Manuscript Details

Manuscript number	JENVRAD_2019_405_R1
Title	Iodine immobilization by silver-impregnated granular activated carbon in cementitious systems
Article type	Research Paper

Abstract

Silver (Ag)-based technologies are amongst the most common approaches to removing radioiodine from aqueous waste streams. As a result, a large worldwide inventory of radioactive AgI waste presently exits, which must be stabilized for final disposition. In this work, the efficacy of silver-impregnated granular activated carbon (Ag-GAC) to remove iodide (I-), iodate (IO3-) and organo-iodine (org-I) from cementitious leachate was examined. In addition, cementitious materials containing I-, IO3-, or org-I loaded Ag-GAC were characterized by iodine K-edge XANES and EXAFS to provide insight into iodine stability and speciation in these waste forms. The Ag-GAC was very effective at removing I- and org-I, but ineffective at removing IO3- from slag-free grout leachate under oxic conditions. I- or org-I removal was due to the formation of insoluble AgI(s) or Ag-org-I(s) on the Ag-GAC. When I--loaded Ag-GAC material was cured with slag-free and slag grouts, I- was released from AgI(s) to form a hydrated I- species. Conversely, when org-I loaded Ag-GAC material was cured in the two grout formulations, no change was observed in the iodine speciation, indicating the org-I species remained bound to the Ag. Because little IO3- was bound to the Ag-GAC, it was not detectable in the grout. Thus, grout formulation and I speciation in the waste stream can significantly influence the effectiveness of the long-term disposal of radioiodine associated with Ag-GAC in grout waste forms.

Keywords	Iodine speciation, cement, slag, immobilization, redox, silver-impregnated granular activated carbon
Taxonomy	Environmental Chemistry, Environmental Radioactivity, Environmental Management
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Submission Files Included in this PDF

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Responses to Comments from the editors and reviewers:

Comments from the editors and reviewers:

-Reviewer 1

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Journal: Journal of Environmental Radioactivity

Summary:

The authors present an investigation of the mobility of various anionic iodine species (iodide, iodate, and organic iodine) from cementitious leachate through silver-impregnated granular activated carbon (Ag-GAC) as indicated by distribution coefficient values. Iodide was determined to be the least mobile (highest K_d) followed by organic iodine and finally iodate (lowest K_d) confirming previous work. The authors also assessed and compared the efficacy of various Ag concentrations within the GAC for immobilizing iodine. The speciation of iodine after loading on Ag-GAC was assessed using K-edge XANES and EXAFS. Different formulations and treatments of grout were also assessed and compared in terms of their abilities to retain the iodine associated with the solid state. From this investigation the authors identified the importance of iodine speciation and grout formulation for the efficacy iodine immobilization by Ag-GAC.

This work is applicable to and has implications for the management of radioactive iodine in waste streams and the long-term management the radioactive iodine waste inventory. The content is appropriate for the Journal of Environmental Radioactivity.

Title:

The title appropriately describes the manuscript.

No change

Abstract:

The abstract provides an appropriate stand-alone summary of the work presented in the manuscript.

No change

Highlights:

The highlights provide a good summary of the significant and novel results determined from this investigation.

No change

Introduction:

The Introduction provides sufficient explanation for the importance of the investigation, most notable the increasing radioactive iodine inventory, its occurrence in waste streams, its toxicity, and the challenges it poses due to its mobility in the environment.

The authors provide an extensive literature review of work using Ag-impregnated materials to capture the various species of iodine by precipitation as solid AgI. For completeness, it may be worth mentioning some of the previous work completed by one of the co-authors of the current manuscript (Kaplan) along with others that utilized anion-exchange resin to remove aqueous iodine species as an alternative.

Agreed. A relevant statement and associated references were added.

Materials and Methods:

Overall, the method for the batch experiments appears sound. I am unfamiliar with grout formulation techniques, so I cannot comment on those. See specific comments below:

Page 3, line 53 and Table S1: The reasoning behind the presentation of calcined Ag-GAC materials in the present work based on their current industrial use makes sense. However, I'm not sure Table S1 supports the claim of "very similar" K_d values for both calcined and non-calcined materials without further explanation of the very large relative standard deviations for some samples. Also, are standard deviations of 0 due to the analysis of only one sample of that type?

Agreed. Because of this, we deleted the whole Table S1, and removed the statement in line 53, page 3. Also, made corresponding change for Table S2 to Table S1 and its citation in the main text.

Page 5, line 94: Was any correction or accounting made for aqueous phase that remained with the wetted Ag-GAC after filtration?

No.

Page 6, line 124: Concentrations are "unrealistic" for expected environmental concentrations, but not for industrial waste streams, correct? Perhaps clarify this statement.

Agreed. This sentence was re-written.

Results and Discussion:

Section 3.1 clearly presents the expected relative efficacy of Ag-GAC for capturing different iodine species based on the literature (iodide > organic iodine > iodate) and the increased removal capacity for higher Ag formulations. Can the authors offer any possible explanations or clarify the reasons for the difference in efficacy for these 3 species?

Agreed. A sentence was added for explanation.

Page 8, line 174: "…at the end of the 14-day experiment,.."

Agreed and made correction.

Section 3.2 describes SEM and EDS analyses used to show the formation of insoluble AgI on the GAC in order to confirm that the iodide removal mechanism is, in fact, due to the precipitation of insoluble AgI. This analysis seems concise and straight-forward.

Agreed.

Section 3.3, 3.4, and 3.5 examine iodine speciation for iodide-amended grout, iodate-amended grout, and organic iodine-amended grout, respectively) under various conditions using XANES and EXAFS. I am unfamiliar with these techniques, but the explanations and conclusions drawn from this section seem reasonable if the analysis is accurate. However, I would ask if the authors can offer any explanation for the mechanism(s) that allows for the stable immobilization of non-transformed organic iodine and iodide while iodate is largely non-capturable?

Agreed. Some explanation statements were added, line 178, page 9; line 275, page 16; and a paragraph on page 21.

Figures 3, 4, and 5 have very small font that may be difficult for some readers. Also, the use of color to differentiate data types is problematic for any article that is printed in gray scale. Perhaps these lines can be more easily differentiated with a number and corresponding label system?

We believed that the fond was reasonably large enough for reading. In addition, our most recent paper was published on J. Environ. Radioact. in 2018, the color line graphs were re-printed. We hope the color line figures are still acceptable.

Conclusions:

The conclusion describes covalent bonding of organic iodine to surface functional groups on the Ag-GAC. It would be helpful to have a more detailed discussion of this mechanism in the Results and Discussion section.

Agreed. More detailed discussion was added to the Results and Discussion Section.

Highlights

- Ag-granular activated carbon (Ag-GAC) removed I^- and organic I, but not IO_3^-
- I^- was immobilized in AgI, but organic I remained unchanged, binding with Ag
- AgI in Ag-GAC was dissolved as it was mixed/cured with slag-free and slag grouts
- Organic I in Ag-GAC remained unchanged as it was mixed/cured with both grouts

ABSTRACT: Silver (Ag)-based technologies are amongst the most common approaches to removing radioiodine from aqueous waste streams. As a result, a large worldwide inventory of radioactive AgI waste presently exits, which must be stabilized for final disposition. In this work, the efficacy of silver-impregnated granular activated carbon (Ag-GAC) to remove iodide (I^-), iodate (IO_3^-) and organo-iodine (org-I) from cementitious leachate was examined. In addition, cementitious materials containing I^-, IO_3^-, or org-I loaded Ag-GAC were characterized by iodine K-edge XANES and EXAFS to provide insight into iodine stability and speciation in these waste forms. The Ag-GAC was very effective at removing I^- and org-I, but ineffective at removing IO_3^- from slag-free grout leachate under oxic conditions. I^- or org-I removal was due to the formation of insoluble $AgI_{(s)}$ or Ag-org-$I_{(s)}$ on the Ag-GAC. When I^--loaded Ag-GAC material was cured with slag-free and slag grouts, I^- was released from $AgI_{(s)}$ to form a hydrated I^- species. Conversely, when org-I loaded Ag-GAC material was cured in the two grout formulations, no change was observed in the iodine speciation, indicating the org-I species remained bound to the Ag. Because little IO_3^- was bound to the Ag-GAC, it was not detectable in the grout. Thus, grout formulation and I speciation in the waste stream can significantly influence the effectiveness of the long-term disposal of radioiodine associated with Ag-GAC in grout waste forms.

Iodine immobilization by silver-impregnated granular activated carbon in cementitious systems

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KEYWORDS: Iodine speciation, cement, slag, immobilization, redox, silver-impregnated granular activated carbon

1. Introduction

Iodine-129 (^{129}I) is a major long-lived fission product generated during nuclear power production and nuclear weapon development. Over the years, ^{129}I contamination has been inadvertently introduced into the environment from leaks at waste storage facilities and currently is one of three key risk drivers at several US Department of Energy (DOE) sites (Kaplan et al., 2014). The health risks associated with ^{129}I originate from its high toxicity as a thyroid seeker. When radioactive ^{129}I is ingested, 90% of it concentrates in the thyroid, which only weighs14 g for adults, thereby, creating a small region of concentrated radiation. In addition, ^{129}I commonly exists as multiple anionic species (i.e., iodide (I^-), iodate (IO_3^-) and organic iodine (org-I)) in the environment and liquid nuclear wastes. These species often co-exist and display limited adsorption onto common sediment minerals or even expensive synthetic sorbent materials, making them highly mobile and difficult to remove from environmental systems (Kaplan, 2003; Kaplan et al., 2014; Kaplan et al., 2000; Li et al., 2014; Li et al., 2018; Mattigod et al., 2003a). As the stockpile of ^{129}I-bearing nuclear waste continues to increase rapidly due to nuclear energy production, novel and practical sequestration technologies are needed to reduce its potential contamination of the environment and living organisms.

Anion-exchange resins have been utilized to remove aqueous iodine species (Othman et al., 2017; Parker et al., 2014; Tachibana et al., 2016). However, the most effective technologies for iodine sequestration from aqueous and gaseous phases utilize silver (Ag)-containing materials that presumably lead to the formation of insoluble AgI. These Ag remediation agents include silver chloride (Denham et al., 2010; Zhang et al., 2011; Zhang et al., 2010), argentite (AgS) (Asmussen et al., 2016), and Ag modified activated carbon, zeolites and porous silica (Asmussen et al., 2016; Chapman et al., 2010; Hoskins and Karanfil, 2002; Jubin et al., 2014; Kikuchi et al., 1978; Mattigod et al., 2003a; Mnasri et al., 2014; Nan et al., 2017; Nenoff et al., 2014; Sadasivam and Rao, 2016; Sanchez-Polo et al., 2006; Scheele et al., 2002; Sheppard et al., 2006). Silver impregnated granular activated carbon (Ag-GAC) is among the most commonly used materials for iodine sequestration. However, the Ag-based materials are only effective for removing I^- and maybe some forms of org-I (Chebbi et al., 2016; Mattigod et al., 2003b; Nenoff et al., 2014; Qafoku et al., 2014), but not IO_3^-. Conversely, IO_3^- has been demonstrated to substitute for carbonate (CO_3^{2-}) in calcite (Podder et al., 2017), $Na_4UO_2(CO_3)_3$ (Wu et al., 2013) and aragonite (Feng and Redfern, 2018), thereby providing an additional mechanism by which this species can be sequestered and stabilized. There is a worldwide need to identify a long-term disposal pathway for the growing inventory of ^{129}I-loaded solid secondary waste created due to deployment of the Ag-based iodine separation technologies.

There were three objectives to this research: 1) quantify the uptakes of I^-, IO_3^-, and org-I by Ag-GAC from cementitious leachate as a function of Ag loadings on Ag-GAC materials, 2) characterize I and Ag distribution on Ag-GAC materials after exposure to I^- in the cementitious leachate using electron scanning microscopy (SEM) and energy dispersive spectroscopy (EDS), and 3) identify iodine speciation in grout samples that contain Ag-GAC amended with I^-, IO_3^- or org-I using I K-edge X-ray absorption near structure (XANES) and extended X-ray absorption fine structure (EXAFS). The first two objectives were addressed through experiments studying various iodine speciation in cementitious leachate solutions and Ag-GAC, while the third objective was addressed by spectroscopic experiments of slag-free grout ($Grout_{-Slag}$) and slag-containing grout ($Grout_{+Slag}$) with or without Ag-GAC amended with I^-, IO_3^-, or org-I in oxic grout leachate.

2. Materials and methods

2.1 Materials

Ag-GAC materials containing 0, 1, 5, 10, and 14.1 wt% Ag were acquired from Calgon Carbon (Pittsburgh, PA, USA; CE 20 × 50 and OLC WW 20 × 50) and then calcined at 200 ^{o}C under N_2 for 24 hrs. Potassium iodide (KI) and potassium iodate (KIO_3) used in this study were purchased from Fisher Scientific (Hampton, NH, USA), and 4-iodoaniline (C_6H_6IN) was obtained from Thermo Fisher Acros Organics (Geel, Belgium). The 4-iodoaniline was specifically used in this study as an example of one of many possible organo-iodine species that may exist in waste streams. It contains an aromatic ring, a dominant organic carbon moiety for forming covalent bonds with iodine (Xu et al., 2013; Xu et al., 2012) and it is relatively more soluble than other aromatic iodine compounds. The chemicals were used as received. The ingredients used for making grouts included class-F fly ash (FA; LaFarge North America Inc., Pasco, WA, USA), grade-120 blast furnace slag (BFS; LaFarge North America Inc., Pasco, WA, USA), and type-I/II Portland cement (OPC; Ash Grove Cement West Inc., Durkee, OR. USA).

2.2 *Aqueous I^-, IO_3^- or 4-iodoaniline uptake by Ag-GAC*

Aqueous I^-, IO_3^- or 4-iodoaniline uptake by GAC containing 0, 5, and 10 wt% Ag (i.e., $Ag_{0\%}$GAC, $Ag_{5\%}$GAC, and $Ag_{10\%}$GAC) was determined under bench top conditions. In order to simulate a grout porewater, 100 g <2 mm ground $Grout_{-Slag}$ (Table 1) was combined with 1 L of de-ionized water for 14 days and then the grout leachate was collected following 0.2-µm filtration of the liquid. The grout leachate had a pH value of 12.21, Eh value of +423 mV, a background total I concentration of 112 µg/L, and a dissolved organic carbon (DOC) concentration of 4.28 µg/L (Kaplan et al., 2019). The 1:10 solid:liquid grout leachate was amended with about equal iodine concentrations from KI (measured 7615 µg I/L), KIO_3 (measured 7753 µg I/L), and 4-iodoaniline (measured 7672 µg I/L). The KI and KIO_3 solutions were prepared by dissolving the solids in Milli-Q water, while the 4-iodoaniline had to be dissolved first in methanol prior to introducing it into the grout leachate. These iodine concentrations were selected to represent the ^{127}I (natural stable) and ^{129}I (radioactive) concentrations that may exist in waste streams, but they are greater than those commonly reported in contaminated environmental groundwater systems. For example, ^{127}I concentrations in Savannah River Site groundwater are in the order of 2 µg/L (Otosaka et al., 2011) and the concentrations in disposal waste may be in the 1000s of µg/L levels, depending on the waste streams (Kaplan et al., 2019). The waste streams that involve large amounts of nitric acid commonly have elevated stable iodine as a trace impurity, while contaminated groundwater rarely exceeds 200 µg/L ^{129}I. We also wanted sufficient iodine mass in the leachates to ease analytical measurements after contact with these strong sorbents (i.e., we did not want to report a less-than K_d value, defined below).

The batch treatments included a no-solid control for each iodine species amendment, which demonstrated that no detectable aqueous iodine was lost to the glassware or filters. All treatments were conducted in duplicate, resulting in a full-factorial experimental design of 24 tubes (3 iodine species (I^-, IO_3^-, and 4-iodoaniline) × 4 solid treatments ($Ag_{0\%}GAC$, $Ag_{5\%}GAC$, $Ag_{10\%}GAC$, no-solids control) × 2 replicates). After a 14-day equilibration period on a platform shaker, the phases were separated using a 0.2-µm pore-size filter, and pH and Eh were measured immediately. The filtrate samples were analyzed for total Ag by ICP-MS following standard methods and for total iodine by derivatization to 4-iodo-N,N-dimethylaniline, followed by solvent extraction with cyclohexane and then quantification by GC-MS (Zhang et al., 2010).The iodine uptake by Ag-GAC was described as a distribution coefficient (K_d value, mL/g) as defined by Equations 1:

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{M} \quad (1)$$

where C_0 (µg/L) is the I concentration in the no-solid control samples at the end of the 14-day equilibration period, C_e (µg/L) is I concentration in the solution at the end of the 14-day equilibration period, V is the volume of the solution (mL) and M is the mass of the sorbent (g).

Similarly, a separate batch experiment was conducted to study aqueous I^- uptake as a function of Ag concentrations on GAC, with GAC samples containing 0, 1, 5, 10, or 14.1 wt% Ag. The Ag-GAC samples were put in contact with grout leachate (in a 0.5 g:10 mL ratio) that was amended with 259 µg/L $^{127}I^-$ from KI.

2.3 Grout preparation

Grout samples were prepared for I K-edge XANES and EXAFS analyses. Ingredients and proportions used to make the grout samples with and without iodine-amended Ag-GAC are shown in Table 1. The recipes for the $\text{Grout}_{+\text{Slag}}$ and $\text{Grout}_{-\text{Slag}}$ samples are based on existing waste-form recipes presently being used or under consideration at the Savannah River Site, South Carolina USA and the Hanford Site, Washington USA. Dissolved iodine as I^-, IO_3^-, and 4-iodoaniline were added directly to the water that was used to make the grout paste for the $\text{Grout}_{+\text{Slag}}$ and $\text{Grout}_{-\text{Slag}}$ samples. For the grout samples containing Ag-GAC+iodine as I^-, IO_3^-, and 4-iodoaniline, the iodine species were added in a suspension containing the $\text{Ag}_{5\%}\text{GAC}$ and permitted to equilibrate overnight (Table 1). The iodine-amended $Ag_{5\%}GAC$ was mixed with the slag-free and slag grout at air temperature on the bench top. As noted above, these I amendment concentrations were selected in part to represent concentrations expected in industrial waste streams and to permit iodine detection in the presence of Ag. A nominal I load of ~9,000 mg/kg was used in these samples to permit detection by synchrotron I K-edge X-ray absorption spectroscopy. This iodine concentration was perhaps three orders of magnitude greater than that expected in most environmental samples, but it was not unrealistic for industrial waste streams.

Grouts were prepared by adding the dry feed materials to a beaker containing the appropriate amount of water that was calculated based on the water/dry blend ratio and stirred by an overhead mixer. Ingredients were mixed for 5 min and the mixer speed was slowly increased to a speed that maintained a vortex in the grout. Occasionally the mixer was stopped to “burp” the grout and remove air pockets. Once the mixing was complete the grout was immediately decanted for fresh property testing and poured into molds to cure. Monoliths were typically cured for a minimum of three months at room temperature and 100% humidity. The grout monoliths with slag (i.e., $Grout_{+Slag}$, $Grout_{+Slag}$+(Ag-GAC+I^-), $Grout_{+Slag}$+(Ag-GAC+IO_3^-) and $Grout_{+Slag}$+(Ag-GAC+org-I)) were cured in an inert glovebox (5% H_2/95% N_2), while those without slag (i.e., $Grout_{-Slag}$, $Grout_{-Slag}$+(Ag-GAC+I^-), $Grout_{-Slag}$+(Ag-GAC+IO_3^-), $Grout_{+Slag}$+(Ag-GAC+org-I)) were cured on the bench top. Grout samples containing the AgI-GAC were cured for 1 month and the grout samples with iodine spiked directly into the dry mix were cured for 3-months. After curing, grout subsamples were ground with a mortar and pestle to pass through a 0.1 mm sieve under the appropriate oxic or anoxic atmosphere. The slag-free grout and slag grout samples were charatcerized by chemical analysis (Table S1) and powder X-ray diffraction (Fig. S1).

Table 1.

Ingredients and proportions (% in dry blend) used to make the grout samples

Ingredients	$Grout_{-Slag}$ (wt%)	$Grout_{+Slag}$ (wt%)	$Grout_{-Slag}$+(Ag-GAC+iodine) (wt%) [a]	$Grout_{+Slag}$+(Ag-GAC+iodine) (wt%) [a]
Cement	25	8	20	6.4
Fly ash	75	47	60	37.6
Slag	0	45	0	36
AgI-GAC	0	0	20	20
Water/dry blend ratio	0.29	0.45	0.29	0.45

[a] The iodine used to amend the Ag-GAC was either I^-, IO_3^-, or 4-iodoaniline.

2.4 SEM and EDS characterization

Selected solids from the I^- update experiment by Ag-GAC were then washed three times with deionized water, dried, and analyzed by SEM and EDS using a Zeiss Supra 40 VP with an Oxford X-Max EDX detector. To do this, the samples were mounted on Al specimen stubs using double-sided carbon tape. SEM images and EDS data were typically collected at 15 kV, a working distance of 8.5 mm and a 60 µm aperture. Samples were stable and not affected when exposed to the electron beam.

2.5 I K-edge XANES and EXAFS

The I K-edge XANES and EXAFS spectra of selected grout samples were collected using the Materials Research Collaborative Access Team (MRCAT) Sector 10-BM beamline at the Advanced Photon Source (APS) (Argonne National Lab, Argonne, IL). To do so, 50 mg of each of the air-dried powder samples was pressed into a 6.3-mm diameter disk pellet that was mounted on sample holder. The MRCAT Sector 10-BM beamline used a double crystal water cooled Si (111) monochromator, detuned to 50% of peak intensity (Kropf et al., 2010). The monochromators were calibrated using the first inflection point at 31,814 eV of the K-edge of tellurium foil. The I K-edge XANES and EXAFS spectra were collected in transmission mode for the energy range of 33,000-34,000 eV at room temperature. Spectra were processed and analyzed using the IFEFFIT software package including Athena and Artemis (Ravel and Newville, 2005). Data from multiple scans were processed using Athena by aligning and merging the spectra followed by background subtraction using the AUTOBK algorithm.

3. Results and Discussion

3.1 Ag-GAC uptake of I^-, IO_3^- and 4-iodoaniline in grout leachate

K_d values of the three I species by Ag-GAC materials with different Ag loadings, together with the pH and Eh data at the end of the 14-day experiment, are shown in Table 2. As Ag loading on the GAC increased from 0 to 10 wt%, pH values of the slag-free grout leachate significantly decreased by ~0.7 units ($p \leq 0.05$, $n = 4$), while the Eh values did not show a consistent trend. For the GAC without Ag (i.e., $Ag_{0\%}$-GAC), the K_d values for all I species (i.e., I^-, IO_3^- and 4-iodoaniline) were <10 mL/g, which meant that the GAC alone had very little capacity for binding these I species from the grout leachate. With incremental increases in Ag loading onto the GAC, the K_d values increased sharply. For example, the K_d value for I^- was 8 ±

10 mL/g for Ag$_{0\%}$GAC and increased to >4423 mL/g for Ag$_{10\%}$GAC. For GAC with the same Ag loadings, the K_d values tended to increase in the following order of I^- > 4-iodoaniline >> IO_3^-, because I^- is favorable to react with Ag to form AgI precipitation for its removal. For example, the K_d values for the Ag$_{5\%}$-GAC were >3924 mL/g for I^-, 1212 mL/g for 4-iodoaniline, and 32 mL/g for IO_3^-.

Table 2.

Ag-GAC uptake (K_d values) of I^-, IO_3^-, or 4-iodoaniline in a grout leachate solution

Aqueous I amendment	Ag loading on GAC (%)	K_d (mL/g)^a	pH	Eh (mV)
I^-	0	8 ± 10	11.82 ± 0.00	273 ± 11
	5	>3924^b	11.30 ± 0.04	284 ± 1
	10	>4423^b	11.12 ± 0.01	287 ± 2
IO_3^-	0	-2 ± 5	11.83 ± 0.02	186 ± 1
	5	32 ± 0	11.32 ± 0.05	196 ± 18
	10	612 ± 25	11.16 ± 0.07	163 ± 13
4-iodoaniline	0	5 ± 1	11.75 ± 0.01	196 ± 29
	5	1212 ± 1023	11.22 ± 0.06	169 ± 8
	10	>1942^b	11.10 ± 0.01	131 ± 13

[a] Solid:Liquid was 0.5 g:10 mL; initial iodine concentration as I^-, IO_3^-, or org-I (4-iodoaniline) was 1 mg I/L; contact time = 2 weeks; pH and Eh were measured after the equilibrium period; all measurements conducted in duplicate; total iodine was measured by the method described previously (Zhang et al., 2010).

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[b] These greater-than-K_d values were calculated based on the I detection limit of ~0.2 μg/L or 1.6×10^{-9} M; differences in detection limits of K_d values is attributed to slight differences in solids or liquids mass. Differences in greater-than-K_d values originate from slight differences in solid:liquid ratios and initial iodine concentrations.

Because Ag-loaded GAC was most effective for I^- removal from grout leachate, but less effective for removal of 4-iodoaniline and especially IO_3^-, a separate batch experiment was conducted to more specifically illustrate how the I^- K_d values, pH, Eh and aqueous Ag concentration data changed as a function of Ag loadings onto GAC. Fig. 1A shows that the I^- K_d values tended to increase from 0 to 2.7×10^4 mL/g with an increase in the Ag loading on GAC from 0 to 14.1 wt%. It also shows that the variability of the duplicate K_d values were quite low (1-σ error bars are often hidden by the symbol for the mean in Fig. 1A).

The pH values decreased from 12.3 (0% Ag) to 11.5 (14.1% Ag) (Fig. 1B). As shown in Fig. 1C, the Eh values gradually decreased from 391 mV (0% Ag) to 374 mV (10 % Ag). With a further increase in the Ag loading onto the GAC, the Eh value drastically decreased to 207 mV (14.1% Ag). It is noted that the system remained partially reducing with respect to the I^-/IO_3^- standard redox couple ($Eh^0 = 0.380$ mV at pH 12.2). It is presently unclear how the increased loading of Ag on the GAC promoted the pH and Eh value changes. One possibility is that Ag, initially added as Ag^+, may have undergone some reduction after attachment to the GAC to form Ag^0, which in turn promoted a more reducing system. The aqueous Ag concentration gradually increased with Ag loading in GAC, from ~0.2 μg/L without Ag loading to ~7 μg/L with 10 wt% Ag loading. With a further increase in Ag loading onto the GAC, the aqueous Ag concentration drastically increased to 167 μg/L (14.1% Ag). It is likely that at the lower Ag loading, the aqueous Ag concentration was controlled by AgI solubility under these relatively oxic conditions. However, from a regulatory point of view, only the $Ag_{14.1\%}$-GAC exceeded the regulatory standard for the Secondary Maximum Contaminant Level of 100 µg/L Ag. Our I detection limit was about 2.8×10^{-9} mol/L (or 0.35 µg/L) (Xu et al., 2016), which is slightly greater than the estimated AgI solubility in this system: 7.9×10^{-10} mol/L (Kaplan et al., 2019). Therefore, our analytical method was not sensitive enough to measure aqueous iodine concentrations when AgI solubility was controlling iodine concentrations.

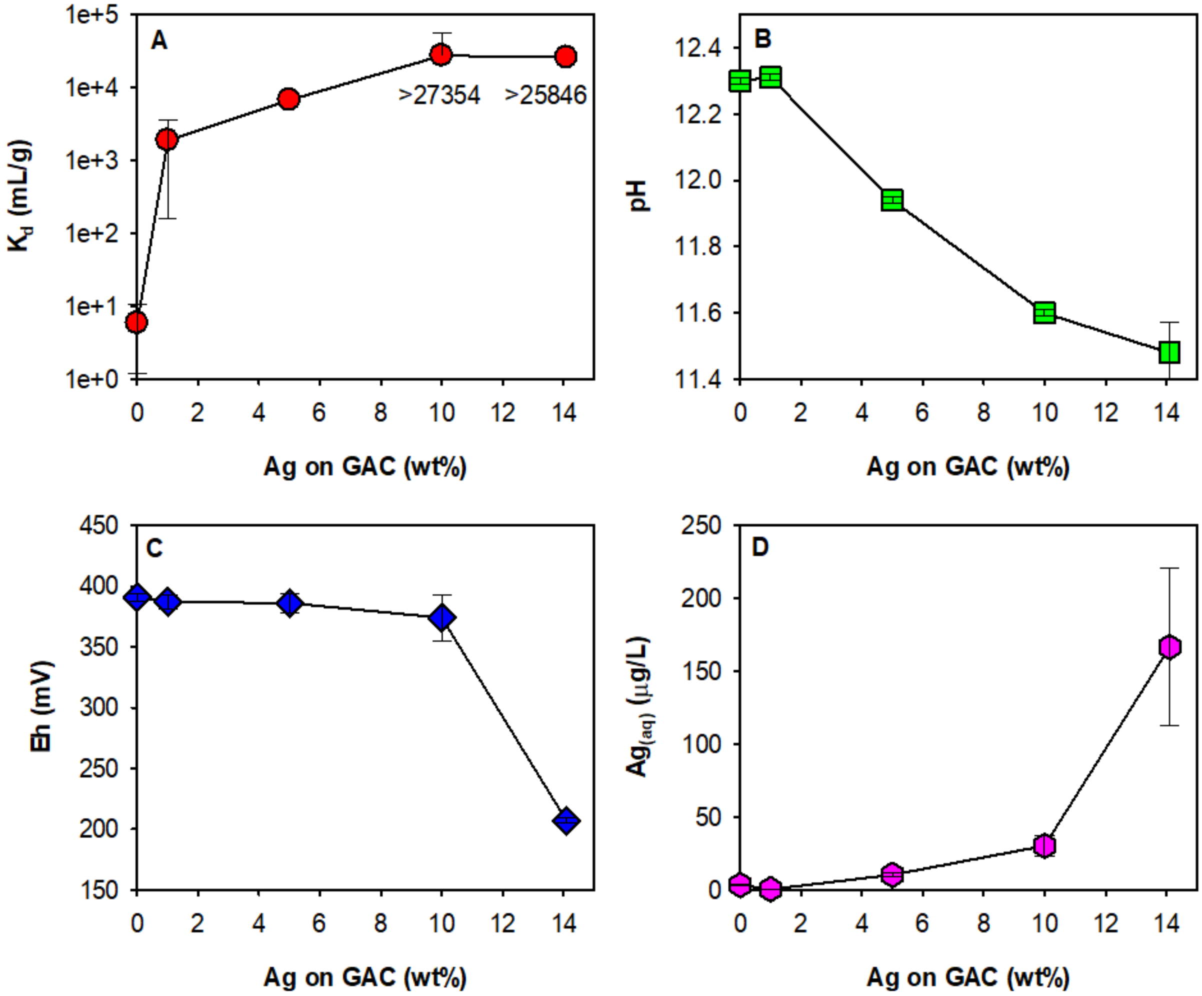


Fig. 1. Iodide uptake and aqueous chemistry as a function of percent Ag impregnated on GAC: (A) K_d values, (B) aqueous pH, (C) aqueous Eh, and (D) Ag concentration in solution, $Ag_{(aq)}$.

Experimental conditions were 0.5 g Ag-GAC, 10 mL $\text{Grout}_{\text{-slag}}$ leachate that had a pH value of 12.21, Eh value of +423 mV, background I concentration of 112 µg/L and DOC carbon concentration of 4.28 µg/L, 7272 µg/L I^- (from KI) spike amendment, 14-day equilibration on bench top in contact with air, 2 replicates (1-σ error bars may be hidden by the symbol identifying the mean).

3.2. SEM and EDS analyses of Ag-GAC after contact with $I^-_{(aq)}$

Ag-GAC was most effective for I^- removal from aqueous media, as demonstrated in Table 2 and literature (Chebbi et al., 2016; Mattigod et al., 2003b; Nenoff et al., 2014; Qafoku et al., 2014). Figure 2 shows SEM images and an EDS spectrum of the 1 wt% and 14.1 wt% Ag loaded GAC materials that were in contact with I^- in slag free grout leachate under oxic conditions. With 1% Ag-GAC, essentially all the Ag was located within the throat of the pore openings, Ag particles were evenly distributed on GAC, and the size of the Ag particle aggregates were between ~0.1 and 1 µm. As Ag loading in the GAC increased to 14.1%, the Ag clusters became larger, somewhat less evenly distributed, and more Ag appeared on GAC surface, as opposed to in the GAC pore openings. The EDS spectra indicated that no detectable I existed directly on the GAC and that it was exclusively associated with the Ag. Together the SEM and EDS data confirm that Ag-GAC was highly effective at removing I^- from this slag free grout leachate under oxic conditions via the formation of insoluble AgI.

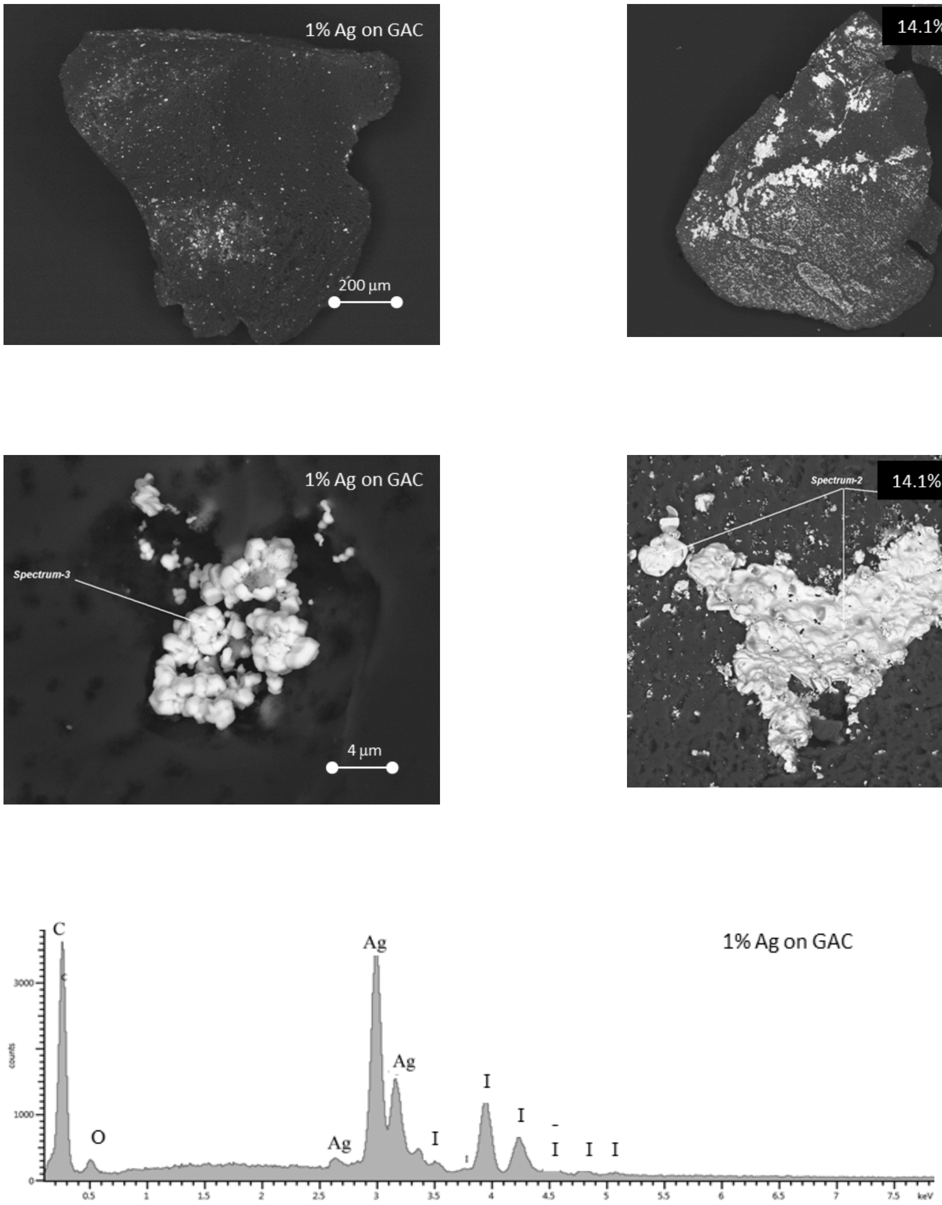
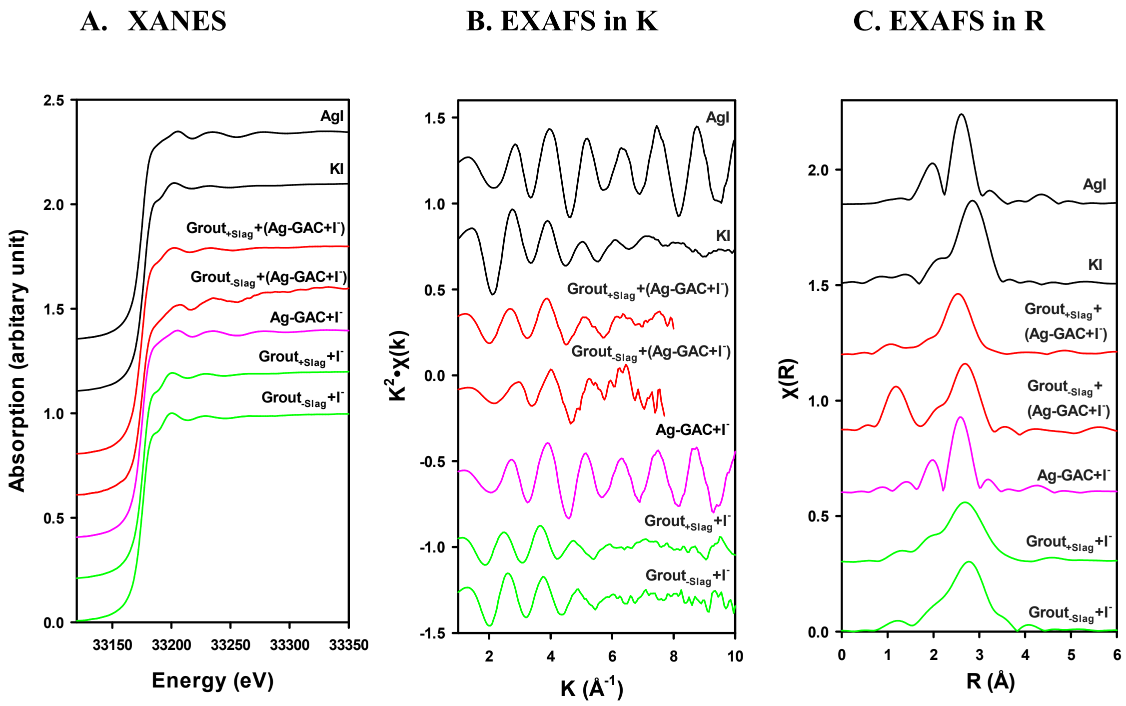


Fig. 2. SEM images and an EDS spectrum of $Ag_{1\%}$-GAC and $Ag_{14.1\%}$-GAC after contact with I^- amended grout leachate solution under oxidizing conditions.

3.3. I speciation in grout samples containing I^--amended Ag-GAC

Iodine K-edge XANES (Fig. 3A) and EXAFS (Fig. 3B and 3C) spectra of the slag-free grout and slag grouts cured with iodide (i.e., $\text{Grout}_{\text{-Slag}}$+$I^-$ and $\text{Grout}_{\text{+Slag}}$+$I^-$, respectively), the Ag-GAC amended with I^- (Ag-GAC+I^-), the slag-free grout and slag grouts cured with Ag-GAC amended with iodide (i.e., $\text{Grout}_{\text{-Slag}}$+(Ag-GAC+$I^-$) and $\text{Grout}_{\text{+Slag}}$+(Ag-GAC-$I^-$), respectively) samples were collected and compared with the spectra of two reference materials (i.e., KI and AgI). These spectra provided information about the I speciation in the solid phases. The spectra of the $\text{Grout}_{\text{-Slag}}$+$I^-$ and $\text{Grout}_{\text{+Slag}}$+$I^-$ samples (green lines) were identical to that of KI reference sample (black line), indicating that the I species in these grout samples was primarily I^- (Kodama et al., 2006; McKeown et al., 2015; Shimamoto et al., 2010; Shimamoto et al., 2011; Yamaguchi et al., 2010). The hydrated I^- species is surrounded by water molecules. The stronger signal-to-noise ratio in the $\text{Grout}_{\text{+Slag}}$ sample can be attributed to both the greater retention of I^- compared to the $\text{Grout}_{\text{-Slag}}$ sample and the slightly higher I^- loading for the $\text{Grout}_{\text{+Slag}}$ (see Table 1).

The I K-edge XANES and EXAFS spectra of Ag-GAC+I^- (pink line; Ag-GAC after exposure to I^- in oxic water solution) were identical to the corresponding spectra of AgI (black line), which indicated that the I species in Ag-GAC+I^- was I^- in the form of AgI, in good agreement with its EDS spectrum (Fig. 2) and as expected. After Ag-GAC+I^- was stabilized into the $\text{Grout}_{\text{-Slag}}$ and $\text{Grout}_{\text{+Slag}}$, the I K-edge XANES and EXAFS spectra (red lines) of $\text{Grout}_{\text{-Slag}}$+(Ag-GAC+$I^-$) and $\text{Grout}_{\text{+Slag}}$+(Ag-GAC+$I^-$) samples were completely different from the corresponding spectra of AgI-GAC and AgI, indicating that the AgI compound underwent some form of transformation after the Ag-GAC+I was stabilized in the slag-free and slag grouts. The I K-edge XANES and EXAFS of the grout samples containing Ag-GAC+I^- were similar to those of the grout samples in which I$^-$ was hydrated within the samples (green lines), which indicated that I species in the grouts that stabilized Ag-GAC+I$^-$ was hydrated I$^-$ species surrounded by water molecules, and not I$^-$ bound to Ag.


A. XANES

B. EXAFS in K

C. EXAFS in R

Fig. 3. I K-edge XANES (A) and EXAFS (B and C) spectra of grout samples with iodide loading, in comparison with the spectra of AgI and KI as reference materials. For the Grout$_{\text{-Slag}}$+I$^-$ and Grout$_{\text{+Slag}}$+I$^-$ samples, I$^-_{(aq)}$ was mixed with the grout dry blend. For the Grout$_{\text{-Slag}}$+(Ag-GAC+I$^-$) and Grout$_{\text{+Slag}}$+(Ag-GAC+I$^-$) samples, the I$^-_{(aq)}$ was first added to the Ag-GAC, washed, and then the dried (AgI-GAC+I$^-$) was mixed into the appropriate grout dry blend. Grout formulations are presented in Table 1. At the time of the measurements, the Grout$_{\text{+Slag}}$+I$^-$ and Grout$_{\text{+Slag}}$+(Ag-GAC+I$^-$) had been hydrating (curing) in an inert environment for 40 days, while the Grout$_{\text{-Slag}}$+I$^-$ and Grout$_{\text{-Slag}}$+(Ag-GAC+I$^-$) had been hydrating on a bench top for 40

days. It is noted that the peak at ~1 Å in the EXAFS in R (Fig. 3C) for sample Grout$_{-\mathrm{Slag}}$+(Ag-GAC+I$^-$) was likely an artifact due to the noisy nature of the data at K > 6 Å^{-1} (Fig. 3B).

Thus, aqueous I$^-$ was effectively sequestered by Ag-GAC as I$^-$ reacted with Ag species to form AgI precipitation (Denham et al., 2010; Hoskins and Karanfil, 2002; Kaplan et al., 2019). When iodide-loaded Ag-GAC (i.e., Ag-GAC+I$^-$) was mixed with the slag grout (i.e., Grout$_{+\mathrm{Slag}}$), it is possible that the strongly reducing conditions created by the slag caused reductive dissolution of AgI, resulting in the partial formation of $\mathrm{Ag}^0_{(s)}$ and $\mathrm{I}^-_{(aq)}$. In an earlier related study, a 1:10, Grout$_{+\mathrm{Slag}}$:water suspensions had a steady state Eh of -307 mV (Kaplan et al., 2019). Geochemical modeling indicated that even under moderately reducing cementitious conditions of <200 mV, the Ag$^+$ of the $\mathrm{AgI}_{(s)}$ undergoes reduction to Ag^0, resulting in the release of $\mathrm{I}^-_{(aq)}$ (Fig. S2). They also confirmed the occurrence of this reductive dissolution process by measuring very high I$^-$ concentration in the grout leachate containing the slag grout that stabilized iodide-loaded Ag-zeolite (Kaplan et al., 2019). The I K-edge XANES and EXAFS data of the Grout$_{+\mathrm{Slag}}$+(Ag-GAC+I-) sample (Fig. 3) support the occurrence of reductive dissolution of the AgI. Overall, these results indicated that the slag grout is not an appropriate technology for stabilization of iodide-loaded Ag-GAC secondary solid waste.

When Ag-GAC+I$^-$ was mixed with the slag-free grout (i.e., Grout$_{-\mathrm{Slag}}$), the slag-free system is generally more oxidizing and therefore the AgI would not be expected to undergo reductive dissolution. In the previous related study mentioned above, a 1:10, Grout$_{+\mathrm{Slag}}$:water suspensions had a steady state Eh of +423 mV (Kaplan et al., 2019). Thus, it is difficult to explain why the dominant I species is also hydrated I$^-$, rather than AgI, in the Grout$_{-\mathrm{Slag}}$+(Ag-GAC+I$^-$) sample (Fig. 3). One possible explanation for the absence of AgI in this grout sample is that even under oxidizing condition, the GAC and grout ingredients may provide additional reducing capacity to promote the reductive dissolution of AgI. There are various oxidative or reductive functional groups on GAC surfaces, depending on sources of raw materials, manufacturing processes and post treatments (Li, 2012; Shafeeyan et al., 2010; Yin et al., 2007). For example, GAC materials have been shown to reduce NO_2 (Ghouma et al., 2018) and Cr^{6+} (Han et al., 2000). Thus, in this complex system under oxic conditions, there are many factors that may impact the iodine speciation and immobilization, which warrants future investigation. Overall, the available results appear to indicate that the slag-free grout appears to be effective for stabilizing iodide loaded on Ag-zeolite (Kaplan et al., 2019), but not Ag-GAC secondary solid waste. Additional studies designed to quantify and characterize the iodine released from Ag-GAC in cementitious systems are needed to validate these results.

3.4. I speciation in grout samples cured with IO_3^--amended Ag-GAC

Iodine K-edge XANES and EXAFS spectra of the $Grout_{-Slag}$+IO_3^-, $Grout_{+Slag}$+IO_3^-, Ag-GAC+IO_3^-, $Grout_{-Slag}$+(Ag-GAC+IO_3^-) and $Grout_{+Slag}$+(Ag-GAC+IO_3^-) samples were collected. The I K-edge XANES spectra of these grouts were compared with the spectrum of a reference material (i.e., KIO_3) in Fig. 4A. The XANES spectra of the $Grout_{-Slag}$+IO_3^-, $Grout_{+Slag}$+IO_3^- samples (green lines) were identical to that of KIO_3 (black line) (Kodama et al., 2006; McKeown et al., 2015; Shimamoto et al., 2010; Shimamoto et al., 2011; Yamaguchi et al., 2010), indicating that the IO_3^- once cured in the two grout formulations did not undergo any detectable transformation. There was no detectable amount of reduced iodine species like I^-, even in the slag grout. The I K-edge EXAFS spectra in K space (Fig. 4B, green lines) and R space (Fig. 4C, green lines) of these two grouts were also compared with the corresponding spectra of KIO_3 (black line), which confirmed that the I species in the slag-free and slag grouts was primarily IO_3^-.

The I K-edge XANES spectrum of the Ag-GAC+IO_3^- sample (pink line) showed only a very weak signal, indicating that there was little uptake of IO_3^- by the Ag-GAC (Fig. 4). As a result, the spectra of the grout samples cured with the Ag-GAC+IO_3^- (i.e., $Grout_{-Slag}$+(Ag-GAC+IO_3^-) and $Grout_{+Slag}$+(Ag-GAC+IO_3^-) samples) were also weak, as shown in Fig. 4A. Therefore, the EXAFS data of these three samples were not presented in Fig. 4B and 4C. These results support the low IO_3^- K_d values reported in Table 2 and previous studies (Chebbi et al., 2016; Mattigod et al., 2003b; Nenoff et al., 2014; Qafoku et al., 2014).

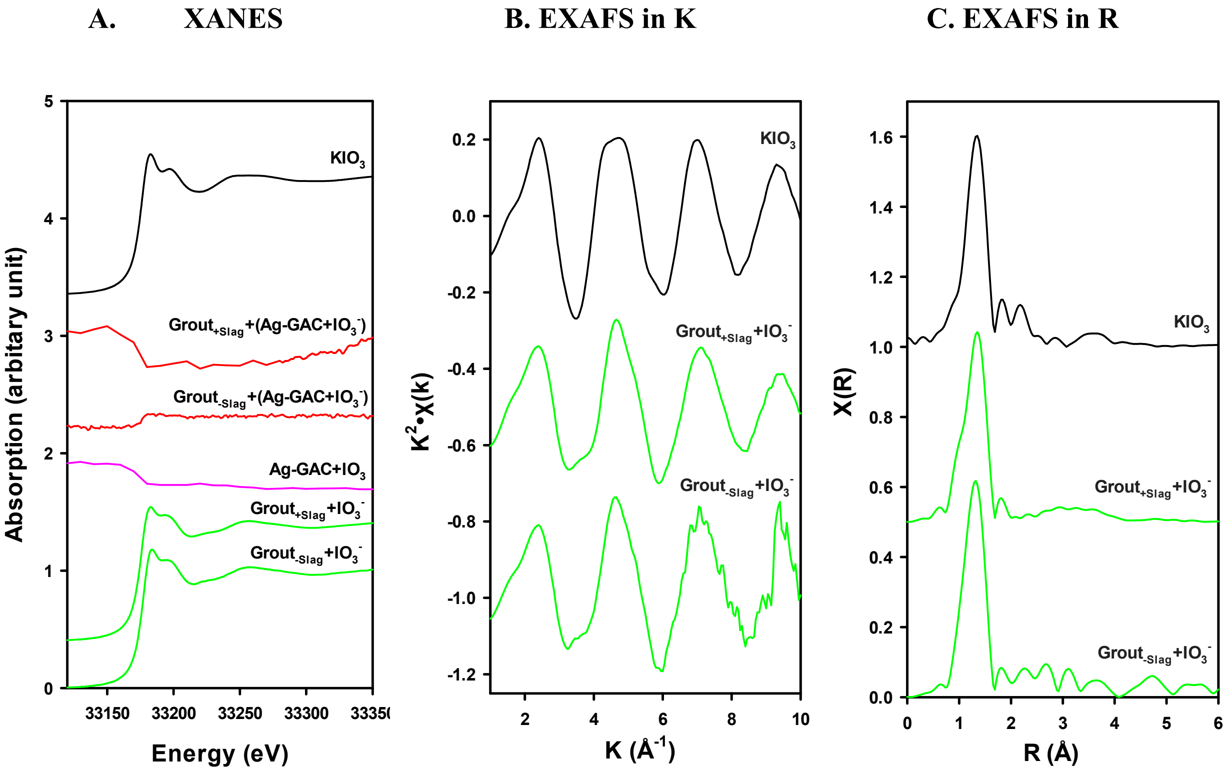


Fig. 4. I K-edge XANES (A) and EXAFS (B and C) spectra of grout samples with iodate loading, in comparison with the spectra of KIO_3 as a reference material. IO_3^- was mixed with grout formulations, or initially added to the Ag-GAC and then the (Ag-GAC+IO_3) was added into the dry blend of the two grout formulations. At the time of the measurements, the $Grout_{+Slag}$+IO_3^- and $Grout_{+Slag}$+(Ag-GAC-IO_3^-) had been hydrating (curing) in an inert environment for 40 days, while the $Grout_{-Slag}$+IO_3^- and $Grout_{-Slag}$+(Ag-GAC-IO_3^-) had been hydrating on a bench top for 40 days.

3.5. I speciation in grout samples cured with org-I-amended Ag-GAC

Iodine K-edge XANES (Fig. 5A) and EXAFS (Fig. 5B and 5C) spectra of the $Grout_{-Slag}$+org-I, and $Grout_{+Slag}$+org-I, Ag-GAC+org-I, $Grout_{-Slag}$+(Ag-GAC+org-I) and $Grout_{+Slag}$+(Ag-GAC+org-I) samples were collected and compared with the spectra of two reference materials (i.e., AgI and 4-iodoaniline) (Shimamoto et al., 2011; Yamaguchi et al., 2010). The spectra of the $Grout_{-Slag}$+org-I, and $Grout_{+Slag}$+org-I samples (green lines) were nearly identical to those of 4-iodoaniline (black line), indicating that the I species in these grout samples did not undergo any detectable speciation transformation. The I K-edge XANES and EXAFS spectra of Ag-GAC+org-I (pink line; Ag-GAC after exposure to 4-iodoaniline in oxic water solution) were identical to the corresponding spectra of 4-iodoaniline reference sample, rather than AgI (black line), which indicated that the I species in the Ag-GAC+org-I sample remained as 4-iodoaniline, rather than undergoing some form of transformation to form AgI. After the Ag-GAC+org-I was cured in the $Grout_{-Slag}$ and $Grout_{+Slag}$, the I K-edge XANES and EXAFS spectra (red lines) of $Grout_{-Slag}$+(Ag-GAC+org-I) and $Grout_{+Slag}$+(Ag-GAC+org-I) samples were fairly similar to the corresponding spectra of 4-iodoaniline, which means that the 4-iodoaniline bound to the Ag-GAC also did not undergo any detectable speciation transformations after being cured in the slag-free and slag grout samples.

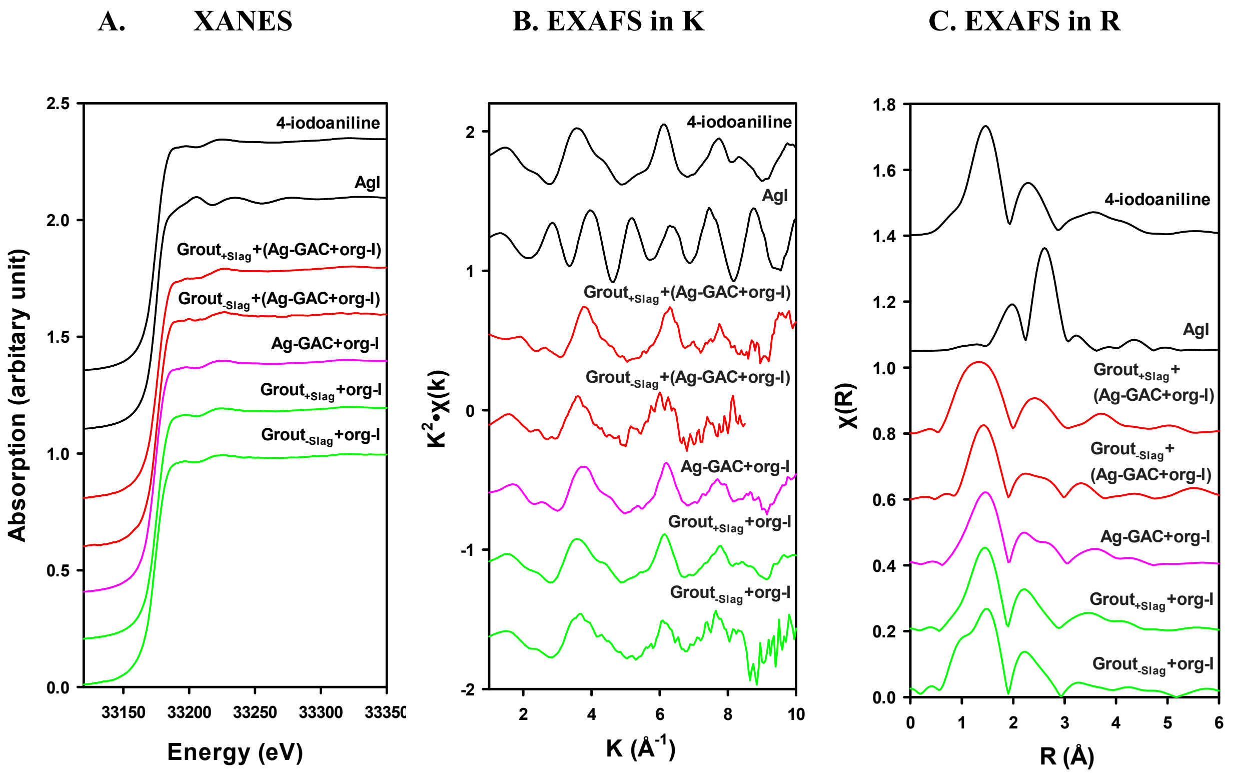

A. XANES B. EXAFS in K C. EXAFS in R

Fig. 5. I K-edge XANES (A) and EXAFS (B and C) spectra of grout samples with org-I loading, in comparison with the spectra of AgI and 4-iodoaniline as reference materials. Org-I (i.e., 4-iodoaniline) was mixed with grout formulations, or initially added to the Ag-GAC and then the (Ag-GAC+org-I) was added into the dry blend of the two grout formulations. At the time of the measurements, the Grout$_{+\mathrm{Slag}}$+org-I and Grout$_{+\mathrm{Slag}}$+(Ag-GAC+org-I) had been hydrating (curing) in an inert environment for 40 days, while the Grout$_{-\mathrm{Slag}}$+org-I and Grout$_{-\mathrm{Slag}}$+(Ag-GAC+org-I) had been hydrating on a bench top for 40 days.

It is expected that much of the iodine in high-level nuclear waste, especially those waste streams with high organic carbon concentrations, and in groundwater with moderate to high dissolved organic carbon concentrations will contain a large fraction of org-I species (Kaplan et al., 2014). The iodine in org-I compounds is covalently bound to the organic ligands, and therefore would need to be reduced to I^{-1} before it could form the sparingly soluble AgI compound. This process was expected to compromise the effectiveness of Ag-GAC to remove org-I, because GAC is not able to reduce org-I to I^-, and the AgI precipitation is not expected to occur. However, Ag-GAC has a moderate capacity for removing org-I from grout leachate, with a K_d value of >1942 mL/g for $Ag_{10\%}$-GAC (Table 2), probably through the chemical bonding of org-I with the surface functional groups of GAC.

When the Ag-GAC+org-I was cured with $Grout_{+Slag}$ in an inert atmosphere or with $Grout_{-Slag}$ on the bench top, the org-I did not undergo any transformations, and its speciation remained unchanged (Fig. 5). These results demonstrated that the immobilized org-I on the Ag-GAC was stable without observable speciation change under either reducing or oxidative grout conditions (Kaplan et al., 2019). Based on previous studies of the grout leachate chemistry used in this study, the $Grout_{+Slag}$ porewater may have approached an Eh of -307 mV and a pH of 12.37, whereas the $Grout_{-Slag}$ porewater may have approached an Eh of 423 mV and a pH of 12.21 (Kaplan et al., 2019). Thus, based on the large K_d values (Table 2) and the lack of iodine speciation transformation, it appears that both slag-free or slag grout formulations may be effective for stabilization of organic I-loaded Ag-GAC secondary solid waste. Nevertheless, while these results are encouraging, it is important to bear in mind that only one compound of this large class of org-I compounds was tested.

4. Conclusions

This study demonstrated that grout composition and I speciation may have a significant impact on the effectiveness of grout waste forms to immobilize radioiodine from Ag-GAC secondary solid waste. While the AgI technology is extremely effective at converting I^- from a highly mobile to a highly immobile form, the stability of the formed $AgI_{(s)}$ is sensitive to the redox conditions of the system. In this study, the strong reducing system approached subsurface disposal conditions that might exist in young (> ~1 year) to moderately old (< ~500 years) slag grout systems, while the more oxidized systems approached conditions that might exist in aged (>~500 years) slag-free grout. These results demonstrated that either slag or slag-free grouts may not be effective for stabilization and disposal of I^- loaded Ag-GAC secondary solid waste, because the grout ingredients and GAC may have sufficient reduction capacity, so that even a slag-free grout could potentially promote reductive dissolution of AgI under repository subsurface systems. While Ag-GAC was not effective at removing IO_3^-, it was effective for org-I removal. As the org-I loaded Ag-GAC secondary solid waste were loaded into the grout formulation, the organic I speciation remain unchanged under either reducing or oxidative grout condition. Thus, based on these initial results, the slag-free and slag grouts may be effective for stabilization of org-I loaded Ag-GAC secondary solid waste.

This study also has implications on appropriate subsurface disposal sites. For example, some proposed disposal sites under consideration, such as in China (Wang, 2010) and Belgium (Won et al., 1997), were selected in part because they possess naturally reducing system. Reducing conditions are expected to reduce the mobility of some key aqueous radionuclides that are redox-sensitive, most notably Np, Tc, Pu, and U. However, such reducing systems may exacerbate safe disposal of I^- loaded Ag-GAC secondary solid waste.

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Iodine immobilization by silver-impregnated granular activated carbon in cementitious systems

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Supplemental Information

Table S1.

Chemical composition (wt%) of grout samples

Element[a]	**Grout$_{-slag}$**	**Grout$_{+slag}$**
CaO,	22.5	27.4
SiO_2	38.3	35.0
Al_2O_3	13.1	13.7
Fe_2O_3	4.5	3.0
SO_3	0.8	1.1
MgO	3.7	4.5
K_2O	1.1	0.9
TiO_2	0.6	0.7
Na_2O	2.2	1.8
SrO	0.2	0.2
P_2O_5	0.2	0.1
Mn_2O_3	0.1	0.1
Org-C	0.12±0.02	0.13±0.02
Inorg-C	1.64±0.03	1.45±0.05

[a] XRF analysis except Organic C and inorganic C were conducted by a CHNS Analyzer (furnace oxidation followed by an infrared detection method).

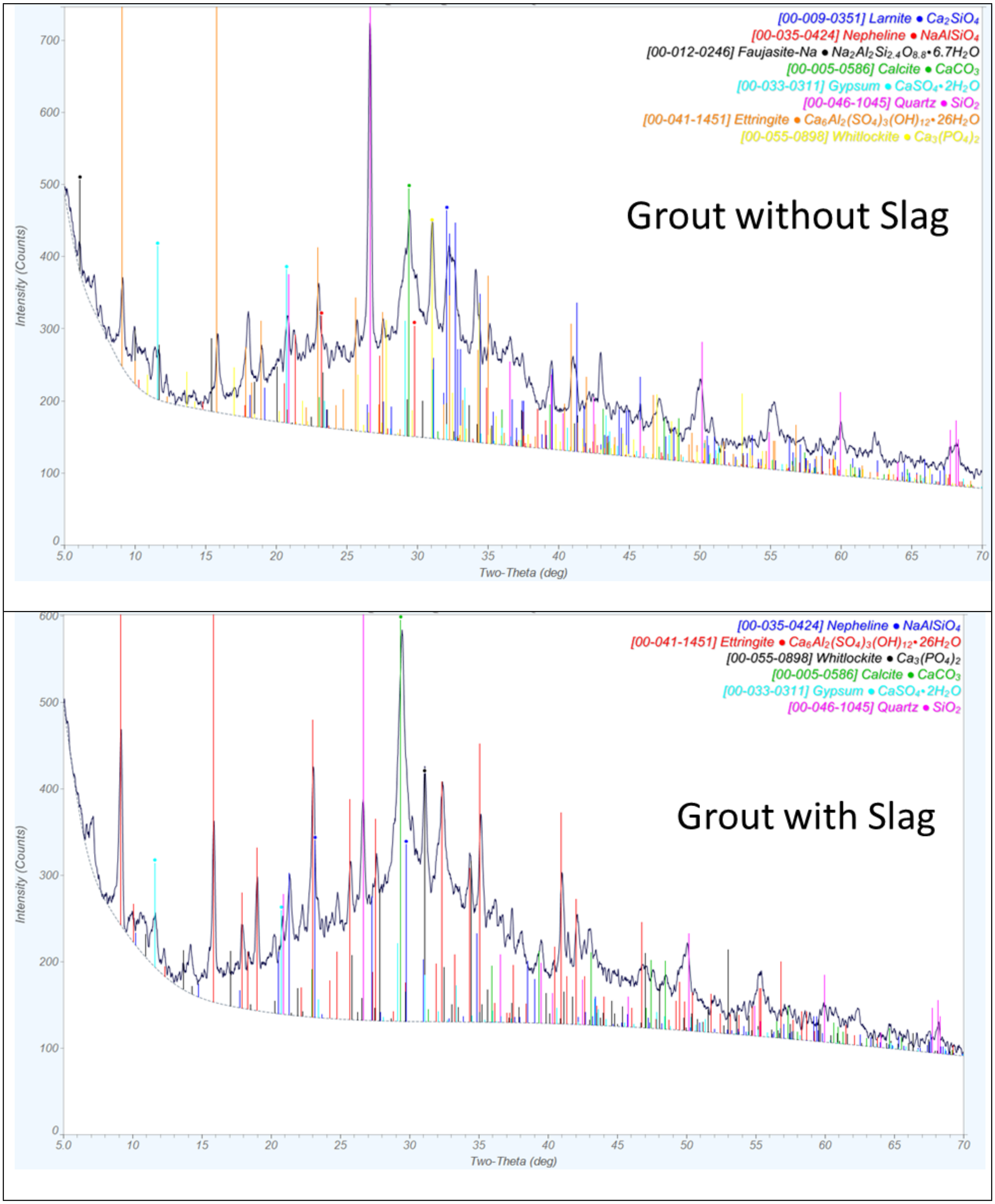

Fig. S1. Powder X-ray diffraction (XRD) patterns of grout samples without slag (top) and with slag (bottom).

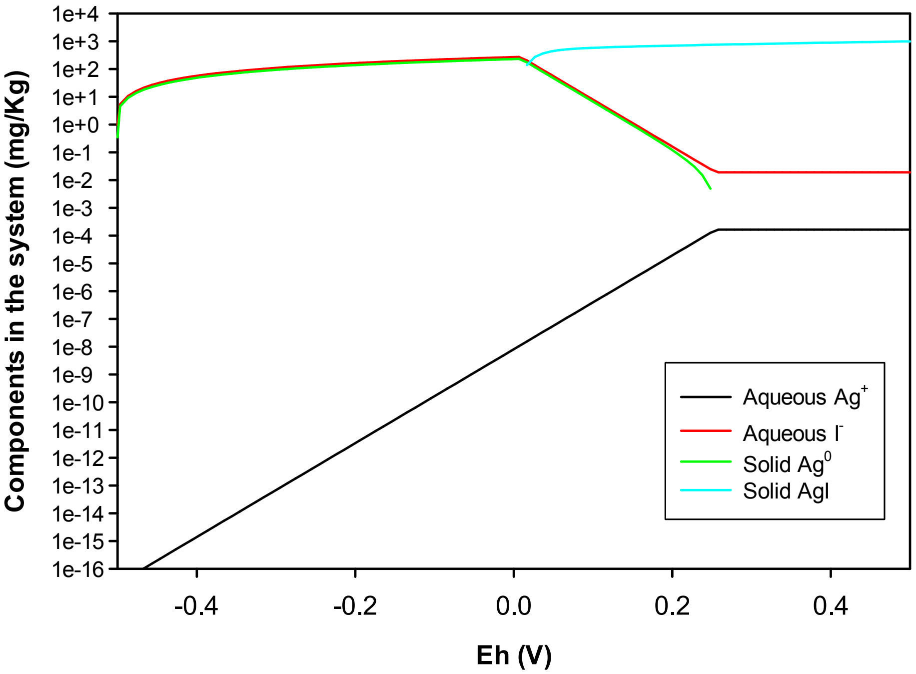

Fig. S2. Concentrations of components in a Grout$_{+Slag}$+AgI system as a function of Eh. Model conditions included the aqueous chemical composition of slag grout leachate, including a pH of 12.41 and an AgI concentration of 1 g/kg (1 g of AgI was dispersed in aqueous slag grout porewater solution). The AgI solubility in the grout leachate solution was conducted using Geochemical WorkBench® v.8, [2]. The database, Thermo.dat, came with the software and was amended to include the solubility product for AgI (k_{sp} = -16.1) [3].

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