

**LEACHING FROM ARSENIC-BEARING SOLID RESIDUALS UNDER
LANDFILL CONDITIONS**

BY

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AMLAN GHOSH

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ABSTRACT

The recent lowering of the arsenic MCL from 50 ppb to 10 ppb in 2006 will cause many utilities to implement new technologies for arsenic removal. Most of the affected utilities are expected to use adsorption onto solid sorbents for arsenic removal, especially in the arid Southwest, where conserving and re-using water is of utmost importance. This would cause the generation of more than 6 million pounds of arsenic residuals every year, which then would be disposed of in landfills. This thesis effort focuses on the testing of different aluminum and iron (hydr)-oxide based sorbents that are likely to be used for arsenic removal and assessing the behavior of these Arsenic Bearing Solid Residuals (ABSRs) under landfill conditions. It was demonstrated that the Toxicity Characteristic Leaching Procedure (TCLP) test underestimates the arsenic mobilization in landfills. Desorption of arsenic from ABSRs was quantified as a function of the range of pH and concentrations of competitive anions like phosphate, bicarbonate, sulfate and silicate and NOM found in landfills. The effect of pH is much more significant than the anions and NOM. Arsenic release due to competition of different anions is neither additive nor purely competitive. Landfill conditions were simulated inside long-term, continuous flow-through column reactors, and arsenic mobilization from sorbents was measured under those conditions. The results indicate that under reducing conditions, and in the presence of other competitive anions and high organics, microbes reduce arsenate to arsenite, which is a much more mobile species. Fe(III) is also reduced to Fe(II) under these conditions. Arsenic is transported in the particulate phase, associated with the iron, much more than

in the dissolved phase. It was also observed that the sorbent itself might leach away at a faster rate than the arsenic sorbate causing a depletion of surface sites and a sudden spike in the release rate of arsenic, after a long residence time. Finally, investigation of different solid sorbents indicate, that the rate of leaching and the form of arsenic released varies widely and is independent of the respective adsorption capacities, even under similar leaching conditions.

CHAPTER 1

INTRODUCTION AND OVERVIEW

Motivation and Overview

Arsenic is a naturally occurring element widely distributed in the earth's crust. Arsenic does not form in its elemental state and is more common in sulfides and sulfosalts such as arsenopyrite, orpiment, realgar, lollingite and tennantite. Inorganic arsenic compounds are used to preserve wood. Organic arsenic compounds are used as pesticides, primarily on cotton plants. Arsenic is both a toxin and a carcinogen, implicated in cardiovascular, pulmonary, immunological, neurological and endocrine disorders as well as skin, lung, bladder and kidney cancers (NRC, 1999, NRC 2001). Long-term exposure to contaminated drinking water has been cited as the most widespread threat to human health posed by arsenic (Nordstrom, 2002, Smedley and Kinniburgh, 2002).

On January 22, 2001, The United States Environmental Protection Agency (USEPA) lowered the drinking water arsenic MCL (Maximum Contaminant Limit) from 50parts per billion (ppb) to 10ppb and public water supplies must comply with the new standard beginning January 23, 2006 (USEPA, 2001). The World Health Organization (WHO), The European Union (EU) and several other countries also recently lowered their recommended or required arsenic limit to 10ppb. In order to meet the new norm, approximately 4000 water utilities in the U.S. will either have to blend with higher quality waters, modify existing technologies or implement completely new ones for

arsenic removal (USEPA, 2001). There is a disproportionate frequency of occurrence of arsenic in the arid, western states and about 90% of the affected utilities are small-scale operations serving 3,301 or less consumers.

Of the EPA identified treatment options, adsorption onto solid media seems to be the most attractive option, particularly for small treatment facilities. This is especially true in the arid regions of the western U.S., due to water wastage, water reuse and reagent handling issues. An estimated six million pounds of arsenic residuals would be generated every year after the implementation of the new arsenic MCL. However if the arsenic from the disposed solid residuals remobilizes, the large, concentrated volume of arsenic poses an obvious environmental concern.

In the U.S., the Toxicity Characteristic Leaching Procedure (TCLP) (Federal Register, 1986) assesses the hazard presented by toxics leaching from solid surfaces. Consequently, the TCLP has been used in several studies to quantify the leaching potential of arsenic from the likely sorbents that will be used in arsenic removal operations (Amy et al., 2000). The leachate from all solid residuals has been less than the present toxicity characteristic (TC) of 5mg/L and, hence, EPA has suggested the solids may be classified as non-hazardous and disposed of in non-hazardous waste landfills.

The underlying premise for the TCLP is that the contaminant-laden solid should be subjected to aqueous leaching conditions that favor desorption and mobilization of the

contaminant at least as much as any likely non-hazardous disposal environment. The concentration of the contaminant in the leachate of the TCLP is measured and this value is compared to the TC regulatory level set as hazardous for the particular contaminant. At the time of development of the TCLP, the metals of environmental interest with respect to aqueous leaching from solids were predominantly cations such as lead (Pb^{2+}), copper (Cu^+ and Cu^{2+}) and cadmium (Cd^{2+}). Thus the TCLP was devised to create conditions that particularly challenge the stability of sorbed, metallic cations. However, environmental surface chemistry has shown that the sorption and desorption behavior of different metals is different and, more significantly, that the ionic character is a primary determinant of behavior.

Unlike the cationic metals, arsenic occurs in natural waters almost exclusively in either the uncharged arsenous acid form, H_3AsO_3 , or the negatively charged arsenate anionic forms, H_2AsO_4^- and HAsO_4^{2-} . For water treatment, if arsenous acid is present, it is oxidized to arsenate to enhance sorption and removal. Anions typically exhibit sorption behavior that is distinctly different from cations. For instance, metallic cations sorb most strongly at high pH, while metal oxy-anions (such as arsenate) typically sorb most strongly at low pH and are most mobile at high pH. Since arsenic will be sorbed on treatment solids in a state, which is critically different than the chemical state of the sorbed metals for which the TCLP was designed, the question arises whether the TCLP realistically predicts the leaching potential and subsequent environmental hazard posed by ABSRs. Landfill conditions are projected to be very different than conditions

simulated by the TCLP test. Alkaline pH, anaerobic microbial activity, mineralogic aging, low redox potential and concentrated organics are characteristics typical of mixed solid waste (MSW) landfills. These same conditions are likely to be very conducive to mobilizing sorbed arsenic.

Thus, the appropriateness of the TCLP as the primary protocol for evaluating the leaching potential of sorbed anionic toxic contaminants must be verified. As a short-term solution, the effectiveness of alternative tests to the TCLP like the state designated California Waste Extraction Test (WET) (California Register, 1985) need also be examined. However, as a long-term solution, the likelihood of environmentally significant mobilization of arsenic from ABSRs must be evaluated under landfill conditions, rather than merely from the legal perspective of compliance with the TCLP. The key to better predict arsenic leaching is to identify and understand the various controlling mechanisms that cause arsenic desorption and leaching. Once the key controlling parameters that govern the amount of leaching are successfully isolated, then, the development of an alternative, more appropriate protocol for the hazard assessment of ABSRs (and other oxy-anion bearing residuals) can be initiated. However, from a practical point of view, the size of landfills, the amount of waste in a landfill, the rate of leachate generation and flow, the hydraulic residence time of the leachate, the chemical parameters like pH, alkalinity, ORP, organic concentration, and the biological composition of an MSW landfill can vary by orders of magnitude and hence it is difficult to identify representative values for those parameters.

The work detailed in this thesis is a step toward determining the extent and mechanisms of the mobilization of arsenic from ABSRs under landfill conditions. This research effort is primarily application oriented. Mechanistic evaluation of arsenic desorption and mobilization from metal oxide surfaces was only limited in scope. The primary aim was to provide an immediate, practical evaluation of the hazard posed by the disposal of solid residuals in landfills. The applied bias was taken in response to the realization that the hazard has not been reasonably evaluated, while at the same time utilities are selecting and installing removal technologies to meet the 2006 revised arsenic rule compliance deadline. Thus the most pressing issue is to evaluate the appropriateness of present ABSR assessment and disposal strategies and develop practical guidance where these strategies are inadequate.

Arsenic Adsorption/Desorption

Arsenic in drinking water supplies is present either as arsenite, As(III) or as arsenate As(V). In near-neutral waters arsenite is present primarily as fully protonated and uncharged arsenous acid up to the pK_{a1} of 9.2, above which an arsenite anion predominates. In contrast, arsenate is in an anionic form at all pH above 2.2, which is the pK_{a1} of arsenic acid (H_3AsO_4). The pK_{a2} for arsenate is 7.0 and the pK_{a3} is 11.0 (Wagman et al., 1982). Since metal oxy/hydroxide adsorption of ions is typically more efficient than of neutral species (Stumm and Morgan, 1996), water containing a significant amount of arsenite would generally undergo pre-oxidation prior to the application of an arsenic

removal technology (Federal Register, 2001). Thus all arsenic in residual streams will be in the anionic, oxidized arsenate form.

Nearly all solid residuals that are expected to be produced from arsenic removal systems are composed of aluminum or iron (hydr)oxides. The EPA has recommended activated Alumina (AA) as a Best Available Technology (BAT). GFH studies have shown that it may be preferred to AA due to its 5X greater capacity (Amy et al., 2000). Most other alternative sorbents (i.e. Bayoxide E33, green sand, Aqua-bindTM and iron modified AA) exhibit an alumina or iron (hydr)oxide surface (USEPA, 2001a).

Arsenate sorption to AA shows stronger pH dependence than iron oxide sorption with optimal sorption at about pH 6.0 and a rapidly decreasing sorption capacity as pH increases above 6.0 (Rubel and Hathaway, 1985, Clifford et al., 1998). Adsorption site competition and/or arsenic sorption inhibition have been reported for various competing anions, like carbonate/bicarbonate on ferrihydrite (Holm, 2002, Fuller et al. 1993, Meng et al., 2000, Apello et al., 2002), phosphates on iron oxide (Dixit and Hering, 2003, Hongshao and Stanforth, 2001, Manning and Goldberg, 1996, Jain and Loeppert, 2000), sulfate on AA (Xu et al., 1988), silica on hydrous ferric oxides (Holm, 2002) and NOM on AA (Xu et al., 1991).

The effect of NOM is much harder to predict than the effect of pH, ionic strength and other competitive anions. NOM may directly compete with the ion of interest for the

surface sites (Parks, 1990), it may sorb to the surface and create additional surface attraction and enhanced sorption (Schwarzenbach et al., 1993), it may act as a soluble partitioning agent to bind with the ion and keep it in solution (Stumm and Morgan, 1996), or it may directly react with the sorbent surface to enhance dissolution of the surface and loss of sorption sites (Schwarzenbach et al., 1993). Because of the variety of mechanisms and potentially contradictory effects of NOM on ion sorption, relevant studies to date have been largely empirical and should only be cautiously interpreted outside the conditions in which they were applied.

Most studies have looked at arsenic uptake by sorbents rather than release from sorbents. Even though the direction of change of the system in response to a change of a given parameter (i.e., pH, NOM concentration) is expected to be the same for both adsorption and desorption, neither the kinetics nor the mechanisms of adsorption/desorption are always analogous. Metal adsorption-desorption studies on amorphous ferric hydroxides (AFH) show significant hysteretic desorption, the degree of which varies with residence time, pH, and organic complexation of the sorbent/sorbate. The reversibility of some sorption processes has been found to be slow, on the order of weeks. (Schultz et al., 1987, Coughlin et al., 1995, Ainsworth et al., 1994). Myneni et al. (1997) found similarity between adsorption and desorption equilibrium concentrations of arsenic on Ettringite, but desorption was much slower than adsorption. The work suggested that once sorbed on the surface, the surface bond to arsenate changes. Grossl et al. (1997) and Fendorf et al. (1997) observed a two-step adsorption process of arsenate on goethite. There was

relatively rapid monodentate, inner sphere adsorption followed by a slower relaxation to a more stable bidentate, inner sphere bonding state. In addition, surface precipitation may occur. When an ABSR is exposed to a leaching solution, the solid substrate surface may solubilize and release ions that subsequently participate in re-precipitation reactions forming new solid phases, which can potentially incorporate arsenate or cover over previously sorbed arsenate (Hongshao et al., 2001). These considerations motivate study of the desorption behavior of arsenate from sorbent surfaces as a unique process distinct from adsorption.

Arsenic Treatment: Solid Residuals

Although EPA lists thirteen (eleven for systems serving populations less than 500) feasible treatment trains for small system compliance with the final arsenic rule, these trains encompass only seven treatment technologies. These technologies include lime softening, coagulation/filtration, anion exchange, coagulation-assisted microfiltration, oxidation/filtration with iron (including green sand), activated alumina and reverse osmosis (only in a point of use (POU) device). If the solid residual streams are identified for each of these treatments, it is seen that all solid residuals are in the form of either aluminum oxide or iron oxide (Amy et al., 2000). Furthermore, most of the treatment technologies are inappropriate for small utilities, particularly those located in water scarce, arid regions. Few small treatment systems have lime softening or coagulation/filtration already in place, which is a precondition for the feasibility of these technologies. Small utilities are not advised to use anion exchange or reverse osmosis

(USEPA 2001, USEPA 2000) due to safety issues with reagent handling and water wastage issues in arid regions. Thus for small water suppliers, the predicted solid residual streams are narrowed to throw-away activated alumina, throw-away iron-based sorbents (e.g., GFH and E33). Even if other technologies (i.e., membrane filtration, ion exchange) that produce a liquid residual stream are implemented, solid adsorption processes may also play a role, since any removal of arsenic from the concentrate stream will typically involve iron precipitation with concomitant arsenic adsorption, forming arsenic-laden iron sludge (ferric hydroxide, $\text{Fe}(\text{OH})_3$).

TCLP and other Leaching Tests

The EPA specifies the TCLP as the defining test for determining if a solid waste is hazardous. Although the inadequacies of this test for certain types of wastes and conditions (including alkaline wastes in landfills) has been suggested (USEPA, 1996), it is used as the default determinant of the hazard potential of the ABSRs in the arsenic final rule. California adopted an alternative test, the WET, in response to perceived inadequacies of the TCLP. The main difference between the TCLP and the WET is the identity of the conjugate base of the weak acid that is used to lower pH to about 5. The TCLP base is acetate, while the WET base is citrate, which is a somewhat stronger complexing ligand than acetate for cationic metals (Hooper et al., 1998).

Concern has been expressed that leaching of certain oxy-anion forming elements may be underestimated by the TCLP and other existing methods. Hooper et al. (1998) showed

that when actual municipal solid waste leachate was used as the extracting solvent, arsenic leaching increased by as much as two orders of magnitude from what was observed with the TCLP. The US EPA Science Advisory Board (1999) has also written to the chief administrator calling attention to the need for a review and improvement to the existing leachate tests. As noted by the EPA final rule, the TCLP creates conditions that are conducive for arsenate sorption onto metal oxides and thus might be a poor standard by which to gauge the potential environmental hazard of the residual disposal.

In order to better simulate leaching conditions, a host of other leaching test protocols have been developed for the evaluation of leaching potential of arsenic from contaminated soils, sediments and solid residuals of water treatment. Most of these are batch leaching tests which assume that arsenic concentration in the leachate will be equal to that measured during a single batch extraction and is constant with time (“infinite source” assumption) (Kosson, 2002). The various parameters often taken in consideration in these tests include leaching kinetics, liquid-to-solid ratio, pH, potential for colloid formation, particle size reduction, aging, volatile losses, and commingling of the material with other wastes. The limitation of most of these leaching tests is that they tend to simulate contaminant release under a specific environmental scenario (e.g. TCLP), instead of assessing fundamental leaching parameters (Van der Sloot, 2003). As a result they do not provide information on release under environmental scenarios different from the one being simulated, thus leading to misinterpretation of the test results and over- or under- prediction of leaching potentials.

Kosson (2002) provides the most comprehensive analysis of leaching test protocols done so far. It lays out a detailed, tiered, flexible framework capable of incorporating a range of site conditions that affect waste leaching, and estimating long-term release under field management scenarios. Variations of the basic testing protocols, and examples of applications of these protocols can be found in Sanchez (2002, 2003), Garrabrants (2002, 2003a, 2003b, 2004), and Van der Sloot (2003). These protocols are also the basis for the development of the European standard CEN TC 292 for evaluating release of inorganic constituents from solid wastes. The Kosson tests have 3 tiers: Tier 1 – Screening tests (availability), Tier 2 – Equilibrium (over a range of pH and liquid-solid ratio conditions), Tier 3 – Mass transfer based assessment. Based on the results of the above tests, and knowing the appropriate environmental data (precipitation frequency and amounts), and design information (placement geometry, infiltration rates), the long-term release estimates may be obtained. Depending on the circumstances, two different leaching scenarios can be envisioned: percolation-controlled and mass transfer-controlled. For each scenario, a different estimation method can be used to predict the total mass released over a long period of time.

Variations of the Kosson protocol have been applied to soils and solidified wastes for which matrix alkalinity and species activity in pore water were measured to better characterize the waste matrix. Long term mass transfer leaching tests were also done for up to 4 months to better assess dynamic release. (Sanchez 2003). The effect of storage in

an inert atmosphere on the release of constituents during intermittent wetting was studied by alternate cycles of leaching in deionized water and storage under nitrogen at different levels of Relative Humidity (0, 50 and 100% RH) (Garraabrants, 2002).

This approach of identifying the fundamental leach-controlling parameters, instead of simulating a specific leaching environment, seems to be the better way to assess leaching potentials. However, for the specific case of ABSR disposal in mixed solid waste landfills, the chemical conditions do not seem to be sufficiently aggressive. For example, organic concentration, competitive anions, redox potential and microbial activity have an impact on arsenic leaching in MSW landfills, yet none are directly accounted for in the Kosson tests. Various other leaching tests which simulate a particular set of leaching conditions or use a dynamic or sequential extraction procedure have also been designed and tested (Comacho, 2004, Leist, 2003, Miller, 2000, Khan, 2004, Kartal 2003, Gaskova, 2003, Gao, 2004, Benzaazoua, 2004, Sahuquillo, 2003), but none of these tests seem to be able to simulate the “worst-case scenario” that might be experienced by ABSRs when disposed of in MSW landfills.

MSW Landfills

Several salient conditions associated with non-hazardous landfills distinguish them from the conditions created in a TCLP test and directly impact the potential for leaching of arsenic from ABSRs. The aqueous leachates in the unregulated, non-hazardous landfills typically exhibit neutral or alkaline, not acidic, pHs and very high concentrations of

dissolved, complex organics (Hooper et al., 1998). Of perhaps equal importance with respect to leaching of arsenic, landfill fluid residence times are long, reducing conditions and salinity zones are common, and mineralogical aging and dissolution may be significant over the long time-scales that characterize solid disposal.

Landfill leachate pH normally ranges from 6 to 9 with a median value of 8.2 (Christensen et al., 2001). The total organic carbon (TOC) content of the leachate ranges from a few hundred to several thousand mg/L (Bagchi, 1994) and is several orders of magnitude higher than the TOC levels considered in arsenate adsorption studies (Amy et al., 2000). Although it is difficult to predict the effect of these very high TOC concentrations on arsenic sorption, and there is scant research data available, Hooper et al. (1998) noted that when solid wastes are exposed to municipal landfill leachates, that the highest extraction efficiencies of all metals coincided with the highest TOC concentrations. It is also significant that the composition of the solid sorbent was observed to significantly affect the leaching of arsenic, so the observed response of one sorbent could not be extrapolated readily to the response of other sorbents. Arsenic release from iron oxyhydroxide has been observed in groundwater in an intermediate pe range (i.e. $-4.0 < pe < 0$) where the transformations between reduced and oxidized phases take place (Meng et al., 2001). Very similar pe in the low-intermediate range would be expected in a mature landfill leachate, and thus significant mobilization of arsenic can take place due to such reducing conditions.

Due to the oxygen demand created by microbial degradation of the abundant organics in landfills, anaerobic, reducing conditions are common. Under such conditions, arsenate can be reduced to arsenite by both microbial (Zobrist et al., 2000) and abiotic (Rochette et al., 2000) processes. Sorption of arsenite to metal oxides is significantly lower than arsenate, and thus its mobility is enhanced. The reduction and mobilization of arsenic specifically sorbed onto the surfaces of AA (Sierra-Alvarez et al., 2005) and ferrihydrite (Zobrist et al., 2000, Langner et al., 2000) have been demonstrated. Under these same reducing conditions with high TOC, reduction of ferric to ferrous iron (Fe(III) to Fe(II)) is commonly observed, which coincides with dissolution of iron oxides (Stumm and Morgan, 1996). Thus not only may landfill conditions enhance arsenic solubility by converting the arsenic to the more mobile and toxic arsenite form, but it may also lead to dissolution of the iron oxide sorbents.

The final salient characteristic that distinguishes landfill conditions from TCLP conditions is the long residence times. The TCLP is a short-term extraction test of 18 hours. Fluid residence times in landfills range from weeks to tens of years (LaGrega et al., 1994). In the Hooper et al. (1998) study, extraction trials conducted for 48 hours produced significantly increased arsenic leach concentrations than extraction trials run for 18 hours.

Objectives

What becomes apparent in the preceding discussion is that the TCLP might be particularly inadequate to predict the leaching behavior of arsenic from ABSRs under MSW landfill conditions. If this is true, then an alternative assessment method is needed for ABSRs and similarly behaving wastes. So, in order to design a more appropriate leaching test, a basic understanding of the various phenomena that might occur when an ABSR is disposed of in a landfill is needed. The various parameters that might influence the leaching of arsenic in a landfill need to be identified, isolated and evaluated for their individual and synergistic effects on arsenic leaching. Since different sorbents might behave differently when placed under similar leaching environments, representatives of the characteristic types need to be evaluated individually. The overall objective of this thesis was to investigate arsenic leaching from ABSRs under landfill conditions and identify and evaluate different parameters that influence arsenic leaching. A nontrivial corollary to this endeavor was to evaluate the difference in the performance and leaching characteristics of the different arsenic sorbents when placed under similar leaching conditions. The specific objectives were:

1. Development of adsorption isotherms for two sorbents, AA and GFH, using small volume batch experiments. pH and arsenic loading are expected to be the two most significant mechanisms controlling sorbed arsenic retention and hence these two parameters would need to be studied in detail. The equilibrium solid-water concentrations of arsenic and the primary ions would be modeled using HYDRAQL software for surface complexation modeling to give insights into the potential mechanistic underpinnings for the observed behavior. This in turn would

be used in subsequent work to help elucidate desorption and leaching behavior from these representative sorbents.

2. Comparison of ABSR leaching in response to exposure to various, batch, abiotic environments. Arsenic loaded solid residuals, AA and GFH, would be subjected to the various leaching tests like TCLP, WET, an actual landfill leachate and a synthetic leachate solution prepared in the laboratory. Several physical design variables like duration of tests, aggressiveness of agitation and the addition of a N₂ headspace would be investigated. The results should indicate whether the standard tests like the TCLP and WET are appropriate for the evaluation of arsenic leaching or whether an alternative, more appropriate protocol should be developed.
3. Determination of the kinetic rates and equilibrium concentrations of desorption of arsenate from AA and GFH with variations of pH, competitive anions (phosphate, sulfate, bicarbonate and silicate) and NOM concentrations. The results obtained from these studies would then be compared to the results from the TCLP and actual landfill leachate tests to quantify their relative contribution to arsenate leaching from ABSRs.
4. Establishment of a set of conditions inside a column-reactor that would be representative of a MSW landfill and to which different ABSRs can be subjected. The leaching of arsenic and iron in the dissolved phase and particulate phases would be measured. The leaching response to a change in leachate property like pH, alkalinity or organic concentration would be measured. Finally the

differences between the short-term and long-term leaching characteristics due to the change (i.e., aging, dissolution, reprecipitation) of the sorbent would need to be understood.

5. Comparison of the leaching behavior of the different representative sorbents when they are subjected to similar, aggressive leaching conditions. Effort would be made to identify the dominant leaching mechanisms for each particular ABSR and whether these differences can be explained by the differences in the sorbent structure and chemistry and the arsenic bonding by the sorbents.

Dissertation Overview

The five core chapters of this dissertation (Chapters 2-6) have been written in a journal article format for submission to peer-reviewed journals for publication, with the exception of modifying each chapter's format to conform to specific journal's requirements. Because journal articles must be stand-alone manuscripts, some text, figures and tables may appear in more than one place in this thesis in either identical or similar form. This duplication of material has been kept to a minimum, yet particularly with introduction sections, some duplication is unavoidable.

This first chapter to the thesis is intended to be introductory in nature; providing a broad summary of the significance of the project, the particular project objectives, the format of the thesis and a brief literature review of arsenic adsorption/desorption, residuals assessment, leaching test critique and analysis of landfill conditions. A somewhat

shortened version of Chapter 2 was submitted as an article for inclusion in *Journal of Environmental Engineering*. Chapter 3 was submitted and published in *Environmental Science and Technology*. Chapter 4 has been accepted for publication in *Science of the Total Environment*. The fourth and fifth articles (Chapters 5 and 6) will be submitted shortly. The final chapter (Chapter 7) provides a summary of the conclusions gathered in the five core chapters with comments as to the significance of these conclusions for future environmental engineering research and work. The specific focus of the five journal format chapters follows.

Chapter 2 was submitted as a paper entitled “Arsenic Adsorption on Activated Alumina under Landfill pH Conditions” with Amlan Ghosh as the first author and Dhananjay Mishra and Wendell P. Ela as co-authors. This chapter describes the adsorption of arsenic on activated alumina through kinetic and equilibrium trials. Freundlich and Langmuir isotherm equations are used to describe the partitioning behavior of the system. The pH dependence of equilibrium adsorption is also studied and results were simulated through surface complexation modeling using HYDRAQL software.

Chapter 3 was published under the title “TCLP Underestimates Leaching of Arsenic from Solid Residuals under Landfill Conditions” in *Environmental Science and Technology* with Amlan Ghosh (first author), and Muhammed Mukiibi and Wendell P. Ela as co-authors. The paper quantifies leaching of arsenic from AA and GFH that are subjected to the TCLP, WET, an actual landfill leachate and two synthetic leachate solutions. The

effects of the duration of the tests, presence/absence of a N₂ headspace and shaker-table/end-over-end tumbler agitation are investigated.

Chapter 4 has been accepted for publication in *Science of the Total Environment* under the title “Effect of pH, Competitive Anions and NOM on the Leaching of Arsenic from Solid Residuals” with Amlan Ghosh (first author), Eduardo Sáez and Wendell P. Ela as coauthors. This chapter quantifies the desorption of arsenic from AA and GFH as a function of the range of pH and concentrations of the competitive anions (phosphate, bicarbonate, sulfate and silicate) and NOM found in landfills. Leaching tests are also conducted to compare the fraction of arsenic mobilized by the TCLP vis-à-vis an actual landfill leachate and a synthetic leachate with similar anionic concentration as the landfill leachate.

Chapter 5 is near submission. It will be submitted under the title “Column Experiment Demonstrates the Leaching of Arsenic from GFH Residual under Landfill Conditions” with Amlan Ghosh (first author), Muhammed Mukiibi, Eduardo Sáez and Wendell P. Ela as co-authors. Muhammed Mukiibi did a significant portion of the work on column sampling and analysis. This chapter describes the simulation of landfill-like conditions in a flow-through column reactor. The degradation of GFH and the leaching of arsenic under those conditions are evaluated. A discussion on the various mechanisms that might cause leaching and mobilization of arsenic under landfill conditions is included in this chapter.

The final research chapter, Chapter 6, is planned for submission with the title “Different ABSRs Behave Differently when Subjected to Similar Landfill Leaching Conditions” with Amlan Ghosh (first author), Muhammed Mukiibi, Eduardo Sáez and Wendell P. Ela as co-authors. Three ABSRs, AA, GFH and E33 are subjected to reducing, anaerobic environments inside landfill simulation columns. The differences in the leaching patterns of these three residuals under long-term exposure to landfill-like conditions are mapped. The differences are correlated with the differences in the structure of the sorbents themselves and the arsenic bonding to the surface of the sorbents.

Four appendices follow Chapter 7, the thesis conclusions chapter. In Appendix A, the results of the adsorption trials on GFH are shown. In Appendix B, actual leached concentrations from the different leaching tests under different conditions (as described in Chapter 3) are supplied. In Appendix C, the results for a different set of batch experiments, Kosson trials are shown. In Appendix D, the raw data from the AA and E33 columns are shown. Separate plots show the leached arsenic and iron concentrations in both the dissolved and the particulate fractions as well as the pH, alkalinity, ORP and DOC in the column effluents throughout the duration of the column runs.

CHAPTER 2

ARSENIC ADSORPTION ON ACTIVATED ALUMINA UNDER LANDFILL pH CONDITIONS

Introduction

The recent review of the arsenic in drinking water regulation resulted in a decrease in the maximum contaminant level (MCL) to 10ppb and a concomitant need for many water providers to implement additional technologies for arsenic removal (USEPA, 2001). Of the EPA identified treatment options, adsorption onto solid media seems to be the most attractive for the over 3500 small treatment facilities, impacted by the new rule. For other technologies (i.e., membrane filtration, ion exchange) producing a liquid residual stream, solid adsorption processes may also play a role, since any removal of arsenic from the residuals stream will typically involve iron precipitation with arsenic adsorption/co-precipitation. The arsenic bearing solid residuals from these adsorption processes are to be disposed in non-hazardous landfills (USEPA, 2000).

Due to the potential for toxics remobilization, the large volume of arsenic bearing solid residuals presents an obvious environmental concern after landfill disposal. In the U.S. the hazard posed by toxics leaching from solid's surfaces is quantified using the Toxicity Characteristic Leaching Procedure (TCLP). Consequently, the TCLP has been used in several studies to quantify the leaching potential of arsenic from the likely sorbents that will be used in arsenic removal operations (Amy et al., 2000). However, it is doubtful

that the TCLP correctly estimates the leaching potential of arsenic residuals if disposal is in mixed solid waste (MSW) landfills. The TCLP poorly simulates the alkaline pH, anaerobic microbial activity, mineralogic aging, high phosphate, and concentrated organic characteristics of these landfills. These same conditions are expected to favor mobilization of arsenic from metal oxide adsorbents. This study quantifies leaching of arsenic under alternative, more realistic pH conditions and models the observed behavior using a surface complexation model (SCM) approach.

Activated Alumina (AA) has been identified as one of the adsorbents to be most widely used for arsenic removal. It is a Best Available Technology (BAT) identified by EPA. It has a strong selectivity for the arsenate ion (Clifford, 1990), and is already being tested for use by many small water treatment plants. (Chen et al., 1999). The AA surface also represents a reasonable surrogate for the variety of alumina surfaces that are suggested for direct arsenic removal or subsequent liquid residual stream treatment.

In this study's adsorption trials, small volume batch experiments were used to identify pH and loading effects, as these were posed as the most significant independent variables controlling sorbed arsenic retention. The resulting equilibrium solid-water concentrations of arsenic and the primary ions were modeled using HYDRAQL software for surface complexation modeling. This modeling can suggest potential mechanistic underpinnings for the observed behavior and allows prediction of leaching potentials under a wide range of conditions.

Materials and Methods

Sorbent: Activated Alumina

Conventional Activated Alumina has been successfully implemented as an adsorptive treatment media for the selective removal of arsenic from potable water. Although it removes other inorganic and organic contaminants from water, it is somewhat selective for arsenic. To achieve maximum performance, arsenite must be oxidized to arsenate, which is accomplished by treatment with an oxidizing agent, typically chlorine. The AA used in the current research is AA400G, manufactured by Alcan. The properties of the sample as obtained from the manufacturer's product specifications are listed in Table 2.1. This sample can be regenerated once it is saturated with arsenic, although this is not expected to be frequently practiced by facilities using AA for arsenic removal. (USEPA 2001 a).

Kinetic and equilibrium pH trials

Sodium Arsenate Heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, MW: 312 g/mol, KR Grade Aldrich Sigma) was used as the arsenic salt. Ionic strength was adjusted to 0.1M using NaCl. The samples were analyzed using ion chromatography, IC (Dionex, DX-500), or graphite furnace atomic absorbance, GFAA (Perkin Elmer 4100ZL), depending on the sensitivity required. The detection limit in this study was established as 5 $\mu\text{g/L}$ of total arsenic, and analyses of replicates were within $\pm 5\%$. Total dissolved aluminum was measured by GFAA. The detection limit was established as 10 $\mu\text{g/L}$ of aluminum, and analyses of replicates were within $\pm 10\%$. The alumina solubility was also modeled using Phreeqc software (USGS, 1998).

Table 2.1: Properties of Activated Alumina as reported by Alcan (Alcan, 2003).

Bulk Density (g/cc)	0.65
Particle Size (m)	80-100 mesh
Specific Surface Area (m ² /g)	350-380
Pore Volume (cc/g)	0.50

For the kinetic trials, three different pHs of 7, 8 and 10 were tested. The experiments were conducted using 250mL glass conical flasks placed on a reciprocating shaker table (Orbit, reciprocating speed 125 rpm), and were purged with N₂ gas. The solid (alumina) loading was fixed at 2.5g/L and two arsenic loadings of 0.05mM and 0.0125mM were tested. Every 6 hours samples were collected and the pH readjusted using hydrochloric acid (Spectrum) or sodium hydroxide (Sigma) to within ± 0.1 of the predetermined pH. After collection, samples were filtered through a 0.45 μ m filter and analyzed. The kinetic trials were conducted for 60 hours.

Equilibrium trials were conducted with the same arsenic to solid loadings as used in the kinetic trials. Seven pHs from 5 to 12 with five different arsenic loadings of 0.125mM (9.38ppm), 0.05mM (3.75ppm), 0.0125mM (938ppb), 0.005mM (375ppb) and 0.00125mM (94ppb) were sampled for total solution phase arsenic. Total dissolved aluminum was measured in all samples for the 0.005mM, 0.05mM and 0.125mM initial arsenic loadings. PH was adjusted after every 6 hours with either 1N HCL or 1N NaOH. Samples were collected after 48 hours and filtered with 0.45 μ m filter. Similar equilibrium trials were conducted for Granular Ferric Hydroxide (GFH) for 4 different arsenic loadings and in the pH range between 5 and 11, even though the results were not modeled using HYDRAQL. The equilibrium trials data are shown in Appendix A.

The adsorption data were fitted with Langmuir and Freundlich isotherm equations. The Langmuir equation states

$$q = \frac{q_m b C}{1 + q_m C} \quad [1]$$

where q is the solid phase concentration of arsenic ($\text{g}_{\text{As}}/\text{g}_{\text{sorbent}}$), C is the aqueous concentration at equilibrium ($\text{g}_{\text{As}}/\text{cm}^3_{\text{solution}}$), q_m is the adsorption capacity of monolayer ($\text{g}_{\text{As}}/\text{g}_{\text{sorbent}}$), and b the empirical constant ($\text{cm}^3_{\text{solution}}/\text{g}_{\text{sorbent}}$).

The Freundlich equation states

$$q = KC^{1/n} \quad [2]$$

where, K ($(\text{g}_{\text{As}}/\text{cm}^3_{\text{sorbent}})/(\text{g}_{\text{As}}/\text{cm}^3_{\text{solution}})^{-n}$), and n are the empirical constants.

Adsorption Modeling

Surface Complexation Models (SCM) were developed to simulate the surface binding of ionic solutes on mineral oxide surfaces (Davis and Kent, 1990; Stumm, 1987). Four SCMs are commonly used: the diffuse double layer, DLM, the constant capacitance model, CCM, the triple layer model, TLM, and the four layer model, FLM (Davis and Kent, 1990). These models differ conceptually in the structure of the interfacial region and the structure of complexes sorbed at the mineral water interface. All SCMs treat the oxide surface groups as reactive entities that can interact with solution atoms and ions in the standard chemical fashion (Dzombak and Morel, 1990).

For this chapter two SCM were considered: the simple DLM and the more complex TLM. The DLM posits ion interaction (broadly termed adsorption) with the solid by two modes: specific coordination bonding of ions with variously protonated surface hydroxyl groups or non-specific, dissociated electrostatic attraction of counterions in the diffuse layer extending out from the surface (Davis and Kent, 1990). For this work the proton was modeled as not only the single surface potential determining ion, but also as the only ion exhibiting inner sphere (specific, non-hydrated) adsorption. This is in accordance with other DLM work (Hayes et al., 1990) investigating the simplest, electrostatic control of adsorption. In the DLM all ions may undergo non-specific (hydrated) interaction with the solid surface in the diffuse double layer. In contrast the TLM simulates three possible planes of interaction (Davis et al., 1978). As in the DLM, strongly bound ions specifically bond (primarily chemically) to the surface plane. A second plane, the inner Helmholtz or β plane, weakly binds hydrated counterions, while the diffuse layer plane defines the closest distance of approach for all dissociated ions. The TLM allows differentiation between weakly and strongly bound ions and thus typically is able to better simulate such observations as ionic strength and variable ion speciation with pH effects. Detailed descriptions of the structure and implementation of SCMs, including the DLM and TLM, can be found elsewhere (Davis and Kent, 1990, Dzombak and Morel, 1990).

Discussion and Results

Kinetics of Adsorption

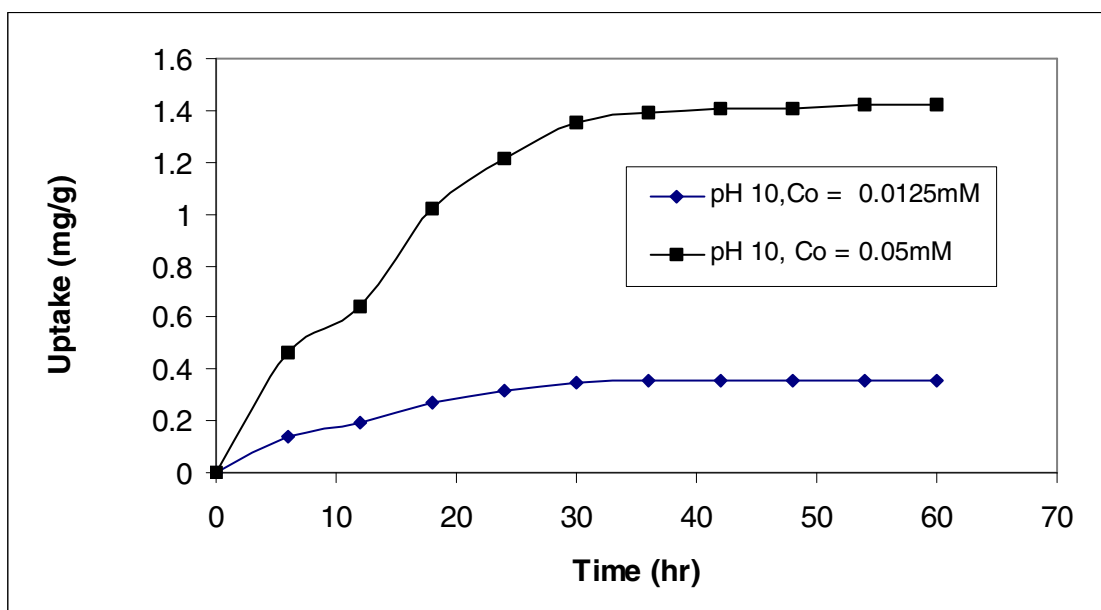


Figure 2.1: Rate of uptake of arsenate by activated alumina at pH 10. Uptake is defined as mass of arsenic adsorbed per unit mass of activated alumina.

Kinetic trials were conducted at pH 7, 8, and 10 and with loadings of 0.05mM and 0.0125mM. The observed kinetics for pH 10 is representative of the results (Figure 2.1). Minimal change in arsenic adsorption was observed after 30 hours for either arsenic loading. This result differs from an earlier study by Lin and Wu. (2001) who observed equilibrium was reached in about 17hr. This difference is probably due to a difference in the properties of the AA used. In this study, the AA had a lower bulk density, higher specific surface area and higher particle size range than the one used by Lin et al. (2001). Based on these results all subsequent equilibrium experiments were conducted with a 48-hour duration to ensure near-equilibrium conditions. The results indicate that it is unlikely that activated alumina will reach equilibrium in the 18 hours of exposure specified in the TCLP.

Equilibrium Adsorption

Arsenic adsorption on activated alumina was tested over the pH range of 5 to 12, which brackets the range of pH expected in landfills. The onset of the arsenic adsorption edge lies between pH 6.0 and 9.0 for all the loadings tested (Figure 2.2). Above this pH the solution arsenic concentration increases rapidly, with the adsorption edge occurring at a more acidic pH as the arsenic loading increases. These results are consistent with previous work by Amy et al. (2000), and Lin et al. (2001), where it was found that arsenic sorption was about 60% greater at pH 5.5 than 8.5. The decreasing concentration

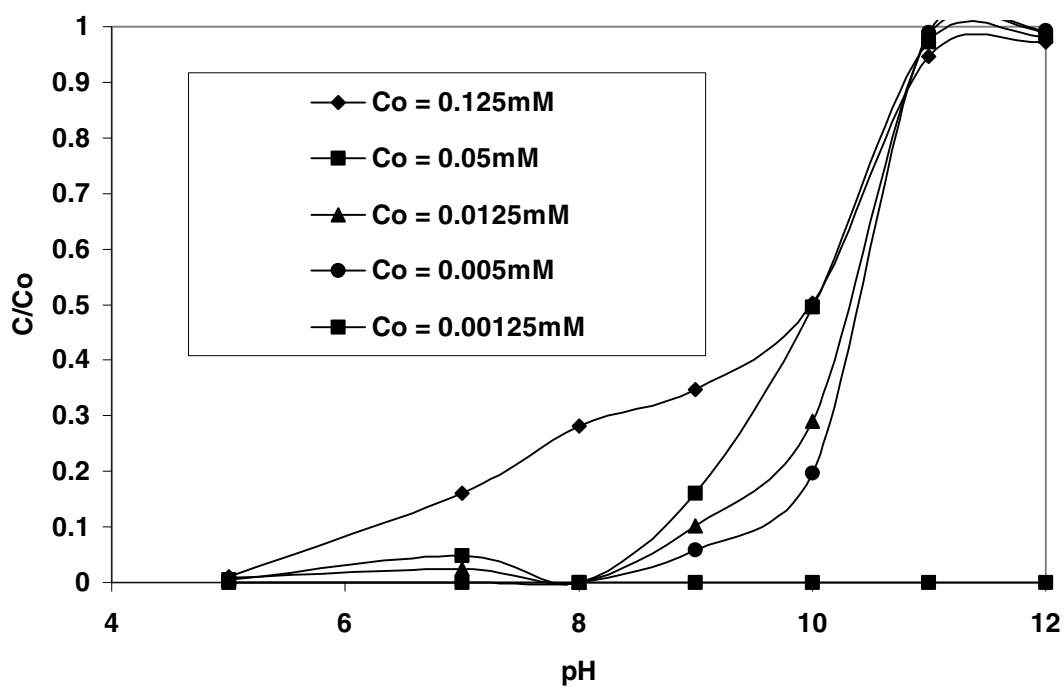


Figure 2.2: Observed equilibrium concentrations of arsenate on activated alumina. C denotes the concentration of arsenic in solution at equilibrium and C_0 denotes the total concentration of arsenic in the system. The curves indicate different arsenic loadings.

of solution protons as pH increases drives more protons from the adsorbent surface, thus making it more negatively charged. As a consequence, the arsenate, anion (H_2AsO_4^- or HAsO_4^{2-}) is progressively more repelled from the double layer to compensate for the increasingly negative surface charge and an arsenate increase in the bulk solution is observed. Conversely, if the pH decreases, preferential anion adsorption onto the surface is expected and anions, like arsenate, will be adsorbed. This increase in concentration of arsenate in solution at high pH is of particular significance in mature landfills where the pH ranges from 7.5 to 9.0 with a median value of approximately 8.2 (Christensen et al., 2001). For all system arsenic loadings, except for the minimum loading of 0.00125mM where no pH sensitivity was observed, the concentration in solution at the median landfill pH of 8.2 was greater than at the TCLP pH of 4.95.

From Figure 2.2, it is also evident that as the total arsenate in the system increases for a constant AA concentration, the relative proportion of adsorbed arsenate decreases. For instance, at pH 9 about 93% of the arsenate is sorbed when 0.005mM arsenate is initially added to the system, whereas when the total system arsenate increases 10 fold (0.05mM), only about 83% is sorbed. This behavior may be explained by a distribution of binding affinities of the surface sites. That is as high affinity sites become progressively saturated, a lower proportion of available arsenate is subsequently bound by lower affinity sites.

The effect of pH and arsenic system loading on equilibrium solid/liquid partitioning is often reported from the perspective of specific uptake (mass of sorbed arsenate / mass of AA). The specific uptake was found to be directly proportional to the initial arsenic

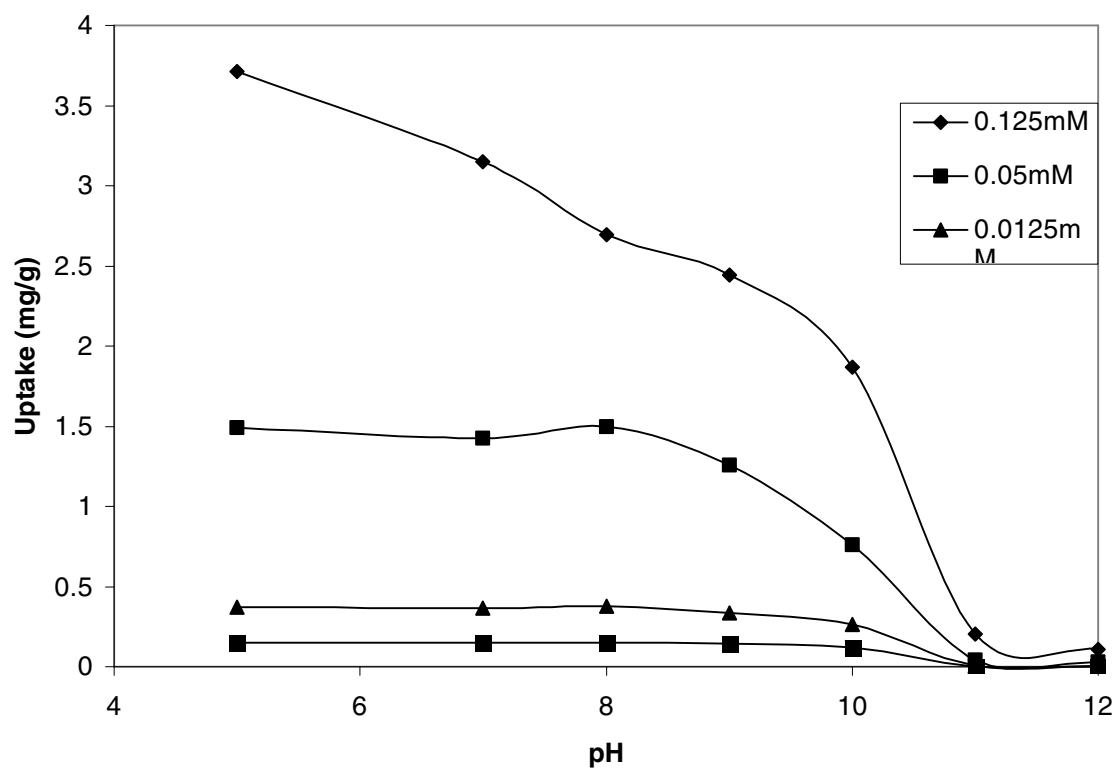


Figure 2.3: Observed adsorption capacity of arsenate on activated alumina. Uptake denotes the mass of arsenic adsorbed per unit mass of activated alumina. The curves indicate different arsenic loadings.

Table 2.2: Uptake (in mg/g) of arsenate on AA as a function of pH and loading.

pH	9.38mg/L		3.75mg/L		94µg/L	63µg/L
	Ghosh ¹	Lin ²	Ghosh ¹	Lin ²	Ghosh ¹	Wang ³
5	3.71	9.17	1.49	3.40		
7	3.15	8.03	1.43	3.22		
8					0.92	1.09
9	2.45	2.27	1.26	1.36		

¹Current Study²Lin et al., 2001³Wang et al., 2002

loading. For a given pH, the uptake was much greater for a higher loading than a lower loading. (Figure 2.3). The observed adsorption capacity of AA is compared to reported values in Table 2.2. It is evident that the adsorption capacities found in this study are in the range of, but differ somewhat from earlier values obtained by Lin et al. (2001) and Wang et al. (2002). It is suggested this is because of the differences in the properties of the activated alumina and much lower arsenic loadings used in this case.

The adsorption data were fitted with Langmuir and Freundlich isotherms to describe the equilibrium partitioning behavior between the aqueous and solid phases for arsenate. The parameters fitted are listed in the Table 2.3. The parameters for pH 8 could not be ascertained because at that pH the partitioning was such that the arsenate in solution was below the detection limit of 10ppb. It is clear from the preceding results and the Table 2.3 isotherm parameters that the pH sensitivity of arsenate sorption on AA limits the usefulness of isotherms to constant pH conditions. Adsorption and desorption data gathered without pH control or without reporting the pH condition is of little comparative value and could easily lead to erroneous conclusions. It was found in this work that it was insufficient to merely establish the initial pH at the desired concentration for the trial of interest. Without preequilibration of the AA surface to the pH of interest (commonly for 24 hours), continuous purging by N₂ and small pH corrections at 6-hour intervals during the sorption phase, the pH drift in many cases was a full pH unit or more during the course of the trial.

Modeling Equilibrium Adsorption

Table 2.3: Isotherm parameters for arsenate sorption on activated alumina. The values for pH 8 were omitted because the concentration in solution was below the detection limit of 10 ppb.

Langmuir Isotherm				Freundlich Isotherm		
pH	q_m (mg/g)	b (L/mg)	R^2	K $(\text{mg}/\text{cm}^3)/(\text{mg}/\text{cm}^3)^{-n}$	N (-)	R^2
5	2.033	2.510	0.99	66.50	1.813	0.99
7	5.910	3.000	0.99	100.2	1.933	0.97
9	5.345	1.327	0.97	79.91	1.707	0.98
10	1.791	1.008	0.97	49.44	1.571	0.98
11	0.213	0.020	0.98	198.3	0.675	0.99
12	0.163	0.016	0.99	92.64	0.689	0.99

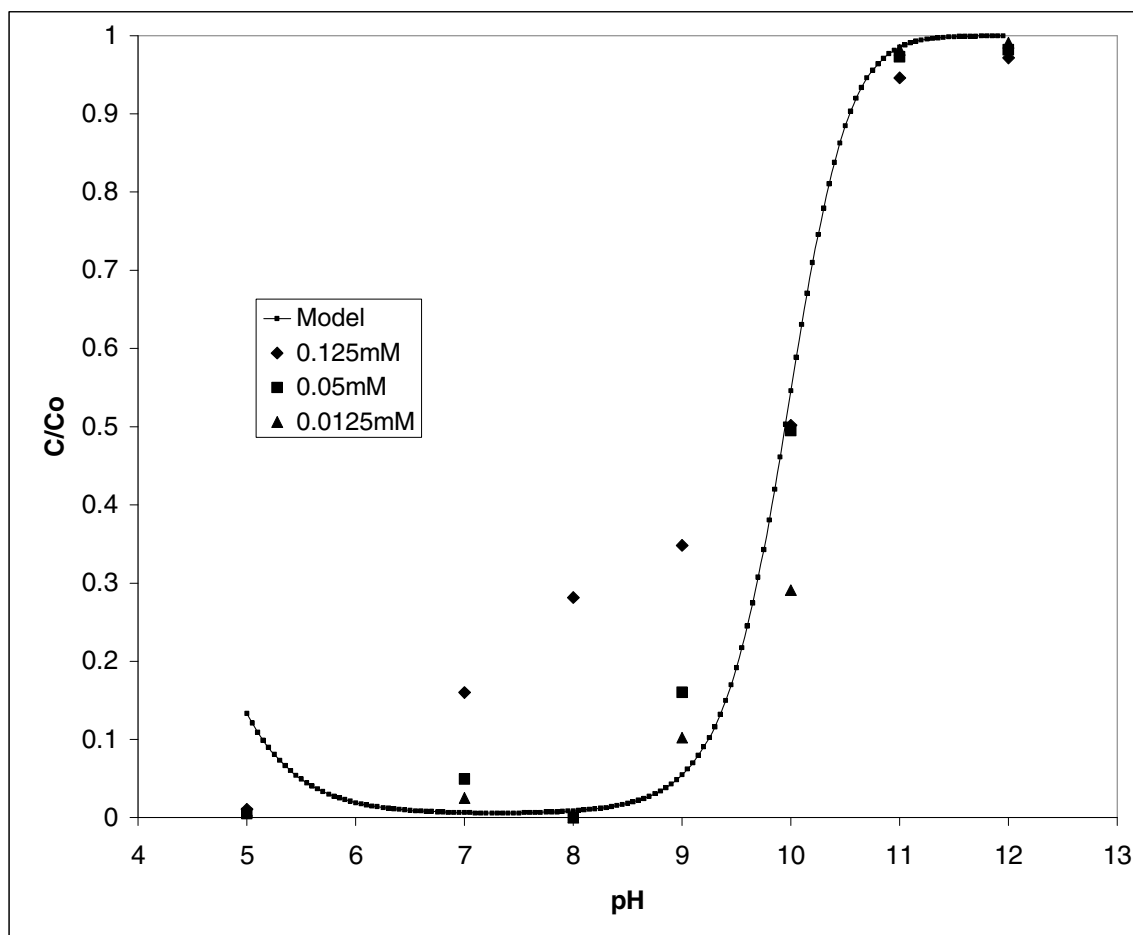


Figure 2.4. Diffuse Layer Model (DLM) simulation of arsenate adsorption on activated alumina. Using a single set of fitted equilibrium constants based on the 0.05mM data, the model simulations for all arsenic loadings fall on the single line shown.

The DLM and TLM surface complexation models were tested for their ability to simulate the data. The best-fit DLM was found using literature equilibrium constants for the surface protonation reactions and the electrolyte (Na^+ and Cl^-) adsorption constants (Prasad, 2001). The specific surface area of $300 \text{ m}^2/\text{g}$ and site density of 7 nm^{-2} were also taken from Prasad (2001). The adsorption equilibrium constants for HAsO_4^{2-} and H_2AsO_4^- were manually adjusted until the visual best fit was achieved. The DLM could be fitted to reasonably simulate the pH dependence of sorption at a single loading (i.e., 0.05 mM as shown in Figure 2.4). However a single set of model equilibrium constants could not be fit to reasonably model both the pH and loading dependence observed.

When different arsenic loadings (ratios of total arsenate mass to solid mass) were modeled, all DLM simulations fell essentially on the same line. The DLM simulates the experimental trend of increasing arsenate desorption with increasing pH, but it shows little sensitivity for the effect of loading observed in the higher pH range. In the lower pH range studied, the model predicts the behavior very well, although there is little effect of pH or loading in this range.

Because of the poor ability of the DLM to simulate the measured behavior, the more flexible TLM was tested. The TLM allows more differentiation between the ways ions can bind to the surface. The model essentially provides extra fitting parameters to describe the specific adsorption of target ions as both inner-sphere complexes and as outer-sphere complexes undergoing non-specific adsorption. Figure 2.5 shows the

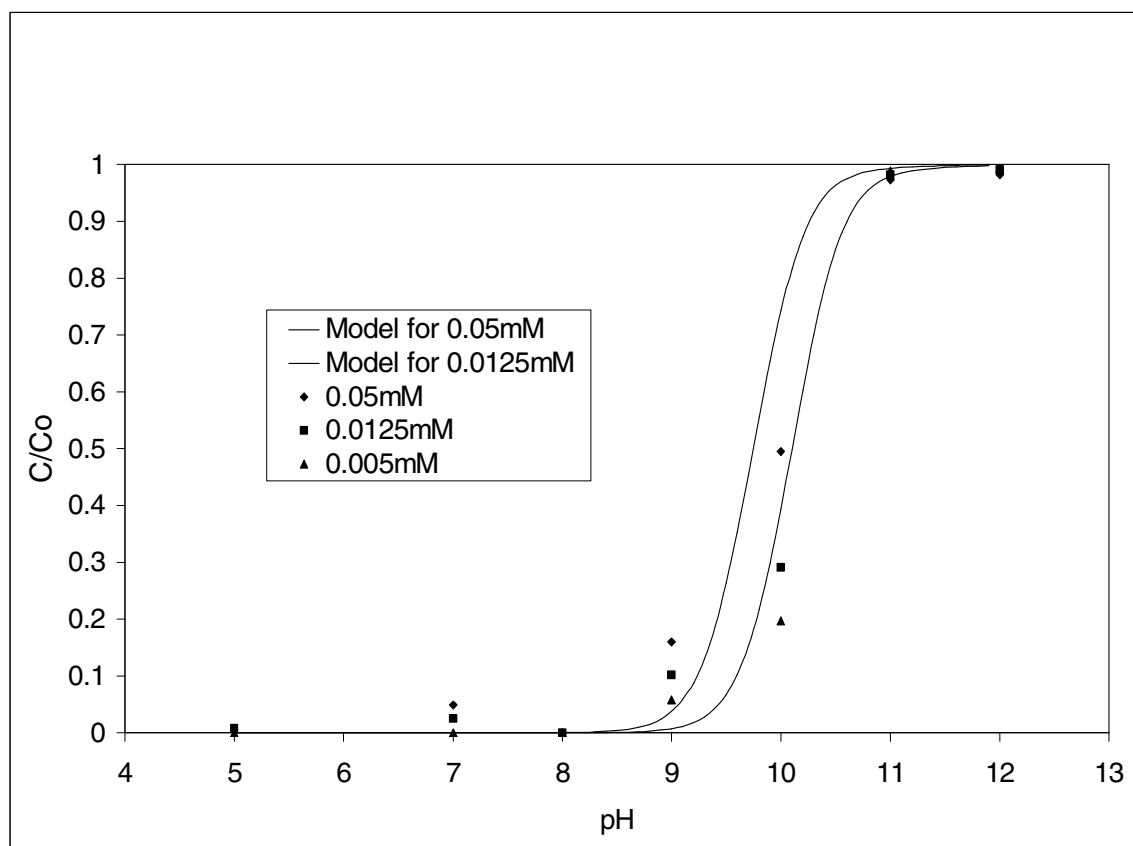


Figure 2.5. Triple Layer Model (TLM) simulation of arsenate adsorption on activated alumina. Equilibrium constants for the model fits shown were based on the 0.05mM loading and then utilized to model behavior at the three loadings. The model curve for 0.05mM loading is indistinguishable from the one shown for 0.0125mM loading.

results. The TLM was fitted using literature equilibrium constants for the surface protonation reactions, AA specific surface area and site density (Prasad, 2001), just as for the DLM. The Na^+ and Cl^- adsorption constants were adjusted manually until a visual best fit was achieved, as were the equilibrium constants for HAsO_4^{2-} and H_2AsO_4^- . TLM results show the experimental trend of increasing arsenic mobility with increasing pH at different loadings of arsenic. However, the TLM also does not do a very good job predicting the extent of the experimental behavior. For instance, considering the model fit based on the 0.05mM data, nearly complete desorption of arsenate is predicted at pH 10 with only about 20% observed for a system loading of 0.005mM.

The observed nearly complete sorption of arsenate at all pHs for low system loadings, but high proportion of arsenate solubilization at high pH and high loadings is consistent with a solid surface with a significant distribution of site binding affinities. To simulate this condition a two site approach was investigated for the TLM. The two-site approach assumes one population of surface sites exhibits a high binding affinity and chemisorption of arsenate, while a second population of surface sites is low energy binding sites, which electrostatically adsorb arsenate from solution. This multi-site approach is consistent with observations of the adsorption behavior of other hydrous oxide surfaces (van Riemsdijk et al., 1987), although often such behavior can be modeled successfully using various single-site type SCM techniques (Hayes, 1987). The low affinity binding sites release arsenate to solution more readily than the high affinity sites as the surface charge becomes more negative with increasing pH. Thus, depending on the proportion of the total surface sites of low and high affinities, the partitioning will exhibit more or less

sensitivity to pH changes. To evaluate this two-site possibility, first the low arsenic loading experimental data was fitted to determine the number of high affinity binding sites. It was found that by designating somewhat less than one percent of the total surface sites as high affinity the lack of sensitivity to pH at a loading of 0.00125mM could be simulated (simulation not shown).

After fixing the number of and equilibrium constants for the high affinity sites the equilibrium constants for the remaining population of low affinity sites was fitted. For all simulations the high affinity sites were modeled using the 0.00125mM data and the low affinity sites were modeled using the data from the remaining loadings. For the high affinity sites the Na^+ , Cl^- , AsO_4^{3-} , HAsO_4^{2-} and NaHAsO_4^- adsorption constants were adjusted manually until a visual best-fit was achieved. The constants for the low energy and high energy binding sites are listed in Table 2.4.

The TLM two-site approach is able to simulate the observed pH insensitivity of the lowest system arsenic loading (0.00125 mM) and also the pH sensitivity of a single higher system loading. However, once the equilibrium constants for and site density of the high affinity population was fixed, it was found that no single set of low affinity site equilibrium constants could reasonably simulate the combined effect of pH and system arsenate loading for the remaining experimental data. This shortcoming of the modeling is illustrated by comparing Figures 2.6 and 2.7. The former shows the best model fit based on fitting the high and low affinity populations on the 0.00125mM and 0.0125mM

loadings data respectively, while the latter is based on the 0.00125mM and 0.125mM loadings respectively. Because none of the SCM model efforts (DLM, TLM or two-site TLM) were able to reasonably simulate the observed partitioning behavior, no effort was made to determine if the best-fit parameters for a particular case were unique. In other SCM work it has been found that multiple, disparate parameter sets may give comparably good fits (Hayes et al., 1991), but this data set was not amenable to such an evaluation.

Aluminum Analysis

Total dissolved aluminum concentration was measured in the equilibrium trial samples for 0.005mM, 0.05mM and 0.125mM loadings. The total aluminum concentration in solution was found to be the least between pH 6-7 (Figure 2.8), which is consistent with the minimum predicted by the equilibrium model, Phreeqc (USGS, 1998). In addition Phreeqc predictions and experiment observations agree that aluminum solubility increases more slowly on the acid than base leg above the minimum. However the

Table 2.4: TLM equilibrium constants fitted for single site (S.S.) approach and two-site approach with high energy (H.E.) and low-energy (L.E.) binding sites. The arsenate loading on which the model fitting parameters were based is shown in parenthesis.

Species	S.S. Log (K)	H.E. (0.00125mM) Log (K)	L.E. (0.0125mM) Log (K)	L.E. (0.125mM) Log (K)
Na^+	-12.5	5.0	5.0	5.0
Cl^-	2.5	5.0	5.0	5.0
AsO_4^{3-}	7.6	4.2	-10.25	-6.25
HAsO_4^{3-}	22.7	44	9.2	21.3
NaHAsO_4^{3-}	N/A ¹	42	28	19.5

¹Not Applicable

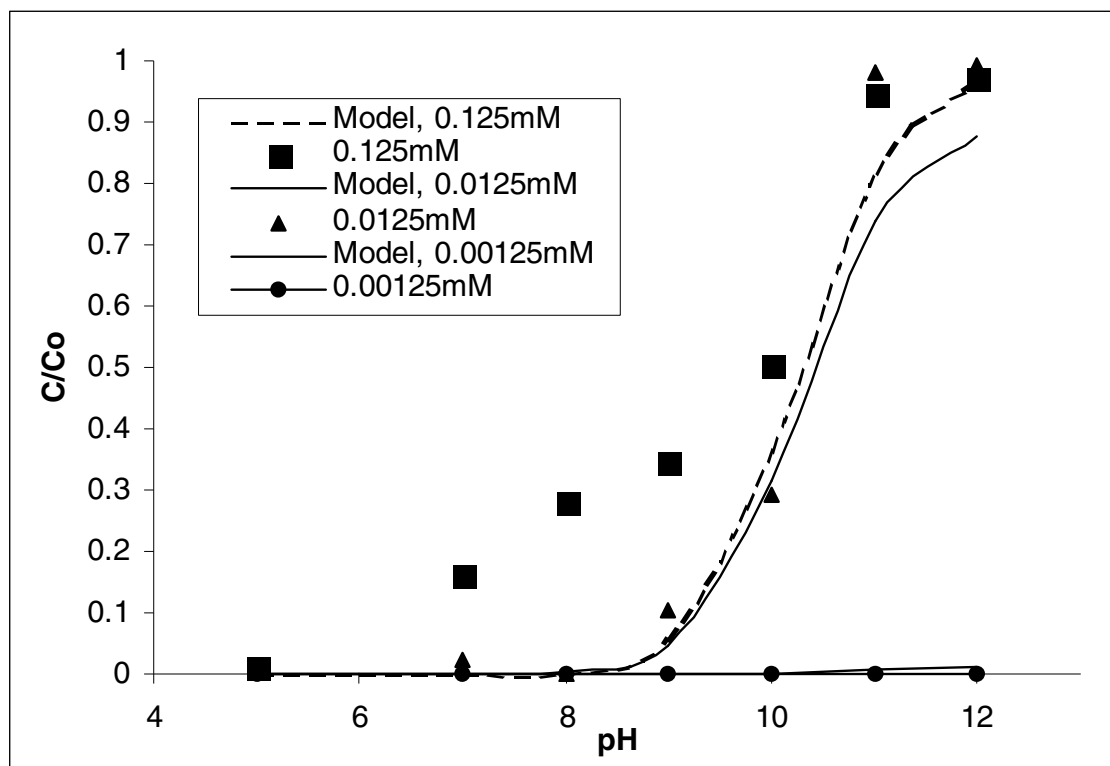


Figure 2.6. Modified two-site approach simulating the adsorption of arsenate on activated alumina using Triple Layer Model (TLM). The model equilibrium constants for the high and low affinity populations are fit based on the 0.00125mM and 0.0125mM loadings, respectively. The constants are then used in tandem to simulate the 0.125mM, 0.0125mM and 0.00125mM loadings with fits as shown.

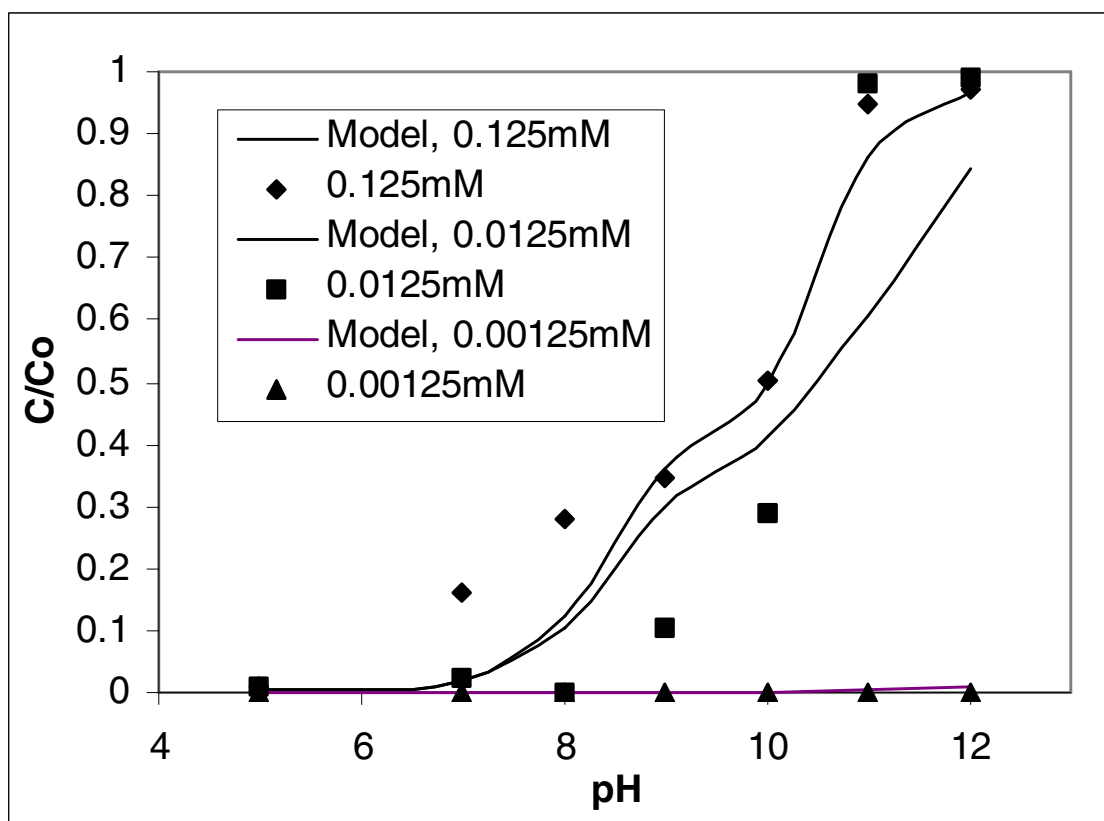


Figure 2.7: Modified two site approach simulating adsorption of arsenate on activated alumina using Triple Layer Model (TLM). The model equilibrium constants for the high and low affinity populations are fit based on the 0.00125mM and 0.125mM loadings, respectively. The constants are then used in tandem to simulate the 0.125mM, 0.0125mM and 0.00125mM loadings with fits as shown.

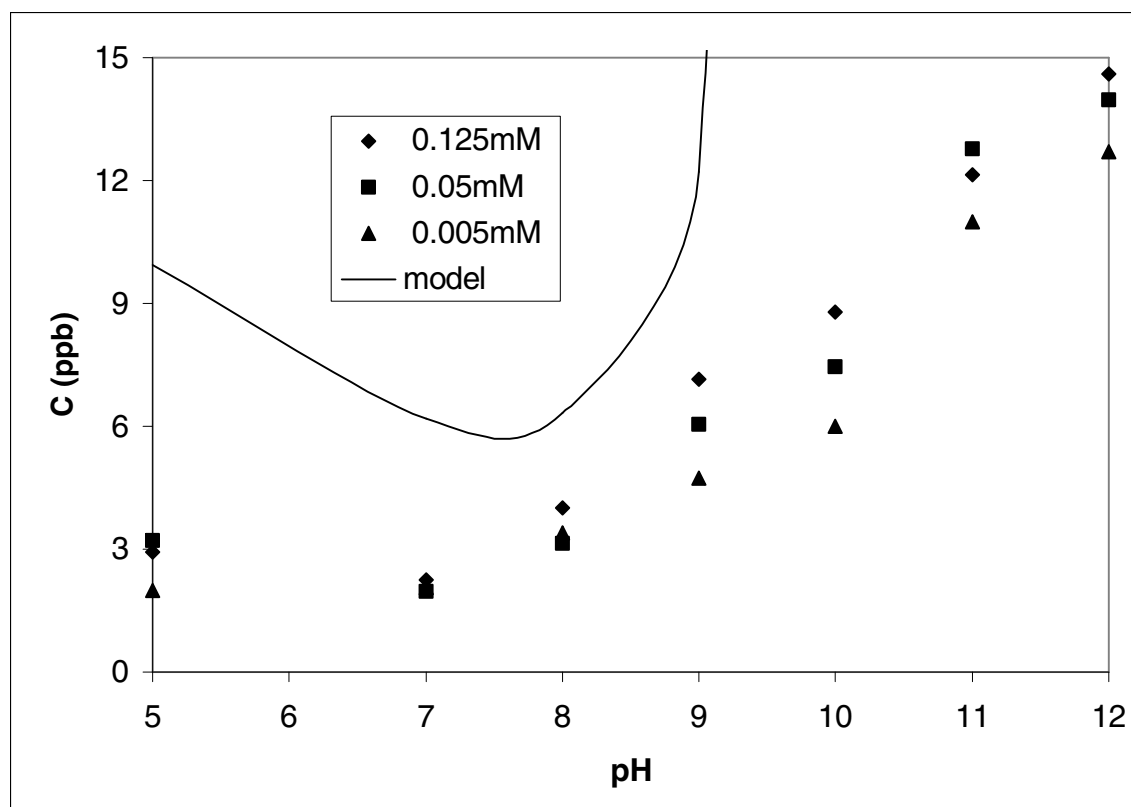


Figure 2.8: Experimental and model predicted equilibrium concentrations of aluminum in solution. C is the concentration of aluminum in solution.

equilibrium model predicts a two-fold or greater concentration in solution aluminum than was measured for any experimental pH or arsenic loading. The divergence of model predictions and experimental observations is particularly pronounced in the pH range greater than 9. This discrepancy could be due to the formation of alumina/arsenate solution complexes, however, no literature references to the formation of any such complexes were found. It is more likely the lack of agreement is due to the fact that the equilibrium experiments were run for 48 hours after which the samples were filtered and analyzed. This trial duration was based on the arsenic kinetic study described above, whereas the kinetics of aluminum dissolution may not be similar. Thus, the dissolution of activated alumina may have been kinetically limited. The other important observation was that the model predicts the same equilibrium concentration of aluminum for all three arsenate loadings. The arsenate concentrations were so small that they did not have any significant effect in altering the activity of the overall solution and no arsenate/aluminum complexes are included in the model database. From the model results, we also find that at no pH, does all of the alumina in the system solubilize. Maximum solubility occurs at pH 12 where 0.43% of the initial solid AA would be in solution at equilibrium. This is significant because it indicates that even if the system reaches equilibrium (i.e. long residence time, characteristic of a landfill), a substantial reservoir of solid AA would still remain for the arsenate to sorb on.

Conclusions

The capacity of activated alumina obtained was about 3 fold lower than the capacity obtained in earlier research by Lin et al. (2001). The difference in capacity is likely due to the difference in the characteristics of the activated alumina used in the two studied and to the much lower arsenic loadings used in this study. Although addressing a lower range in arsenate loading than previous studies, the sorption experiments confirmed the relationship noted by other researchers that the adsorption capacity of activated alumina is highly dependent on the pH of the solution. The increase in mobility of arsenic with increasing pH is of particular significance when contrasting the low pH of the TCLP and the alkaline pH of landfills. The desorption edge for activated alumina was found between pH 8 and 10, which roughly brackets the typical mature landfill leachate pH in the range of 7 to 9. At the same pH and solid concentration, a greater fraction of the total arsenic partitioned to the aqueous phase as the total arsenic in the system was increased, indicating a significant distribution in surface site binding energies. The Langmuir and Freundlich isotherm equations were able to describe the partitioning behavior for the system at a single pH. Surface complexation models (DLM and TLM) were able to simulate the pH dependence of a single arsenate loading, but poorly simulated the effect of variable arsenate loadings even when a two-site approach was tested with the TLM.

¹CHAPTER 3TCLP UNDERESTIMATES LEACHING OF ARSENIC FROM SOLID RESIDUALS
UNDER LANDFILL CONDITIONS

Introduction

The Maximum Contaminant Level (MCL) of arsenic in drinking water was recently lowered from 50µg/L to 10µg/L. Utility compliance with the new standard is required by the years 2006-2011, depending on the size of utility. This will cause over 3,300 U.S. utilities to implement new or modified technologies for arsenic removal (Federal Register, 2001). Arsenic bearing solid residuals (ABSR) from these removal operations are expected to be disposed in landfills, where the potential for arsenic remobilization presents an environmental concern. The suitability of toxic bearing solids for landfill disposal is assessed by the Toxicity Characteristic Leaching Procedure (TCLP) (Federal Register, 1986), although a few areas use the California Waste Extraction Test (WET) (California Register, 1985). The TCLP is designed to expose the waste material to conditions more conducive to toxic leaching than landfill conditions and, by comparing the concentration leached toxic's to a toxicity characteristic (TC) regulatory level, determine if the waste can be disposed in a non-hazardous landfill. Consequently, the TCLP has been used to quantify the leaching potential of arsenic from the spent sorbent residuals (Amy et al., 2000, Hooper et al., 1998, Cornwell et al., 2003). Currently the residuals from most arsenic removal technologies pass the TCLP and are considered safe

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for disposal in non-hazardous, mixed solid waste (MSW) landfills. The current arsenic TC is 5mg/L, but even if the TC is lowered to 1mg/L in line with the new arsenic MCL, the Environmental Protection Agency (EPA) believes that arsenic residuals would not be classified as hazardous waste and would remain suitable for non-hazardous landfilling (USEPA, 2001).

Of the EPA identified treatment options, adsorption onto solid media is favored for the small facilities (those serving populations of less than 3,301), which comprise over 92% of the impacted utilities (USEPA, 2001). Activated alumina (AA) and granular ferric hydroxide (GFH) have been identified as solid adsorbents that will be widely used for arsenic removal. Although activated alumina is a best available technology (BAT), GFH trials indicate it may be preferable due to a capacity more than 5X that of AA (Amy et al., 2000). A large number of other alternative sorbents have been developed (i.e., Bayoxide E-33, green sand, Aqua-bindTM, iron modified AA), but nearly all exhibit an alumina or iron oxy/hydroxide surface (USEPA, 2001a) and all will generate ABSR. For other technologies (i.e., membrane filtration, ion exchange) producing a liquid residual stream, the liquid residuals will need to be treated on-site. The recommended process is adsorption/co-precipitation with amorphous ferric hydroxide (AFH ($\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$)) induced by addition of ferric chloride. The residual for final disposal will be AFH, which like other ABSR, would be evaluated using the TCLP (USEPA, 2000).

The arsenic in potable water supplies is in either the arsenite, As (III), or arsenate, As (V), oxidation states (USEPA, 2000). The oxidation state of arsenic greatly affect its adsorption/desorption behavior. In near-neutral waters arsenite is primarily fully protonated and uncharged as arsenous acid (H_3AsO_3) (pK_{a1} 9.2). In contrast, arsenate is predominantly in an anionic form (pK_{a1} 2.2, pK_{a2} 7.0 and pK_{a3} 11) (Wagman et al., 1982). Metal oxy/hydroxide adsorption/desorption of ions is typically more efficient than of neutrals (Stumm and Morgan, 1996). This electrostatic enhancement is in response to the amphoteric nature of surface functional groups, whereby pH adjustment protonates or deprotonates surface functional groups (i.e., hydroxides) and decreases or increases, respectively, the surface attraction for anions such as arsenate (Stumm, 1992, Dzombak and Morel, 1987, Lin and Wu, 2001). Thus water containing a significant fraction of arsenite is recommended to undergo preoxidation of arsenite to arsenate prior to the application of an arsenic removal technology (USEPA, 2001). Consequently, in this research, sorption of only arsenate onto the metal oxides is looked into, and not that of arsenite.

The concentration and nature of other anions affects the fraction of arsenate sorbed/leached, as ions compete for the surface sites. Most of the research that is conducted on arsenic sorption has looked into the adsorption characteristics. Very little information is available on desorption. Myneni et al. (1997) compared the adsorption and desorption of arsenate in Ettringite and found very little similarity between adsorption and desorption behavior. This work has been done exclusively on desorption and the

results should be interpreted as such. It is not implied here that the adsorption kinetics would be the same as desorption kinetics, nor that the other competing anions impact adsorption and desorption in a similar way. However, the very same factors which impact adsorption would also impact desorption so a discussion of these factors is relevant. In general, as the ionic strength increases the fraction of contaminant sorbed decreases. However, individual ions have differing affinities for surface groups, so their effectiveness in displacing a target ion depends not only on the relative concentrations of the ions, but also on the identity of both the ions and the surface. Anions like sulfate and phosphate may directly compete with arsenate for surface sites (Jain and Loeppert, 2000, Driehaus and Jeckel, 1998). The concentration of Natural Organic Matter (NOM) also impacts arsenic sorption. Xu et al. (1991) found the presence of NOM to significantly decrease anion adsorption on metal oxide solids. Amy et al. (2000) confirmed this observation for arsenic sorption on ion exchange resins, iron oxide coated sand and activated alumina. Not only does the composition of the water affect ion sorption by solids, but so also does the nature of the sorbent. This effect is manifested both as a difference between different metal oxides, and as a difference between the different mineralogical forms of the same metal oxide. Thus, aluminum oxide sorption of arsenate is known to be more affected by the presence of other anions than iron oxide sorption (USEPA, 2000). Also the iron oxide, ferrihydrite ($\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$), has a much different sorption capacity than the iron oxide, goethite (FeOOH), into which ferrihydrite naturally ages by dehydration (Nowack et al., 1996).

A leaching test must present the residuals with an environment that is equal or more aggressive than the final disposal environment. For the case of an ABSR the degree of leaching will depend on numerous factors including pH, ionic strength and composition, NOM concentration and composition, and detention time. Consequently the appropriate leaching test for ABSRs must expose the waste to a solution in which the combination of the above-mentioned factors provide a more aggressive condition than a non-hazardous landfill. Table 3.1 shows the characteristics of typical landfill leachate parameters of interest. In an actual landfill the pH can be as high as 9, the alkalinity as high as 11500mg/L and the TOC 29000mg/L. The residence time can range from a few days to weeks or months. In contrast, the TCLP conditions include an acidic pH, an oxidizing and abiotic environment and a short (18hr) contact duration. The TCLP was initially designed to test the leaching potential of cationic metals which partition most strongly to electrostatic sorbents at high pH, whereas arsenate as an oxyanion partitions most strongly at the low pH such as created by the TCLP, but not a landfill. A component of this study's batch trials exposed ABSRs to actual landfill leachate as well as to TCLP and WET specified leachates. We report here on the results of these primarily abiotic tests. Parallel studies are being conducted using the combined biotic and abiotic conditions characteristic of landfill conditions. This study does not intend to quantify all individual factors affecting appropriateness of TCLP and WET protocols for evaluating the hazard posed by landfilling of ABSR, but does attempt to answer whether these standard tests are appropriate for evaluation of ABSR and indicate whether an alternative, equally easy to apply and more appropriate protocol might be developed.

Table 3.1: Characteristics of the Synthetic Extracting Solutions and Landfill Leachates

Test	pH	ORP (mV)	Alkalinity (mg/L as CaCO ₃)	TOC (mg/L)	TDS (mg/L)	Ionic Strength (M)
TCLP	4.95	-68.2	766	38.6	1480	0.08
WET	5.05	-101	7940	55.8	5160	0.10
SL1	7.03	-48.4	1500	1050	5200	0.03
SL2	7.55	-224	12500	1310	8600	0.49
LL ¹	6.82	-143	1100	160	3600	0.33
LL ²	4.5-9.0	N/R [*]	300-11500	30-29000	2000-60000	N/R
LL ³	6.5-8.2	N/R	1250-8050	N/R	1960-16800	N/R
LL ⁴	6.2-7.1	N/R	N/R	236-3160	N/R	N/R

N/R^{*} - Values Not Reported

LL¹ – Leachate used in this study and collected from Tangerine Road Landfill, Tucson, AZ.

LL² – Leachate composition reported in Christensen et al., 2001 (23)

LL³ – Leachate composition reported in Jang et al., 2003. (24)

LL⁴ – Leachate composition reported in Hooper et al., 1998. (5)

Materials and Methods

Sorbents

Conventional AA has been implemented for the selective removal of arsenic from potable water (Rubel and Hathaway, 1985). Although it also removes other contaminants (i.e. fluoride, sulfate), it is somewhat selective for arsenic. The AA used in the current research is AA400G, manufactured by Alcan. The properties of the sample according to the manufacturer's product specifications are particle size, 80-100mesh; specific surface area, 350-380m²/g; and pore volume, 0.50cc/g. This sorbent can be regenerated once it is saturated with arsenic, although this is not expected to be frequently practiced. (USEPA 2000, USEPA 2001).

Granular ferric hydroxide (GFH) is a weakly crystalline β -FeOOH produced by conditioning previously compacted iron hydroxide slurry (Driehaus and Jeckel, 1998). It is in the form of irregular grains up to 2mm diameter. In order to preserve its activity, the material must not be dried and the mechanical stability of the granules is less than that of activated alumina. GFH particles specifically adsorb As(V). Under comparable conditions, the capacity of the GFH is estimated to be 5X greater than that of conventional alumina (Amy et al., 2000). GFH® is manufactured by GEH and distributed in the US by U.S. Filter. It is designed as a throw-away media and would not be regenerated.

Leaching Trials

Prior to all leaching experiments, a single batch of AA and GFH were pre-equilibrated with arsenate. For each, a solution was prepared with 150.0g of sorbent and 1.00L of solution. The initial concentration of arsenic added was 190mg/L (as As) and 1080mg/L (as As) for AA and GFH respectively. After equilibration the aqueous concentration was 21.8 μ g/L (as As) and 31.0 μ g/L (as As) for AA and GFH respectively. The sorbed concentration on the solids were 1.27mgAs/gAA and 7.2mgAs/gGFH. All solutions were made using purified water (Milli-QTM Water System by Millipore). Arsenate was added as Sodium Arsenate Heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, KR Grade Aldrich Sigma). Solution ionic strength was adjusted to 0.1 M with NaCl (GR Grade EM Science). After 48 hours of equilibration on a shaker table (Orbit, reciprocating speed 125 rpm), liquid samples were collected and analyzed. All subsequent TCLP, WET, actual leachate and simulated leachate tests used GFH and AA from these single batches.

The TCLP specifies that samples be rotated end over end during leaching, whereas the WET specifies shaker table agitation. The duration of extraction is 18 ± 2 hr for the TCLP and 48 hr for the WET. In both cases, the leaching temperature is 23°C. Finally, for the WET the headspace for the extraction vessel is purged vigorously with N_2 prior to sealing and agitation, whereas for the TCLP the headspace is ambient air. For this study, all leaching tests were compared for both extraction durations (18 and 48 hrs), both agitation means (shaker table and tumbler), and both headspace treatments (N_2 and ambient). Following extraction, the liquid for all samples was filtered through a 0.45 μ m

glass fiber filter before analysis. The initial characteristics of the different leaching solutions are shown in Table 3.1.

TCLP The appropriate extraction fluid for both AA and GFH is extraction fluid #1 of the TCLP (Federal Register, 1986). Extraction fluid #1 is prepared by adding 5.7mL of glacial acetic acid ($\text{CH}_3\text{CH}_2\text{OOH}$) and 64.3mL of 1N NaOH and bringing it up to 1000mL with reagent water. The pH is 4.93 ± 0.05 . When a waste contains both solid and liquid phases, with the solid being more than 0.5% by weight, the TCLP prescribes a sample size of 100g (solid plus liquid phase) and that 97.5mL of extraction fluid be added to each sample. For this work, the TCLP tests were run at 0.05 scale, but checks on the reproducibility of results showed no drawback with this approach. Solids were separated from the supernatant using vacuum filtration. The solids did not need any size reduction.

WET According to WET (California Register, 1985), the ABSRs studied in this research are classified as Type (ii) substances. The solids and liquids are separated by vacuum filtration. The solids thus obtained passed through a No10 sieve, so no further milling was required. The WET extraction solution consists of 0.2M sodium citrate at pH 5.0 ± 0.1 , prepared by titrating analytical grade citric acid in Milli-Q water with 4N NaOH. 5g of the solid waste is placed in a glass container with 50mL of the extraction solution.

Landfill Leachate (LL). The landfill leachate used in this research was obtained from the Pima County, Tangerine Road Landfill, Tucson, Arizona. The leachate was extracted

Table 3.2: Composition of Simulated Leachate 1 (SL1) and Simulated Leachate 2 (SL2):

SL1	Concentration (mg/L)
Acetic Acid	576
Propionic Acid	192
Butyric Acid	422
Valeric Acid	163
Caproic Acid	232
Ammonium Chloride	2680
Sodium Bicarbonate	2520
TOC	1050
pH	Adjusted to 7.0 with 0.1N HCl or 0.1N NaOH
SL2	
Calcium Carbonate	1100
Sodium Carbonate	11500
Ammonium Chloride	650
TOC (VFA mixture)	10000
Sodium Citrate	46400
Hydroxylamine Hydrochloride	31.7
pH	Adjusted to 7.5 with 0.1N HCl or 0.1N NaOH

from a landfill cell containing mixed municipal leachate. The composition of the actual leachate along with literature values (Hooper et al., 1998, Christensen et al., 2001, Jang et al., 2003) is shown in Table 3.1. Consistent with the TCLP protocol, 5g of solid was treated with 97.5mL of leachate.

Simulated Leachate 1 (SL1) A solution of volatile fatty acids (VFA) was prepared consisting of 5 different acids of low molecular weight in order to mimic the TOC concentration and approximate make-up of landfill leachate. The composition of the solution is shown in Table 3.2. Ammonium chloride and sodium bicarbonate were added to mimic concentrations found in a mature landfill leachate. The pH was adjusted to 7.0 using 0.1N NaOH. Analogous to the TCLP protocol, 97.5mL of this solution was added to 5g of the solid waste.

Simulated Leachate 2 (SL2) A second, more aggressive simulated leachate solution was prepared consisting of higher organic concentrations, ionic strength and pH. Table 3.2 shows the composition of the SL2. In addition to the 5 VFAs that were used in the SL1, sodium citrate was added at the concentration used in the WET test. Hydroxylamine was added to create a reducing environment commensurate with the low ORP of typical, mature landfills. The pH was adjusted to 7.5 using 0.1M NaOH. Consistent with other leaching solution tests, 97.5mL of this solution was added to 5g of the solid waste.

Analytic Methods

Arsenic was analyzed by using HPLC for pretreatment and species separation followed by Ion Coupled Plasma Mass Spectrometer(ICP-MS, Agilent 7500a) for subsequent detection. The HPLC system consists of an Agilent 1100 HPLC (Agilent Technologies, Inc.) with a reverse-phase C18 column (Prodigy 3u ODS(3), 150x4.60mm, Phenomenex, Torrance, CA), maintained at 50°C. The mobile phase (pH 5.85) contained 4.7mM tetrabutylammonium hydroxide, 2mM malonic acid and 4% (v/v) methanol at a flow rate of 1.2mL/min. The detection limit for this instrument was 0.1µg/L for arsenic speciation, and 0.01µg/L for arsenic totals. Analysis of replicates was within $\pm 5\%$. ORP measurements were made with a Cole Palmer Platinum Single-Junction Electrode calibrated using ZoBell's solution ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ / $\text{K}_3\text{Fe}(\text{CN})_6$ redox couple). Aluminum concentration was measured using a Graphite Furnace Atomic Absorbance Spectrometer (Perkin Elmer, 4100ZL, detection limit 10 µg/L for Al) while iron concentration was measured using the phenanthroline method using a Spectrophotometer (Hitachi, U-2000).

Discussion and Results

Activated Alumina

Separate trials subjected arsenic loaded AA to extraction by TCLP, WET, landfill leachate (LL), and simulated leachates (SL1 and SL2) under the standard conditions for both the TCLP (18-hour duration, end-over-end tumbler, ambient air headspace), WET (48-hour duration, shaker table, N_2 headspace) and variations thereof. Figure 3.1 shows

arsenic concentrations for AA samples, agitated by tumbler for 18 hours with and without a N₂ headspace. The standard TCLP protocol does not introduce a N₂ headspace. The concentrations of arsenic for all tests are above 21.81µg/L, the initial aqueous arsenic concentration in equilibrium with the loaded AA. Figure 3.1 shows that the TCLP test extracts the lowest amount of arsenic while the LL and the SL2 extract the highest amounts of arsenic. The concentration of total arsenic in LL is about an order of magnitude greater than that found in the TCLP test. This suggests that the TCLP is not a sufficiently aggressive test to conservatively predict arsenic (or likely other anionic metal) leaching from AA residuals exposed to the landfill fluids. The high leachate pH presumably contributes to the result since the TCLP has a pH of 4.93, whereas the pH in the LL is 6.82 and arsenic mobilization increases as pH increases (Lin and Wu, 2001). In addition, the TCLP test is conducted with lower total organic concentrations than LL

(albeit only by a factor of about four), which may decrease solubilization by organic complexes. The TOC of the LL is at the lower limit of the range observed for typical MSW landfills (Table 3.1), although SL1 solution with a much higher TOC and comparable pH exhibits only about one-third the arsenic leaching of LL. Perhaps some of the wide range of organic species present in LL, but not introduced in SL1, form soluble complexes with arsenic and explain the increased solubilization. This is consistent with the results of Amy et al. (2000), who found the presence of 4mg/L natural organic matter

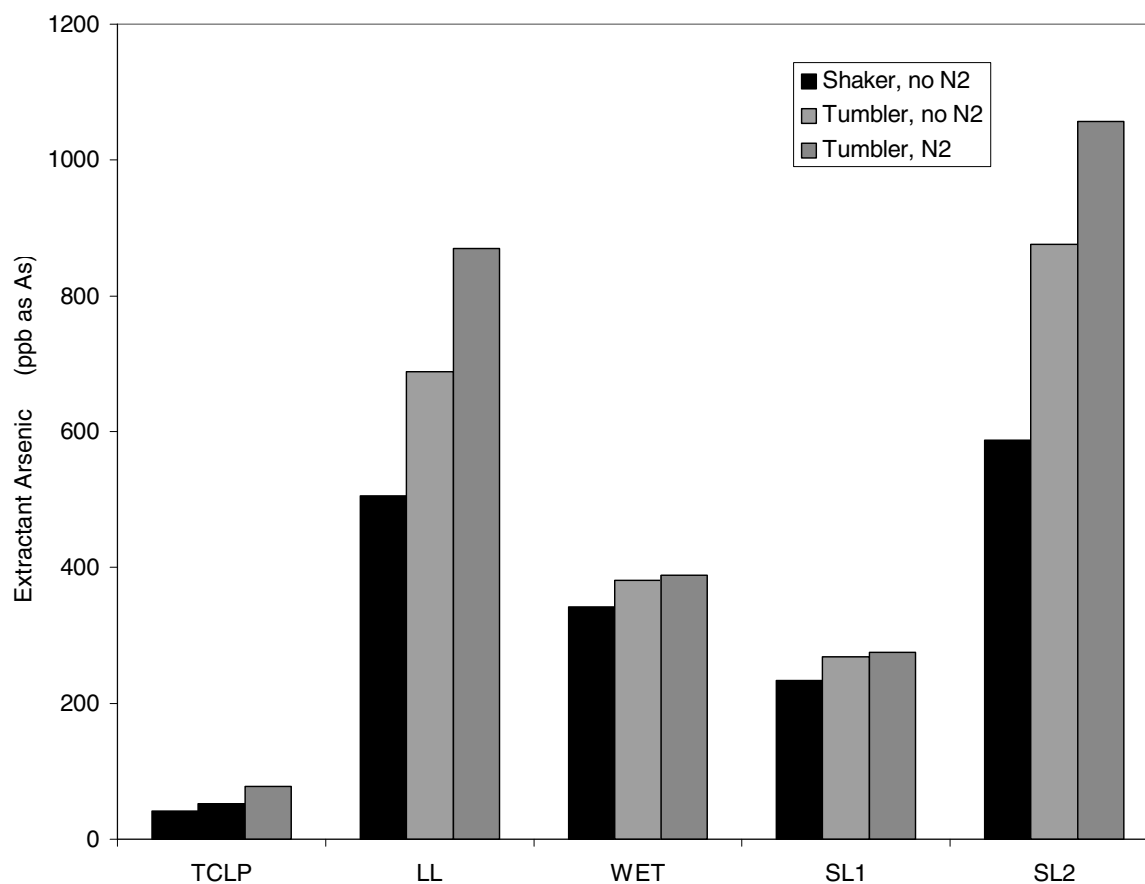


Figure 3.1: Concentration of total arsenic (arsenite + arsenate) in solution from AA samples run for 18 hours on the tumbler with and without a N₂ headspace and on the shaker without a N₂ headspace. (TCLP: Toxicity Characteristic Leaching Procedure, WET: Waste Extraction Test, SL1: Simulated Leachate 1, SL2: Simulated Leachate 2, LL: Landfill Leachate)

(NOM) decreased arsenate adsorption on AA by a factor of 3. Other factors, like competition from other ions (phosphate, sulfate, silica, etc.) present in LL, also might enhance arsenic leaching from the AA residual by LL.

The LL and SL2 generate As(III) in addition to As(V), whereas the WET and SL1 do not. This is expected as the LL and the SL2 leachates are the most strongly reducing of the leachates (Table 3.1). However for the TCLP tests, small amounts (about 12% of total) of As(III) were observed confirmed in duplicate tests, even though the ORP was not sufficiently low (Appendix B).

Differences in the TCLP and WET solid to extractant ratio further impedes direct comparison of results. The TCLP prescribes a solid to extractant ratio of about 1:20 (w/w), while the WET prescribes 1:10 (w/w). The actual leachate and the two simulated leachates used ratios of 1:20 so that the results could be directly compared to the TCLP test. Without knowledge of the isotherm for each fluid/solid mix, the exact impact of this disparity could not be quantified, but qualitatively as the mass fraction of solid decreases the final leachate arsenic concentration should also decrease. Thus, the higher concentration of arsenic in solution for the WET versus TCLP test (Figure 3.1) is partially due to the higher solid fraction in the test. However the WET extracted only about half the arsenic of the LL, which has the same solid concentration as the TCLP.

When the tests follow the WET procedure (48 hour exposure, shaker table, N₂ head), the results are amplified (Figure 3.2). Again the WET leaches more than the TCLP test, yet the WET results are only 60% of the total arsenic leached by LL. Furthermore, the 48 hour WET yields about 8 times the arsenic leaching of the 18 hour TCLP test. In separate kinetic trials it was found that the As concentration in the leachate increased in all tests between 18 and 48 hours, and infact increases even beyond 48hours. Upto 10% more leaching was observed when the solutions were allowed to equilibrate upto 6 weeks.(Data not shown). Some of the 48 hour trials on the LL and SL2 also showed traces of methylated arsenic species like MMA suggesting that microbial activity can also be expected with a longer leaching time.

The three non-standard leachates behave very differently (Figure 3.1), even though both simulated leachates show compositional similarities to the landfill leachate. SL1 is much less aggressive than LL, while the SL2 is consistently more aggressive than LL (as well as the TCLP and WET). SL2 has a very high organic concentration, very high ionic strength and, due to the presence of hydroxylamine, a strong reducing character. The organic matter will enhance arsenic solubility although this is not likely a major factor since SL1 has a TOC close to SL2 and about six fold greater than LL. Both SL2 and LL

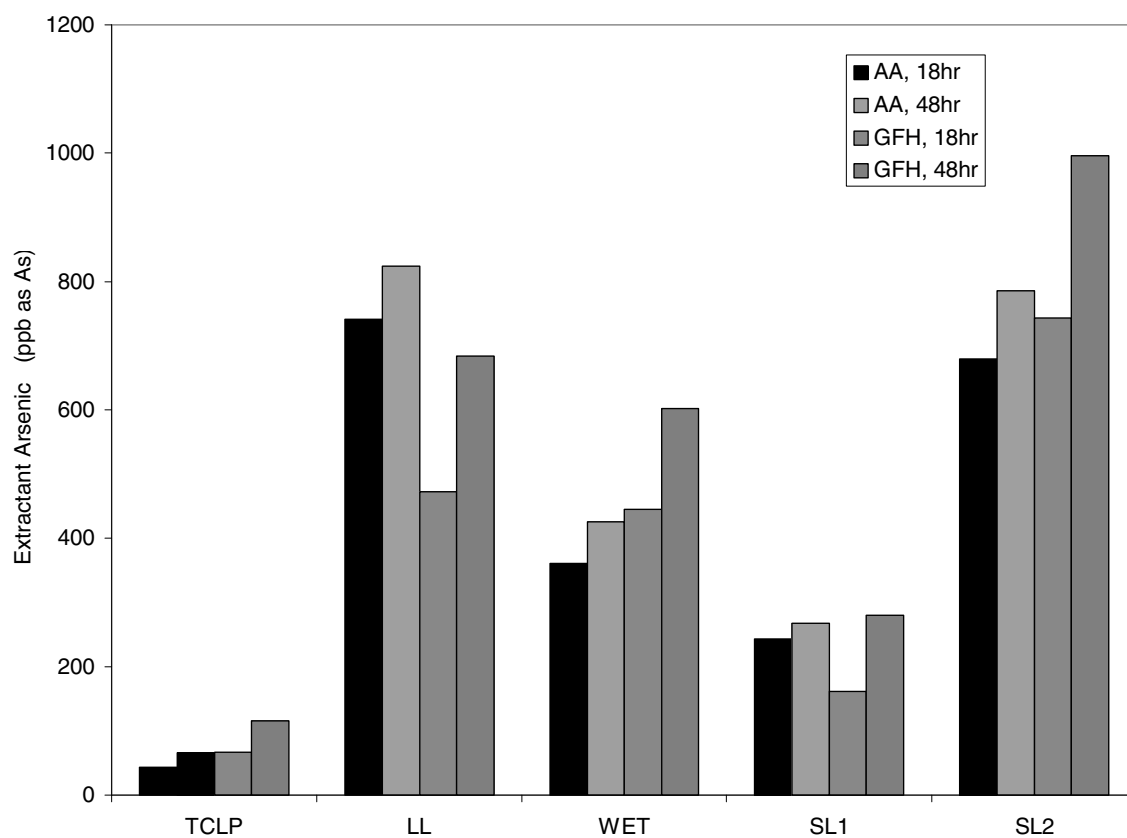


Figure 3.2. Concentration of total arsenic (arsenite + arsenate) in solution from AA and GFH run on the shaker table for 18 and 48 hours with a N₂ headspace.

have higher ionic strengths (a factor of 3 or greater) than any of the other leachates. A greater ionic strength will potentially produce two counteracting (although unlikely to be equal) effects. The greater concentration of anions (particularly multivalent) will lead to greater direct competition with arsenate for the available surface adsorption sites (in the manner of ion exchange) and greater partitioning of the sorbates to the surface due to compression of the electrostatic double layer (assuming non-specific adsorption). In both WET and SL2, there is a high concentration of citrate (0.2M). The pK_a s of citric acid are 3.13, 4.72 and 6.33 (Benjamin, 2002). At the pH of the WET and SL2 tests, there will be significant concentrations of doubly and triply charged citrate anions. Thus, if the interaction of citric acid with the sorbent surface is significant, its competition with AsO_4^{3-} would increase leaching of arsenic in WET and SL2. This may apply to LL too, but it will be dependent on the unknown concentrations of polyvalent anions in LL. However, the most likely explanation for the greater aggressiveness of the LL and SL2 lies in the lower pe of these leachates (Table 3.1). As (V) partitions much more strongly to AA than As (III) at acidic or near neutral pH (Lin and Wu, 2001). In both SL2 and LL As (III) is found in the leachate indicating arsenate reduction is occurring during exposure. The reductive nature of SL2 and LL mimic the highly reducing character of mature MSW landfills and the mobilization of arsenic via reduction of arsenate to arsenite would be expected to play a significant role in actual landfill disposal. Although

not studied here, the anaerobic microbial activity characterizing mature MSW landfills is expected to further enhance arsenic mobilization from AA (Ela et al., 2003).

Aluminum analysis was done after the leaching tests in samples that were expected to have the most aggressive leaching, and hence the highest concentrations of dissolved aluminum. Both 18 and 48-hour samples were analyzed for all leaching tests conducted in the tumbler with a N₂ headspace. With the exception of LL, all samples analyzed had an aluminum concentration of less than 100µg/L (Appendix B). The LL sample was not analyzed for aluminum before the experiment was run, so it could not be concluded whether the high aluminum concentration in the leachate was due to leaching or its presence in the LL matrix. Concentrations of less than 100µg/L were considered non-hazardous since the Secondary Maximum Contaminant Level (SMCL) for aluminum is 200µg/L. Using this criterion the test results indicate that aluminum dissolution from any of the leaching procedures does not pose an environmental hazard. By the same token it is not expected that dissolution of the activated alumina surface greatly affects arsenic loading.

GFH

The GFH results show similar (albeit often amplified) trends to the AA results. Figures 3.3 and 3.4 show the arsenic and iron leaching observed from the GFH samples run on the tumbler for 18 hours with a N₂ headspace. (An arsenic concentration of 45.5µg/L was observed using the standard TCLP with ambient air headspace). The leached arsenic

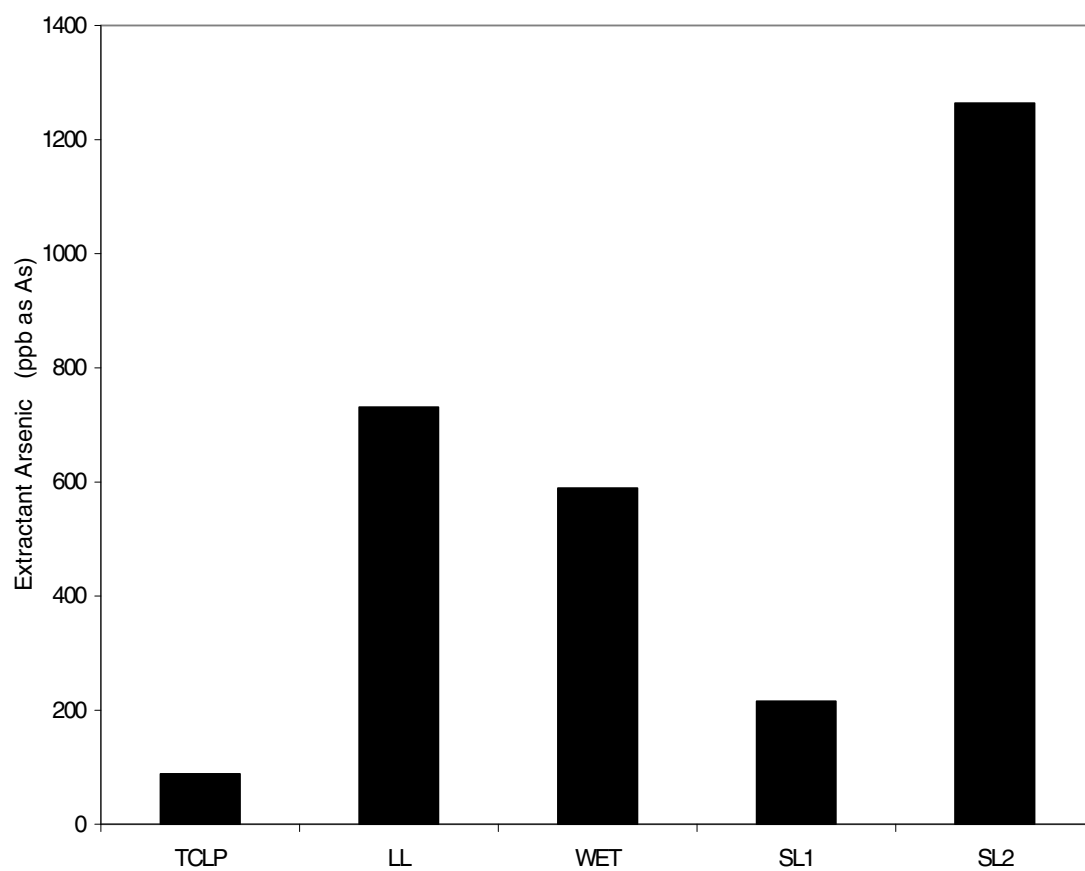


Figure 3.3. Concentration of arsenate in solution from GFH samples run on the tumbler for 18 hours with a N₂ headspace.

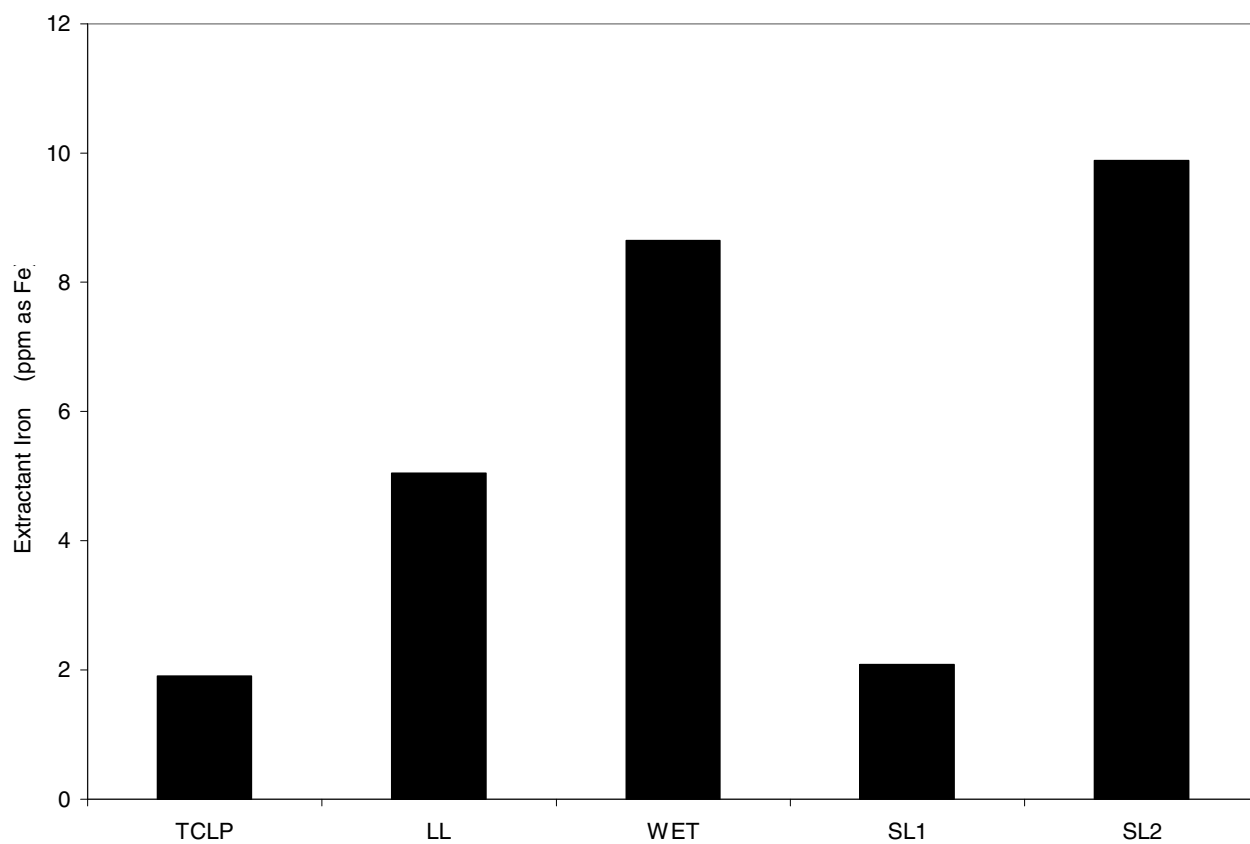


Figure 3.4. Concentrations of iron in solution from GFH samples run on the tumbler for 18 hours with a N_2 headspace. The background concentration of iron in the landfill leachate was 28ppm.

concentration is highest in SL2, followed by LL with the TCLP showing the least leaching. Although the WET better matches the LL results, it is still an insufficiently challenging environment for the leaching of arsenic from GFH to predict landfill disposal behavior. The TCLP is the least conservative test for estimating GFH arsenic leaching expected in landfills.

For all tests the leached arsenic from GFH ranges from 1.5 times to 4 times higher than the corresponding concentration from activated alumina. The GFH capacity for arsenic is much higher than that of the AA. The GFH and AA batches prepared at equilibrium with 31.0 and 21.8 $\mu\text{g/L}$ arsenic carried solid concentrations of 7.81mg/g and 1.25mg/g, respectively. Thus, similar percentages of leaching would result in about 6X higher solution concentrations with GFH than AA. Although the leached arsenic concentration from GFH is greater than from AA, the relative fraction of arsenic extracted from GFH (mass in solution/mass in solid) is less than AA. For example, in the WET test the fraction of arsenic extracted from GFH is 1.6E-5, whereas for AA it is 5.4E-5. The arsenic binding on the GFH surface is more stable than on the activated alumina, although the higher capacity results in GFH leachate concentrations greater than for AA. This would be accentuated if dissolution of the iron substrate continued to the point that the solid surface area changed significantly as might occur over long exposure to leachate in a MSW landfill. This should not be a factor in the batch leaching tests reported here, where the maximum iron mass leached (SL2) accounted for less than 0.1% of the total

GFH mass. (The landfill leachate had a background iron concentration of 28mg/L in solution). Citrate is a strong ligand for ferric iron complexation (Hooper et al., 1998), so the citrate (34g/L) present in WET and SL2 contributes to higher iron solubilization in these solutions.

Interestingly for the GFH vis-a-vis the AA, no As(III) is observed, even though some of the samples showed the presence of very small amounts of methylarsonous acid, MMA(V). A significant amount of iron was dissolved during the GFH leaching tests (Figure 3.4). This is expected since the standard electrode potential of the Fe(III)/Fe(II) couple is more positive than the As(V)/As(III) couple (Bockris and Khan, 2003). This explains both the high concentration of iron in solution in the GFH samples and the absence of As(III). However, there is no similar couple in play in the alumina system, and hence there is not much dissolution of the the alumina, but As(III) is formed.

Effect of Duration of Tests

All tests were done for two different durations: 18 and 48 hours. For the different leaching tests done on the shaker table with a N₂ headspace (Figure 3.2), none reach equilibrium in 18 hours. Arsenate adsorption on AA and GFH reached greater than 95% of equilibrium in 48 hours (Chapter 4). The disequilibrium observed upto and beyond 48 hours suggest that the leaching is not mass transport limited, rather it is controlled by the slower reaction rate. For AA, the adsorbed arsenic concentration increased 15-32% from 18 to 48 hours, whereas for GFH the increase was between 8-20%. The LL and SL2 have

the greatest absolute value of concentration increase between 18 and 48-hour periods. However the fractional increase in concentration is the highest in the TCLP, although it exhibited the lowest absolute concentration of arsenic leached. This accentuates the conclusion that for the long fluid residence times characteristic of landfills, the 18 hour TCLP will particularly underestimate arsenic leaching from both GFH and AA.

Effect of Agitation

The TCLP prescribes agitation in an end-over-end tumbler, whereas the WET test is performed on a shaker table. All tests were duplicated under both agitation modes. Figure 3.5 shows the results for AA and GFH respectively, with the tests done for 48 hours with no N₂ headspace. The concentrations in the tumbler were between 25 and 65% higher than those obtained by the shaker table. The samples contain about 5% by weight of solid (10% for the WET case) and it was noticeable with shaker table agitation that the solids settled to the bottom without substantial suspension, thus, reducing the flow of bulk water over the solid surfaces. The GFH samples show a bigger difference in concentration between the tumbler and the shaker table than the AA samples (Figure 3.5). The possible explanation for this behavior is that the end-over-end rotation tends to break up the relatively fragile GFH granules, in addition to turbulently mixing them. However this was not further investigated by measuring the particle size of the GFH granules before and after the leaching trials.

Effect of N₂

The effect of N_2 was investigated by duplicating all the tests in the presence and absence of a N_2 headspace on the tumbler for 48 hours (Figure 3.6). In all the tests a N_2 headspace increased arsenic concentration after leaching. Also the ORP of the solutions with a N_2 headspace was 20 to 60mV lower than those in the absence of N_2 at the end of the experiment (Appendix B). This shows that the anoxic environment is more reducing and helps in mobilizing the arsenic from the surface. Among the different solutions, for both AA and GFH, the LL and SL2 exhibit 30-50% higher concentrations with the application of N_2 . The TCLP, WET and the SL1 have between 10 and 20% increase in total arsenic concentration with N_2 . LL and SL2 have the lowest initial ORP values while the TCLP, WET and SL1 have much higher ORP values (Table 3.1). For LL and SL2, the presence of N_2 results in anoxic conditions, which in turn preserves the reducing capacity and results in greater arsenic leaching. The sensitivity of arsenate leaching to pe from ferrioxhydryde sludges has been previously reported (Meng et al., 2001).

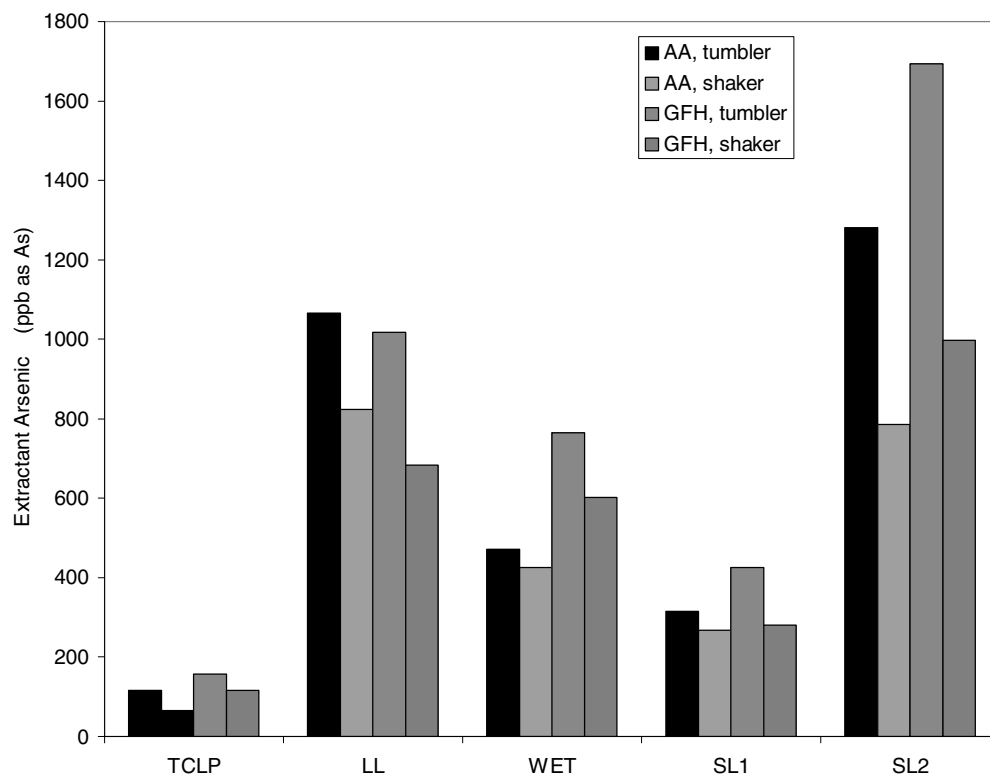


Figure 3.5. Concentration of total arsenic (arsenite + arsenate) in solution from AA and GFH samples run on the shaker table and tumbler for 18 hours with no N₂ headspace.

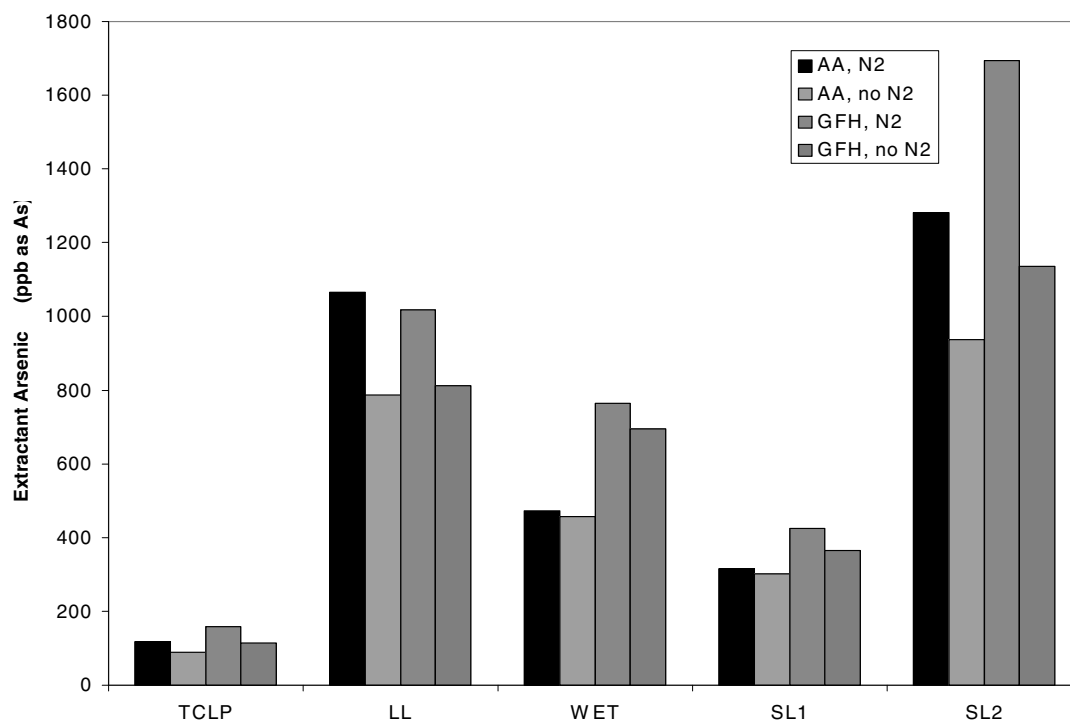


Figure 3.6: Concentration of total arsenic (arsenite + arsenate) in solution from AA and GFH samples run on the tumbler for 48 hours with and without a N₂ headspace.

Aggressiveness of Protocols

SL2 leached more arsenic under all conditions than the other tests. LL, SL1 and WET leach less aggressively, while the TCLP is the weakest extractant. SL2 was formulated with a high organic concentration comparable to that in a mid-strength landfill (as well as matching the citrate concentration of WET) and a higher ionic strength and pH than all the remaining solutions. SL2 has a much higher TDS value than the other solutions (Table 3.1), while the TCLP has the least TDS. Thus, some of the explanation for the weak performance of the TCLP may lie in the paucity of competing ions. In other work (Amy et al., 2000), it was observed that 10-20% less arsenate sorption occurred on iron oxide coated sand for sulfate concentrations of 100mg/L than for sulfate-free conditions. In some leaching conditions like LL and SL2 with high organic concentrations, in addition to the generation of inorganic As(III) and As(V), organic arsenic as MMA (V) was generated. However in all cases the MMA(V) concentration was small.

In a number of cases, the arsenic solution concentration exceeded 1000 μ g/L. This level is significant, because if the toxicity limit is lowered to 100X the MCL as is customary, some of the leaching tests, especially on GFH, would classify the residual as a hazardous waste. The comparative results indicated the WET test was more challenging than the TCLP and increased arsenic leaching by a factor of 5 or more. The TCLP mobilized less arsenic from both sorbents than any of the other leaching methods and leached significantly less arsenic than when an actual landfill leachate was used. Overall, the

study suggests the TCLP poorly predicts the stability of arsenic on AA and GFH and, in most cases, the WET procedure also under-predicts arsenic leaching. An ideal short-term leaching protocol would indicate the highest concentration of arsenic that could be expected under actual landfill conditions. From an ease of protocol application perspective, an abiotic, short-term batch test would be preferred to a biotic, long-term, continuous flow test, although the latter would most accurately mimic the most aggressive landfill conditions. Of the protocols investigated, LL is obviously the closest analog to the leachate from a MSW landfill, but it is likely it also underestimates actual landfill leaching, as it does not include the anaerobic microbial and long-term processes that would be expected to further increase arsenic leaching (Ela et al., 2003). Consequently, SL2, which produced arsenic mobilization greater than LL is arguably the most appropriate of the protocols investigated. However, this still requires quantitative comparison with long-term, biologically active tests before it is accepted as a conservative predictor of arsenic leaching from water treatment residuals under MSW landfill conditions.

²CHAPTER 4EFFECT OF pH, COMPETITIVE ANIONS AND NOM ON THE LEACHING OF
ARSENIC FROM SOLID RESIDUALS

Introduction

Recent revision of the Maximum Contaminant Level (MCL) for arsenic in drinking water from 50 µg/L to 10 µg/L by the Environmental Protection Agency (EPA) will impact over 4000 U.S. utilities (*USEPA, 2001*). Of the EPA identified treatment options, adsorption onto solid media is the most attractive for the small utilities (serving populations of less than 3,301), which comprise over 92% of the utilities affected (*USEPA, 2001*). Activated Alumina (AA) and granular ferric hydroxide (GFH) are representative of the solid sorbents that will be most widely used. Activated alumina has been recommended as a Best Available Technology (BAT) by the EPA, whereas GFH studies have shown it may be preferred to AA due to its greater adsorption capacity (*Amy et al., 2000*). Most other alternative sorbents, (i.e., Bayoxide E-33, green sand, Aqua-bindTM, and iron-modified AA) exhibit either an alumina or iron oxy/hydroxy surface (*USEPA, 2001a*). All arsenic treatment technologies will generate a residual stream containing the arsenic removed from the drinking water. Solid sorption processes as well as several other technologies (i.e., modified lime softening, coagulation assisted microfiltration, enhanced coagulation) will generate arsenic-bearing solid residuals (ABSRs). The Toxicity Characteristic Leaching Procedure (TCLP) (*Federal Register*,

1986) is used to assess the leaching potential of arsenic from ABSRs. Currently most ABSRs pass the TCLP and are considered safe for disposal in non-hazardous, mixed solid waste (MSW) landfills. However, recent research has shown that the TCLP does not appropriately estimate the leaching potential of arsenic residuals under landfill conditions (Ghosh *et al.*, 2004), so the potential for arsenic mobilization from landfilled ABSRs presents an obvious environmental concern. In a landfill, many biotic and abiotic factors may influence the leaching of arsenic from the ABSRs and there has been scant research evaluating the relative significance of the various factors in terms of arsenic mobilization from landfill disposed ABSRs. Among the abiotic factors, pH, NOM and competitive anions like phosphate, bicarbonate, sulfate and silicate are potentially important. Consequently, this paper reports on work undertaken to comparatively evaluate the importance of these abiotic factors in the context of landfill conditions and arsenic leaching from ABSRs. Previous research has investigated the impact of most of these abiotic factors on sorption of selected anions on various metal oxy/hydroxides (i.e., arsenate on Ettringite (Myneni *et al.*, 1997), arsenate on goethite (Hongshao and Stanforth, 2001), arsenate/arsenite on ferrihydrite (Jain and Loeppert, 2000). However, this work specifically investigates the previously unreported impact of these factors on actual sorbents used in drinking water arsenic removal processes and for the range of concentrations characteristic of the range of conditions in actual mixed solid waste, non-hazardous landfills. Limiting the scope of this work to the abiotic factors listed is not to suggest that these are the only potentially important factors dictating ABSR behavior under landfill conditions and additional work not reported here is underway to evaluate

additional factors such as microbial activity, redox conditions and the hydraulic environment.

Arsenic in drinking water supplies is present as either arsenite, As(III), or arsenate, As(V). In near-neutral pH waters, arsenite is present primarily as uncharged arsenous acid whereas arsenate is predominantly in the anionic form. Since metal oxy/hydroxide adsorption of ions is typically more efficient than of uncharged species (*Stumm and Morgan, 1996*), EPA recommends preoxidation of water containing a significant amount of arsenite prior to an arsenic removal technology (*USEPA, 2001*). Consequently, in this research only arsenate desorption from residuals is studied. Several studies have investigated the effect of abiotic parameters on the adsorption of arsenic onto solid sorbents. Recent works by Lin *et al.* (2001) and Dixit *et al.* (2003) investigated the effect of pH on the adsorption of arsenic on activated alumina and iron oxide minerals, respectively. Adsorption site competition and/or arsenic sorption inhibition have been reported for carbonate/bicarbonate on ferrihydrite (*Holm, 2002, Fuller et al., 1993, Meng et al., 2000, Apello et al., 2002*), phosphates on iron oxide (*Dixit et al., 2003, Hongshao et al., 2001, Manning et al., 1996, Jain et al., 2000*), sulfate on AA (*Xu et al., 1988*), silica on hydrous ferric oxides (*Holm, 2002*), and NOM on AA (*Xu, 1991*). Significantly less literature is available on the desorption of arsenic, which is the focus of concern for ABSR disposal. Even though the direction of change of the system in response to a change of a given parameter (i.e., pH, NOM concentration) is expected to be the same for both adsorption and desorption, neither the kinetics nor the mechanisms of adsorption/desorption are always analogous. Metal adsorption-desorption studies on

amorphous ferric hydroxides (AFH) show significant hysteretic desorption, the degree of which varies with residence time, pH, and organic complexation of the sorbent/sorbate. The reversibility of some sorption processes has been found to be slow, on the order of weeks. (*Schultz et al., 1987, Coughlin et al., 1995, Ainsworth et al., 1994*). Myneni *et al.* (1997) found similarity between adsorption and desorption equilibrium concentrations of arsenic on Ettringite, but the desorption was much slower than adsorption. The work suggested that once sorbed on the surface, the surface bond to arsenate changes. Grossl *et al.* (1997) and Fendorf *et al.* (1997) observed a two-step adsorption process of arsenate on goethite. There was relatively rapid monodentate, inner sphere adsorption followed by a slower relaxation to a more stable bidentate, inner sphere bonding state. In addition, surface precipitation may occur. When an ABSR is exposed to a leaching solution, the solid substrate surface may solubilize and release ions that subsequently participate in re-precipitation reactions forming new solid phases, which can potentially incorporate arsenate or cover over previously sorbed arsenate (*Hongshao et al., 2001*). These considerations motivate study of the desorption behavior of arsenate from sorbent surfaces as a unique process from adsorption.

This study's objectives are (i) to determine the kinetic rates of desorption of arsenate from actual treatment sorbents with variations of pH, competitive anions and NOM concentration, (ii) to measure the equilibrium desorption (as opposed to adsorption) of arsenate when exposed to the range of pH and concentrations of competitive anions and NOM expected in a landfill, and (iii) to compare the results to the extent of desorption observed in TCLP and actual landfill leachate tests. The materials and methods evaluated

are specifically chosen to be representative of the actual ABSRs that will be generated from water treatment processes, and the experimental conditions to be representative of the concentration ranges reported in the non-hazardous, mixed solid waste landfills in which ABSRs are to be disposed.

Materials and Methods

Sorbents

Conventional AA is well accepted for the semi-selective removal of arsenic from potable water. The AA used is AA400G, manufactured by Alcan Corp., with particle size, 80-100 mesh (149-177 μm); specific surface area, 350-380 m^2/g ; and pore volume, 0.50 cm^3/g (manufacturer's product specifications). This sorbent can be regenerated, although this is not expected to be frequently practiced due to issues of cost and handling of hazardous chemicals onsite. (USEPA, 2001, USEPA, 2001a).

Granular ferric hydroxide (GFH) is a weakly crystalline $\beta\text{-FeOOH}$ produced by conditioning compacted iron hydroxide slurry into irregular grains up to 2 mm diameter (Driehaus *et al.*, 1998). GFH[®] is manufactured by GEH and distributed by U.S. Filter. The properties are: grain size 0.2-2.0 mm, specific surface area, 250-300 m^2/dm^3 , and a bulk density of 1.22-1.29 kg/dm^3 . It is designed as a throwaway media.

Pre-equilibration of the solids

Single batches of AA and GFH were pre-equilibrated with arsenate. For each, an aqueous suspension was prepared with 200 g of sorbent in 1 L of solution. All solutions were

made using purified water (Milli-QTM Water System by Millipore). The initial concentration of arsenic added was 204 mg/L (as As) and 1196 mg/L (as As) for AA and GFH, respectively. Arsenate was added as sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, KR Grade, Aldrich Sigma). Solution ionic strength was adjusted to 0.1 M with NaCl (GR Grade EM Science). The pH was adjusted to 7.0, using hydrochloric acid (Spectrum) or sodium hydroxide (Sigma). The batches were equilibrated for 6 days on a shaker table (Orbit, reciprocating speed 125 rpm). After equilibration, the aqueous concentration was 10.27 $\mu\text{g/L}$ (as As) and 20.91 $\mu\text{g/L}$ (as As) for AA and GFH, respectively, which is within the concentration range of concern of arsenic in drinking water. The sorbed concentrations were 1.02 mgAs/gAA and 5.98 mgAs/gGFH. All subsequent kinetic, pH and competitive anion tests used AA and GFH from these single batches.

Kinetic Trials

Kinetic trials were conducted at pH 8.0, 9.0 and 10.0, as well as for one concentration each of a competitive anion at pH 7.0. All kinetic experiments were performed in duplicates. An amount of 5.0 g of the arsenic-sorbed-solid was transferred to a 125 mL Nalgene bottle and 97.5 mL of Milli-Q water was added (following the TCLP protocol). The solutions were placed on the shaker table. Every 6 hours samples were collected and the pH adjusted to within ± 0.2 of the predetermined pH. The concentrations of the anions used in the tests were 1.2 g/L for bicarbonate, 200 mg/L for NOM (as TOC), 20 mg/L for phosphate, 10 mg/L for silicate and 500 mg/L for sulfate. Sodium bicarbonate

(NaHCO_3 Aldrich), sodium phosphate (NaH_2PO_4 , Sigma), sodium sulfate (Na_2SO_4 , Sigma) and silicic acid (H_2SiO_3 , Mallinckrodt) salts were used for stock preparation. Humic acid, sodium salt (Aldrich, carbon content 39.03%) was used as the NOM source. When 1.0 g of this humic acid was dissolved in 1.0 L of water, the TOC measured 341.1 mg/L. Kinetic experiments were run for 96 hours in sealed, Nalgene bottles with minimal headspace. The temperature for all tests was kept constant at 23°C and all samples were filtered through a 0.45 μm filter.

Desorption Trials

For the desorption experiments, 5.0 g of solid from the original arsenic sorbed batch were treated with 97.5 mL Milli-Q water. Values of pH tested were 8.0, 9.0 and 10.0. The samples were allowed to equilibrate for 48 hours at 23°C, on the shaker-table, with pH adjusted after every 6 hours. Liquid samples were 0.45 μm filtered before analysis.

For the competitive anion experiments, 5 concentrations for each anion were selected (Table 4.1). These concentrations bracket the highest and lowest concentrations of the respective anions expected to be found in a typical landfill leachate. For each of the trials, 5.0 g of the solid were placed in a 125 mL Nalgene bottle and 97.5 mL of Milli-Q water containing the competitive anion was added. The pH was adjusted after the addition of the anions to either 7.0 or 9.0 for each loading of each anion. The samples were equilibrated on a shaker table for 48 hours, and 0.45 μm filtered before analysis. For the case of pH dependency, a separate set of adsorption trials was conducted alongside the desorption trials. For the adsorption experiments, an aqueous suspension was prepared

Table 4.1: Typical pH and concentration ranges of anions in landfill leachate and the concentrations of anions used in this work

Parameter	Landfill Leachate Range (in mg/L)*	Concentrations in Los Reales Landfill, Tucson, AZ (in mg/L)	Concentrations used in this work (in mg/L)
pH	3.7-8.9	7.16	7.0, 8.0, 9.0, 10.0
Bicarbonate	34- 15050	2219	60, 120, 1200, 2400, 12000
Phosphate	0.11- 234	0.17	0.2, 2, 20, 100, 200
Sulfate	105- 4900	267	50, 250, 500, 2500, 5000
Silicate	5.1-51	6	2.5, 5, 10, 20, 40
NOM (as TOC)	76-40000	378	10, 20, 200, 2000, 20000

* Bagchi (1994) is a compilation of municipal waste leachate data

with 5 g of arsenic-free-sorbent in 97.5 mL of solution. The initial concentration of arsenic added was 0.51 mg/L (as As) and 2.99 mg/L (as As) for AA and GFH, respectively. Solution ionic strength was adjusted to 0.1 M with NaCl. The pH was adjusted to 7.0, 8.0, 9.0 or 10.0, depending on the experiment, using HCl or NaOH. The batches were equilibrated for 48 hours on a shaker table, with pH being adjusted every 8 hours. The adsorption experiments were conducted in duplicates.

Leaching Trials

Solids were subjected to three leaching protocols, the TCLP, Landfill Leachate (LL) and Synthetic Landfill Leachate (SLL).

TCLP The appropriate extraction fluid for both AA and GFH is extraction fluid #1 of the TCLP (*Federal Register, 1986*). This is prepared by adding 5.7 mL of glacial acetic acid ($\text{CH}_3\text{CH}_2\text{OOH}$) and 64.3 mL of 1N NaOH and bringing it up to 1000 mL with purified water. The pH is 4.93 ± 0.05 . When a waste contains both solid and liquid phases, with the solid being more than 0.5% by weight, the TCLP prescribes a sample size of 100 g (solid plus liquid phase). For this work, the TCLP was run at 0.05 scale; meaning 5.0 g of solid and 97.5 mL of extraction fluid. The solids did not require size reduction. The TCLP test is done in an end-over-end tumbler for 18 ± 2 hours. Sealed Nalgene bottles were used with minimal headspace of ambient air. An additional test followed the TCLP protocol, but for 48 hour duration.

Landfill Leachate (LL). Landfill leachate was obtained from the Pima County, Los Reales Landfill, Tucson, Arizona. The leachate was extracted from a cell containing mixed solid waste (MSW). The leachate (Table 4.1) included no detectable arsenic. LL experiments were done for 18 and 48 hours, otherwise following the TCLP procedure (5 g solid, 97.5 mL leachate, tumbler agitation with minimal ambient air headspace).

Synthetic Landfill Leachate (SLL). A synthetic solution was prepared with the same pH and composition (HCO_3^- , SO_4^{2-} , PO_4^{3-} , and TOC) as the LL (Note: all reagents used were sodium salts specifically chosen to avoid cationic complexation). The major differences between this solution and the LL were the absence of microbial populations, the higher redox potential and the complexity of the organic material. SLL trials were done for 48-hour duration on the tumbler with ambient air headspace.

Analytic Methods

Arsenic was measured by Inductive Coupled Plasma Mass Spectrometer (ICP-MS, Agilent 7500a) using HPLC for pretreatment. The system is an Agilent 1100 HPLC (Agilent Technologies, Inc.) with a reverse-phase C18 column (Prodigy 3u ODS(3), 150x4.60mm, Phenomenex, Torrance, CA) maintained at 50°C. The detection limit for this instrument was 0.01 µg/L and analysis of replicates was within ± 5%. Sulfate and phosphate were analyzed using Dionex DX 500 Ion Chromatography System, with a detection limit of 10 µg/L for both sulfate and phosphate. The TOC in NOM was measured using a Shimadzu Total Organic Carbon Analyzer, with a detection limit of 0.01 mg/L. Silicate was analyzed using the Molybdosilicate method (*Standard Methods*,

1989), and a Hitachi U-2000 Spectrophotometer. Bicarbonate was analyzed by titration with hydrochloric acid to pH 4.3.

Results and Discussion

Kinetics of Desorption

Figure 4.1 shows the time dependent desorption of arsenic from AA and GFH at pH 8.0, 9.0 and 10.0. Minimal change in arsenic concentration was observed for pH 9.0 and 10.0 after 36 hours for both ABSRs. For pH 8.0, the solutions reached near-equilibrium by 48 hours. Lin *et al.* (2001) observed equilibrium was reached in about 17 hours for adsorption of arsenate on AA. The difference between adsorption and desorption kinetics may be related to the difference in rates of bond formation and breakage. Myneni *et al.* (1997) also found slower desorption than adsorption kinetics for arsenate on Ettringite. The observed kinetics might be a consequence of mass transfer effects, interfacial rates of desorption, or a combination of both mechanisms. Intraparticle mass transfer is controlled by the effective diffusivity of the ions in the particle pores. For a representative particle with a diameter of $d=200\text{ }\mu\text{m}$, a characteristic time of $t=24\text{ hours}$ would require an effective diffusivity of $D_{\text{eff}} \sim d^2/t = 5 \times 10^{-9}\text{ cm}^2/\text{s}$, which seems too low for the relatively high internal porosity of both GFH and AA particles. This suggests that interfacial desorption kinetics play a role in the results obtained.

Figure 4.2 shows kinetics of desorption of arsenate from ABSR when competitive anions are added. For sulfate and silicate, the solutions reached near-equilibrium within 24 hours. For phosphate and bicarbonate, the desorbed fraction increased up to 36 hours.

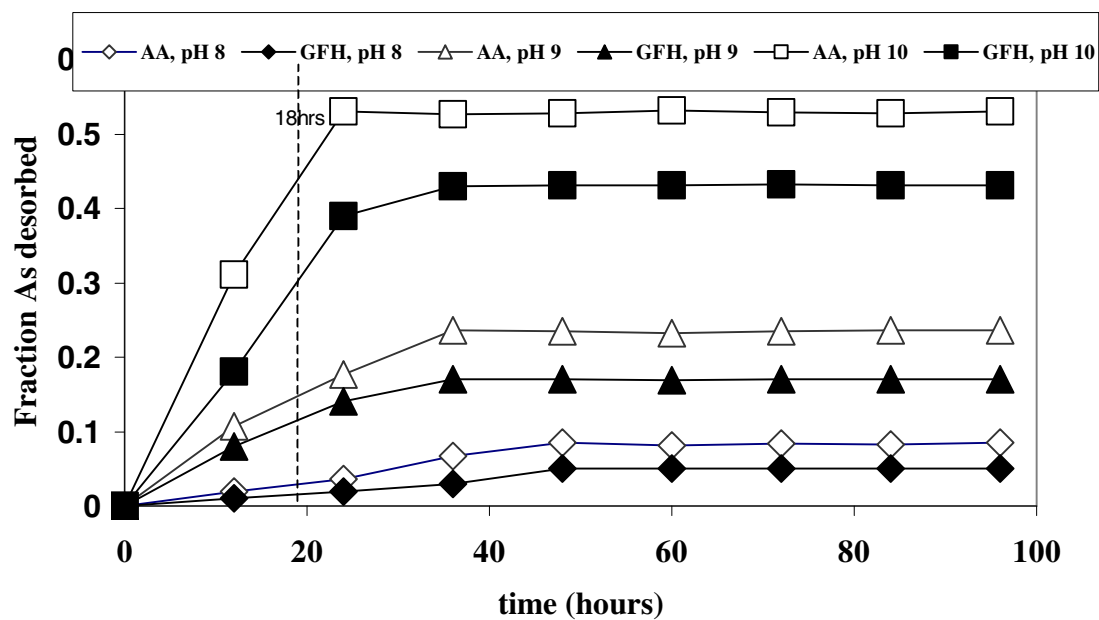


Figure 4.1: Time dependent desorption of arsenate from AA and GFH at pH 8.0, 9.0 and 10.0 for a solid: liquid ratio of 5.0g: 97.5mL at 23° C. Error bars deleted for clarity – maximum relative error in fraction As desorbed is $\pm 0.1\%$.

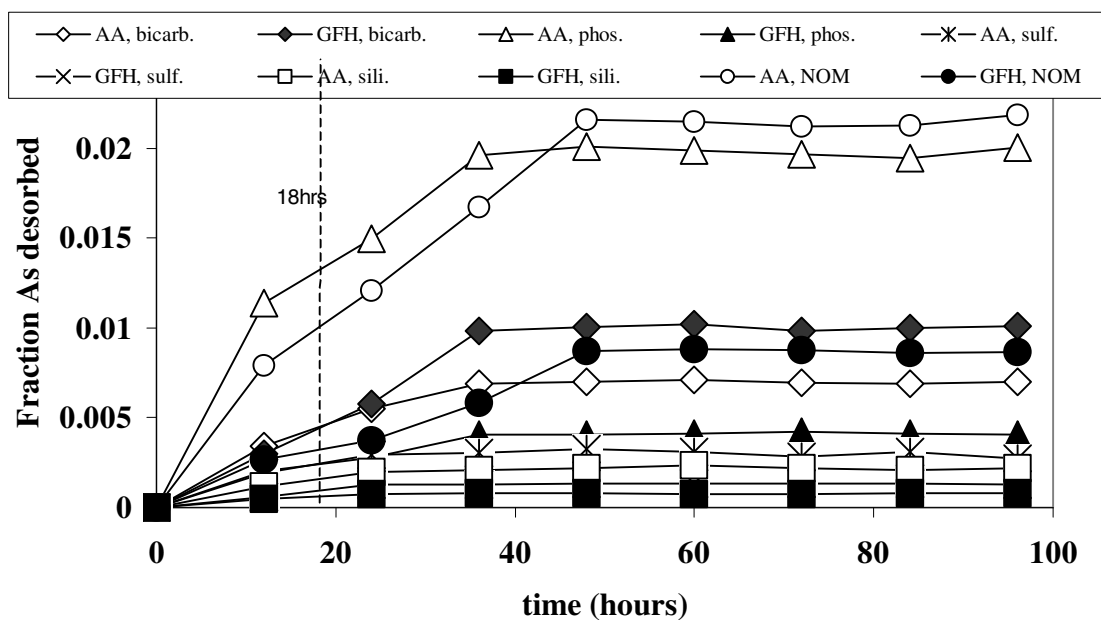


Figure 4.2. Time dependent desorption of arsenate from AA and GFH in the presence of phosphate (20mg/L), bicarbonate (1.2g/L), sulfate (500mg/L), silicate (10mg/L) and NOM (200mg/L as TOC) at pH 7.0 for a solid: liquid ratio of 5.0g: 97.5mL at 23° C. bicarb.= bicarbonate, phos.= phosphate, sulf.= sulfate, sili.= silicate. Error bars deleted for clarity - maximum relative error in fraction As desorbed is $\pm 0.3\%$.

The NOM solutions only reached equilibrium after about 42 hours. In general, the AA solutions reached near-equilibrium faster than the GFH solutions, which could reflect their lower particle size and its contribution to intraparticle diffusion. However, the difference in rates observed for the various competitive ions points to an interfacial kinetic limitation, since diffusion rates of the various ions should not differ much in magnitude. Based on these results, all subsequent equilibrium experiments (excluding the standard TCLP) were performed with a 48-hour duration to ensure near-equilibrium conditions. None of the solutions reach equilibrium in 18 hours (shown with vertical lines in Fig 4.1 and 4.2), accentuating the previous observation (*Ghosh et al, 2004*) that the 18-hour duration specified for TCLP probably does not achieve equilibrium for extraction of arsenic from ABSRs.

Effect of pH on Adsorption/Desorption

Figure 4.3 shows the equilibrium fraction of arsenic in the liquid measured in adsorption and desorption experiments with AA and GFH at pH 7.0, 8.0, 9.0 and 10.0. This covers the range of pHs expected in a mature landfill (Table 4.1). Significant desorption of arsenic is observed with the increase of pH and a hysteretic behavior is observed. Note that both adsorption and desorption equilibrium fractions are the same at pH 7, since this is the original pH used in the loading of the solid with arsenic. The effect of pH is comparable with results presented by Amy *et al.*(2000) and Lin *et al.*(2001) pH 6.5 and 9.0. As pH increases, the decreasing concentration of solution protons drives more protons from the adsorbent surface, thus making it more negatively charged. The pH_{PPZC}

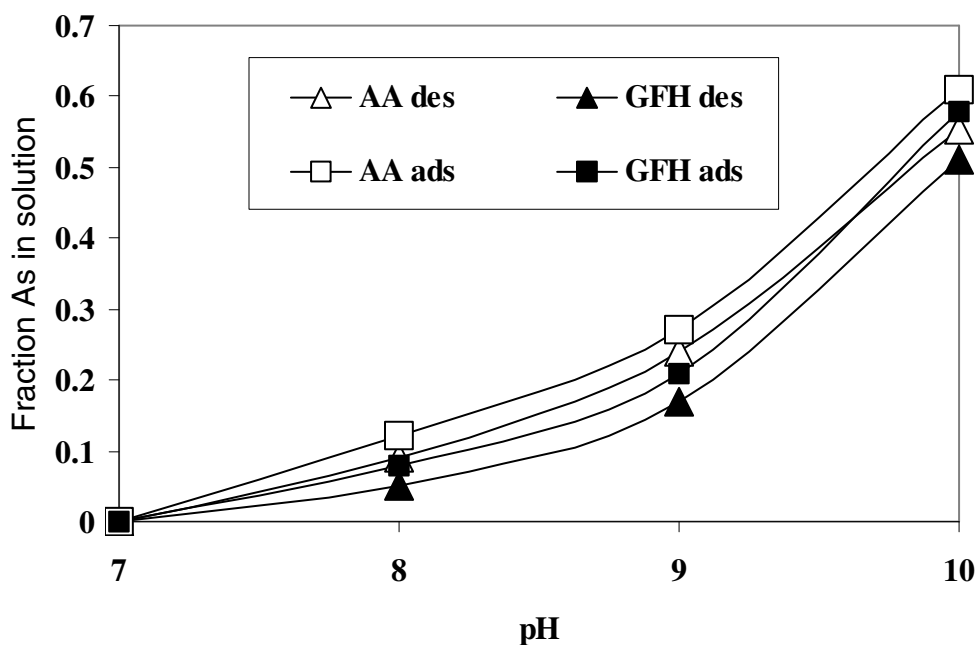


Figure 4.3. Fraction of arsenate in solution in adsorption and desorption experiments from AA and GFH at pH 7.0, 8.0, 9.0 and 10.0. The solid: liquid ratio was 5.0g: 97.5mL and the temperature was 23° C. Error bars deleted for clarity - maximum relative error in fraction As desorbed is $\pm 0.1\%$.

(pristine point-of-zero charge) for $\gamma\text{-Al}_2\text{O}_3$ is 8.5, while for goethite ($\alpha\text{-FeOOH}$) is 7.3 (Davis *et al.*, 1990). The anionic arsenate (H_2AsO_4^- or HAsO_4^{2-}) is increasingly repelled and desorbed as the surface negativity increases. As the pH increases, desorbed arsenate is progressively out-competed by hydroxyl ions for sorption onto surface sites. The increase in arsenate desorption at high pH is of particular significance in mature landfills where the pH ranges from 7.5 to 9.0, with a mid value of approximately 8.2 (Christensen *et al.*, 2001). At any given pH, the fractional desorption of arsenate from GFH is about 5-10% lower than from AA (Figure 4.3), although the absolute concentration of dissolved arsenate in solution is always greater from GFH than AA. This suggests more specific bonding between arsenate and the GFH surface than the AA surface, in addition to a GFH specific capacity exceeding that of AA.

The higher fraction of arsenic in solution in the adsorption experiments than in the desorption experiments might be due to the presence of an energy barrier that must be overcome to mobilize sorbed arsenic. This would indicate the presence of sites on the surface on which arsenate is irreversibly bound within the operating conditions employed in this work.

Phosphate-Induced Desorption

At pH 7.0, about a ten-fold increase in fractional arsenic desorbed is observed between the lowest (0.2 mg/L) and highest (200 mg/L) phosphate concentrations expected in landfills (Table 4.2). The trend is observed for both AA and GFH, even though at any

Table 4.2: Fractional arsenic leached from AA and GFH with NOM and competitive anion addition

Anions	Activated Alumina					GFH				
	0.2	2	20	100	200	0.2	2	20	100	200
Phosphate (mg/L)										
pH 7.0	0.00	0.00	0.01	0.02	0.0307	0.0007	0.0024	0.0041	0.0052	0.0062
	2	98	93	59						
pH 9.0	0.24	0.24	0.24	0.25	0.256	0.1705	0.1716	0.1726	0.1731	0.1737
	15	46	85	36						
Bicarbonate (mg/L)	60	120	1200	2400	12000	60	120	1200	2400	12000
pH 7.0	0.00	0.00	0.00	0.01	0.0136	0.0021	0.0041	0.0103	0.013	0.0141
	16	25	7	05						
pH 9.0	0.24	0.24	0.24	0.24	0.2484	0.1712	0.1722	0.1748	0.1758	0.1767
	11	2	36	68						
Sulfate (mg/L)	50	250	500	2500	5000	50	250	500	2500	5000
pH 7.0	0.00	0.00	0.00	0.00	0.0042	0.0004	0.0008	0.0013	0.0016	0.0017
	07	18	3	35						
pH 9.0	0.24	0.24	0.24	0.24	0.2431	0.1703	0.1706	0.1707	0.1709	0.171
	09	14	22	25						
Silicate (mg/L)	2.5	5	10	20	40	2.5	5	10	20	40
pH 7.0	0.00	0.00	0.00	0.00	0.003	0.0003	0.0006	0.0008	0.001	0.0012
	04	12	2	27						
pH 9.0	0.24	0.24	0.24	0.24	0.2424	0.1702	0.1705	0.1706	0.1707	0.1708
	04	09	19	2						
NOM (mg/L)	10	20	200	2000	20000	10	20	200	2000	20000
pH 7.0	0.00	0.00	0.02	0.03	0.0422	0.0014	0.0029	0.0087	0.0105	0.0123
	38	7	17	5						
pH 9.0	0.24	0.24	0.25	0.25	0.2619	0.1713	0.1718	0.1731	0.1736	0.174
	35	62	42	84						

given phosphate loading, the fraction of arsenic desorbed from GFH is much lower than for AA. For example, at the highest phosphate loading, the fraction of arsenic desorbed from AA is about 3.0% while it is only 0.6% for GFH. At pH 7.0, arsenic release is a function of phosphate added for low phosphate additions, but becomes insensitive at high phosphate addition (Figure 4.4). This insensitivity to amount of phosphate added is observed throughout at pH 9.0. For AA, 279 mmol of As are released per mole of phosphate added between the two lowest phosphate loadings, while only 4.7 mmol of As are released per mole of phosphate added between the two highest phosphate loadings (calculated from Table 4.3). The corresponding numbers for the GFH are 357 and 6.1 mmol of As per mole of phosphate between the two lowest phosphate loadings and the two highest phosphate loadings, respectively. At low concentrations of phosphate added, the amount of arsenic desorbed from the ABSR surfaces approximately matches the amount of phosphate sorbed by the solid. For example, at pH 7 and 0.2 mg/L initial phosphate loading, about 0.03 $\mu\text{molAs/gAA}$ is desorbed, as 0.025 $\mu\text{molPO}_4/\text{gAA}$ is sorbed onto the surface. For GFH at the same pH and phosphate added, 0.135 $\mu\text{molAs/gGFH}$ desorbed as 0.04 $\mu\text{molPO}_4/\text{gGFH}$ adsorbed. The results suggest that both AA and GFH have a number of sites where arsenate ion can be exchanged by phosphate, but the indifference of arsenate desorption to phosphate addition at higher phosphate loadings suggests that not all arsenate sites are exchangeable. Hongshao *et al.* (2001) found in pH 5.15 adsorption trials that arsenate binds more strongly than phosphate on goethite and that the non-exchangeable fraction of arsenic increases with the pre- They found that after a 144 hour pre-equilibration time (the time in our study), 14 μmol

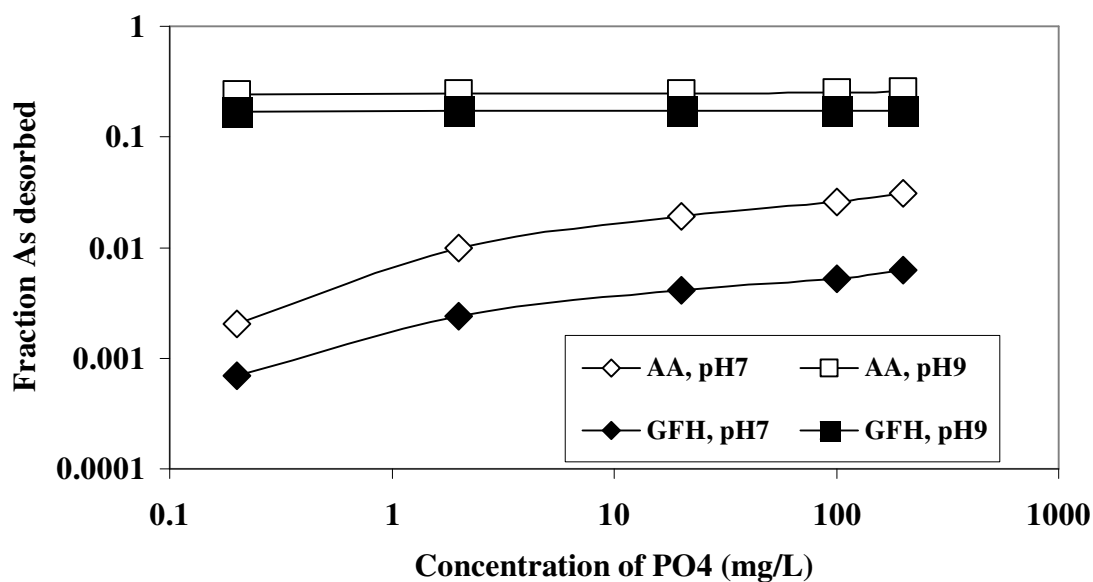


Figure 4.4. Fraction of arsenate desorbed from AA and GFH at pH 7.0 and 9.0, as a function of phosphate concentration between 0.2 and 200mg/L. The solid: liquid ratio was 5.0g: 97.5mL and the temperature was 23° C. Error bars deleted for clarity - maximum relative error in fraction As desorbed is $\pm 0.2\%$.

Table 4.3: Release of arsenic from AA and GFH as a function of the concentration of competitive anions and NOM

Anion	mmol As released/ mol of anion						Fraction sorbed As expected to leach due to concentration of anion in LL ⁴	Calculated fraction of total leaching attributable to each anion in the SLL-calc ⁵
	Maximum Slope ¹		Minimum Slope ²		Average Slope ³			
	pH 7	pH 9	pH 7	pH 9	pH 7	pH 9		
Activated Alumina								
Phosphate	279	113	3.05	1.52	9.24	4.69	0.002	0.04
Bicarbonate	0.92	0.58	0.014	0.007	0.043	0.025	0.008	0.15
Sulfate	0.352	0.143	0.017	0.014	0.045	0.028	0.002	0.04
Silicate	12	8.6	0.56	0.68	2.6	2	0.001	0.02
NOM	391	336	0.41	0.23	2.35	1.13	0.040	0.75
Granular Ferric Hydroxide								
Phosphate	357	244	4.02	2.09	10.5	6.07	0.0007	0.03
Bicarbonate	8	4	0.027	0.023	0.24	0.11	0.012	0.48
Sulfate	0.698	0.458	0.021	0.005	0.098	0.054	0.0008	0.03
Silicate	32	21	2.1	0.62	5.4	3.7	0.0013	0.05
NOM	1064	374	0.7	0.19	3.9	0.97	0.010	0.40

¹ Maximum Slope is the increase in arsenic leaching between the two lowest concentrations of anion, per unit mole of anion.

² Minimum Slope is the increase in arsenic leaching between the two highest concentrations of anion, per unit mole of anion.

³ Average Slope is the increase in arsenic leaching between the lowest and highest concentrations of anion, per unit mole of anion.

⁴ Calculated as the average slope at pH 7 multiplied by the molar concentration of the anion present in LL.

⁵ SLL-calc is the Calculated Leaching Expected in the Synthetic Landfill Leachate.

equilibration time prior to addition of phosphate. For their study, 42-58 $\mu\text{molAs/gGoethite}$ was initially sorbed compared to 79.7 $\mu\text{mol As/gGFH}$ in this study.

As/gGoethite was exchangeable when 40 μM phosphate was added in solution. In our case when 21 μM phosphate was added, 0.19 $\mu\text{molAs/gGFH}$ was desorbed. The difference (almost two orders of magnitude) suggests that GFH has more specific binding and a higher adsorption capacity for arsenate than goethite.

It is also seen that at pH 9.0, the arsenic fraction desorbed from both AA and GFH is more than 10-fold higher than at pH 7.0 (Figure 4.4). However, based on the pH results alone, much of the effect is due to the increase in pH rather than the addition of phosphate. If the fraction of arsenic desorbed at pH 9.0 with no phosphate present (Figure 4.3) is subtracted from the amount desorbed at pH 9.0 with phosphate added, the difference indicates the additive effect of phosphate (Figure 4.5). For both AA and GFH, the phosphate-driven arsenic desorption at pH 9.0 is far less than at pH 7.0. As the pH increases, the surface becomes more negatively charged and hydroxide ion competition becomes more intense, so the adsorption of both arsenate and phosphate anions becomes less suitable. It was also observed that at high pH, very little phosphate disappeared from solution, indicating few exchangeable or non-exchangeable sites are present for phosphate. Table 3 shows that (i) at any given loading of phosphate, the competitive effect is greater at pH 7 than at pH 9, (ii) the relative competition is far greater at the lower loadings than the higher loadings, and (iii) the absolute release of arsenic is higher in GFH than AA, but the fractional release is much higher in AA than in GFH. The third observation is probably due to the much higher capacity of GFH for arsenic than AA, and

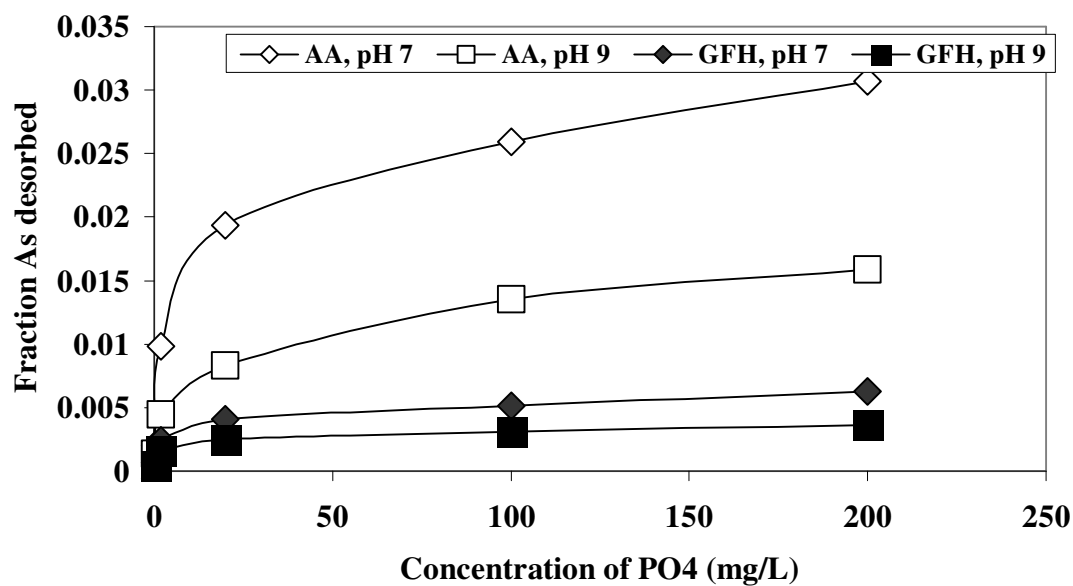


Figure 4.5. Incremental fraction of arsenate desorbed from AA and GFH due to presence of phosphate, at pH 7.0 and 9.0, as a function of phosphate concentration. The fraction of arsenate desorbed at zero phosphate concentration has been subtracted from the total arsenate desorbed. Error bars deleted for clarity - maximum relative error in fraction As desorbed is $\pm 0.2\%$.

not because of a greater competitive effect of phosphate for arsenate when sorbed onto AA rather than GFH.

Other Anion-Induced Desorption

Other anions, bicarbonate, sulfate and silicate, have lesser impact than phosphate on the release of arsenic from both AA and GFH surfaces (Tables 4.2 and 4.3). For all anions (other than bicarbonate), the trends are similar when comparing GFH and AA, even though the molar arsenic release from GFH is higher than from AA. This effect is much greater at pH 7.0 than at pH 9.0. For equal moles of the anions, silicate has a greater competitive effect than bicarbonate, which in turn is greater than sulfate. Between the lowest (2.5 mg/L) and highest (40 mg/L) concentrations of silica at pH 7.0, the fraction of arsenic desorbed from both sorbents increased by an order of magnitude. Meng *et al.* (2000) found that when silica concentration is increased from 1 mg/L to 10 mg/L, the removal of As(V) by co-precipitation with ferric chloride decreased from 90% to 45%. Although our results cannot be directly compared with theirs because of differences in sorbents, concentrations of As and silica, and adsorption versus desorption; their suggestion that silicate interacts with Fe(III) to form soluble polymers and highly dispersed colloids should also be a factor in our trials. The interaction increases iron solubility and lowers the adsorption capacity due to the formation of surface complexes and electrostatic repulsion.

Bicarbonate addition caused less desorption of arsenate than either phosphate or silicate on a mole released per mole added basis (Table 4.3). However, because the bicarbonate concentration added (and observed in landfills) is much higher than that for silicate or phosphate, the contribution of bicarbonate to the total arsenic leaching is greater than for any of the other anions investigated (Table 4.3). Bicarbonate is the only anion that extracted a higher fraction of arsenic from GFH than AA. The greater effect of bicarbonate on GFH than AA may be due to the formation of aqueous As-HCO_3 complexes as well as competitive displacement of arsenic (Apello *et al.*, 2002). Fuller *et al.* (1993) and Meng *et al.* (2000) found very little effect of bicarbonate on co-precipitation of As in iron hydroxide. However, bicarbonate concentration in those experiments was orders of magnitude lower than observed here and than that which would be expected in a landfill environment. Surface complexation models estimate that high bicarbonate concentrations reduce the sorption capacity of arsenic on ferrihydrite significantly (Apello *et al.*, 2002). This study's results may not be as dramatic as the model results because the arsenic is sorbed onto the GFH surface prior to the addition of the bicarbonate.

Sulfate extracted the least amount of arsenic on a per mole basis among all the anions tested from both sorbents. Even at the highest sulfate loading of 5000 mg/L, only about 0.4% arsenic from AA and 0.1% of arsenic from GFH were desorbed at pH 7.0. This is consistent with other studies (Meng *et al.*, 2000, Jain *et al.*, 2000) that showed negligible influence of sulfate on arsenic adsorption onto ferrihydrite.

The concentrations of the anions in the Los Reales Landfill Leachate (Tucson, AZ) are within the normal landfill range (Table 4.1), albeit somewhat weaker than average. Table 4.3 (second-last column) shows the fraction of arsenic that would be expected to leach from the sorbents due the presence of the anions studied at their Los Reales leachate concentrations. Bicarbonate leaches out 2-3 orders of magnitude lower arsenic than phosphate on a per mole basis. However, since it is present at up to a 20,000-fold higher molar concentration, it extracts 4 times the fraction of arsenic from AA and 17 times the fraction from GFH. Sulfate is present in a concentration three orders of magnitude higher than phosphate, but phosphate and sulfate prompt similar fractional leaching from both AA and GFH. Finally, silica is present in a low concentration and only leaches a small fraction of arsenic from both sorbents.

NOM induces a molar (mole As)/(mole anion) release of arsenate greater than or comparable to any of the anions studied (Table 4.3). NOM also shows a greater difference in the molar leaching observed between the lowest and highest concentrations (Table 4.3). NOM is a heterogeneous mixture of different fulvic and humic acids. Consistent with previous work (*Xu et al., 1991*), our calculations use a characteristic molecular weight of 1800 for the NOM. It is recognized that a single molecule of NOM might have multiple functional groups associated with it, however no effort is made to incorporate such a factor in our calculation. NOM may affect the desorption of arsenic from AA and GFH through various mechanisms: (1) by directly competing with the

arsenate for surface sites (*Parks, 1990*), (2) by sorbing to the surface and creating additional surface attraction and enhanced sorption (*Schwarzenbach et al., 1993*), (3) by acting as a soluble partitioning agent to bind the ion and keep it in solution (*Stumm and Morgan, 1996*), (4) by directly reacting with the sorbent surface to enhance dissolution of the surface and loss of sorption sites (*Schwarzenbach et al., 1993*) or (5) by deposition of NOM onto the solid surface to shield active sites. In all likelihood, the net effect is probably the effect of the various different mechanisms in tandem. However, as seen in Table 4.2, NOM is likely to be present in a very high concentration in a landfill leachate, and hence play a significant role in leaching of arsenic from both AA and GFH.

Leaching tests

The results of the TCLP, Landfill Leachate (LL) and Synthetic Landfill Leachate (SLL) extractions are shown in Figure 4.6. The TCLP extracts the least arsenic, more than an order of magnitude lower than the LL, for both AA and GFH. A primary reason is that the LL pH is 7.16 -much higher than the TCLP pH of 4.95. In addition, the LL's higher organic concentration and the presence of other competing ions (phosphate and bicarbonate) also enhances the leaching. Although outside the scope of this study, it is expected that the low redox potential of the LL relative to the TCLP also increases arsenic leaching (*Ghosh et al., 2004*). Even when the TCLP is continued for a 48-hour duration, the leaching does not increase substantially, and it extracts less arsenic than the phosphate, bicarbonate and NOM, even at their lowest concentrations.

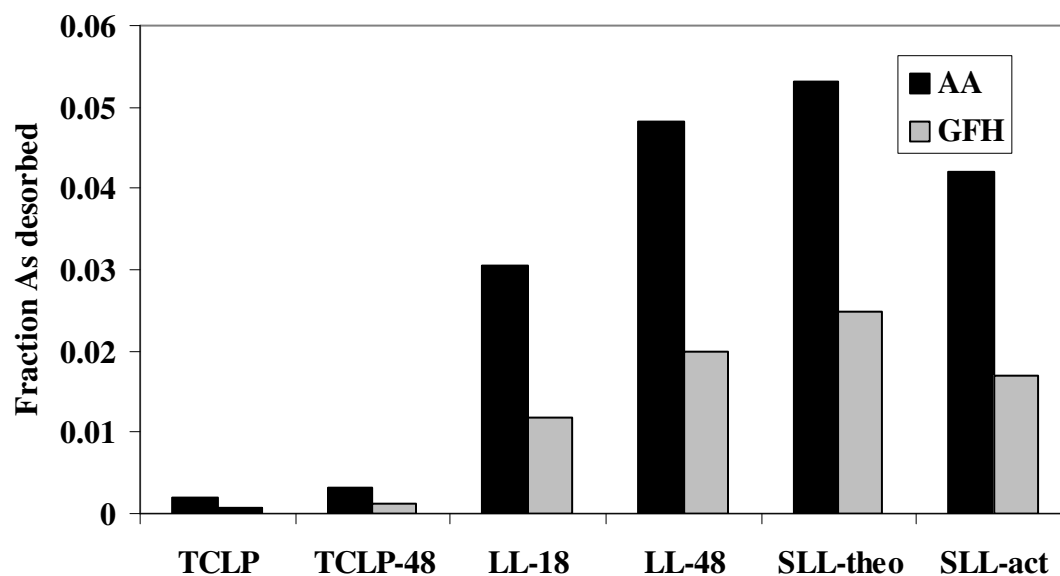


Figure 4.6. Fraction of total arsenate desorbed from AA and GFH by different leaching protocols. (TCLP: Toxicity Characteristic Leaching Procedure, LL-18: Landfill Leachate, 18 hours, LL-48: Landfill Leachate, 48 hours, SLL-theo: Synthetic Landfill Leachate, theoretical, SLL-act: Synthetic Landfill Leachate, actual). Error bars deleted for clarity - maximum relative error in fraction As desorbed is $\pm 0.4\%$.

The leaching calculation (Figure 4.6, SLL-calc) assumes that the effect of each anion is additive (a worst-case assumption, in that an additive hypothesis would imply that each anion sorbs to a different set of arsenic-sorbed sites so as not to compete with each other, which is not what our results show in general). The Synthetic Landfill Leachate Calculated Leaching (SLL-calc) calculated here is the sum of the fractions leached by the individual anions (Table 4.3). The last column in Table 4.3 shows the fraction of the total arsenate that is expected to be leached by the SLL-calc that is attributable to a given constituent. However, the additivity premise fails as the SLL-calc gives about 1.3 and 2 times the actual leaching that is observed in the SLL (SLL-act) for AA and GFH, respectively. This and previous research (*Lin et al., 2001*) indicate that electrostatic bonding plays a significant role in arsenic adsorption/desorption on most metal oxide surfaces. The multivalent anions (*e.g.* PO_4^{3-}) would be expected to be particularly significant. For both AA and GFH, the LL leached a much higher fraction of arsenic than the SLL-act. Although not specifically proven, it is suspected that the low redox potential and the heterogeneous matrix of complex organics and inorganics in addition to those mimicked in the SLL play a role.

Conclusions

Among the abiotic factors that would influence desorption of arsenic from the sorbents when disposed of in a landfill, pH seems to be the most important parameter of those considered. An increase in one unit of pH from 8.0 to 9.0, causes desorption of 15% and 12% of the arsenate from AA and GFH, respectively. This effect increases with increase

in pH, consistent with an adsorption edge between pH 7.5 and 11.0 for AA and pH 7.0 and 12.0 for GFH (data not shown). For an 10-fold increase in concentration, NOM gives the highest leaching among all anions. However, even in that case (2000 mg/L to 20000 mg/L TOC) the increase in the fractional leaching of arsenic is only 2.05% for AA, and 0.5% for GFH, which is far less than observed for one unit increase in pH (a 10-fold increase in OH⁻). Among the different anions, NOM has the greatest impact on arsenic desorption both per mole of anion as well as by virtue of being present at a very high concentration. Phosphate has a significant competitive effect with arsenic, but is generally not present at high concentrations, and hence would not typically play a large role (Table 4.3). The same is true for silicate. Bicarbonate and sulfate do not compete strongly with arsenate, but are likely to be present in high concentrations in a leachate, and hence their influence cannot be ignored. No single anion dominates influence over arsenic leaching under landfill conditions. In addition, the leaching experiments show that the effects of the various anions, when present in tandem, are not additive, but to various degrees compete with each other in displacing arsenate.

Of the abiotic factors considered in this study, the difference in pH between actual landfill leachate and the TCLP solution most accounts for the under-prediction of leaching exhibited by the TCLP. The influence of NOM, bicarbonate or phosphate at landfill concentrations (and their absence in the TCLP), also explain some of the discrepancy of the leaching observed. However, the small contributions of the competing anions and NOM relative to that of the hydroxyl ion indicates that their omission in alternate leaching test formulations would not be significant, if an appropriately

aggressive, high pH is maintained. This is not to suggest that the influence of other factors not considered in this study, such as microbial activity and redox conditions would not have an equal or greater impact than pH on arsenic mobilization from ABSRs.

CHAPTER 5

LEACHING OF ARSENIC FROM GRANULAR FERRIC HYDROXIDE RESIDUAL UNDER LANDFILL CONDITIONS

Introduction

The Toxicity Characteristic Leaching Procedure (TCLP) is the primary, United States, Environmental Protection Agency (USEPA) assessment protocol for distinguishing hazardous from non-hazardous wastes (Federal Register, 1986). However, a growing body of work in the last decade has indicated the TCLP may poorly predict contaminant leaching for a number of contaminants and disposal scenarios (Hooper et al., 1998; Ghosh et al., 2004; USEPA, 1999; Halim et al., 2003; Halim et al., 2004). Consequently, development of alternative leaching protocols and associated decision trees has become a research priority. A successful alternative protocol must provide a sufficiently aggressive test to safeguard human and environmental well being without being so cautionary that appropriate waste disposal becomes economically or technologically infeasible. Therefore, leaching test results must be calibrated against the leaching that would occur in reality after waste disposal in the actual environment of interest. Behavior of arsenic-bearing solid residuals (ABSR) disposed in non-hazardous landfills is poorly predicted by the TCLP (Ghosh et al., 2004; Jing et al., 2005). Consequently, this study evaluates the magnitude and time dependence of leaching from an ABSR in a mixed solid waste landfill simulation column in order to provide a benchmark against which to judge the appropriateness of standard and alternative leaching protocols.

The USEPA has recently lowered the Maximum Contaminant Level (MCL) of arsenic in drinking water from 50 µg/L to 10 µg/L, and compliance begins in 2006. In response, over 4000 U.S. utilities must reduce the arsenic level in their delivered water (USEPA, 2001). Removal of arsenic by adsorption onto solid media seems to be the most attractive option for small utilities (serving populations less than 3,301), which comprise more than 92% of the impacted utilities (USEPA, 2001). The sorbents most commonly expected to be used employ an iron oxy/hydroxide surface such as Granular Ferric Hydroxide (GFH), Bayoxide E-33, iron-modified AA, iron-impregnated sand (IIS), and hybrid ion exchanger (HIX) (USEPA 2003, Amy et al., 2000, Vaishya et al., 2003, DeMarco et al., 2003). The commercial sorbent GFH was chosen as the solid media of interest in this work.

Arsenic in circum-neutral water is present either as arsenite, As(III) or as arsenate As(V). Arsenite is present primarily as uncharged arsenous acid, whereas arsenate is predominantly in a combination of two anionic forms: H_2AsO_4^- and HAsO_4^{2-} . USEPA recommends that water containing a significant amount of arsenite undergo pre-oxidation prior to the application of an arsenic removal technology (USEPA, 2001). Consequently, only arsenate-loaded GFH was used in this research.

Currently, most ABSRs pass the TCLP and the Waste Extraction Test (WET), an alternative leaching test used in California. As a consequence, ABSRs may be considered

safe for disposal in non-hazardous, mixed solid waste (MSW) landfills. Microbially active, mildly alkaline, anaerobic conditions characterize MSW landfills (Christensen et al., 2001, Kjeldsen et al., 2002). Under such conditions, several factors influence arsenic leaching. Among them, microbial reduction of iron and arsenic is suspected to be a major factor. Numerous researchers have studied anaerobic reduction of both iron and arsenic. Ferric-iron reducing bacteria have been isolated from a great diversity of anoxic environments including sediments, soils, deep terrestrial subsurfaces, and hot springs (Straub et al., 2001, Lovley, 1997). Also, microorganisms of various taxonomies have demonstrated the ability to utilize As(V) as an electron acceptor for anoxic respiration, yielding energy to support their growth (Oremland and Stolz, 2003). Dissimilatory arsenate reducing prokaryotes (DARPs) have been isolated from wetland, lake and pond sediments with a cell count of as high as 10^4 cells/g sediment (Harrington et al., 1998, Kuai et al., 2001, Oremland and Stolz, 2003). Other microorganisms including bacteria, archaea and fungi exhibit arsenic resistance by reduction of intracellular As(V) to As(III) by arsenic reductases, where As(III) is the substrate of efflux pumps (Oremland and Stolz, 2003, Rosen, 2002). The dissimilatory reduction and mobilization of arsenic specifically adsorbed onto the surface of ferrihydrite has also been studied (Zobrist 2000, Langner 2000).

Abiotic characteristics also may influence arsenic leaching from disposed ABSR. Arsenic partitioning to the liquid phase increases as pH increases, as well as in the presence of the typical concentrations of natural organic matter and competitive anions found in landfill

leachates (Ghosh et al., 2005; Holm, 2002; Meng et al., 2000; Jain and Loeppert, 2000). In addition, MSW landfills have widely varying waste composition, rates of leachate generation, rates of percolation from local precipitation, and leachate hydraulic residence times. All of these factors potentially could influence arsenic mobilization. The waste in a landfill is a heterogeneous mixture of organic and inorganic wastes with organic wastes expected to be more influential in the mobilization of arsenic (Christensen et al., 2001, Kjeldsen et al., 2002). The dissolved organic content observed in MSW landfill leachates can vary between 76 and 40000 mg/L (Bagchi, 1994). In addition, once materials like arsenic and iron are leached from a residual, they may subsequently reaction with other materials, and either sorb or precipitate onto other surfaces. Finally, the ABSR will reside in the landfills for multi-year duration, so relatively slow (scale of years) aging and transformation of the ABSR may also influence leaching. Thus, a realistic landfill simulation must incorporate a variety of biotic and abiotic factors in ranges characteristic of the MSW environments that will most strongly challenge arsenic retention within the system.

The goals of the present research are: a) to establish a set of conditions inside a flow-through column reactor that would be representative of an MSW landfill, b) to measure and characterize the leaching of arsenic from the column, and c) to observe the leaching response to changes in influent water composition, such as pH, alkalinity and organic concentration. This is the first study to our knowledge in which an actual ABSR has been subjected to a long-term, dynamic, simulation of actual landfill conditions. The results

are aimed at providing a broad understanding of the primary physicochemical and biological factors that control arsenic leaching from ABSR under landfill conditions, as an indication of the fate of arsenic on an ABSR disposed of in a landfill and as a first step towards the design of a more realistic leaching test for the evaluation of arsenic residuals.

Materials and Methods

Column Design

A schematic of the experimental setup is shown in Figure 5.1. The column used in this study was a cylindrical PVC column, 76.2 cm in length, and 15.9 cm in diameter. It was closed with flat PVC plates on both ends, and was operated in downflow mode. All joints and connections in the column were sealed with silicon rubber to ensure airtight conditions. The gas generated in the column was allowed to escape via a vent at the top, and collected over a Mariotte Flask. The influent was pumped from a conical flask into the column by a syringe pump (Dayton, Model 2Z798B). Small diameter PTFE tubes (inner diameter 1 mm) were used to deliver the influent to the column and transport the effluent out of the column to the collection jar. The water level was maintained at 61 cm from the bottom of the column and the saturated bed volume was 12.1 L out of a total volume of 15.1 L. The liquid flow rate through the column was 0.44 mL/min. In terms of leachate flow per unit mass of waste, the selected flow rate was more than two orders of magnitude higher than average mass fluxes in a Virginia landfill that had a leachate generation rate of 9.73×10^{-4} L/kg day (Gillispie and Lancaster, 2003). The hydraulic residence time in the column was 10-15 days, whereas the residence time in a landfill can

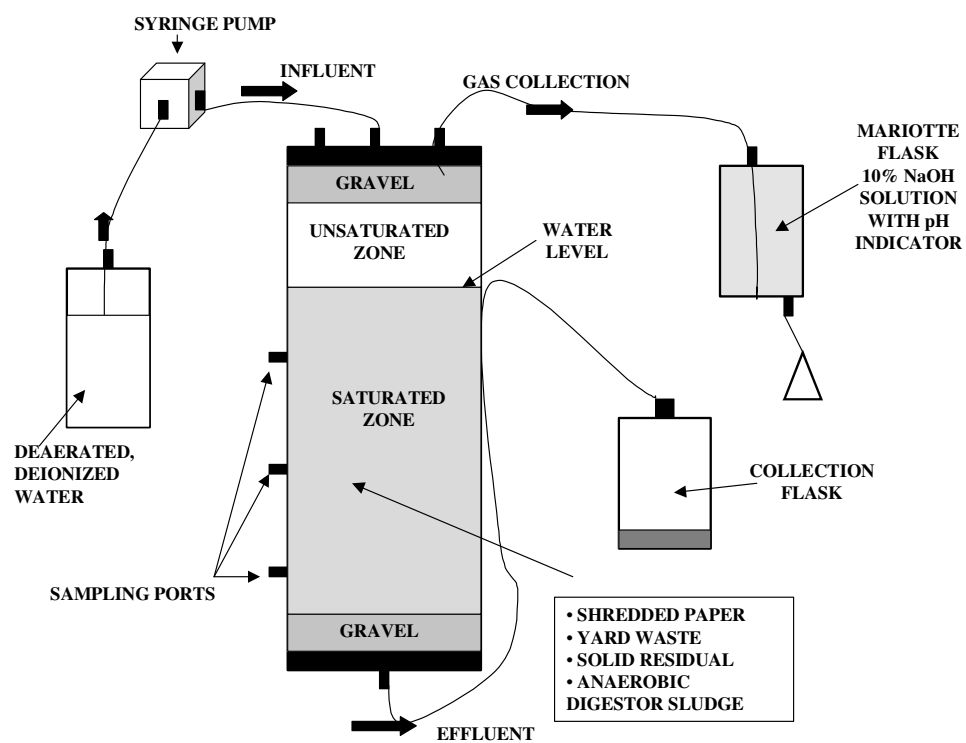


Figure 5.1: Schematic diagram of the column reactor setup used for the experiments.

vary anywhere between weeks to years. The relatively high leachate throughput in our laboratory system was selected to allow for an observation time scale that would be tractable in terms of leachate concentration measurements. The entire set up was kept in a temperature-controlled room maintained at 30°C, which ensures optimal performance of the microbes.

Column Composition

Two sections occupying 5 cm from the bottom and 3 cm from the top of the column were packed with gravel ranging between 0.3 cm and 1 cm in size. The active bed sat between the gravel beds. The gravel was added to provide even distribution of water flow through the bed.

The reactive bed was made out of the following components:

Sorbent: Granular ferric hydroxide (GFH) is a weakly crystalline β -FeOOH produced by conditioning previously compacted iron hydroxide slurry (Dreihaus et al., 1998). It is in the form of irregular grains up to 2 mm diameter. GFH particles specifically adsorb As(V). GFH[®] is manufactured by GEH and distributed in the US by U.S. Filter. It is designed as a throwaway media and would not be regenerated.

The GFH sample used in this study contained 55.4% water. The iron content of the GFH was 69% of the dry weight of the sample and about 30.8% of the overall weight. Prior to the start of the column experiment, a batch of GFH was pre-equilibrated with arsenate. A

GFH suspension was prepared with 1 kg of GFH and 2 L of purified water (Milli-Q™ Water System by Millipore). Arsenate was added as sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, KR Grade Aldrich Sigma). The initial concentration of arsenic added was 2.7 g/L (as As). The pH was adjusted to 7.0, using hydrochloric acid (Spectrum) or sodium hydroxide (Sigma). After 48 hours of equilibration on a shaker table (Orbit, reciprocating speed 125 rpm), liquid samples were collected and analyzed. After equilibration, the aqueous concentration was 25.7 $\mu\text{g/L}$ (as As), which is in the range expected for drinking water treatment systems. The sorbed concentration was 12.04 mgAs/gGFH (dry), which translates to 17.6 mgAs/gFe.

Compost: Domestic yard waste, consisting primarily of fruit and vegetable waste, dry leaves and soil was added to the column. This compost contained about 12% water and 72% organic matter. When 1 g of compost was digested with 100 mL of concentrated nitric acid, iron (1.6 mg/g) and aluminum (0.93 mg/g) were found to be the major metallic components.

Paper: White Econosource Smooth DP paper was shredded using a paper shredder. The paper was soaked in de-ionized water and squeezed to pulp, in order to reduce its volume.

Digester Sludge: Sludge was collected from the anaerobic digester at the Ina Road Water Pollution Control Facility in Tucson, Arizona. The sludge consisted of 76% water, and 18% organic matter. When 1 g of the dry sludge was digested with acid, iron (9 mg/L), copper (6.3 mg/L) and nickel (2.9 mg/L) were found to be the major metallic components of the sludge. The sludge was added to the column mixture to provide an initial microbial population to the column. Presumably, it consisted of a diverse population of anaerobic

microorganisms, including methanogens, fermentative bacteria, and sulfate- and iron-reducers.

To assemble the column filling, 542 g of the GFH (with sorbed As) were mixed with 1.5 kg of compost, 750 g of paper and 4 L of anaerobic digester sludge. This mixture formed the active bed. The mixture approximated the composition that would be expected in municipal garbage in the United States (Bagchi, 1994).

Influent

At the beginning of the experiment, the influent was de-aerated, de-ionized water. However, with the progress of the experiment, as the dissolved organic carbon (DOC) and alkalinity of the effluent began to drop, the influent was spiked with sodium bicarbonate and a mixture of volatile fatty acids (VFA) (which served as the electron-donating substrate) and the pH was adjusted to a desired value. Effort was made to keep the pH, alkalinity, ORP and DOC of the column leachate within the range of values expected in MSW landfill leachates. The VFA mixture had the following composition: 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 to desired values using either hydrochloric acid (Spectrum) or sodium hydroxide (Sigma). The composition of the influent at various times during the column operation is shown in Table 5.1. Each of the different periods defined in Table 5.1 were designed with a particular objective to assess the column response to a particular set of conditions. The results will be presented in order of periods, discussing the dose-response of the column in each phase of operation.

Table 5.1: Table showing the influent composition for different operational periods of the column

Period	Time (days)	pH	VFA (g/L)	Bicarbonate (g/L)
I	0-304	6.1	-	-
II	305- 643	7.0	1.58	2
III	644-766	7.0	15.8	4
IV	767- 837	4.8	15.8	4
V	838- 892	5.8	15.8	4

Column Operation

Samples were collected from the effluent of the column after every 7 days. The samples were sequentially filtered through 5 μm , 0.8 μm and 0.45 μm polycarbonate membrane filters (Millipore). The 0.45 μm filtered samples were frozen under N_2 headspace prior to analysis, while the other samples were acidified with concentrated nitric acid (Spectrum) and digested in a Microwave Digester (CEM), before being frozen. The pH, ORP and alkalinity of the samples were measured in-situ, to avoid exposure to air. The iron analysis was done within 30 min of collection and acidification of the samples. The samples for DOC were acidified and refrigerated prior to analysis.

Analytical Methods

The samples were analyzed for arsenic using Ion Coupled Plasma Mass Spectrometer (ICPMS). The HPLC system consists of an Agilent 1100 HPLC (Agilent Technologies, Inc.) with a reverse-phase C18 column (Prodigy 3u ODS(3), 150x4.60 mm, Phenomenex, Torrance, CA). The mobile phase (pH 5.85) contained 4.7 mM tetrabutylammonium hydroxide, 2 mM malonic acid and 4% (v/v) methanol at a flow rate of 1.2 mL/min. The column temperature was maintained at 50°C. An Agilent 7500a ICP-MS with a Babington nebulizer was used as the detector. For arsenic totals, an ASX500 autosampler (CETAC Technologies, Omaha, NE) was used with the Agilent 7500a ICP-MS. The detection limit for this instrument was 0.1 $\mu\text{g/L}$ for arsenic speciation, and 0.01 $\mu\text{g/L}$ for arsenic totals. Analysis of replicates was within $\pm 5\%$. Iron was measured by the Phenanthroline Method (Standard Methods,

1993) using a Hitachi U-2000 Spectrophotometer. DOC was measured using a Shimadzu Total Organic Carbon Analyzer, the detection limit for which was 0.01 mg/L. pH was measured using an Orion (Model 720) pH meter. ORP measurements were made with a Cole Palmer Platinum Single-Junction Electrode calibrated using ZoBell's solution ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}/\text{K}_3\text{Fe}(\text{CN})_6$ redox couple). Alkalinity was determined by titration with 1 N HCl solution. Methane gas was collected using an inverted glass serum flask filled with a 3% (w/v) NaOH solution to scrub out the carbon dioxide and then analyzed by a Gas Chromatograph (Hewlett Packard, Series 5790A).

Results and Discussion

The results are presented according to the performance of the column reactor as a response to the influent characteristics in each of the 5 different periods of the column operation (Table 5.1). In period I, the influent was de-ionized water. By the end of period I, the effluent DOC and alkalinity had dropped significantly and were below typical mature MSW landfill leachate values (Figure 5.2). For this reason, a moderate amount of VFA (1.58 g/L) and alkalinity (2 g/L of NaHCO_3) were added to the influent and the pH was adjusted to 7.0. This influent composition was continued throughout period II. The alkalinity and DOC in the column leachate exhibited recoveries during period II, but eventually started to decline. Consequently, for period III, the influent was amended with increased organics (15.8 g/L), high alkalinity (4 g/L) and the pH was adjusted to 7.0. However, the pH of the column leachate increased up to values that would be unrealistic in an MSW landfill (Figure 5.3). Therefore, in period IV, the influent pH was

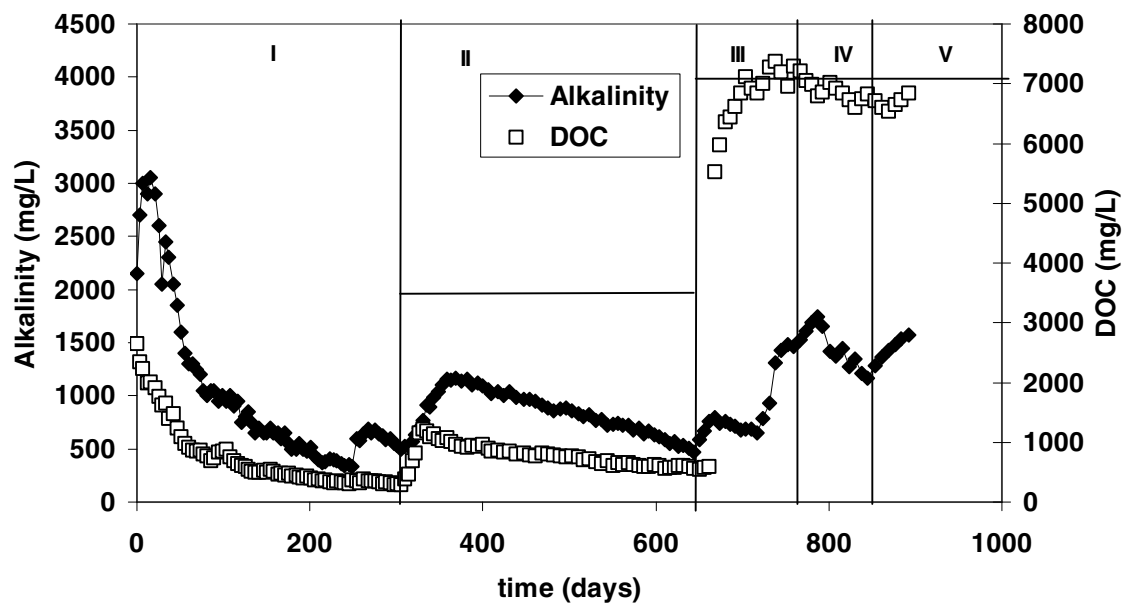


Figure 5.2: Alkalinity (in mg/L) and Dissolved Organic Carbon (in mg/L) in the effluent throughout the duration of the column run. The horizontal lines show the influent alkalinity during different periods of the column operation.

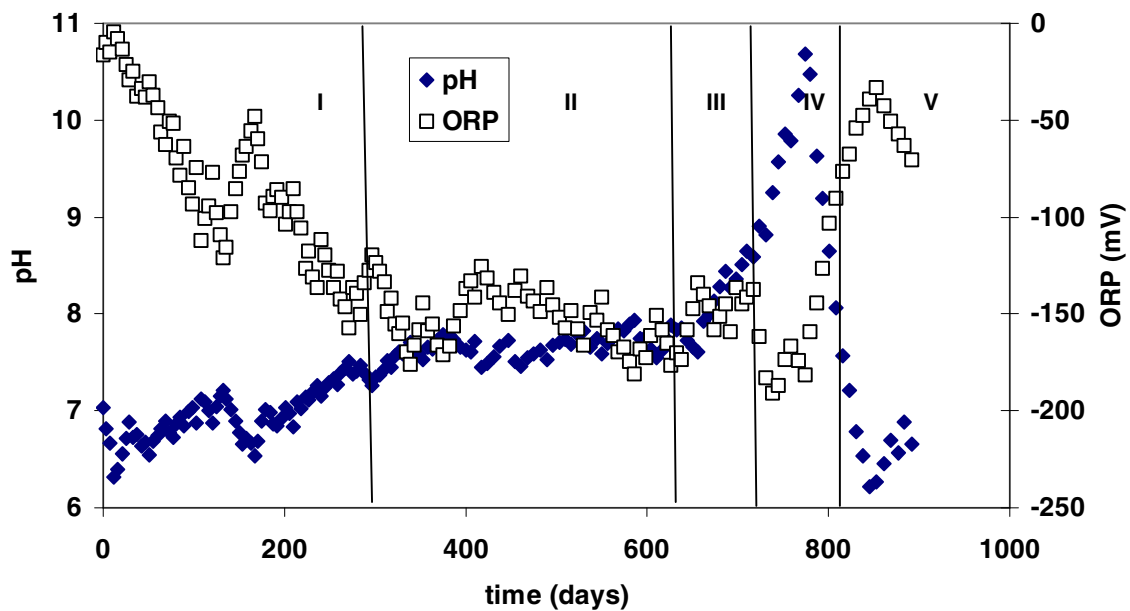


Figure 5.3: pH and ORP (in mV) in the effluent throughout the duration of the column run.

lowered from 7.0 to 4.8, which is close to the pK_{a1} of the VFAs in the influent, which range from 4.7 to 4.9. By the end of period IV, the leachate pH had dropped below the expected range of pH in a mature landfill. For this reason, in period V, the influent pH was adjusted to 5.8 instead of 4.8.

Period I

Figure 5.4 shows iron and arsenic concentrations in the dissolved/colloid fraction of the column effluent. As defined here and throughout the work, the term *dissolved/colloid* refers to the portion of the leachate that passes through a 0.45 μm filter and *particulates* refer to solid fractions with particle size greater than 0.45 μm in size. It should be noted that most iron colloids are between 10-60 nm in size (Tadanier et al., 2005) so that they are part of the dissolved/colloid fraction. Figure 5.5 shows a comparison between the total and dissolved iron and arsenic concentrations in the effluent. The total (digested) concentrations reflect contributions from both the dissolved/colloid and the particulates fraction.

From Figure 5.4, it can be seen that more than 95% of the total dissolved/colloid iron was present as Fe (II) throughout period I of the column run, indicating the microbial reduction of Fe(III) to Fe(II). Since the GFH media only has Fe(III) hydroxide, all the Fe(II) was generated inside the column, presumably by microbial reduction of Fe(III). The Fe(II) concentration in the dissolved/colloid phase increased substantially during the

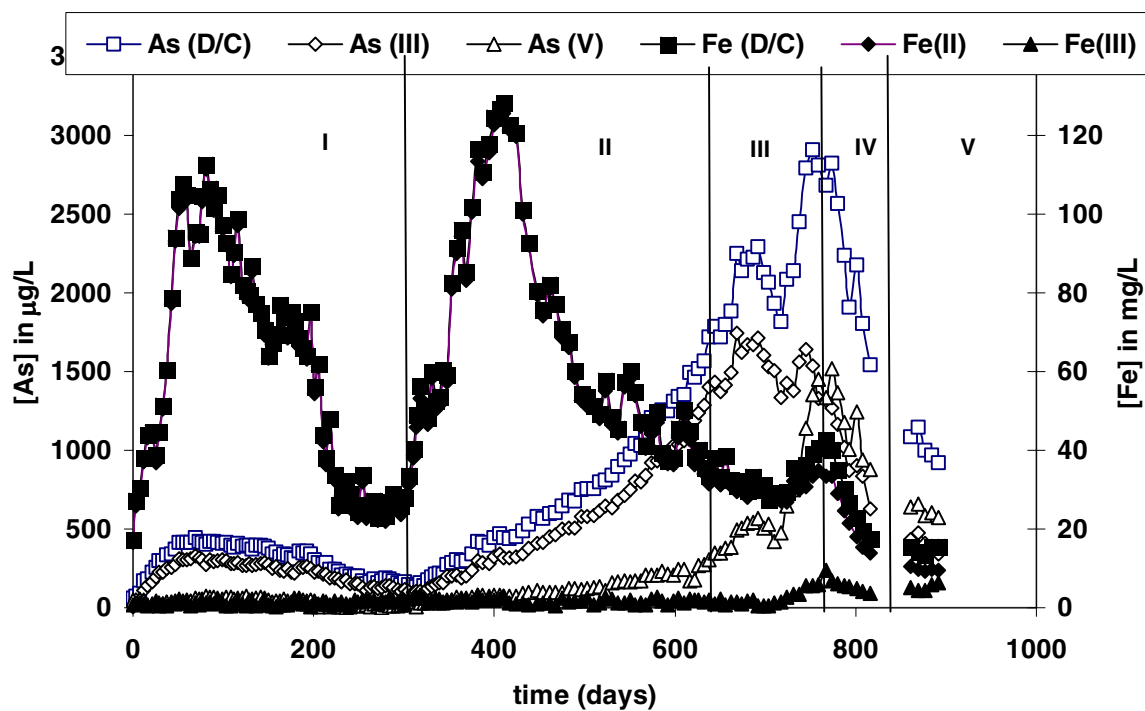


Figure 5.4: Concentration of the dissolved/colloidal (D/C) arsenic, As(III), As(V) (in $\mu\text{g/L}$) and dissolved/colloidal (D/C) iron, Fe(II) and Fe(III) (in mg/L) in the effluent throughout the duration of the column run.

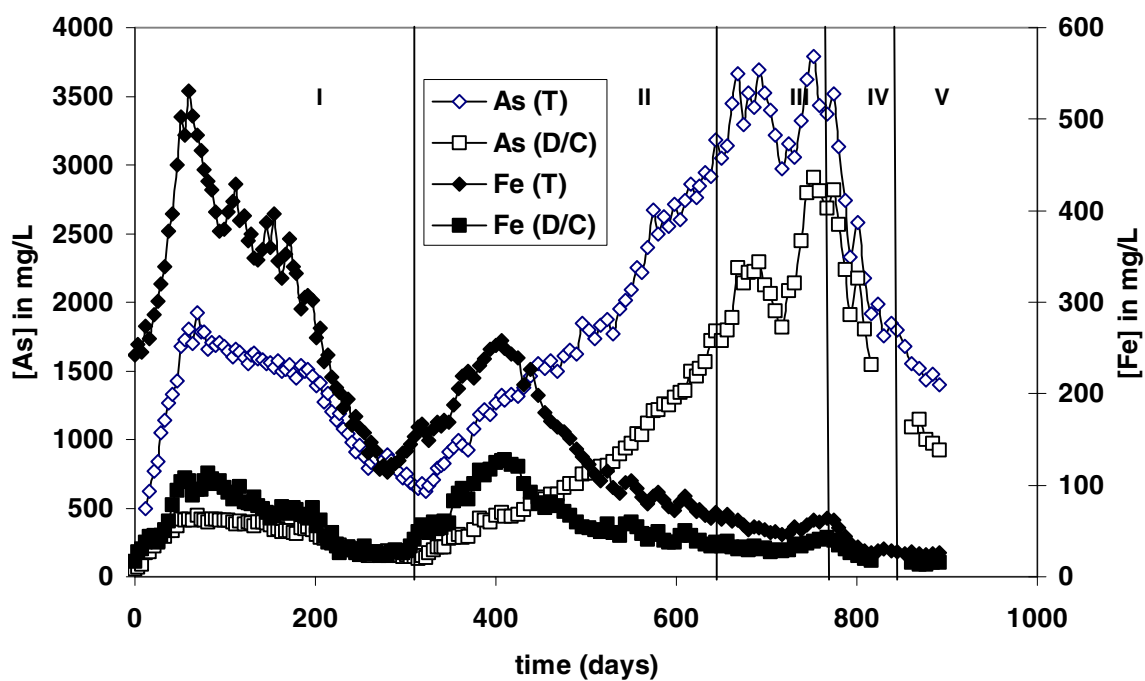


Figure 5.5: Concentration of the total (T) digested arsenic and dissolved/colloidal (D/C) arsenic (in $\mu\text{g/L}$) and total (T) digested iron and dissolved/colloidal (D/C) iron (in mg/L) in the effluent throughout the duration of the column run.

first 80 days of operation, but then dropped steadily to reach levels comparable to those obtained in the first days of operation towards the end of period I. Along with Fe(II), a relatively small amount of Fe(III) was observed in the dissolved phase, although it never exceeded 3 mg/L in period I. However, the solubility of Fe(III) within the pH range of the experiment (Figure 5.3) should be in the range 10^{-10} to 10^{-16} mg/L. The observed concentration was much higher than the theoretical solubility limit because of the presence of iron colloids. To test this hypothesis, the 0.45- μm filtrate was ultra-filtrated with a 30000 Dalton (pore size 0.02 μm) regenerated cellulose membrane, yielding a permeate with Fe(III) concentration below the detection limit of 0.1 mg/L, which confirms that most of the iron is in particles smaller than 0.45 μm . This observation is in agreement with Tadanier et al. (2005), who report that a significant fraction of the colloids generated by the microbial de-flocculation of ferrihydrite are in the size range 10-60 nm. However, the fraction of iron leached as particulates during period I had a median value of 69%, indicating that most of the iron leached was in the form of particles larger than 0.45 μm .

From Figure 5.4, it is also seen that, in period I, As(III) was the dominant species in the dissolved/colloid fraction of arsenic, indicating microbial reduction of As(V) to As(III). The occurrence of As(III) can be rationalized by microbial reduction supported with VFA, dissolved organics from compost, and endogenous substrate of the inoculum's biomass as electron donors. The ratio of As(III):As(V) in the dissolved fraction of the

column effluent was as high as 3:1 during the peak reducing phase. Given that reducing conditions were present in the column, as indicated by the measured ORP values (Figure 5.3), a higher fraction of As(III) would have been expected. However, inside the column there were two competing redox couples, Fe(III)/Fe(II) and As(V)/As(III). During the peak reducing period of the column run, more than 95% of the total dissolved iron was present as Fe(II). Literature data show that the Fe(III)/Fe(II) couple has a higher ORP than the As(V)/As(III) couple (Meng, 2001). However, GFH might be a mixed oxide and hence the exact ORP of Fe(III)/Fe(II) would be difficult to determine. In a similar anaerobic experiment in the absence of the competing iron couple, the As(III):As(V) ratio has been observed to be as high as 9:1 (Sierra-Alvarez et al., 2005).

Other than As(III) and As(V), there were some methylated arsenic species were detected namely methylarsonous acid (MMA(V)) and dimethylarsonous acid (DMA(V)). No methylated species of As(III) were detected ever in the effluent. The concentrations of these species were almost insignificant, varying between 0 and 25 µg/L throughout the column run and so the values of the methylated species have not been reported here.

A comparison of Figures 5.4 and 5.5 shows that the trends followed by arsenic and iron concentrations in the leachate were similar for both the dissolved/colloid fraction and the total (dissolved/colloid plus particulates fractions). The decline in the leaching concentrations towards the end of period I might reflect a decrease in microbial activity, which would be consistent also with the observed drop in ORP (Figure 5.3).

The results of period I show a correlation between the iron concentration and the arsenic concentration in the leachate: the higher the iron concentration at any given time, the higher was the arsenic concentration. As shown in Figure 5.6, the ratio of arsenic to iron concentration during period I remained fairly constant and relatively low (below 0.01). The correlation between iron and arsenic concentration seems to be a consequence of the association of the arsenic to the iron surfaces, even on the mobilized particulates and colloids. Similar results were obtained by Tadanier et al. (2005), who demonstrated that arsenic remained associated with nanometer-sized colloids generated by the microbial deflocculation of ferrihydrite.

It is clear that particulate leaching is a significant factor in the mobilization of iron and arsenic from the GFH media, and particularly dominant during the initial phase of leaching. The flow rate in the column was very low, about 0.44 mL/min, which translates to a superficial velocity of 0.022 mm/min. It does not seem likely that fluid stresses on the solid sorbent could explain the generation of the particulates inside the column. We postulate that the main reason for the generation of the particulates is microbial erosion of the GFH media, reduction of Fe(III) to Fe(II) followed by re-precipitation, or nucleation of smaller sized colloids into larger sized ones. A recent study (Tadanier et al., 2005) demonstrated that the anaerobic bacterium *Geobacter metallireducens* reduces Fe(III) in ferrihydrite, resulting in deflocculation of ferrihydrite aggregates into nanometer sized colloids.

Figures 5.7 and 5.8 show the breakdown of the particle size fractions in the particulate

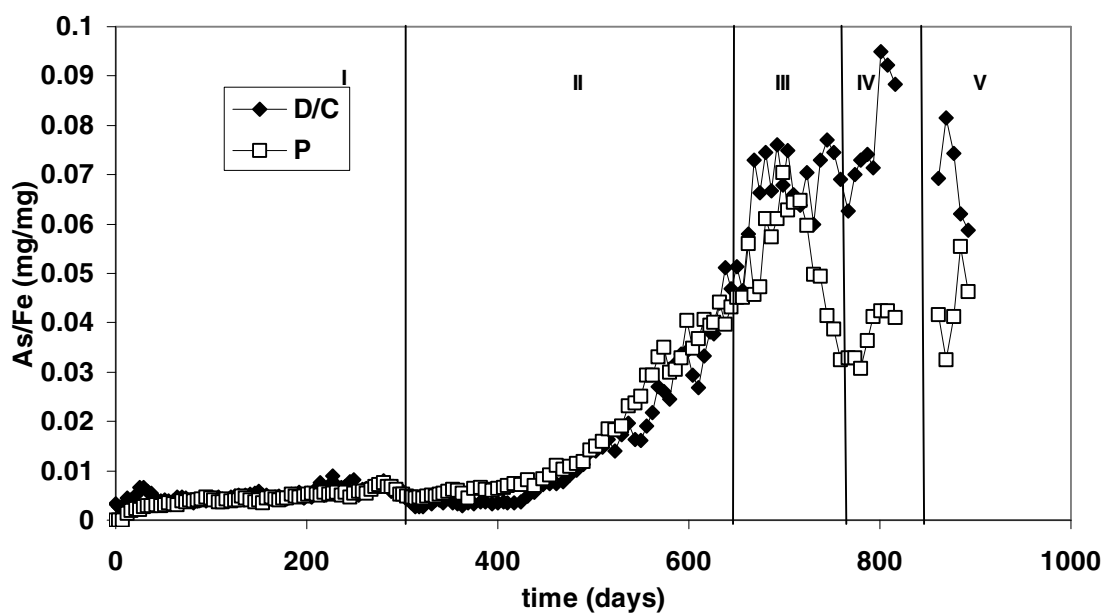


Figure 5.6: Ratio of As:Fe in the dissolved/colloidal (D/C) and particulate (P) fractions (in mg/mg) in the effluent throughout the duration of the column run.

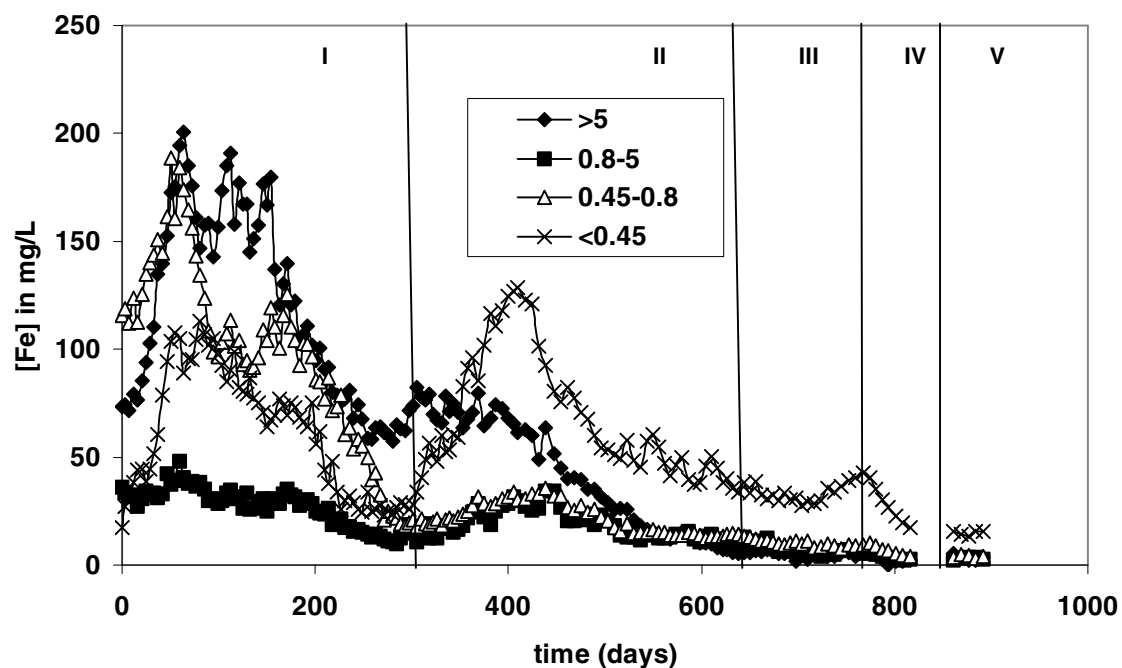


Figure 5.7: Concentration of iron leached in particulate sizes greater than 5 μm , between 0.8 μm and 5 μm , between 0.45 μm and 0.8 μm , and less than 0.45 μm (dissolved/colloidal fraction) in $\mu\text{g/L}$ in the effluent throughout the duration of the column run. Numbers in the legend denote particle sizes in μm .

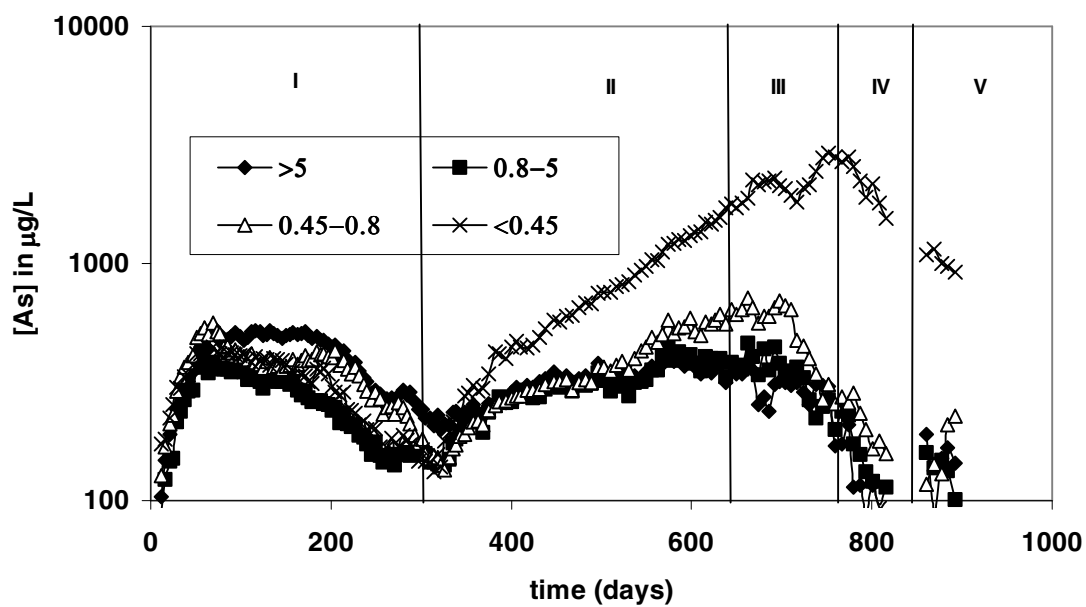


Figure 5.8: Concentration of arsenic leached associated with particulate sizes greater than $5\mu\text{m}$, between $0.8\mu\text{m}$ and $5\mu\text{m}$, between $0.45\mu\text{m}$ and $0.8\mu\text{m}$ and less than $0.45\mu\text{m}$ (dissolved/colloidal fraction) in $\mu\text{g/L}$ in the effluent throughout the duration of the column run. Numbers in the legend denote particle sizes in μm . [Note: y-axis is plotted on log-scale.]

phase for iron and arsenic, respectively. From Figure 5.7, it can be seen that in period I the fraction greater than 5 μm was the most dominant one, closely followed by the size fraction between 0.45 μm and 0.8 μm . In this period, when the total digested iron concentration was the highest, the principal carrier of iron was large particulates, which could be agglomeration of granules broken off from the parent GFH mass.

Figure 5.8 shows the arsenic concentration in the different particulate phases. Comparing Figure 5.7 and Figure 5.8, it can be seen that there is a general agreement between the amount of iron transported in each particulate phase, and arsenic transported in the same phase. For example, the arsenic found in the greater than 5 μm fraction was the highest in period I, the same interval when the iron found in that fraction was also the highest.

It is interesting to note that the As/Fe ratio in the leachate during period I is appreciably lower than the ratio in the original sorbent (about 0.017). If colloids and particulates were a consequence of solid phase breakup, one would expect the As/Fe ratio to be at least equal to that of the original sorbent, and perhaps higher, considering that break-up particles come from the sorbent's surface, which is where the arsenic is concentrated. A possible explanation for this observation is that the particles in the leachate are actually composed of re-precipitated iron that does not have either enough residence time in the GFH bed to re-equilibrate with the dissolved arsenic or a capacity for arsenic equal to that of the original sorbent. An interesting consequence of this is the fact that the amount

of arsenic that remains in the column per unit mass of sorbent remaining increases during period I. This increased apparent capacity of the sorbent will be detrimental to the leaching process in subsequent stages of operation (see below). The apparent increased capacity of the sorbent might be a consequence of other processes that contribute to the fixation of arsenic. Even though the leaching of iron will create new surface area on the sorbent, it is difficult to believe that re-adsorption of arsenic on the new surfaces would yield an increased apparent capacity of the sorbent: if this were the case, the experiment would be creating a sorbent with a higher specific capacity of the original GFH, a fact that seems unlikely. At this point, we do not have a definite explanation on how the arsenic is retained in the column over the original specific capacity. We speculate that arsenic might be sorbed or co-precipitated in processes that involve the organic matter present in the column.

Figure 5.3 shows the pH and ORP in the effluent of the column for the entire duration of operation. It can be seen that the pH at the start of the experiment was about 7.0. In period I, the pH initially fell to pH 6.3 and then steadily climbed up to pH 7.4. The initial low pH was indicative of the generation of organic acids during the degradation of the compost. This is similar to the acetogenic leachate phase in an actual municipal landfill scenario (Westlake, 1995). The ORP of the leachate was about -15 mV at the start of the column, but it steadily decreased over time. The ORP in the effluent showed an exact opposite behavior to the pH, which was expected. At any given point during the run of the column, when the pH plot had an upward slope, the ORP plot had a downward slope

and vice versa.

Figure 5.2 shows the alkalinity and DOC measured in the column effluent. In period I, the influent was de-ionized water with a pH 6.1 and alkalinity less than 30 mg/L, and close to zero DOC. Hence all the alkalinity and DOC observed in the effluent was generated within the column. The effluent alkalinity and DOC steadily dropped. Initially, the DOC was high because it consisted of soluble organics in the compost, the organics formed by the microbes due to the degradation of the compost, and also the endogenous organics present in the anaerobic digester sludge.

Period II

By the end of period I, the microbiological activity inside the column seemed to decrease due to the lack of electron-donating organic substrate. To compensate for this, a moderate amount of VFA (1.58 g/L) and alkalinity (2 g/L of NaHCO_3) were added with the influent and the pH was adjusted to 7.0. As a result, the pH had a stable value in the range 7.5 – 7.9 (Figure 5.3). This is similar to the methanogenic leachate generation phase in an actual landfill. When methane gas generated in the column was measured, methane comprised about 39% of the total gas on day 79 of the column run, whereas it was 51% of the total gas generated on day 296. During the most stable period of the column run (between days 200 and 660), the ORP was in the range –130 mV to –180 mV with a median value of –165 mV (Figure 5.3). This range of ORP values is within the typical range expected in a municipal landfill leachate (Nanny, 2002). The alkalinity of the

leachate increased due to the addition of the bicarbonate, but by the end of period II it had dropped down to values similar to those at the beginning of the period (Figure 5.2). The DOC showed a similar behavior (Figure 5.2). However, the effluent alkalinity and DOC were always lower than the influent alkalinity (shown by the horizontal line in Figure 5.2) in period II, as a consequence the consumption/deposition of bicarbonate and organics inside the column. The decrease in effluent DOC between the start and end of period II may not indicate progressively increasing microbial activity, but rather it is probably a result of the gradual washing away of the indigenous organics from the compost inside the column.

From Figure 5.4, it can be seen that the addition of VFA and alkalinity had an immediate effect on the leaching of iron. The iron concentration in the dissolved/colloid fraction increased sharply to levels that were much higher than the highest concentrations observed in Period I of the experiment. More than 98% of the dissolved/colloid iron was Fe(II), indicating that the supplemented organics helped boost microbial activity which in turn reduced Fe(III) to Fe(II). From Figure 5.2, it can be seen that the arsenic concentration in the leachate also started to increase with the addition of VFA and alkalinity. The total dissolved/colloid arsenic concentration exhibited more than a 10-fold increase between the beginning and end of period II. All through period II, the ratio As(III):As(V) in the dissolved fraction varied between 3:1 and 5:1, signifying arsenic reduction in addition to iron reduction in this period.

During period II, the total iron concentration increased at first, but the dissolved/colloid iron concentration ended up being higher than the sum of all three particulate fractions. An explanation for this observation is that the loosely attached agglomerates on the periphery of the parent GFH mass gradually got depleted, the GFH mass inside the column got more consolidated, and biochemical dissolution and re-precipitation accounted for most of the loss of iron from the column.

One of the most important observations during this period is the sharp increase in the As/Fe ratio (Figure 5.6). We believe that the depletion of the iron might be partly the cause of this behavior. At the end of period II, we estimate that 64% of the original iron has leached out of the column, while only 29% of the arsenic has. This behavior indicates that arsenic leaching is becoming less dependent on iron leaching: note the strong increasing trend in arsenic concentration at the end of period II while the iron concentration decreases (Figure 5.4).

Period III

By the end of period II, the alkalinity and DOC in the column leachate had dropped once again to values out of the range of a typical landfill. Even though the dissolved/colloid arsenic concentration was on the rise, the iron concentration was on the decline. Microbial activity in the column was again being limited by the availability of organic substrates. For this reason, in period III, the influent was amended with an excess of organics (15.8 g/L), high alkalinity (4 g/L) and the pH was adjusted to 7.0. As a result,

the leachate pH exhibited a sharp increase from 7.7 at the beginning of period III to 10.7 by the end of the period (Figure 5.3). The increase in pH was due to the reduction of the VFAs by the microbes inside the column. Coupled to this, the buffering capacity of the column ingredients had decreased which resulted in the rise in pH. In this period, the ORP dropped from -130 mV to -180 mV. The effluent alkalinity and DOC also increased reflecting the increase of VFA and bicarbonate in the influent (Figure 5.2). However, as can be seen from Figures 5.4 and 5.5, the increase of VFA had minimal impact on the leached iron concentration, which remained flat all through period III. The dissolved/colloid arsenic concentration, on the other hand, continued to increase throughout period III. This was evidently arsenic not associated with iron, since the iron concentration did not increase at all in this period, which is consistent with the high values of the As/Fe ratio observed in this period (Figure 5.6). The other important observation in period III is that the As(V) fraction of the dissolved arsenic started to increase. The increase in the dissolved As(V) concentration is probably due in part to desorption of arsenic from GFH surface as a result of the increase in pH. The other factors contributing to the increased As(V) concentration could be the loss of the reductive capability of the microbes inside the column and the oxidation of some of the reduced arsenic by the excess VFA in solution.

Period IV

By the end of period III, the pH of the column leachate had increased up to 10.7 and such a high pH would be unrealistic in an MSW landfill. Consequently, the influent pH was

lowered from 7.0 to 4.8, which would be close to the pK_{a1} of the VFAs in the influent. This resulted in the immediate drop of pH, and, by the end of period IV, the leachate pH dropped below 6.5 (Figure 5.3). This was also associated with a sizable increase of ORP. The ORP changed from -170 mV to -48 mV during period IV (Figure 5.3). The alkalinity in the effluent also dropped substantially during this period, while the DOC was still in excess (6700-7200 mg/L). Both arsenic and iron concentrations decreased throughout period IV (Figures 5.4 and 5.5). Both dissolved/colloid arsenic concentration and dissolved iron concentration had decreased by more than 50% between the start and end of period IV. This was an indication that the microbial population inside the column was on the decline. In period IV, the As(III) concentration also decreased and for the first time during the entire column run, the As(V) concentration was more than the As(III) concentration. The Fe(II): Fe(III) ratio had also dropped down to 4:1 by the end of period IV.

Period V

By the end of period IV, the leachate pH had dropped off to 6.3. So, in period V, the influent pH was adjusted to pH 5.8 instead of pH 4.8. This resulted in an increase of the effluent pH and a drop in its ORP (Figure 5.3). The effluent alkalinity also increased and there was no impact on the DOC. There was almost no change in the total dissolved iron concentration between period IV and period V, even though the Fe(II):Fe(III) ratio continued to drop. The dissolved arsenic concentration, on the other hand, continued to decrease and by the end of period V, which reflects a depletion in the remaining arsenic

in the column.

Implications

The GFH column was run for a length of 892 days, and about 487L of influent had flown through the column. The iron leached out in that period of time was about 69% of the total iron inside the column. However, this estimate is approximate, since column samples were only collected once in every 7 days, and the concentrations averaged over the 7-day period. The possibility of significant diurnal variation of the amount of leaching, especially in the initial, most aggressive leaching phase of the experiment cannot be discounted and must be factored in during the analysis of total mass balance. The total arsenic leached out in the duration of the column run was about 49% of the total, and the concentrations spiked in the last stage of the run of the column. This proves the fact that if the residual is exposed to leaching conditions for long enough duration, the sorbent itself might leach away at a higher rate than the sorbate. If that occurs, eventually there will be a significant increase in the concentration of the sorbate in the leachate. From a practical standpoint, the accelerated leaching of arsenic once significant depletion of the sorbent has occurred would be an undesirable feature of landfill operation, since concentration of arsenic in the landfill leachate might achieve unacceptable levels at that point.

Acknowledgements

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CHAPTER 6

DIFFERENT ABSRS BEHAVE DIFFERENTLY UNDER SIMILAR LANDFILL LEACHING CONDITIONS

Introduction

Chronic exposure to low levels of arsenic in contaminated drinking water has been known to cause cardiovascular, pulmonary, immunological, neurological and endocrine disorders as well as skin, lung, bladder and skin cancers (NRC, 2001). This has caused the United States Environmental Protection Agency (USEPA) to lower the drinking water standard for arsenic from 50 to 10 parts per billion (ppb) with compliance in early 2006 (USEPA 2001). This will cause about 4000 water utilities in the US to either modify or implement new technologies for removal of arsenic from drinking water in order to comply with the new guidelines. Most of the affected utilities are small-scale operations serving a population of less than 3,301 (USEPA, 2001). Among the EPA identified Best Available Technologies (BAT) for the removal of arsenic, adsorption onto solid sorbents seems to be the most attractive option for small utilities due to issues with conservation of water and on-site chemical handling. Aluminum and iron oxides/hydroxides are long known for their effectiveness as packed-bed adsorbent systems for removal of arsenic from water (Chen et al., 1999, Jekel and Seith, 2000). The EPA has recommended Activated Alumina (AA) as a BAT. However, recent studies have shown that iron oxides/hydroxides like Granular Ferric Hydroxide (GFH) and Bayoxide (E33) might be a better sorbents than AA under comparable conditions (Amy et al., 2000, Bayer, 2005). In

this research AA, GFH and E33 were studied as they are likely to be among the most popular media for removal of arsenic from drinking water.

Using EPA published frequency of occurrence and concentration data (USEPA, 2001), we estimate that about 6 million pounds of Arsenic Bearing Solid Residuals (ABSRs) will be generated each year after the implementation of the new arsenic MCL. The Toxicity Characteristic Leaching Procedure (TCLP) (Federal Register, 1986) is used to assess the leaching potential of arsenic from ABSRs. Currently most ABSRs pass the TCLP and are thus considered safe for disposal in non-hazardous mixed solid waste (MSW) landfills. However, the TCLP poorly simulates the alkaline pH, anaerobic microbiological activity, mineralogic aging, low redox potential and high organic concentrations typical of MSW landfills (Christensen et al. 2001, Kjeldsen et al., 2002). These same conditions are expected to favor mobilization of arsenic from metal oxide sorbents (Ghosh et al., 2005). Previous research has shown that TCLP does underestimate the leaching potential of arsenic residuals under landfill conditions (Ghosh et al., 2004).

Microbiological reduction and mobilization of iron and arsenic are suspected to be major factors driving landfill leaching. Anaerobic reduction of iron and arsenic in a wide variety of environments has been well documented (Straub et al., 2001, Lovley 1997, Oremland and Stolz, 2003, Harrington et al., 1998, Kuai et al., 2001, Rosen 2002). Microbial mobilization of arsenic from Fe-(hydr)oxides, whether adsorbed on or contained within the mineral structure, has also been demonstrated (Islam et al., 2004, Langner et al.,

2000, Zobrist et al., 2000, Jones et al., 2000, Cummings et al., 1999). Several mechanisms including competitive desorption, reductive desorption and reductive dissolution can lead to mobilization. Even though mature MSW landfill conditions would be ideal to support and promote such microbial mobilization, the TCLP test does not simulate these conditions.

The TCLP test also specifies filtration (0.6 μ m to 0.8 μ m) of the leachate after the extraction procedure and prior to analysis. However, in an actual landfill, much of the arsenic may be mobilized with particles of diameter greater than 0.8 μ m. A recent study (Tadanier et al., 2005) demonstrated the formation of As-bearing colloids through microbially mediated reduction of Fe-(hydr)oxides, thereby enhancing arsenic mobility. The work showed that the bioreduction of Fe-(hydr)oxide by microorganisms leads to arsenic mobilization by deflocculation of aggregated nanoparticles. This is consistent with the GFH column work reported in the preceding chapter, in which up to 70% of the arsenic in the effluent was particulate associated.

Whether from groundwater or surface water for use as drinking water, arsenic in drinking water is present either as arsenite, As(III) or as arsenate, As(V). In near-neutral conditions arsenite would be present predominantly as arsenous acid whereas arsenate will be present primarily in an anionic form. Metal oxide/hydroxide adsorption of ions is typically more efficient than of neutral species (Stumm, 1996) and so water containing a significant concentration of arsenite would generally undergo pre-oxidation prior to the

application of an arsenic removal technology (USEPA, 2001). Thus when solid arsenic residuals are generated they would be loaded with arsenate only. Consequently, in this research, the three sorbents were loaded only with arsenate prior to their placement in the column reactors.

The goals of the present research are: a) to establish a set of conditions inside flow-through columns that would be representative of a MSW landfill, b) to measure the leaching of arsenic and iron in the dissolved versus particulate phases from the three representative ABSR, c) to quantify temporal changes in arsenic leaching over the long-term, and d) to comparatively assess different ABSR performance and arsenic release mechanisms under mixed solid waste (MSW) landfill conditions. Due to the broad range of MSW landfill conditions, the results reported here cannot indicate the arsenic or iron concentrations that would be observed in all landfill leachates after ABSR disposal. However, they do provide a broad understanding of the various physical, chemical and biological phenomena that might occur in and around the residual and the magnitude of leaching that would be expected through time. This understanding of the various leaching mechanisms in a landfill is key to assessing the hazard posed by landfill disposal of ABSR and designing more appropriate leaching tests for ABSRs.

Materials and Methods

Sorbents:

Activated Alumina (AA): Conventional AA has been implemented for the semi-selective removal of arsenic from potable water (Rubel and Hathaway, 1985). The AA used in the current research is AA400G, manufactured by Alcan (Cleveland, OH). The properties of the sample according to the manufacturer's product specifications are particle size, 80-100mesh; specific surface area, 350-380m²/g; and pore volume, 0.50cc/g. This sorbent can be regenerated once it is saturated with arsenic, although this is not expected to be frequently practiced. (USEPA, 2001,USEPA, 2001a).

Granular Ferric Hydroxide (GFH): GFH is a weakly crystalline β -FeOOH produced by conditioning previously compacted iron hydroxide slurry (Dreihaus and Jeckel, 1998). It is in the form of irregular grains up to 2mm diameter. The GFH sample used in this study contained 55% water. Based on whole sample digestion, iron constitutes 69% of the dry weight and about 31% of the overall weight of the sample. In order to preserve its activity, the material must not be dried and the mechanical stability of the granules is less than that of activated alumina. Under comparable conditions, the capacity of the GFH is estimated to be 5X greater than that of conventional alumina (Amy et al., 2000). GFH® is manufactured by GEH and distributed in the US by U.S. Filter. It is designed as a throw-away (non-regenerable) media. GFH is shipped wet and will not maintain its properties if dried.

Bayoxide SORB 33 (E33): The E33 media manufactured by Bayer for Severn Trent is a synthetic iron oxide hydroxide, which is mostly α -FeOOH (Bayer, 2005). The E33 spent

media (as received, in wet condition) contained 46% water (vacuum filtration, followed by drying to constant weight). Based on whole sample digestion, iron constitutes 48% of the dry weight and about 26% of the overall weight of the sample. The medium is in the form of dry granules with particle sizes ranging from 0.5mm to 2mm. The specific surface area ranges from 120m²/g to 200m²/g and the bulk density is 0.4-0.6g/cm³ (Bayer, 2005). The E33 medium was chosen for this research because it demonstrated 3 times the adsorption capacity (for arsenic) of GFH in a pilot plant operation in Mesa, Arizona (Figure 6.1) and is shipped dry, making it more easily handled than GFH.

Pre-equilibration of the Sorbents:

The AA and GFH were pre-equilibrated with arsenic prior to their placement in the columns. For the AA, a solution was prepared with 1.5kg AA and 3L water (Milli-QTM Water System by Millipore). Sodium Arsenate Heptahydrate (Na₂HAsO₄·7H₂O, KR Grade Aldrich Sigma) was used to prepare an initial aqueous arsenic concentration of 517mg/L (as As). For the GFH, 1kg (bulk weight) of GFH was equilibrated with 2L water. The initial concentration of arsenic in the GFH solution was 2.71g/L. Solution ionic strength was adjusted to 0.1M with NaCl (GR Grade EM Science). The pH was adjusted to 7.0, using Hydrochloric Acid (Spectrum) or Sodium Hydroxide (Sigma). After 48 hours of equilibration on a shaker table (Orbit, reciprocating speed 125 rpm), liquid samples were collected and analyzed. After equilibration, the aqueous concentration was 193 µg/L (as As) and 25.66 µg/L (as As) in the AA and GFH solutions respectively, which are in the range expected for arsenic in drinking water that would

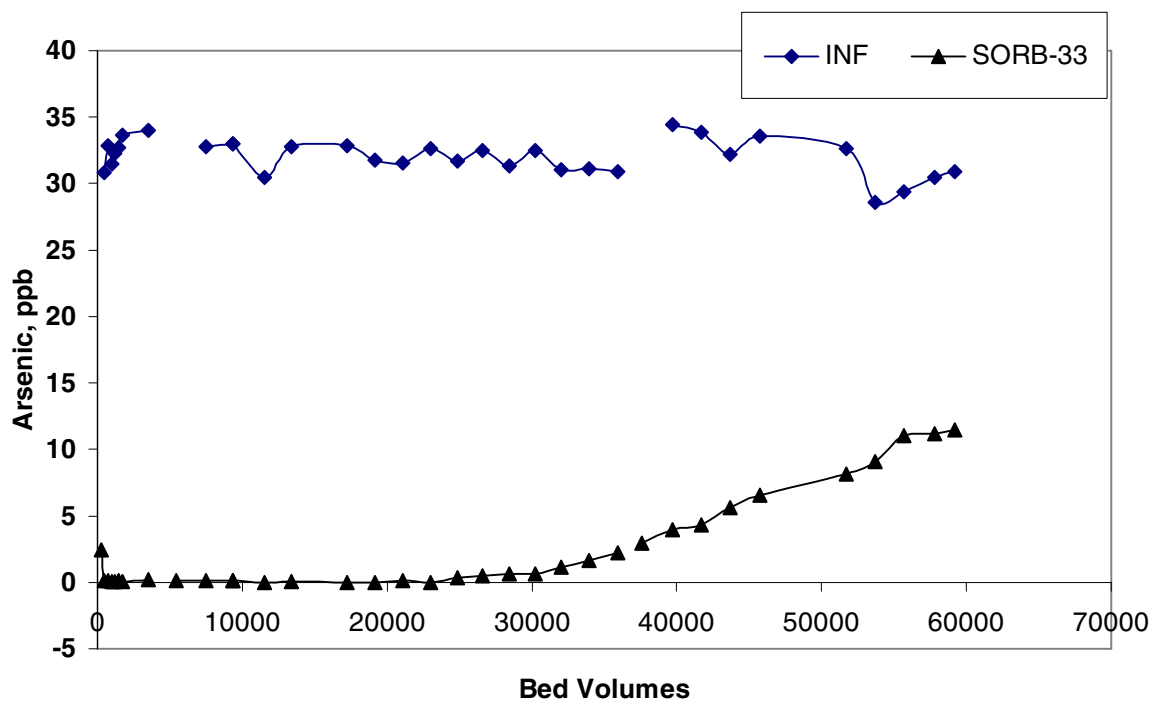


Figure 6.1: Influent arsenic concentration and breakthrough curve for E33 media used in Mesa Pilot Treatment Plant.

need treatment. The sorbed concentrations of arsenic on the solid were 1.04mgAs/gAA and 12.04mgAs/gGFH (dry) (which translates to 17.44mgAs/gFe).

The E33 used in this research was a residual obtained from a pilot plant that removed arsenic from drinking water in Mesa, AZ. The breakthrough curve for the E33 media is shown in Figure 6.1. The flowrate in the columns at the pilot plant was 10gpm with an empty bed contact time (EBCT) of 5mins. The media from the top half of the column had higher arsenic loading than the media from the bottom half of the column. So a 50-50 (by mass) mixture was made from the two halves and this mixture was placed in the E33 column. The average sorbed concentration of arsenic on the mixed E33 media was 9.09mgAs/gE33 (dry) (which translates to 18.94mgAs/gFe).

Flow-through Columns:

The details of the column geometry, operation and analytic techniques are presented in the previous chapter (Chapter 5). All columns were operated in downflow mode and the flowrate in each was fixed at 0.44mL/min. The saturated bed volume in all columns was 12.1L and the hydraulic residence time varied between 10 and 15 days. All the columns were placed in a climate controlled room at 30°C. The same protocol was followed for the sampling from all columns and analysis of all samples was done with the procedure as described in Chapter 5.

Column Composition: Two sections occupying 5cm from the bottom and 3cm from the top of the columns were packed with gravel with a diameter from 0.3cm to 1cm. The active beds sat between the gravel layers. The gravel was added to properly distribute the hydraulic flow at the inlet and the outlet of the columns. The composition of the active beds is shown in Table 6.1. Details on the individual components are provided in the previous chapter (Chapter 5).

Influent: For the initial period of operation with all columns, the influent was de-aerated, de-ionized water. For the AA column, no amendments were needed to the influent throughout the duration of run. However, with the progress of the other columns, as the Dissolved Organic Carbon (DOC) and alkalinity of the effluent began to drop, the influent was spiked with sodium bicarbonate and a mixture of Volatile Fatty Acids (VFA) (which served as the electron-donating substrate) with the pH adjusted to a desired value, as described below. Effort was made to keep the pH, alkalinity, ORP and DOC of the column leachate within the range of values expected in MSW landfill leachate. The details on the VFA composition and the influent preparation are provided in the previous chapter. For the GFH column, the influent had different compositions in five different periods of operation (Chapter 5). For the E33 column, there were three periods of operation. In period I, the influent was de-ionized water. In period II (starting on day 218) the influent was supplemented with organics (15.8g/L) and alkalinity (4g/L) and the pH was adjusted to 7.0. In period III (starting from day 343 onwards) the organics and

Table 6.1: Table showing the composition of the three column reactors

Parameter	Activated Alumina	Granular Ferric Hydroxide	E33
Mass of sorbent	1.014kg	542g	474g
Mass of As	1.05g	2.86g	2.33g
Compost	1kg	1.5kg	1.5kg
Paper	750g	750g	750g
Anaerobic digester sludge	3L	4L	4L
Duration of Run	302 days	892 days	383 days
Bed Volumes	25	64	32
Total Leachate Generated	166L	487L	208L

alkalinity were maintained at the same levels, but the influent pH was adjusted to 4.8 instead of 7.0.

Results and Discussion

Operation of the Columns

The goal of this project was to simulate conditions that would be expected in an MSW landfill. To that end, the column operating parameters were designed so that the pH, ORP, alkalinity and DOC of the column leachates were within the window of the values for those variables that would be expected in the leachates from actual MSW landfills (Bagchi, 1994). Table 6.2 shows the maximum, minimum and median values for pH, alkalinity, ORP and DOC of the effluents from all three column reactors. As can be seen from Table 6.2, both the maximum and minimum values of all the variables are within the limits that might be expected in a MSW landfill. If at any point during a columns' run, one of the variables exceeded or fell below the limits of a MSW leachate for a parameter (i.e., pH, alkalinity), the influent to the column was immediately amended to return it to within the boundaries of landfill parameters. There were sudden spikes of organics and alkalinity at various points of the column runs, which would not be expected in an actual landfill leachate and that resulted in a corresponding increase or decrease of the rates of arsenic and iron leaching. The GFH column had the most number of adjustments during its operation and they have been described in detail in the previous chapter. Due to operational shortcomings as well as differential rates of arsenic depletion, the three columns were operated for different durations. Due to media compaction and

Table 6.2: Table showing the maximum, minimum and median values of pH, ORP, alkalinity and DOC in the three column reactors

Sorbent	pH			Alkalinity (mg/L)			ORP (mV)			DOC (g/L)		
	Max ¹	Min ¹	Median ²	Max ¹	Min ¹	Median ²	Max ¹	Min ¹	Median ²	Max ¹	Min ¹	Median ²
AA	7.4	6.1	6.8	3650	350	600	-31.6	-134	-98.2	4.1	1.05	1.5
GFH	10.7	6.2	7.4	3050	335	795	-4.6	-191	-133.8	7.4	0.3	0.8
E-33	8.3	6.3	7.3	3120	995	1975	-36.8	-215	-103.7	8.0	0.5	2.8

¹ The maximum and minimum values measured in the effluent during each column's run duration. However, column run lengths differed and the values may not reflect the values that would have been measured had all runs been for equal duration.

² The median value of the measured parameters in the effluent during each column's run duration. However since column run lengths differed, the median is calculated from different number of available data points and may not reflect the values that would have been measured had all runs been of equal duration.

plugging of the E33 column, it was terminated at 383 days. The AA column also had operational problems due to leaking and it was terminated after 302 days.

Dissolved Phase Leaching

Figure 6.2 shows the dissolved phase arsenic concentration from all three columns and Figure 6.3 shows the dissolved phase iron concentration from the GFH and the E33 columns. The dissolved aluminum concentration in the effluent of the AA column was periodically sampled, but never exceeded 173 $\mu\text{g/L}$. From Figure 6.2 it is evident that the sorbents leach arsenic differently from each other, when responding to very similar leaching conditions. Both GFH and E33 are iron oxide sorbents and had similar initial sorbed arsenic concentrations (12.04mgAs/gGFH (dry) and 9.09mgAs/gE33 (dry)). Even though E33 had slightly less arsenic sorbed on to it (per unit mass), it leached 4-5 times the concentration of arsenic as leached by GFH during the initial period (first 200 days) of operation (Figure 6.2). Batch desorption experiments done in the laboratory show that arsenic desorption/dissolution from E33 media is more strongly pH dependent than the GFH media (Appendix C, Kosson Trials, Solubility as a function of pH). Thus, the more rapid leaching from the E33 than GFH can be partially explained by the higher pH in the E33 column relative to the GFH column in the initial period (first 150 days) of column operation (Figure 6.4).

In the E33 column it was also observed that there was a significant increase in the dissolved arsenic concentration as a response to the increase in VFA (15.8 g/L) and

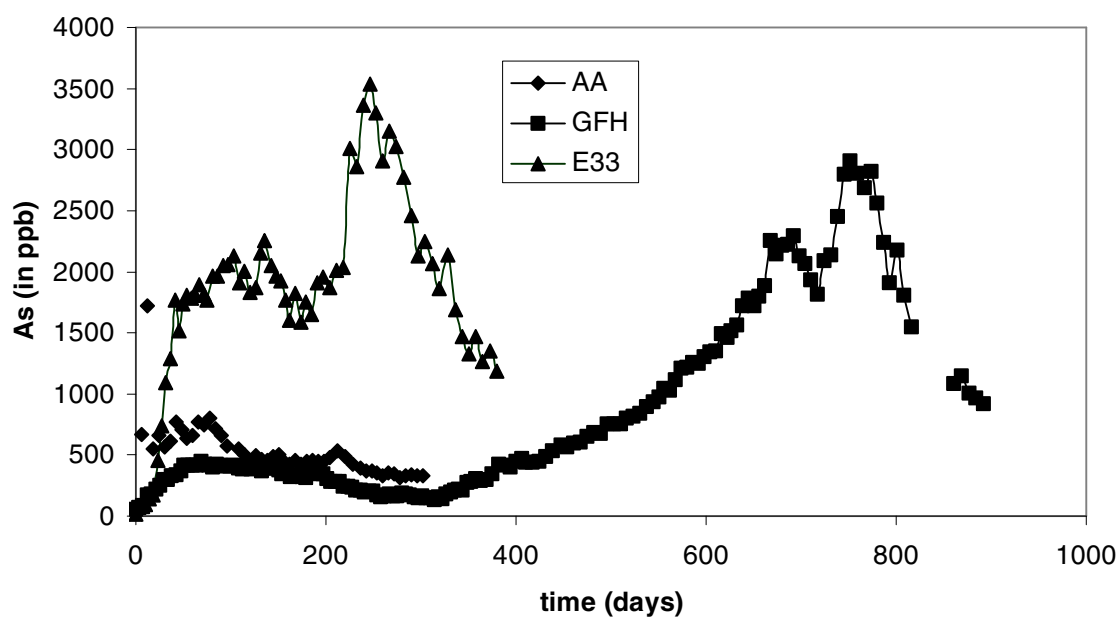


Figure 6.2: Concentration of the total arsenic in the dissolved phase (in $\mu\text{g/L}$) in the effluent for the entire duration of the three column runs.

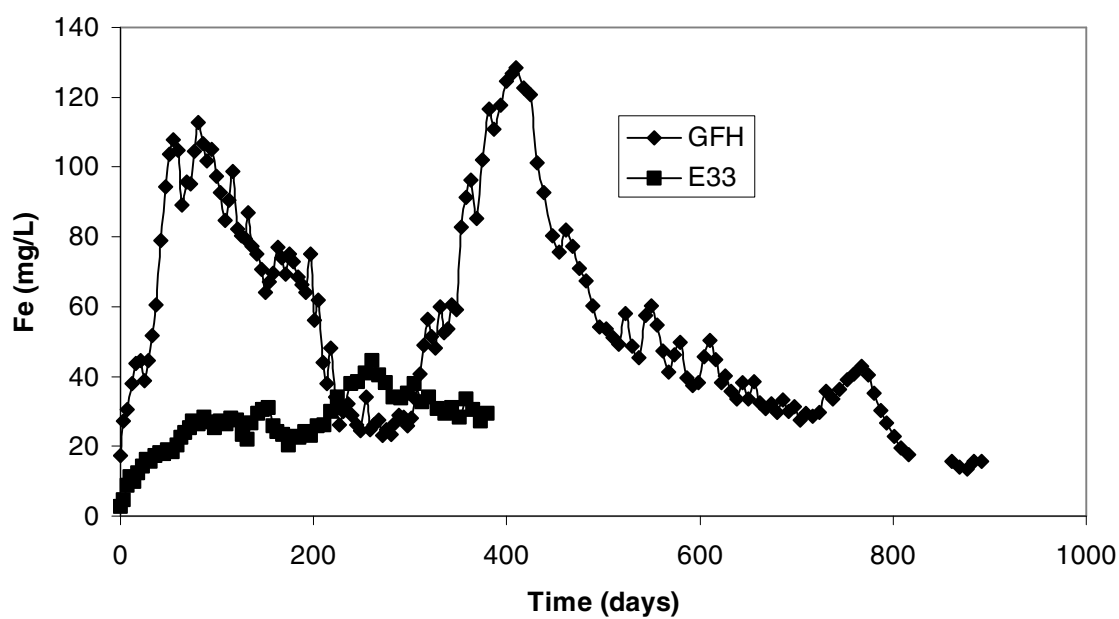


Figure 6.3: Concentration of the total iron in the dissolved phase (in mg/L) in the effluent for the entire duration of the three column runs.

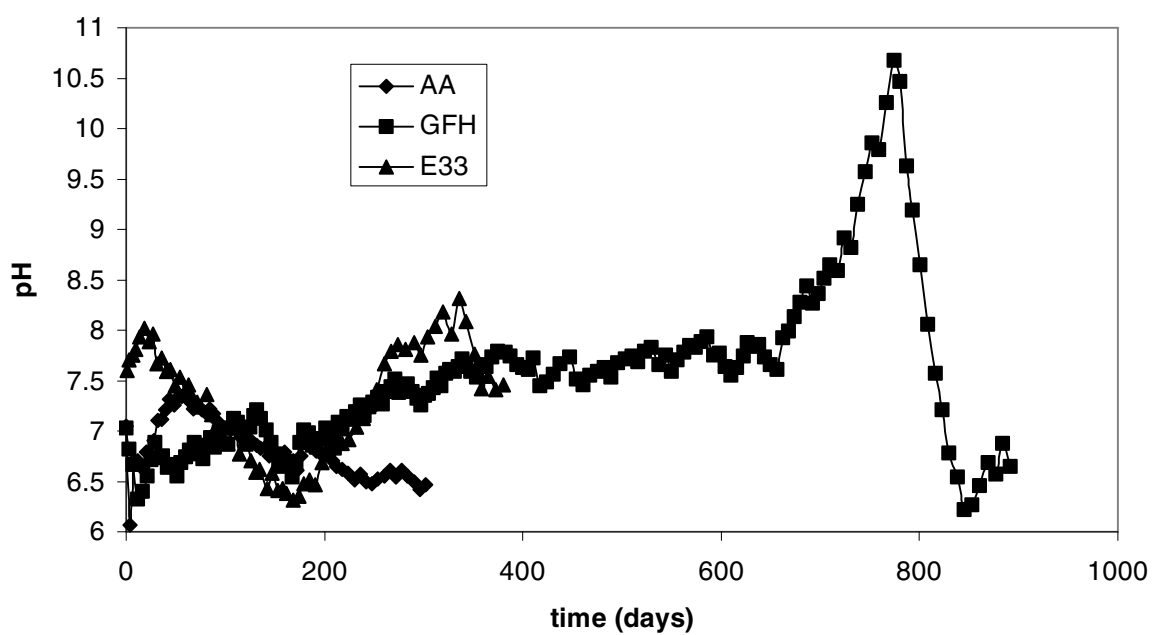


Figure 6.4: pH measured in the effluents of the three columns for the entire duration of the column runs.

alkalinity (4g/L) after 218 days. The dissolved arsenic concentration in the E33 leachate increased from 2037 $\mu\text{g/L}$ to 3539 $\mu\text{g/L}$ in the short period between 218 days and 246 days. However, in the same period the changes in pH (from 6.9 to 7.3) and ORP (from -89mV to -133mV) were not significant (Figure 6.4 and Figure 6.5). This suggests that the increase in the dissolved arsenic concentration was possibly due to a biotic response to the VFA addition. The VFAs probably served as electron donating substrates, thus boosting microbial activity and arsenic dissolution. However, the VFAs themselves could lead to increased arsenic desorption and dissolution through several mechanisms: (1) by directly competing with arsenate/arsenite for surface sites, (2) by sorbing to the surface and creating additional surface attraction and enhanced sorption, (3) by acting as a soluble partitioning agent to bind the ion and keep it in solution, (4) by directly reacting with the sorbent surface to enhance dissolution of the surface and loss of sorption sites or (5) by deposition of NOM on to the solid surface to shield active sites (Stumm and Morgan, 1996, Parks, 1990, Schwarzenbach 1993). The addition of organics in the GFH column did not have a similar effect. When additional organics were supplied to the GFH column (15.8 g/L on day 644), there was some increase in arsenic leaching, but the change was much less pronounced than observed with E33. Comparing the iron leached in the dissolved phase, from the GFH and E33 columns (Figure 6.3), an exact opposite trend to arsenic was observed. In the initial 200 days, 4-5 times the iron leached out from the GFH column than the E33 column. It is useful to point out that both the media had similar amounts of iron in them. Iron makes up about 31% of the bulk weight of the GFH media and about 26% of the bulk weight of the E33 media, the total amount of iron in the

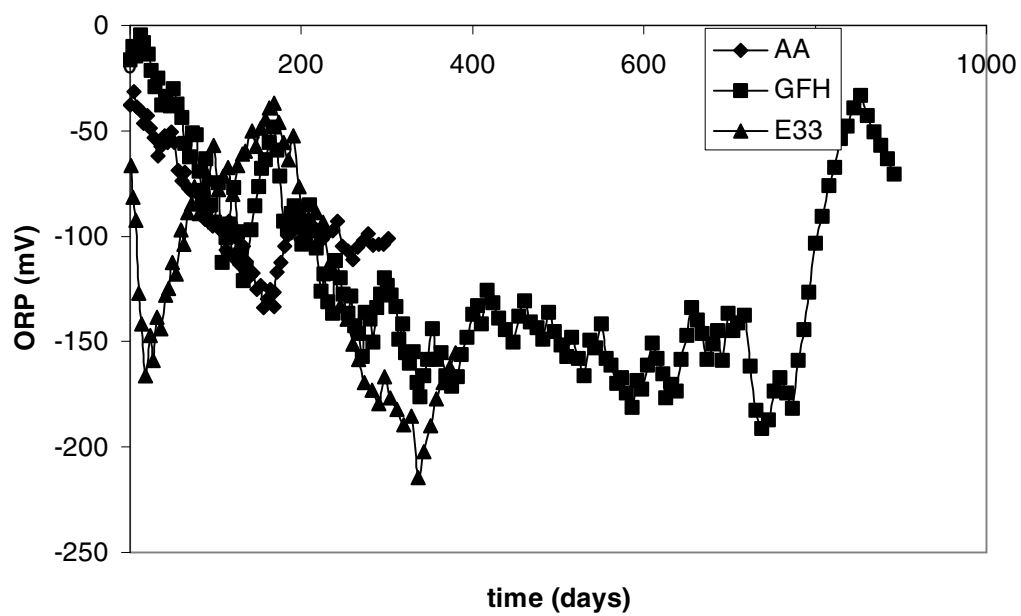


Figure 6.5: ORP (in mV) measured in the effluents of the three columns for the entire duration of the column runs.

GFH column was about 163g, whereas that in the E33 column was 123g. Evidently, the iron phases in the two sorbents are sufficiently different to result in a much higher iron release from GFH than E33. It is also seen that for the GFH column, when a small amount of organics (1.58g/L) and alkalinity (2g/L) is added after day 204, the dissolved iron concentration increases significantly. In the period between day 204 and 410, the dissolved iron concentration increased from 62mg/L to 128mg/L. However, for the E33 column, a 10-fold higher increase in the organics (and twice the alkalinity) on day 218 did not cause a similar increase in dissolved iron concentration, which only increased from 29mg/L to 40mg/L between day 218 and day 267. This suggests that the crystal structure in E33 is more recalcitrant than GFH and hence iron is bonded more strongly in the matrix. Finally, comparing AA and GFH behavior (Figure 6.2), the leached arsenic concentration from AA was about 1.5 times that from GFH during the duration of the AA column run. This is despite the fact that the GFH had about 3 times more arsenic loaded on it than AA (Table 6.1). This has to do with both the difference in bond strengths of the arsenic to AA and GFH as well as the fact that most of the surface area of the GFH is inside the individual grains, and diffusive transport of arsenic can limit the rate of arsenic leaching. Previous work on the kinetic studies of adsorption of arsenic on to AA and GFH demonstrated that the AA reaches equilibrium faster than GFH (Ghosh et al., 2005). Figure 6.6 shows the As(V)/As(III) ratio in the dissolved phase in the effluent from all three columns. The common result is that for most of the run duration the As(V)/As(III) ratio in all columns is much less than 1. It is to be noted that for all three sorbents,

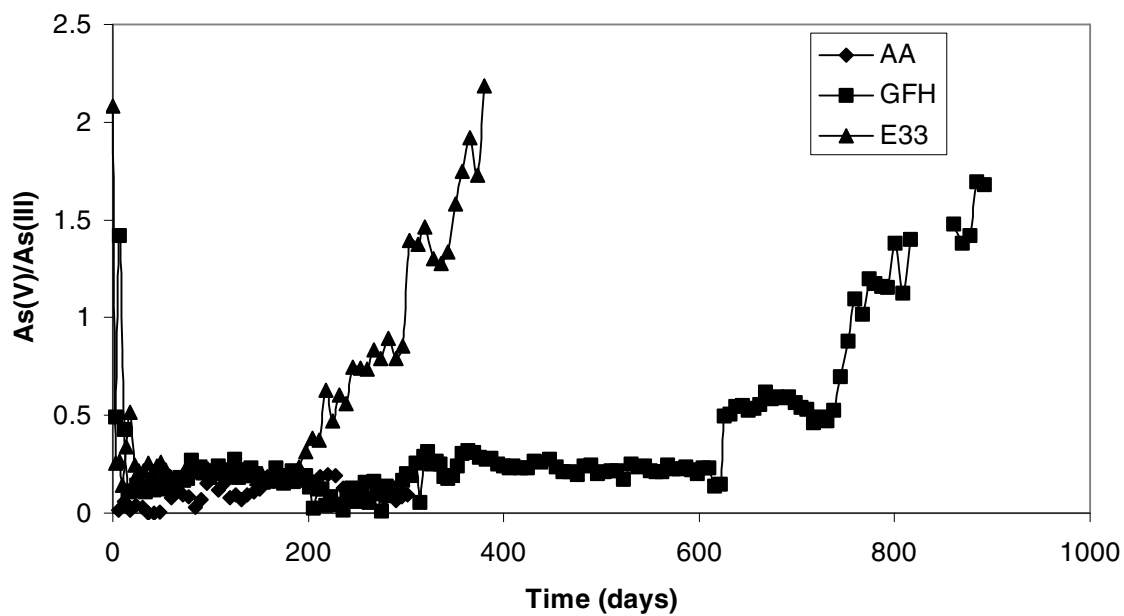


Figure 6.6: As(V)/As(III) ratio in the dissolved phase of the effluent from the three columns.

initially only As(V) was sorbed on to them. Thus, all the As(III) in the effluent is due to chemical and microbiological reduction processes. Microorganisms of various taxonomies have shown the ability to utilize As(V) as an electron acceptor for anoxic respiration, yielding energy to support their growth (Oremland and Stolz, 2003). The dissimilatory reduction and mobilization of arsenic, specifically adsorbed on iron oxide surfaces has also been demonstrated (Zobrist, 2000, Langner 2000). Thus, the formation of As(III) is an indirect confirmation of the presence of reductive conditions and anaerobic microorganisms inside the columns as would be expected in mature MSW landfills. Comparing the AA to the two iron sorbents, we find that the median As(V)/As(III) value for AA is 0.05 whereas that for both iron sorbents in the first 300 days of the column runs is 0.25-0.3. This means that there was 5-6 fold more conversion of the As(V) to As(III) in the AA column than in the GFH and E33 columns. This is probably because in the AA column oxidation is relative to the As(V)/As(III) redox couple, whereas in both the GFH and E33 columns there is a more positive Fe(III)/Fe(II) redox couple, in addition to the arsenic couple. Literature data shows that the standard electrode potential of Fe(III)/Fe(II) is 0.77V. At neutral pH, arsenate would be equally distributed between H_2AsO_4^- and HAsO_4^{2-} anions, whereas arsenite would be uncharged (HAsO_2). The standard potentials for $\text{H}_2\text{AsO}_4^-/\text{HAsO}_2$ and $\text{HAsO}_4^{2-}/\text{HAsO}_2$ are 0.666V and 0.881V respectively (Bard et al., 1985). From the standard potentials alone, Fe(III)/Fe(II) and As(V)/As(III) ratios would be expected to be similar to one another. However, most of the Fe(III) that is formed might be precipitated and retained in the column thus accounting for such a low Fe(III)/Fe(II) ratio measured in the effluent. From

the ORP figure (Figure 6.5), it can be seen that the ORP of the AA column was slightly more negative than the GFH column during the first 200 days of the column operation, which is in agreement with the higher proportion of As(III) observed in the AA column effluent. However the ORP in the E33 column was far more negative than both the AA and GFH columns in the initial 100 days of the E33 column operation. From the ORP data alone, a lower ratio of As(V)/As(III) would be expected in the E33 column. However, since the total dissolved arsenic was much higher in E33 than in both GFH and AA in the initial period of operation, it is possible that a higher fraction of the available As(V) could not be reduced to As(III) by the microbes. Direct evidence of the reduction of iron in the GFH and E33 systems is shown in Figure 6.7, which shows the Fe(III)/Fe(II) ratio in the dissolved phase in the respective column effluents. From the figure, it is evident that for both GFH and E33, the Fe(III)/Fe(II) ratio in the effluent is much less than 1, meaning that there is much more Fe(II) than Fe(III) in the effluents. Both iron sorbents in their virgin state have only Fe(III), so all the Fe(II) that is measured in the effluent must have been generated inside the column by chemical and microbiological reactions. A great diversity of microorganisms have been isolated from different anoxic environments like sediments, soils, deep terrestrial subsurfaces and hot springs that are capable of anaerobic dissimilatory ferric iron reduction (Straub et al., 2001, Lovley 1997). So, the observation that between 80-95% of the total dissolved iron in the effluent from both columns is in the ferrous state was an expected outcome. From Figure 6.7, it can be seen that the median Fe(III)/Fe(II) value for the GFH column is 0.03 whereas that for the E33 column is about 0.17. The difference between these two

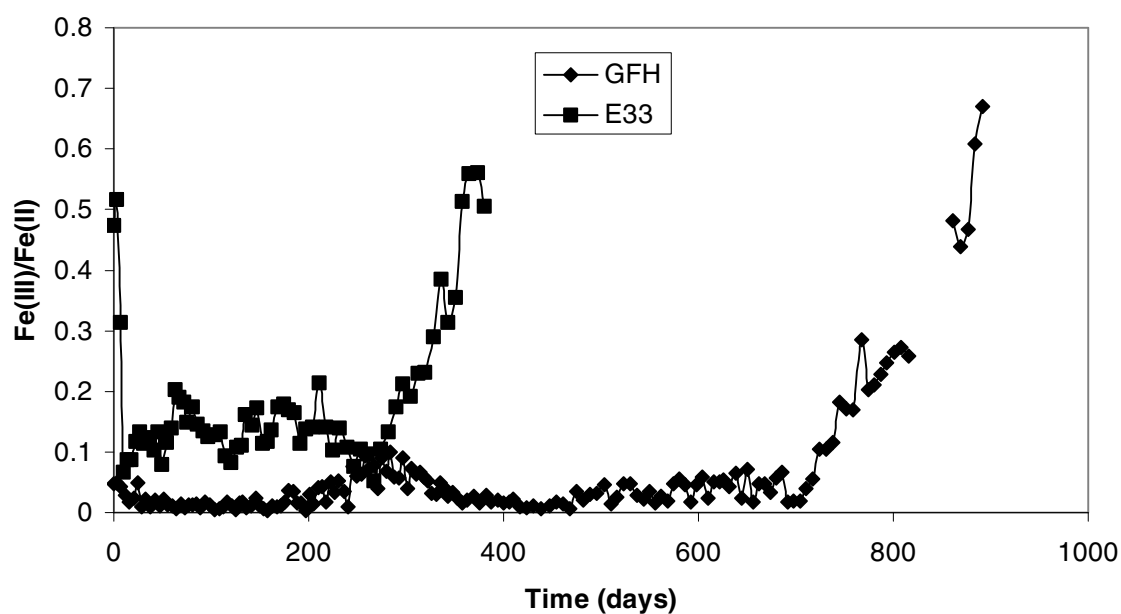


Figure 6.7: Fe(III)/Fe(II) ratio in the dissolved phase of the effluent from the GFH and E33 columns.

numbers is due to the fact that the total dissolved iron in the GFH is 4-5 times as much as in the E33 (Figure 6.3). In the effluents from both columns the Fe(III) concentrations were similar, ranging between 0 and 12mg/L throughout the duration of run. However, the Fe(II) in the GFH column was 4-5times as high as that in the E33 column. The lower concentration of Fe(II) in the E33 column does not necessarily indicate lower microbial activity than in the GFH column. It could be explained by the lesser amount of iron present in E33 than GFH and a less bioavailable iron structure in the E33 crystals than the GFH. Looking at Figures 6.6 and 6.7, it can also be seen that for both the GFH and E33 columns, there is a huge increase in the As(V)/As(III) as well as the Fe(III)/Fe(II) ratios towards the end of the column runs. This increase corresponds to the 10-fold increase in the VFA concentrations in both columns.

Particulate Phase Leaching

Figure 6.8 shows the total arsenic concentrations in the three column effluents after digestion with nitric acid in the microwave digester. Comparing the two iron sorbents, GFH and E33, E33 leached significantly more total arsenic than the GFH throughout the first 400 days. However, comparing Figure 6.8 with Figure 6.2, it can be observed that most of the arsenic leached in E33 is in the dissolved phase, while that in the GFH is in the particulate phase. In fact 55% of the total arsenic leached from E33 is in the dissolved phase, while for the first 500 days of the GFH column, about 70% of the total arsenic is leached in the particulate phase. It is hypothesized that the GFH granules are mechanically weak and more easily broken off from the parent mass. On the other hand,

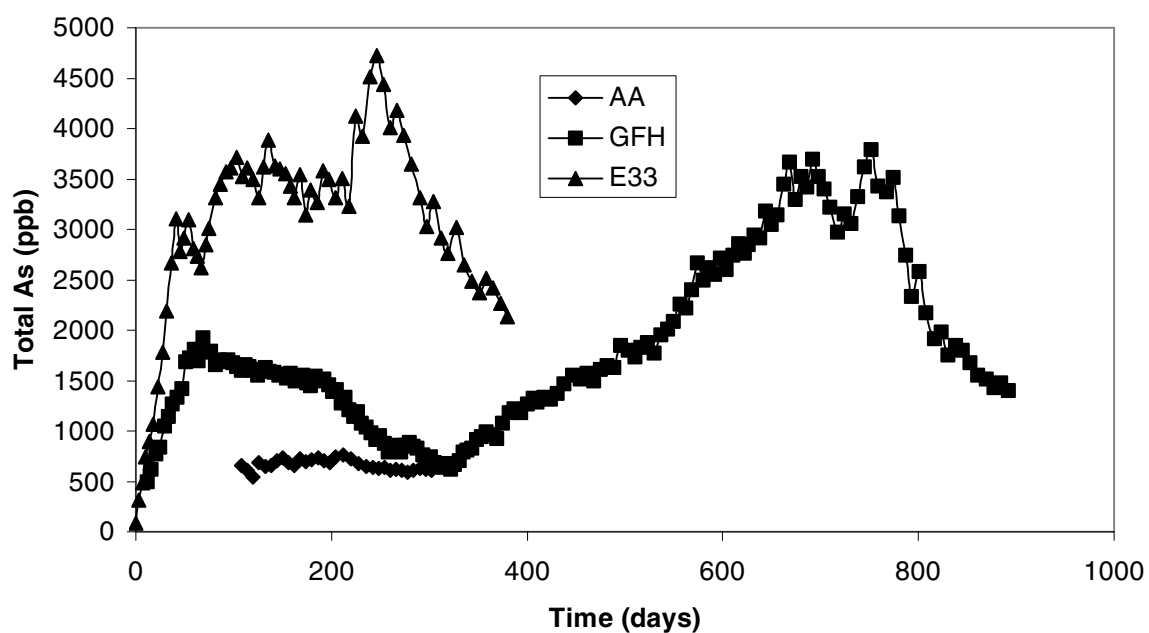


Figure 6.8: Concentration of total arsenic (in $\mu\text{g/L}$) after digestion in the effluent from the three columns.

the E33 grains are much more regularly shaped and crystalline and may remain attached more strongly to the parent mass. It is also notable that the GFH effluent arsenic concentration was increasing, whereas the E33 concentration was decreasing rapidly at the time the E33 column operation was stopped. Thus, it is likely that if the E33 column had functioned longer, its effluent arsenic concentration would have soon been surpassed by that from the GFH column.

Figure 6.9 shows the total iron concentrations from the GFH and E33 columns after digestion. The total iron plots are very similar to the dissolved iron plots (Figure 6.3). The total digested iron in GFH is 10-12 times the total digested iron concentration in E33. If the dissolved iron concentrations are subtracted from the total iron concentrations for both column effluents, the results become more dramatic. It is observed that the particulate iron concentration in the GFH is about 25-30 times the particulate iron concentration in E33. This further accentuates that if both sorbents are disposed of in a landfill environment, the primary mechanism of arsenic leaching and transport will be very different for these two sorbents. While the GFH leaching is more likely to be dominated by particulate phase transport, the leaching from E33 is expected to be primarily in the dissolved phase, even though particulate phase leaching cannot be ignored. Sequential filtration of the samples from the column effluents showed the fraction of iron and arsenic in each size fraction of the particulates. The results from the sequential filtration of the GFH column effluent have been shown in the previous chapter. The results from the sequential filtration of the E33 column showed a very similar trend

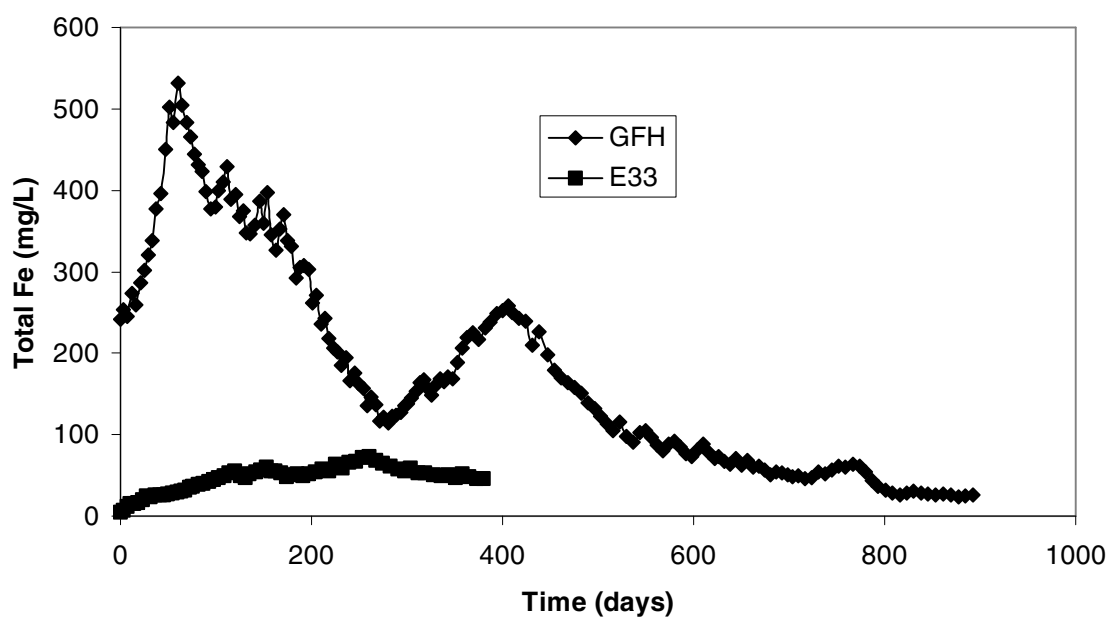


Figure 6.9: Concentration of total iron (in mg/L) after digestion in the effluent from the GFH and E33 columns.

to the GFH (Appendix D). The absolute values of the concentrations of the iron and arsenic in the different size fractions of the E33 column effluent were far lower than those observed in the GFH column. However, the common observation in both column effluents was that there is a direct correlation in trends between the amount of iron and the amount of arsenic transported in each size fraction. The higher the amount of iron in any size fraction on any sampling time, the higher was the amount of arsenic in the same size fraction. This observation was consistent all through the run duration of both columns, and thus indicates that arsenic in the particulate phase is associated with the particulate iron and not with organics or any other particles in the column leachate. The second observation which held true for both columns was that the fraction of the particulates in the highest size fraction ($> 5\mu\text{m}$) had the highest concentrations for both GFH and E33 during the earlier part of the column runs. However, this fraction gradually decreased with time and by the end of the column run the size fraction between $0.45\mu\text{m}$ and $0.8\mu\text{m}$ constituted the highest fraction of the particulates. This shows that for both sorbents, aggressive microbial and chemical activity in the initial phase of the column run was able to cleave off chunks from the parent sorbent mass, which were then transported out of the reactors. However with time, the parent mass surface may have been smoothed, so that there were less big chunks available to be worn off and only smaller sized particulates were being released. The appearance of the small particulates/colloids could also be due to reduction and/or dissolution followed by re-precipitation in a different phase. It is expected that both of these mechanisms may contribute to the total particulate

concentration observed in the effluent. However, further characterization of the particulates was beyond the scope of this project.

Comparing the total to the dissolved arsenic concentration in the effluent from the AA column (Figures 6.2 and 6.8), it is observed that particulate phase leaching was minor for AA. It is to be noted here that for the first 120 days of the run of the AA column, the digested arsenic concentration was not measured and hence, the probability that a greater fraction of the arsenic might have been leached in the particulate phase cannot be discounted for that early period. However, after the digested arsenic concentration measurement began, the total fraction of arsenic leached in the particulate phase increased gradually from 20% to about 45% of the total arsenic leached. This was due to a faster decrease in the amount of total arsenic released than decrease in the particulate fraction. All told, it appears that for AA, dissolved phase transport is probably a more dominant leaching mechanism than particulate phase transport.

In order to further illustrate the role of particulates in the overall leaching of arsenic and iron the particulates as a fraction of the total arsenic and iron have been shown in Figures 6.10 and 6.11, respectively. As mentioned before, the amount of arsenic in the particulate phase is the most significant for GFH. For the first 400 days of the column run, particulate arsenic accounts for at least 75% of the total arsenic leached from the column. Thereafter the fraction of particulates begins to decrease and by the end of the column run, the particulates accounted for only 25-30% of the total arsenic leached. On the other

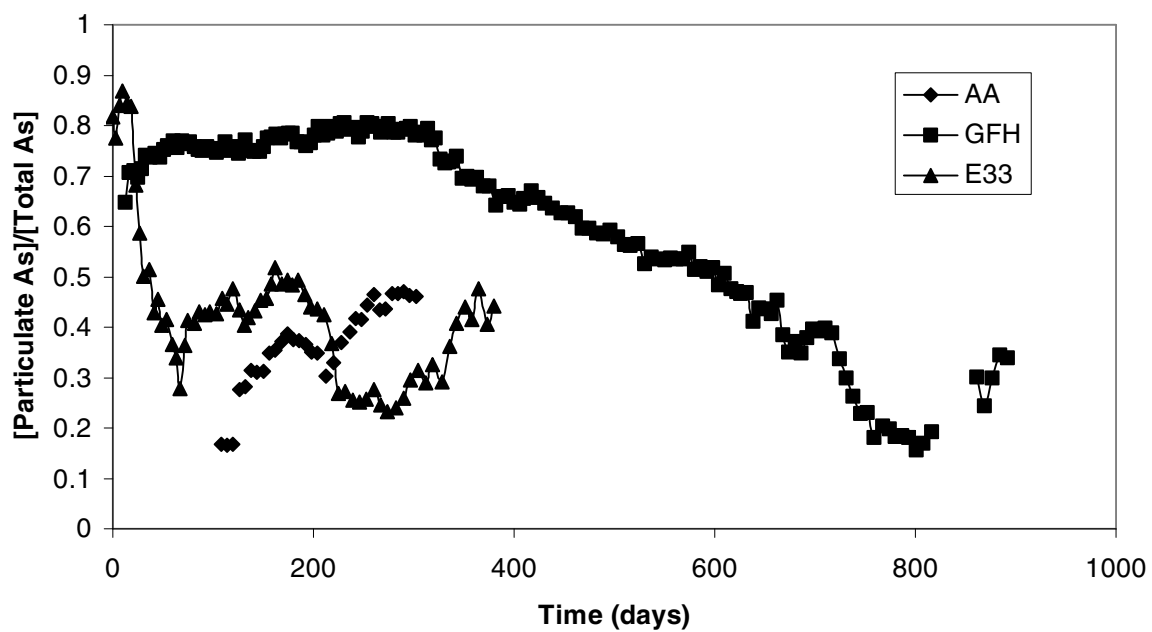


Figure 6.10: Amount of arsenic leached as particulates as the fraction of total leaching from the three columns.

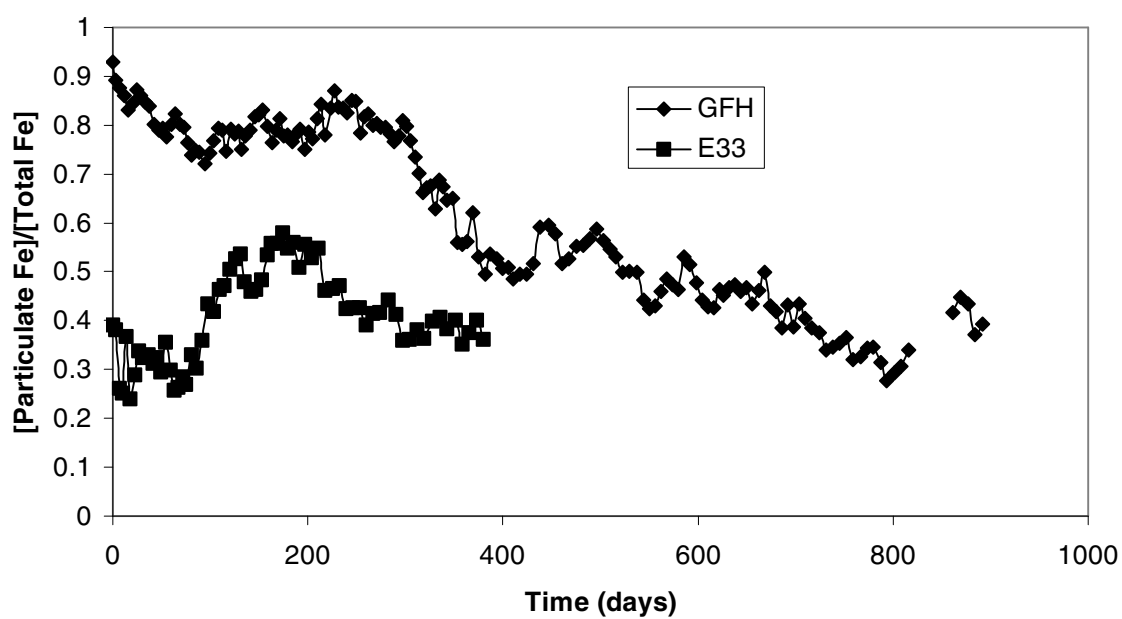


Figure 6.11: Amount of iron leached as particulates as the fraction of total leaching from the GFH and E33 columns.

hand, for E33, the particulate fraction was between 40-50% of the total arsenic leached. A very similar trend is observed for the iron particulates in GFH and E33 (Figure 6.11). For the first 200 days of the GFH column run, particulates constituted close to 75-80% of the total leached iron, after which the fraction gradually decreased and by the end of the column run particulate iron was about 35-40% of total. For the E33 column, the fraction of iron leached in the particulate phase was comparatively lower. The particulate fraction was about 30% at the beginning of the column run, then it increased to up to 60% of the total during the peak period before falling back to about 40% by the end of the column run. It is to be noted that after E33 digestions, a very small fraction of undissolved solids (suspected to be silica) remained and it is possible that some iron might have remained in the undissolved fraction and couldn't be accounted for by this analysis.

Mass Balance Comparison

Figure 6.12 shows the cumulative fractional arsenic leached from the three sorbents as a function of time. It is important to note that the total arsenic content of the three sorbents was initially very different. The total arsenic in the AA column was 1.05g, while the GFH column contained almost 3 times that amount (Table 6.1). The total arsenic content in the E33 column was slightly less than GFH but more than twice that of AA. Also, the amount of iron present in GFH is higher than that in E33. Comparing the fractional arsenic released from AA and GFH in Figure 6.12, the fractions almost coincide with one another throughout the duration of run of the AA column. This means that the overall rate of arsenic release from AA and GFH are similar to one another. [Note: Here “rate of

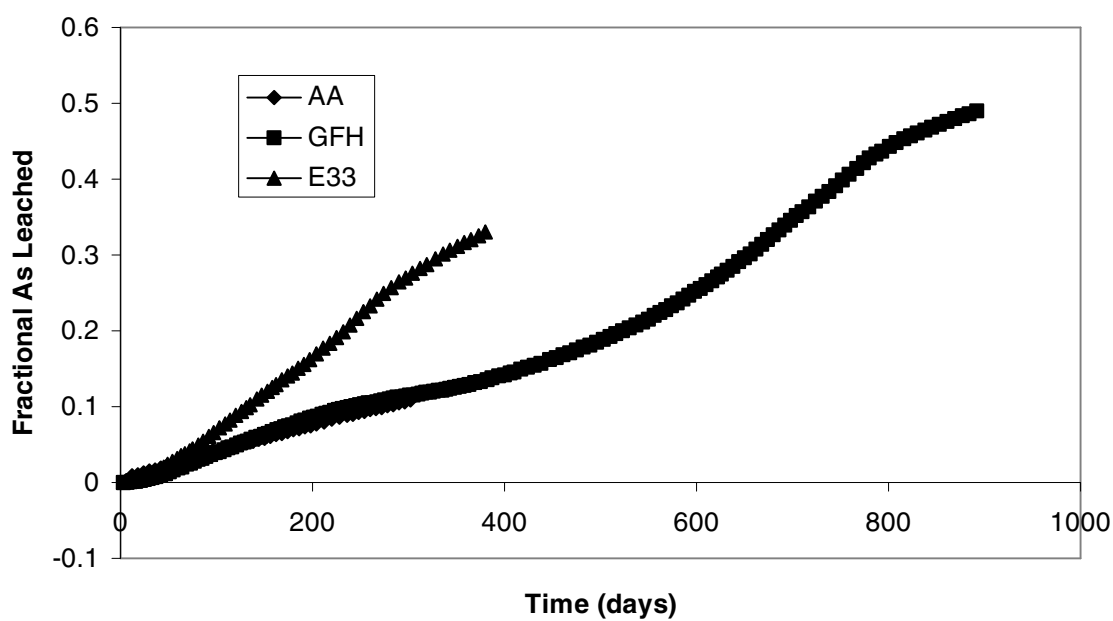


Figure 6.12: Cumulative fractional arsenic leached from all three columns as a function of time.

release” is defined as (amount leached)/(amount initially available)/time]. However, there is a key difference between the leaching in the AA and GFH columns. While most of the arsenic in the AA leached in the dissolved phase, most of the observed leaching from the GFH column in the initial period of column operation was in the particulate phase. However, it is also observed that for GFH there is a sharp inflection point around day 500, after which the fraction of arsenic released tends to increase much faster. This might be due to the fact that in the initial phase of the GFH column run; arsenic that was being released from the parent GFH could either re-precipitate with iron forming a new phase or could re-adsorb on the surface that is freshly exposed by the dissolution of surface iron. Detailed description of the comparative leaching rate of the iron and arsenic from the GFH column was provided in the previous chapter. Since aluminum was not being leached from AA at a rate nearly as fast as the iron from GFH, it is unlikely that there was significant formation or exposure of new surfaces for arsenic to re-adsorb on. Comparing the fractional arsenic leached plots of GFH and E33 (Figure 6.12), it can be seen that the slope of the E33 plot is nearly twice that of the GFH plot. There are several possible explanations for the higher rate of arsenic release from E33 than from GFH. It can be due to the stronger bonding of arsenic to GFH than to E33, the more negative ORP of the E33 column compared to the GFH column in the initial periods of column operation as well as more bioavailability of the E33-sorbed arsenic than the GFH-sorbed arsenic. When the fractional iron leaching from GFH and E33 are compared in Figure 6.13, an exact opposite behavior is observed. The slope of the GFH iron plot is almost 4 times the slope of the E33 iron plot in the initial phase of the column runs. (GFH had a

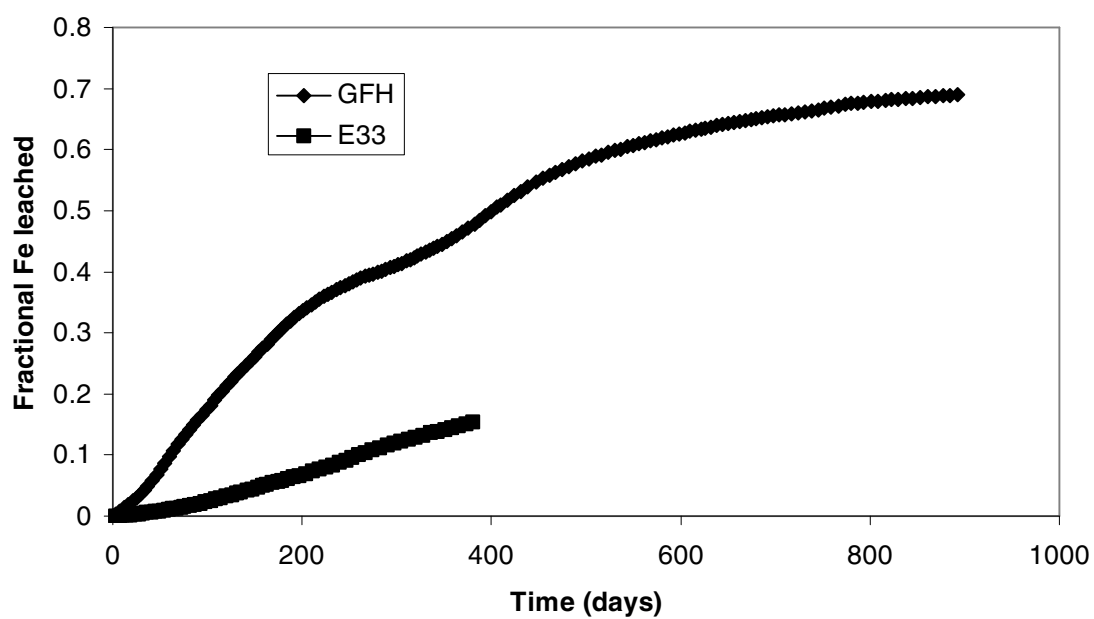


Figure 6.13: Cumulative fractional iron leached from the GFH and E33 columns as a function of time.

slightly higher iron content than E33 (163g Fe in GFH to 123g Fe in E33)). The opposite behavior of iron and arsenic leaching rates for GFH and E33 points to some key differences between the two iron-oxide sorbents themselves. The iron in E33 seems to be in a more stable strongly bonded matrix whereas that in GFH is in a more weakly crystalline form. The arsenic sorbed onto E33, once desorbed under reducing, anaerobic conditions does not re-adsorb or re-precipitate with iron in any appreciable quantity. In contrast, in GFH, much of the arsenic that would otherwise be mobilized may be re-adsorbed or re-precipitated by some freshly formed iron-oxide phase. . The summary of the total leaching of both iron and arsenic from all three columns for the first 200 days of operation is provided in Table 6.3. The table gives an overall idea of the differences in the leaching behavior of the three sorbents. From the table it is clear that particulate leaching of both arsenic and iron is the most likely mechanism for leaching in GFH whereas it is not as dominant in E33 and AA. As(III) is likely to dominate over As(V) in the dissolved phase for all three sorbents and Fe(II) is likely to be at a much higher concentration than Fe(III) in the leaching of GFH and E33 under the conditions expected in a mature MSW landfill.

Table 6.3: Table showing the summary of arsenic and iron leached in the first 200 days from the three columns

Parameter	AA	GFH	E33
Total arsenic leached	7.2%	7.9%	17%
Total iron leached		27%	8%
Arsenic in particulates	29%	75%	45%
Arsenic in dissolved	71%	25%	55%
Iron in particulates		78%	41%
Iron in dissolved		22%	59%
As(III) fraction of dissolved	87%	83%	73%
As(V) fraction of dissolved	13%	17%	27%
Fe(II) fraction of dissolved		96%	87%
Fe(III) fraction of dissolved		4%	13%

CHAPTER 7

SUMMARY AND CONCLUSIONS

The research effort undertaken in this project focused on the two broad themes of 1) evaluating the appropriateness of the Toxicity Characteristic Leaching Procedure (TCLP) and other batch leaching tests for the measurement of arsenic leaching potential from arsenic bearing solid residuals (ABSRs) and 2) investigating the various processes that might act individually or in tandem in non-hazardous, mixed solid waste (MSW) landfills to cause leaching and mobilization of arsenic from ABSRs. The TCLP has been in use for over two decades as the primary standard protocol for evaluating the leaching hazard posed by ABSRs. This is despite the fact that arsenic is sorbed on the treatment solids in a state, which is critically different from the chemical state of the sorbed metals for which the TCLP was designed. In addition based on geochemical theory, the conditions in a MSW landfill (the currently accepted disposal destination for ABSRs) are predicted to be conducive to mobilizing sorbed arsenic. Thus, the question arises whether the TCLP realistically predicts the leaching potential and subsequent environmental hazard posed by ABSRs. Because of the large mass of a known carcinogen involved, it is critically important to evaluate and understand the various physical/chemical/microbiological conditions that would cause leaching of arsenic from ABSRs under landfill conditions. The work described in this thesis has aimed to identify the limitations of the TCLP and other similar short-duration batch tests and to provide useful insight into the various

phenomena at play during arsenic leaching from ABSRs in a landfill environment. The project yielded the following results and conclusions.

1. Adsorption isotherms have been developed and Langmuir and Freundlich parameters determined for two commercially available, popularly used sorbents, activated alumina (AA) and granular ferric hydroxide (GFH). It is observed that the arsenic loading on GFH at neutral pH for an equilibrium concentration of about 20 ppb, is about 4 times that of AA. For both sorbents, the onset of the arsenic adsorption edge lies between pH 6.0 and 9.0. Below that pH range, most of the arsenic remains on the surface of the solids, while for higher pHs most of the arsenic is mobilized in solution. For AA, arsenic sorption was 60% greater at pH 5.5 than 8.5. For GFH, for a 0.05mM initial arsenate concentration, 98% of the arsenate was sorbed onto the solid at pH 6.0, while only 31% on the solid at pH 9.0. The diffuse double layer model (DLM) fails to simulate the experimental data for adsorption of arsenate on AA and GFH because it seemingly does not differentiate between the ways the ions can bind to the surface. A single site triple layer model (TLM) also fails to show the observed sensitivity towards the different arsenate loadings, but a two-site approach shows better agreement to the experimentally observed data because it simulates a solid surface with a significant distribution of site binding affinities.

2. The TCLP results were compared to those from the waste extraction test (WET), actual landfill leachate (LL) and two different synthetic leachate solutions (SL1 and SL2) for AA and GFH loaded with arsenic. Leaching tests only extract a very small fraction ($<0.2\%$) of the total arsenic on the ABSRs tested. The total arsenic leached is higher from GFH than AA, but the fractional arsenic leached is higher in AA than GFH. Up to 10-fold higher concentration is extracted by the LL than by the TCLP. The WET test results in a higher arsenic concentration than the TCLP but lower than the LL. SL2 leached more arsenic than all the other tests because it has a high organic concentration, high ionic strength and due to hydroxylamine, a strong reducing character. Equilibrium conditions are not achieved within 18 hours leaching time (the TCLP duration) and as had been shown by kinetic experiments, it takes close to 30 hours to attain equilibrium. The most aggressive physical leaching conditions (independent of leaching solution composition) were end over end tumbling, N_2 headspace, high solid to liquid ratio (low LS ratio) and 48-hour duration. In a few cases, the arsenic solution concentration exceeded 1000ppb, which is significant because if the TC were to be brought down from 5mg/L to 1mg/L (as it is customary to have the TC set at 100X the MCL), the residual would be classified as a hazardous waste.
3. Desorption of arsenic from arsenic-loaded AA and GFH is a strong function of pH and a weak function of the concentrations of anions like phosphate, bicarbonate, sulfate and silicate and NOM found in landfills. An increase of one

unit of pH (between 8.0 and 9.0) causes desorption of 15% and 12% of arsenic from AA and GFH, respectively. This effect increases with increase of pH. For a 10-fold increase in concentration, NOM gives the highest leaching among all anions (about 1% increase in arsenic concentration between 2000 mg/L and 20000 mg/L), even though the observed effect is far less than an increase in one unit of pH (10-fold increase in the $[\text{OH}^-]$). Among the different anions, NOM has the greatest impact on arsenic desorption both per mole of anion as well as by virtue of being present at a very high concentration in landfills. Phosphate and silicate have significant competitive effect with arsenate, but generally are not present at high concentrations and hence would not typically play a large role. Bicarbonate and sulfate do not compete strongly with arsenate, but are likely to be present in high concentrations in a leachate, and hence their influence cannot be ignored. Bicarbonate, if present at its highest concentration, leaches out about 1.5% of the sorbed arsenic while sulfate at its highest concentration leaches out about 0.4% of the sorbed arsenic from both sorbents. The effects of the various anions, when present in tandem, are not additive, but to various degrees compete with each other in displacing arsenate.

4. Landfill-like conditions were established inside a flow-through column reactor and arsenic-laden GFH was subjected to leaching under those conditions. It is demonstrated that in a high organic, reducing, anaerobic environment, both the iron and the arsenic are susceptible to reduction and mobilization. Results indicate

that arsenic and iron mobilization can occur by a) reductive dissolution of Fe(III) to soluble Fe(II) thereby mobilizing both iron and arsenic sorbed onto the Fe(III) surfaces, b) direct biological reduction of either sorbed or dissolved As(V) to As(III), which would be less sorbed to the iron surface and hence more mobile, c) de-flocculation of GFH into micron and sub-micron sized particulates which mobilizes both iron and arsenic in the particulate phase and in association with each other. In two and half years of leaching duration, 69% of the iron leached out while in the same period of time only 49% of the arsenic is mobilized in the leachate. This progressive increase in surface concentration of the sorbed arsenic, during early phases of column operation leads to an increased arsenic mobilization at a later date. Particulate and colloidal transport is about 4-5 times more than transport in the dissolved phase, especially during the early, most aggressive leaching period.

5. Three different ABSRs, AA, GFH and E33 were subjected to reducing, anaerobic environments (inside column reactors) similar to those that would be expected in a MSW landfill. Key differences were noted in the leaching patterns of the three sorbents under similar leaching conditions, and these differences can be attributed to the differences in the structure of the sorbents themselves and the arsenic bonding to the surface of the sorbents. Arsenate to arsenite reduction was observed with all three sorbents, even though there was 20-35% more reduction in AA than in the two iron-based sorbents. This might have been due to the presence

of the Fe(III)/Fe(II) redox couple in the iron based sorbents as Fe(III)/Fe(II) is more positive than the As(V)/As(III) couple. Particulate phase transport was significant for all three sorbents and in certain cases the particulate phase leached 4-5 times more than the dissolved phases. Particulates were most significant for GFH, which, based on observation, is mechanically the weakest among the three media tested, whereas AA and E33 are much stronger, regular, crystalline matrices than GFH. It was also observed that even though arsenic leaching is associated with sorbent leaching, the leaching rates of the arsenic and sorbent can be very different from each other which would have implications in the quantification of the long-term estimates of arsenic leaching rates.

Environmental Significance and Future Work

The results of this work show beyond doubt that the TCLP is a very misleading gauge for the estimation of hazard risk posed by ABSRs disposed of in landfill environments. Much of the effort and significance of this project is about understanding the different means and mechanisms by which arsenic might be mobilized from residuals under landfill conditions. It is expected that the results observed in this work will motivate future projects that would seek to design a more realistic leaching test for ABSRs. However, certain conclusions drawn from this work have immediate environmental engineering and management significance and indicate the direction and path that future research should take. These immediate impacts are discussed below.

One of the most serious challenges of this project was to provide a sound theoretical explanation for the observed leaching behavior. In a heterogeneous environment like a MSW landfill, several parallel, potentially synergistic mechanisms would determine overall leaching behavior. To explain such behavior, a reductionist approach needs to be taken. Processes such as diffusion, dissolution, desorption, re-precipitation, reduction, mechanical breakage, particle aggregation and de-flocculation need to be taken in consideration. Each mechanism needs to be isolated, mathematically formulated and modeled. Finally, these mechanisms need to be coalesced together to obtain the overall leaching scenario. It should be noted that leaching occurs in two distinct but interdependent phases – dissolved and particulates and each phase is governed by its own equilibrium behavior with respect to the environment.

The column experiments performed in this work have two basic limitations: a) they needed to be run for impracticably long time durations, in the order of years (the longest column experiment was performed for 32 months) and b) they gave a cumulative impact of the various mechanisms without de-lineation of the effect of each mechanism. In order to estimate the effect of each individual mechanism, a suite of shorter duration small column experiments need to be run with parallel control reactors. Each parameter like pH, ORP, organic concentration, microbial activity needs to be isolated and their impacts evaluated.

It needs to be re-emphasized that experiments in the laboratory would never be able to simulate actual landfill conditions. A MSW landfill is a very complex, heterogeneous entity and one landfill can differ significantly from another in its physical, chemical and microbiological properties. Also, the properties of the same landfill with respect to waste amount, leachate generation and flowrate, pH, ORP, DOC, alkalinity can change over time and with seasons. Finally, the ABSR itself might undergo significant changes in its physical and chemical properties with aging. Hence, the most realistic test should take an ABSR and place it in an actual landfill. Leaching profiles of arsenic and iron as well as variations in the chemical parameters of the leachate with time should be recorded with data loggers placed on lysimeters. If different ABSRs are subjected to field-tests under different field conditions, the data generated should give valuable insight of leaching which would be impossible to investigate inside a laboratory setting.

The ultimate goal, which motivated the inception of this research, was to design a more appropriate, realistic batch leaching protocol, which would be a better substitute for the TCLP. In order to design such a batch test, all mechanisms, which affect the arsenic leaching in a column reactors and in a field setting need to be accounted for. A non-trivial task in this process would be to correlate the column (and field) leaching data to the observed batch data. Processes such as microbial activity or generation of particulates would be especially difficult to simulate in a short-duration batch testing protocol. However the ideal leaching test should incorporate all these complex processes. The other way to solve this problem might be do to away with the idea of “leaching tests” for

ABSRs. The properties of the individual sorbent, the quantity of arsenic sorbed on to it, as well as the characteristics of the disposal environment should be analyzed and decisions should be taken regarding the fate of the residuals on a case-by case basis.

It is expected that the entire process of development of a new protocol, its veracity guaranteed by scientific research and its passage through legislation before it can be enforced as a rule would take 5-10 years at a minimum. In the meantime, the water treatment utilities would generate millions of pounds of waste and need to dispose them in a safe manner. Current recommendations are to isolate the wastes in a separate cell inside the landfill, where it does not come in contact with high concentrations of organics that would be able to support microbial reduction and mobilization from the waste. However, solidification-stabilization of the waste either with cement or polymers have shown sufficient promise to be pursued as an avenue for the reduction of leaching potential of arsenic from ABSRs. Research needs to be directed to identify or develop a particular polymer or binding agent that would be specific to the retention of arsenic. The encapsulation binder itself needs to be robust enough to withstand the aggressive leaching conditions inside a MSW landfill.

APPENDIX A

ADSORPTION OF ARSENIC ON GFH

Batch Adsorption Trials were conducted on GFH, similar to the ones described for Activated Alumina in Chapter 2. Four different initial arsenic loadings were selected and the experiments were done at 7 different pHs between pH 5 and 11. The solid loading was 2.5g and the liquid volume was adjusted to 100mL for each experiment. All experiments were conducted for 48-hour duration. The results are shown below.

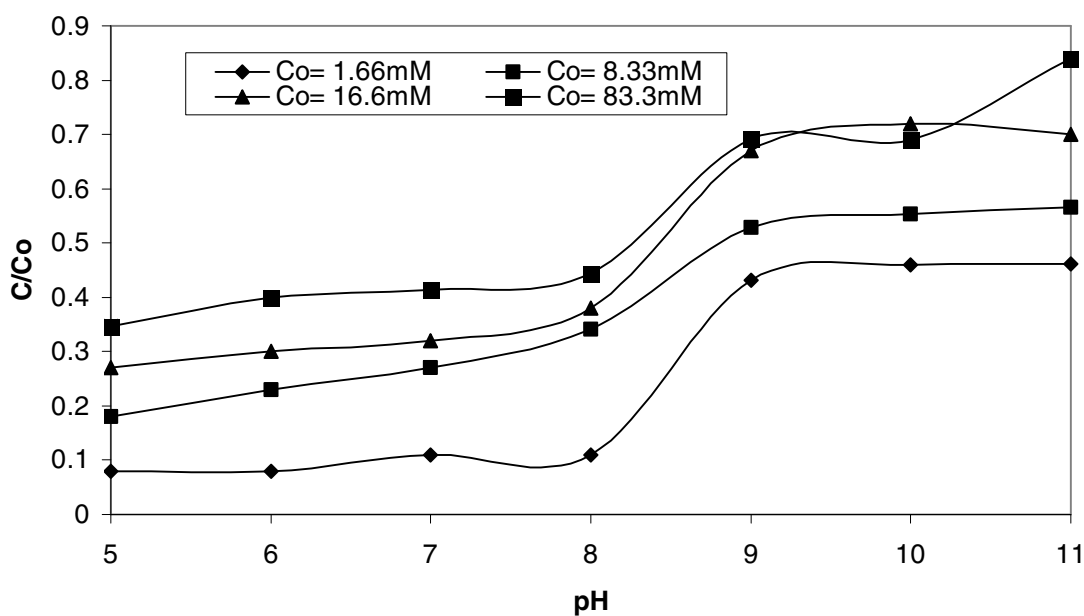


Figure A-1. Observed equilibrium concentrations of arsenate on GFH. C denotes the concentration of arsenic in solution at equilibrium and C_o denotes the total concentration of arsenic in the system. The curves indicate different arsenic loadings.

APPENDIX B

SUPPLEMENTARY INFORMATION FOR THE LEACHING EXPERIMENTS
DESCRIBED IN CHAPTER 3

Actual Concentrations of Arsenic, Aluminum and Iron in solution for the different leaching experiments conducted on AA and GFH. The ORPs at the end of the experiments are also shown.

Table B-1: Leaching results for Activated Alumina: Equilibrium concentration 21.81 µg/L (All concentrations in µg/L)

Test	Tumbler				Shaker			
	With N ₂		No N ₂		With N ₂		No N ₂	
	18hrs	48hrs	18hrs	48hrs	18hrs	48hrs	18hrs	48hrs
	As (V)	As (V)	AsV	As (V)	As (V)	As (V)	As (V)	As (V)
TCLP	59	99	52	76	44	57	41	55
LL	707	827	582	610	617	679	414	449
WET	389	452	381	433	361	425	341	397
SL1	275	315	268	302	243	267	233	255
SL2	919	1128	755	812	589	675	523	601

Table B-2: Leaching results for GFH: Equilibrium concentration 31.03 µg/L (All concentrations in µg/L)

Test	Tumbler				Shaker			
	With N ₂		No N ₂		With N ₂		No N ₂	
	18hrs	48hrs	18hrs	48hrs	18hrs	48hrs	18hrs	48hrs
	As (V)	As (V)	AsV	As (V)	As (V)	As (V)	As (V)	As (V)
TCLP	88	157	45	113	66	115	48	75
LL	731	1018	645	812	472	684	450	637
WET	589	764	514	695	444	602	432	557
SL1	215	425	188	365	161	280	105	178
SL2	1264	1693	978	1135	743	996	653	829

Table B-3: Concentration of Aluminum in the extractant at the end of the leaching trials.
(All concentrations in µg/L as Al)

Tests	Tumbler				Shaker			
	With N ₂		No N ₂		With N ₂		No N ₂	
	18hrs	48hrs	18hrs	48hrs	18 hrs	48hrs	18hrs	48hrs
TCLP	*	16	12	45	*	24	*	*
LL	102	183	94	136	87	145	69	118
WET	*	42	*	34	22	59	*	30
SL1	12	54	*	49	15	46	13	57
SL2	50	91	42	103	43	74	48	87

* - Concentrations of Al below the detection limit of 10ppb.

Table B-4: Concentration of Iron in the extractant at the end of the leaching trials. (All concentrations in mg/L as Fe)

Tests	Tumbler				Shaker			
	With N ₂		No N ₂		With N ₂		No N ₂	
	18hrs	48hrs	18hrs	48hrs	18 hrs	48hrs	18hrs	48hrs
TCLP	1.91	3.52	1.66	2.54	2.04	4.63	1.57	3.08
LL	5.05	9.59	5.31	8.57	4.26	7.94	4.77	7.49
WET	8.65	13.52	7.43	11.35	6.09	11.50	5.91	10.55
SL1	2.08	4.11	1.25	2.78	1.80	4.02	2.15	3.83
SL2	9.88	15.69	7.46	13.17	8.47	14.44	8.33	13.76

Table B-5: ORP (in mV) at the end of the AA leaching trials (in mV). Initial ORP of all the extractants are listed in Table 3.1, main text.

Tests	Tumbler				Shaker			
	With N ₂		No N ₂		With N ₂		No N ₂	
	18hrs	48hrs	18hrs	48hrs	18 hrs	48hrs	18hrs	48hrs
TCLP	121.9	133	146.8	161.8	119	125.3	142.9	158.8
LL	66.4	77.3	95.1	115.3	62.1	81.3	92.9	109.9
WET	97.5	111.7	119.8	128.1	102.5	113	127.9	139.3
SL1	136.8	143.1	147.8	156.3	135.1	152.9	151.9	160.9
SL2	21.4	46	70.1	85.2	10.1	41.1	77.8	94.9

Table B-6: ORP (in mV) at the end of the GFH leaching trials (in mV). Initial ORP of all the extractants are listed in Table 3.1, main text.

Tests	Tumbler				Shaker			
	With N ₂		No N ₂		With N ₂		No N ₂	
	18hrs	48hrs	18hrs	48hrs	18 hrs	48hrs	18hrs	48hrs
TCLP	100.3	108.2	119.2	133.5	95.8	105.7	113.1	141.5
LL	43.5	53.9	78.1	91.2	40	65.6	70.6	84.3
WET	72.7	87.1	89.3	103.2	84.6	95.8	100.3	116.4
SL1	121.1	127.4	118.8	130	104.2	127.9	128.6	144.7
SL2	-8.9	17	41.6	60.3	-13.5	17.8	54.4	69.1

APPENDIX C

KOSSON TRIALS

A small number of batch trials were conducted following the protocol outlined in the paper “An Integrated Framework for Evaluating Leaching in Waste Management and Utilization of Secondary Materials” (Kosson, et al., 2002). GFH and E33 spent media, as received from a Mesa Pilot Treatment Plant were used as raw materials for this study. The sorbed arsenic concentrations were 5.6mgAs/gGFH(dry) and 9.09mgAs/gE33(dry) respectively. Solubility as functions of LS ratio and pH were investigated. The results are shown below.

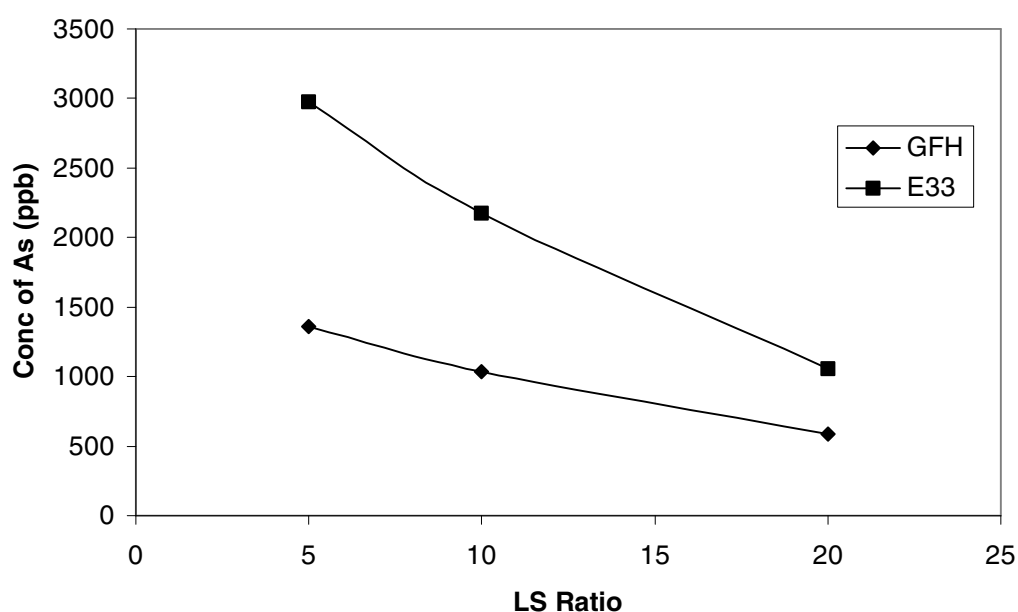


Figure C-1. Aqueous concentration of arsenic as a function of LS Ratio for GFH and E-33. For all experiments solid loading was kept constant at 5g.

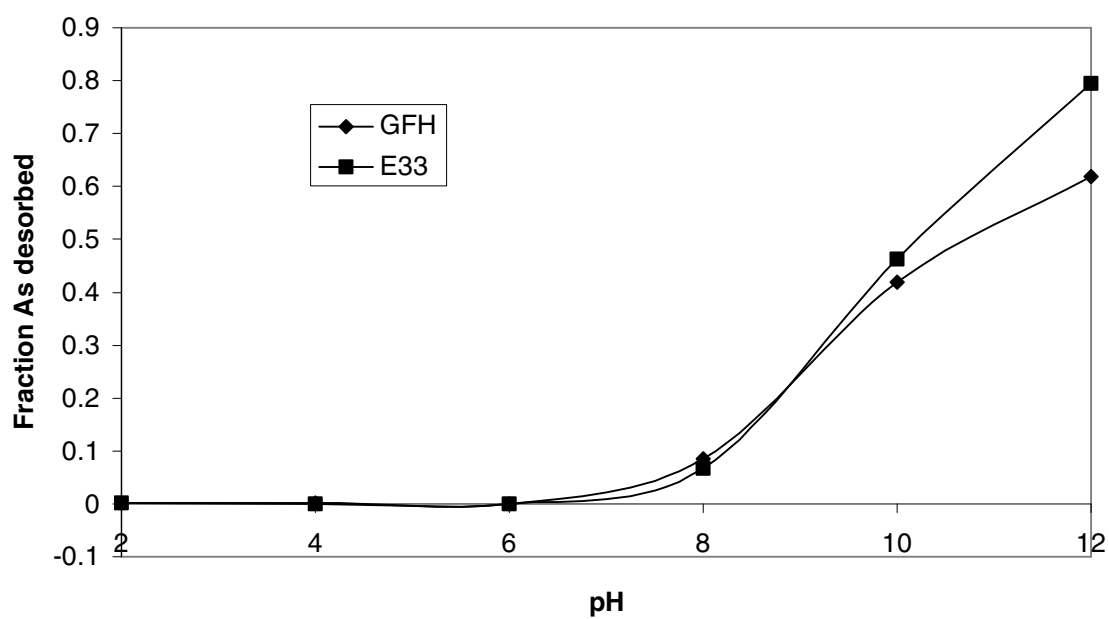


Figure C-2. Aqueous concentration of arsenic as a function of pH for GFH and E-33.

APPENDIX D

SUPPLEMENTARY INFORMATION FOR ACTIVATED ALUMINA AND E-33

COLUMN TRIALS

The Alkalinity and DOC in the effluents of the AA and E33 columns are shown. The iron and arsenic in the different particulate size fractions in the effluent of the E33 column are also shown.

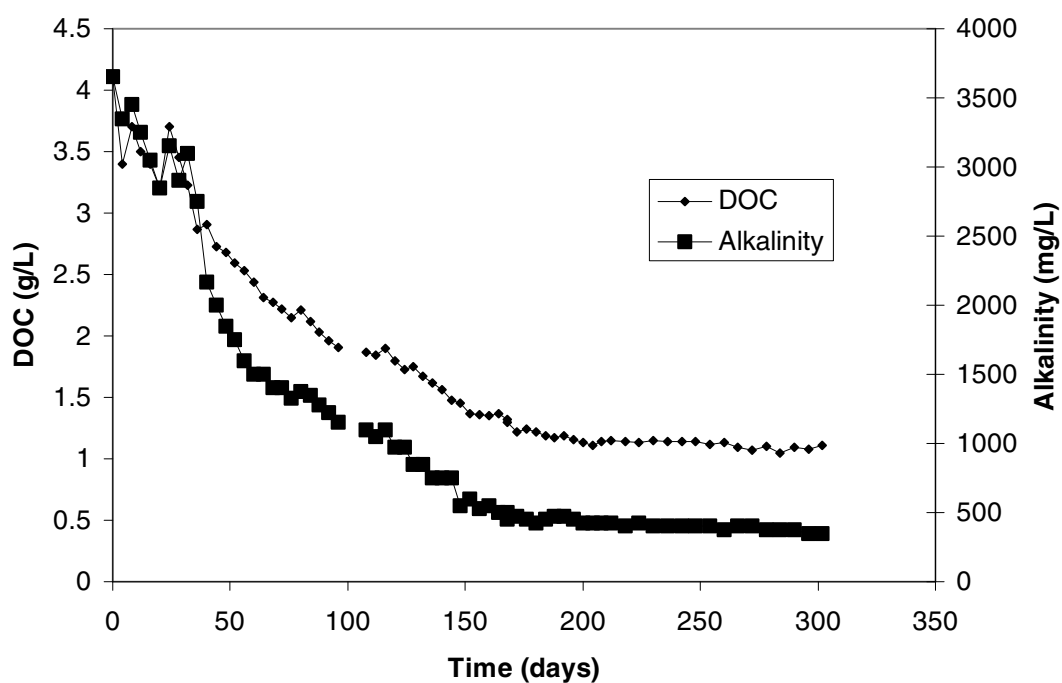


Figure D-1. DOC and Alkalinity as measured in the effluent of the AA column.

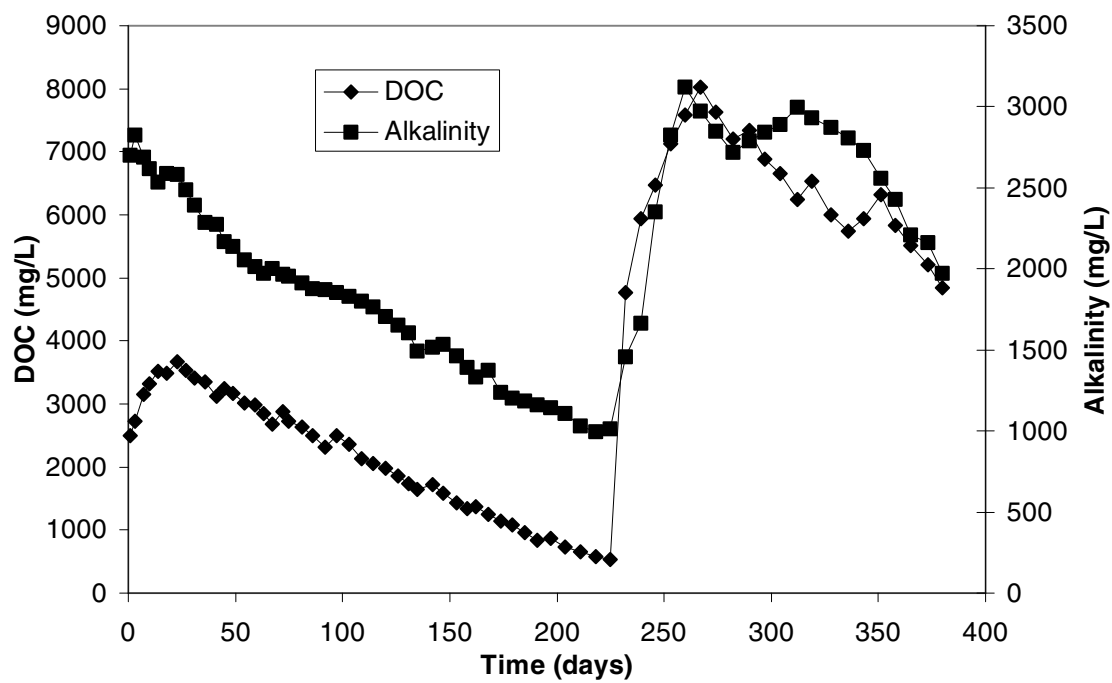


Figure D-2. DOC and Alkalinity as measured in the effluent of the E33 column.

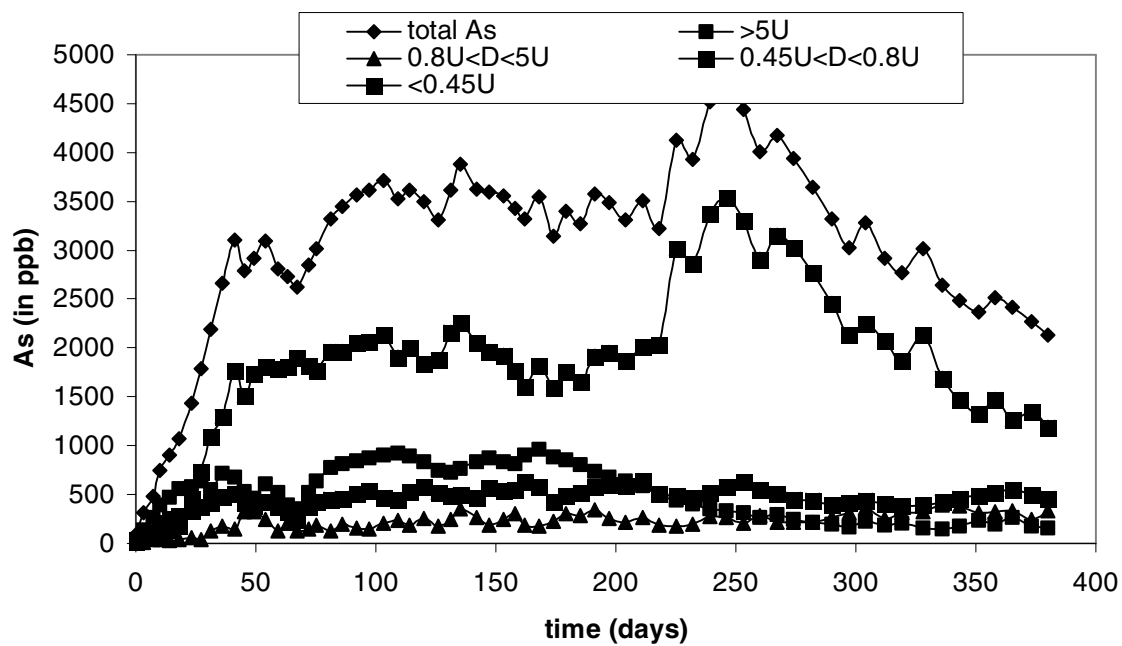


Figure D-3. Arsenic in the different particulate size fractions in the effluent from the E33 column.

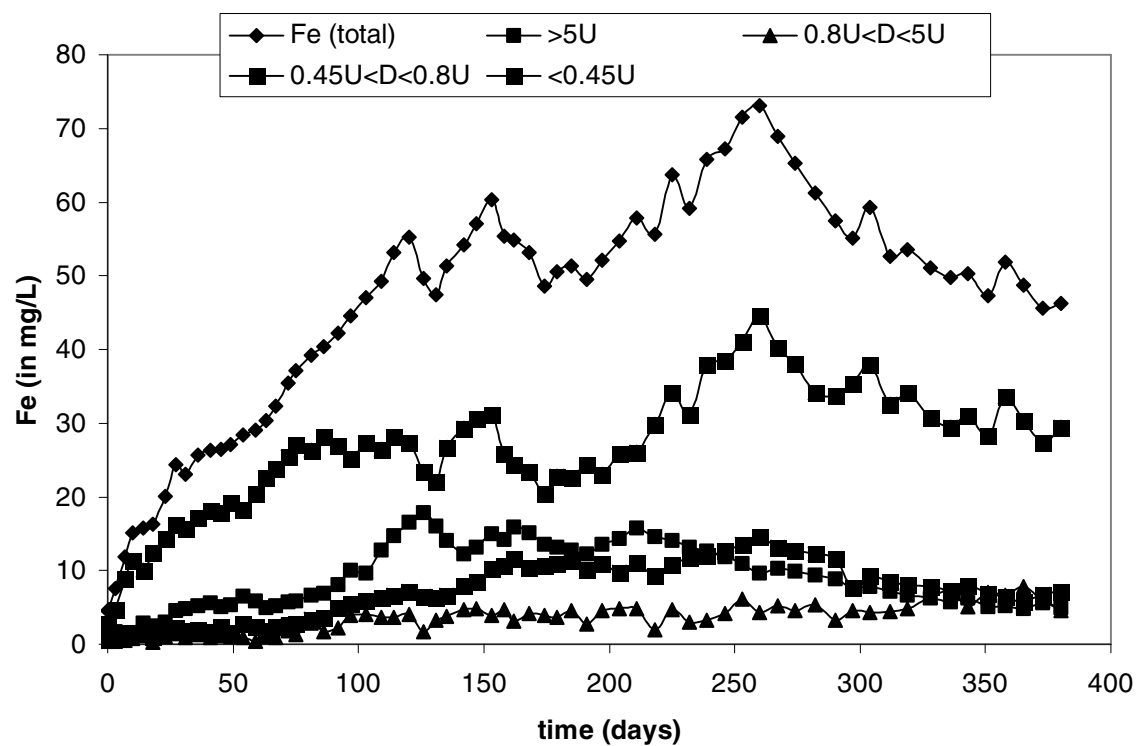


Figure D-4. Iron in the different particulate size fractions in the effluent from the E33 column.

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