

**ARSENIC STABILITY IN FRESH AND AGED AMORPHOUS FERRIC
HYDROXIDE SLUDGES GENERATED FROM BRINE TREATMENT
PROCESSES**

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DEDICATION

To my parent Elias Mutyaba and Namutebi Yudaya Mutyaba, who taught me the value of good ethics, hard work, respect and responsibility. They have always believed in me and also constantly encouraged me to pursue my dreams.

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ABSTRACT

Using Environmental Protection Agency occurrence and concentration data, it is estimated that about 6 million pounds of arsenic-bearing residuals (ABSR) will be generated annually in the United States when full compliance with the new standard for arsenic in drinking water (10 $\mu\text{g/L}$) is realized. Effective management of disposal of ABSR requires both a full characterization of the materials and an understanding of the environment in which the disposal will occur. Currently, there are different testing methods to evaluate the stability of ABSR, the principal of which is the EPA Toxicity Characteristics Leaching Procedure (TCLP). These tests indicate that common ABSRs may be disposed in mixed-solid waste landfills. However, this and previous work shows that these testing methods may significantly underestimate the degree and mechanism of arsenic mobilization from the residuals, because critical physical and chemical dissimilarities exist between the tests and landfill conditions. In addition, no current testing methods simulate the mineralogic aging in those ABSR, which exhibit further complexity. Landfill disposal involves liquid and solid residence times on the order of months and decades, respectively, whereas leaching tests are completed in two days or less. Consequently, time dependent re-mineralization of residuals that would be routinely expected in landfill time scales is not addressed by standard leaching tests. Treating arsenic brines by co-precipitation with iron oxyhydroxides is an established and effective remediation method for small quantities of highly concentrated liquid arsenic waste, such as brines derived from mine tailings, ion exchange resin regeneration, and reverse osmosis treatment of drinking water. However, amorphous ferric hydroxide (AFH) is expected to exhibit mineralogical aging analogous to the observed natural evolution of ferrihydrite to goethite and

hematite. The aim of this research is to develop methods for characterization of AFH sludges precipitated from concentrated arsenic brines which exhibit mineralogical aging and to evaluate the impact of such aging on arsenic leachability. Overall, aging the sludge resulted in consistently higher arsenic release.

Key words: Arsenic, Mineralogical Aging, Water Treatment Residuals, Amorphous Ferric Hydroxide.

CHAPTER 1

INTRODUCTION AND OVERVIEW

History of Arsenic

For centuries arsenic has been best associated or is best known for its use as a poison, although it has been suggested that low levels of arsenic could be beneficial as a nutrient (Frost, 2000). The ancient Romans used arsenic as a way to resolve personal matters or conflicts, since arsenic contamination or poisoning of food and or water can result in illness and in death. “Arsenic in the form of Fowler's solution, Asiatic pills, Donovan's solution and DeValagin's elixir, was commonly used into the nineteen fifties as a therapy for anorexia, neuralgia, rheumatism, asthma, cholera and many other conditions” (Frost, 2000).

Occurrence (within the United States)

Arsenic can be found on earth in rocks, soil, animals, water, etc. The presence of arsenic in ground water can be attributed to arsenic-bearing minerals dissolving over time as rocks and soils are weathered. Commonly arsenic concentrations in ground water are a result of either up flow of geothermal waters, dissolution of sulfide minerals or evaporative concentrations (USGS, 1998). Since mineral dissolution is very slow process, high arsenic concentrations are normally associated with ground water rather than surface water due to the much longer contact of the water with arsenic bearing minerals in a subsurface environment.

Within the United States, naturally occurring arsenic in ground water will vary from region to region as a result of the unique climate and geology. The western U.S. generally has a higher concentration of arsenic, with values frequently above 10 $\mu\text{g/L}$. However, USGS reports that investigators in Maine, Michigan, Minnesota South Dakota, Oklahoma and Wisconsin within the last decade suggest that arsenic concentrations exceeding 10 $\mu\text{g/L}$ are more frequent than previously suggested (USGS, 1998).

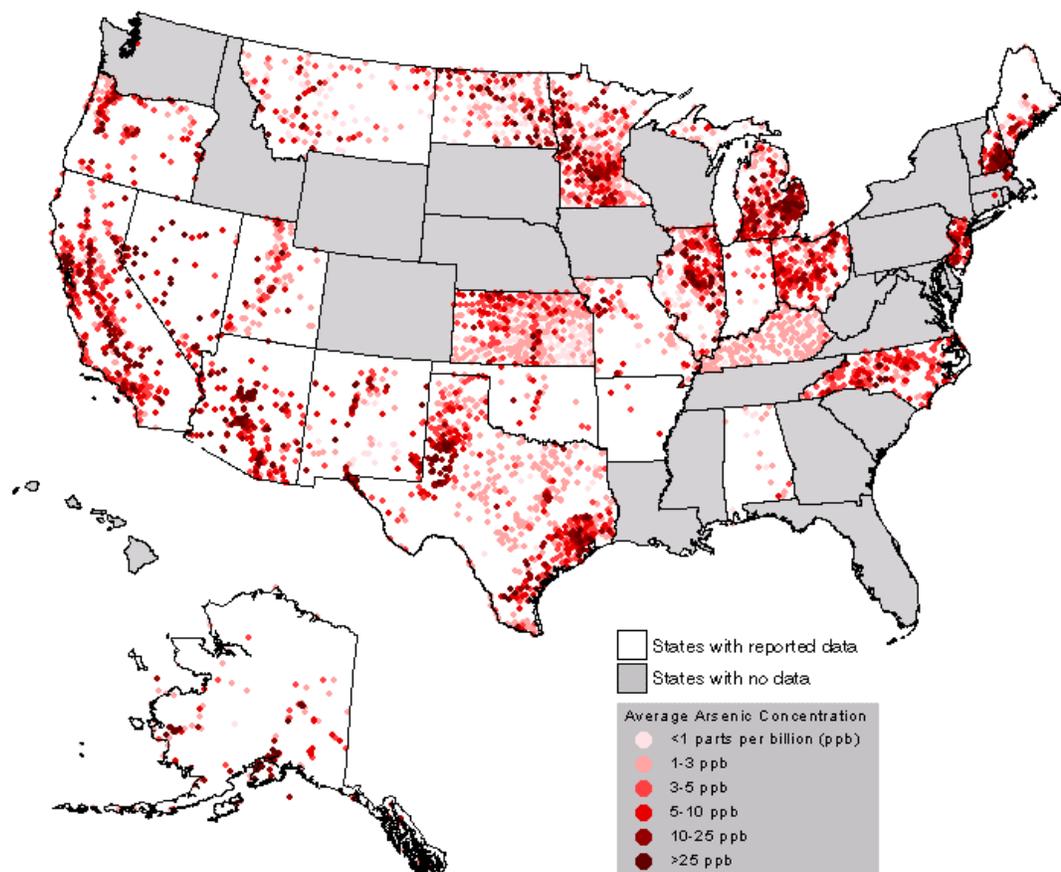


Figure 1.1. Arsenic concentrations in ground water of the United States (USGS, 2000).

Because elevated arsenic levels are normally associated with groundwater and the arid Southwest of the U.S. is primarily dependent on groundwater as a drinking water source, this region is particularly impacted by changes to the arsenic standards. The most frequent reason of arsenic exceeding a concentration of 10 µg/L in ground water is arsenic release from natural iron oxide.

Chemistry of Arsenic

Arsenic in potable water supplies is almost entirely in either the arsenite, As (III), or arsenate, As (V), oxidation states (US EPA, 2000). In near neutral waters arsenite is primarily fully protonated and uncharged as arsenous acid (H_3AsO_3) ($\text{pK}_{\text{a}1}$ 9.2). In contrast, arsenate is predominantly in an anionic form in the pH range typical waters ($\text{pK}_{\text{a}1}$ 2.2, $\text{pK}_{\text{a}2}$ 7.0 and $\text{pK}_{\text{a}3}$ 11) (Wagman et al, 1982). Because metal oxy/hydroxide sorption of ions is more efficient than of neutrals (Stumm et al, 1996b), water containing a significant fraction of arsenite is recommended to undergo pre-oxidation of arsenite to arsenate prior to the application of an arsenic removal technology (USEPA, 2001).

Overview of Treatment Techniques for Arsenic Removal

As a requirement of the Safe Drinking Water Act (SDWA), the United States Environmental Protection Agency (USEPA) recommended different best available technologies (BATs) to comply with the new arsenic maximum contaminant regulation (USEPA, 2001). These technologies include precipitation/coagulation, adsorption and ion exchange. The technologies available and under development for arsenic removal by small utilities depend primarily on adsorption of arsenic onto a

throwaway or regenerable solid media. Arsenate adsorption on metal oxy/hydroxide solids is a strong function of electrostatic attraction. The electrostatic effect responds to the amphoteric nature of surface functional groups, whereby pH adjustment tends to increasingly protonate or deprotonate surface functional groups (i.e., hydroxides) and decrease or increase, respectively, the surface attraction for anions such as arsenate (Stumm, 1992a; Dzombark et al, 1987a; Lin et al, 2001b). Adsorption also occurs due to non-electrostatic attraction (termed specific adsorption), which explains some sorbents (e.g.: iron, manganese) increased selectivity for arsenate over other equally charged anions. In this case a stronger chemical bond, termed specific or chemical sorption, occurs between the sorbate and sorbent (Parks, 1990).

Of the EPA identified treatment options, adsorption onto solid media is strongly favored for the small treatment facilities (those serving populations of less than 3,301), which comprise over 92% of the impacted utilities (USEPA, 2001). A brief description of each of these technologies is described below.

Precipitation/Coagulation: In water treatment operations, soluble arsenic is most commonly removed by co-precipitation with ferric salts, and this method has been designated as “The Best Demonstrated Available Technology” (BDAT) for the removal of dissolved arsenic by the United States EPA. Precipitation/Coagulation technology is based on growth and aggregation of particles in water. A single process can involve both coagulation and co-precipitation. Co-precipitation refers to the formation of an insoluble complex by an inorganic complex and coagulant. In all forms of coagulation, soluble arsenic is converted to insoluble particles, which can

then be removed by sedimentation or filtration. Ferric chloride and ferric sulfate are the most common coagulants used. The best arsenic removal rates are obtained at a pH of less 8.5 (Cadena et al, 1995; Kartinen et al, 1995). A variety of practical coagulation systems are based on similar principles and display short-term results ranging from 50-98% removal of detectable arsenic contamination. However, in all cases, disposal of the sludge from these approaches remains a significant pollutant trade off issue. This is because the most efficient available arsenic removal technologies with high adsorption capacities generates large amount of solid residuals, which require disposal (Selvin et al; 2002).

Adsorption techniques, which concentrate solutes (arsenic) on the surface of a sorbent, resulting in reduction of their concentration in the bulk water, phase. This technique employs adsorptive media such as activated alumina (AA) and granular ferric hydroxide (GFH) and many other commercially available products such as Bayoxide E-33.

Ion Exchange and Ion exchange treatments produce a liquid residual brine stream, which must be either treated on-site or discharged to a sanitary sewer (EPA, 2001). However, technically based local limits (TBLL) dictate sewer limits due to increased TDS (salt content) accompanying arsenic treatment. Consequently, it is expected that this liquid (brine) stream residuals will need to be treated on-site. The recommended process in this case 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 and corresponding pH adjustment above the solubility product.

Practically, all the above arsenic removal techniques produce arsenic bearing solid residuals, which would be evaluated using the Toxicity Characteristic Leaching Procedure, TCLP and may require disposal in non-hazardous landfills.

Limitation of Treatment Technologies

The concentration and nature of other anions in solution affects the fraction of arsenic sorbed, as ions compete for the surface sites. In general, as the ionic strength increases, the fraction of contaminant sorbed decreases. However, individual ions have differing affinities for the surface groups, so the effectiveness of competing ions 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. For instance, sulfate competes effectively with arsenate for most anion exchange resin sites, whereas it has much less effect on arsenate adsorption by activated alumina (Clifford et al, 1990a). Likewise, phosphate concentration is observed to strongly influence arsenate adsorption on granular ferric hydroxide, GFH (Driehaus et al, 1998). The concentration of natural organic matter (NOM) is also expected to impact the degree of arsenic adsorption. The effect of NOM on sorption is much harder to predict than the effect of pH or ionic strength, and only a few studies have been conducted on anion sorption in the presence of variable concentrations and types of NOM. Natural organic matter 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 complexion agent to bind with the ion and keep it in solution, or it may directly react with the sorbent surface to enhance dissolution of the surface and cause loss of sorption sites

Schwarzenbach et al, 1993). Very little research has been conducted on the effect of NOM on arsenic sorption. However, 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. 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 (Nowark et al, 1996).

Residuals Characterization and Landfill Conditions

Many methods are used to characterize arsenic mobility and the risk associated with arsenic in soils and other materials. The toxicity characteristic leaching procedure (TCLP) is a method required for the determination of characteristic waste properties for solid waste under the Resource Conservation and Recovery Act (RCRA), and it has been used as a reference method in determining the mobility of arsenic in contaminated soils or other materials. In accordance, the TCLP has been used to quantify the leaching potential of arsenic from water treatment residuals (Hooper et al, 1998; Cornwell et al, 2003). Even though the residuals from most arsenic removal technologies pass the TCLP and, consequently, are considered safe for disposal in non-hazardous, mixed solid waste (MSW) landfills, characterization of arsenic

mobility in samples using TCLP may be inadequate. The state of California uses a different leaching method called the waste extraction test (WET), which is used to determine a solid waste's soluble threshold limit concentrations (STLC). The regulatory threshold in California is the same as in RCRA: 5.0 mg/L arsenic in the leachate. The California WET method uses a longer extraction period and different extractants than TCLP; in the WET method, citrate is used rather than acetate because it is a more efficient chelating agent (Wellman et al, 1999).

Many types of methods described above are used to characterize arsenic mobility and risk associated with arsenic bearing solid residual materials. The TCLP and WET extraction methods, which are designed to simulate landfill-leaching conditions, have been shown to be inadequate at representing mobilization of arsenic in landfill conditions.

It is important to note that the long-term chemical stability of arsenic compounds depends on a number of factors, including the landfill site characteristics, the degree of aging and crystallinity, distribution, and the presence of oxygen, presence of complexing agents, or naturally occurring organic ions and presence of competing ions.

Mixed solid waste landfills progress through an acidic phase, characterized by the accumulation of volatile organic acids and subsequently an alkaline, methanogenic phase as the system reaches maturity (Christensen et al, 2001b; Kjeldsen et al, 2002). Landfill leachate from the methanogenic phase has neutral to alkaline pH (6.5 – 9)

and high concentrations of anions (carbonate, phosphate, and sulfate), which favor arsenate extraction. Landfill leachate is also high in readily biodegradable substrates reflected in very high biochemical oxygen demand values (Table 2.3). In the acidic phase, high BOD values are accounted for largely by volatile fatty acids that can serve as electron donors to support microbial reduction of arsenate and ferrihydrite. In the methanogenic phase, BOD values decline, yet high residual levels of chemical oxygen demand are accounted for by humic and fulvic acids (Kang et al, 2002; Christensen et al, 1998a). Landfill leachates support a diverse population of microorganisms, including methanogens, fermentative bacteria, and sulfate and iron reducers (Christensen et al, 2001b; Van et al, 2004; Ludvigsen et al, 1999). Although microbial transformations are not expected to contribute significantly to arsenic dissolution during the short duration of standard leaching tests, they are likely major contributors to arsenic dissolution that would occur in the long residence times of landfills and, consequently, their impact should be incorporated into an appropriate leaching protocol. The long residence time of landfill fluids may contribute to arsenic leaching. Our previously published data Ghosh et al, 2004a compared the effect of different leachates (TCLP, the California WET, simulated landfill leachates, and actual collected landfill leachate) on arsenate desorption from activated alumina and granular ferric hydroxide. These sorbants are expected to be widely used in small water treatment facilities to comply with the modified Maximum Contaminant Limit (MCL) for arsenic. It was observed that the TCLP method mobilized arsenic at significantly lower levels than the other methods. The California WET method also mobilized arsenic at lower levels than the other methods, except for the TCLP method.

Table 2.3 shows the characteristics of typical, mature landfill leachate parameters of interest. In an actual landfill the pH can be as high as 9, the alkalinity as high as 11500 mg/L and the TOC 29000 mg/L. Also, the residence time in an actual landfill can range from a few days to weeks or months. In contrast, the TCLP conditions include an acidic pH of 4.9, an oxidizing and abiotic environment and a short (18 hr) contact duration. The TCLP was designed to mimic the leaching potential in young landfills, characterized by high volatile fatty acid concentrations (including acetic acid, the acid in the TCLP). These conditions are particularly conducive to leaching of cationic metals which partition most strongly at high pH when amphoteric sorbent surfaces are negatively charged. Arsenate and other oxyanions partition most strongly at low pH (Lin et al, 2000a) such as created by the TCLP. However, as the landfill matures (typically over 1-5 years disposal) the conditions move to those shown in Table 1, which are dominated by an alkaline pH, which is particularly conducive to leaching of anionic metals (e.g., arsenate) but not mimicked by the TCLP.

The behavior of arsenic under reduced conditions was summarized by Hopkin et al, 1989 who concluded that: Arsenates are stable in oxygenated systems such as surface and shallow waters, soil and rocks. Within limits, arsenate is very strongly adsorbed and efficiently immobilized by weakly acidic or alkaline ferric oxyhydroxides (e.g., ferrihydrite) and to a lesser extent by other high surface area hydroxides such as those of manganese and aluminum. Arsenites dominate in mildly reducing anaerobic conditions where ferrous ions are also stable. Adsorption is weaker in such shallow soils and ground waters, and in the pore waters of, for example, marine or lacustrine sediments. In more strongly reducing conditions where sulfate-reducing bacteria are

active as in deep sediments, the arsenical sulfides form essentially insoluble species, the origins of minerals of the future.

The Changes in the redox potential found landfills can cause interconversion of these species, mainly catalyzed by biochemical processes, and thus potentially can result in the liberation or fixation of arsenic (Hopkin et al, 1989). Bacterial activity can have an important effect on the speciation of arsenic (Newman et al, 1998). Besides microorganisms, which are capable of direct As(III) oxidation and direct As(V) reduction, the iron reducing and the sulfate-reducing bacteria can have an important effect on the arsenic solubility.

In an iron-rich environment, iron oxyhydroxides bind arsenic; however, iron-reducing bacteria can utilize iron hydroxides as terminal electron acceptors, releasing bound arsenic. Production of aqueous sulfide by sulfate-reducing bacteria can directly reduce both arsenate and iron oxyhydroxides (Harrington et al, 1998).

There is no definitive test to determine the behavior of hazardous compounds under landfill conditions and over long periods of time. The development of such a protocol would be useful. It has become customary to determine the stability of compounds by subjecting them to leachate tests, usually the United States EPA TCLP test, which involves mixing the solid with a measured volume of buffered acetic acid solution (pH 5) and determining the dissolution of elements into the aqueous solution. The TCLP test cannot objectively be a comprehensive and legal test of a hazardous waste;

it can be of value only as a preliminary screening test, applicable to the very short term and to the particular test conditions.

Consequently, to circumvent the limitations of the United States EPA TCLP test, other non standard characterization methods which have been developed include use of sequential extraction method which has been mainly used on minerals and soils, (Keon et al, 2001; Kim et al, 2003) and landfill leachate and simulated leachates (Ghosh et al, 2004a, 2006b)

Dissertation Objectives

It is apparent that the TCLP is particularly inadequate to predict the leaching behaviour of arsenic from ABSRs under MSW landfill conditions. The development of a long-term dynamic leaching test is important. 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. The aim of this work is to simulate landfill conditions in the laboratory and examine how they impact stability of AFH. The overall objective of this work was to investigate arsenic leaching from fresh and aged AFH under simulated landfill conditions and identify and evaluate different parameters that influence arsenic leaching. The specific objectives were:

1. Comparison of fresh and aged AFH sludge leaching when subjected to various leaching tests like TCLP, WET, an actual landfill leachate and a synthetic leachate solution prepared in the laboratory. The results obtained from these

tests reveals the appropriateness of the standard tests, the TCLP and WET, as well as non standard tests such as landfill leachate, water, synthetic leachate to arsenic leaching.

2. Quantification of the kinetics and equilibrium concentrations of desorption of arsenate from fresh and aged AFH with variations of pH, ionic strength, competitive anions (phosphate and sulfate) and NOM concentrations. The results obtained from fresh studies can be compared to the results obtained from aged sludge so as to quantify the relative contribution of aging to arsenate leaching.
3. Simulation of long-term arsenic leaching of fresh and aged sludges under landfill conditions. This simulation is carried out in a dynamic down flow column reactor and the results are used to compare how those conditions affect leaching of fresh and aged sludges. Throughout the simulation run, the change in column characteristics such pH, alkalinity or organic concentration are measured as the column matures. The leaching of arsenic and iron in the dissolved phase and particulate phases is also monitored in the trials.
4. Comparison of long-term leaching behavior of fresh AFH at Fe/As ratios 1:5:7 (representative of brine treatment) and 1:20 (representative of water treatment) when subjected to aggressive leaching conditions.
5. Overall, differences between the short-term and long-term leaching characteristics and the contribution of aging to overall leaching are foci of interest.

Dissertation Overview

The dissertation is divided into 8 chapters. A brief description of each of the chapters is indicated below.

Chapter 1 of the dissertation 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 dissertation and a brief literature review of arsenic adsorption/desorption, residuals assessment, leaching test protocols and weakness, and analysis of landfill conditions.

Chapter 2 is near submission as a journal article. It is entitled “Arsenic Stability in Fresh and Aged Amorphous Ferric Hydroxides Sludges Generated from Brine Treatment Processes”. This chapter describes the effect of aging of AFH on arsenic leachability. The work quantifies leaching of arsenic from fresh and aged sludges when they are subjected to TCLP, WET, actual landfill leachate, and two synthetic leachate solutions. The effect of pH, both that at which the material is synthesized and aged, and also the pH of the chemical leaching environment is discussed.

Chapter 3 is entitled “Comparative Effect of pH, Competitive Anions NOM and Aging on the Leachability of Arsenic from AFH Generated from Brines.” This chapter quantifies the desorption of arsenic from fresh and aged sludges as a function of the range of ionic strength, pH, and the concentrations of the competitive anions (phosphate and sulfate) and NOM found in landfills.

Chapter 4 is entitled, "Simulation of Landfill Long Term Stability of Amorphous Ferric Hydroxides Sludges Generated from Arsenic Brine Treatment Processes." This chapter describes the simulation of landfill conditions in a flow-through column reactor. A discussion of the various mechanisms that might cause leaching and mobilization of arsenic under landfill conditions is included in this chapter.

Chapter 5 is entitled, "Simulation of Landfill Long-Term Stability of Aged Ferric Hydroxides Sludges Generated from Arsenic Brine Treatment Processes." This chapter describes the effect of aging on the long-term stability of AFH under reducing environments

Chapter 6 is entitled, "Comparative Leachability of Encapsulated and Unencapsulated AFH, Under Landfill Conditions." This chapter describes the performance of AFH stabilized by polymer encapsulation when subjected to simulated landfill conditions and how this compares with unencapsulated sludge leaching.

Chapter 7- has been accepted by the New York Academy of Sciences (PBC) for publication under title "Ferrous Iron Effect on Arsenate Sorption to Amorphous Ferric Hydroxide" The set of experiments described in this chapter were designed to understand whether sorption of Fe(II) onto AFH enhances sorption of arsenic.

Chapter 8. This section contains conclusions of the study undertaken in this research

CHAPTER 2

ARSENIC STABILITY IN FRESH AND AGED AMORPHOUS FERRIC
HYDROXIDE SLUDGES GENERATED FROM BRINE TREATMENT
PROCESSES

Abstract

Treating arsenic brines by co-precipitation with iron oxyhydroxides is an established and effective remediation method for small quantities of highly concentrated liquid arsenic waste, such as brines derived from mine tailings, ion exchange resin regeneration, and reverse osmosis treatment of drinking water. This work deals with the stability of arsenic in amorphous ferric hydroxide, (AFH) sludges precipitated from concentrated arsenic brines. The effect of aging of AFH on arsenic mobilization was studied with regard to sludge with Fe/As molar ratio 5.7:1. Aging kinetics was examined by suspension leaching in 0.4 M HCl. Overall, aging the sludge resulted in consistently higher arsenic release.

Key Words: Aging, amorphous ferric hydroxide, leaching, arsenic

Introduction

According to Environmental Protection Agency estimates, the implementation of the recently enacted arsenic drinking water standard will lead to generation of over 6 million pounds of Arsenic Bearing Solid Residuals (ABSR) every year containing over 30,000 pounds of arsenic (Federal registrar, 2001). Among these ABSR are ferrihydrites, which are a group of poorly crystalline, high surface area iron oxide minerals, with somewhat variable composition in terms of water/Fe ratio (Schwertmann et al, 2004c). Amorphous ferric hydroxide (AFH) is a term commonly used to describe mixtures of various ferrihydrite forms. It occurs naturally in soils and it is commonly generated as a chemical sludge from removal of contaminants such as arsenic in water/waste water treatment operations.

Typically, water treatment processes such as ion exchange (IX) and membrane filtration (MF) yield liquid residual streams (brine) that require treatment. The liquid residuals stream must be either treated on-site or discharged to a sanitary sewer (USEPA, 2001). The recommended process treatment of these residuals 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 followed by neutralization. The type, physicochemical condition and composition of the resultant sludge depend on the type of treatment and the composition of the source water. Sludges resulting from IX treatment could have a pH ranging from 7-12, depending on precipitation pH, while sludges generated from membrane filtration are usually at neutral pH. Generally, the removal of arsenic by co-precipitation is effective for small quantities of highly concentrated liquid arsenic waste.

Sludges containing arsenic typically pass the TCLP and therefore may be disposed in mixed-solid waste landfills. However, the TCLP was designed to simulate co-disposal with municipal (putrescible) waste using acetic acid as organic promoter of dissolution (Janusa et al, 1998; Hardaway et al, 1999; Chang et al, 2001; Meng et al, 2001b). It is known that conditions used in the TCLP are very different from typical conditions prevalent in a landfill. High pH, a reducing environment, long residence time, and anaerobic microbial activity are landfill characteristics not simulated by the TCLP. Previous researchers have shown that leaching of arsenic from ABSR under simulated landfill conditions is much faster than what would be expected by TCLP characterization (Gosh et al, 2004a; 2006b).

It has been established that better crystalline forms develop from less crystalline ABSR precursors by aging (Schwertmann, 2004c). Over time, ferrihydrite may transform (age) slowly into more crystalline and dehydrated forms such as goethite [α -FeO(OH)] and /or hematite [α -Fe₂O₃.nH₂O] (Nowack et al, 1996; Cornell et al, 1985a), which may have different sorptive capacities from the parent sludge. Mechanistically, it has been noted that the formation of goethite and hematite occurs by two mutually exclusive and competitive processes. Hematite is formed by an internal rearrangement of the ferrihydrite structure that also involves dehydration, while goethite formation involves dissolution of the ferrihydrite and its subsequent nucleation and crystallization from solution. This has been the subject of several investigations (Cornell et al, 1985a; 1986b; 1989d). It has also been established that the presence of foreign ions, such as those found in brine solutions, can retard and/or

enhance the aging of ferrihydrite. (Cornell, 1988c; Meng et al, 2001b; Karlis et al; 1996).

Studies involving extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy indicate that As (III) and As (V) species are adsorbed on the iron oxy-hydroxide substrate through formation of inner sphere complexes (Waychunas et al, 1993; Sherman et al, 2003; Manning et al, 1998; Farquhar et al, 2002; Christopher et al, 2006) between the surface and the arsenic oxy-anion. The strength and number of adsorptive sites and the reactivity of the surface might change considerably during aging, since this process involves changes in the physicochemical state of the surface. In general, this reduces the adsorptive capacity of the iron oxides for arsenic and increases extractability of arsenic. The effect of factors that affect such a transformation on arsenic retention has been investigated (Ford et al, 2002a). However, the leachability and stability of the aged material under landfill environments is still poorly understood.

Most of the previous studies have focused their attention on only the factors affecting transformation upon aging of fresh sludge (Cornell 1989d; Karlis et al, 1996; Waychunas et al, 1993; Ford, 2002a) and a limited number on both transformation and leachability (Meng et al, 2002c). Little is known about leachability of aged sludge under MSW alkaline landfill environments. In this work, we study the aging of AFH and its contribution to leachability of arsenic and iron.

The specific objectives of this work are:

1. To assess and compare iron and arsenic leachability from fresh and aged sludges and
2. To investigate the physicochemical conditions that affects the rate of aging of AFHs and their impact on arsenic and iron leaching behaviour.

Materials and Methods

Sludge Preparation and Aging

Two iron sludges with different Fe: As molar ratios (5.7:1 and 87:1) were prepared. The procedure employed to make the 5.7:1 sludge is detailed in what follows. The Fe:As 87:1 sludge was prepared by a similar procedure. Sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, KR grade Aldrich Sigma) was used as the arsenic salt. The results presented refer to the Fe:As 5.7:1 sludge unless specified otherwise.

A 0.169 M As solution was prepared by dissolving 12.64 g of sodium arsenate heptahydrate in 1 L Milli-QTM water (Water Systems by Millipore). A 0.964 M Fe solution was prepared by dissolving 259.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1 L Milli-QTM water. The resultant solution was rapidly stirred at 100 rpm. This mixture (molar ratio Fe/As = 5.7:1) was allowed to equilibrate for 1 hr and the solution adjusted to pH 7 using 10 M NaOH solution with vigorous stirring. The mixture was buffered using 0.001 M NaHCO_3 . The sludge mixture was then shaken on a reciprocating shaker table (Orbit, reciprocating speed of 30 rpm) for 30 minutes to ensure homogenization without causing the break up of the flocculated particles. The batch was then allowed to settle and equilibrate for 14 days at 25°C. During this period, fluctuations in pH of ± 0.5

units were observed. These fluctuations were mitigated by periodic adjustment with 0.1 M HCl or 0.1 M NaOH. A liquid sample was withdrawn for analysis to determine the equilibrium concentration of As and Fe. Duplicate aliquot samples, 100 mL each, were withdrawn from the batch and placed in 250 mL Erlenmeyer flasks. Free water was decanted off. The pH in each flask was set to a predetermined value, which we will call the synthesis pH, ranging from 7 through 12 and allowed to equilibrate for 2 days. Every 5 hours, the fluctuations in synthesis pH were mitigated by periodic adjustment with 0.1 M HCl or 0.1 M NaOH. Solid-liquid separation of each batch was achieved by vacuum filtration in a 0.45 μm pore size cellulose acetate membrane filter to achieve 50-60% wt/wt water content in the separated solids, which would be suitable for sludge disposed in a landfill.

Duplicate sludge samples, 2 g each, were withdrawn from each synthesis pH batch, and placed in 75 mL well-stoppered high density polyethylene bottles. The bottles were purged with nitrogen and the sludge was aged in an oven at 40° C for 11 weeks. The effect of temperature was also investigated by aging the sludge at 40° and 70°C. Unless otherwise specified, aging temperature was 40°C.

Total Fe and As in the prepared sludges was determined by digestion of a 0.5 g sample using 70% by volume HNO₃ in a CEM microwave digester, using the SW 821-8051 method. The total loading of the sludges after digestion are shown in Table 2.1.

Table 2.1. Loading Characteristics of the sludges used in this study

Sludge type	Fe loading (mg Fe /g dry sludge)	As loading (mg As /g dry sludge)
Fresh, (Fe:As 5.7:1, pH 7)	381.3	106.4
Aged, (Fe:As 5.7:1 , pH 7)	296.3	42.9
Fresh, (Fe:As 5.7:1,pH 12)	326.1	80.0
Aged, (Fe:As 5.7:1, pH 12)	258.6	32.6
Fresh, (Fe:As 87:1, pH 12)	387.2	7.3
Aged, (Fe:As 87:1 , pH 12)	279.5	2.8

Characterization of Arsenic and Iron Leaching

The sludges prepared in this work were subjected to various liquid environments that included standard leaching tests (TCLP and the CA-WET), and more realistic conditions in terms of what might be expected in a MSW landfill. Table 2.2 summarizes the main difference among protocols employed and typical conditions of actual landfills. Both freshly synthesized and aged sludges were subjected to the various leaching protocols. The procedure employed in each protocol is briefly described in what follows. All leaching experiments were conducted at room temperature (approximately 25° C).

Table 2.2 Characteristics of Leaching Protocols and actual landfill conditions

TEST	TCLP	WET	SL	LL	Actual Landfill
Chelator	Acetic acid	Citric acid	VFA mixture	Mixture	Multiple
Duration	18 hr	48 hr	18 hr	18 hr	Weeks – years
PH	4.95	5.05	7.36	7.4	7.5-9.0
Bioactivity	Abiotic	Abiotic	Abiotic	Biotic	Biotic
ORP (mV)	-68.2	-101	-224	-165.6	Anoxic, variable

SL refers to synthetic leachate and LL is actual Landfill leachate.

Standard leaching tests

Sludge samples were separately leached with acetic acid at pH 4.95 according to the TCLP/EPA procedures SW846-method 1311. During leaching, the samples were rotated end-over-end for 18 ± 2 hr at room temperature. Sludge samples were also subjected to CA-WET test (California Register, 1985), which includes maintaining the slurry under a nitrogen headspace. The mixture was shaken at 125 rpm on a reciprocating shaker table.

Non-standard leaching tests

The sludge samples were mixed with leaching solutions as described below. All non-standard tests involved contacting the leaching solution and the sludge for 48 hours, following the modified TCLP procedure (5 g solid, 97.5 mL of the extraction fluid,

tumbler agitation with nitrogen headspace). After each test, solid-liquid separation was achieved by filtering each batch in a 0.45 μm pore size cellulose acetate membrane filter.

Landfill Leachate (LL) solution

Actual leachate was collected from Los Reales MSW Landfill, in Tucson AZ and was used as leaching fluid. To minimize alteration after collection, the LL was kept at 4°C and used within 1 day of collection. The landfill leachate was fully characterized for composition and physical chemical properties prior to leaching. Table 3 shows properties of various landfills leachates from this work and other sources for comparison purposes. Only the landfill leachate labelled LL was used in this work.

Table 2.3: Physicochemical characteristics of various landfill leachates

	PH	ORP (mV)	Alkalinity (mg/L CaCO ₃)	TOC (mg/L)	TDS (mg/L)	Ionic Strength (M)	Nitrogen (mg/L)
LL	6.9-8.5	-166	3850-4550	67-120	3500-4400	N/R	13-145
LL1	6.82	-143	1100	160	3600	0.33	120
LL2	4.5-9.0	N/R	300-11500	30-29000	2000-60000	N/R	50-50000
LL3	6.5-8.2	N/R	1250-8050	N/R	1960-16800	N/R	20.6-2030
LL4	6.2-7.1	N/R	N/R	236-3160	N/R	N/R	N/R

N/R - Values not reported

LL – Leachate collected from Los Reales MSW Landfill, Tucson, AZ and used in this work.

LL1 – Leachate from Tangerine Road Landfill, Tucson, AZ (Ghosh et al, 2004a)

LL2 – Leachate composition in reference (Kjeldsen et al, 2002)

LL3 – Leachate composition in reference (Jang et al, 2003)

LL4 – Leachate composition in reference (Hooper et al, 1998)

Synthetic Simulated Leachate (SSL)

This leaching solution was designed to represent an approximation of the condition of a mature landfill leachate, in order to have a representative and reproducible leaching protocol that is close to the physicochemical condition of an actual landfill. In order to mimic the TOC concentration and approximate make-up of landfill leachate, a mixture of 5 low molecular weight volatile fatty acids (VFA) was prepared and added to 1 L reactor. Ammonium chloride and sodium bicarbonate were added to mimic ionic strength of in a mature landfill leachate. 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. Sodium Bicarbonate was added to provide for the required typical alkalinity. The pH of the mixture was adjusted to 7.5 using 1 N NaOH. The composition of the SSL used in shown in Table 2.4.

Table 2. 4. Composition of the SSL used in this work

Component	Concentration (mg/L)
Acetic Acid	576
Valeric Acid	163
Propionic Acid	192
Butyric Acid	422
Cuproic Acid	232
Ammonium Chloride	650
Sodium Bicarbonate	11500
Sodium Citrate	46400
Hydroxylamine Hydrochloride	31.7
Calcium Carbonate	1100

Deionized Water Extractant (DI)

Milli-QTM water was used as the extracting fluid. This test is designed to mimic leaching under scenarios where the wastes are in contact with non-buffered environments as such as rainwater.

Controlled-pH leaching

An amount of 0.05 g dry wt of sludge was added to 200 mL of Milli-Q water. The pH of the mixtures was adjusted to 6.5 using 0.1 M HCl (Spectrum) or NaOH (Sigma). The mixture was then purged with a nitrogen headspace, shaken at 125 rpm on a reciprocating shaker table (Orbit) at room temperature for 20 days with periodic

adjustment of pH (to compensate fluctuations of up to 2 pH units) with 0.1 M NaOH. Solid-liquid separation was achieved by filtering each batch in a 0.45 μm pore size cellulose acetate membrane filter. The above procedure was repeated for pHs of 7, 8, 9, 10 and 10.5.

Acid Extraction (AE)

Leaching in an acidic solution was performed on aging sludges to assess changes in arsenic and iron extractability with time. At a specific aging time, a sample of 0.2 g of solid was taken from the sludge and contacted for 30 minutes with a 0.4 M HCl (the solid to liquid ratio was 100 mg solid /100 mL solution). Both iron and arsenic concentrations were measured in the leaching liquid. The purpose of this test was to solubilize amorphous iron phases in the sludge, whose solubility in acidic solution is appreciably higher than that of crystalline phases (Cornell et al, 1996e).

Instrumentation and Analysis

In all cases, the filtrate and liquid samples were analyzed for total arsenic and iron by ICPMS, which consists of an Agilent 1100 HPLC (Agilent Technologies, Inc) with a reverse-phase C 18 column (Prodigy 3u ODS 150 \times 4.60mm, Phenomenex, Torrance, CA) fitted with Agilent 7500a ICP-MS with a Babington nebulizer detector. Bulk mineralogy of the solid samples was analyzed by taking 0.2 g of dry aged solid and then characterizing it by XRD fitted with a graphite monochromator filter, detector slit of 0.15 and a Scintag XDS 2000 diffractometer employing Cu-K alpha radiation scanning at 2 degrees/minute.

Results and Discussion

The changes, which occur when AFH ages are distinct and visible. Figure 2.1 below shows the comparison between the fresh and aged AFH of the same preparation conditions and chemical composition.

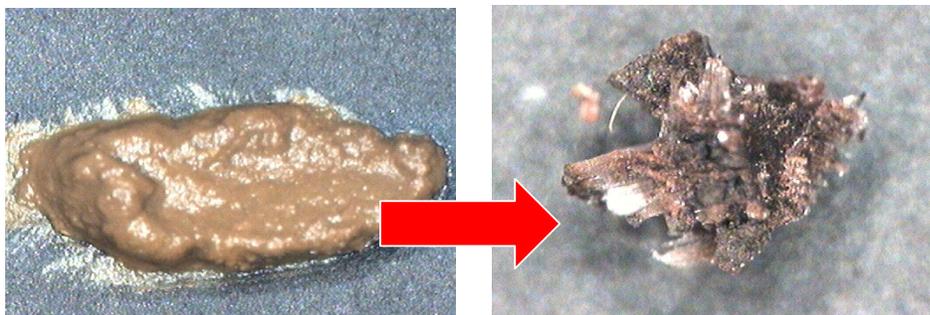


Figure 2.1. Optical Microscope images of AFH showing the transformation fresh AFH to aged solid. The sludge was synthesized at pH 12, Fe:As 5.7:1

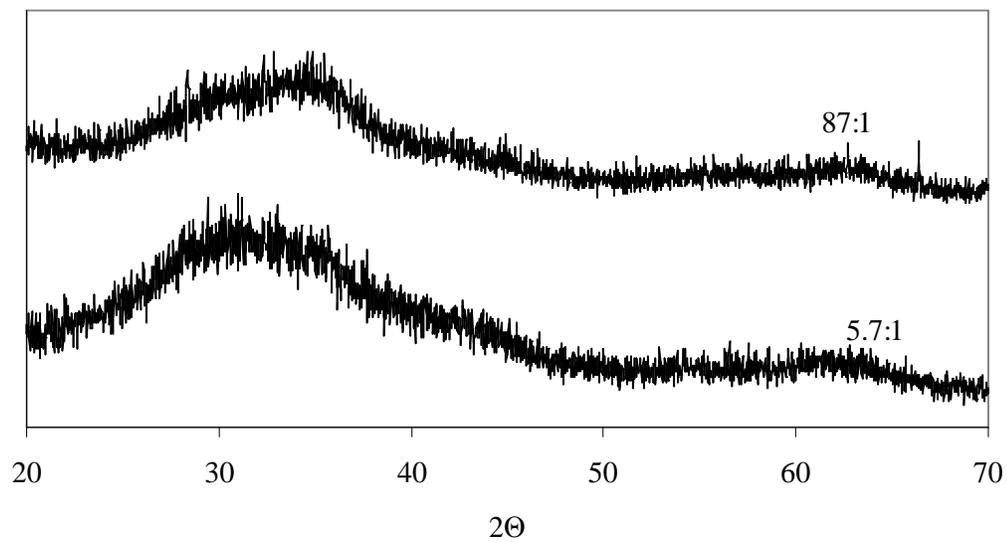
Other analytical methods were used to quantify the effects of such transformations on arsenic and iron retentions. The results are discussed in the proceeding sections of the chapter.

XRD Analysis

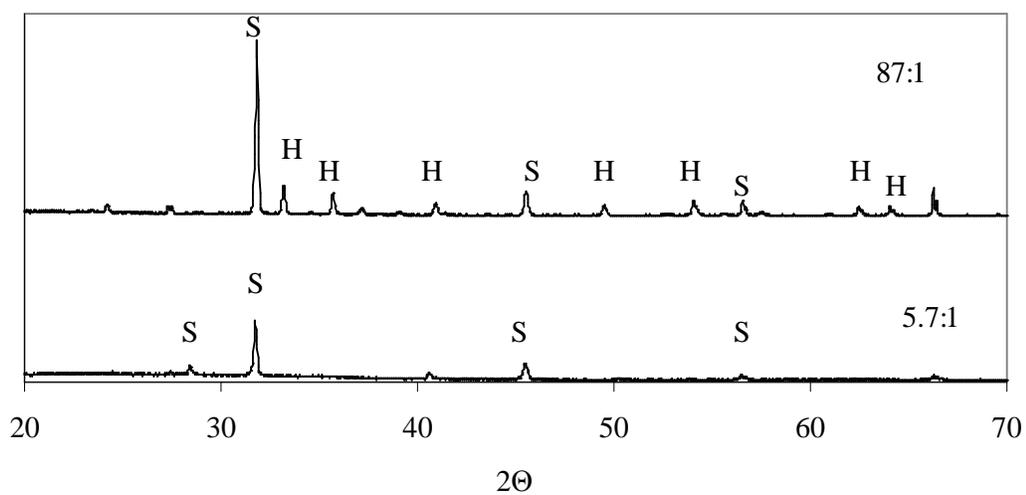
X-ray diffraction patterns of the sludges at different aging times and water content are presented in Figure 2.2 for sludges synthesized at pH 12. Fresh sludges exhibited very broad and shallow diffraction peaks (Figure 2.2a). Bragg reflections of this nature possessing very broad and low intensity peaks indicate that the analyzed phase possesses a short-range order; i.e., it is amorphous or very poorly crystalline in nature.

Note that the diffractograms obtained from the sludges were very similar but no iron or arsenic-containing phases were detected, implying that they were either amorphous, poorly crystalline or below the detection limit. Both fresh and aged sludges synthesized at pH 7 showed diffractograms similar to Figure 2.2a (results not shown). The broad peak around $2\Theta=30^\circ$ has been attributed by Carlson et al, 2002 to the precipitation of a disordered iron (III)/arsenate phase. On the other hand, Rancourt et al 2001 postulated that it results from an AFH phase containing high levels of adsorbed arsenate and the precipitate is made up of extremely fine-grained particles. We hypothesize that, irrespective of Fe/As ratio, this peak may be distorted as a result of ordering of the ferrihydrite into more morphological crystal forms, either incorporating or excluding high levels of As in the inner restructured Fe crystallite solid. However, due to the short range and low intensity nature of the broad peak, XRD could not, unfortunately, provide proof of our hypothesis. Therefore, the fate of arsenic in the solid remained unknown and was further investigated using other chemical tests. The results are presented in subsequent sections of this paper.

(a) Aging time: 0 days, water content: 55



(b) Aging time: 80 days, water content: 55 wt%



(c) Aging time: 80 days, excess water

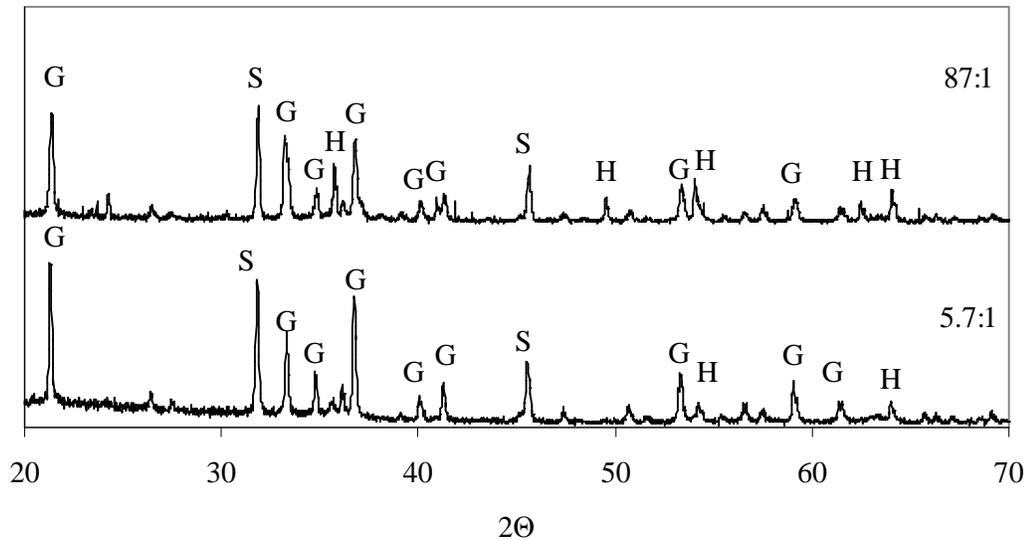


Figure 2.2. X-ray powder pattern for synthesis pH 12, Fe:As 5.7:1 and 87:1 sludges. S=sodium chloride, H=Hematite and G=Goethite. Both sludges were X-ray amorphous at day 0 (a) For water content of 55% in 5.7:1 sludge no detectable iron phases were observed, whereas the 87:1 yielded hematite (b) Both sludges aged to goethite at excess water levels (c).

After aging the sludges for 80 days at 70°C, generated XRD diffractograms revealed that the 5.7:1 sludge did not undergo any change in phase composition and structure; i.e. no identifiable crystalline iron phases were found (Figure 2.2b) and only NaCl crystals were resolved. On the other hand, the 87:1 sludge aged to crystalline hematite (Fe_2O_3). This observation is consistent with previous works (Paige et al, 1997) in which the formation of hematite was documented in aged sludges at higher Fe:As ratios. The diffractogram does not allow us to assess what proportion of the AFH transformed into hematite.

In an MSW landfill, accumulation of landfill leachate may result in water saturation of the disposed AFH sludge, which will induce overall water content of the material

greater than its initial amount, as predetermined by the EPA's Paint Filter Liquid Test (PFLT) SW-846 method 9095A. For this reason, we conducted sludge aging under completely water-saturated conditions (excess water). Figure 2.2c shows that, after 80 days of excess water aging, X-ray diffraction of samples from both sludge ratio batches led to detection of goethite and minor traces of hematite. However, by comparing the intensity of the peaks, it is apparent that goethite was the more prevalent crystalline iron phase. This observation is consistent with results presented by Schwertmann et al, (1989a; 2000b) who stated that amorphous hydrous ferric oxides are thermodynamically unstable and age by dehydration to goethite (FeOOH) and hematite (Fe_2O_3).

The XRD microanalysis did not reveal the impact of sludge aging on arsenic adsorption and retention (no identifiable arsenic mineral phases could be detected). These patterns only provided snapshots of iron phase transformations at a certain time during the aging process. In order to investigate the effect of sample mineralogy on fate and stability of arsenic, leaching tests were performed.

Acid Extraction

The change in the solid structure of the sludge during aging was quantified by acid extraction (AE). This was based on the premise that the 0.4 M HCl solution would dissolve the amorphous fraction of the sludge, leaving the crystalline aged phase undissolved. Figure 2.3 shows the results obtained as a function of the aging temperature (40°C and 70°C) and synthesis pH (7 to 12). The results are presented in terms of the mass fraction of iron (Figure 2.3a) and arsenic (Figure 2.4b) that the

weak acid extracts from a sludge sample over 30 minutes of contacting. For both fresh (aging time=0) pH 7 and 12 sludges, AE is capable of extracting practically all iron and arsenic in the sludge. However, as the sludges age, iron and arsenic extraction decreases with time. It is interesting to note that both iron and arsenic extracted follow the same trends under all conditions, which points to a co-dissolution of both elements in the extraction tests.

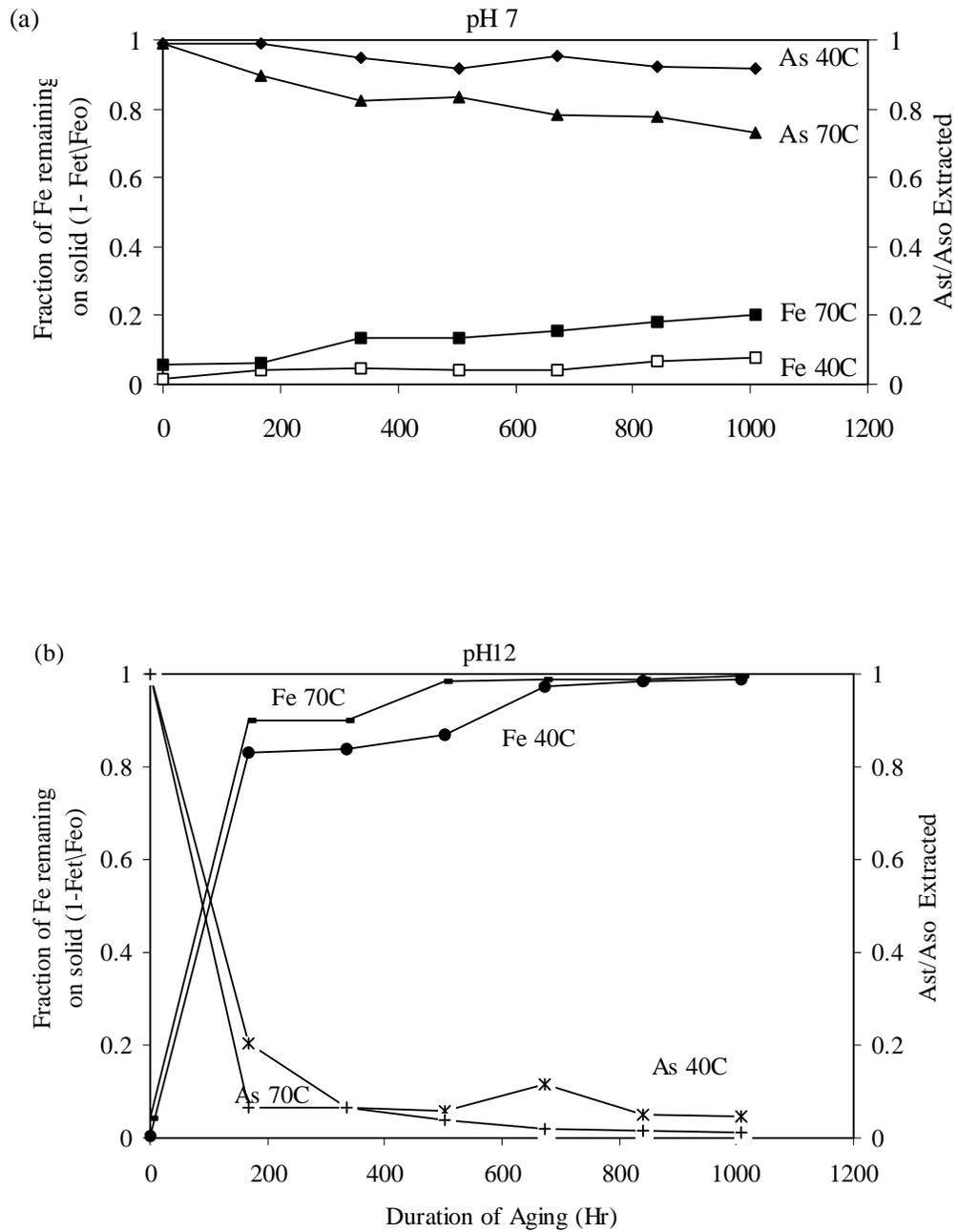


Figure 2.3. The mass fraction of iron (a) and arsenic (b) extracted from sludges by acid (0.4 M HCl) as a function of aging time, for two synthesis pHs: pH 7 (solid symbols) and pH 12 (open symbols), and two aging temperatures: 40°C (circles) and 70°C (squares).

The sludge synthesized at pH 7 exhibits slow changes throughout the duration of the study. A slight increase in the stability of iron and arsenic is seen over 1000 hr, which might be the product of a gradual change in the solid structure over this period. On the other hand, the sludge synthesized a pH 12 showed a dramatic increase in both iron and arsenic stability during the first 200 hr of aging. There is also an indication that transformations continued to occur in the aging period between 200 and 700 hrs, as evidence by the additional decline in iron extraction during this period (Figure 2.3a). In combination with the XRD results discussed above, the WAE results indicate that the pH 12 sludge ages relatively rapidly to a partially crystalline phase, whose stability is appreciably better than that of the original amorphous sludge. Previous works have reported that an increase in hydroxyl ions leads to increases in the degree of crystallinity of AFH sludges (Kim et al, 2003; Paige et al, 1997).

The solid phase transformations that lead to a lower solubility of both iron and arsenic during aging are accelerated by an increase in aging temperature from 40 to 70°C (Figure 3). However, the mechanism responsible for the change seems not to change, since the trend with synthesis pH changes is the same at the two temperatures.

Our results show that it would be desirable, from the standpoint of sludge disposal, to manufacture the sludge at high pHs and age it for at least 200 hr to increase arsenic stability. However, this does not seem practical in applications that involve relatively large amounts of materials. The sludge synthesized at pH 7 is closer to what would be expected in most practical applications and thus it will be the focus of the rest of this study.

Overall, for all conditions tested, the observed decrease in the iron and arsenic fraction in the WAE experiments as the age of the sludge increased is qualitatively consistent with Calvin et al, 1994 who investigated desorption/sorption of metal ions as a function of hydrous ferric oxide aging. They concluded that during aging of HFO, some metals might become incorporated into the transforming solid, which may reduce their extractability. Once the crystalline product is formed, the majority of arsenic becomes immobilized and not readily extractable. Lin et al, 2000a hypothesized that dehydration and hydrothermal treatment could enhance the bonding of arsenic to the adsorptive sites of AFH and hence reducing its extractability. It should be noted, however, that AE probes extractability at a low pH whereas in a mature landfill, the pH of the leachate in contact with the aging solid is usually in the range 6.5-9. The pH dependence of arsenic leachability from water treatment sorbents has been previously investigated (Jing et al, 2005b) but, to the authors' knowledge, there is no available literature on the behavior of aged AFH sludge under variable pH environments. The effect of varying solution pH to stability of arsenic was further investigated and results presented below.

Effect of pH on Leaching

The pH of the leaching solution is one of the most important factors affecting the magnitude of arsenic leaching and for this reason it was investigated in detail. According to Hooper et al, 1998, quantification of arsenate desorption at high pH is of particular significance in mature landfills where the pH ranges from 7.5 to 9.0, with an average value of approximately 8.2. Figure 2.4 shows the fractions of iron and arsenic extracted from the solid at various pHs in the range 6.5-10.5.

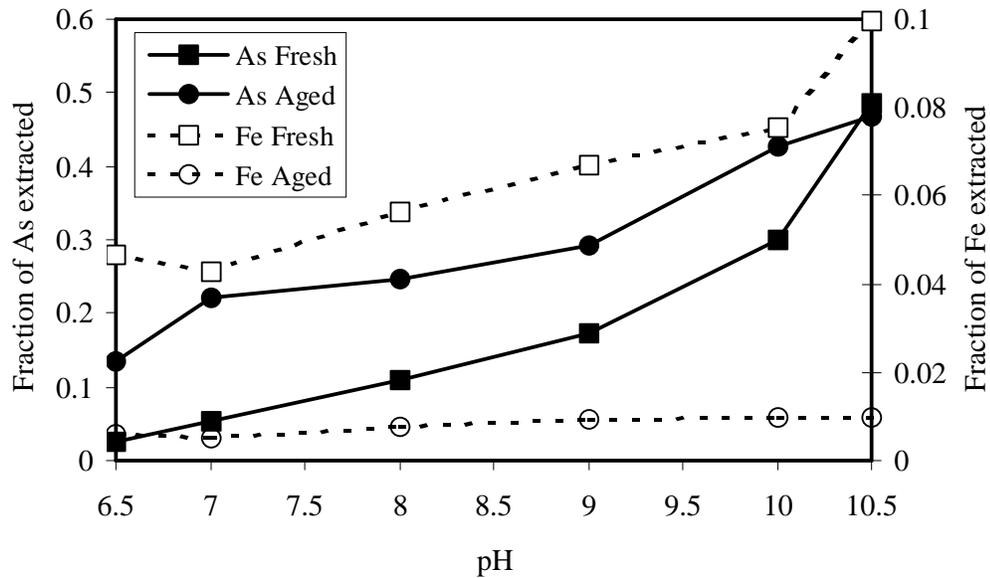


Figure 2.4. The mass fraction of arsenic and iron extracted from fresh and aged sludges as a function of pH. Synthesis pH: 7.

The first important observation is that, in contrast with acid extraction, the fraction of arsenic extracted is appreciably higher than the fraction of iron extracted. In addition, iron is comparatively very stable in the aged sludge while at the same time arsenic becomes easier to extract. These results suggest that the leaching of arsenic in this case is associated with desorption rather than co-dissolution. For this reason, it seems more reasonable to characterize these results in terms of a partition coefficient,

$$\text{defined as } K_d = \frac{q_A}{C_A} \quad (1)$$

where q_A is mass of arsenic in the solid per unit mass of Fe in the solid, and C_A is molar concentration of arsenic in the liquid. Results for the partition coefficient as a function of pH are shown in Figure 2.5. At low pHs (≤ 8), arsenic has a higher affinity for fresh sludge. It has been reported that during crystal growth there is elimination of

adsorptive coordination sites for surface arsenic (Waychunas et al, 1993). It is appealing to think that this will be the case at lower pHs, where electrostatic adsorption of arsenate ions should be favored.

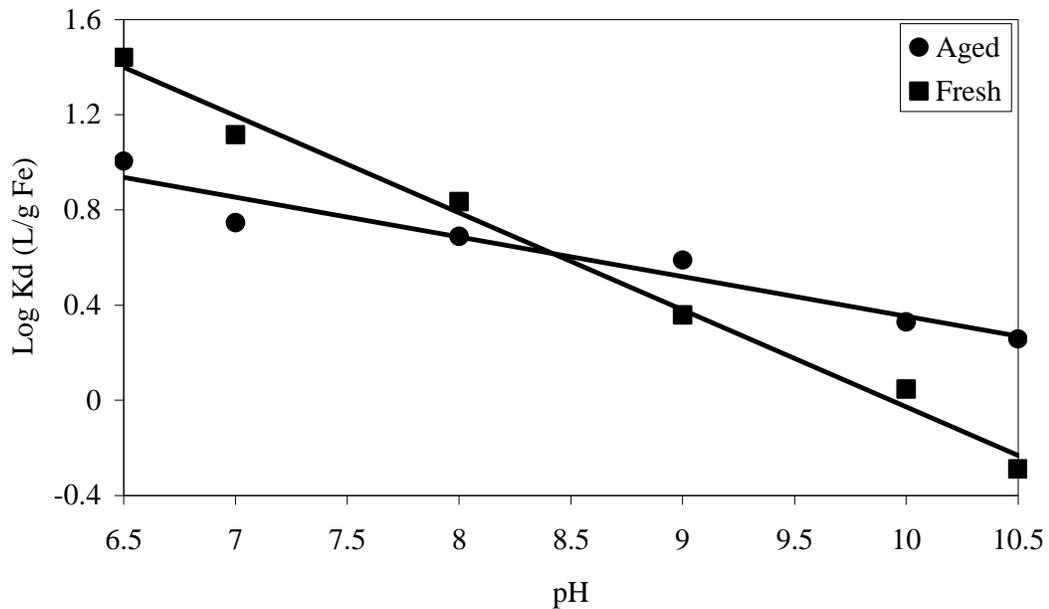


Figure 2. 5. Partition coefficient for arsenic in fresh and aged sludges. Synthesis pH: 7. Solid lines represent linear fits.

It is interesting to note that pH 8.3, the crossover point for the partition coefficient of fresh and aged sludge (Figure 2.5) coincides with the pH of zero point charge (ZPC) of pure ferrihydrite and amorphous $\text{Fe}(\text{OH})_3$ (Cornell et al, 1996; Stumm et al, 1992a; Klaus et al, 1998). Since the XRD analysis revealed that the sludge remains mostly amorphous even after aging, it is not surprising that both fresh and aged sludge would have the same ZPC. The fact that both partition coefficients are the same at the ZPC suggests that the difference in arsenic affinity for both sludges could be related mostly to electrostatic sorption. The aged sludge has less available adsorption sites for arsenic, which accounts for the lower affinity at low pHs for which electrostatic effects become more important, but higher affinity at high pHs, for which the density of negative charges on the surface should be lower for the aged sludge.

Leaching Tests

The results presented above indicate that pH and aging can have a significant effect on arsenic stability. However, in practice, decisions on whether the sludge is or is not a hazardous waste are made in terms of standard leaching tests. For this reason, we investigated arsenic leachability of fresh and aged sludge by subjecting them to standard leaching tests (TCLP and CA-WET) and other extraction fluids (H₂O, LL and SSL). Figure 2.6 shows the leachate concentration of total iron and arsenic for fresh and aged sludges. As shown in Figure 2.6b, the order of leached arsenic concentration was as follows: WET > SSL > DI > LL > TCLP. It is remarkable that the TCLP test is less capable of leaching arsenic from the sludge than distilled water. This is a consequence of the lower pH of the TCLP test (Table 2.2), at which arsenic becomes more stable. For the fresh sludge, the TCLP leachate has an arsenic concentration of 2.5 mg/L, which is well below the EPA 5 mg/L toxicity characteristic limit. Previous works (e.g Ghosh et al, 2004a; Hooper et al, 1998) on leachability of As from commercial sorbents (GFH, activated alumina) showed that the acetate in the TCLP has a minimal effect on arsenic leachability.

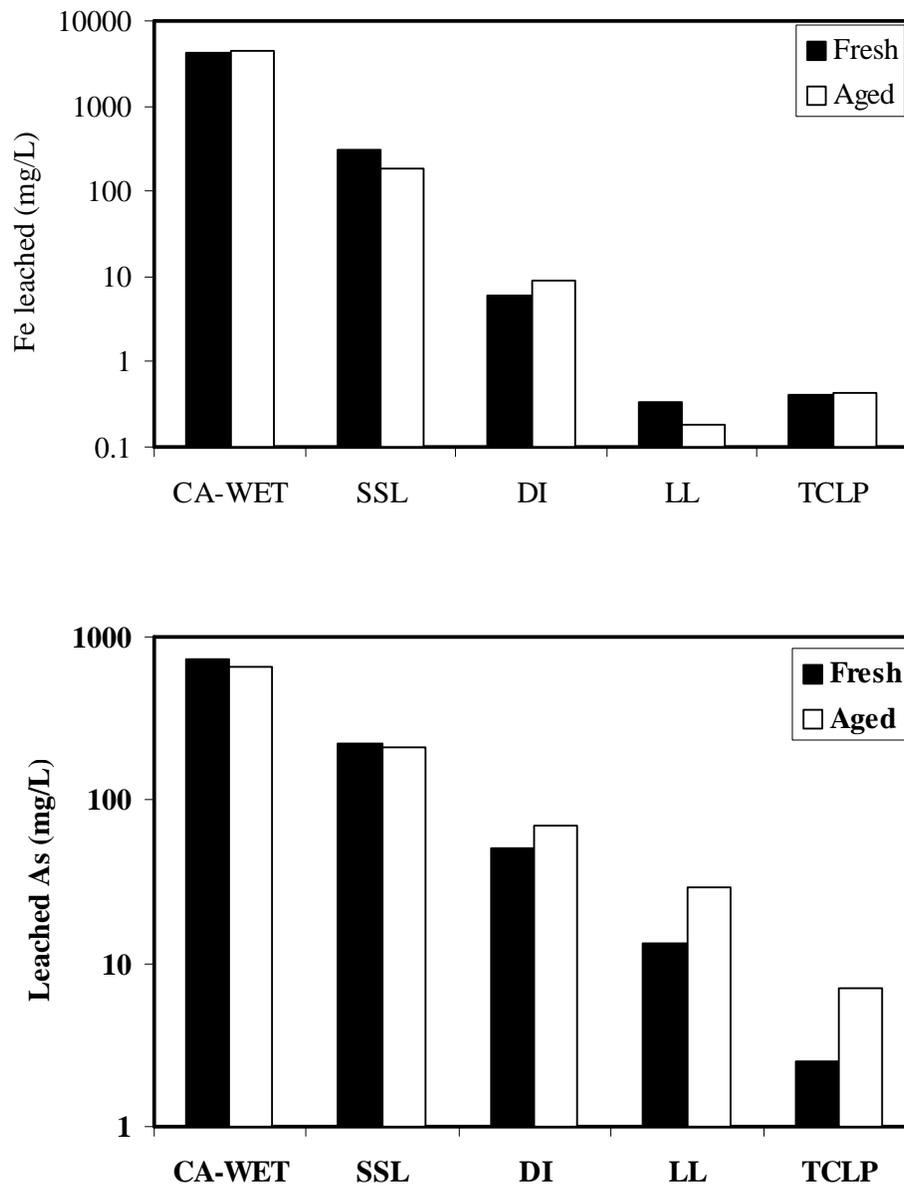


Figure 2. 6: Comparative concentrations of Fe (a) and As (b) leached from fresh and aged sludge. Synthesis pH: 7.

Comparatively, DI water leached more arsenic from fresh and aged sludge than actual landfill leachate. This clearly indicates that, unless a strong chelating agent for iron, such as citrate, which is present as in the WET and synthetic leachate, is available,

purified water is the most aggressive leaching environment. During DI water leaching, hydrolysis of ferric hydroxide releases OH^- ions in the bulk solution. Since DI is not buffered, accumulation of OH^- ions in solution results in an alkaline pH in the final slurry, which favors arsenic leaching. In the experiments reported in Figure 2.6, the final pH of the DI water leachate was about 9.

The CA-WET induced the highest arsenic leaching. The ability of the citric acid in the CA-WET to extract iron was explained by Jing et al, 2003a who observed that citric acid forms surface complexes on iron oxides that are much stronger than acetic acid (TCLP). These complexes compete with arsenic for available adsorption sites. In addition, citrate solubilizes iron, which, in turn, leads to further arsenic release. Because of the strong complexation strength of the citrate, which overshadows the contribution of aging, quantification of the contribution of aging to overall leachability of arsenic was not possible under standard test conditions.

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CHAPTER 3

COMPARATIVE EFFECT OF pH, COMPETITIVE ANIONS, NOM AND AGING ON THE LEACHABILITY OF ARSENIC FROM AFH GENERATED FROM BRINES TREATMENT

Introduction

According to Environmental Protection Agency estimates, the implementation of the recently enacted arsenic drinking water standard will lead to generation of over 8 million pounds of Arsenic Bearing Solid Residuals (ABSR) every year containing over 30,000 pounds of arsenic. Among these ABSR are ferrihydrites, which are a group of poorly crystalline, high surface area iron oxide minerals, with somewhat variable composition in terms of water/Fe ratio (Schwertmann et al, 2004c). Amorphous ferric hydroxide (AFH) is a term commonly used to describe mixtures of various ferrihydrite forms. It occurs naturally in soils and it is commonly generated as a chemical sludge from removal of contaminants such as arsenic in water/waste water treatment operations.

Typically, water treatment processes such as ion exchange (IX) and membrane filtration (MF) yield liquid residual streams (brine) that require treatment. The liquid residuals stream must be either treated on-site or discharged to a sanitary sewer (USEPA, 2001b). The recommended process treatment of these residuals 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 followed by neutralization.

Sludges containing arsenic typically pass the TCLP and therefore may be disposed in mixed-solid waste landfills. However, the TCLP was designed to simulate co-disposal with municipal (putrescible) waste using acetic acid as organic promoter of dissolution (Janusa et al, 1998; Hardaway et al, 1999; Chang et al, 2001; Meng et al; 2001b). It is known that conditions used in the TCLP are very different from typical conditions prevalent in a landfill. High pH, a reducing environment, long residence time, and anaerobic microbial activity are landfill characteristics not simulated by the TCLP.

Over time, ferrihydrite may transform (age) slowly into more crystalline and dehydrated forms such as goethite [α -FeO(OH)] and /or hematite [α -Fe₂O₃.nH₂O] (Cornell et al, 1985; Nowack et al, 1996), which may have different sorptive capacities from the parent sludge.

The strength and number of adsorptive sites and the reactivity of the surface might change considerably during aging, since this process involves changes in the physicochemical state of the surface. In general, this reduces the adsorptive capacity of the iron oxides for arsenic and increases extractability of arsenic. The effect of factors that affect such a transformation on arsenic retention has been investigated (Ford, 2002a) however, the stability of the aged once in contact with anions in the landfill leachate under landfill environments has never been investigated and is poorly understood.

The concentration and nature of other ions in solution also affects the fraction of arsenic desorbed, as ions compete for the surface sites. In general, as the ionic strength increases the fraction of contaminant sorbed decreases. However, individual ions have differing affinities for the surface groups, so the effectiveness of competing ions 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. For instance, sulfate (SO_4^{2-}) competes effectively with arsenate for most anion exchange resin sites, whereas it has only minimal effect on arsenate adsorption by activated alumina (Clifford, 1999b).

The concentration of natural organic matter (NOM) is also expected to impact the degree of arsenic absorption. The effect of NOM on sorption is much harder to predict than the effect of pH or ionic strength and only a few studies have been conducted on anion sorption in the presence of variable concentrations and types of NOM. 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 et al, 1996b), or it may directly react with the sorbent surface to enhance dissolution of the surface and loss of sorption sites (Schwarzenbach et al, 1993). However, 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. Whereas little research has been

conducted on the effect of NOM on arsenic desorption from AFH, no known available literature is available on the effect of NOM on aged sludge.

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. 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). It is expected that once AFH ages into more crystalline forms, the anions present in solution might compete for the fraction of binding sites available for arsenic sorption. Since the aged material has been implicated to have less available sites for arsenic binding, it is therefore expected that competition for the available sites will be greater in the aged solid than in the parent fresh AFH sludge. To the author's knowledge, there is limited available literature data, which attempts to quantify and compare the above competition of anions between the fresh and aged solids.

The aim of this research was:

To determine the impact of iron oxide mineralogy on the reversibility of arsenic partitioning on AFH under various environmental conditions in which it may be in contact.

Materials and Methods

Sludge Preparation and Aging

The materials, methods and procedures used in sludge preparation and its aging is similar to that described in chapter 2. Refer to chapter 2 for detailed description.

Characterization and kinetics of arsenic desorption

The sludges prepared in this work were used to investigate two types of experiments namely kinetic trails and desorption trials using various liquid anion environments that included various SO_4^{2-} , PO_4^{3-} , NOM, H^+ , OH^- and ionic strength concentrations.

The ranges of concentration used in desorption trials represented more realistic conditions in terms of what might be expected in a MSW landfill. Table 3.1 summarizes the average composition of typical conditions of actual landfills.

Table 3.1: Typical pH and concentration ranges of anions in landfill leachate and the concentrations of anions used in this work.

Parameter	Landfill Leachate Range (mg/L)*	Concentrations in Los Reales Landfill, (mg/L)	Concentrations used in this work (in mg/L)
PH	6.7-8.9	7.16	6.5, 9.0, 10.5
Phosphate	0.11- 234	0.17	0.2, 2, 20, 100, 200
Sulfate	105- 4900	267	50, 250, 500, 2500, 5000
NOM (as TOC)	76-40000	378	10, 20, 200, 2000, 20000

*Bagchi, 1994; a compilation of municipal waste leachate data.

Both freshly synthesized and aged sludges were subjected to the various kinetic and desorption protocols. The procedure employed in each protocol is briefly described in what follows. All leaching experiments were conducted at room temperature (approximately 25° C).

Kinetic Studies

The kinetic desorption of arsenic from fresh and aged sludge was investigated in pH range 6.5-10.5 for a period of 100 hours. The experiments were conducted in a separate 125 mL Nalgene bottles following the modified TCLP procedure (5 g solid, 97.5 mL of the extraction fluid, tumbler agitation with nitrogen headspace). The solution was placed on a reciprocating shaker table (Orbit, reciprocating speed 125 rpm). Every 2 hours, the fluctuations in solution pH were mitigated by periodic adjustment with 0.1 M HCl or 0.1 M NaOH. At 10 hr time interval, a bottle was withdrawn, and liquid samples were filtered through 0.45µm filter and analysed.

Desorption Trials

In an attempt to quantify the leaching behavior of fresh versus aged sludge, batch parametric leaching tests were used to evaluate the influence of a single characteristic (e.g., pH, NOM etc) of the leaching solution composition. These tests were conducted to comparatively evaluate the aggressiveness of these differing formulations and to determine if aging differentially affects arsenic leaching under ion composition conditions.

Controlled-pH leaching

An amount of 0.05 g dry wt of each type of sludge was added to 200 mL of Milli-Q water. The pH of the mixtures was adjusted to 6.5 using 0.1 M HCl (Spectrum) or NaOH (Sigma). The mixture was then purged with a nitrogen headspace, shaken at 125 rpm on a reciprocating shaker table (Orbit) at room temperature for 20 days with periodic adjustment of pH (to compensate fluctuations of up to 2 pH units) with 0.1 M NaOH. Solid-liquid separation was achieved by filtering each batch in a 0.45 μm pore size cellulose acetate membrane filter. The above procedure was repeated for pHs of 7, 8, 9, 10 and 10.5.

Effect of Sulfate, Phosphate, Ionic Strength and NOM

Other than H^+ and OH^- ions described above, parallel sets of desorption experiments were conducted for other ions. These experiments were conducted in a separate 125 mL Nalgene bottles following the modified TCLP procedure (5 g solid, 97.5 mL of the extraction fluid, tumbler agitation with nitrogen headspace). Stock solutions of the extraction fluids included SO_4^{2-} and PO_4^{3-} solutions, which were prepared from sodium sulfate and sodium phosphate respectively. For studies involving ionic strength, equi-molar concentrations of NaCl (GR Grade) and CaSO_4 was measured to achieve the desired ionic strength whereas NOM source included a humic acid – sodium salt (Aldrich) which consisted of 39% carbon and 352 mg TOC /g NOM.

After addition of the anion, the pH of the slurry was adjusted to either 7 or 9. The solution was placed on a reciprocating shaker table (Orbit, reciprocating speed 125 rpm). Similarly, every 2 hours, the increase in solution pH supposedly caused by

specific adsorption of oxyanions through OH^- exchange at the solid surface, was mitigated by periodic adjustment with 0.1 M NaOH. The samples were equilibrated for 60 hrs, and liquid samples were filtered through 0.45 μm filter and analyzed.

Instrumentation and Analysis

In all cases, the filtrate and liquid samples were analyzed for total arsenic and iron by ICPMS, which consists of an Agilent 1100 HPLC (Agilent Technologies, Inc) with a reverse-phase C 18 column (Prodigy 3u ODS 150 \times 4.60mm, Phenomenex, Torrance, CA) fitted with Agilent 7500a ICP-MS with a Babington nebulizer detector. The TOC in NOM was measured using Shimadzu Total Organic Analyser with a detection limit of 0.01 mg/L.

Results and Discussion

Kinetic of Desorption

This experiment was designed to describing the rates of desorption of arsenic from fresh and aged solids. The kinetic desorption of arsenic from fresh and aged sludge was investigated in pH range 6.5-10.5. Figure 3.1 shows the time dependent desorption of arsenic from fresh and aged sludge at pH 6.5, 9.0 and 10.5. It is clear that there is a significant difference in kinetic desorption behavior between the fresh and aged sludge. It is evident that fresh sludge exhibited only one kinetic regime and reached near-equilibrium in 30 hours.

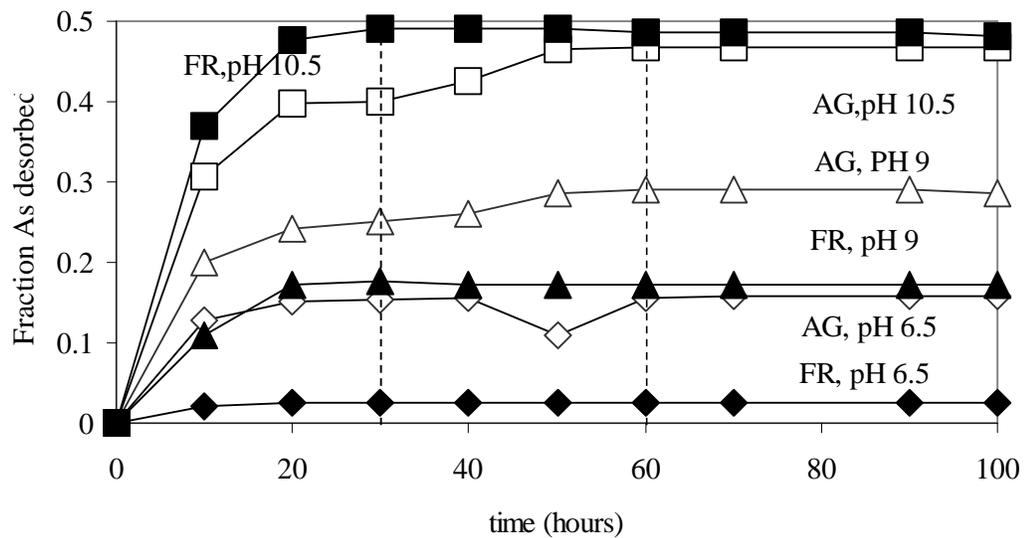


Figure 3.1: Kinetic desorption of arsenate from fresh sludge at pH 6.5, 9.0 and 10.5.

However, aged sludge seems to have exhibited two kinetic regimes, the fast regime (0-30 hrs) and the slow regime (30-60 hrs). The fast kinetic desorption of arsenic from aged sludge can be explained by the fact that the aging of fresh sludge results into a solid which is more structured, not totally crystalline (as revealed by XRD) but with less exposed iron surface area for arsenate binding. Consequently, in the aged sludge, a greater fraction of the arsenate occupies weak electrostatic binding sites and is more readily released into solution (Waychunas et al, 1993) and that could account for fast kinetic regime. The slower desorption kinetic regime observed from aged sludge (bigger particle size) could be a consequence of intra particle diffusion, mass transfer limitations, interfacial rates of desorption, or a combination of all mechanisms. (Ghosh et al, 2006c). Overall, it took 60 hours for aged sludge to reach equilibrium, which is twice the time required by the fresh sludge.

Modelling of Desorption Kinetics

In the absence of experimental data to elucidate desorption mechanism of arsenic from fresh and aged sludge, fitting experimental data to known desorption models is important because it provides clues to kinetic mechanisms which dominate desorption of arsenic. Two reaction rate equations were used to interpret the mechanism dictating As release from fresh and aged sludges. These kinetic models included the traditionally used Lagergren rate equation.

$$\ln (A_{s_e}-A_{s_t}) = \ln A_{s_e}-K t \dots\dots\dots(1)$$

Where A_{s_t} ($\mu\text{g/g}$) represents the mass of arsenic desorbed at time t (hr), A_{s_e} ($\mu\text{g/g}$) is mass of arsenic desorbed at equilibrium. K is the sorption rate constant. Testing of first order behavior was evaluated by plotting $\ln (1- A_{s_e}/ A_{s_t})$ against t . The results of lagergren simulation modeling are shown in figure 3.2 below.

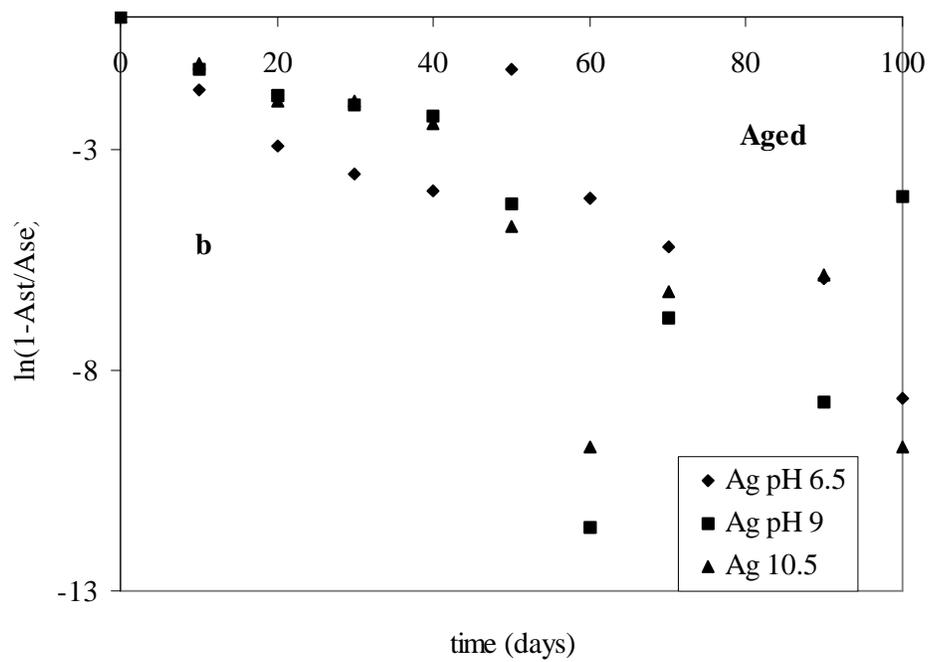
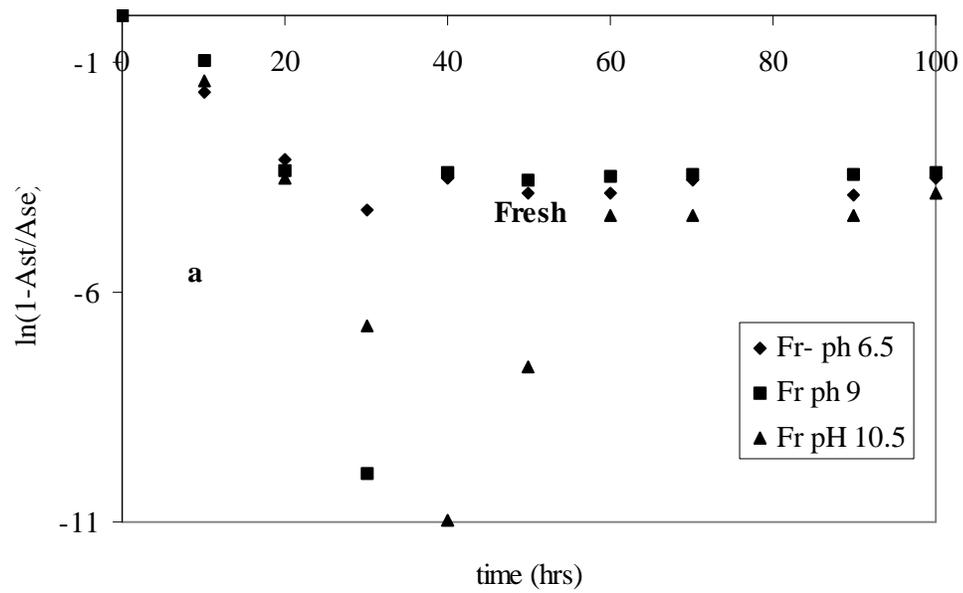


Figure 3.2. Plots of Langregan equation fitted to experimental data for arsenates desorption from fresh (a) and aged AFH (b) at pH ranges 6.5, 9, 10.5.

The empirical parabolic diffusion model as described by equation 2 below,

$$[1/t][A_{s_t}/A_{s_e}] = [4/\pi^{0.5}] [(D/r^2)^{0.5}] [1/t^{0.5}] - [D/r^{0.5}] \dots \dots \dots (2)$$

was used to evaluate whether diffusion controlled phenomenon in the aged and fresh sludge are rate limiting. In the diffusion parabolic model, r is the average radius of the respective AFH particles, D is the diffusion constant. A_{s_e} and A_{s_t} carry the same meaning as described in Lagregan equation above. The agreement between our experimental data and the parabolic diffusion law was by tested by plotting $[A_{s_t}/A_{s_e}] / t$ against $t^{-0.5}$ and the results are shown in figure 3.3b.

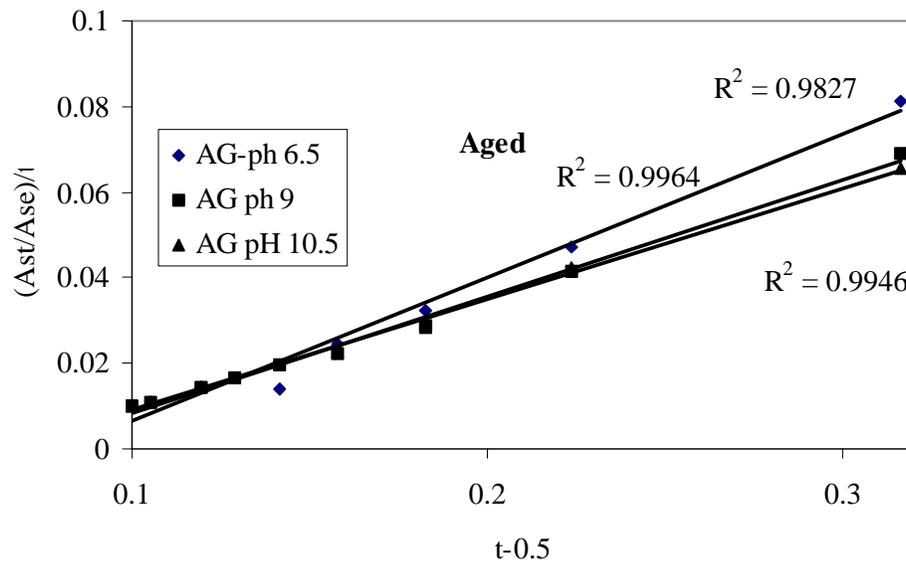
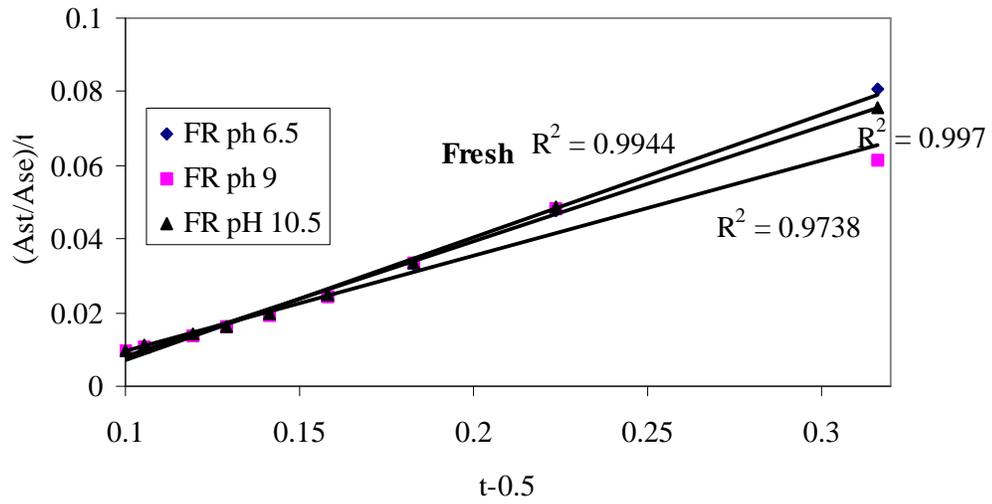


Figure 3.3 Plots showing parabolic diffusion equations fitted to experimental data for arsenate desorption from fresh and aged AFH at pH ranges 6.5, 9.0, 10.5.

Looking at the figure 3.2a, irrespective of the solution pH, fresh sludge approximated a linear relationship for the first 40 hrs. In that region, desorption of sludge approximated near first order kinetics behaviour. Linearity, however, wasn't all the way. Soon after 40 hrs, arsenic desorption deviated from first order kinetics. Interestingly, aged sludge (figure 3.2b), approximated first order kinetics in the first 30 hrs, followed by deviations from first order over a longer time periods. This trend is interestingly a similar behaviour exhibited by fresh sludge and noted above. However, over the longer periods of time (<30 hr), the aging sludge data approximated first order kinetics better than fresh sludge. This characteristic behaviour, has been previously observed by Seidel et al, 2005 who explained that the deviations from first order kinetics of this nature are often observed at longer periods of time and noted that changing slopes could be due to multiple first order desorption reactions or other reaction order reactions occurring due to different sites or mechanism of arsenic sorption on the fresh sludge. Irrespective of the solution of the pH, our experimental data generated from both fresh and aged sludge (figure 3.3) fitted the parabolic diffusion model with correlation coefficient being > 98%. This result is consistent with Raven et al, 1998 who tested different kinetic models and reported a good kinetic data fit of arsenate-ferrihydrate system with the parabolic model.

Justification of a good fit for parabolic model

It is well established that sorption of arsenic on amorphous iron oxhydroxides is faster (fuller et al, 1993a) than desorption rate (Seidel et al, 2005). The slow rate of arsenic desorption from amorphous iron oxhydroxides has been explained in terms of high

activation energy of adsorption resulting from the formation of inner sphere multidentate, binuclear surface complexes (Wachuyanas et al, 1993) or to slow diffusion out of the micropores (Cornell et al, 1996e). This could explain why our experimental data fit the diffusion parabolic model.

Even though aging the AFH can produce a more, structured, not totally crystalline but with less specific iron surface area for arsenate binding, its has also been proven and reported to stabilize a portion of arsenic initially loaded on the ferrihydrate into its crystalline phase (Kim et al, 2003; Ford, 2002a). Looking at our results, this seems to be the case and it is therefore not surprising that a portion of arsenic, which desorbs off the aged solid into solution, could have diffused out of the crystal matrix and this could explain why the desorption of arsenic from aged AFH was best described by the diffusion model.

Effect of pH on Desorption of arsenic

The pH of the leaching solution is one of the most important factors affecting the magnitude of arsenic leaching quantification of arsenate desorption at high pH is of particular significance in mature landfills where the pH ranges from 7.5 to 9.0, with an average value of approximately 8.2 (Hopper et al, 1998). It should be noted that the effect of pH on arsenic desorption has been previously discussed and noted in details in chapter 2. To avoid duplication of material, this section only summarizes the key findings of pH effect study. These include:

- i) The fraction of arsenic extracted is appreciably higher than the fraction of iron extracted.
- ii) Iron is comparatively very stable in the aged sludge while at the same time arsenic becomes easier to extract. At pH 10.5, aged sludge leached into solution a mass fraction under 1% of total Fe in the system whereas the fresh sludge leached 10-fold higher mass fraction.
- iii) Despite the significant difference in mass fraction of Fe leached from the two solids, there was minimal difference in mass fraction of leached As from both fresh and aged sludges i.e. just under 50% of the total compositional As.
- iv) In the aged solid, since the leached iron mass fraction was very low, the contribution of surface dissolution to total Fe and As leachability was minimal. These results suggest that the leaching of arsenic in this case associated with desorption rather than co-dissolution.
- v) At low pHs (≤ 8), arsenic has a higher affinity for fresh sludge.
- vi) pH 8.3, is the cross-over point for the partition coefficient of fresh and aged sludge (Figure 2.4) and it coincides with the pH of zero point charge (ZPC) of pure ferrihydrite and amorphous $\text{Fe}(\text{OH})_3$ (Stumm et al, 1992a; Cornell et al, 1996e; Klaus et al, 1998; Jain et al, 2000).
- vii) Since the XRD analysis revealed that the sludge remains mostly amorphous even after aging, it is not surprising that both fresh and aged sludge would have the same ZPC. The fact that both partition coefficients are the same at the ZPC suggests that the difference in arsenic affinity for both sludges could be related mostly to electrostatic sorption.

- viii) The aged sludge has less available adsorption sites for arsenic, which accounts for the lower affinity at low pHs for which electrostatic effects become more important, but higher affinity at high pHs, for which the density of negative charges on the surface should be lower for the aged sludge.

Overall, from the disposal point of view, our results indicate that, that neutrality should be an important consideration for the long-term storage and disposal of these materials.

Competitive Desorption

Phosphate addition

Batch equilibrium trials were conducted to evaluate the effect phosphate competition on arsenic retention of fresh and aged AFH sludges. Since phosphate is abundantly found in relatively high amounts in landfill leachates ~300 ppm (table 3.1,) it is expected to compete with arsenic for sorption sites on fresh and aged sludge. The trials included the range of phosphate concentrations typical of landfill leachates so as to quantify the desorption behavior that would be expected due to phosphate competition for both aged and fresh AFH residuals when co- disposed in MSW landfills.

Overall, Irrespective of the solution pH, phosphate extracted considerably more arsenic than any other ions. Our results show that the percentage of sorbed arsenic displaced by phosphate from sorption sites on either sludge was influenced by

phosphate concentration. For instance, at pH 7, as the phosphate concentration increased from 25 – 250 mg/L, a sharp increase in the fraction of arsenic extracted from fresh sludge was observed (figure 3.4). This observation is not surprising since phosphate has been implicated to compete with arsenic for sites (Jackson et al, 2000).

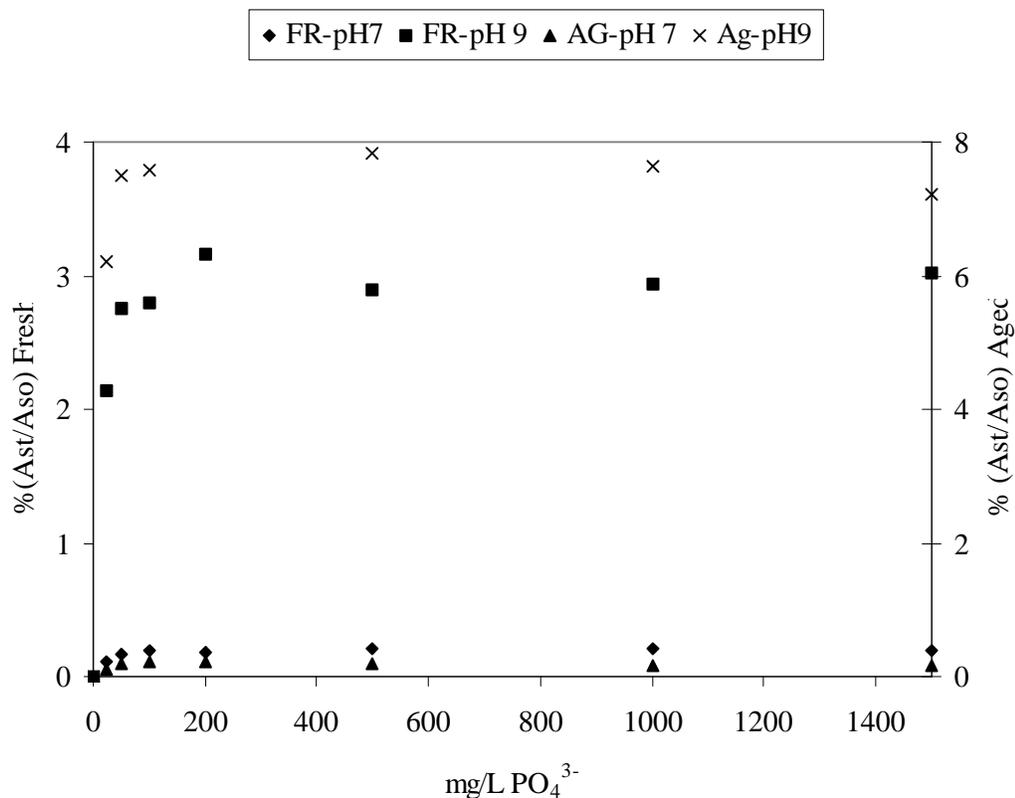


Figure 3.4: Fractional arsenic desorption from fresh and aged AFH as a function of PO_4^{3-} concentration. Both fresh and aged AFH were synthesised at pH 7 and equilibrated pH 7 and 9.

For phosphate concentrations above 500 mg/L, the differences in the fraction of desorbed arsenic with increasing phosphate added concentrations were not significant. This suggests that for a given sludge, not all arsenate sites can be exchanged by phosphate competing ion.

At a phosphate a concentration 200 mg/L when desorption was maximum, the fraction of arsenic extracted from either sludges at pH 9 was about 6 times the amount extracted from their respective parallel batches at pH 7. This could be due to the combined additive effect of pH and phosphate. It was possible to quantify the contribution of phosphate alone to overall desorption at a fixed pH by calculating the quantity using this formula below:

$$\text{Competitive phosphate Effect} = [\% \text{ desorbed As with phosphate added}] - [\% \text{ Desorbed As without phosphate added}].$$

Table 3.2 showing the contribution of phosphate (only) addition to the overall mass fraction of arsenic desorbed at two pHs 7 and 9 for both fresh and aged sludges.

Anion PO ₄ ³⁻ mg/l	Fresh		Aged	
	pH 7	pH 9	pH7	pH 9
0	0.0000	0.0000	0.0000	0.0000
25	0.0009	0.0005	0.0154	0.0008
50	0.0013	0.0007	0.0162	0.0059
100	0.0013	0.0008	0.0166	0.0062
200	0.0015	0.0009	0.0164	0.0081
500	0.0015	0.0013	0.0161	0.0072
1000	0.0015	0.0013	0.0161	0.0064
1500	0.0015	0.0013	0.0160	0.0048

The results of this calculation and presented in the table above proved that the contribution of pH effect to overall desorption was greater than the contribution from phosphate added. At 200 mg/L the effect of phosphate alone at pH 7 was a factor of two higher than at pH 9. The fact that there is minimum difference in the fraction of desorbed arsenic at pH 7 and 9 is not surprising and it confirms that irrespective of the

solution pH, both fresh and aged solids have a specific number of sites, which can be exchanged by the phosphate. This result is qualitatively consistent with Meng et al, 2002c who by determining binding affinities for iron hydroxides using equilibrium concentrations and surface site concentrations showed As(V) has a binding affinity which is 7 times greater than that for phosphate. Since arsenic was already bound to AFH prior to desorption, it is therefore not surprising that overall, phosphate only desorbed a relatively small fraction of total arsenic (less than 2%) from the aged solid.

Table 3.2 shows that for a given sludge type, the fraction of desorbed arsenic by phosphate was greater at pH 9 than pH 7 by factor of above 6 and that the absolute release of arsenic at a fixed pH was higher from aged sludge than fresh sludge. For example, irrespective of the solution pH and with no phosphate added, the fraction of arsenic released was over 7 X greater in aged sludge than fresh sludge. This clearly indicates that aging had a more aging effect on arsenic release from aged sludge, which leads to detachment of arsenic.

NOM Concentration

Typically, the NOM concentration in landfills varies widely and ranges from 75 – 40,000 mg/L. Therefore, a range of NOM concentrations used in this study consequently, for this work NOM concentrations used represent a wide range of concentrations found in a landfill.

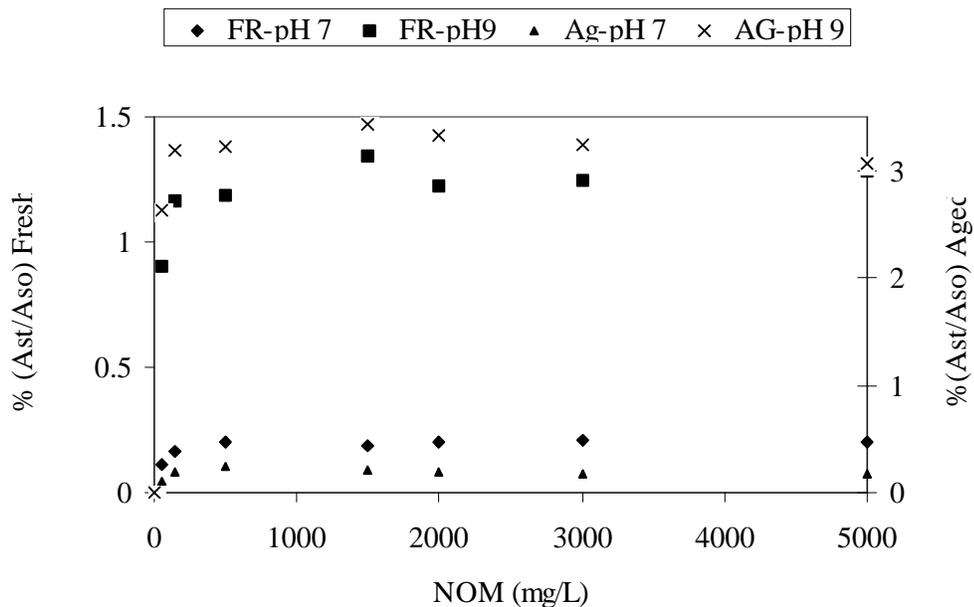


Figure 3.5 Fractional arsenic desorption from fresh and aged AFH as a function of NOM concentration. Both fresh and aged AFH were synthesised at pH 7 and equilibrated pH 7 and 9.

For both fresh and aged sludges, an impact of increasing NOM concentrations on arsenic desorption was only observed for concentrations below 1500-mg/L beyond which concentration, there was minimum effect. NOM extracted a greater % of arsenic than any other ion used in this study.

The effectiveness of NOM as an extractant is dependent on solution pH and the type of sludge used. Referring to pH dependence results documented in figure chapter 2, at higher pH>7, the fraction of arsenic extracted from aged sludge was appreciably higher than the fraction of iron extracted. Therefore, in the aged solid, iron is comparatively very stable while at the same time arsenic becomes easier to extract. Its not therefore surprising that at pH 9, the extractable fraction of arsenic is 3X higher for aged than fresh sludge. These results suggest that the leaching of arsenic from

aged sludge in this case was associated with desorption rather than co-dissolution. However, the properties of the solids are not the only mechanism, which released arsenic in solution. For instance, after subtracting out the pH effect, at NOM concentration of 1500 mg/L, maximum fraction of arsenic was extracted from fresh sludge was over 10X higher at pH 9 than pH 7 whereas the maximum fraction of arsenic extracted from aged sludge was just slightly higher at pH 9 than pH 7 (figure 3.5). Also, the absolute release of arsenic at a fixed pH was higher from aged sludge than fresh sludge.

Possible explanations to this difference lies in the fact that NOM has been found to impact desorption of arsenic through various mechanism. For instance, high desorption from aged solid at pH 9 could also been caused by either NOM competing with arsenate for surface sites (park, 1990) or NOM acting as a soluble partitioning agent to bind the arsenic and keep it in solution (Stumm et al, 1996b). Therefore, the net observed high leachability at pH 9 might be a result of both NOM effect and the solid properties.

Ionic Strength

The effects of ionic strength on As (V) desorption onto fresh and aged AFH was studied by varying the concentration of equimolar CaSO₄ and NaCl solution at pH 7.0 and 9.

Figure 3.6 shows that both the fresh and aged sludges showed increased desorption of arsenic as the ionic strength increased up to about 0.03 M and showed no further increase with greater concentrations of ionic strength.

For example, fresh sludge at pH 7, about a four-fold increase in fractional arsenic desorbed was observed between the lowest IS (0.0045 M) and highest (0.03M) whereas a six-fold factor was observed for aged sludge at the same pH. The fractional increase in desorbed As was a factor of 3 X higher between the lowest and the highest ionic strength value for both fresh and aged sludges at pH 9. The higher desorption observed at high ionic strength was attributable to changes in the electrostatic forces out from the AFH surface, rather than specific (chemical) binding competition on the surface of the AFH. This explanation holds because variation in ionic strength variation was accomplished by addition of equimolar concentrations of NaCl and CaSO₄, so that only nonspecific binding electrolytes were added to solution.

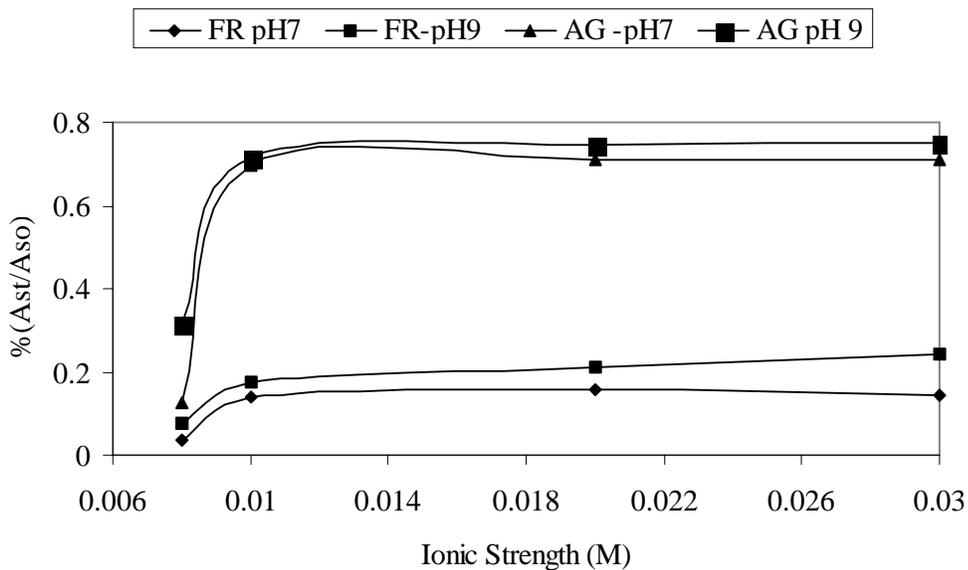


Figure 3.6: Fractional arsenic desorption from fresh and aged AFH as a function of Ionic Strength of the leachant solution. Both fresh and aged AFH were synthesised at pH 7 and equilibrated pH 7 and 9.

As stated by Ramesh et al, 2007, studying the influence of ionic strength is a simple approach to distinguish between the inner-sphere and outer-sphere surface complexes when direct evidence from microscopic data is absent. Therefore, the contrasting behavior of the fresh and aged AFH therefore indicates the differences in primarily electrostatic forces than bind a larger fraction of the arsenic is associated with the fresh AFH than aged AFH. According to the Hayes et al, 1997, if the adsorption is not affected by the variations of the ionic strength, then an inner-sphere surface complexation should form; whereas the presence of outer-sphere complexes is indicated by changes in sorption with changing ionic strength. Based on the theory and consistent with previous researchers who have reported similar behaviour on hydrous oxides (Cox et al, 1994), and Goethite (Manning et al, 1998), it is therefore possible that the adsorbed As(V) on fresh sludge may have take place by the

formation of inner sphere bidentate surface complexation whereas a larger % As(V) on the aged solid was formed by outer-sphere complexation and therefore easily desorbed.

Sulfate Concentration

Batch equilibrium trials were conducted to evaluate the effect sulfate competition on arsenic retention of fresh and aged AFH sludges. Since sulfate is abundantly found in relatively high amounts in landfill leachates ~5000 ppm (table 1,) it is expected to compete with arsenic for sorption sites on fresh and aged sludge. The trials included the range of sulfate concentrations typical of landfill leachates (table 3.1) so as to quantify the desorption behavior that would be expected due to sulfate competition for both aged and fresh AFH residuals when co- disposed in MSW landfills.

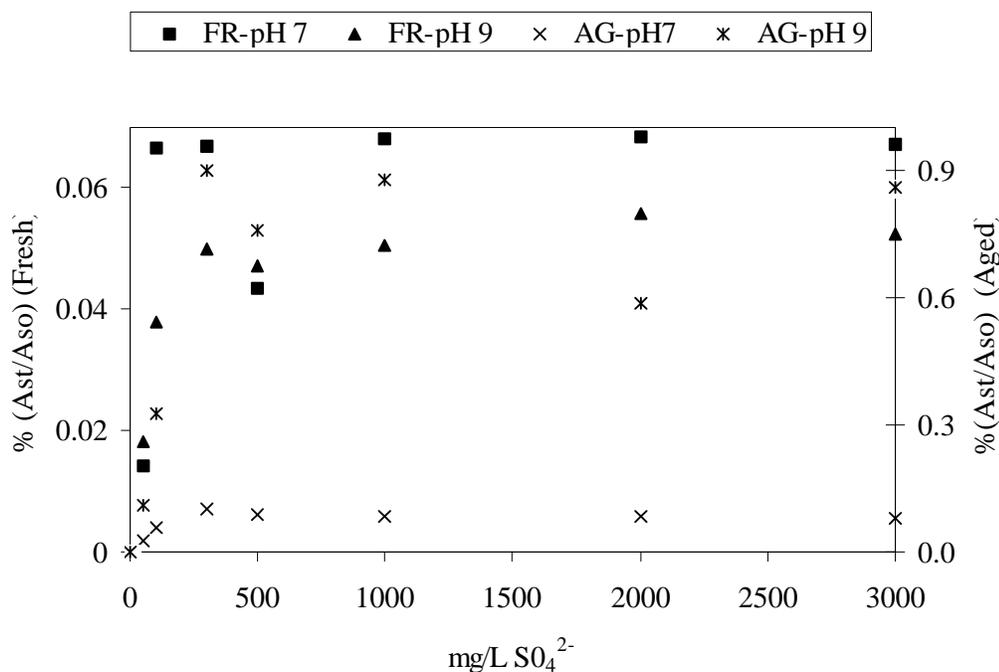


Figure 3.7 Fractional arsenic desorption from fresh and aged AFH as a function of sulfate concentration. Both fresh and aged AFH were synthesised at pH 7 and equilibrated pH 7 and 9.

Referring to figure 3.7, it is evident that the fraction of arsenic extracted from aged sludge at pH 9 was over 20 times that extracted at pH 7. However, after subtracting out the fraction of arsenic desorbed due to pH effect alone, that sulfate extracted twice the mass fraction from fresh sludge at pH 7 than at pH 9 whereas the opposite was true for the aged sludge (table 1, appendix A). Noticeably, in the fresh batch, the amount of sulfate present in solution decreased at pH 7 whereas a negligible amount of sulfate was removed from the pH 9 batches. Clearly, this shows that in the fresh batch, as the pH increased, the increased negative charge resulted in increased {surface/OH⁻/arsenate/SO₄²⁻} repulsions, resulting in decreased arsenic or sulfate partitioning on fresh solid. Therefore sulfate alone at pH 9 had least effect on arsenic desorption from the fresh solid. In the aged solid, since it has been confirmed that at high pH, aged sludge has been found to have less available adsorption sites for arsenic binding, the density of negative charges on the surface is therefore appreciably higher for the aged sludge than for fresh sludge. Consequently, in the aged solid, electrostatic effects become less important at higher pH than in the fresh sludge.

Overall, for fresh and aged sludges at pH 7, less than a 0.1% change in the fractional arsenic in solution over a sulfate range from 0 to 3000 ppm was observed indicating that there is little effect of sulfate addition to total desorption. For example, at the highest sulfate loading of 3000 mg/L, only about 0.08% arsenic from fresh sludge desorbed into solution. Again, this result is consistent with our previous work (Ghosh, 2005) on GFH where we showed that at the highest sulfate loading (5000 mg/L), only 0.1% arsenic was desorbed. Also other researchers have demonstrated the negligible influence of sulfate addition on arsenic adsorption onto ferrihydrite precipitates

(Meng et al, 2000a). However, no known published data has attempted to quantify the effect of anions on aged sludge and therefore, direct comparison of our observed data on aged sludge was not possible.

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CHAPTER 4

SIMULATION OF LONG TERM STABILITY OF AMORPHOUS FERRIC
HYDROXIDES SLUDGES GENERATED FROM ARSENIC BRINE
TREATMENT PROCESSES UNDER LANDFILL CONDITIONS.

Abstract

Using Environmental Protection Agency occurrence and concentration data, it is estimated that about 8 million pounds of arsenic-bearing residuals (ABSR) will be generated annually in the United States when full compliance with the new 10 $\mu\text{g/L}$ arsenic in drinking water standard is realized. Among these ABSR, are high surface area, cost effective amorphous ferric hydroxides (AFH) with variable water/Fe/As compositional ratios. Effective management of disposal of ABSR requires both a full characterization of the materials and an understanding of the environment in which the disposal will occur. Currently, there are different testing methods to evaluate the stability of ABSR, the principal of which is the EPA Toxicity Characteristics Leaching Procedure (TCLP). These tests suggest non-hazardous landfill disposal of most residuals will not pose an unacceptable environmental hazard. However, our ongoing work shows these testing methods may significantly underestimate the degree and mechanism of arsenic mobilization from the residuals, because critical physical and chemical dissimilarities exist between the test and landfill conditions. Some of the key landfill characteristics that are not simulated by the TCLP include: alkaline pH, organic characteristics, competing ions like phosphate, reducing environments, long residence times and anaerobic microbial activities. These landfill characteristics can promote both changes in redox potentials and also biochemical

processes which can potentially cause transformation of AFH resulting in the liberation of arsenic and iron. More so, landfill disposal involves liquid and solid residence times on the order of months and decades whereas leaching tests are completed in two days or less.

This chapter describes the work undertaken on fresh AFH to predict arsenic and iron release under simulated landfill disposal conditions.

Introduction

According to Environmental Protection Agency estimates, the implementation of the recently enacted arsenic drinking water standard, will lead to generation of over 8 million pounds of Arsenic Bearing Solid Residuals (ABSR) every year containing over 30,000 pounds of arsenic. Among these ABSR are ferrihydrites, which are a group of poorly crystalline, low solubility, high surface area iron oxide minerals, with somewhat variable composition in terms of water-OH/Fe ratio (Cornwell et al, 2003, Schwertmann et al, 2004c). Amorphous ferric hydroxide (AFH) is a term commonly used to describe mixtures of various ferrihydrite forms. It occurs naturally in soils and it is commonly generated as a chemical sludge from removal of contaminants such as arsenic in water/waste water treatment operations.

Typically, sludge generated from water treatment processes such as ion exchange (IX) and membrane filtration (MF) yields liquid residual streams (brine) that require treatment. The liquid residuals stream must be either treated on-site or discharged to a sanitary sewer (USEPA, 2001b). The recommended process treatment of these residuals 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 followed by pH neutralization. The type, physicochemical condition and composition of the resultant sludge depend on the type of treatment and the composition of the source water. Sludges resulting from IX treatment could have a pH ranging from 7-12, depending on precipitation pH. On the other hand, sludges generated from membrane filtration are usually at neutral pH. Generally, the removal of arsenic by co-precipitation is effective for small quantities of highly concentrated liquid arsenic waste.

Sludges containing arsenic typically pass the TCLP and therefore may be disposed in mixed – solid waste landfills. However, the TCLP was designed to simulate codisposal with municipal (putrescible) waste using acetic acid as organic promoter of dissolution (Janusa et al, 1998; Hardaway et al, 1998; Meng et al, 2001b). It is known that conditions used in the TCLP are very different from typical conditions prevalent in a landfill. High pH, a reducing environment, long residence time, mineralogical aging and anaerobic microbial activity are landfill characteristics not simulated by the TCLP. Currently, there is no legal, long-term definitive and predictive test, which simulates and predicts leachability of ABSRs under reducing, microbial rich complex landfill environments over long periods of time.

The biggest drawback of AFHs to landfill disposal is their sensitivity to redox variations. AFH are therefore considered as (bio)available Fe(III) (hydr)oxide for dissimilatory iron reducing bacteria (Lovely et al, 1986). Microbially mediated reduction can have an important effect on the speciation of both arsenic (Ahmann et al, 1997; Newman et al, 1998; Wilke et al, 1998; Christopher et al, 2006; Gihring et

al, 2001; Thomas et al, 2004) as well as the iron to which arsenic binds (Ponnampurna et al, 1996; Puling et al, 2003; Hansel et al, 2003a; Ghosh et al, (2004a, 2006b); Van et al, 2004; Islam et al, 2005a). Consequently, the changes in the landfill redox potentials catalyzed by biochemical processes potentially can cause a transformation of AFH resulting in the liberation (release of sorbed ions) or fixation (reductive immobilization via redox active metabolites) of arsenic (Hopkins et al, 1998; Colleen et al, 2004a).

Such changes also initiate biogeochemical processes like biomineralization of Fe, which has been demonstrated to result in formation of more crystalline and dehydrated secondary minerals such as magnetite [α -Fe₃O₄], lepidocrocite (δ -FeOOH) and goethite [α -FeO(OH)] from less crystalline ABSR precursors under reductive environments. The formation of these crystalline minerals has been a subject of several investigations (Shawng et al, 2002; Hansell et al, 2003a; Jang et al, 2003; Fredickson et al, 2003; Collen et al, (2004a, 2005b)). These biominerals have different and lesser sorptive capacities of arsenic compared to the parent sludge.

The differences in sorptive capacities of the different mineral phases for arsenic is supported by evidence involving extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy, which indicate that As (III) and As (V) species are adsorbed on the iron oxy-hydroxide substrate through formation of inner sphere complexes (Waychunas et al, 1993; Manning et al, 1998; Farquhar et al, 2002; Sherman at al; 2003) between the surface and the arsenic oxy-anion. In formation of biominerals, the strength, the number of adsorptive sites and

the reactivity of the surface might change considerably, since this process involves changes in the physicochemical state of the surface. This may reduce the adsorptive capacity of the iron oxides for arsenic and potentially increases extractability of arsenic.

There are conflicting reports on effects of biomineralization on the fate of arsenic mobility. Some authors report that reduction of As(V) bearing Fe(III) oxides results in mobilization of arsenic (Ghosh et al, (2004a, 2006b), Van et al, 2004)) whereas others argue that in situ formation of biogenic Fe(II) minerals can act as sinks for As (Islam et al, 2005a). In view of this, the long-term contributions of pathways like biomineralization to total leachability of As is still poorly understood.

Another important parameter, which has been found to significantly affect fate and transport of arsenic that is not correctly addressed by the conventional batch leaching trials, is the role of colloids. It is thought that landfill disequilibria resulting from in situ-redox reaction shifts may directly or indirectly generate organic/inorganic colloids. Some researchers have demonstrated that the Fe redox cycle affects colloid generation through the stoichiometry of oxidation/reduction (Ponnamperuma et al, 1986) as well as by consuming high surface area ferric solids and producing catalytically reactive ferrous species (Hansel et al, 2003a). These processes may enhance dissolution of AFH, reduce surface area for As attachment and negatively impact the long term stability of the already thermodynamically unstable AFH material. Some portion of the arsenic contained in these AFH may be transported on

colloids and ultimately end up in the landfill leachate or the groundwater beneath the landfill.

In lieu of all the above, there is an on-going controversy about the long-term stability of Fe based arsenic sorbents, because of strong disagreements between different short term batch laboratory study outcomes and long term landfill column simulation observations. For instance, our previously published work on GFH showed that iron arsenates are unstable under reducing conditions and that they would eventually decompose, releasing soluble arsenic Ghosh et al, (2004a, 2006b). On the other hand, a number of experimental studies have shown that, under proper storage conditions, high-iron (Fe/As molar ratio >3) arsenate compounds are stable for at least several years (Kontopoulos et al, 1988; Harris et al, (1989a, 1993b); Kraus et al, 1989; Vircikova et al, 1998).

Besides the controversy, to the author's knowledge, the long-term leachability of sludge obtained from brine treatment process solutions has not been previously observed in an actual disposal sites. Therefore, it is apparent that long-term stabilities of arsenic bearing AFH generated from brine treatment is undoubtedly unknown and needs to be tested to evaluate and determine whether special precautions are necessary for its final disposal.

This work focuses on long term leaching assessment of sludge generated from brine treatment, under simulated landfill conditions. The goal is to simulate landfill leachate characteristic, which include high pH, high organic biodegradable substrates, diverse

population of microorganisms including methanogens, fermentative bacteria, and sulfate and iron reducers etc. We use a column experiment, which allowed the landfill simulation of microbially mediated, reductive leaching of Fe and subsequent release of As from ferric hydroxide. The experiment was performed under saturated flow conditions, which simulated saturation conditions in a typical landfill as leachate collects and flows through it.

We hypothesized that simulation of a combined effect of microbial activity, shifts in both pH and ORP, may offset colloidal formation and/or secondary pathways, as those found in landfills, might negatively impact long-term stability of arsenic bearing AFH.

Our primary objectives is to examine the effectiveness of high loading Fe/As = 5.7:1 sludge generated from brine treatment, as a long term storage agent by examining and measuring leaching from a simulated landfill column. We provide data of the overall leachability of As and Fe which occur from brine sludge when most important competing physical and microbial processes typical of landfills are present. The findings have relevance to other subsurface environments with similar reducing conditions.

Experimental Procedures and Methods

Sludge Preparation by Co-precipitation

The procedure employed to make the 5.7:1 sludge is detailed in what follows. Sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, KR grade Aldrich Sigma) was used as the arsenic salt.

A 0.169 M As solution was prepared by dissolving 12.64 g of sodium arsenate heptahydrate in 1 L Milli-QTM water (Water Systems by Millipore). A 0.964 M Fe solution was prepared by dissolving 259.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1 L Milli-QTM water. The resultant solution was rapidly stirred at 100 RPM. Two solutions were mixed to obtain 5.7:1 Fe:As ratio. The final mixture containing precipitated sludge was allowed to equilibrate for 1 hr and the solution adjusted to pH 7 using 10 M NaOH solution with vigorous stirring. The mixture was buffered using 0.001 M NaHCO_3 . The sludge mixture was then shaken on a reciprocating shaker table (Orbit, reciprocating speed of 30 rpm) for 30 minutes to ensure homogenization without causing the break up of the flocculated particles. The batch was then allowed to settle and equilibrate for 14 days at 25°C to ensure complete sorption of As and complete hydrolysis of Fe in solution. During the sorption-hydrolysis period, fluctuations in $\text{pH} \pm 0.5$ were observed. These fluctuations were mitigated by periodic adjustment with 0.1 M HCl or 0.1 M NaOH.

A liquid sample was withdrawn for analysis to determine the equilibrium concentration of As and Fe. Duplicate aliquot samples, 100 mL each, were withdrawn from the batch and placed in 250 mL Erlenmeyer flasks. Free water was decanted off. The pH in each flask was set to a predetermined value, (which we will call the synthesis pH), ranging from 7 through 12 and allowed to equilibrate for 2 days. Every 5 hours, the fluctuations in synthesis pH were mitigated by periodic adjustment with

0.1 M HCl or 0.1 M NaOH. Solid-liquid separation of each batch was achieved by vacuum filtration in a 0.45 μm pore size cellulose acetate membrane filter to achieve 50-60% wt/wt water content in the separated solids, which would be suitable for sludge disposed in a landfill. Using this sludge as a parent arsenic host, long-term column leachability of arsenic and iron was simulated.

Biotic Column Design, Composition, Flow Conditions and Operation

This experiment was aimed at simulating and predicting the long-term effects of reducing conditions on leaching of arsenic from AFH using unadapted, natural microbial populations, under saturated flow conditions. It was expected that the simulated landfill column test would provide the most important results in terms of managing AFH residuals.

The column was fabricated from PVC cylinder with dimensions outer diameter (OD) 15.9 cm and height 76.2 cm as shown in figure 4.1. It was then fitted with 3 sampling ports at every 20 cm along the column depth so as to provide varying sampling points within the column. The bottom end of the simulator was fitted with a mesh (opening 2.5 mm) to act as a filter and to retain porous material during operation. The bottom end of the column was then tightly sealed with flat PVC plates 30 X 30 X 2 cm fitted with o-rings to provide leak proof joints.

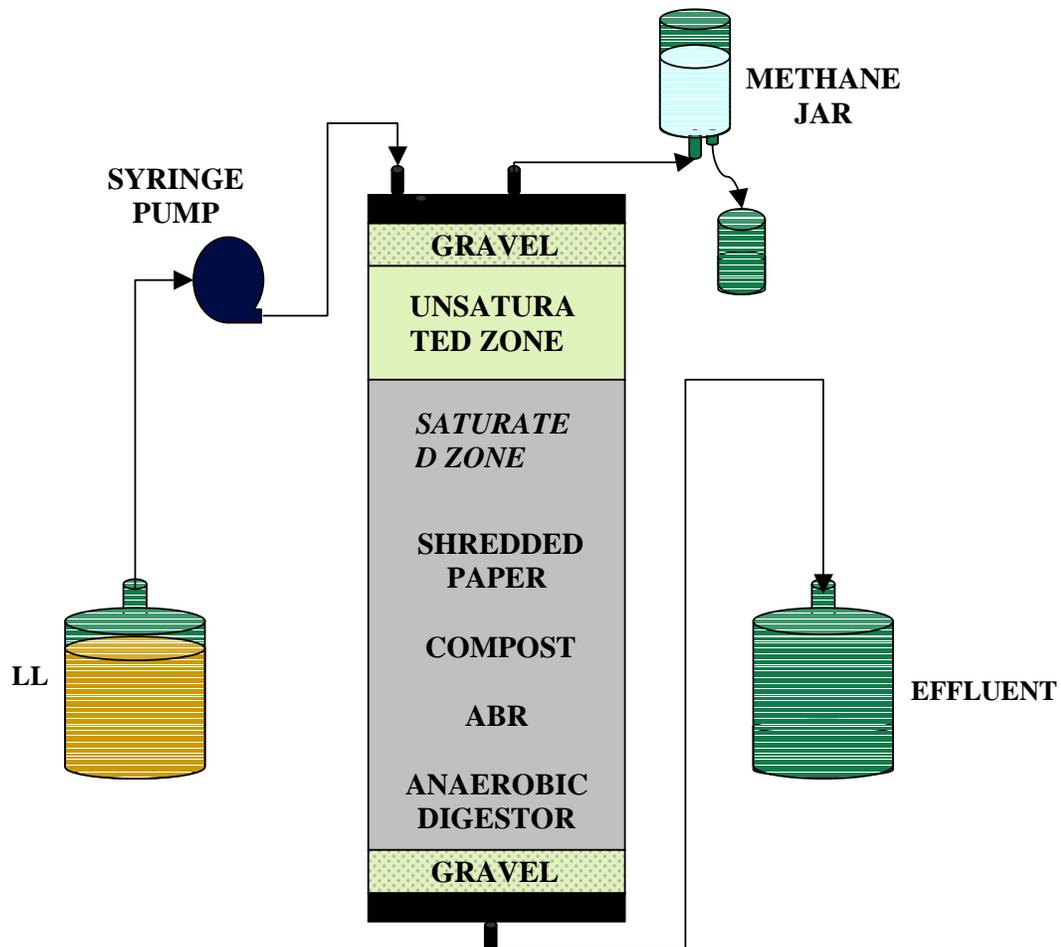


Figure 4.1: Schematic of column bio leaching reactor. The active bed is located between the unsaturated zone and bottom level gravel.

The column was loaded with the following materials 0.3 -1 cm size gravel material (5 cm from top and 3 cm from bottom), 1.6 kg of Compost, (a mixture of dry leaves, soil, vegetables, and organic matter). Shredded paper (0.5 kg) and anaerobic digester sludge (4L) that was obtained from Ina Road Wastewater treatment plant, Tucson, Arizona. This was used as microbial inoculum. A sample of this anaerobic sludge was characterized for physical characteristics like pH etc. Chemical composition of both

anaerobic sludge and compost were evaluated by separately digesting 1 g of material in 100 mL of concentrated nitric acid. The results obtained from both samples are presented in table 4.1 below.

Table 4.1. Key Characteristics of compost and anaerobic digester sludge in column

Parameter space	Anaerobic Digester Sludge	Compost
pH	7.4	NA
ORP (mV)	-320	NA
(%)Total water Content (g water/g dry weight)	78	88
Total Alkalinity (mg/L)	5820	NA
Fe (mg/g dry wt)	0.28	2.1
Cu (mg/g dry wt)	0.19	0.06
Ni (mg/g dry wt)	0.09	0.02
Al (mg/g dry wt)	ND	0.93
As (mg/g dry wt)	ND	ND

NA- Not applicable, ND - Non Detect

In addition to the anaerobic digester sludge inoculums and compost, the column was loaded with sludge 500 g of fresh (Fe/As= 5.7:1) that translates to 5 g Fe/L of active bed (defined as the volume between the two gravel layers mentioned above). To enhance anaerobic conditions in the reactor, the column was then flushed 100 times with nitrogen gas. Before delivering landfill leachate to the column, the top part of the column was then sealed with PVC plates of same dimensions as the bottom plates previously described above.

Landfill leachate Collection and Preservation

Actual leachate was then collected from Los Reales MSW Landfill, in Tucson AZ and was used as leaching fluid. Leachate sampling from the cell was conducted according to the ADEQ standard operating procedures using a collection pump and a dedicated Teflon bailer. Typically, over the course of the entire column run, 20 L/week of landfill leachate were collected per sampling event and stored in dark plastic collection jar (20L). The sampling frequency was 2 times a month. After collection, to minimize alteration of its original hydrogeochemical characteristics, the LL was purged with nitrogen, kept at 4° C and used within 1 day of collection. The landfill leachate was fully characterized for composition and physical chemical properties prior to delivery into the column. Table 4.2 shows average properties of landfills leachates for comparison purposes. Only landfill leachate Los Reales landfill leachate was used in this work.

Table 4.2. Average Physicochemical Characteristics of Los Reales landfill leachate compared with typical landfill ranges.

Parameter space	Los Reales Landfill	Typical landfill range
pH	7.16	3.7-8.9*
ORP (mV)	-165	NR
Alkalinity (mg/L HCO_3^-)	4219	34- 15050*
TOC (mg/L)	8016	76-40000*
Fe (mg/L)	3.7	10-1000**
As (mg/L)	0.065	0.37-26.7 ***
SO_4^{2-} (mg/L)	634	10-1000**
PO_4^{3-} (mg/L)	267	105- 4900*
SiO_4^{2-} (mg/L)	0.17	0.11- 234*
NO_3^- (mg/L)	6.3	5.1-51*

- * Bagchi ,1994 is a compilation of municipal waste leachate data.
- ** Lin et al ,1986a compilation of municipal waste leachate data
- *** Ela et al , 2006. Disposal of Arsenic Bearing Water treatment Residuals:
- NR- Not reported

A syringe pump (Dayton, Model 2Z798B) was used to deliver the fresh Landfill Leachate (LL) to the column at 0.44 mL /min, operated in a down flow mode. This flow rate was estimated from the observed Virginia leachate generation rates (Gillispie et al, 2003). PTFE tubes (inner diameter 1mm) were then used to transport landfill leachate from the influent reservoir (10L) into the column and also to deliver the column effluent into the effluent collection system (20L).

Once the landfill leachate was delivered to the column, the leachate level was maintained at 62 cm from the bottom of the column and the saturated bed volume was 11 L out of a total volume of 15 L. During the column run, off gases were collected in an inverted glass methane collection jar filled with a 3% (w/v) NaOH solution to absorb the carbon dioxide. The leachate samples were also periodically collected from the effluent tube located at the bottom of the column (figure 4.1) as well as from the sampling side ports. Total Fe and As in the liquid samples were determined by digestion of a 20 mL sample using 70% by volume HNO₃ in a CEM Inc. microwave digester. The dissolved fraction was determined by filtering the sample through a 0.45µm pore size cellulose acetate membrane filter prior to digesting it with 70% by volume HNO₃ as described above.

Instrumentation and Sample Analysis

In all cases, the liquid column effluent samples were analyzed for total and dissolved arsenic / iron concentration by ICPMS, which consists of an Agilent 1100 HPLC (Agilent Technologies, Inc) with a reverse-phase C 18 column (Prodigy 3u ODS 150* 4.60mm, Phenomenex, Torrance, CA). The system is fitted with Agilent 7500a ICP-MS with a Babington nebulizer detector. Speciation of As was measured by ICPMS and that of Fe by Hitachi U-2000 Spectrophotometer, using hollow cathode lamps of Fe at a wavelength of 510 nm. Alkalinity was determined by acid titration with 1 N HCl solution. Methane gas was then analysed by a Gas Chromatograph (Hewlett Packard, Series 5790A). Orion Model 720 meter and Cole Palmer's Platinum Single-Junction Electrode measured changes in pH and ORP respectively. TOC was measured using a Shimadzu. Total Organic Carbon Analyzer. Sulfate, nitrate and

phosphate were analyzed using Dionex DX 500 Ion Chromatography System whose detection limit for both sulfate and phosphate is 10 $\mu\text{g/L}$.

Results

Landfill leachate supports a diverse consortium of microorganisms as well as organic and inorganic matter, all which can support anoxic conditions in reduced environments. SEM (Figure 4.2) analysis provided images of the complex solid network of the matrix found in the landfill leachate.

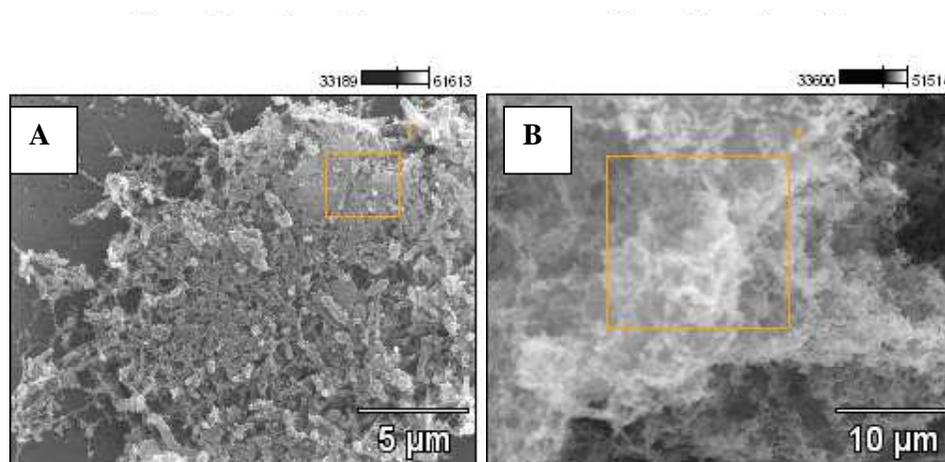


Figure 4.2 SEM images of solid cake left on a filter paper after sequentially filtering landfill leachate through a 0.45 μm (A) filter and through 0.22 μm filter (B).

This complex network shown in figure 4.2 could be a mixture of organic/inorganic material present in the leachate. These materials could facilitate transport of As in landfills.

Evidence of anoxic conditions present in the bioreactor, resulting from dissimilatory reduction of arsenic and iron reduction was confirmed by measuring ORP as well as the appearance of Fe (II) and As (III) concentrations in the dissolved phases. The fraction of As associated with colloids was determined by quantifying the difference between the totals and dissolved concentrations. Since in any give regime, the composition and characteristics of the feed solution were well known and remained averagely constant (table 4.2), therefore, the observed compositional and physicochemical differences in the effluent leachate over the duration of leaching primarily reflected changing processes within the bioreactor. The results are presented in 4 different kinetic regimes, which reflect changing observed patterns within the biosimulator over the course of the column run.

Regime I. This is a period between 0 - 63 days of the column run. This period coincides with initiation of dissimilatory Fe (III) reduction. Figure 4.3. shows that in the first 63 days, the observed pH of the column effluent leachate initially decreases from 8.4 to 7.1 whereas the ORP correspondingly decreased from +256 mV to - 40 mV.

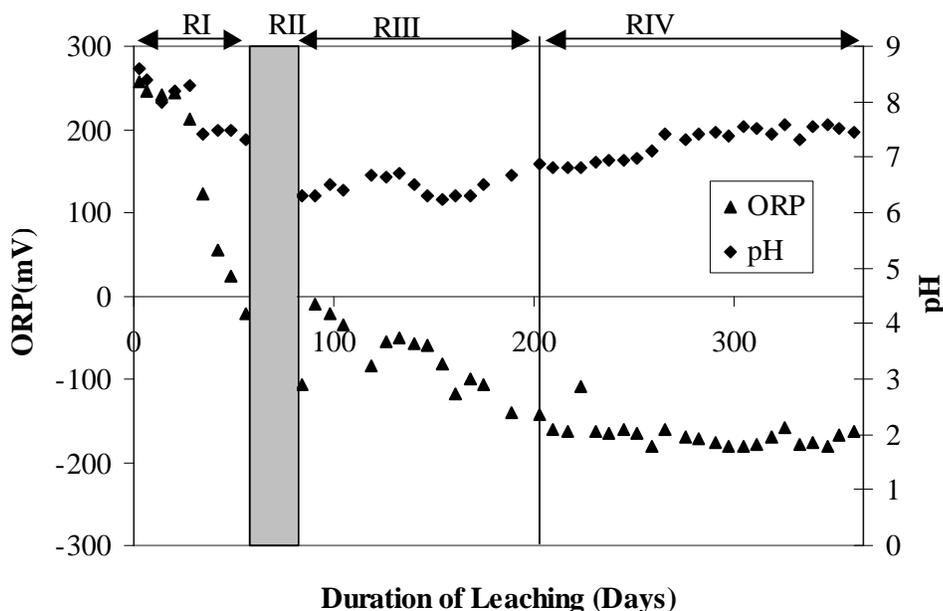


Figure 4.3 .ORP (mV) and pH variations during the column run. The regime representing DI leaching is presented as a block on the plot for easy distinction. The “R” labels refers to the different regimes of the column run numbered from 1-4.

Since, the average initial pH and ORP of the influent leachate remained averagely constant, obviously, the observed decrease in leachate pH and ORP is linked to other processes occurring in the bioreactor such as the initiation of dissimilatory Fe (III) reduction. Theoretically, If the initiation of dissimilatory Fe (III) reduction, as documented by other researchers, occurs in the range 20-50 mV (Collen et al; 2004a), then, we should notice an increase in Fe^{2+} concentration leached from the bioreactor when the ORP reaches that range. Indeed at day 42, over 50% of the dissolved fraction leaching from the column was in Fe (II) (figure 4.4) when the ORP was 54 mV (figure 4.3).

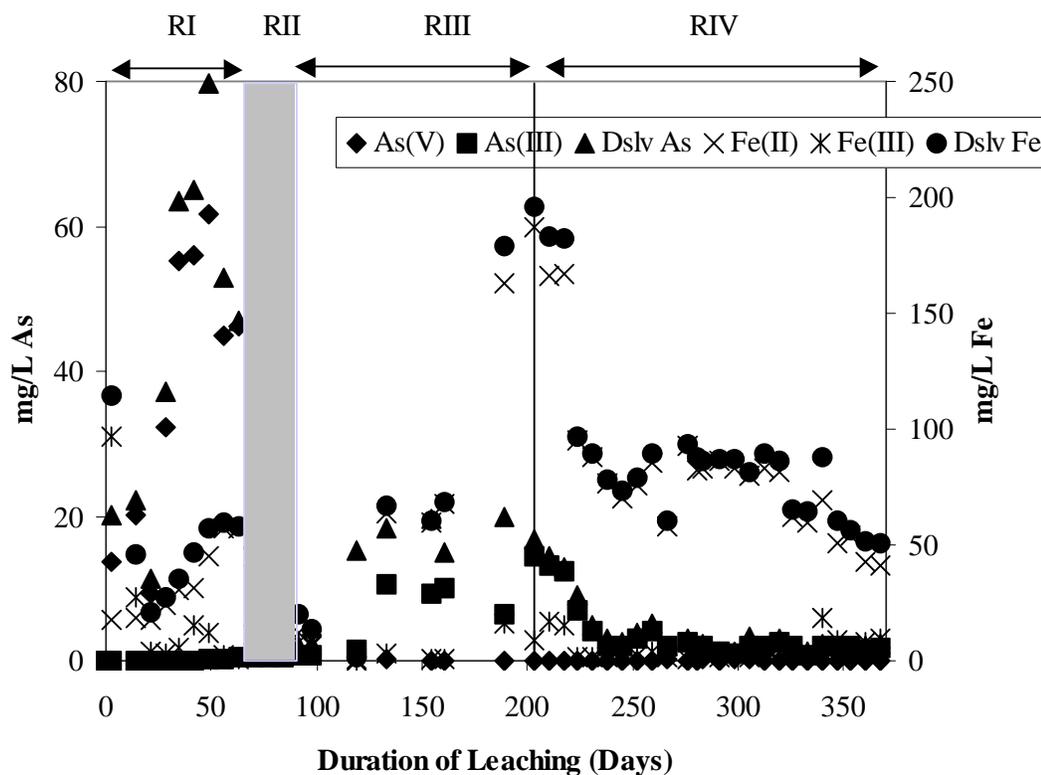


Figure 4.4. Concentration of As and Fe speciation in the dissolved fraction of the effluent solution. Note, As and Fe track each other implying coupling of processes which lead to mobilization of arsenic and iron.

By day 49, the ORP had dropped to 20 mV and the fraction of Fe (II) had increased to about 80 % of the total dissolved fraction.

The decreasing pH and increasing Fe^{2+} concentration is characteristic of onset of microbial Fe respiration coupled to incomplete oxidation of organic acids found in the landfill leachate. This process normally results in decrease in leachate pH, as H^+ / Fe^{2+} competition for iron oxide surface is promoted. Mechanistically, It is well known that the onset of microbial iron reduction is characterized by production of ferrous iron

(Shawng et al, 2002; Collen at al, 2004a). The half-reaction for this process is shown.



This process is followed by competitive desorption of H^+ by Fe^{2+} from the Fe oxide surface hence releasing H^+ in solution. It is this large proton flux into the leachate solution, which overwhelmed the solution alkalinity and was responsible for the initial observed decrease in pH (Figure 4.3). One would however expect that a drop in pH would result in increase of the ORP. This was not the case during this period of the column run. The disequilibria still present in the column could have resulted in an expected drop in ORP. It is possible that the drop in ORP was mainly caused by consumption of the remnant oxygen by the surviving aerobes still present in the column and not less dependent on pH fluctuations. However, the drop in pH and ORP was not all the way of the column run. Once equilibrium was established, an increase in pH evidently tracked a decrease in ORP as will be demonstrated later in the text.

Previous researchers (Kretzschmar et al, 1999) have evidently confirmed that microbially mediated proton production of the nature described above and coupled to Fe redox chemistry has direct influence on colloidal mobilization via deflocculation/reductive dissolution of iron and indirectly via changes in solution chemistry and surface charge. These colloids are characteristic of high specific surface areas ($>10 \text{ m}^2\text{g}^{-1}$), high reactive site densities and variable range particles sizes (1 nm -1 μm). The above particle characteristics can significant contribute to the mobilization and transport of arsenic in the subsurface. In this study, we demonstrated role and contribution of particles $>0.45\mu\text{m}$ to As leaching. Figure 4.5 shows the total arsenic concentration in comparison to the concentration of dissolved arsenic in the column effluent. Generally, arsenic and iron concentrations track each other and there are

obvious correlations between total As and Fe and their corresponding dissolved fractions.

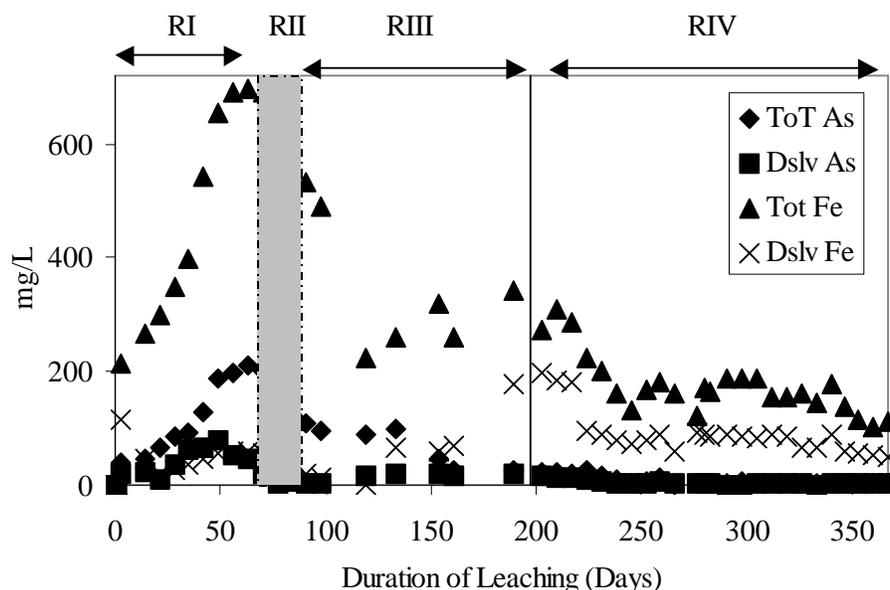


Figure 4.5. Total and dissolved As and Fe concentrations, in the effluent leachate solution. Tot = Total (Dissolved + Particulates $>0.45 \mu\text{m}$) and Dslv = Dissolved ($<$ than $0.45 \mu\text{m}$).

For example, a maximum total Fe concentration of 690 mg/L at day 70 coincided with the maximum concentration of 240 mg/L As on the same day. This trend is also true for the dissolved fraction where the maximum and minimum concentrations coincide.

It is also evident that the fraction of particulate to total iron/arsenic remained near 60%. This suggests that much of the arsenic mobilization was due to adsorption onto the colloidal iron with particle size $> 0.45 \mu\text{m}$ that is leaving the column as suspended solids. This result is agreement with our previously published results on GFH (Ghosh et al., 2006b) and is consistent with previous researchers who established that

reduction of ferric oxides under suboxic conditions can promote colloid dispersion by dissolving Fe-oxide that hold aggregates together (Tadanier et al, 2005). Not all colloids are purely Fe based. The high concentration of organic matter in the landfill leachate (table 4.2) may also trigger the in situ neof ormation of Fe-NOM complexes and / or stable Fe-oxide particle greater than 0.45 μ m (Peiffer et al, 1999; Pullin et al, 2003) and hence promoting the mobilization of high levels of arsenic.

Even though there is an association between Fe and As concentrations, their relative rates of leaching differ in different regions of the leaching period. For example, Figure (4.5) shows that in the first 50 days, the rates of leaching of Fe and As were initially high and tracked each other. In that period, the cumulative fraction of iron and arsenic leached was approximately 22% of their respective initial totals in the system.

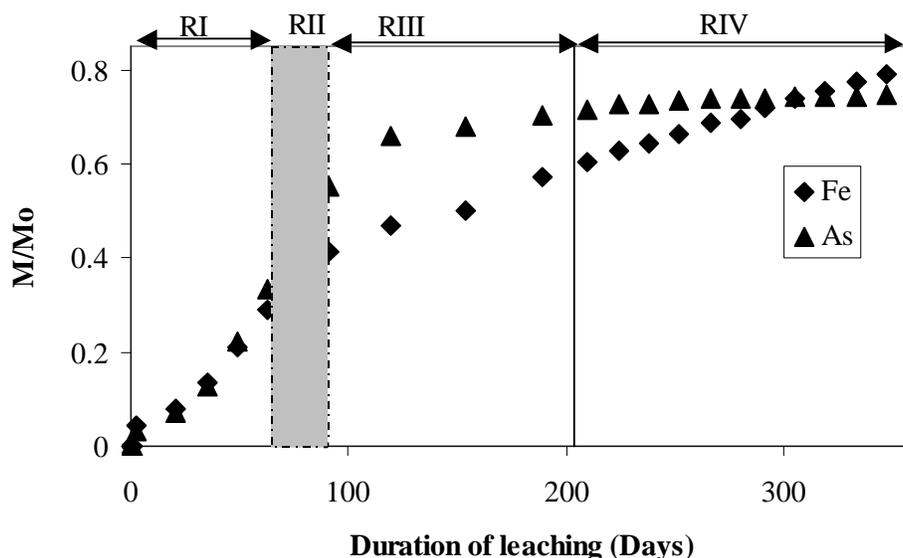


Figure 4.6. Cumulative mass fraction of arsenic and iron mobilized from a simulated landfill column over one year of operation. Note, the rate of arsenic leaching slowed down after 100 days whereas that of arsenic kept increasing.

However, the correlation was not all the way. Soon after that, the rate of iron leaching started to slow down while the arsenic leaching rate kept increasing. By the 63rd day (end of regime I), 34% of total arsenic had leached out whereas only 28 % iron leached out. The change in kinetic regimes after 50th day of the column run, which resulted in higher rates of arsenic leaching, could be attributed to initiation of processes such as secondary mineralization occurring during microbial reduction of ferric (hydr)oxides. It is probable that formation of secondary minerals e.g magnetite, lepidocrocite, and/or goethite on the ferrihydrite surface lead to decreased sorption capacity of arsenic and slower dissolution rates of iron.

Regime II. This region spans from day 63-91 of the column run. It is represented as a block on all the plots for easy distinction from the rest of the leaching eras. The main feature of this region was interrupting the landfill leachate supply and using DI water

(pH 6.9) as the feed solution for 30 days. This solution lacked electron donating organic substrate and nutrients, which are required for microbial growth. The aim of this step was to simulate the leachability of As and Fe under disequilibrium conditions which may occur in landfills due to perturbations on redox equilibrium, created by percolation of rain water. As expected, this perturbation resulted in a sudden increase in ORP from -210 to -11 mV (indicating decreased microbial activity) whereas the pH suddenly dropped from 7.1 (day 63) to 6.3 ± 0.1 . Obviously, the sudden drop in pH was indicative of a drop in solution alkalinity (120 mg/L CaCO_3) which was closer to the lowest alkalinity range of most landfills (table 4.2) and certainly too low to resist continuous flux of protons generated from the dissimilatory reduction of iron (regime I).

Similarly, the measured DOC in the column leachate dropped progressively to 108 mg/L, which was less than DOC range of most landfill leachates (table 4.2). A drop in ORP and DOC confirmed that microbiological growth and activity were limited by supply of electron-donating organic substrates, which were absent in DI feed solution. One would expect that the observed changes in the system redox chemistry and declining microbial activity noted above directly impacted the relative levels of arsenic and iron leached. Indeed, after introduction of DI water, the concentration of total Fe and As dropped drastically by 30% and 54% respectively of the maximum observed value right before introduction of DI water. Similarly, in the dissolved fraction, the iron concentration suddenly dropped by 76%, of its maximum observed value just before introduction of DI water whereas the dissolved As concentration dropped by a factor of over 90% of its initial value. By the 91st day, the ratio of iron

Fe(II) : Fe (III) had reduced from 20:1 (end of regime1) to 1:1 by the end of regime 2 and the ratio of As(V) to As (III) had however reduced from over 20:1 to about 2:1.

Note, the decreasing microbial activity does not however explain why we were able to generate As (III) without addition of any exogenous electron donors to the DI water feed. This suggests that in the processes of feeding the reactor with DI water, we provided the right condition for As (III) itself to act as electron donor. Reactions of this nature have been shown to proceed without a lag (Ahmann et al, 1997; Wilke et al, 1998; Gihring et al, 2001; Thomas et al, 2004), which is consistent with our observations as shown in figure 4.4.

Mechanistically, It can be argued that the observed declining trends in both Fe and As concentrations, presumably due to decreasing microbial activity, were not surprising given the fact that DI water lacked suitable nutrients and organic electron donors for microbial activity. The continuous decrease in Fe (II) and As (III) concentration in later days of regime II may be a consequence of declining dissimilatory Fe and As reduction activity, although the reprecipitation of Fe at circumneutral pH could also have occurred producing insoluble iron hydroxides co-precipitating and / or adsorbing high levels of arsenic species and reducing its mobility. The fact that the DI feed solution was deficient in sulfate and any other nutrients needed for biotransformation to occur, makes it unlikely that formation of low solubility alternate iron phases such as mineral sulfides could have significantly contributed to slowing leaching of iron and arsenic as reported by others (Shawng et al, 2002).

The landfill leachate originally in the column was continuously being washed out and substituted with the influent DI water. Even though the fractions of total and dissolved fractions decreased over time, the majority of arsenic leaving the column was still associated with particles with the ratio of particulate to dissolved arsenic reaching more than 10:1 during the entire regime. The generation of colloids coincides with increased Fe (III) in the dissolved fraction and is consistent previous researchers who explained that, iron reduction (regime 1)-oxidation (such as that observed in regime 2) events may initiate wide shifts in the concentration of particulate and dissolved colloidal material because of either Fe mineral dissolution or pH shifts associated with Fe oxidation state changes (Aaron et al, 2006). These particulates and dissolved colloids may be responsible for the transport high levels of arsenic such as those observed in this regime.

Regime III: Switching from DI water back to landfill leachate (day 98 onwards) reestablished the high DOC (electron donating organic substrate) and nutrient conditions required by microbes. Over time, alkalinity and DOC levels increased to 4216 mg/L and 3200 mg/L, which approximated what they were at the beginning of regime I. The pH started to increase from 6.3 to 7.0 by 203rd days. By this time, the H^+ / Fe^{2+} desorption, exchange and adsorption equilibrium had been reestablished and any continued Fe (III) respiration (Ponnamperuma et al, 1986; Vesparaskas et al, 2001; Shawng et al, 2002) process consumed H^+ and this lead to an increase in pH as shown in the following equation.



In the above equation, organics in landfill leachates are described by the general formula RCHOHCOO^- because most organics, which make up the landfill leachate, carry carboxylate group and / or carbonyl functionality in their chemical structure.

In lieu of the above, its not surprising that the increase in pH mentioned above immediately resulted in drop in the ORP from -10 to below -143 mV and remained under -160 mV until the end of the column run. Consistent with previous researchers (Nanny et al, 2002), this ORP range is indicative of maturing of the bio simulator analogous to a typical ORP range of mature landfill. The dissolved Fe concentration increased to a maximum value of 200 mg/L, which was 3 times higher than the maximum observed concentration before feeding the reactor with DI (end of regime I). Analysis of the dissolved phase of the leachate effluent showed that Fe^{2+} concentration constituted over 96% signifying a jump start in dissimilatory Fe (III) reduction probably due to return of electron donating organic matter to the system.

The interplay between Fe (III) /Fe (II) species and the progression of pH/ORP was expected to directly have an impact on As levels and its speciation. Indeed, the minimum measured leachate concentration of As (III): As (V) averaged 2:1 and this ratio increased over time, indicative of continued dissimilatory arsenic reduction. During this phase of the column run, the association between arsenic and particles had weakened as the duration of leaching increased. For example from 154-203 days, the ratio of particulate to dissolved arsenic had reduced to an average ratio 1:1. By the end of regime III, the dissolved As fraction was greater than the particulate fraction,

suggesting the particles ($>0.45\mu\text{m}$) generated originally present or produced in-situ had been largely eluted from the column. By the 203rd day, 70% of As and 58% Fe had come out. As seen from the slopes, (figure 4.6) reintroduction of the landfill leachate did not immediately or in the long run, change the kinetics of leaching of arsenic and iron observed in regime II. The rate of iron leaching kept a steady slowing down while the arsenic-leaching rate kept increasing at a steady state. The difference in relative rates was probably, among other factors, due to desorption of arsenic from AFH as a result of the increasing pH.

Overall, considering all factors noted in this section, it is clear that decreased iron reduction at the end of regime II was not primarily attributable to precipitation of secondary iron minerals which decreased Fe and As availability as we had previously thought and as reported by others (Shawng et al, 2002; Collen et al, (2004a, 2005b) but was linked directly linked to microbe starvation due to decreased organic substrate/nutrient resource.

Regime IV. From day 203 to the end of the column run, the correlation between particulate and dissolved iron and arsenic had weakened further (Figure 4.5).

By this time of the column run, the rates of As leaching had slowed down and the rates of iron were still increasing drastically (figure 4.6). Particularly, the time (about day 203) when the majority of iron leaving the column switches from being particulate to dissolved is also the about the same time as when the majority of arsenic leaving the column changes from being particulate to dissolved. Arsenic and iron concentrations decreased throughout that period. The dissolved Fe fractions decreased

from 200 mg/L at day 203 days to 50 mg/L at the end of the column run whereas the dissolved As concentration decreased from 17 mg/L to 2 mg/L. The oxidation potential (ORP) of the effluent remained averagely about -250 ± 5 mV throughout this period indicating continued dissimilatory microbial activity. Therefore, its not surprising that both Fe (II) and As (III) constituted over 90% of the total dissolved fraction rather than the Fe (III) and As (V) in which there loaded into the column.

One would expect that depletion of total arsenic from the reactor would affect negatively impact the dissimilatory arsenic reducer (DasR) population densities responsible for reduction of As (V) to As (III). Our observations reveal that this is not necessarily true and that As (III) was still more prevalent than As (V). The prevalence of As (III) over As (V) was not surprising considering that most of the documented DasR have been found to be opportunistic (Stolz et al, 1999; Oremland et al, 2003) and are capable of respiratory growth on a wide variety of other electron acceptors such as nitrate which are abundantly present in the landfill leachate (table 4.2). Therefore, depletion of As(V) minimally affect their activity and any small amount of As(V) available in the system could still readily be reduced to As(III).

As shown in figure 4.6, in the course of a year's operation (total column run), sorbent capacity of Fe for arsenic had become limited (80% of the iron had leached). By the end of the column run, about 75% of the arsenic originally loaded into the column on the AFH had leached

Implications

The simulated landfill column test of the fresh AFH provides the most important results in terms of managing AFH residuals. Our results indicate that reductive dissolution of arsenic rich iron oxy hydroxides linked to microbial degradation of organic matter in reduced environments has serious implications to the long term storage of iron based ABSR. Most of the arsenic measured in the effluent from the column was not in the dissolved phase (as defined operationally by filtration through a 0.45 μm filter). Throughout the first 200 days of the column run, particulate mobilization dominated arsenic leaching. This disparity is significant in light of the fact that the standard batch leaching tests, TCLP and WET, measure only the dissolved fraction, while the bulk of arsenic leaching from AFH is via particulate transport.

In addition, the arsenic concentration leaving the column for the first 240 days never decreases below 5 mg/L, which is the arsenic TC limit set for designation as a hazardous waste. Contamination of ground water with arsenic may persist for many years even after closure of a landfill because of the high organic carbon content of landfill leachates which will promote reductive dissolution of AFH and releases arsenic. Reductive dissolution of arseno AFH occurs because degradation of the organics in the leachate deplet the solution of its oxygen content and this translates into favourable reducing conditions for reductive dissolution of arsenic-rich iron oxides.

Overall, even though a number of studies have qualitatively provided evidence that AFH has a higher capacity for binding arsenic than most other Fe based media (Jain et al, 2000; Su et al, 2001; Redman et al, 2002), our results shows that under mature landfill conditions, AFH is more unstable and will release As and Fe at a rate 3 X faster than GFH (data provided elsewhere). One of the reasons which could have caused the difference in the relative rates is the fact that the iron in AFH seems to be in a less stable amorphous form whereas that in GFH is in a more weakly crystalline form. However, It is important to note that the total arsenic content of the two sorbents was initially very different and this could also have contributed to the difference in observed rates. In Lieu of the above, the stability associated with long-term disposal should be evaluated and considered in the choice of sorbent for treatment of liquids brines containing high levels of arsenic.

Acknowledgments

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CHAPTER 5

SIMULATION OF LONG TERM STABILITY OF AGED FERRIC HYDROXIDES
SLUDGES GENERATED FROM ARSENIC BRINE TREATMENT PROCESSES
UNDER LANDFILL CONDITIONS.

Introduction

The long-term chemical stability of AFH loaded with arsenic depends on a number of factors, including the disposal site characteristics, the particle crystallinity and size distribution, the presence of other ions such as phosphate, presence of complexing agents, such as naturally occurring organic ions.

Schwertmann et al, 2004c provided evidence that goethite and hematite develop from ferrihydrite by two different and competitive mechanisms: goethite crystals form in solution from dissolved Fe(III) ions produced by the dissolution of ferrihydrite, whereas hematite forms through an internal dehydration and rearrangement within the ferrihydrite aggregates (Schwertmann et al, 2004c). The transformation mechanisms of ferrihydrite into stable ferric oxyhydroxides or oxides have been studied by Manceau et al, 1993, by means of EXAFS spectroscopy. These researchers concluded that the structure of 6-line ferrihydrite consists of structural anionic ABA and ACA fragments in which Fe cations occupy only octahedral sites forming a three dimensional periodic structure. Over long periods of time, aging of AFH would therefore result in the breaking of these face linkage deeply altering the anionic packings in going from ABACAB... to ABABAB... stacking. This may either release or retain arsenic into solution.

Jambor and Dutrizac (1998) concluded that the adsorption of arsenate while ferrihydrite is polymerizing interferes with the chain-building process, thereby retarding further polymerization and the aging to hematite. Rancourt et al, 2001 worked on extensive characterization of arsenic-rich hydrous ferric oxide samples, using powder X-ray diffraction (pXRD), transmission electron microscopy (TEM). Mössbauer spectroscopy revealed that arsenical ferrihydrite has a fundamentally different structure from natural and synthetic As-free hydrous ferric oxide or As-free ferrihydrite. These researchers concluded that the adsorbed arsenic stabilizes the structure of ferrihydrite and retards the transformation to As and Fe oxides.

On the other hand, a number of experimental studies have shown that, under proper storage conditions, high-iron arsenical ferrihydrite is stable for at least several years (Harris et al, (1989a, 1993b); Krause et al, 1989; Kontopoulos et al, 1988; Vircikova et al, 1998). Furthermore, to the author's knowledge, the decomposition of arsenical ferrihydrite obtained from water treatment processes has not been observed in actual landfill sites.

Based on the above observations, there is an ongoing controversy about the effect of long-term aging and its effects on the stability of arsenical ferrihydrite, because of strong discrepancies between theoretical considerations and practical observations. Robins et al, (1987a, 1990b), on the basis of a comprehensive thermodynamic study of the stability of metal arsenates, concluded that most arsenates are metastable under natural conditions and that they will eventually age, releasing soluble arsenic. Furthermore, the thermodynamic calculations indicate that, over a relatively long

period of time, arsenical ferrihydrite will age to goethite (FeOOH) or hematite (Fe_2O_3) and release arsenic acid into the solution (Robins et al, 1990b).

Currently, there is no definitive test to determine the effect of aging on the leachability behavior of ABSR compounds over long periods of time, and the development of such a protocol would be useful. Also, there is no conclusive evidence from previous studies that arsenical AFH undergoes reduction under landfill conditions. This study provides the first data driven multi evidence of the overall leachability of As and Fe which occur from brine sludge when most important competing physical and microbial processes typical of landfills are present.

Experimental Materials and Procedures

Sludge Preparation and Aging

The procedure and conditions employed to make and age the 5.7:1 fresh sludge was similar to that described in chapter 2. The only difference was that since the more aged sludge was needed (500g), the batch was aged in one big batch container as opposed to many separate smaller vials. The advantage of aging the sludge in a single batch was to avoid the differences in relative rates of aging between the contents of the different vials which had been previously been found to result from non-uniform rates of water loss between the different vials.

Aged Solid Characterisation

The aged solid was characterized by X-ray diffraction analysis as well as by digesting 0.5 g sample using 70% by volume HNO_3 in a CEM Inc microwave digester, using

the SW 821-8051 method. Characterization of arsenic and iron leaching from the aged solid was evaluated using standard leaching tests (TCLP and the CA-WET) as well as using acid extraction procedure described in methods section of chapter 2.

Biotic Column Design, Composition, Flow Conditions and Operation

The reactor design, flow condition and mode of operations of the aged column was same as detailed in experimental section of chapter 4. The procedure for collecting landfill leachate and its preservation was the same as described earlier in chapter 4. The average influent leachate characteristics and composition were the same as that described in table 4.2.

Instrumentation and Sample Analysis.

Instrumentation and analytical procedures used in obtaining the results in this study are the same as described in chapter 4.

Results and Discussions

Aged Solid Characterization

Consistent with results obtained from XRD analysis of pH 7 Fe:As 5.7:1 aged sludge and presented in chapter 2, X-ray diffraction data confirmed that aged material used in this study produced, as expected, very broad and low intensity peaks which indicated that the analysed phase possessed a short-range order; i.e., it is amorphous or very poorly crystalline in nature. After digestion, the total As and Fe loading of the pH 7 aged sludge used in this study approximated and confirmed the values previously obtained and shown in Table 2.1. Results obtained from weak acid extraction and

standard leaching procedures were comparable to those presented in the results section of chapter 2.

Changing processes within the bioreactor were monitored by measuring pH, ORP, speciation of Fe and As of the effluent solution as well as their corresponding total and dissolved fractions. The results are presented in 4 different kinetic regimes, which are based on the observed changing leaching patterns for Fe/As during the column run. The details of each regime are discussed below.

Regime I. This is a period between 0 - 74 days of the column run during which Fe and arsenic concentrations rose to their corresponding maximum values before decreasing (start of regime 2). As demonstrated in chapter 4, this period coincides with initiation of dissimilatory Fe (III) reduction. Figure 5.1 shows that in the first 45 days, pH and ORP variations were linked. The effluent leachate initially increases from 6.4 to 7.3 whereas the ORP correspondingly decreased from -22 mV to -150 mV.

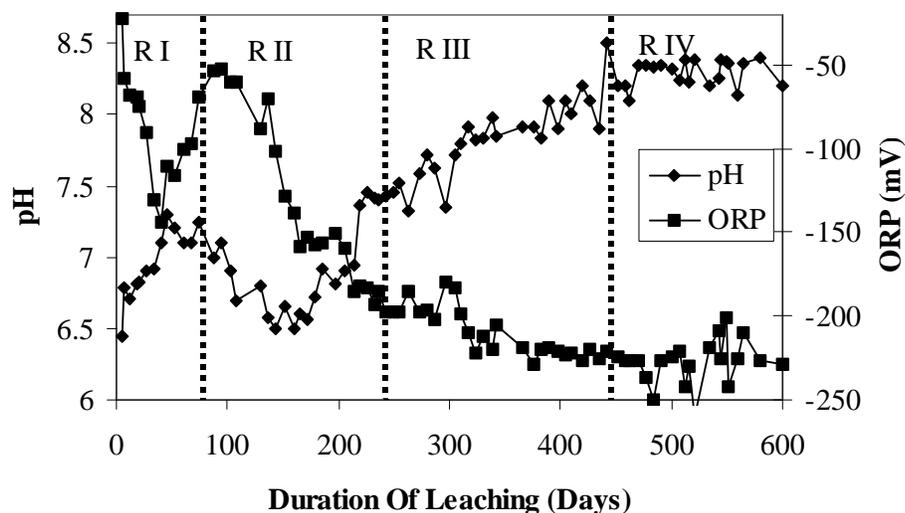
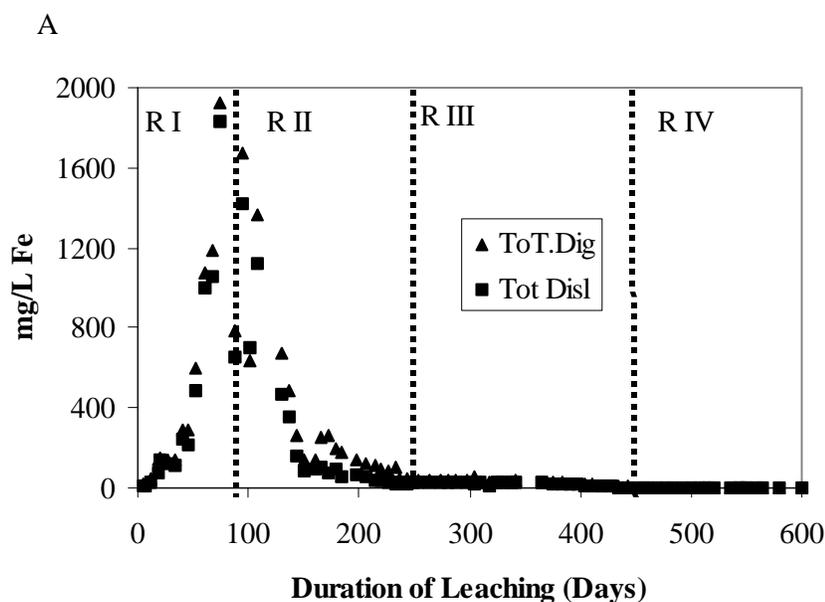


Figure 5.1 ORP (mV) and pH variations during the column run. “R” stands for “Regime” which represents the different periods of the column run numbered from 1-4.

Analysis of the dissolved phase of the leachate effluent showed that Fe^{2+} concentration constituted over 90% signifying the initiation of dissimilatory Fe (III). From day 45-74, the ORP had increased from -150 mV to -70 whereas there were minor fluctuations in solution pH (probably due to high solution alkalinity present in the landfill leachate). The disconnect in the ORP and pH trends between day 45-74 could have been caused by the disequilibria still present in the column. This disconnect between ORP and pH was not all the way of the column run. Once equilibrium was established, an increase in pH evidently tracked a decrease in ORP as will be demonstrated latter in the chapter.

As noted in chapter 4, under reduced conditions, microbial processes linked to Fe reduction has direct influence on colloidal mobilization and transport of arsenic. The

extent to which these iron colloids are mobilized from ABSR is also a function of the nature of the sorbent. Since our AE results revealed that aging of AFH resulted into a solid which is crystalline with less available iron (see results section of chapter 2), intuitively, the contribution of Fe colloids to arsenic leachability may be more significant in the fresh sludge and less significant in the aged sludge. Figure 5.2 and 5.3 shows the total iron and arsenic concentration respectively in comparison to their respective of dissolved arsenic concentration in the column effluent.



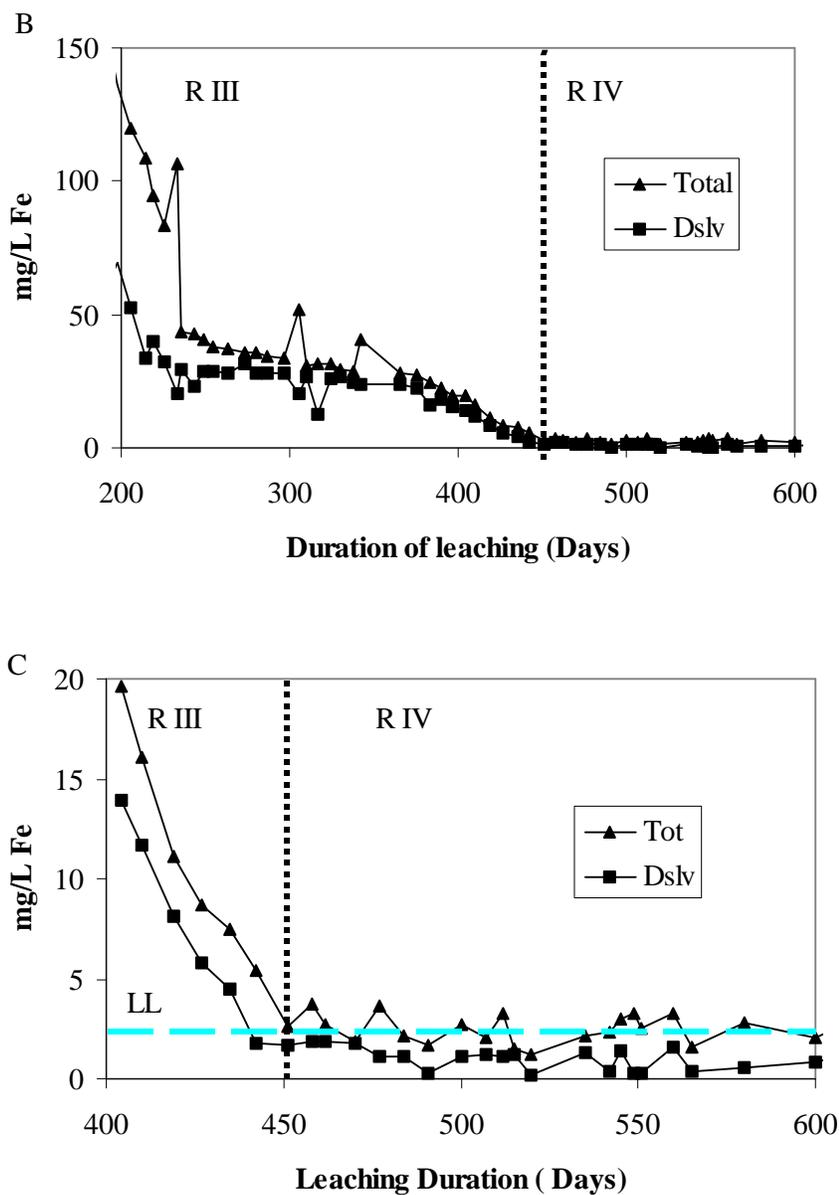
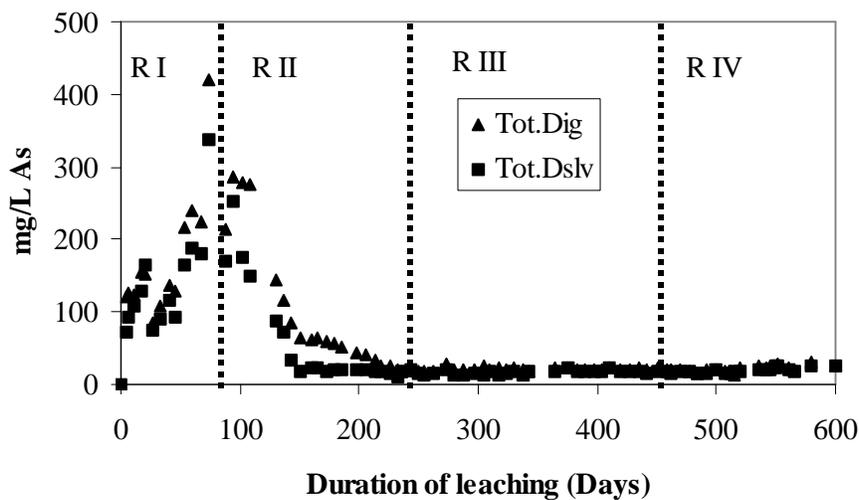


Figure 5.2. (A) Total and dissolved Fe concentrations, in the effluent leachate solution over the entire column run. B and C are expanded scales representing lower concentration of iron in latter days of the column run. Horizontal dotted line represents Avg influent Fe concentration.

Generally, arsenic and iron concentrations track each other and there are obvious correlations between total As and Fe and their corresponding dissolved fractions. For example, a maximum total Fe concentration of 1930 mg/L (figure 5.2 A) at day 74

coincided with the maximum concentration of 420 mg/L As (figure 5.3A) on the same day. However, a more pronounced but similar trend was observed for fresh sludge of the same initial Fe: As sludge.

A



B

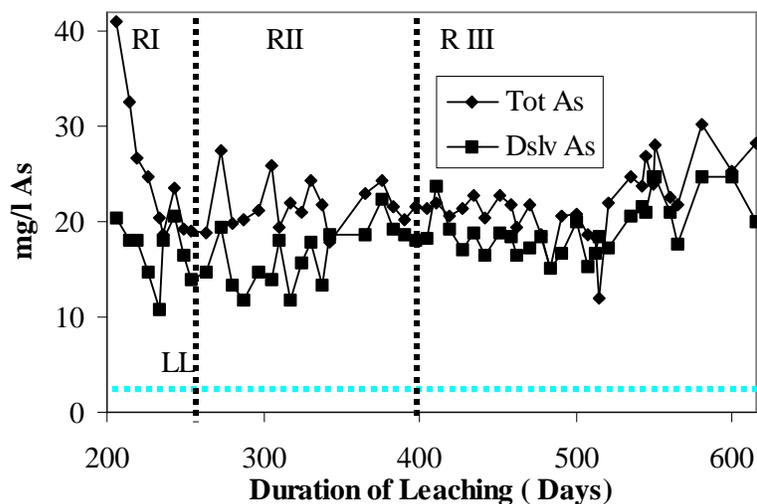


Figure 5.3. (A) Total and dissolved As concentrations, in the effluent leachate solution over the entire column run. B is an expanded scales representing lower concentration of arsenic in latter days of the column run. The horizontal line represents the influent leachate concentration.

This suggests that in the fresh sludge, among other leaching mechanism occurring, much of the arsenic mobilization was due to adsorption onto the particulate iron or organic $> 0.45 \mu\text{m}$ that is leaving the column as suspended solids. In the aged sludge, since the majority of Fe in the sludge has been found to be crystalline and not readily available, it is therefore likely that the high concentration of organic matter in the landfill leachate may also have triggered the formation of As-NOM complexes greater than $0.45\mu\text{m}$ (Peiffer et al, 1999; Pullin et al, 2003) and hence promoting the mobilization of high levels of arsenic.

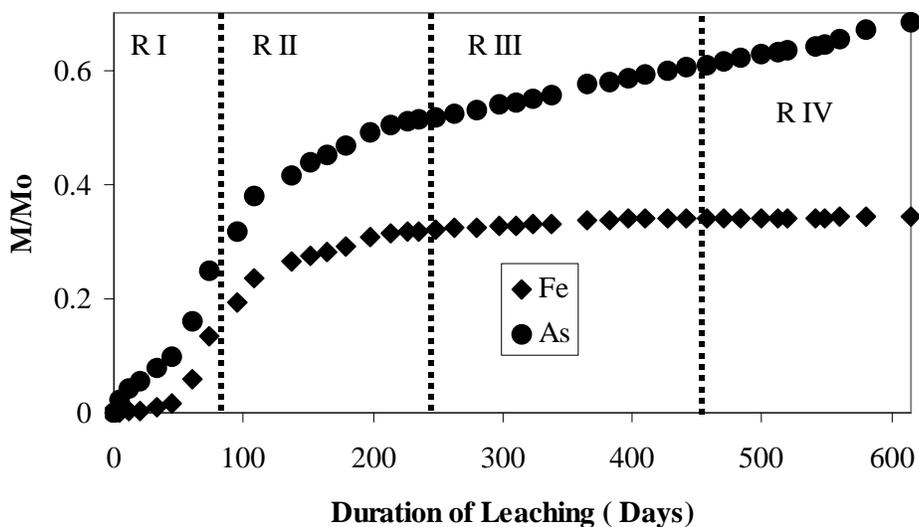


Figure 5.4. Cumulative mass fraction of arsenic and iron over a period of 600 days of operation. Note, the rate of Fe leaching slowed down after 100 days whereas that of arsenic kept increasing.

It should be noted that even though there is an association between Fe and As concentrations, their relative rates of leaching differ. For example, Figure (5.4) shows that in the first 74 days, the cumulative mass fraction of As increased more rapid than that of Fe and they followed the same trend. By the 74th day (end of regime 1),

cumulative 26 % and 16% of total arsenic and Fe respectively had leached out. This behavior of aged sludge is qualitatively similar to that noted in batch results (results section of chapter 2) in which the leaching solution contained a greater fraction of the total As than Fe. Soon after day 74, the rate of iron leaching started to slow down while the arsenic leaching rate kept increasing.

Regime II. This region spans from day 74-250 of the column run. This regime is characterized by decreasing Fe/As concentrations in the effluent liquid of the column. In this regime, the pH decreased even further from 7.2 at day 74 to 6.5 at day 160 meaning that the flux of protons into solution over whelmed the solution alkalinity. In the same time scale, the ORP decreased from -52 to -152 mV (Figure 5.1). The observed decrease in pH in regime II could have been caused by accumulation of VFA as the reactor progresses through acidic phase to methanogenic phases whereas the decrease in ORP could have been caused and governed by consumption of the remnant oxygen by the surviving aerobes still present in the column due to disequilibria still present in the column.

Soon after day 160, the pH started to increase while the ORP dropped further. By 250th days, the pH was 7.4 whereas the ORP was -200 mV. By this time, the H^+/Fe^{2+} desorption, exchange and adsorption equilibrium had been established and any continued Fe (III) respiration (Ponnamperuma et al, 1996; Vesparaskas et al, 2001 Shawng et al, 2002) process consumed H^+ and this lead to an increase in pH as the biosimulator reached maturity (Nanny et al, 2002).

During this period of the column run, the association between arsenic and iron particles started to decline. Greater than 60% of the effluent arsenic concentration was measured As (III) indicative of continued dissimilatory arsenic reduction. During this regime, colloidal transport dominated As leachability (Figure 5.3 A) because most of readily accessible iron particles from the aged sludge (Figure 5.2 A) had come out. The dissolved As concentration approximated the total concentrations. The cumulative mass fraction of iron kept steadily slowing down while that of As kept increasing steadily (figure 5.4). By the 250th day, 51% of As and only 32% Fe had come out.

Based on evidence obtained from weak acid extraction and other leaching tests, which proved that aged sludge is more crystalline than fresh sludge, intuitively, in the aged solid, less Fe may be available for microbial mineralization. It is therefore unlikely that the observed decrease in iron and arsenic availability in the effluent at the end of regime 2 was primarily attributable to precipitation of secondary iron-arsenic minerals we had previously thought and as reported by others (Shawng et al, 2002; Collen et al, (2004a, 2005b) working on fresh AFH. It is probable that by this time, the readily available iron has been washed out of the column and traces of iron appearing in solution could be coming from the dissolution of the crystalline aged sludge.

Regime III. This regime is characterized by decrease by a break down in correlation between arsenic and iron concentrations in the effluent. Overall, iron concentrations decreased throughout that period (Figure 5.2 B and 5.3 A) whereas arsenic concentrations leveled. The dissolved Fe fractions decreased from 22 mg/L at day 250

days to 2 mg/L at day 450 whereas the dissolved As concentration averaged 20 ± 4 mg/L. The correlation between particulate and dissolved iron and arsenic had also weakened further. From day 250 to day 450, the oxidation potential (ORP) of the effluent continued to decrease throughout this period indicating continued dissimilatory microbial activity. It is therefore not surprising that through out this period, both Fe (II) and As (III) constituted over 90% of the total dissolved fraction rather than the Fe (III) and As (V) in which there loaded into the column. By this time of the column run, the cumulative mass fraction of Fe had slowed down even further and that of As was still increasing drastically (Figure 5.4) probably due to continued desorption of arsenic from the crystallite Fe surface.

Regime IV. This is a period between 450-600 days in which the iron dissolution from the aged solid had completely stopped. In this regime, most of the measured iron concentration approximated the influent Fe concentration in the landfill leachate whereas most of the measured arsenic concentration was over X40 the influent leachate concentration. This signifies that the desorption rather than dissolution of Fe contributed to total leachability of As. It is therefore not surprising that total iron and arsenic leaving the column and their corresponding dissolved fractions (figure 5.3) approximated.

In the course of 2 years operation (total column run), 35% of the iron had leached whereas about 69% of the arsenic originally loaded into the column on the AFH had leached

Implications

It should be noted that standard batch leaching tests, TCLP and WET were not designed to quantify the contribution of aging on total arsenic leachability. However, our results indicate that aging of arsenic rich iron oxy hydroxides under landfill conditions has serious implications to the long term storage of iron based ABSR. It appears that desorption of arsenic from the crystallite Fe is the major driving force behind arsenic leachability and has profound effects over long periods of time. The benefit of aging sludge prior to disposal is that leaching 70% arsenic from aged sludge took 600 days whereas fresh sludge took one year under similar conditions.

Noticeably, arsenic concentration leaving the column for the during the entire column run never decreases below 5 mg/L, which is the arsenic TC limit set for designation as a hazardous waste. Contamination of ground water with arsenic due to aging may persist for many years .

Overall, our results shows that under mature landfill conditions, aged AFH is more unstable and will release As. Therefore, stability associated with aging should be evaluated and considered in the choice of sorbent for treatment of liquids brines containing high levels of arsenic.

Acknowledgments

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CHAPTER 6

COMPARATIVE LEACHABILITY OF ENCAPSULATED AND UNENCAPSULATED AFH, UNDER LANDFILL CONDITIONS

Abstract

This research investigates the use of polymeric matrices to encapsulate AFH sorbent which is widely used to remove arsenic from drinking water. Arsenic-containing amorphous ferric oxy/hydroxide residuals were encapsulated in a synthetic polymeric matrix. The polymer was synthesised from poly(styrene butadiene) and an epoxy resin. The polymeric- waste forms produced were loaded up to 60 wt% of sorbent (dry basis), while keeping good mechanical properties. Arsenic leaching from encapsulated and unencapsulated residuals was evaluated using short term and long-term biotic landfill simulator columns. The results of short term leaching are contained in our previous work (Shaw et al, 2007). This chapter evaluates the long-term behaviour of this material under column saturated flow conditions. The results show that waste forms of the polymer-encapsulated residuals resists leaching when evaluated, yielding leachate arsenic concentrations below the Toxicity Characteristic (TC) standard of 5 mg/L. When the unencapsulated residuals were subjected to the same leaching conditions, arsenic leached up to 700 times greater concentrations than that observed from the encapsulated residuals.

Introduction

As described in the previous chapters, all practical industry arsenic removal processes produce arsenic bearing solid residuals containing arsenic and iron, which require disposal in non-hazardous landfills. The Toxicity Characteristic Leaching Procedure

(TCLP) is the standard test procedure recommended by USEPA to determine if this solid residual can be disposed into non-hazardous or hazardous landfills. It is now evident that whereas most residuals from most arsenic removal technologies currently pass the TCLP and are eligible to be disposed of in non-hazardous landfills, the TCLP under predicts the leaching of arsenic species (Hooper et al, 1998; Ghosh et al, (2004a; 2006b)). There is therefore an urgent need to stabilize the ABSR to reduce their leaching risk, which in turn reduces the disposal and clean up costs. Current, the most commonly used techniques for stabilization of ABSR are described as below.

Vitrification is the best-demonstrated available technology for stabilisation according to USEPA. The processing requires melting the mixture of sludge under extremely high temperature (2630-3330°C) and cooling it back down to room temperature in order to form a solid structure. Vitrification treatment has been found to be very effective in reducing leachability of arsenic and other related contaminants. The biggest draw back of this technology is that it is not economically feasible due to high-energy costs associated with high processing temperatures.

Solidification/Stabilization (S/S) or chemical fixation. The S/S process physically binds arsenic or other contaminants and this reduces the hazardous potential of waste by converting the contaminants into less mobile forms. Some of the stabilisation materials available on the market include lime, cement and polymer materials etc.

To the author's knowledge, S/S process has not yet been well characterised. For instance, it was long thought that using cement as a stabilising agent leads to the formation of calcium-arsenic compounds which is very effective in immobilization

arsenic (Phenrat et al, 2004). However, it has now been established that under landfill conditions, calcium arsenates are unstable and may disintegrate releasing arsenic. It is therefore not surprising that the USEPA doesn't preclude use of S/S method for treatment of arsenic waste, due to its long-term stability issues and increased waste volume, but recommends site-specific treat ability study.

Crystallisation: Also referred to as mineral crystallisation, this technology employs the ability of certain minerals to incorporate arsenic with a goal of returning arsenic to its natural mineral states. It is expected that synthesis of these with high enough mechanical strength may reduce the mobility of As.

For sludges like AFH, the proposed technology involves a two-step process (Forstner et al, 1998): (1) Arsenic-bearing sludge is treated under certain conditions (temperature, pH, humidity...) with or without additives. Aging of sludge may cause molecules and chemical functional groups to rearrange to form the expected arsenic-rich mineral structure in which arsenic can be stored in a low mobility and stable phase. (2) These minerals are stabilized under natural landfill conditions. The goal is to convert amorphous As-Fe sludge into a crystalline structure with a high chemical and mechanical strength. Upon crystallization the mobility of arsenic may be reduced significantly enough to meet both the non-hazardous waste disposal regulation and long-term leachability concern.

Encapsulation Technique: This technology attempts to stabilize AFH by using a water-based emulsion procedure that forms an epoxy matrix to encapsulate arsenic waste. The development of this process was based off previous work by Rengifo et

al, 2004 who attempted to stabilize soluble salts. The procedure for making the polymer, processing of the waste and making of the dipped rods used in this work is described in details (Shaw et al, 2007).

Experimental Methods and Procedures

Sludge Preparation by Co-precipitation

The procedure and conditions employed to make the 20:1 fresh sludge is similar to that described in making 5.7:1 fresh sludge detailed in chapter 2. The only differences between the two procedures were the ratio of Fe:As in the sludge. In this procedure, 22.34 g Sodium arsenate salt (5.37 g/L As) was dissolved in 1 L MQ water and stirred completely. 245.6 g FeCl_3 (86.3 g Fe) was rapidly injected into the mixture and the resultant solution rapidly stirred at 100 RPM. The influent leachate characteristics are the same as that described in table 4.3. The rest of the procedure for making the fresh sludge is the same as described in chapter 2.

Biotic Column Design, Composition, Flow Conditions and Operation

To demonstrate that polymeric encapsulation is effective at reducing arsenic leaching, two landfill simulation columns were built. One column contained freshly precipitated AFH (sludge) and the other contained polymer encapsulated sludge (dipped rods, 60% loading by weight). Figure 6.1 shows the experimental set up.

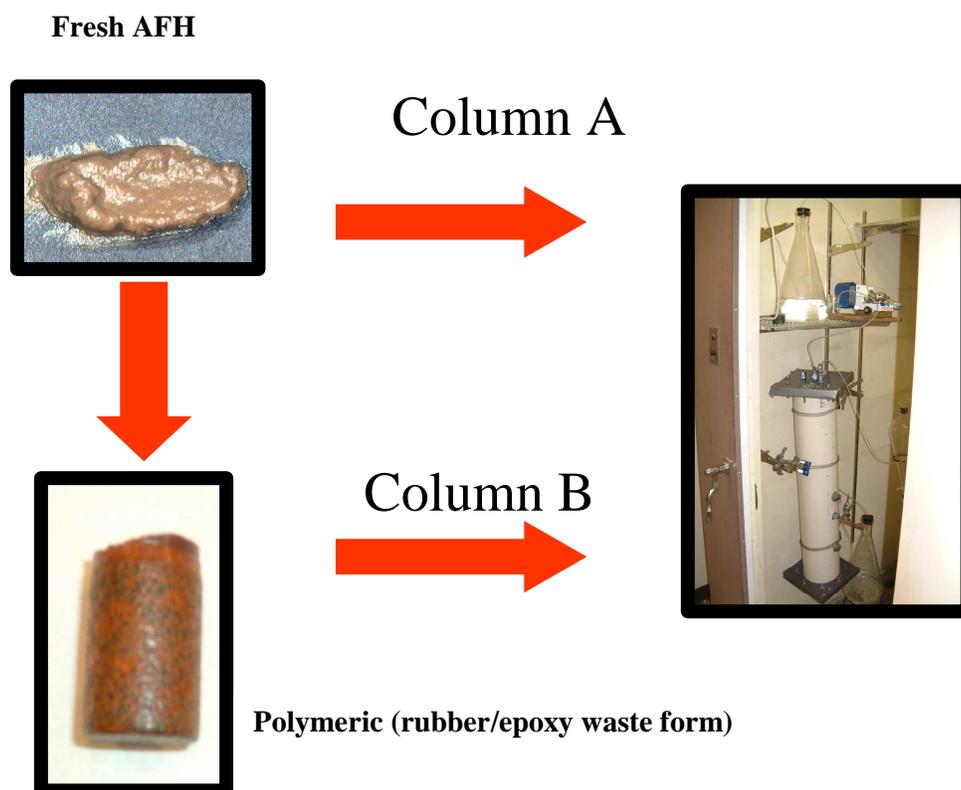


Figure 6.1: Schematic of experimental steps in setting up of encapsulated and unencapsulated bio leaching reactors.

The reactor design, flow condition and mode of operations of both the encapsulated and unencapsulated columns were same as detailed in experimental section of chapter 4 and 5. The only difference between the two columns lay in the type of ABSR loaded into each type. One reactor contained encapsulated sludge (dipped rods) and the other contained unencapsulated sludge (fresh) of the same starting Fe/As ratio (20:1). The unencapsulated (fresh) column consisted of 500g fresh sludge (60% water content) while the other column consisted of dipped rods contain up to 60% sludge (dwt). To maintain the same loadings between the two columns, each column was loaded with sludge so as to provide Fe content of 5 g/L of active bed.

For comparison purposes, both columns were loaded with equal amounts of the each component and were also fed from the same influent landfill leachate reservoir collected from Los Reales landfill.

Results and Discussion

Unencapsulated (Fresh) Column

Regime I. This is a period between 0 -107 days of the fresh column run. As described in the previous chapters, this regime describes the increase in both arsenic and iron concentrations to their corresponding maximum values. In this regime, even though there was an association between Fe and As concentrations in the earlier days of the column run, their relative rates of leaching differed in latter days of this leaching period. For instance by day 70, Fe leaching had reached a maximum concentration of 1800 mg/L (figure 6.3) whereas arsenic leaching continued to increase and reached a pick value of 20 mg/L at 107 days (figure 6.4) before it started slowing down. The observed pH of the column effluent leachate initially decreases from 8.4 to 7.2 whereas the ORP correspondingly decreased from +72 mV to - 157 mV (figure 6.2). These conditions are indicative of reducing conditions as those found in landfills. The decrease in pH is characteristic of maturing of MSW landfills. Cornwell et al, 2003, explained that MSW landfills goes through an acidic phase caused by the microbial production of volatile organic acids. This phase is normally followed by an alkaline, methanogenic phase as the landfill reaches maturity.

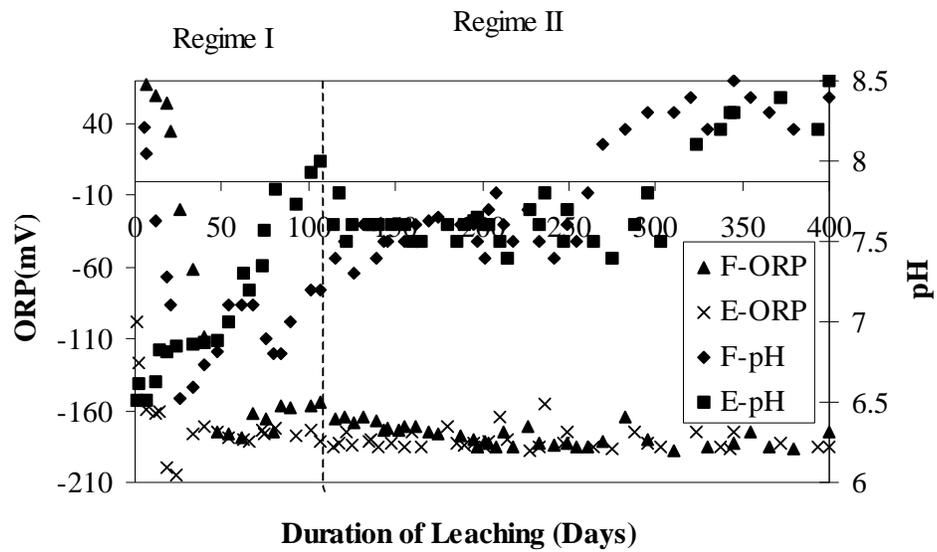
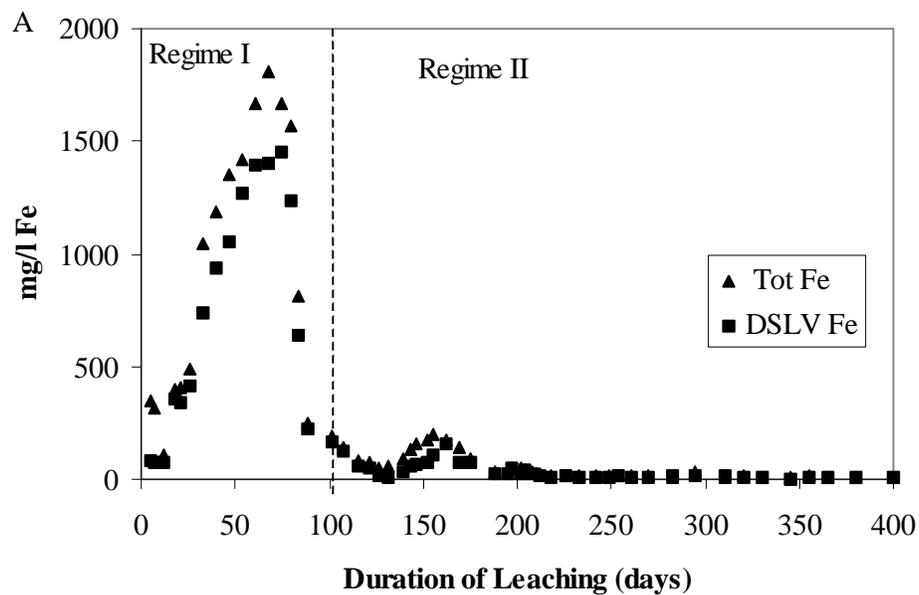


Figure 6.2 .ORP (mV) and pH variations of the two columns. Note that the pH and ORP trends of the two columns track each other though the columns run. The dotted lines separate the different kinetic regimes of the column run.



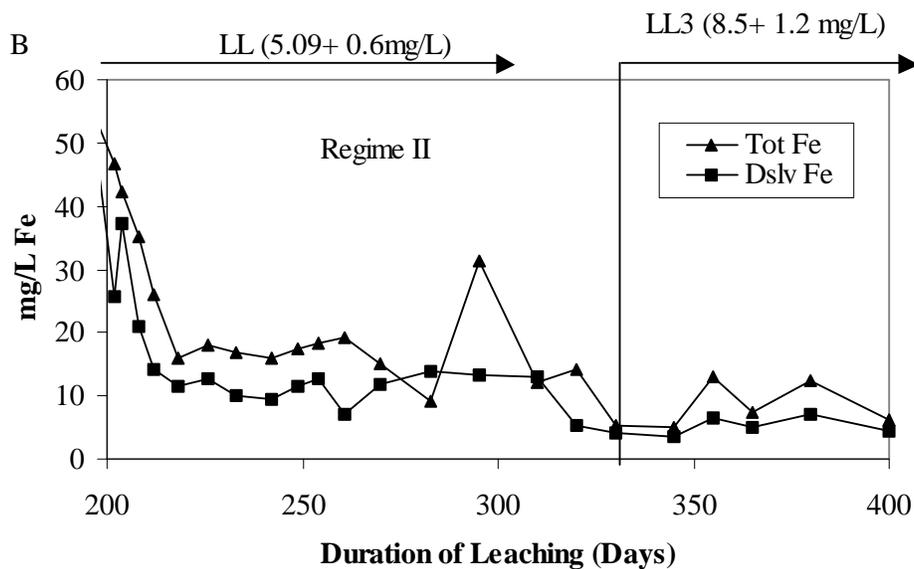
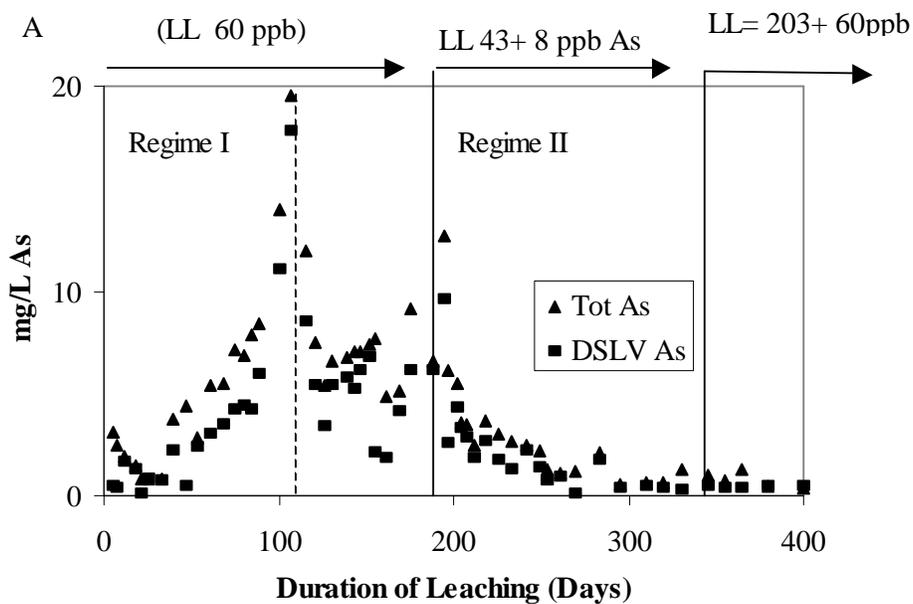


Figure 6.3. Total and dissolved Fe concentrations, in the effluent leachate solution from fresh column. (A) represents the entire column run and (B) represents the expanded scale of graph a after 200 days. Tot = Total (Dissolved + Particulates >0.45 μm) and Dslv = Dissolved (< than 0.45 μm).



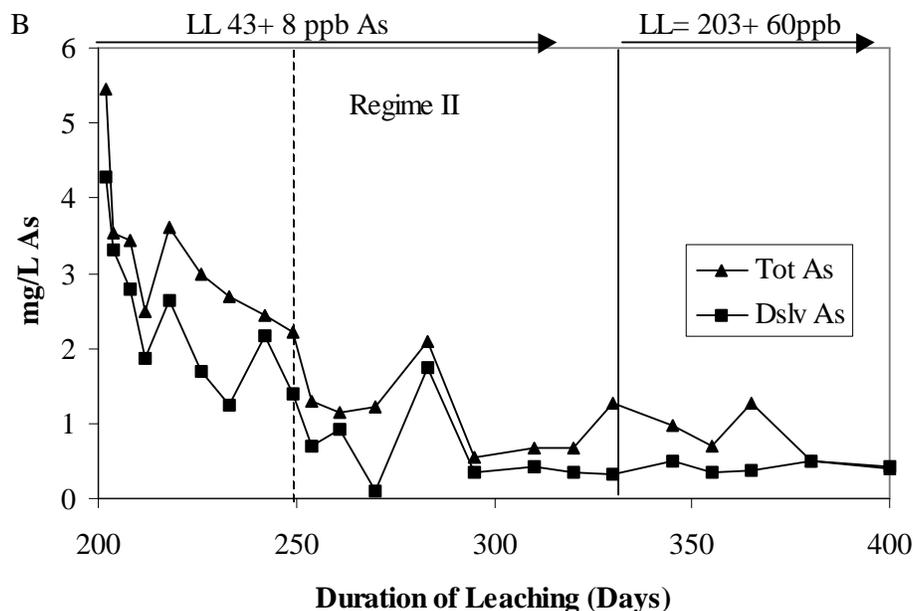


Figure 6.4. Total and dissolved As concentrations, in the effluent leachate solution from fresh column. (A) Represents the entire column run and (B) represents the expanded scale of graph a after 200 days. The dotted lines represent different Kinetic regimes whereas the solid lines represent days when there was a significant change in effluent LL concentration.

It is also evidently clear that in the first 100 days, arsenic and iron leaching from unstabilized AFH progressively increased with arsenic reaching values greater than the TC limit of 5 mg/L (Figure 6.4 A). The difference in rates of leaching between Fe and As during the latter days of this regime can be explained by a number of processes including mineral precipitation at elevated ion levels. It is also possible the complexation between ferrous complexes with carbonate, phosphate, and organic species that may be present in these landfill leachate lead to scavenging a significant proportion of iron thereby limiting its availability in effluent landfill leachate.

By the end of regime I, the cumulative fraction of iron and arsenic approximated 7% and 40% of their respective initial totals in the system (Figure 6.5). Soon after that, the rate of iron leaching started to slow down while the rate of iron leaching kept increasing (Figure 6.4).

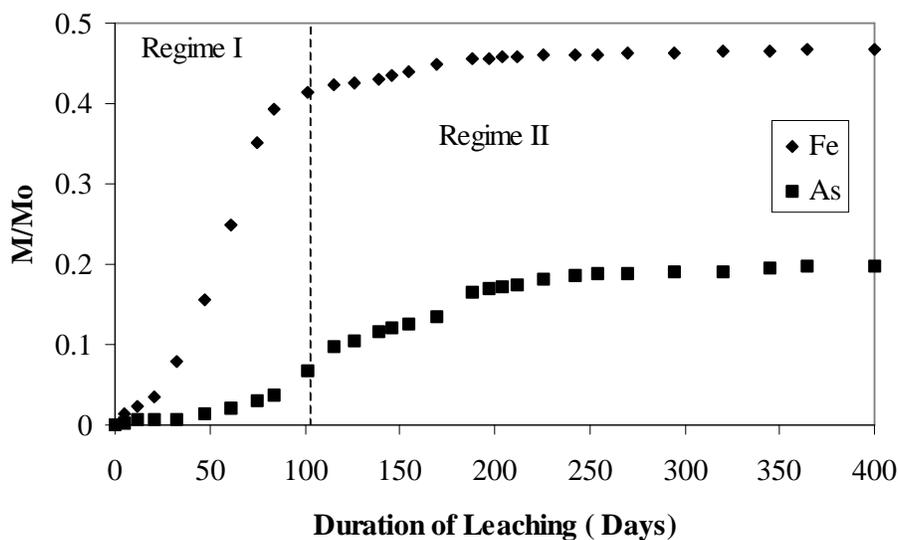


Figure 6.5 Cumulative mass fraction of arsenic and iron mobilized from a simulated landfill column over one year of operation. Note, the cumulative mass fraction of iron slowed down after 100 days whereas that of arsenic kept increasing.

Regime II.

This is a period between 100 - 400 days of the fresh column run. This period is characterised by a rapid and sudden drop in Fe and As concentration followed by a slow drop in their corresponding concentrations. During this period, the pH increased from 7.2 to 7.8 whereas the ORP, as expected decreased from -158 to -185 mV (figure 6.2). Both total and dissolved arsenic and iron concentrations continued to decrease. By 250 days, Fe leaching had dropped to 12 mg/L, which was 150X times lower than the maximum value recorded at the end of regime 1. Similarly, arsenic

leaching declined to about 1 mg/L, which was X20 less than the maximum recorded in regime I. Since the effluent Fe and As leachate composition was still higher (Figure 6.3B and 6.4B) than the influent landfill leachate amounts, this signifies that the extra iron and arsenic measured in the effluent leachate was coming from dissolution of the AFH previously loaded in the column.

By the end of the 250th day, had slowed down further. From then till the end of the column run, the pH and ORP had stabilised and averaged 8.4 and -182 mV respectively inductive of maturing of reduced landfill conditions. The total effluent Fe concentrations of Fe and arsenic were averaging 10 and 1 mg/L respectively, which is comparable to the range of the landfill leachate influent composition (figure 6.3B and 6.4B). This implied that mineral dissolution had even reduced further to very low levels. By the 400th day (end of regime 3), the rate of Fe and As leaching had slowed even further. By the end of the column run, 46% of total Fe had leached out whereas only 20 % As leached out (figure 6.5).

Discussion of Fresh AFH Column Results

There are a number of processes, which could have caused the different kinetic regimes shown above. The slowing down of the rate of leaching 100th day for Fe and 250 days for As could be attributed to initiation of processes such as:

- (1) Secondary mineralization occurring during microbial reduction of ferric (hydr)oxides.
- (2) The possibility of precipitation (beyond solubility product, K_{So}) of minerals like ferrous arsenate at high concentration of arsenic, which may immobilize arsenic.

(3) It is also probable that Fe (II) sorption on the on the ferrihydrite surface may have lead to enhanced sorption capacity of arsenic and slower dissolution rates of both iron and arsenic.

Secondary mineralization precipitations have been extensively studied. However, little is know about Fe (II) sorption on the on the ferrihydrite surface and its implication to arsenic mobility. For this reason, we conducted batch experiment to investigate whether Fe (II) sorption on ferrihydrite surface may have lead to enhanced sorption capacity of arsenic as well as slower dissolution rates of iron. The details of the methodology and study outcomes are described in chapter 7.

Encapsulated AFH Column

It is evident from Figure 6.2 that the pH and ORP had stabilised and averaged 8.4 and -185 mV respectively, which in the range of conditions noted from the fresh column. Based on this observation, leachability of the unencapsulated and encapsulated AFH can be compared since the conditions in both columns were similar. The dissolved and total (particulate plus dissolved) fractions of iron and arsenic leaching for the polymer encapsulated AFH columns are shown in figure 6.6 and 6.7 respectively.

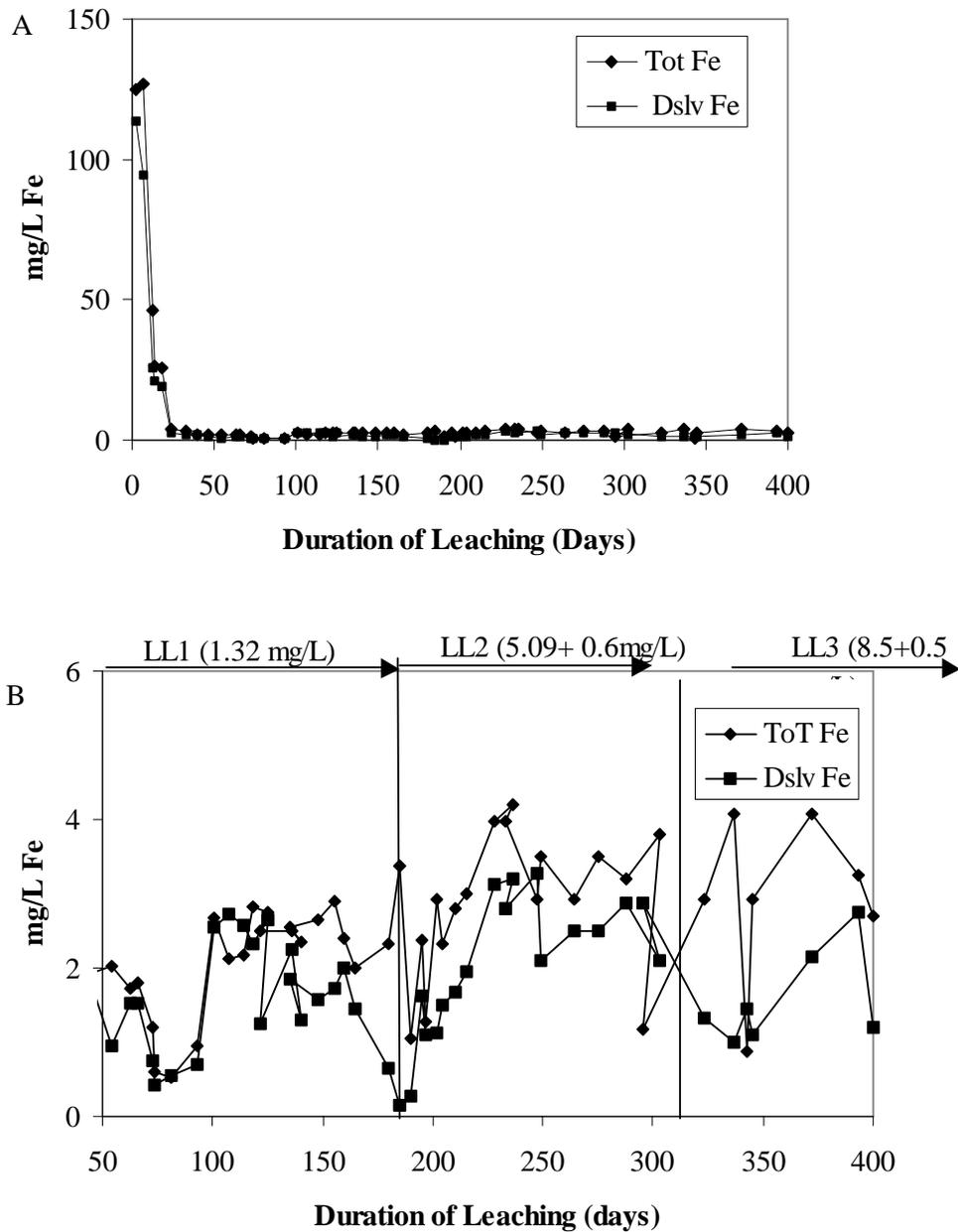
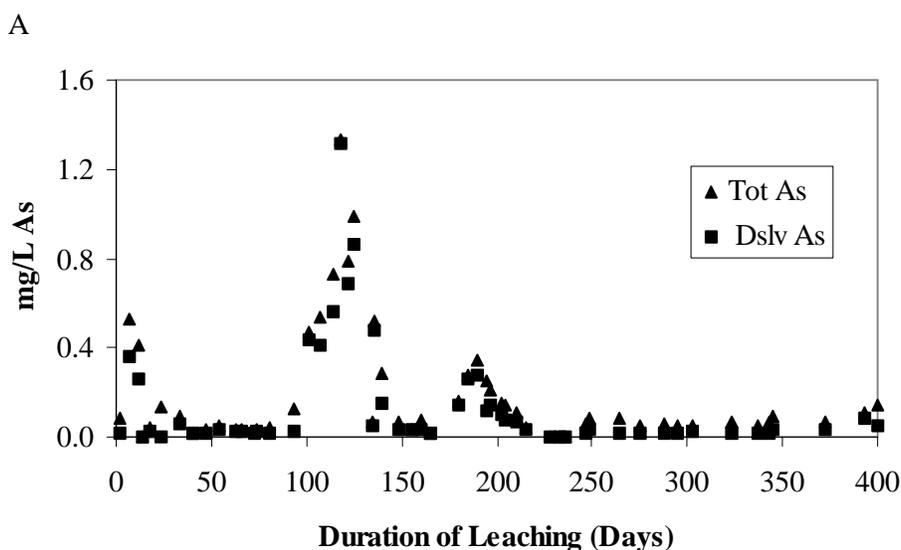


Figure 6.6. Total and dissolved Fe concentrations, in the effluent leachate solution from encapsulated column. (A) represents the entire column run and (B) represents the expanded scale of graph a after 50 days.

The expanded scale in figure 6.6 B shows that most of the total and dissolved Fe in the column leachate effluent was not due to AFH leaching but was due to Fe originally present in the landfill leachate. The composition of Fe and As present in the column influent is shown on the top most part of 6.6B and 6.7 B respectively. Arsenic leaching followed the same trend as Fe with the exception of the two peaks of arsenic at 1.3 ppm and 0.4 at day 105 and 190 days (Figure 6.7 A). Considering the 1.3 ppm peak, the calculated cumulative mass fraction leached over a period of 50 days approximated the mass As loaded in one rod. Therefore, it can be concluded that disintegrating of one the rods previously loaded in the column could have caused this spike. It is hypothesized that the disintegration could have been caused by active bed compression and /or microbial attack on the weak spots of the affected rod, which in turn exposed the AFH to strong reducing conditions and hence releasing arsenic.



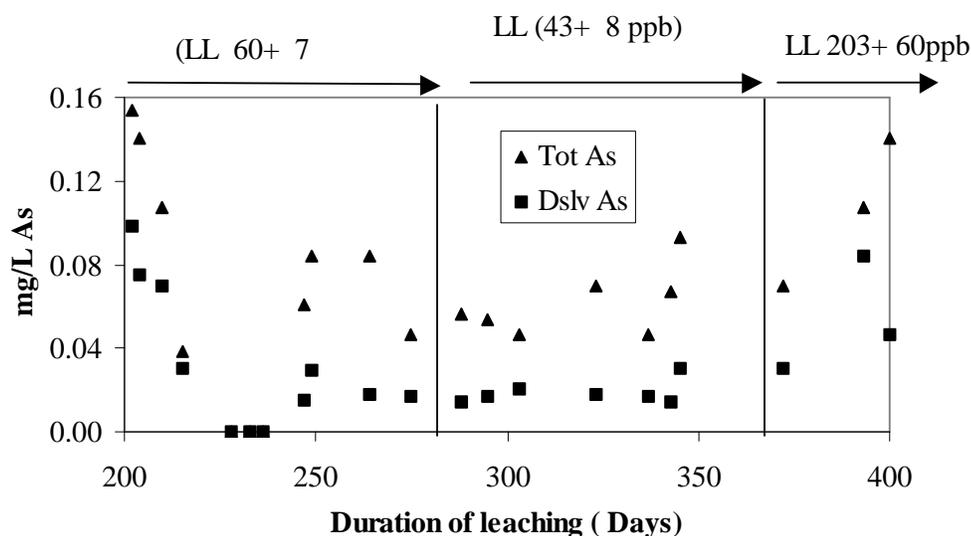


Figure 6.7. Total and dissolved As concentrations, in the effluent leachate solution from fresh column. (A) represents the entire column run and (B) represents the expanded scale of graph a after 200 days. The solid lines represent days when there was a significant change in effluent LL concentration.

Even with the breaking of one rod, which created a spike, the effluent concentration was still below the TCLP TC limit of 5 mg/L and of course far below the arsenic concentrations of unencapsulated AFH noted in figure 6.4. Once the exposed arsenic was washed out the column, arsenic concentrations remained close to detection levels (figure 6.7 B) for the rest of the column run with over 95% of arsenic in the effluent balancing the amount originally present in the landfill leachate.

Discussion of Encapsulated AFH Column Results

Polymer encapsulated AFH remains stable under fully biotic simulated landfill conditions, leaching arsenic concentrations of less than 0.5 ppm. Since the measured arsenic concentration in the effluent balances the influent concentration. These results

prove that this is a viable and effective technique for stabilizing ABSR. The waste forms are capable of containing high loadings (60% of more) of residuals with good leaching characteristics and excellent mechanical properties. As observed, encapsulation reduced arsenic leaching drastically by more than 100 orders of magnitude in leachate arsenic concentrations. It is now established that polymeric waste material is durable and can withstand aggressive simulated landfill conditions.

Acknowledgments

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CHAPTER 7
FERROUS IRON EFFECT ON ARSENATE SORPTION TO AMORPHOUS
FERRIC HYDROXIDE

Abstract

Amorphous ferric hydroxide (AFH) sorbents are commonly utilized for removal of arsenate from water. When disposed in microbially active, reducing environments such as landfills, Fe (II) will be generated by reductive dissolution of the AFH surface and arsenate will be desorbed. However, the observed ratio of arsenate (and, in fact, total arsenic) to total iron in the leachate is not consistent with the original ratio of arsenate to iron on the AFH. This paper describes work to determine if ferrous iron readsorption to the AFH can partially explain this inconsistency. As pH increases above 7, Fe (II) increasingly sorbs onto the AFH surface. This sorption is largely independent of ionic strength and somewhat irreversible at high pH. In contrast, arsenate partitioning to AFH decreases with increasing pH. However, over the pH range from 5 - 9, the presence of Fe(II) sorbed to the AFH surface increases the capacity for arsenate sorption. The experimental results indicate when no Fe(II) is present, arsenate binding is largely to surface sites inaccessible to Fe(II) binding. The results are also consistent with Fe(II) sorption to AFH sites, otherwise unfavorable to arsenate binding, and transformation of those sites into arsenate amenable binding sites.

Introduction

Fate of Iron in the Reduced Environments

Substantial quantities of arsenic-bearing solid residuals (ABSRs) are being generated as a consequence of the large-scale removal of arsenic from drinking water by adsorption processes currently being implemented in the United States and, to a lesser degree, worldwide. These residuals may be sorbents that are close to equilibrium saturation with aqueous arsenic at the source water concentration or largely amorphous solid sludges resulting from adsorption/co-precipitation of arsenic from the brines produced in the regeneration of those primary sorbents that are amenable to reuse. The reactivity of most common primary arsenic sorbents depends on iron (hydr)oxide surfaces, which have a relatively high capacity to adsorb both arsenate and arsenite oxyanions at near neutral pH. Likewise in the secondary processes used for arsenic removal from brines, adsorption/co-precipitation of arsenic occurs readily with ferric iron precipitation and constitutes the most common technique for treatment of arsenic-laden brines. Based on current EPA assessment tests, both primary and secondary iron-based ABSR typically are characterized as non-hazardous wastes and, consequently, may be disposed in municipal solid waste (MSW), non-hazardous landfills. However, recent work by a number of research groups shows that in mature MSW landfills, the high organic carbon content results in microbially-driven reducing conditions, which combined with slightly alkaline pH, an abundance of organic ligands, and spatially fluctuating redox fronts, are conducive to arsenic leaching (Ghosh et al, (2004a, 2006b, 2006c); Hooper et al, 1998; Jing et al, 2005b; Ford et al, 2006b)). Ghosh et al, 2006b, studied arsenic and iron leaching from an ABSR consisting of granular ferric hydroxide (GFH, a weakly crystalline α -FeOOH in

irregular grains up to 2 mm diameter) when exposed to simulated mature landfill conditions. Most of the iron and arsenic in the ABSR were released in less than three years of simulated disposal conditions. A significant portion of the iron leaching out from the column was dissolved Fe(II). It was concluded that reduction of the original sorbent's Fe(III) substrate to Fe(II) facilitated its dissolution. The loss of surface to dissolution released part of the sorbed arsenic, and this constituted the most important mechanism in the leaching of arsenic from the sorbent. It is noteworthy that the original arsenic sorbed on the GFH was in the form of arsenate, As(V), but the arsenic leached was largely reduced As(III). Other studies support the finding that reductive dissolution of iron and/or arsenic are important mechanisms in the mobilization of arsenic to the environment (Ford et al, 2006b; Delemos et al, 2006; Zobrist et al, 2000; Kocar et al, 2006; Langner et al, 2000; Pederson et al, 2000).

It is known that bacterial-driven dissimilatory iron reduction is self-inhibited by the accumulation of ferrous iron (Roden et al, 1999a; Hansel et al, 2003a; Royer et al, 2004). The inhibition has been connected with mass transfer limitations of the solubilized Fe(II), but evidence of secondary mineralization of the surface has also been identified in the case of ferrihydrite dissolution, leading to formation of magnetite and goethite (Hansel et al, 2005b; Zobrist et al, 2000, Zachara et al, 2002b). The picture becomes more complicated when the possible adsorption of Fe(II) to the solid ferric oxy/hydroxide is considered (Icopini et al, 2004; Roden et al, 2002b). It has been argued that Fe(II) sorption is partly responsible for inhibition of microbial respiration of Fe(III) (Ghosh et al, 2004a; Roden et al, 2002b, Zachara 2000a). However, experimental evidence has indicated that Fe(II)-Fe(III) electron

transfer at the aqueous/ferric oxy-hydroxide interface leads to oxidation of the sorbed Fe(II) by the solid phase Fe(III) matrix. In a recent work, Larese-Casanova and Scherer 2007 used Mössbauer spectroscopy tried to determine if a stable sorbed Fe(II) species would be possible on hematite. Their conclusion was that, at relatively low Fe(II) concentrations in the aqueous phase and near-neutral pH, the hematite surface becomes a complex mixture of Fe(II)-Fe(II) interacting sites, along with precipitated Fe(OH)₂. At higher Fe(II) concentrations, a stable sorbed layer of Fe(II) is formed. It is interesting to point out that systems in which convective motion of the aqueous phase removes dissolved Fe(II) from the vicinity of the interface probably will fall into the low-Fe(II) concentration regime.

Since Fe(II), As(V) and As(III) are all released into solution from ABSR as a consequence of its disposal in mature MSW landfill conditions, re-adsorption of Fe(II) to the remaining ABSR surface and its impact on re-adsorption of As(V) and As(III) directly impacts the timing, magnitude, and speciation of arsenic mobilized into the effluent leachate from the landfill. This role that adsorption of Fe(II) may play in altering the capacity of the sorbent's surface to retain and/or re-adsorb arsenic has received little attention. Although a lack of competition for possible surface sites between As(III) oxyanions and Fe(II) has been reported for goethite, only limited literature is available on the impact of Fe(II) adsorption on arsenic mobility (Dixit et al, 2006b). In this work, we examine the effects of the presence of Fe(II) on adsorption of arsenate ion on the surface of an amorphous ferric hydroxide (AFH). The AFH was synthesized using a method analogous to the process used for removing arsenate from drinking water by ferric chloride precipitation (Amy et al, 2000). The

main objective is to assess the possible role of soluble Fe(II) on arsenic mobilization in reducing environments. These results will provide needed information to assess the stability of ABSRs under landfill conditions.

Experimental Materials and Procedures

AFH Sludge Preparation

A 0.964 M Fe(III) solution was prepared by dissolving 259.4 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 1.00 L Milli-QTM water. The resultant solution was rapidly stirred at 100 rpm and allowed to equilibrate for 1 hr before adjusting the solution to pH 7 using a 10 M NaOH solution with vigorous stirring. The mixture was buffered using 0.001 M NaHCO_3 . The sludge mixture was then shaken on a reciprocating shaker table (Orbit, reciprocating speed of 30 rpm) for 30 minutes to ensure homogenization without causing the break-up of flocculated particles. The batch was allowed to settle and equilibrate for 14 days at 25°C. During this period, fluctuations in synthesis pH of ± 0.5 units were observed. These fluctuations were corrected by periodic adjustment with 0.1 M HCl or 0.1 M NaOH. Final solid-liquid separation was achieved by vacuum filtration through a 0.45 μm pore size cellulose acetate membrane filter resulting in 57 % (wt/wt) water content of the separated solids. This sludge passes the Paint Filter Test and would be suitable for disposal in a landfill. Liquid samples of the filter permeate and solid samples of the sludge (for digestion) were taken to verify the equilibrium solid and liquid concentrations and to close a mass balance on the iron originally introduced as reagents.

Experimental Setup and Procedures

Stock Preparation

All sorption experiments were conducted in continuously stirred batch reactors (CSBRs) at $25\pm 2^\circ\text{C}$ in the absence of light. Nitrogen gas was continuously bubbled through each reactor to displace oxygen and minimize the rate of oxidation of Fe(II). All solutions were prepared with degassed reagent-grade water prepared by boiling for 30 min and purging with ultra-high purity N_2 during cooling. A stock solution of 1.8 M Fe(II) was prepared by dissolving 89 g of $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$ in 250 mL of deoxygenated water, and pH was adjusted to 4.0 using NaOH. After stirring for 15 min, the solution was filtered through a 0.45- μm filter to remove any solids. The filtrate was then acidified to pH 2.0 with HCl, and its concentration verified by comparison with Fe(II) standards. The stock solutions were diluted to provide initial concentrations that were in the range 10-100 mg/L Fe(II). An arsenate stock solution (15 mM) was prepared using sodium arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$, KR grade, Aldrich/Sigma). Aqueous suspensions of AFH sludge (1.7 g dry AFH/L) were allowed to equilibrate at the pH of interest for at least 2 days and then deoxygenated by purging with ultra-high purity N_2 prior to contacting with arsenic and/or ferrous solutions. A description of the experiments performed follows.

Fe and As Sorption Kinetics

Fe and As kinetic sorption experiments were conducted in parallel to:

- 1) Select appropriate reaction times to be used for the “equilibrium” sorption/desorption experiments.
- 2) Quantify the dynamics of Fe (II)/As (V) uptake by AFH

Continuously stirred aqueous suspensions were prepared in 125-mL polypropylene bottles by adding appropriate volumes of water to AFH stock suspension. Suspension pH was then adjusted as necessary ranging from 6-8 (below and above the PZC of AFH). Using small volumes of 0.1 M HCl or NaOH. The ionic strength was fixed at 0.02M, which represents the background ionic strength of the sludge in water. The slurry was allowed to equilibrate overnight.

A small volume of Fe (II) stock solution was then added to initiate the kinetic reactions and achieve an overall Fe (II) concentration of 1000 μM in the suspensions. Preliminary adsorption experiments showed that these concentrations resulted in intermediate and nearly maximum Fe adsorption.

Aliquots of suspension were then regularly collected for a period of 30 days.

Another set of parallel As sorption kinetics experiments were also conducted at pH 6 and 8 (below and above the PZC of AFH). To have a final As(V) surface coverage on AFH of about 100% as reported by Pigna et al; 2006, 15.04 mM As(V)/L were initially added to the initially prepared and equilibrated aqueous suspensions of sludge solid phase (1.7 g dwt AFH /L) reactors . This concentration provides surface coverage maximum sorption density value of 4.9 mMolAs(V)/g AFH sorbed on the AFH at pH 6.

Equilibrium experiments for Fe(II) and As(V) Sorption

These experiments were conducted to determine the effect of the primary variables; pH, ionic strength, and total Fe(II) and As(V) concentration; on the extent of Fe(II)

and As(V) sorption on AFH. For these experiments, duplicate CSBRs corresponding to different pH or ionic strength solutions were prepared in 200-mL polypropylene bottles, while keeping all other factors constant. Degassed water and pre-equilibrated AFH (0.35 g AFH/ 200 mL solution) were added to each CSBR. The pH was readjusted, as needed using 0.1 M HCl or NaOH solutions. After equilibrating for 48 hr, Fe(II) at concentrations ranging from 0 to 1.9 mM, was added to the AFH suspensions, for the first set of experiments. In the second set of experiments, appropriate quantities of As(V) ranging from 0 to 15.0 mM As(V) were added to each AFH suspension. The reaction time was 48 hr, which was determined to be enough to reach quasi-equilibrium solution concentrations of all species (see Results and Discussion section). This reaction time is adequate to ensure near-constant aqueous concentrations, but avoid long-term structural changes to the surface of the AFH, which were observed to occur over periods of weeks.

At the end of the equilibrium sorption experiments with Fe(II), the pH of the solution in contact with the solid was lowered slightly using 0.1 M HCl. The slurry was then re-equilibrated for 48 hr. Dilution effects due to pH adjustments were assumed negligible, because the total added HCl solution volume was <1% of the volume of each reactor. The objective of these experiments was to determine whether the Fe(II) was reversibly sorbed onto the solid and would partition back into water or irreversibly sorbed and would stay on the surface. The latter case would be consistent with both simple irreversible sorption and transformation of Fe(II) into a mixed iron phase after sorption.

Co-sorption of Fe(II) and As(V)

Equilibrium experiments were conducted to quantify the effect of presorbed Fe(II) on arsenic adsorption in the pH range 6-8. Total concentrations of 1,128 mg/L As(V) and 75 mg/L Fe(II) were used in this study. In this series of experiments, the procedure employed for Fe(II) sorption and equilibration at a fixed pH was repeated as described above. After equilibration of AFH with Fe(II), As(V) was added to each reactor to achieve an initial solution concentration of 1,128 mg/L As(V). The reaction was allowed to equilibrate for 48 hr. The final pH of each CSBR was measured and recorded. Similarly, equilibrium experiments were conducted to quantify the effect of presorbed As(V) on Fe(II) adsorption in the pH range 6-8. Total concentrations of 1,128 mg/L of As(V) and 75 mg/L Fe(II) were also used in this study.

At the end of each of the experiments described above, liquid samples were withdrawn from each reactor, filtered through 0.45 μm cellulose nitrate syringe filters, pH-adjusted to 2.0 using 0.1 M HNO_3 (for arsenic determination) or as required for Fe determination using the SSA method (see below). In all cases, the amount of Fe(II) or As(V) sorbed to the AFH solids was calculated as the difference between the amount added initially and what remained in solution at equilibrium.

Fe(II) sorption reversibility

At the end of the equilibrium sorption experiments with Fe(II), the pH of the solution in contact with the solid was lowered slightly using 0.1 M HCl. The slurry was re-equilibrated for 48 hr. Dilution effects due to pH adjustments were assumed negligible because the total added HCl solution volume was <1% of the volume of

each reactor. As the results will show, sorption of Fe(II) increases monotonically with pH. Hence, lowering the pH should release Fe(II) into solution. The objective of these experiments was to determine whether Fe(II) sorbed on the solid would partition into water or would stay irreversibly sorbed on the surface. The latter case would suggest transformation of Fe(II) after sorption.

Instrumentation and Analysis

Liquid samples were analyzed for total arsenic and iron by ICPMS, consisting of an Agilent 1100 HPLC (Agilent Technologies, Inc) with a reverse-phase C18 column (Prodigy 3u ODS 150×4.60mm, Phenomenex, Torrance, CA) fitted with Agilent 7500a ICP-MS with a Babington nebulizer detector. Ferric ion concentration was determined by colorimetric measurement of the red ferric–sulfosalicylate complex formed at pH 2 obtained by addition of 5-sulfosalicylic acid to the sample. Total Fe determination in the sample was based on addition of ammonia to the sample to increase pH to 10. Total iron is measured at a wavelength of 425nm. The ratio between the volumes of the iron solution and volumes of SSA and ammonia solutions was 100:3:3 (Karamanev et al, 2002). The ferrous iron concentration was calculated as a difference between the total and ferric iron. Absorbance was measured using a Hitachi U-2000 Spectrophotometer.

Results and Discussion

Sorption Kinetics

Kinetic experiments for sorption of both Fe(II) and As(V) were performed at pH 6 and 8 (Figure 7a). More rapid sorption of As(V) occurred at a pH 6, while faster sorption of Fe(II) occurred at pH 8 (figure 7.1).

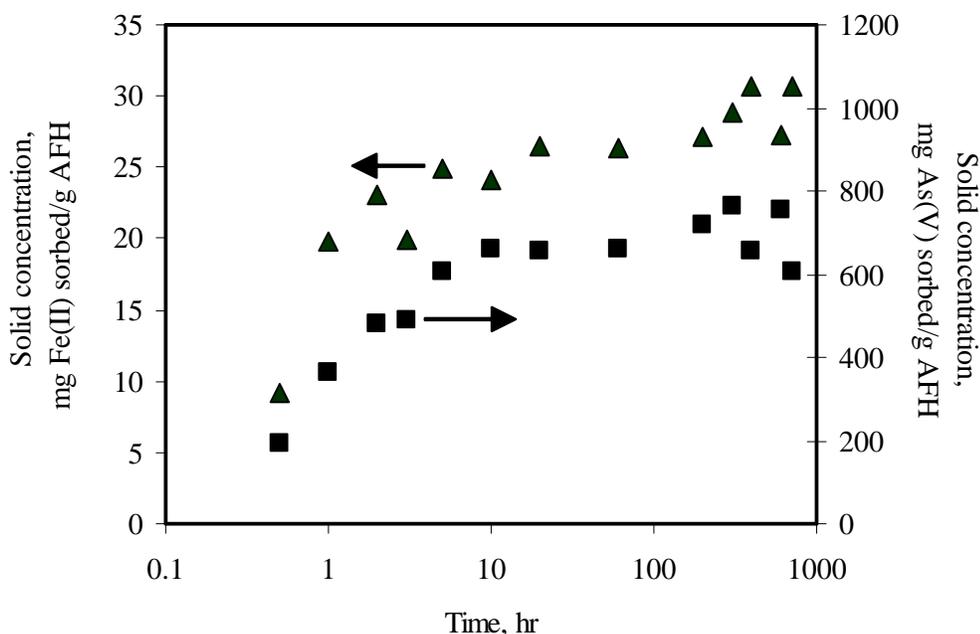


Fig. 7.1. Kinetics of Fe(II) (\blacktriangle) and As(V) (\blacksquare) sorption. The initial liquid concentrations were 60 mg/L for Fe(II) and 2,250 mg/L for As(V). Results shown correspond to pH 8. The solids were free of Fe(II) and As(V) initially. The ionic strength is 0.02 M and the suspension contained 1.7 g AFH/L.

Sorption of up to 60% of final mass of As occurred during the first hour, increasing to over 90% over the next 5 hours. 78% of Fe(II) sorption occurred during the first few hours. It was observed that the concentration of Fe(II) in solution kept decreasing with time over periods of weeks even in an anoxic environment. This behavior could be simply an indication of an inability to completely stop iron oxidation (and subsequent

precipitation). It might also be an indication of irreversible transformations of the sorbed Fe(II), such as the formation of new mixed Fe(II)/Fe(III) phases (Jeon et al, 2003; Welch et al, 2003) which would drive more of the dissolved iron onto the surface. Furthermore, the time scale for these changes is the same as that over which transformation of the AFH surface occurs (Ford et al, 2002a). At this point, there is not enough evidence to clearly suggest which one or more of these mechanisms is responsible for the long-term loss of Fe(II) from solution. Although the answer to this question is of some interest in understanding long timeframe sorption behavior, the objective of this work was concerned with the shorter-term behavior that is commensurate with the residence time of fluid movement through disposal environments. Thus, the data presented below are based on the end point of the initial pseudo-equilibrium achieved after 48 hr.

Fe (II) and As (V) Sorption

Equilibrium sorption measurements were carried out to quantify the effects of pH, total Fe(II) and As(V) concentration, and ionic strength on the extent of Fe(II) and As(V) sorption on AFH. The results of these experiments are presented in Figures 7.2 and 7.3 respectively.

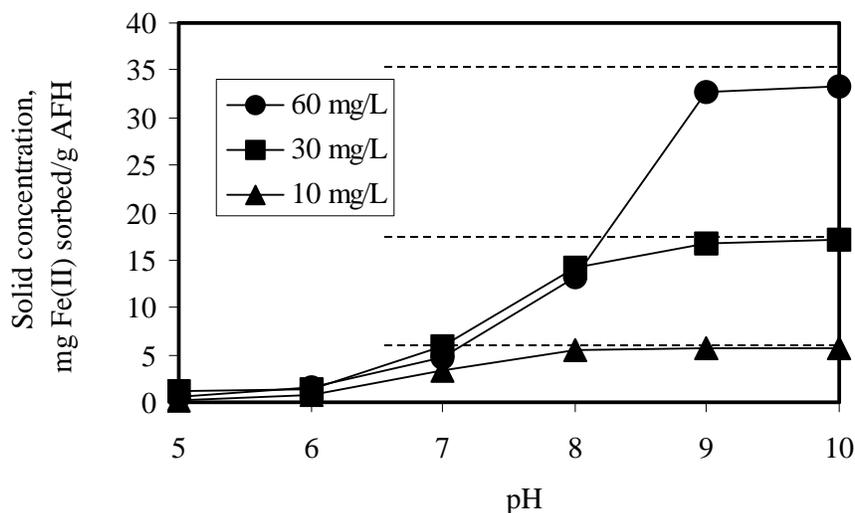


Figure 7.2. Effect of pH on sorption of Fe(II) to AFH in the absence of As(V). The legend represents initial Fe(II) concentration in the solution contacted with AFH. The ionic strength is 0.02 M and the suspension contained 1.7 g AFH/L. The horizontal dashed lines represent the solid concentration if 100% of the initial Fe(II) added were sorbed. Lines between data points are a visual guide.

As expected from surface charge considerations, sorption of Fe(II) increases with pH as the surface becomes more electronegative. Increases in the sorbed concentration with pH become more substantial around the point of zero charge of the surface, which is around pH 8 for ferrihydrite (Zhang et al, 1992, Strathmann et al, 2006). Similarly, sorption of As(V) decreases with increasing pH, since the negatively charged arsenate ions are less strongly attracted by the surface as it becomes more electronegative (figure 7.3). It is important to point out that significant dissolution of the AFH may occur at the extreme pHs used in the experiments (pHs 5 and 10).

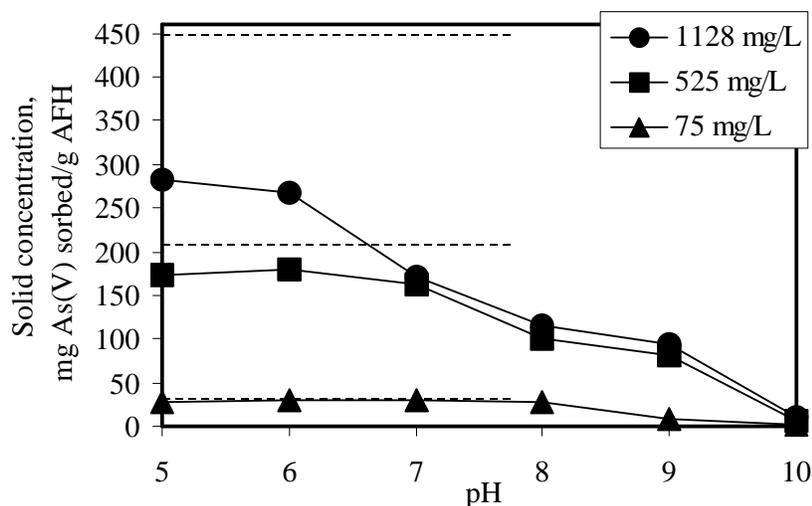


Figure 7.3 Effect of pH on sorption of As(V) to AFH in the absence of Fe(II). The legend represents the initial As(V) concentration in the solution contacted with AFH. The ionic strength is 0.02 M and the suspension contained 2.5 g AFH/L. The horizontal dashed lines represent the solid concentration if 100% of the initial As(V) added were sorbed.

In the range of the initial concentrations of Fe(II) employed (Figure 7.2), it is clear that, at high pH, the surface never becomes saturated; i.e. even at the highest initial concentration of 60 mg/L Fe(II), close to 100% of the Fe(II) is adsorbed at high pH. At intermediate pH, however, even though only a fraction of the initial Fe(II) is sorbed, there is a definite saturation effect. This is better appreciated in Figure 4 where the results of Figure 1 are plotted as an adsorption isotherm.

In the range of initial concentrations of Fe(II) employed (Figure 7.2), it is clear that, at high pHs, the surface never becomes saturated; i.e. even at the highest initial concentration of 60 mg/L Fe(II), close to 100% of the Fe(II) is adsorbed at high pHs. At intermediate pHs, however, even though only a fraction of the initial Fe(II) is

sorbed, there is a definite saturation effect. This is better appreciated in Figure 7.4 where the results of Figure 7.2 are plotted as an adsorption isotherm.

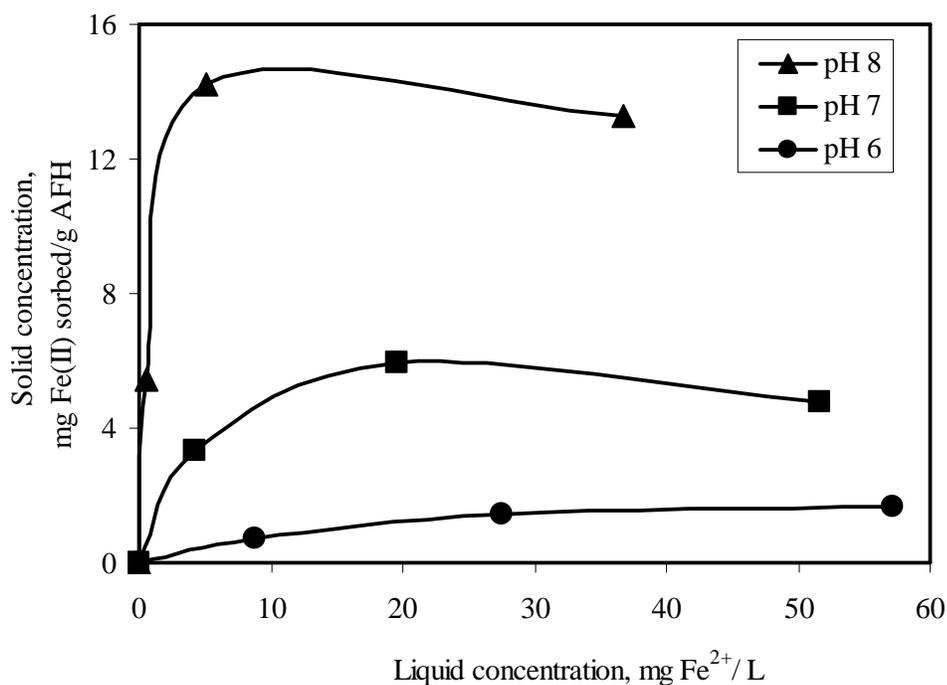


Figure 7.4. Adsorption isotherms for Fe(II) at room temperature and an ionic strength of 0.02 M. Solid lines are visual guides.

It is important to point out that significant dissolution of the AFH may occur at the extreme pHs used in the experiments (pH 5 and 10) and this may add an additional convoluting factor at these pH values. For the case of arsenic sorption (Figure 7.3), at the lowest initial solution concentration (75 mg/L) almost 100% adsorption is obtained at pH below 8. However, at higher system arsenic concentrations, significantly less than 100% of the total arsenic partitions to the AFH, even in the acidic pH range where the surface is positively charged. For the initial solution concentration of 1,128 mg/L, a maximum of only about 60% of the initial added arsenic was adsorbed at pH 5. Isotherms for As(V) are presented in Figure 7.5. A

saturation of available sites is evident in the range of concentrations evaluated for pH 7 and 8, but not for pH 6.

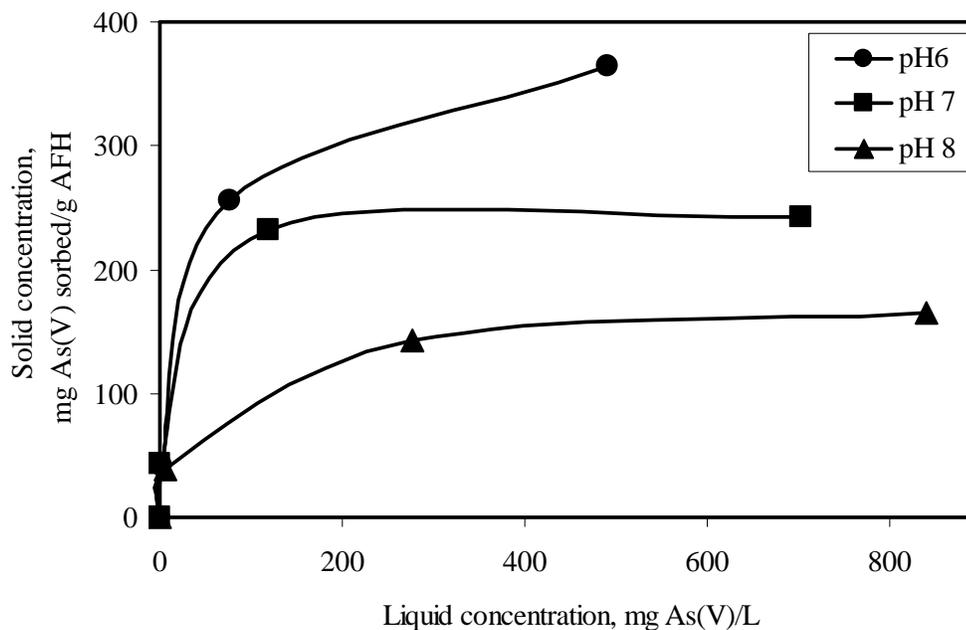


Figure 7.5. Adsorption isotherms for As(V) at room temperature and an ionic strength of 0.02 M. Solid lines are visual guides.

The AFH saturated surface site density at pH 7 can be calculated based on the observed maximum concentrations for Fe(II) and As(V) of 5.7 mg Fe(II)/g AFH and 220 mg As(V)/g AFH, respectively. The site density calculated for As(V) sorption (2.94 mM sites/g AFH) is about 30-fold greater than that calculated for Fe(II) sorption (0.10 mM sites/g AFH). This suggests that at neutral pH most of the AFH sites available for As(V) sorption are not favorable for Fe(II) sorption, so that the impact of direct competition by Fe(II) for As(V) sites should be minimal. The results also indicate that the best pH range to observe effects of combined Fe(II) and As(V) adsorption is pH 7-8 in which both species are sorbed in significant proportion. For

this reason, this range was adopted for the experiments with Fe(II)/As(V) mixtures described below.

Effect of Ionic Strength

It is clear from the pH study, that arsenic and iron sorption is affected by the charge of the AFH surface. In addition, access of dissolved ions to the surface can be affected potentially by the properties of the double layer that forms on the surface. The effect of solution ionic strength on sorption illustrates this dependency. Figure 7.6 shows that increasing ionic strength from 0.02 to 1.0 M has minimal effect on Fe(II) sorption.

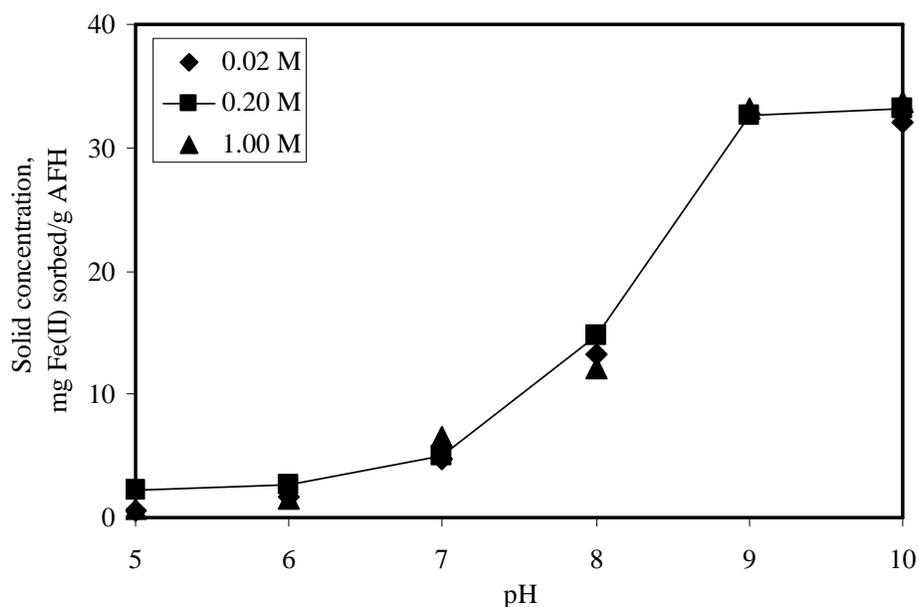


Figure 7.6. Effect of ionic strength on sorption of Fe (II). The initial Fe(II) concentration was 60 mg/L. The suspension contained 1.7 g AFH /L. Values in the legend are the ionic strength of the solution, adjusted by addition of NaCl.

Compression of the double layer at high ionic strength does not have an appreciable effect on the equilibrium sorption of Fe(II), indicating the bonding is primarily due to chemisorption (as opposed to weaker outer-sphere, physisorption). The practical implication of this result is that Fe(II) sorption at a given pH will not vary appreciably whether the process is occurring in a drinking water or a brine ionic strength matrix. Experimentally, the results indicate that the effect on adsorption of the ionic strength change caused by addition of arsenate to an Fe(II)/AFH slurry (as described below) will be negligible, since the ionic strengths utilized are always less than the concentrations shown in Figure 7.6.

Sorption reversibility

The results of the Fe(II) sorption reversibility experiments are shown in Figure 7. Solutions equilibrated at initial pH of 5, 7 and 8 were acidified to obtain final pH of 4, 6.5 and 7.5, respectively. For a given initial concentration of Fe(II), the equilibrium concentration increases monotonically with pH (Figure 7.2).

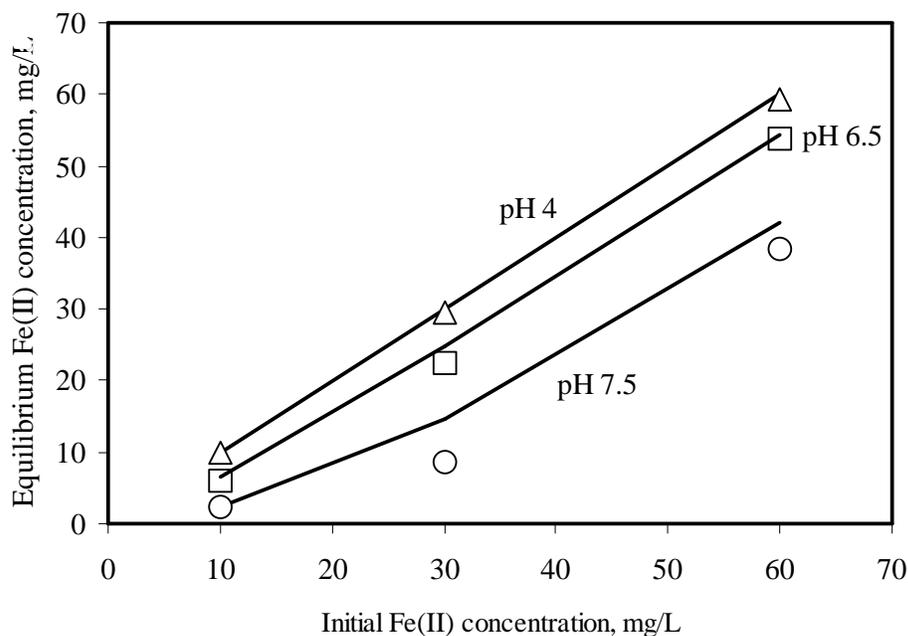


Figure 7.7. Reversibility of Fe(II) sorption as a function of the equilibration pH and ferrous iron concentration. Solid lines: expected equilibrium solution concentration at indicated pH. Symbols: measured concentrations when pH is lowered from 8 to 7.5 (O), 7 to 6.5 (\square), and 5 to 4 (\triangle). Conditions are as in Figure 7.2.

Hence, acidification of solutions should result in release of Fe(II) to achieve a new equilibrium. In Figure 7.7, the solid lines are the expected equilibrium concentration of Fe(II) after acidification (obtained by linear interpolation from the data in Figure 7.2), and the symbols are the new, observed equilibrium concentrations measured after acidification. For pH 4 and 6.5, no appreciable difference is observed. However, for pH 7.5, the new equilibrium concentrations are clearly lower than expected. This indicates that, at the more alkaline (and favorable) pH, a fraction of the Fe(II) has been adsorbed irreversibly. This is evidence that part of the sorbed Fe(II) has been incorporated to the solid phase either in the form of an irreversible chemical bond, or

by electron transfer to form a new surface species. It is interesting to note that this is only appreciable at high pH, which is the condition that favors Fe(II) sorption.

Weak Acid Extraction

The change in the solid structure of the sludge after adding Fe(II) to AFH was quantified by weak acid extraction (WAE). This procedure is based on the premise that short duration exposure to 0.4 M HCl solution will preferentially dissolve the amorphous iron solids, while leaving the crystalline phase largely undissolved. WAE is often used in sequential extraction procedures to separate the contributions of amorphous phases from those of crystalline phases (Tessier et al, 1979). The results in Figure 7.8 are presented in terms (i) of the fraction of total initial solid phase iron remaining in the solid phase after extraction and (ii) of the concentration of Fe (II) sorbed on the solid after extraction. The independent variable is the pH at which the AFH was initially equilibrated and for all samples 60 mg/L of Fe(II) was added to the AFH and allowed to equilibrate for 48 hours before WAE.

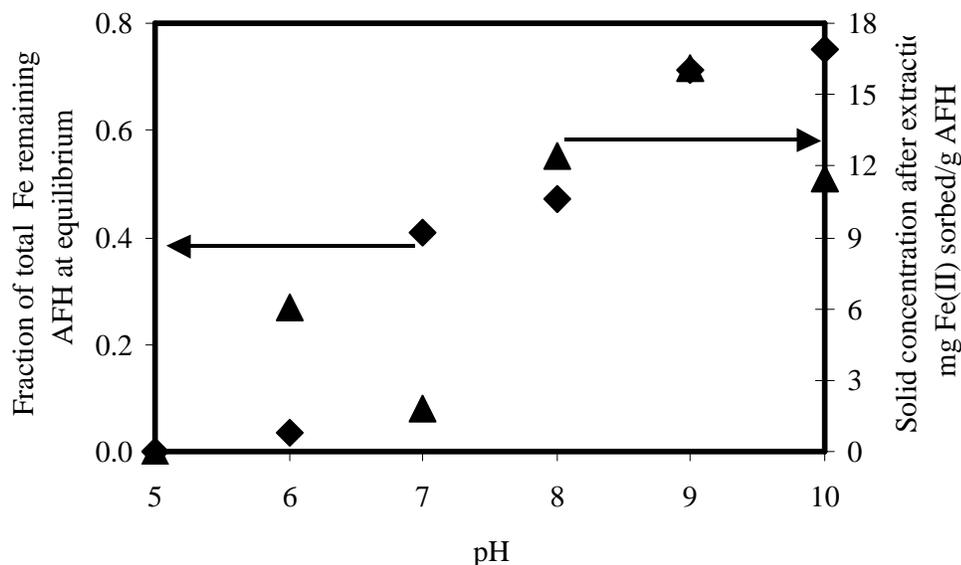


Figure 7.8 Weak acid extraction results as a function of pH. The suspensions initially contained 1.75 g AFH/L and 60 mg Fe(II)/L.

WAE solubilizes practically 100% of the iron in pH 7 AFH sludge when no Fe(II) is introduced into the system. However, as the fraction of adsorbed Fe(II) and pH increase, the fraction of total iron extracted by WAE decreases.

It is interesting to note that both the Fe(II) and total Fe extracted follow the same trends under all conditions, which points to a co-dissolution of both elements in the extraction tests. Figure 8 shows that the extent of transformation of fresh AFH is directly linked to the amount of adsorbed Fe(II) onto its surfaces at a fixed pH as well as the pH of the solution in contact with the AFH. Since high pH has been confirmed to favor increased adsorption of Fe (II) (Figure 7.2), some of the decrease in Fe(II) measured as pH increases can be attributed simply to greater adsorption with higher pH.

However, the sorbed concentration of Fe(II) associated with the crystalline fraction at a given pH is much less than that associated with the amorphous fraction. For instance at pH 9 with 60 mg/L Fe(II) in the system, the total sorbed Fe(II) is about 33 mg/g AFH (Figure 7.2), whereas there is only about 16 mg/g AFH in the crystalline phase (Figure 7.8). Accounting for a loss of about 25% of the solid with WAE (Figure 7.8), the aqueous phase concentrations of Fe(II) in equilibrium with the AFH before and after WAE are 2.9 mg Fe(II)/L and 40 mg Fe(II)/L, respectively. Thus, the crystalline phase of the AFH has about a 2-fold lower Fe(II) loading at about a 14-fold greater equilibrium aqueous concentration. Although insufficient data was gathered to plot a full isotherm for the crystalline phase adsorption of Fe (II), it is obviously much less than for the amorphous phase component of AFH.

Generally, the AFH is composed of an amorphous component that is extracted by weak HCL and an unextractable, partially crystalline phase. In earlier trials not shown here, samples of AFH with no Fe(II) added and equilibrated at various pH were examined by X-ray Diffraction (XRD). In no case were crystalline peaks observed by XRD, for AFH aged less than one month (as is the case in the trials described here). Thus, the crystalline phase alluded to be an operationally defined recalcitrant phase with respect to WAE, but not further identified as to specific mineralogic species. It does however seem to exhibit a significantly different adsorption capacity for Fe (II). The proportion of the partially crystalline component to the amorphous component increases with pH. This is consistent with other research that has reported that an increase in hydroxyl ion concentration also leads to increases in the degree of crystallinity of AFH sludges (Paige et al, 1997; Kim et al, 2003).

Co-sorption of Fe(II) and As(V)

An additional set of experiments investigated directly if there is competition between As(V) and Fe(II) for AFH surface sites. Figure 7.9 shows As isotherms with and without preequilibration of the AFH with 75 mg/L Fe(II).

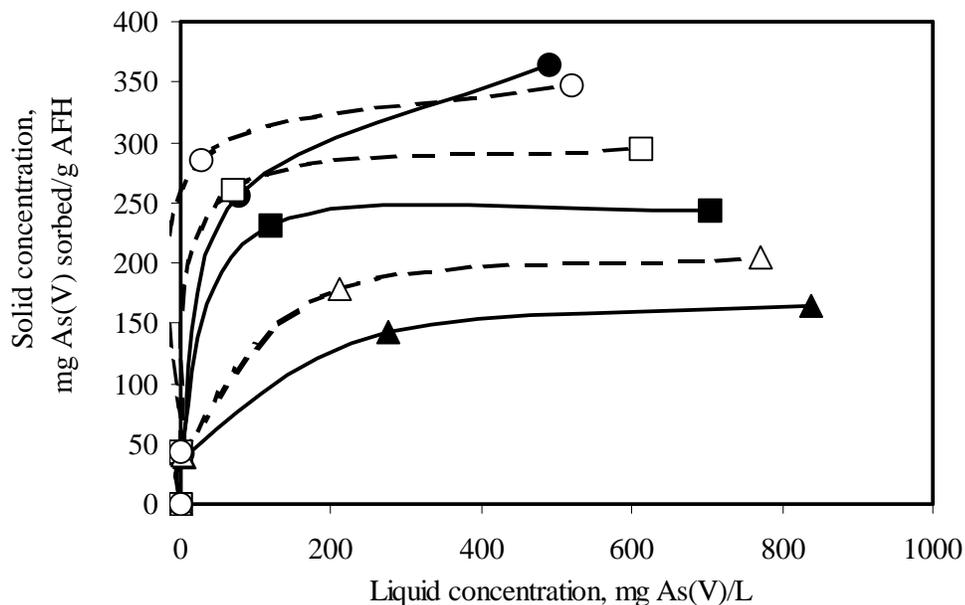


Figure 7.9 Adsorption isotherms for As(V) at room temperature and an ionic strength of 0.02M at three pH: pH 6 (\circ , \bullet), pH 7 (\square , \blacksquare) and pH 8 (Δ , \blacktriangle). Solid symbols and solid lines represent As(V) isotherms in the absence of Fe(II); open symbols and dashed lines represent As(V) isotherms with a solid that has been pre-equilibrated with an initial solution containing 75 mg/L Fe(II).

When AFH was pre-equilibrated with Fe(II), later spiked with As(V) and allowed 2 days re-equilibration, the addition of 15 mM As(V) did not result in desorption of Fe(II) (data not shown). For example, at pH 8 the final aqueous concentration of Fe(II) was $37 \text{ mg/L} \pm 4$, which is consistent with the values that had been previously observed in the absence of arsenic. For all pH values, the pre-addition of Fe(II) increased the capacity of the solid phase for subsequent sorption of As(V) (figure

7.9). The results do not suggest an electrostatic effect due to screening of negative surface charge by sorbed Fe(II), since the trend seems to be the same for all pH values considered. The fact that sorbed Fe(II) does not hinder arsenate sorption under conditions of near saturation for arsenic (as evidenced by the change in slope of the isotherms as the concentration of arsenate in the liquid increases) seems to indicate that either the two species occupy different sites on the surface or that there is cooperation between the two species upon sorption (i.e., arsenate would bind to sites already occupied by Fe(II)). This is supported by the earlier Fe(II) and As(V) saturation site density calculations indicating that most As(V) sites are not available for Fe(II) sorption. Addition of Fe(II) caused darkening of the ferrihydrite to a blacker, more magnetite-like color and suggests that a mixed iron oxide phase may be forming, rather than simple adsorption of Fe(II) on the AFH surface. However, this possibility was not verified by more definitive means.

To investigate if sorption of arsenic enhances sorption of Fe(II), additional experiments were performed in which AFH was pre-equilibrated with As(V), and then Fe(II) was added and allowed to equilibrate for 2 days.

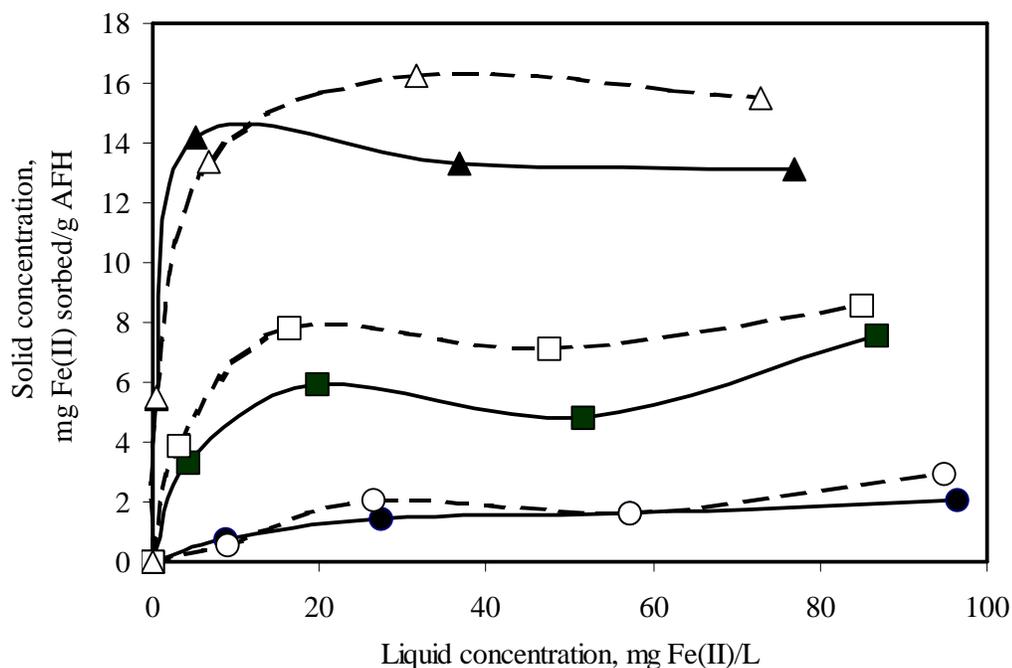


Figure 7.10. Adsorption isotherms for Fe(II) at room temperature and an ionic strength of 0.02 M at three pH: pH 6 (○, ●), pH 7 (□, ■) and pH 8 (△, ▲). Solid symbols and solid lines represent Fe(II) isotherms in the absence of arsenate; open symbols and dashed lines represent Fe(II) isotherms with a solid that has been pre-equilibrated with an initial solution containing 1,128 mg/L As(V).

The addition of Fe(II) did not result in significant desorption of the As(V) previously sorbed on the AFH (results not shown). However, the impact on Fe(II) sorption (Figure 101) seems to indicate that arsenic enhances sorption of Fe(II) at high pH and relatively high Fe(II) concentrations.

Concluding Remarks

The results of these experiments are important in predicting sorption/desorption behavior of AFH when both As(V) and Fe(II) are present in the aqueous phase. This would be the case, for instance, when AFH is produced during water treatment to

remove arsenate from drinking water and the ABSR is subsequently disposed in an MSW landfill as is the current practice. Under landfill conditions the ferric iron of AFH would be reductively released into the leachate as Fe(II) along with the sorbed As(V). Under these types of conditions, the results of this work suggest the following:

1. Fe(II) and As(V) sorb to largely distinct sites on an amorphous ferric hydroxide solid surface,
2. The Fe(II) sorption to AFH is largely unaffected by variation of ionic strength within the range encountered in water treatment and landfill disposal conditions,
3. The Fe(II) sorption to AFH in the alkaline pH range is to some degree irreversible,
4. Fresh AFH equilibrated at pH 7 and above is composed of a weak acid extractable fraction (operationally defined as amorphous) and a non-extractable fraction (operationally defined as crystalline) with the proportion of the latter phase increasing with equilibration pH,
5. The crystalline fraction of fresh AFH has a significantly lower As(V) sorption capacity than the amorphous AFH fraction, and
6. Fe(II) sorbed on AFH can provide new surface sites for arsenate sorption and hence act as a sink for arsenate released by reductive dissolution of a ferric-based sorbent.

Implications

The results of these experiments are important in predicting sorption/desorption behaviour of AFH which may occur when both As(V) and Fe(II) are present in the liquid and are in contact with AFH during the reductive dissolution of arsenic-bearing AFH by Fe(III)-reducing bacteria.

Indeed, our column experiment which attempted to simulate the leachability of a Fe:As 20:1 AFH and discussed in chapter 6 revealed that after one year of operation, only about 20% and 50% total As and Fe respectively had leached out the column. The results also revealed that after 100 days, the rate of leaching of both elements has decreased to very low levels. Based on the evidence presented in this chapter, It is now clear that reductive dissolution of arsenic-bearing AFH by Fe (III)-reducing bacteria may have promoted sorption of arsenic and reducing leachability.

Acknowledgments

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CHAPTER 8

SUMMARY AND CONCLUSIONS

AFH is one of the most commonly used sorbents in arsenic removal because of its high surface area and low cost. Therefore, a great percentage of ABSR will be generated from using AFH for arsenic treatment. It is now apparent that most residuals from most arsenic removal technologies currently pass the TCLP and can be disposed in non-hazardous landfills. Therefore, the evaluation of stability of AFH under reduced landfill conditions becomes important. This research work was aimed at determining and comparing short and long term arsenic stability in fresh and aged sludge amorphous ferric hydroxide sludges generated from brine treatment processes. This dissertation focused on three major areas of research involving arsenic-bearing AFH namely:

- (i) Determining the factors affecting the rate of aging of AFH generated from brine treatment processes
- (ii) Predicting and comparing short/long term stability of fresh and aged arsenic laden AFH.
- (iii) Evaluating the long-term effectiveness of encapsulation of AFH in polymeric matrices as a stabilization technology to reduce the potential for arsenic leaching.
- (iv) Providing evidence that sorption of Fe (II) onto AFH may enhance sorption of arsenic and hence reduce its mobility in the environment.

The outcomes of the study were used to draw the following conclusions below.

1. It was shown that arsenic sorption / desorption, as well the rate of aging of AFH are pH sensitive. Aged sludge has a lower affinity for arsenic at low pHs but higher affinity at high pHs. This is probably because since the aged sludge has less available adsorption sites for arsenic binding, the density of negative charges on the surface should be lower at higher pH. Also, the sludge synthesized at pH 7 exhibits slow rates of aging whereas sludge synthesized a pH 12 showed dramatic increase rates of aging resulting into a partially crystalline phase, whose stability is higher than that of the parent amorphous sludge. Whereas some authors have argued that in the aged solid, an appreciable amounts of arsenic become loosely bound to AFH and becomes readily extractable probably due to elimination of adsorptive coordination sites for surface arsenic, our results indicate that this does not occur at all pH ranges. At high synthesis pH, a considerable amount of arsenic becomes incorporated into the transformed solid and reduces its extractability. Even though pH is a dominate factor affecting arsenic retention, it not the only factor. The extent of how much arsenic is retained is also a function of other factors like the duration of aging, temperature as well as concentrations of anions like phosphate, sulfate and Ionic strength and NOM found in landfills.

2. Under landfill conditions, fresh AFH was unstable and will release As and Fe at a faster rate. In the first 240 days, As never decreased below 5 mg/L, which is the arsenic TC limit set for designation as a hazardous waste. Throughout the first 200 days of the run, particulate mobilization dominated arsenic leaching. This disparity is particularly significant in light of the fact that the standard batch leaching tests, TCLP

and WET, measure only the dissolved fraction, while the bulk of arsenic leaching from AFH is via particulate transport. In the course of a year's operation (total column run), 80% of the iron had leached whereas about 75% of the arsenic originally loaded into the column on the AFH had leached.

3. Aging of arsenic rich iron oxy hydroxides has serious implications to the long term storage of iron based AFH. It appears that desorption of arsenic from the crystallite Fe is the major driving force behind arsenic leachability and has profound effects over long periods of time. In the course of 2 years operation (total column run), 35% of the iron had leached whereas about 69% of the arsenic originally loaded into the column on the AFH had leached. Holistically, from the disposal point of view, aging can be beneficial in the long run because it took 2 years to leach 69% arsenic whereas it only took only 1 year for fresh sludge of the same starting Fe:As ratio to leach an approximate amount. for TCLP and WET where not designed to quantify the contribution of aging on total arsenic leachability.

4. Comparison of the extent of leaching between encapsulated and unencapsulated sludge showed that encapsulation reduced arsenic leaching drastically by more than 20 orders of magnitude in leachate arsenic concentrations. Encapsulated AFH leached arsenic concentrations of less than 0.5 ppm throughout a one period year. It is now certain that the polymeric waste material is stable and can with stand simulated landfill conditions. Polymer encapsulation is attractive, effective and therefore necessary to ensure that arsenic will not be mobilised.

5. The reduction of Fe contained in AFH may not be sufficient to mobilize all the sorbed As (V) as previously thought. Fe (II) sorbed on AFH enhances arsenic sorption

and reducing its mobility. Enhanced retention of arsenic may be resulting from: (i) Either the formation of new Fe (II)-As(V) solid phases or (ii) Incorporation of some As in aged secondary precipitates or (iii) Adsorption of arsenic on the “new” Fe(II)-AFH” precipitate. Sorption isotherms revealed that the extent of arsenic sorption enhancement is a function equilibration pH as well as concentration of Fe (II) concentrations. The optimum adsorption pH to obtain adsorption maxima for Fe(II) and As(V) when both are present in solution is about pH 7-8.

Enhancement of As(V) sorption by Fe(II) can be used to explain that fact that after one year of operation, only about 20% and 50% total As and Fe respectively had leached out the Fe:As 20:1 column. These values were lower than those obtained from leaching Fe:As 5.7:1 sludge (80% of the iron and about 75% had leached). It is now clear that reductive dissolution of arsenic-bearing AFH by Fe (III)-reducing bacteria may have promoted sorption of arsenic in the Fe:As 20:1 column and this could have reduced its mobility/leachability.

APPENDIX A

SUPPLEMENTARY INFORMATION FOR REAL BRINE SOLUTION

Supplementary Information of actual composition of brines solutions obtained from four different locations in the US. The arsenic concentration of the synthetic brine described in the previous chapter 2 and 3 was higher than the average concentration of each of the brine solutions shown in the table below.

TABLE B-1. Composition of four brine solutions obtained from four different locations in USA.

Source	Type of Unit Operation	[Cl-] ppm	[NO3-] ppm	[SO4] ppm	[CLO-] ppm	As ppb	[F-] ppm	pH
Rubidoux, CA	IX	32270.31	1161.19	1026.93	0.57	74.66	0.00	8.3
Rubidoux, CA	IX	53355.55	1420.59	150.92	0.87	80.88	0.00	8.3
Rubidoux, CA	IX	23002.32	1251.55	3942.12	0.54	49.77	0.00	8.3
29 palms, CA	AA	29.70	1.23	2477.60	0.00	0.00	1418.69	8.0
29 palms, CA	AA	19.60	1.53	2027.29	0.00	0.00	1031.27	8.0
29 palms, CA	AA	21.54	1.57	2506.71	0.00	0.00	1137.61	8.0
Ajo, AZ	AA	106.53	3.74	746.73	0.00	734.15	230.49	6.7
Ajo, AZ	AA	101.16	2.79	505.45	0.00	329.74	459.78	6.7
Ajo, AZ	AA	96.18	2.62	314.14	0.00	348.41	810.08	6.7
Fruitland, ID	IX	748.23	1186.09	29193.20	0.00	ND	5.99	7.68
Fruitland, ID	IX	29345.56	2687.45	58.81	0.00	ND	61.99	7.68
Fruitland, ID	IX	22521.71	4053.75	5415.00	0.00	ND	14.56	7.68

APPENDIX B

AGING OF FRESH SLUDGE

SEM images comparing the structural differences between fresh and aged sludges. The effect of such structural changes (caused by aging) on arsenic retention was extensively characterised and described in chapter 2 and 3.

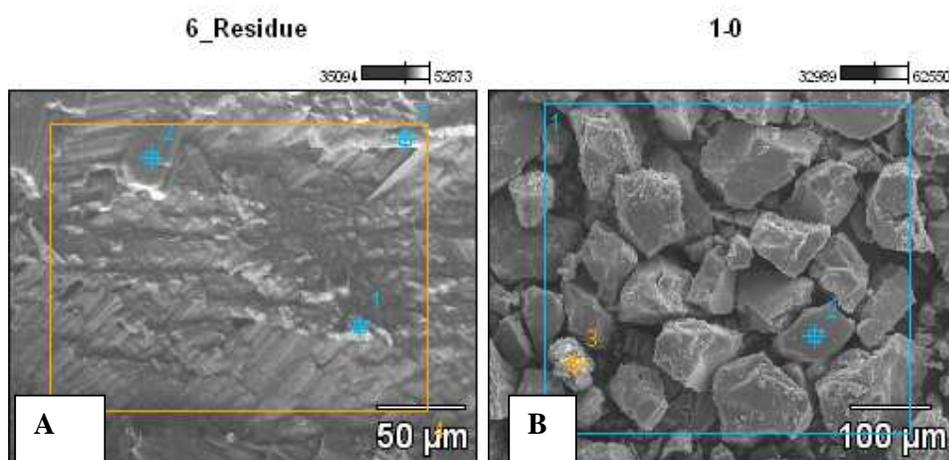


FIGURE B-1. SEM images for fresh sludge (A) and aged sludges (B). The structural changes between the two sludges are distinct.

APPENDIX C

SUPPLEMENTARY INFORMATION FOR LEACHING TRIALS

Batch leaching trials were conducted on fresh and aged sludges in parallel. The synthesis pH for the sludges was 7, 9 and 12. The sludges were then subjected to leaching tests similar to those described in chapter 2. The results are represented as partition coefficient K_d that represents the ratio between concentrations of As on the solid and that in the liquid.

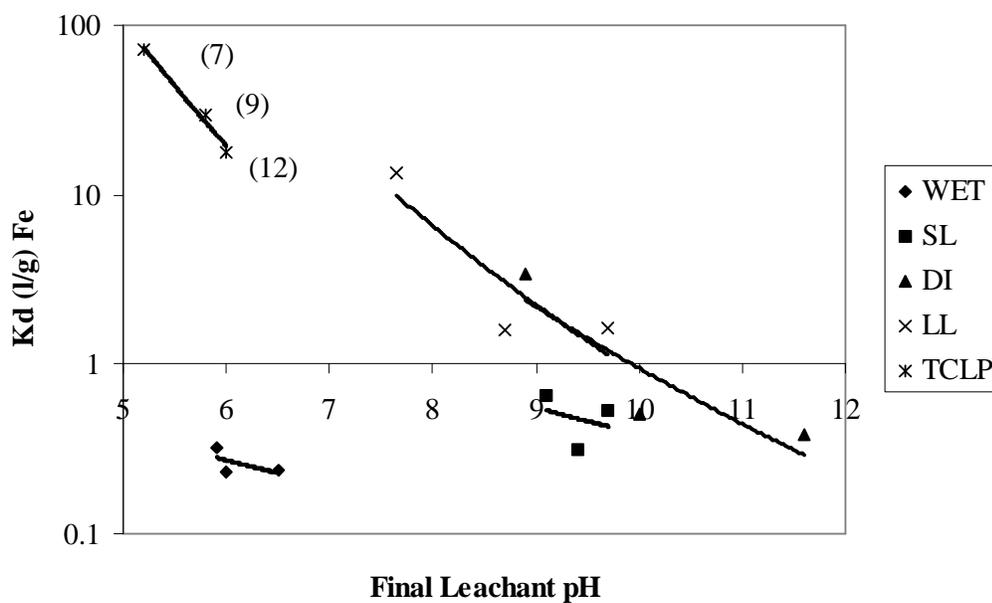


FIGURE C-1. Arsenic partition (K_d) represented as a function of sludge synthesis pH and also equilibration pH of the leachant solution for fresh sludge.

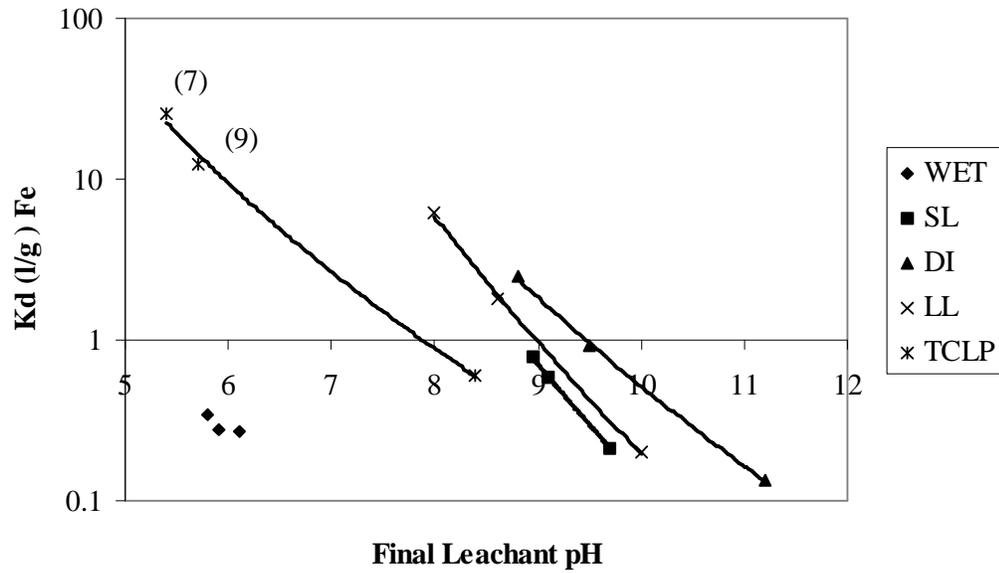
APPENDIX C *continued*.....

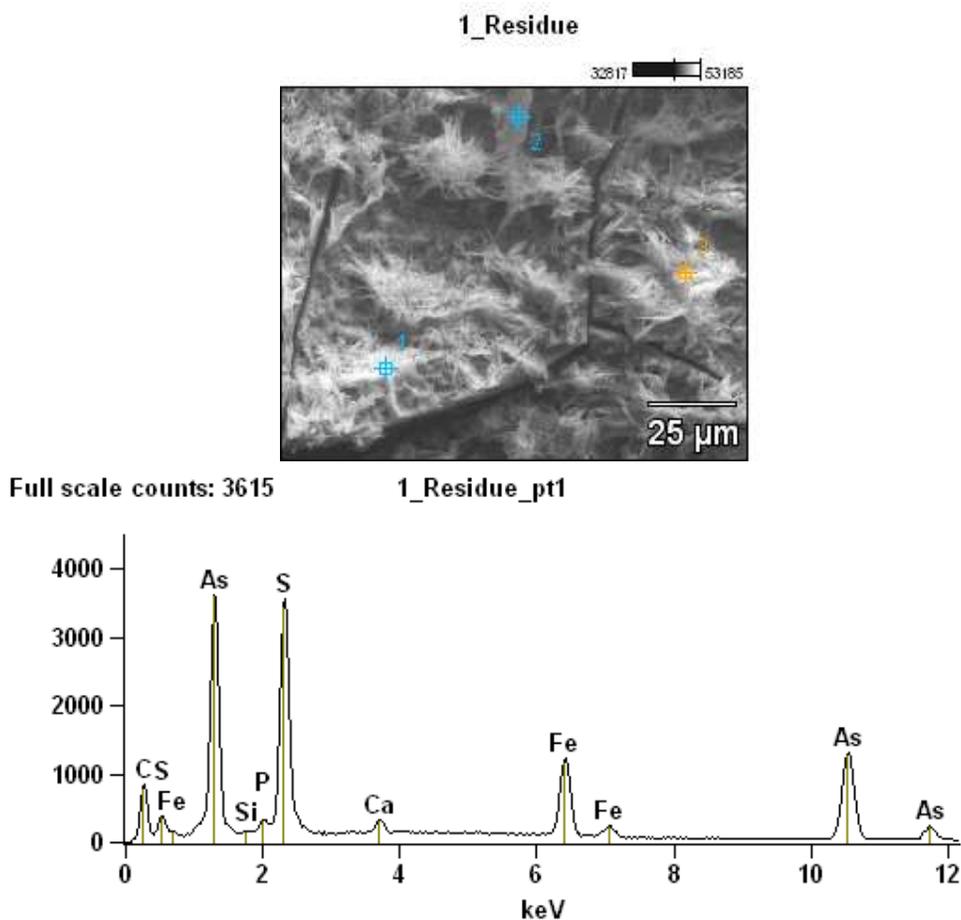
FIGURE C-2. Arsenic partition (K_d) represented as a function of sludge synthesis pH and also equilibration pH of the leachant solution for aged sludge.

APPENDIX D

1:5.7 SLUDGE RESIDUAL LEFT AFTER LONG TERM COLUMN LEACHING.

SEM image showing the residual solid material left after long term column leaching.

Results of the column leaching of AFH were extensively discussed in chapter 4. EDX analysis revealed that the mineral phase described below is rich in Fe-As- Ca.



APPENDIX D *continued*.....

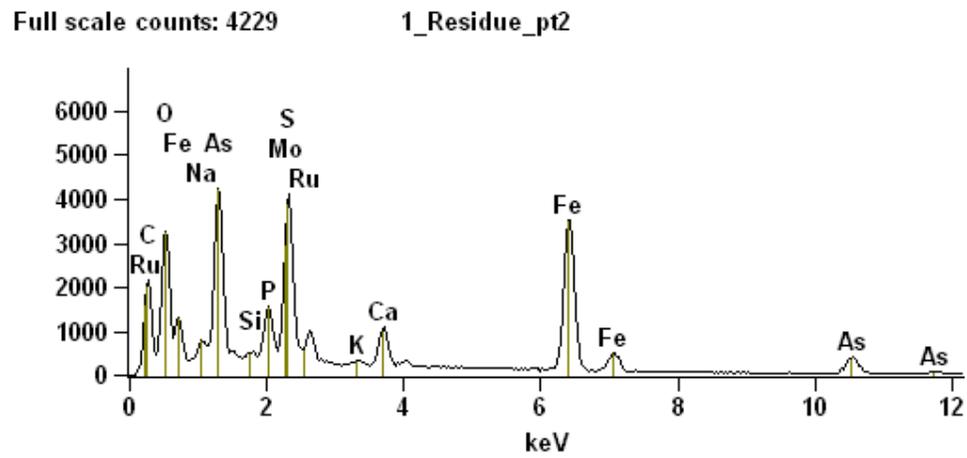
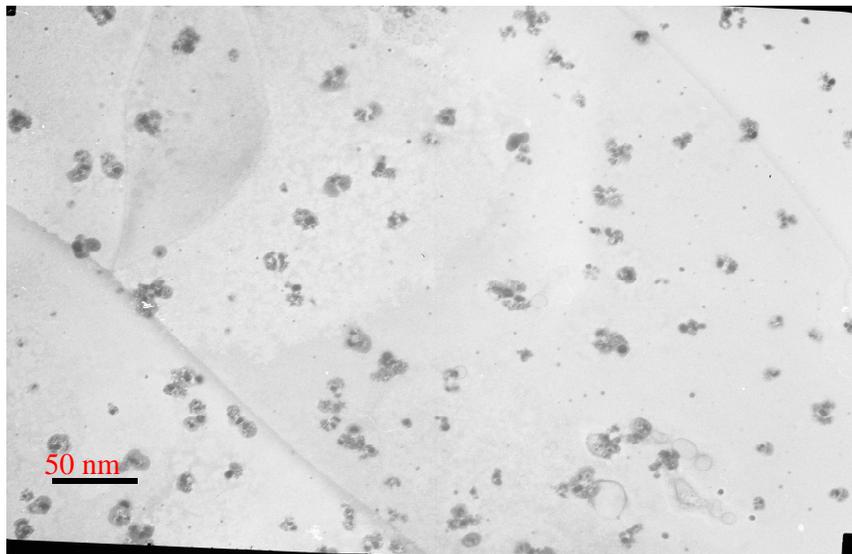


FIGURE D. SEM-EDX analysis showing the ordering sludge into a visibly crystallite mineral solid.

APPENDIX E

TEM IMAGE SHOWING THE DISTRIBUTION OF COLLOIDS IN THE
EFFLUENT COLUMN SAMPLE

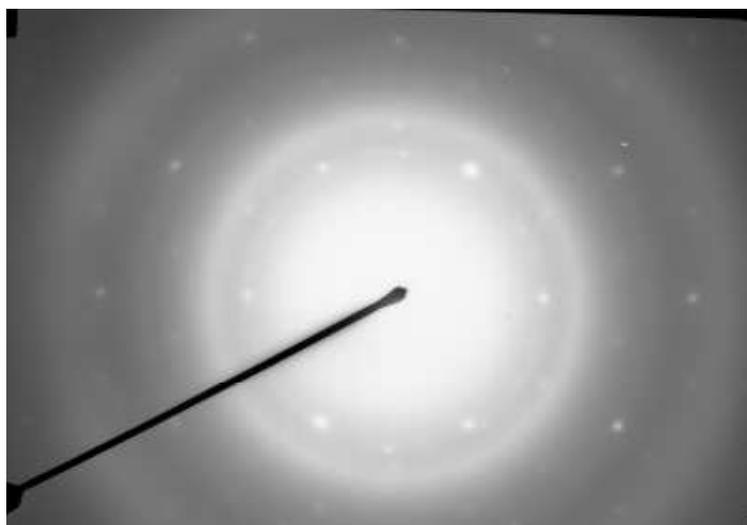
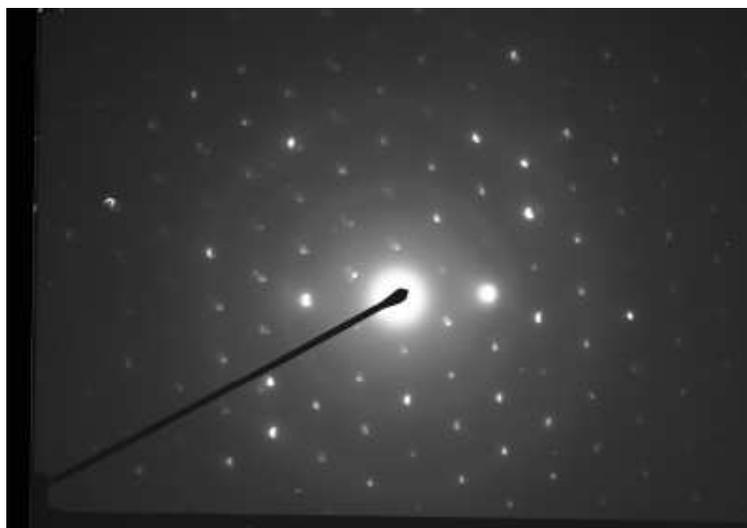
These colloids may be responsible for transporting high level of arsenic.



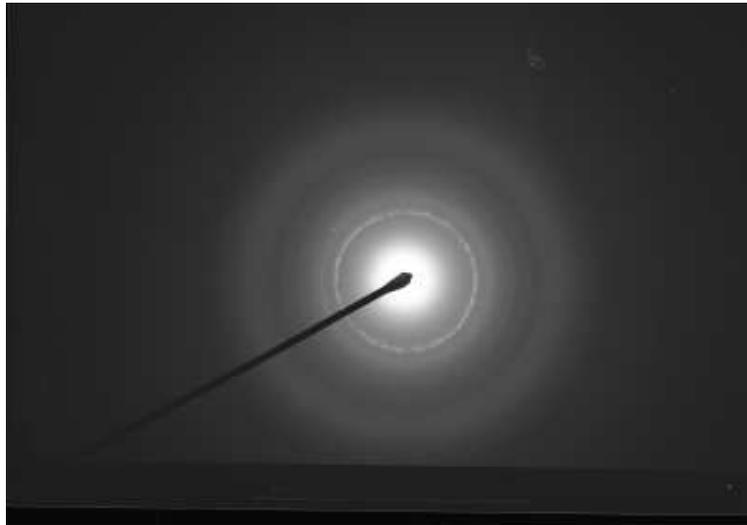
APPENDIX F

TEM IMAGES CHARACTERIZING COLLOIDAL PARTICLES IN THE
EFFLUENT OF THE COLUMN.

These structures revealed that the particle responsible for leaching of could be crystalline in nature.



APPENDIX F *continued*.....



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