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Microscale speciation of arsenic and iron in ferric-based sorbents subjected to simulated landfill conditions

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Abstract

During treatment for potable use, water utilities generate arsenic-bearing ferric wastes that are subsequently dispatched to landfills. The biogeochemical weathering of these residuals in mature landfills affects the potential mobilization of sorbed arsenic species via desorption from solids subjected to phase transformations driven by abundant organic matter and bacterial activity. Such processes are not simulated with the Toxicity Characteristic Leaching Procedure (TCLP) currently used to characterize hazard. To examine the effect of sulfate on As retention in landfill leachate, columns of As(V) loaded amorphous ferric hydroxide were reacted biotically at two leachate sulfate concentrations (0.064 mM and 2.1 mM). After 300 d, ferric sorbents were reductively dissolved. Arsenic released to porewaters was partially co-precipitated in mixed-valent secondary iron phases whose speciation was dependent on sulfate concentration. As and Fe XAS showed that, in the low sulfate column, 75–81% of As(V) was reduced to As(III), and 53–68% of the Fe(III) sorbent was transformed, dominantly to siderite and green rust. In the high sulfate column, Fe(III) solids were reduced principally to FeS_(am), whereas As(V) was reduced to a polymeric sulfide with local atomic structure of realgar. Multi-energy micro-X-ray fluorescence (ME-μXRF) imaging at Fe and As K-edges showed that As formed surface complexes with ferrihydrite > siderite > green rust in the low sulfate column; while discrete realgar-like phases formed in the high sulfate systems. Results indicate that landfill sulfur chemistry exerts strong control over the potential mobilization of As from ferric sorbent residuals by controlling secondary As and Fe sulfide co-precipitate formation.

Keywords

landfill; arsenic; TCLP; μXRF; XANES; EXAFS; realgar

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Supporting Information. Text, tables S11–4, and figures S11–3 describing column preparation and characterization; spectroscopic analysis including details of As and Fe K-edge EXAFS fit results; and ME-μXRF energy map matrix processing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

1. Introduction

Arsenic is a known environmental toxin [1, 2] that is affecting the health of millions of people worldwide through natural and anthropogenic contamination of drinking water sources [3]. Because of its environmental abundance, toxicity, and potential for human exposure, As has been designated the number one priority toxin by the Agency for Toxic Substance and Disease Registry (e.g. 1997–2011). Since 2006, when the USEPA adopted a maximum contaminant level of $10 \mu\text{g L}^{-1}$ in drinking water, more than 4000 US water utilities have been required to reduce concentrations of product water As [4].

The high chemical affinity of arsenic for adsorption to hydrous ferric oxide (HFO) surfaces enables economical methods for removing it from drinking water [5, 6] by exploiting inner-sphere complexation of As(V) under oxic conditions (e.g. [7–9]). The combined low-cost and effectiveness of ferric-based sorbents have contributed to their wide use by water treatment utilities, leading to significant increases in the volume of arsenic-bearing solid residuals (ABSR) [10].

Iron based As “filter” media are typically non-regenerable and, in the US, can be disposed in municipal solid-waste (MSW) landfills if shown to pass the USEPA toxicity characteristic leaching procedure (TCLP). An estimated $3\text{--}12 \times 10^3$ Mg of ABSR are generated annually, typically loaded to $>1:200$ As:Fe mole ratio, creating 15–60 Mg of localized point-source As [11]. ABSR are subjected to landfill (bio)geochemical conditions, including organic-rich reducing environments, which are not simulated by the TCLP [12–14]. Prior studies have shown that reductive dissolution of iron oxides can result in mobilization of sorbed or coprecipitated As (e.g. [15–17]) - a potential fate for ABSR in mature MSW landfills as well [18]. Indeed, the coupled cycling of As and Fe in landfills is impacted by microbial Fe reduction; where spent As sorbent, labile organic matter, and a consortium of heterotrophic reducing bacteria results in release of As and Fe into mobile pore waters [19–21]. Although it is generally recognized that biogeochemical As cycling is closely coupled to the bio-availability of redox sensitive Fe, S, and organic carbon (C_{ORG}) (e.g., [22, 23]), the specific reactions driving arsenic release and sequestration following ABSR disposal in landfills have not been fully characterized. In particular, the influence of sulfate activity is poorly resolved. Sulfate in landfill leachate ranges from 1 to 51 mM, and is likely a key driver of neo-precipitate formation and potential secondary phase As sequestration [24]. For example, in laboratory batch studies of ferric based ABSRs, it was found that reduction of influent dissolved sulfate resulted in precipitation of iron sulfide (FeS_2) coincident with 80–100% reduction of As(V) to As(III) during a 2 year incubation [25].

The current study used X-ray absorption spectroscopy (XAS) and X-ray fluorescence (XRF) imaging to examine the effect of influent sulfate concentration on ABSR under microbially-induced reducing conditions. Briefly, laboratory columns were packed with As(V)-loaded HFO, inoculated with a diverse heterotrophic microbial consortium from a wastewater treatment plant, and reacted with a synthetic landfill leachate (SLL) containing either low (LS) or high (HS) sulfate concentrations (0.064 mM and 2.1 mM, respectively). Effluent samples were collected for complete aqueous chemical analysis as presented elsewhere [26]. The focus of the present study is on the solid phase transformation of ABSR under the two influent sulfate concentrations. By combining X-ray absorption spectroscopy (XAS) and multiple energy micro X-ray fluorescence (ME- μ XRF) mapping (elemental and chemical), we elucidate changes in sorbent and sorbate speciation, binding environments, and co-associations that enable improved prediction of As fate in mature landfills.

2. Experimental Section

2.1 Column Design

Columns (Spectrum Chromatography, 2.5 cm dia; 30 cm long) were packed with 73.3 g (15.1 g dry mass) of As(V) loaded ferric sludge (20:1 molar Fe:As), 120 g of 0.8 mm glass beads to provide tractable porosity ($\phi = 41.7\%$), and 25 ml of anaerobic digester sludge from a wastewater treatment plant (76% water, 18% organic matter; Ina Road Wastewater Treatment Plant, Tucson AZ USA). The anaerobic digester sludge was chosen, in lieu of a pure strain inoculum, for its miscellany of microbes consistent with the broad diversity of anaerobic organisms in a mature MSW landfill. The sludge was a poorly crystalline ferric hydroxide, similar to 2L ferrihydrite (referred to hereafter as AFH), coprecipitated with As(V) by dissolving 0.935 M ferric chloride hexahydrate (ACS reagent, Sigma-Aldrich) and 0.047 M sodium arsenate heptahydrate (KR Grade, Sigma-Aldrich) in 1 L of purified water. The AFH was washed 5x to a supernatant EC $<1\text{mS cm}^{-1}$ and adjusted to pH 7.0 with NaOH. The SLL contained minerals and nutrients necessary for microbial activity and lactate as the organic electron donor and carbon source (Table SI 1). The SLL was sparged with nitrogen and fed continuously with a multi-syringe pump (Braintree Scientific) in up-flow mode at 5.1 ml h^{-1} (2 pore volumes [PV] d^{-1}). The Darcy's velocity was 0.25 m d^{-1} (hydraulic conductivity $\sim 10^{-3}\text{ cm d}^{-1}$) to represent saturated, semi-pervious landfill conditions. Columns were fed SLL with either 0.064 mM (LS) or 2.1 mM (HS) sulfate for 330 days or 331 days, respectively. Sulfate influent concentrations bracketed reported groundwater (average 0.048 mM [27]) and US landfill (2.78 mM [24]) values. The goal was to evaluate the significance of relatively small increments of sulfate in landfill systems relative to natural groundwater environments. Column effluent samples were filtered through $0.22\text{ }\mu\text{m}$ cellulose acetate syringe filters and analyzed for As, Fe^{2+} , SO_4^{2-} , lactate, and acetate. Acetoclastic methanogenic bacteria were inhibited by the addition of 1 mM 2-bromoethanesulfonic acid (BES) sodium salt ($\text{BrCH}_2\text{CH}_2\text{SO}_3\text{Na}$, Sigma-Aldrich) in the influent of the LS column. BES was added to the LS column on day 139 (278 PV). It was observed to not change arsenic and iron leaching patterns compared to other column experiments without inhibition, and was not added to the HS [26]. To preserve the experimental redox environment, post operation column autopsies were conducted in an anaerobic chamber, where reacted AFH was dissected and subsamples were collected before transport in crimp-sealed serum vials to a synchrotron facility for x-ray analysis.

2.2 X-ray Spectroscopy

Column subsections were analyzed with K-edge XAS for speciation of arsenic and iron. Spectra were collected at Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 4-1. Beam energy was calibrated on an arsenic foil with the main edge inflection assigned 11,867 eV and on iron foil with the first edge inflection assigned at 7112 eV. Fluorescence was monitored with a 13-element solid-state Ge detector with a He cryostat sample holder ($\sim 8\text{--}15\text{ K}$, see SI for XAS setup and analysis details). For bulk XAS analysis, 100–200 mg of moist sludge was ground, homogenized, loaded in Teflon sample holders, and sealed with Kapton tape in an anaerobic chamber at the synchrotron facility (Coy, $\text{N}_2/\text{H}_2=95/5$).

2.3 XRF Imaging Collection and Analysis

For XRF analyses, reacted AFH was air dried in the dark in an anaerobic chamber, to minimize post-experiment photochemical/oxidative reaction, and embedded in metal free epoxy (EPO-TEK 301-2FL; Epoxy Technologies, Inc). The suspension was cured for 72 h in a vacuum desiccator, packed under $\text{N}_{2(g)}$ and sent in a low permeability bag for thin-sectioning ($30\text{ }\mu\text{m}$, polished 2-sides) under anoxic conditions (Spectrum Petrographic, WA). Thin sections were transported to SSRL in anaerobic bags (AnaerogenTM) and stored in an anoxic chamber until analyzed.

The X-ray microprobe at SSRL, beamline 2–3, was used to interrogate the local chemical environment by scanning thin-section at energies near the Fe or As absorption edge [28]. Images collected were 400–500 μm^2 with a pixel step size of 2.5–3.0 μm and 50 ms dwell time. For multiple energy (ME) maps, the measured fluorescence (F_m) at a designated energy was used to compile a 2D image relating concentration (ρ) of each element (i) or species (j) to elemental fluorescence yield (ω_i), i.e. (eq.1).

$$F_m = \sum (\rho_{ij} \omega_i) \quad (1)$$

Species specific mapping was conducted by monitoring F_m at multiple energies across the edge jump of As and Fe. The As K-edge is diagnostic for oxidation state, with the white line peak (ca. $\pm 1\text{eV}$) for arsenic sulfides at 11869 eV, As(III) at 11872 eV and As(V) at 11875 eV [22]. Therefore, when the monochromator is tuned to 11869 eV, resultant fluorescence from an arsenic sulfide is measurably different from that of As (III) or As(V). The same concept of multiple energy maps was applied to the Fe edge for phase identification. However, unlike As where a clear spectral peak was associated with oxidation state, the difference in Fe fluorescence at multiple energies was compared in a fluorescence yield - energy matrix selected specifically for phase identification (see Mayhew et al. for details [28]). Briefly, model compound spectra were input to a matrix of normalized fluorescence and energy (eV) at the energies of the XRF maps (Figure SI1 and Table SI3). Generally, the number of energies mapped is greater by one than the number of components that can be resolved (i.e., $n+1$ energy maps for n phases). Iron and As was mapped at discrete energies (7114, 7121, 7124, 7126, and 7137 eV for Fe; and 11869, 11872, 11875, and 11880 eV for As) to assess chemical associations and speciation.

The X-ray energy was calibrated with metal foils as above for bulk XAS. Principal component analysis (PCA) was applied to the $>40k$ pixel images to locate regions of unique components and chemical differences. The application of PCA to image data is common for processing soft X-ray transmission data (e.g. [29, 30]) but has been less extensively applied to hard X-ray μXRF data (see [28]). The unique components highlighted with PCA were probed with X-ray absorption near edge structure (μXANES) and collected at the same spot-size, stage and detector position as image data, to provide additional constraint for reference models and allowed components in the linear combination fits (LCFs) of bulk XAS.

3. Results

3.1 Column leachate aqueous chemistry

The bioreduction of AFH released As and Fe to mobile leachate under both high and low sulfate influent conditions [26]. After 300 d, the LS column leached 84% of the initial solid-phase arsenate and 3.3% of the iron. After 331 d, the HS column released 36% of the initially loaded arsenate and $<1\%$ of the iron. Hence, about three-times more As and Fe were retained under the higher sulfate conditions. Effluent monitoring showed that leachate pH fluctuated around circumneutral with values 7.5–8.0 for LS and 7.5–8.3 for HS. In both columns, e^- donor lactate was oxidized to acetate and carbonate. Nearly all of the lactate was converted to acetate in the effluent from the beginning through to completion of the experiment. Influent and effluent sulfate concentrations were monitored in both columns, with influent sulfate found to be constant throughout the experiment. The HS effluent sulfate decreased from nearly 100% breakthrough at 1 d to 50% at 37 d, 25% at 40 d, and $<10\%$ at 60 d, and for the duration of the experiment. The LS influent sulfate dropped from 100% breakthrough at 5 d to $<10\%$ after 15 d and remained low for the experimental duration. This indicates that sulfate reduction or sorption occurred in both columns.

3.2 As Speciation by Bulk XAS

Normalized As k-edge XANES spectra of LS column solids showed that initial solid phase As(V) had been mostly reduced to As(III) after 300 d. In sections LS-II, LS-III, and LS-IV, XANES showed two distinct peaks at 11872.1 and 11875.3 eV, consistent with As(III) and As(V), respectively (Figure 1a, fits shown in Table 1). Fitting of As XANES to reference spectra of As(III) and As(V) sorbed to ferrihydrite shows that 75–81% of the As(V) in the AFH was reduced to As(III). Arsenic K-edge extended x-ray absorption fine structure (EXAFS) of the LS samples showed the bulk solid to be mixed As(III) and As(V), with spectra fit to first-shell As-O scattering paths, second-shell contributions from As-Fe scattering, and a multiple scattering (MS) contribution corresponding to the As-O-O MS within the arsenate tetrahedra (Figure 1b–c, fits shown in Table SI4). Including the MS paths improved the fit, whereas degeneracy, distance, and the Debye-Waller factor were linked to the determined $\text{As}^{\text{V}}\text{O}_4$ parameters (see e.g., [8, 31]). Multiple scattering was not significant for As(III), likely because of static disorder in the ligating oxygen shell. At 10 cm into the LS column (LS-II), bulk As EXAFS were fit with As-O distances at 1.77 Å and 1.69 Å, corresponding to arsenite pyramidal coordination, and arsenate tetrahedral coordination, respectively. The second shell EXAFS contributions from As-Fe interatomic distances were fit to 3.31 ± 0.01 Å and 3.46 ± 0.01 Å, similar to coordination environments observed in a laboratory experiment of arsenite sorption to 2-line ferrihydrite and a field site where arsenate was sorbed to amorphous hydrous ferric oxide [32, 33]. The EXAFS determined mixed As species was consistent with XANES. Scattering at the As-Fe interatomic distance of 3.31 Å was attributed to a ^2C coordination, bidentate-binuclear corner-sharing between $\text{As}^{\text{III}}\text{O}_3$ pyramids and FeO_6 octahedra, whereas the 3.46 Å As-Fe scattering distance was attributed to ^2C coordination of $\text{As}^{\text{V}}\text{O}_4$ tetrahedra with ferric octahedra (Figure 1c) [8].

Linear combination fits to the As XANES from the HS experiment, using realgar (AsS) as model reference sulfide spectra, showed a gradient from 100% AsS to 100% As(III) from the column influx to the efflux (Figure 1d, Table SI4). Differentiating among As sulfides (e.g. As_4S_4 , As_2S_3 , etc.) with XANES alone is not possible because the associated edge shifts are within energy resolution of the beamline (~1 eV at the As edge). Therefore, while the peak match to realgar is not mineral specific, it is diagnostic of a solid-phase As-sulfide complex. Arsenic XANES of HS-I showed a distinct peak at 11869 eV, fit to a single sulfide component. The intermediate section HS-III had an absorption maximum at 11872 with an asymmetric broadening below the main edge. The lower energy broadening feature was fit with 31% AsS; the main peak was fit with 69% As(III). The As XANES for the sample near the outlet of the column, HS-IV, was fit with a single component of As(III). Arsenic EXAFS of the bulk solid in HS-I showed an As-S distance of 2.25 Å and contributions beyond the first shell of As-As at 2.58 Å, 3.49 Å, and 3.62 Å (Figure 1e). The As-As backscattering features beyond the first shell observed in HS-I are unique to realgar (and associated polymorphs) and are not observed in orpiment (As_2S_3), arsenopyrite (FeAsS), As-thio complexes, or organic As-S ligands (Figure 1f) [34]. Complete reduction of As(V) was observed in the HS column. First shell As-O distance in HS-III and HS-IV were 1.76–1.78 Å, consistent with As(III) in pyramidal coordination. The second shell contributions from Fe backscatters were fit at 3.49 Å, a distance longer than the As(III) ^2C coordination observed in the LS column, consistent with either a monodentate ^1V coordination or ^2C coordination of non-edge sharing iron octahedra.

3.3 Fe Speciation by bulk XAS

Iron XAS data show the reduction of AFH-derived Fe(III) to Fe(II) and secondary Fe (bio)mineralization. Normalized first-derivative Fe K-edge XANES spectra were used for LCFs because they reveal subtle distinctions [35]. Column spectra were well described with

LCF of fractional components of standard ferrous, ferric, and mixed-valent iron reference spectra, incl. ferrihydrite, siderite, carbonate green rust, vivianite, and mackinawite (Table 1). LCFs of the Fe XANES indicated development of a redox gradient in both columns, with the most reducing conditions near the inlet. In the LS column, 68 to 53 % of the AFH was transformed along the redox gradient. The LS spectra showed siderite and ferrihydrite as major components, and carbonate green rust and vivianite as minor components, with components constrained by μ XANES and XRD from LS-II (Figure 2a). In contrast, the HS column showed 100% of the AFH was transformed to ferrous iron sulfide (mackinawite) at the inlet, while ferrihydrite was co-associated with siderite and green rust at the outlet. Mackinawite and ferrihydrite did not co-occur in the HS column and ferric phosphates such as strengite could not be fit to the spectra (Figure 2b). Assignment of the Fe K-edge XANES to a ferrihydrite component is supported by the lack of detectable goethite peaks by XRD. Non-linear least squares fitting of the Fe EXAFS from the bulk solid in HS is consistent with the Fe solids being dominantly a mackinawite-like FeS along with a smaller green rust component (Figure 2c–d, Table SI4). The Fe-S bond distances of 2.27 Å and contributions beyond the first shell from Fe-Fe backscattering at 2.71 Å and 3.62 Å, are unique to the mackinawite structure and are not observed in pyrite or arsenopyrite [36, 37]. Additional backscatterers were needed for a good fit to the EXAFS spectra. An Fe-O distance at 2.02 Å and a Fe-Fe distance at 3.26 Å, both consistent with green rust – a phase also suggested by the Fe XANES – improved the fit significantly. The Fe-Fe distance at 3.26 Å is close to the expected distance for edge sharing iron octahedra found in natural and synthetic green rust (3.18–3.25 Å) [32]. Pyrite was investigated as a possible component in reduced HS sections but was not observed; the Fe XANES LCF was better for mackinawite, as was the unique structural fit from the Fe EXAFS spectra, and XRD showed a lack of diffraction peaks diagnostic of the cubic pyrite structure.

3.4 X-ray Fluorescence

3.4.1 Low Sulfate Column—Elemental correlations from ME μ XRF mapping images for the LS column show As primarily associated with ferrihydrite between the glass beads (Figure 3a–d). Fluorescence yield varies by atomic number; however, comparing per pixel fluorescence counts of Fe to As gives a correlation coefficient of 0.82 and an Fe:As count ratio of 26:1, close to the initial molar ratio of 20:1. ME μ XRF across the As edge indicates that As(III) and As(V) were distributed through the column with localized high concentrations (Figure SI2). The Fe ME μ XRF map shows the predominance of ferrihydrite and siderite in the reacted AFH with rims of green rust (GR) forming at the solid-liquid interface. Both As(V) and As(III) are associated with the areas mapped as ferrihydrite and siderite, whereas the areas mapped as GR are associated with low As counts and As(V) only.

3.4.2 High Sulfate Column—The association of As to Fe differed in the HS column; areas of high As were observed to be mostly independent of Fe rich regions (Figure 3e–h). The abundance of Fe solids appeared to be lower in HS-I versus LS-II, as seen in the fluorescence map (Figure 3a v 3e) and in micrographs (Figure SI3). Arsenic speciation maps showed As associated with sulfide widely distributed throughout the solid matrix, and As(III) located in isolated spots (Figure 3h). The Fe maps indicated that As(III) was generally associated with the area mapped as siderite, and it was not found within the area mapped as FeS.

The HS ME μ XRF showed complete As(V) reduction, mostly to AsS with some As(III). Most of the arsenic in the HS-I section of the column was As-sulfide, consistent with the bulk XAS (Figures 2b and 3h). The Fe phase was mostly FeS with a GR crust co-occurring throughout, consistent with the bulk XAS. Siderite was observed - not associated with AsS

phases - and generally in regions of lowest As fluorescence. The AsS and FeS phases were spatially correlated, but not uniformly; there were areas of FeS without AsS.

4. Discussion

In this long-term flow-through column experiment under sulfidogenic conditions, bulk XAS was used to probe the Fe and As speciation, and μ XRF imaging was employed to determine the localization of secondary phases and As speciation. Reductive transformations of AFH are attributed microbial reduction of Fe(III) and SO_4^{2-} . Once heterotrophic microbial respiration was activated and Fe^{2+} was produced, the resulting reductive dissolution of AFH was likely by both biotic and abiotic pathways as expected in a mature landfill [38]. Results showed that the dissimilatory reduction of these ABSRs produced green rust, vivianite, and siderite in the LS column and mackinawite, siderite, vivianite, and greenrust in the HS column. While solid phase As(V) was reduced, the extent of arsenic mobilization and secondary iron mineral formation were dependent on the influent sulfate concentration.

4.1 As and Fe Speciation in Low Sulfate Column

Mixed valent As is distributed with iron solids in the LS column, indicating mixed coverage and no obvious preference for As(V) over As(III) at this scale at many surface sites. The LS ME μ XRF maps show mixtures As(III) and As(V) in the same $3 \mu\text{m}^2$ pixel space. However, areas of highest As concentration were dominated by As(V) and ferrihydrite, identifying ferrihydrite as the energetically favorable sorbent. Our results indicate that siderite and green rust were not effective sinks for As(III), consistent with previous sorption studies [39]. In general the areas of lowest As fluorescence were associated with regions mapped as green rust indicating that As did not partition strongly to green rust, consistent with previous findings [40]. Green rust occurred as a surface crust on ferrihydrite, whereas siderite was inter-mixed with ferrihydrite. The precipitation of green rust as rims along the ferrihydrite surface suggests that the reducing SLL solution either induced a nucleation of GR at favorable ferrihydrite surface sites, or that it initiated a solid state transformation of ferrihydrite by reaction with free Fe^{2+} [41, 42]. A gradient of solid phase predominance from Fe(II) to Fe(III) was observed in both the LS and HS columns. Fe XANES show ferric, ferrous, and mixed valence phases, with greater predominance of ferrous (ferric) solids near the inlet (outlet). The siderite fraction was greatest at the inlet, owing to the oxidation of lactate to carbonate coupled to Fe(III) reduction. Our results are consistent with a laboratory study showing that the reduction of ferrihydrite by *Shewanella putrefaciens* results in the precipitation of green rust (and vivianite in the presence of phosphate) [42].

4.2 Arsenic and Iron Speciation at High Sulfate Activity

As(V) was reduced to As(III) or AsS at the HS column inlet, and for these simulated landfill solids with localized As(V)-AFH and elevated SO_4^{2-} , SLL was shown to react to precipitate realgar-like AsS and FeS as discrete phases. The precipitation of a realgar-like solid phase is consistent with the neo-formation of arsenic sulfide solids observed in microbially [43, 44] and abiotically [45] reduced sediments. An As sulfide precipitate was reported as the primary product of As(III) reaction with FeS at pH 5, and it occurred as a discrete phase, not associated with Fe, but rather an amorphous hydrous arsenic sulfide with the local structure of realgar [46]. Realgar has been precipitated from the reaction of As(III) with nano-particulate iron sulfide at pH 5, while at pH 9 thio-arsenites were formed [47]. Upadhyaya et al. (2010) showed that under reducing conditions in a fixed-bed bioreactor, generation of iron sulfides sequestered arsenic through surface precipitation of arsenic sulfide on FeS [48]. The precipitation of realgar in a high-sulfate environment subjected to reducing conditions is supported by thermodynamic modeling that predicts the formation of a realgar-like surface precipitate [49].

Similar to the LS experiment, a gradient from Fe(II) to Fe(III) solid phases was observed along the flow path in HS columns. The HS column XANES show FeS and green rust in the zone of greatest sulfidogenesis. It was observed that the inlet region, with the highest HS⁻ activity, promotes the precipitation of sulfides. The observed stability fields of ferrous sulfide and ferric (hydr)oxides do not overlap, unlike ferrous carbonate and phosphate species. Evidently, by mid-column, carbonate activity competed with HS⁻ activity, favoring the precipitation of siderite over FeS, and making green rust unstable. While ferrihydrite-like Fe speciation was kinetically stable near the outlet, it is expected to age to goethite over longer times [50]. The Fe-O distance of 2.02 Å, attributed to GR, is shorter than prior reports (2.06–2.12 Å), possibly indicating a higher ratio of Fe(III)/Fe(II) than ideal green rust, associated with the rapid oxidation of Fe(II), possibly by reaction with As(III) [51]. The Fe-Fe distance at 3.26 Å is close to that expected for edge sharing iron octahedra in natural and synthetic green rust (3.18–3.25 Å) [32]. The EXAFS is best fit to a mixture of 71% FeS and 30% green rust, a higher estimation of the green rust contribution than given by XANES, which shows 85% FeS and 12% green rust. Discrepancies between Fe EXAFS and XANES fits have been shown by O'Day et al., where analysis of known pyrite:phyllosilicate mixtures showed sulfide mass contributions can be underestimated by XANES relative to EXAFS, because of stronger backscattering of sulfur relative to oxygen in the EXAFS first shell [35]. Conversely, the underestimation of FeS by EXAFS in the present study is consistent with an amplitude reduction in $\chi(k) \cdot k^3$, attributed here to low crystallinity or nano-crystalline FeS [52]. Self-absorption was explored as a cause of dampening of the EXAFS signal because it would also manifest in an underestimation in the target phase in the EXAFS relative to XANES, but it was ruled out by concurrently collected transmission spectra that show no dampening of the EXAFS or concomitant enhancement in the XANES (esp. pre-edge region) relative to fluorescence spectra.

4.3 Fe-S-As Reactions in Sulfidic Environments

It has been shown that microbial sulfidogenesis can initiate the reductive dissolution of ferric solids including AFH [38]. Oxidation of lactate, and reduction of sulfate, initiated by microbial respiration will promote ferric solid phase dissolution and subsequent release of Fe²⁺ and HS⁻ to pore waters (eq. 2–3).

Where ferric (hydr)oxide solids are stable, oxyanion $\text{H}_x\text{As}^{\text{V}}\text{O}_4^{2-x}$ has a stronger affinity for reactive surface sites than does neutral $\text{As}^{\text{III}}(\text{OH})_3$ [53]. However, the reduction of As(V) to As(III) alone does not require release of As(III) to solution, the mechanism of As mobilization to porewater is via dissolution of sorbent AFH and subsequent release of sorbate As [54]. If iron reduction is energetically favored over arsenate reduction, the dissolution of ABSR will release oxyanion $\text{H}_x\text{As}^{\text{V}}\text{O}_4^{2-x}$ to solution. The reduction of arsenate to arsenite can then be coupled to microbial respiration (eq. 4) or to abiotic reaction with free HS⁻ (eq. 5) [55];

Excess Fe^{2+} and HS^- in solution at circumneutral pH can then promote the precipitation of mackinawite (eq.6) [56].

Bulk Fe and As XAS showed that at elevated sulfate concentrations (2.1 mM), ABSR were reduced to FeS and As(III) + AsS. We propose a possible explanation for the precipitation of realgar-like solid phases in environments similar to those found in anoxic zones in mature landfills. It has been reported that dissolved As(III) can be removed from porewater as an adsorbed species on FeS [49, 57, 58]. Additionally, it has been shown that As(III) can react with excess sulfide to form soluble thioarsenite complexes that precipitate as As-S solids, such as amorphous arsenic sulfides, orpiment (As_2S_3) at low pH, and realgar (As_4S_4) at circumneutral pH [1, 59, 60]. It has been proposed, and supported with thermodynamic modeling, that dissolved As(III) can adsorb to reactive FeS surface sites [61], followed by its reduction to AsS via oxidation of FeS, forming As-S polymeric (realgar-like) solid phases and precipitation of green rust (eq. 7) [49].

This reaction is consistent with the co-associations of FeS, green rust and polymeric AsS solids observed in the HS column of this study. The identification of intercalated anion in the green rust phase (i.e. CO_3^{2-} or SO_4^{2-}) formed here was not resolved, and (eq. 7) could also be written with sulfate green rust.

In this model for mature landfill conditions it is expected that the formation of AsS is limited by the activity of dissolved As(III) and inhibited by excess HS^- or low pH conditions, conditions that have been reported to favor formation of thio-complexes or precipitation of orpiment [60, 62]. The kinetics of this reaction and conditions favoring AsS precipitation require further study, as our current study examined long term reaction products after 331 d (and 661 PV). A flow-through study with As loading close to this study (and SO_4^{2-} 0.80 mM) was run for 88 d and did not show precipitation of As sulfides [40]. However, a short term (48 h) study showed XAS and XRD evidence of solid phase realgar (or polymorph) after mackinawite (5 g L^{-1}) was reacted in batch reactors with 0.5 mM As(III) (mol As:Fe = 1:14) [63]. Long term (400 d) dissimilatory reduction of arsenic loaded schwertmannite (ferric hydroxysulfate) produced secondary orpiment and mackinawite when excess SO_4^{2-} was absent, but no As-S formed at 100 mM SO_4^{2-} because schwertmannite transformation was inhibited and served as a sorbent for As, thus inhibiting As-sulfide precipitation [64]. This indicates the importance of FeS surface site development and a concomitant lack of alternate energetically favorable sorption sites, such as those from ferrihydrite or schwertmannite, in AsS precipitation.

The present study shows that dissolved arsenic can partition into a realgar-like AsS solid that is spatially associated with $\text{FeS}_{(am)}$ under environmental conditions similar to those in a municipal landfill. The results indicate that the sulfate/sulfide redox couple is important to controlling As mobilization in high-iron environments such as those occupied by landfill-disposed AFH.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

As K-edge XAS of AFH from the synthetic landfill column experiments; LS column (a) XANES (b)unfiltered k^3 weighted EXAFS, and (c) uncorrected for phase shift Fourier transformed EXAFS (FT); HS column in shaded panels d) XANES (e) EXAFS, and (f) FT. Collected experimental spectra (black) and model reference spectra (gray = As(V)=Fh, blue = As(III)-Fh, red = realgar) together with calculated best fits to the data (stippled red). The vertical lines in a) show reference AsS (red), As(III) (blue), and As(V) (gray); vertical lines and arrows in c and f) highlight the structural features corresponding to the calculated coordination and distance, shown with inset schematic, and explained in the text; numerical fit parameters are given in Table SI4.

Figure 2. Normalized first derivative Fe K-edge XANES collected at 8–15K for a) LS and b) HS. Fe K-edge c) EXAFS and d) uncorrected for phase shift Fourier transformed EXAFS (FT). Solid lines are data, stippled lines are best fits, shaded regions in d) are mackinawite FeS (black) and green rust GR1CO3 (green) with Fe-backscatterer pair labeled; all numerical fit parameters are given Table 1.

Figure 3.

Multiple energy μ -XRF maps for the low sulfate (LS: a–d) column experiments after 300 days of bioreduction in inoculated synthetic landfill leachate, and high sulfate (HS: e–h) after 331 days of bioreduction in inoculated synthetic landfill leachate. The top panels show total Fe (a) and As (b) intensity for LS according to the color-scale shown, c.) ternary Fe speciation for LS, ferrihydrite shown in red, carbonate green rust (GR1CO₃) in green, and siderite in blue, and d.) binary distribution of As species for LS with As(III) in red and As(V) in blue, with color intensity corresponding to concentration. The bottom panels show total Fe (e) and As (f) for HS columns, g.) ternary Fe speciation for LS, with FeS shown in red, GR1CO₃ in green, and siderite in blue, and h.) binary As speciation with As sulfide and As(III) in blue. The white dashed lines delineate the edges of glass beads, and color intensity corresponds to the molar concentration of each chemical species per volume in each pixel, mapped at $3\mu\text{m}^2$ and $2.5\mu\text{m}^2$ for LS and HS respectively.

Table 1

Arsenic and Iron K-edge XANES fit results.

Arsenic	fit (%) ^a			ΣAs _i ^b total
	As-S	As(III)	As(V)	
LS-II	-	81	17	98
LS-III	-	77	21	98
LS-IV	-	75	34	109
HS-I	97	-	-	97
HS-III	31	69	-	100
HS-IV	-	102	-	102

Iron	fit (%) ^a				ΣFe _i ^b total	
	Mack	Sid	Viv ^c	GR ^d		
LS-II	-	51	-	17	32	100
LS-III	-	41	5	18	36	101
LS-IV	-	34	5	12	47	98
HS-I	85	-	-	12	-	97
HS-III	30	45	19	-	-	94
HS-IV	-	33	-	17	53	103

^a Results from linear combination least-squares fits with energy varied for each component with reference mineral previously analyzed by XAS[44]. Dash (-) indicates a component not used in the fit.

^b Fit components were not normalized to unity.

^c Fit with synthetic vivianite spectrum, prepared following [65].

^d Fit with green rust 1-hydroxy-carbonate spectrum prepared following [66].

^e Fit with synthetic 2-line ferritrite spectrum, prepared following [67]. Columns sections are numbered (I-IV) from the inlet to the outlet.