg and in Grout$_{\text{+slag}}$ was 9.469 ± 1.981 mg/kg.

[b] Different lowercase letters within a row represent significantly ($p \leq 0.05$, $n = 2$) different values according to Tukey's HSD Range Test.

* indicates a significantly ($p \leq 0.05$, $n = 2$) greater value between Grout$_{\text{-slag}}$ and Grout$_{\text{+slag}}$ according to Student's t-test.

Based on the differences between the uptake and apparent release-K_d values (Tables 2 and 3), it is not surprising that the associated iodine speciation in the suspension of these two tests also differed (Table 2 vs. Fig. 2). Smooth trends were not noted in the iodine speciation distributions in the leachate as a function of contact time (Fig. 2). However, some generalizations were quite evident in this data. Iodide and to a much lesser extent org-I were the first species released from the grout, irrespective of which iodine species was amended to the grout. Averaging the data from all 12 day-1 samples (3 iodine amendments × 2 grout formulations × 2 replicates), the aqueous iodine speciation was 85 ± 17% I^-, 0 ± 0% IO_3^-, and 15 ± 17% org-I. Over the course of the 28-day study, IO_3^- appeared to be unstable; little aqueous IO_3^- was detected and if it was detected, the IO_3^- quickly transformed to another iodine species. Furthermore, IO_3^- was never detected in the I^- amended grout system, indicating that iodine oxidation was not prominent in these systems. These speciation results support the results of Atkins and Glasser (1992) who predicted that I^- would not convert to IO_3^- in cementitious systems because the reaction rate was too slow and cementitious systems tend to have increasingly less oxygen as the materials age.

Even though the $\text{Grout}_{\text{–slag}}$ system did not contain any slag, it still contained some reduction capacity, albeit much less than existed in the $\text{Grout}_{\text{+slag}}$ system. Um et al. (2015) reported that the reduction capacity of the same cement, fly ash, and slag used in this study had a reduction capacity of 79, 77, and 798 meq/kg, respectively, and all three ingredients could reduce Cr(VI). After 28 days of equilibrating, the three iodine-amended $\text{Grout}_{\text{-slag}}$ suspensions had near identical iodine speciation distributions, suggesting the system was approaching equilibrium: 54.6 ± 7.8% I^-, 3.2 ± 5.5% IO_3^-, and 42.2 ± 2.4% org-I (n = 6).

DOC concentrations in the suspensions (<0.45 μm) were also monitored during the study (Fig. 3). Generally, they tended to slightly increase for the initial 7 days, then remained largely constant for the remaining 21 days. There were no significant differences between the DOC concentrations in the $\text{Grout}_{\text{–slag}}$ and $\text{Grout}_{\text{+slag}}$ suspensions. Averaging the DOC concentrations for the $\text{Grout}_{\text{–slag}}$ and $\text{Grout}_{\text{+slag}}$ samples (n = 4): Controls (grout suspensions with no iodine added) were 4.63 ± 0.49 mg/L, I^- amended grout suspension were 14.78 ± 1.85 mg/L, IO_3^- amended grout suspensions were 17.04 ± 1.35 mg/L, and in the 4-iodoaniline amended grout suspensions were 23.63 ± 2.08 mg/L. The greater DOC concentrations in the 4-iodoaniline amended grout suspensions was expected because the DOC measurement would include any 4-iodoaniline that leached from the grout. The DOC concentrations in the I^-, IO_3^-, and 4-iodoaniline amended grout suspension were greater than the no-solids controls, indicating that additional organic carbon had leached from the grout samples during the 28-day desorption period.

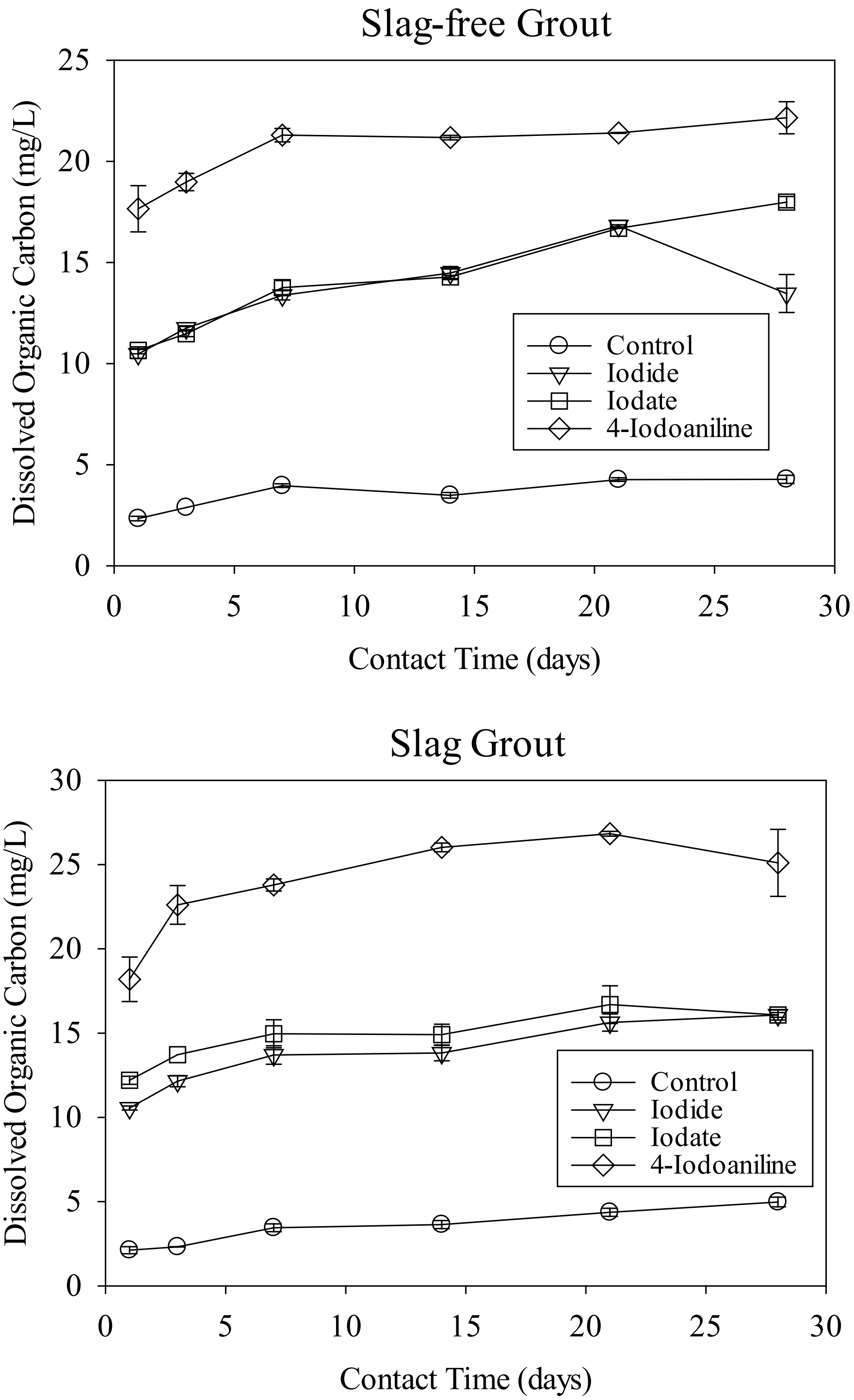

Fig. 3. Dissolved organic carbon concentrations in suspensions containing Grout$_{-slag}$ (top) or Grout$_{+slag}$ (bottom). The grout samples were hydrated for three months with either I^-, IO_3^-, or 4-iodoaniline. The Control treatment contained no solids, only the simulated porewater leachate solution described in Table 1. Suspensions contained 5 g of grout and 20 mL of leachate solution (Table 1).

4. Conclusions

The objectives of this study were to determine iodine speciation in cementitious materials with and without slag, and to determine the impact of iodine speciation on uptake and desorption. These studies were designed not to be diffusion limited; the particles were ground finely (<0.1-mm) and the grout suspensions were mixed vigorously. Together, these experiments demonstrate that: 1) aqueous iodine speciation is dynamic and includes primarily I^- and org-I (a previously unreported species), and relatively little IO_3^-, 2) the form that aqueous iodine is added to the grout impacts remobilization (least to most remobilized: $I^- >> IO_3^- =$ org-I), 3) iodine uptake-K_d values were appreciably less than release-K_d values, and 4) the addition of slag to the grout formulation increased iodine release-K_d values. These results may have important implications on radioiodine waste disposal.

The fact that I^- in solution dominated iodine speciation was expected based on thermodynamic considerations (Ochs et al., 2016). However, thermodynamic calculations did not predict the presence of org-I, and this can be attributed in part to the lack of reliable organic carbon – iodine thermodynamic association constants (Kaplan et al., 2014). Not only did dissolved org-I exist in these systems, but it accounted for a significant percentage of the aqueous iodine (>40% of total dissolved iodine after 28-day desorption). Given the relatively large concentrations of organic C in the grout (~900 mg/kg organic C) and in the aqueous phase (4.28 to 4.98 mg/L), it is not surprising that org-I species formed in these systems. The specific organic moiety involved in the formation of the org-I was not identified but could have originated from any of the three constituents used to make the grout, as suggested by the relatively much greater organic C concentrations in the constituents than added iodine concentrations (cement, flyash, and slag contained 5400 ± 1400, 900 ± 400, and 600 ± 100 mg/kg organic C, respectively).

The speciation of iodine hydrated in the grout influenced the tendency for the iodine to be released into the aqueous phase. Iodine added as IO_3^- or 4-iodoaniline had release-K_d values that were 5x greater than those for I^- amendments. Furthermore, the addition of slag to the grout formulation increased K_d values. This is important, because the addition of slag to cementitious waste forms greatly improves the retention of other redox sensitive radionuclides, such as ^{99}Tc and Np. These latter results do not support the argument that the addition of slag to grout would decrease iodine K_d values by converting iodine to the more mobile I^- form.

Understanding the speciation of iodine in cementitious waste forms is essential because the binding and coordination chemistry of the three iodine species is significantly different (Kaplan et al., 2014). Different engineering approaches would need to be used to promote binding of I^-, IO_3^-, or org-I. For example, the silver-based immobilization technologies (e.g., AgCl, Ag-impregnated granular activated carbon, Ag-mordenite) remove iodine from the aqueous phase by promoting the formation of Ag-iodide precipitates. The solubility of AgI is eight orders of magnitude lower than it is for $AgIO_3$ (Fuge and Johnson, 1986). Similarly, coprecipitation of iodine into calcium carbonate phases occurs only with IO_3^- and not with I^- and org-I (Feng and Redfern, 2018; Lawter et al., 2018; Zhang et al., 2013). Lastly, organo-iodine mobility is mostly driven by the mobility of the organic matter itself, which is determined by its major functional groups and molecular weight, as well as the surrounding environmental pH (Xu et al., 2012). It is anticipated that increased attention directed at understanding and quantifying the speciation of radioiodine, as opposed to simply total radioiodine, will lead to improved results for long-term radioiodine disposal in cementitious waste forms.

Acknowledgements

This project was supported by the SRNL's Laboratory Directed Research and Development program and the Nuclear Energy University Program (DE-EM0004381).

Appendix A. Supplementary Material

Supplementary Material associated with this article can be found online and includes: Estimate of total iodine concentration in SRS grout$_{+slag}$; Table S1, Chemical composition of grout ingredients and grout samples prior to adding iodine to the mix; and Fig. S1, XRD patterns of the Grout$_{+slag}$ and Grout$_{–slag}$.

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