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Leaching of Arsenic from Granular Ferric Hydroxide Residuals under Mature Landfill Conditions

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Most arsenic bearing solid residuals (ABSR) from water treatment will be disposed in nonhazardous landfills. The lack of an appropriate leaching test to predict arsenic mobilization from ABSR creates a need to evaluate the magnitude and mechanisms of arsenic release under landfill conditions. This work studies the leaching of arsenic and iron from a common ABSR, granular ferric hydroxide, in a laboratory-scale column that simulates the biological and physicochemical conditions of a mature, mixed solid waste landfill. The column operated for approximately 900 days and the mode of transport as well as chemical speciation of iron and arsenic changed with column age. Both iron and arsenic were readily mobilized under the anaerobic, reducing conditions. During the early stages of operation, most arsenic and iron leaching (80% and 65%, respectively) was associated with suspended particulate matter, and iron was lost proportionately faster than arsenic. In later stages, while the rate of iron leaching declined, the arsenic leaching rate increased greater than 7-fold. The final phase was characterized by dissolved species leaching. Future work on the development of standard batch leaching tests should take into account the dominant mobilization mechanisms identified in this work: solid associated transport, reductive sorbent dissolution, and microbially mediated arsenic reduction.

Introduction

Recent research indicates that the toxicity characteristic leaching procedure (TCLP) (*1*) significantly underpredicts arsenic leaching from water treatment residuals (*2*−*5*). This creates a need to understand the magnitude and mechanisms of arsenic release from arsenic-bearing solid residuals (ABSR) disposed in municipal solid waste (MSW) landfills—the predicted destination for most ABSR—as a prerequisite to the design of an appropriate alternative leaching test. An alternative leaching test must be sufficiently aggressive to safeguard human and environmental well being without being so cautionary that appropriate disposal becomes economically or technologically infeasible. Therefore, prudent ABSR disposal management and alternative leaching tests must be calibrated against the leaching that would occur in reality in a MSW landfill. This study reports on the behavior of a common iron-based ABSR when subjected to long duration, simulated mature MSW landfill conditions. It is expected that the results presented here provide the baseline understanding that is prerequisite to future development of meaningful leaching tests.

Removal of arsenic by adsorption onto solid media is currently the most widely chosen treatment option among the over 4000 U.S. utilities that must reduce arsenic in their delivered water (*6*). The most common sorbents employ an iron oxy/hydroxide surface such as granular ferric hydroxide (GFH), Bayoxide E-33, iron-modified AA, iron-impregnated sand (IIS), and iron impregnated ion exchange resins (*7*−*10*). The commercial sorbent GFH chosen for this work is one of the most common, iron-based ABSR.

Microbially active, mildly alkaline, anaerobic conditions characterize mature landfills (*11, 12*). Microbial reduction of iron and arsenic is likely a primary landfill process. Ferric iron reducing bacteria have been isolated from a diverse range of anoxic environments including sediments, soils, deep terrestrial subsurfaces, and hot springs (*13, 14*). Microorganisms of various taxonomies have demonstrated the ability to utilize As(V) as an electron acceptor for anoxic respiration (*15*). Dissimilatory arsenate reduction has been reported in lab cultures using granular anaerobic digester sludge and an alumina based ABSR (*16*). The dissimilatory reduction and mobilization of arsenic specifically adsorbed onto the surface of ferrihydrite has also been studied (*17, 18*).

Abiotic processes also influence arsenic leaching from ABSR. Arsenic liquid-phase partitioning increases as pH increases as well as in the presence of the concentrations of natural organic matter and competitive anions found in landfill leachates (*19*−*22*). Landfill waste is a heterogeneous mixture of organic and inorganic material with pH and natural organic matter (NOM) being most influential in arsenic mobilization, while other competitive anions play a negligible role at concentrations reported in MSW leachates (*19*).

The research goal was to establish conditions inside a flow-through reactor that are representative of a mature MSW landfill and to measure and characterize the arsenic mobilization processes from a common iron-based ABSR. This is the first study to our knowledge in which an actual ABSR has been subjected to long-term simulated mature landfill conditions. The results provide insight into the primary physicochemical and biological factors that control arsenic leaching from ABSRs under mature landfill conditions, which are the conditions expected to be most challenging to arsenic retention. The research did not attempt to simulate the initial or old landfill phases of operation but focused only on the mature phase (characterized by methanogenesis and declining CO_2). Specific objectives of the work were as follows: (1) to assess the leaching of arsenic from ABSRs exposed to simulated mature landfill conditions over long time periods (in excess of 2 years); (2) to determine the physicochemical nature of the leached arsenic as a first step toward establishing the mechanisms responsible for arsenic release; and (3) to explore the relation between iron and arsenic leaching.

Experimental Section

A PVC column, 76.2 cm in length and 15.9 cm in diameter, was operated in downflow mode, and the gas generated was collected in a Mariotte Flask (Figure 1). A syringe pump (Dayton, Model 2Z798B) delivered 0.44 mL/min of influent, maintaining the water level at a total saturated bed volume of about 12.1 L with effective porosity of 63%. The hydraulic residence time was approximately 12 days. The hydraulic residence time in the system was selected to allow a tractable observation time for measurements without introducing unrealistically high hydraulic stresses. The column operated

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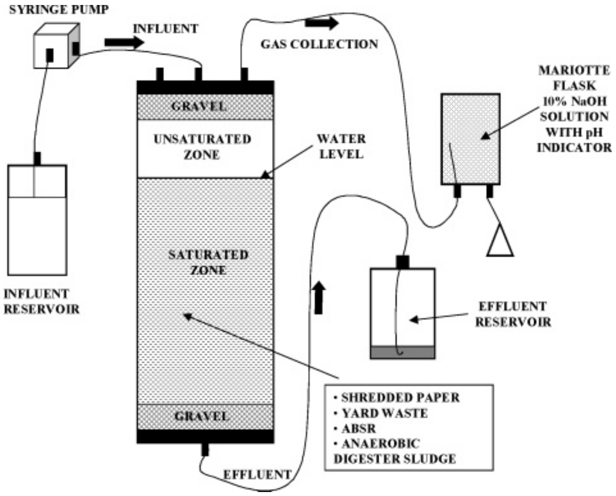

FIGURE 1. Schematic of the column reactor.

in a 30 °C temperature-controlled room. Pea gravel layers (0.3−1.0 cm diameter) 5 cm thick above and below the active bed provided even flow distribution. The active fill was composed of a mixture of 542 g of GFH (wet mass, 55.4% water), 1.5 kg of compost, 750 g of paper, and 4 L of anaerobic digester sludge. The components were lightly, hand mixed before loading (homogeneity at about a 5 cm scale), but mixing was intentionally limited to minimize mechanical degradation of the friable GFH. All chemicals were reagent grade or better. As required, samples were digested in a microwave digestor (CEM, Inc) using concentrated nitric acid (1:5 sample to acid volume). HCl (Spectrum) and NaOH (Sigma) were used for all pH adjustments.

ABSR. Granular ferric hydroxide (GFH) is a weakly crystalline β-FeOOH in irregular grains up to 2 mm diameter (*23*). GFH is manufactured by GEH and distributed in the United States by U.S. Filter. It is designed as a throwaway media. The iron content was 69% of the dry weight. GFH was pre-equilibrated with arsenate using purified water (Milli-Q Water System by Millipore). Arsenate was added as $Na_2HAsO_4 \cdot 7H_2O$ (Aldrich Sigma). The medium was equilibrated at pH 7 for 48 h on a shaker table (Orbit, reciprocating speed 125 rpm) to a final aqueous concentration of 25.7 μg/L (as As) and solid concentration of 12.0 mgAs/gGFH (dry) or 17.4 mgAs/gFe.

Compost. The compost was composed primarily of partially decomposed fruits, vegetable waste, and leaves (12% water, 72% total volatile solids (*24*)). When 1 g of compost was digested, iron (1.6 mg/g) and aluminum (0.93 mg/g) were found to be the major metallic components.

Paper. Strips of white Econosource Smooth DP paper about 2 mm wide were soaked in deionized water and squeezed to pulp prior to mixing with the other components.

Sludge. Anaerobic digester sludge from the Ina Road Water Pollution Control Facility, Tucson, AZ, was used as a microbial inoculum (76% water, 18% organic matter). A sludge sample was microwave-digested, and iron (0.23 mg/g dry sludge), copper (0.16 mg/g dry sludge), and nickel (0.07 mg/g dry sludge) were the major metallic components.

The influent composition was varied during different phases of column operation to maintain the effluent leachate pH, TOC, and alkalinity consistent with the range reported in mature MSW leachates (Table 1). Period 1 influent was deaerated, deionized water. For later periods, the influent contained a deaerated aqueous mixture of volatile fatty acids (VFA) plus sodium bicarbonate at different pH and concentrations. The VFA mixture contained the following: 36 wt % acetic acid (Fisher Scientific), 12 wt % propionic acid (Sigma), 27 wt % butyric acid (Aldrich), 10 wt % n-valeric acid (Sigma), and 15 wt % caproic acid (Aldrich). The influent pH was adjusted as needed. This mixture was chosen to mimic the major VFA species found in actual leachate samples (*11, 12, 16*).

TABLE 1. Influent Composition for Different Operational Periods of the Landfill Simulation Column and Literature Reported Composition of Landfill Leachates

period	time (days)	pH	VFA (mg/L)	TOC (mg/L)	bicarbonate (mg/L)	alkalinity (mg/L as $CaCO_3$)
I	0-304	6.1				
II	305-643	7.0	1580	792	2000	3279
III	644-766	7.0	15800	7919	4000	6557
IV	767-837	4.8	15800	7919	4000	6557
V	838-892	5.8	15800	7919	4000	6557

MSW leachate composition	pH	TOC (mg/L)	alkalinity (mg/L as $CaCO_3$)
Ghosh[a]	6.8	160	1100
Christensen[b]	4.5-9.0	30-29000	300-11500
Clement[c]	7.8-8.6	N/R[e]	585-10950
Hooper[d]	6.2-7.1	236-3160	N/R[e]

[a] Ghosh: ref 3. [b] Christensen: ref 11. [c] Clement: ref 25. [d] Hooper: ref 2. [e] NR: values not reported.

Effluent samples were collected weekly. Some samples were sequentially filtered through 5.0 μm, 0.80 μm, and 0.45 μm polycarbonate membrane filters (Millipore). The 0.45 μm filtered samples were frozen under an N_2 atmosphere prior to analysis, while the other samples were digested before freezing. The pH and ORP were measured in the effluent line to avoid exposure to air, and alkalinity was immediately measured by 1.0 N HCl titration. Iron speciation samples were immediately acidified (100 μL of concentrated HNO_3 per 1.0 mL sample) and analyzed within 30 min. DOC samples were acidified and refrigerated prior to analysis.

Arsenic was measured using ion coupled plasma mass spectrometry (ICP-MS, Agilent 7500a, Agilent Technologies, Inc.) preceded by HPLC (Agilent 1100, Agilent Technologies, Inc.) for species separation. The detection limit was 0.1 μg/L for arsenic speciation and 0.01 μg/L for total arsenic. Analysis of replicates was within ± 5%. Iron was measured by the phenanthroline method (*24*), DOC with a Shimadzu total organic carbon analyzer (0.01 mg/L detection limit), ORP by a platinum single-junction electrode calibrated with ZoBell's solution, and methane by a gas chromatograph (HP, Series 5790A).

Results and Discussion

Results are presented for each of the 5 periods of column operation demarcated by different influent compositions (Table 1). In period I, the influent was deionized water. Responding to a drop in effluent DOC and alkalinity (Figure 2), the influent was amended with VFA (1.58 g/L) and alkalinity (2 g/L of $NaHCO_3$) at pH 7.0 in period II. The alkalinity and DOC initially rose but eventually declined again (Figure 2). Consequently, the influent was amended with additional organics (15.8 g/L) and alkalinity (4 g/L) at pH 7.0 at the start of period III. However during period III, the pH of the effluent rose to values above the range found in mature MSW landfills (Figure 3). Therefore, in period IV, the influent pH was lowered from 7.0 to 4.8, near the VFA pK_{a1}. However after the leachate pH dropped to below the range expected in a mature landfill, in period V the influent pH was adjusted to 5.8. Although the manipulation of the influent likely affected the rates of physicochemical processes, it was important to ensure the continuity of anaerobic microbial activity to simulate mature landfill conditions. This points

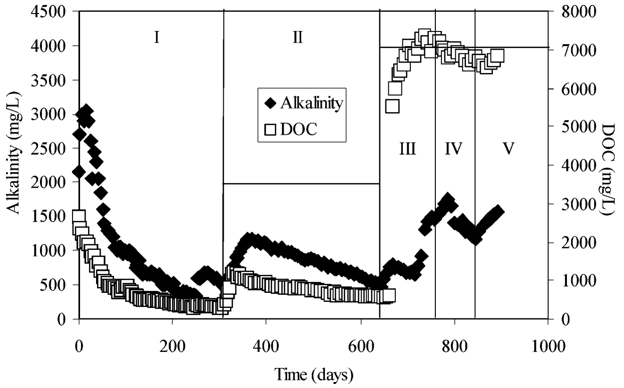

FIGURE 2. Column effluent alkalinity and DOC. Horizontal lines in periods II–IV indicate the influent bicarbonate concentration.

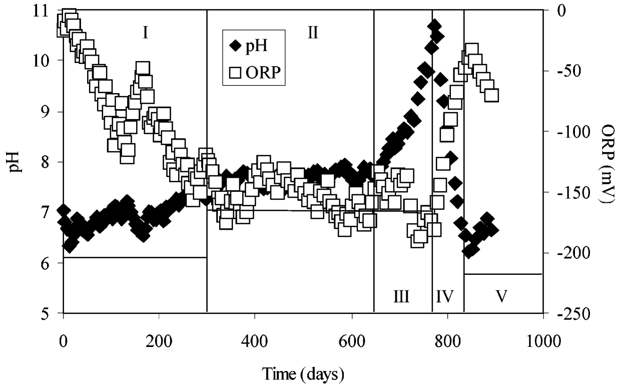

FIGURE 3. Effluent pH and ORP. Horizontal lines in periods I–III and V indicate the influent pH. Period IV influent pH was 4.8.

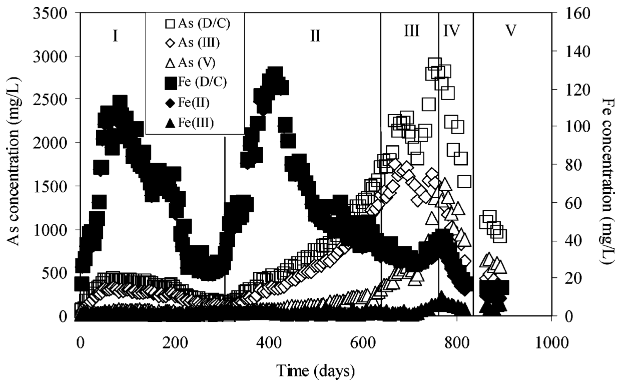

FIGURE 4. Concentration of all arsenic (D/C), As(III), and As(V) (in μg/L) and all iron (D/C), Fe(II), and Fe(III) (in mg/L) in the dissolved/colloidal fraction of the effluent. Note the Fe(II) line falls under the Fe(D/C) line for most of the trial.

to the necessity of including a continuous source of nutrients in the simulation influent flow. It is acknowledged that the need to adjust the influent character could have been avoided by better selecting the initial influent composition and consequently giving a more accurate quantification of the arsenic leaching with time. However, the manipulations were needed to maintain the TOC and alkalinity in the mature landfill range (Table 1) and did not likely change the nature nor qualitative significance of the leaching mechanisms identified.

Period I. In this work *dissolved/colloidal* refers to the leachate passing a 0.45 μm filter and *particulate* refers to the fraction retained. Figures 4 and 5 show the effluent iron and arsenic speciation in the dissolved/colloidal (D/C) fraction and the total versus dissolved/colloidal concentrations, respectively. The total (digested) concentration is the sum of the dissolved/colloidal and particulate fractions.

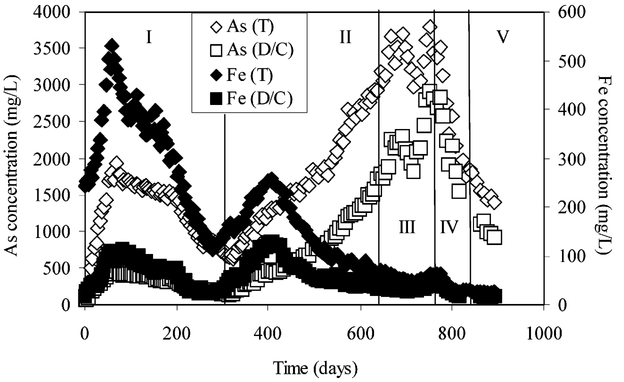

FIGURE 5. Concentration of the total (T) arsenic and iron and the dissolved/colloidal (D/C) fraction of arsenic and iron in the column effluent.

In period I, over 95% of the dissolved/colloidal iron was present as Fe(II). Since GFH only contains Fe(III) hydroxide, all Fe(II) was generated by microbial reduction. The occurrence of methanogenesis was confirmed by measurements of the presence of methane in the gases accumulated in the Mariotte flask: 39% and 51% of the accumulated gas was methane on days 79 and 296, respectively. The Fe(II) concentration increased substantially during the first 80 days but dropped steadily through the balance of period I. As discussed later, this decline was associated with decreasing microbial activity due to limited suitable (e.g., VFA) organic substrate. Fe(III) in the dissolved/colloidal phase never exceeded 3 mg/L nor 10% of the Fe(II) concentration. However, the Fe(III) solubility in the period's pH 6.5–8.0 range should be lower (10^{-10}–10^{-16} mg/L). To test if colloids explained this seeming disequilibrium, the 0.45-μm filtrate was ultrafiltered with a 30,000 Da (~0.02 μm) regenerated cellulose membrane. The permeate Fe(III) concentration was below the detection limit of 0.1 mg/L, suggesting most of the dissolved/colloidal Fe(III) was in colloids. Tadanier et al. (*26*) reported that a significant fraction of the colloids generated by microbial deflocculation of ferrihydrite are in the 10–60 nm size range. However, the particulate fraction accounted for about 69% (median value for period) of total iron mass leached during period I, indicating most iron mass was in particles larger than 0.45 μm.

In period I, the dominant arsenic species in the dissolved/colloidal fraction was As(III) (Figure 4). Microbial reduction of As(V) to As(III) using dissolved organics from compost and the anaerobic digester sludge innoculum as electron donors is not surprising. The ratio of As(III):As(V) in the dissolved/colloidal fraction as high as 3:1 is consistent with the low ORP (Figure 3). There are, at least, two significant redox couples, Fe(III)/Fe(II) and As(V)/As(III), in the system. The Fe(III)/Fe(II) couple has a higher ORP than the As(V)/As(III) couple (*27*). However, GFH is a poorly crystalline goethite phase so the exact magnitude of the redox couple and solubility of Fe(III) is unknown. In an anaerobic column in the absence of iron, the As(III):As(V) ratio was as high as 9:1 (*16*), although other dissimilarities between the trials may also impact this difference.

The trends followed by arsenic and iron in period I were similar for the dissolved/colloidal and particulate fractions (Figure 5). The higher the iron concentration at any given time, the higher was the arsenic concentration. The ratio of arsenic to iron remained fairly constant but was below 0.010 mg/mg, whereas the original ABSR ratio was 0.017 mg/mg (Figure 6). The ratio's similarity between the dissolved/colloidal and particulate fractions suggests similar processes dominated mobilization in both fractions. Other studies have shown the microbial reduction of ferric (hydr)oxides, most significantly ferrihydrite, under advective flow conditions

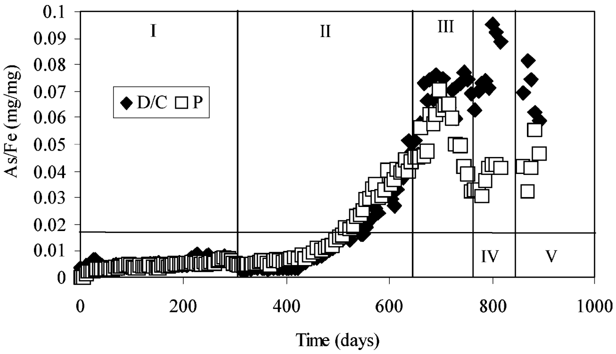

FIGURE 6. Ratio of As/Fe in the dissolved/colloidal (D/C) and particulate (P) fractions in the column effluent. The solid horizontal line indicates the As/Fe ratio of the original GFH loaded into the column.

causes secondary mineral formation of magnetite, lepidocrocite, and/or goethite on the ferrihydrite surface leading to decreased sorption capacity and slower dissolution rates (*28*–*30*). Secondary mineral formation on the mobilized solids (both colloidal and particulate) could explain the lower than original, yet similar As:Fe ratio on the colloidal/dissolved and particulate fractions. This explanation assumes that the truly dissolved arsenic and iron masses are small compared to the colloidal mass in the dissolved/colloidal fraction. Similar results have been found where mobilized arsenic was associated with ferrihydrite colloids with magnetite surface coatings (*26*). Although this biogenic secondary mineralization seems likely based on the studies cited, it is not consistent with the very low Fe(III) fraction (<10% by mass) measured in the dissolved/colloidal iron mass in period I. Although the study's methodology and instrumentation do not allow deeper insight, the consequence is that the mass of arsenic remaining per unit mass of sorbent retained in the column increases during period I (increasing As/Fe ratio).

Particulate transport is significant during the initial phase of leaching. At the column flow rate (0.44 mL/min), the superficial velocity is 0.022 mm/min. This is too low to create sufficient fluid shear on the medium to explain the particle generation. The main reason for the abundance of particles greater than 0.45 μm is expected to be microbial-mediated erosion of the GFH consistent with the microbial reduction of ferrihydrite and generation of submicron sized particles reported elsewhere (*26*).

Period II. The DOC and alkalinity near the end of period I declined to the lower limits of reported values for mature landfill leachates (Table 1) and suggested that microbiological activity may be limited by insufficient, appropriate electron-donating organic substrate. The continuous decrease in Fe(II) late in period I may be a consequence of declining microbial activity, although the biotransformation of the ABSR into alternate iron phases could also contribute to slowing the leaching of iron (*28*). To reestablish simulated mature landfill TOC and alkalinity conditions, the influent was amended with VFA (1.58 g/L) and alkalinity (2 g/L of $NaHCO_3$) at pH 7.0. Between days 300 and 660, the ORP was between −130 mV to −180 mV (Figure 3), consistent with a mature landfill leachate (*31*). Alkalinity and DOC initially increased but then dropped back to approximately what they were at the beginning of period II (Figure 2).

The added VFA immediately impacted iron reduction and leaching (Figure 4). Dissolved/colloidal iron increased sharply to levels much higher than those in period I but then receded back to approximately that at the end of period I. More than 98% of the dissolved/colloidal iron was Fe(II), indicating the supplemented influent organics boosted dissimilatory iron reduction. This suggests the decreased iron reduction at the end of period I was not primarily attributable to precipitation of secondary iron minerals decreasing ferrihydrite availability as reported by others (*28*–*30*) but in this case was linked to limited organic substrate. Unlike iron, the arsenic concentration in the leachate increased throughout period II (Figure 5). The dissolved/colloidal arsenic increased more than 10-fold. Through period II, the As(III):As(V) ratio in the dissolved fraction varied between 3:1 and 5:1, indicating arsenic reduction in addition to iron reduction. An important observation is the sharp increase in the As/Fe ratio (Figure 6). Depletion of iron is the plausible cause. At the end of period II, about 64% of the original iron had leached out of the column, while only 29% of the arsenic was gone. By the end of period II, the iron's dissolved/colloidal fraction was greater than the particulate fraction, suggesting the particles (>0.45 μm) generated previously had been largely lost from the column and biochemical dissolution and colloidal transport now dominated iron loss.

Period III. By the end of period II, the alkalinity and DOC in the effluent had dropped again to values below the range of a typical landfill (Table 1). Despite the rising dissolved/colloidal arsenic concentration, the iron concentration was declining. Microbial activity in the column was again possibly limited by organic substrate availability, so the influent VFA and bicarbonate were increased to 15.8 g/L and 4 g/L with the pH adjusted to 7.0. Consequently, the pH increased to above 10 through period III (Figure 3), presumably due to microbial reduction of the VFA, which consumes protons, while the buffering capacity (mainly bicarbonate) was overwhelmed. In this period, the ORP dropped from −130 mV to −180 mV reflecting increased microbial activity (Figure 2). However, the increase of VFA had minimal impact on the leached iron concentration (Figures 4 and 5). The dissolved/colloidal arsenic concentration, on the other hand, continued to increase throughout period III. This arsenic did not seem associated with colloidal iron, since the iron concentration did not increase (Figure 6). Equally important, the As(V) fraction of the dissolved/colloidal arsenic started to increase. This increase in As(V) is probably partially due to desorption of arsenic from GFH as a result of the pH increase. However, from about 730–820 days the column leachate exhibited unsteady behavior atypical of landfill behavior. This was caused by poor prediction of the required pH adjustment to the influent (see periods IV and V below) to maintain realistic effluent leachate characteristics and not adversely affect microbial activity. However, more steady, realistic column behavior with increased microbial activity in the late periods would not change the conclusions reached as to the importance of particle-mediated transport, reductive dissolution of the iron substrate, and the dissimilar relative rates of iron and arsenic release.

Periods IV and V. By the end of period III, the effluent pH had increased to an unrealistic 10.7 (Table 1). Consequently, the influent pH was lowered from 7.0 to 4.8, near the mean pK_{a1} of the VFA mixture. This resulted in an unexpectedly sharp drop of pH, and, by the end of period IV, the leachate pH was below 6.5 (Figure 3). Arsenic and iron concentrations decreased throughout period IV (Figure 5). Both the dissolved/colloidal arsenic and iron decreased by more than 50% during period IV, due to a combination of lower iron solubility and more favorable arsenic sorption at this pH and the dramatic decrease in microbial activity (based on steep ORP increase). The As(III):As(V) ratio decreased to about 1 and the Fe(II):Fe(III) ratio dropped to 4:1. Because of the low pH at the end of period IV, the influent pH was adjusted to pH 5.8 to start period V. This resulted in an increase in effluent pH and a drop in ORP (Figure 3). The total dissolved/colloidal iron concentration was relatively constant in period V, even though the Fe(II):Fe(III) ratio continued to drop. The dissolved arsenic concentration, on the other hand, continued to decrease, reflecting depletion of the remaining accessible arsenic.

Discussion and Implications. The value of or changes in the As/Fe ratio (Figure 6) cannot be used to prove causal relationships between the transport of arsenic and iron from the column, but it can be used to support or rebut possible explanations for the mobilization observed. The As/Fe ratio in the particulate and dissolved/colloidal fractions are nearly identical during period I and are appreciably lower than the 0.017 mg/mg in the original sorbent. This would not be true, if the colloid and particle composition were simply due to GFH breakup. However, from about day 450 onward the As/Fe ratio increases dramatically and after day 510 exceeds the initial GFH ratio of 0.017 mg/mg. A number but not exhaustive list of possible explanations are discussed here as a prerequisite to follow-on, more hypothesis driven research. One possible explanation is that as particles are eroded, new iron surface is exposed which provides additional sorption sites. However, this would not result in the observed lower As/Fe ratio, unless more new surface is exposed on the immobile granule than on the mobilized particle. This seems unlikely.

Another explanation is that active iron dissolution and recrystallization occurred, so the newly precipitated iron phase(s) had a lower arsenic sorption capacity than the original GFH. Previous literature suggests the secondary iron phases will be magnetite or goethite (*26, 28–30*) which have lower arsenic sorption capacity than the GFH. The other condition for this mechanism to hold is that the secondary minerals form preferentially on the smaller, mobilized particles rather than the stationary GFH granules or that other immobilized phases (i.e., sulfide precipitation, sorption by immobile compost associated sulfur groups) retain the arsenic preferentially over the iron. Given this work's limitations it cannot be verified if this is or is not the case.

It is also possible that the Fe and As leaching are not or are only partially coupled. This explanation is supported by the significant changes in the As/Fe ratio from period II onward (Figure 6). If this is the case, the close tracking between the dissolved/colloidal and the particulate ratios through 600 days suggests that the same type of solids dictate the arsenic and iron mobilization in the particulate fraction as for colloids in the dissolved/colloidal fraction. Another possible, explanation is that the dissimilatory microorganisms responsible for iron reduction more rapidly reduce the GFH surface without adsorbed arsenic, and, as this 'uncontaminated' surface becomes limited, the rate of iron mobilization decreases (period II) at about the same time as the As/Fe ratio noticeably increases.

It should be noted that little sulfate was in the column, and, consequently, the effect of possible sulfide mineral precipitation effects is not investigated although this would not be expected to affect the particle-associated mobilization of arsenic observed. By the same token, arsenic precipitation with sulfides cannot explain the observed relative retention of arsenic compared to iron in early column operation.

The research did not attempt to simulate the arsenic mobilization in the initial landfill phases (O_2 depletion and organic acid production) preceding the mature phase. Thus, any additional mobilization operative during these preceding landfill phases is not accounted for in this work. About 487 L of influent passed through the column during its 892-day run. About 69% of the iron initially present was leached. About 49% of the total arsenic mass was lost, with the most rapid leaching in periods III and IV, after much of the iron had leached. This suggests that, if an iron ABSR is exposed to MSW conditions for a long duration, initially the sorbent itself will leach at a higher rate than the sorbate. In this case, for the first 510 days the As/Fe ratio in the effluent was less than that initially loaded into the column. If that occurs, there will be an increase in the sorbate leaching in a later period when the sorbent capacity becomes limiting. From a practical standpoint, this would result in a late spike in leachate arsenic concentration not predicted by short duration tests. In addition, throughout the first half of the run, particulate mobilization dominated arsenic leaching. Overall, the results indicate that arsenic will be readily mobilized from GFH or similar iron media under mature landfill conditions, and, based on current knowledge, it would be imprudent to dispose of such ABSR in unlined landfills.

Acknowledgments

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