CHARACTERIZATION AND STABILIZATION OF ARSENIC IN WATER TREATMENT RESIDUALS

A Thesis

by

HUN YOUNG WEE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2003

Major Subject: Civil Engineering

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ABSTRACT

Characterization and Stabilization of Arsenic in
Water Treatment Residuals. (August 2003)
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The characterization of water treatment residuals containing arsenic was investigated in the first study. Arsenic desorption and leachability from the residuals were the focus of this study. Arsenic leaching from water treatment residuals was found to be underestimated by the toxicity characteristic leaching test (TCLP) due to the pH of the leachates being favorable for As(V) adsorption. Competitive desorption of arsenic with phosphate was significant because phosphate tends to compete with As(V) on the surface of the metal hydroxide for adsorption sites. However, arsenic desorption by the competition of sulfate and chloride was found to be negligible. The pH in the leachate was a critical variable in controlling arsenic stability in the residuals. The release of arsenic from the residuals was elevated at low and high pH due to the increase dissolution of the adsorbents such as Fe and Al hydroxides.

In the second phase of the study, the stabilization techniques for arsenic contained residuals were examined to develop methods to suitably stabilize arsenic to eliminate and/or minimize leaching. A decrease of arsenic leaching was achieved by the addition of lime to the residuals and believed to be due to the formation of less soluble and stable calcium-arsenic compounds. However, it is suggested that the ordinary Portland cement (OPC) should be added with the lime for the long term stabilization because lime can be slowly consumed when directly exposed to atmospheric CO_2. The solidification and stabilization (S/S) technique with lime and OPC was shown to be successfully applied to the immobilization of a wide variety of arsenic tainted water treatment residuals.

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CHAPTER I

INTRODUCTION

Arsenic is commonly recognized as a toxic and carcinogenic metal compound (Bates et al, 1992; Smith et al, 1992). The adverse health effects when humans are exposed to arsenic compounds are well documented (USEPA, 2000). Anthropogenic and natural sources of arsenic are present in the environment. Human activities generate anthropogenic arsenic compounds through the formulation of herbicides, pesticides, and fertilizers (Ferguson & Gavis, 1972). Riveros et al (2001) rigorously reviewed the arsenic generation problems and disposal practices of the metallurgical industry. Arsenic waste generated from various metal extractions and refining operations is a serious problem (Dutre & Vandecasteele, 1998). Arsenic can be generated naturally in rocks, soil, water, and air. Natural water can be contaminated by the discharge of arsenic through geochemical processes: dissolution of iron oxyhydroxides containing arsenic under reducing conditions, oxidation of arsenic-bearing minerals, and desorption of arsenic by a competing ligand, e.g., phosphate (Bose & Sharma, 2002; Mariner & Willey, 1976).

This thesis follows the style and format of the *Journal American Water Works Association*.

Arsenic contamination of groundwater and/or drinking water has been reported as a critical water quality issue in Vietnam, Bangladesh, and West Bengal, India (Berg et al, 2001; Chakraborti et al, 1999; Nickson et al, 1998). In particular, 70 million people in Bangladesh have been poisoned due to naturally occurring arsenic in wells used for drinking water sources (Lepkowski, 1998). Highly elevated concentrations of arsenic (greater than 1 mg/L) have been commonly detected in the area.

Consequently, arsenic treatment of contaminated surface and groundwater is very important in order to supply people with good standing drinking water. Recently, more attention has been paid to arsenic removal in water treatment due to the U.S. Environmental Protection Agency (USEPA) lowering the Maximum Contaminant Level (MCL) from 50 to 10 μg/L, effective in 2006 (USEPA, 2001). Therefore, it is expected that many water treatment plants (WTPs) may require additional treatment technologies or modification of existing treatment technologies to meet the revised arsenic MCL. Precipitation/coprecipitation with ferric salts is considered to be the " Best Demonstrated Available Technology" (BDAT) for the removal of arsenic in water by U.S. EPA (USEPA, 1990) and has been successfully applied to treat arsenic in groundwater, surface water, mine drainage, drinking water, and industrial wastewater (USEPA, 2002). To meet the revised MCL for arsenic, additional or retrofit treatment may be required at many water treatment plants (WTPs). Thus, appreciable volumes of arsenic-contaminated residuals are expected to be produced which may require further treatment and handling prior to ultimate disposal.

From an economic viewpoint, recovery of arsenic from WTPs residuals is not attractive since demand is low and arsenic has been eliminated for usage in agriculture. Landfill disposal is generally considered to be the best choice for arsenic-contaminated residuals, but treatment of the residuals may be necessary to meet landfill regulations: 1.0 mg/L leachable arsenic measured by the toxicity characteristic leaching procedure (TCLP). Solidification/stabilization (S/S) processes are widely applied to arsenic bearing wastes and soils (USEPA, 2002; Miller, 1996). Arsenic behavior in soils and wastes are similar to residuals since both are solid-phase media. Therefore, S/S processes can be utilized for arsenic immobilization in WTP residuals.

The general objectives of this study were :

1. To characterize field samples of arsenic containing residuals to understand the release of arsenic in natural environments
2. To develop methods to suitably bind the arsenic in order to eliminate or minimize leaching
3. To investigate the feasibility of applying solidification/stabilization (S/S) for arsenic bearing residuals.

CHAPTER II

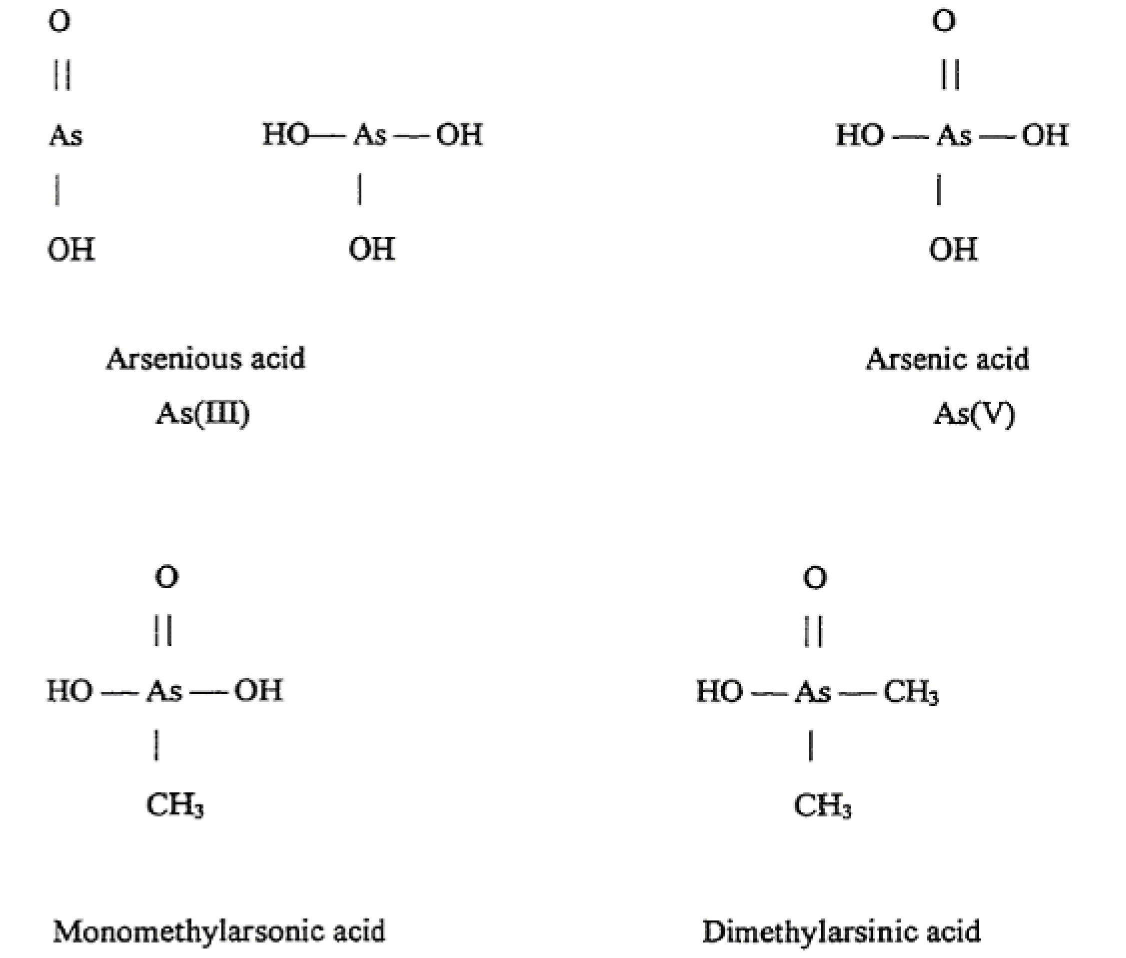
BACKGROUND

2.1 CHEMISTRY OF ARSENIC

2.1.1 Species and Structures

Arsenic chemistry in the aqueous phase is complicated due to the various oxidation states of atomic arsenic. The primary valence states for arsenic are +5, +3, 0 and –3. Both organic and inorganic arsenic species can exist in solution. Major organic arsenic species are monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) (Tamaki & Frankenberger, 1992). However, organo-arsenical compounds are generally accepted as a minor fraction of the total dissolved As. Thus, organic species (methylated arsenic) are commonly considered to be of little significance in waters compared with the inorganic species (Sadiq, 1997; Anderson & Bruland, 1991). The trivalent form of inorganic arsenic [As(III), called arsenite] and the pentavalent forms [As(V), called arsenate] are the inorganic species which tend to be more prevalent in water than the organic arsenic species (Ferguson & Gavis, 1972). Figure 2.1 shows the structural difference between arsenate and arsenite. Arsenic compounds exist in common aqueous environments as oxygen combined forms due to the high affinity (Langmuir, 1997a). Thus, arsenic is present as an anionic form.

FIGURE 2.1 Arsenic species in water



Source: Smith, 1973

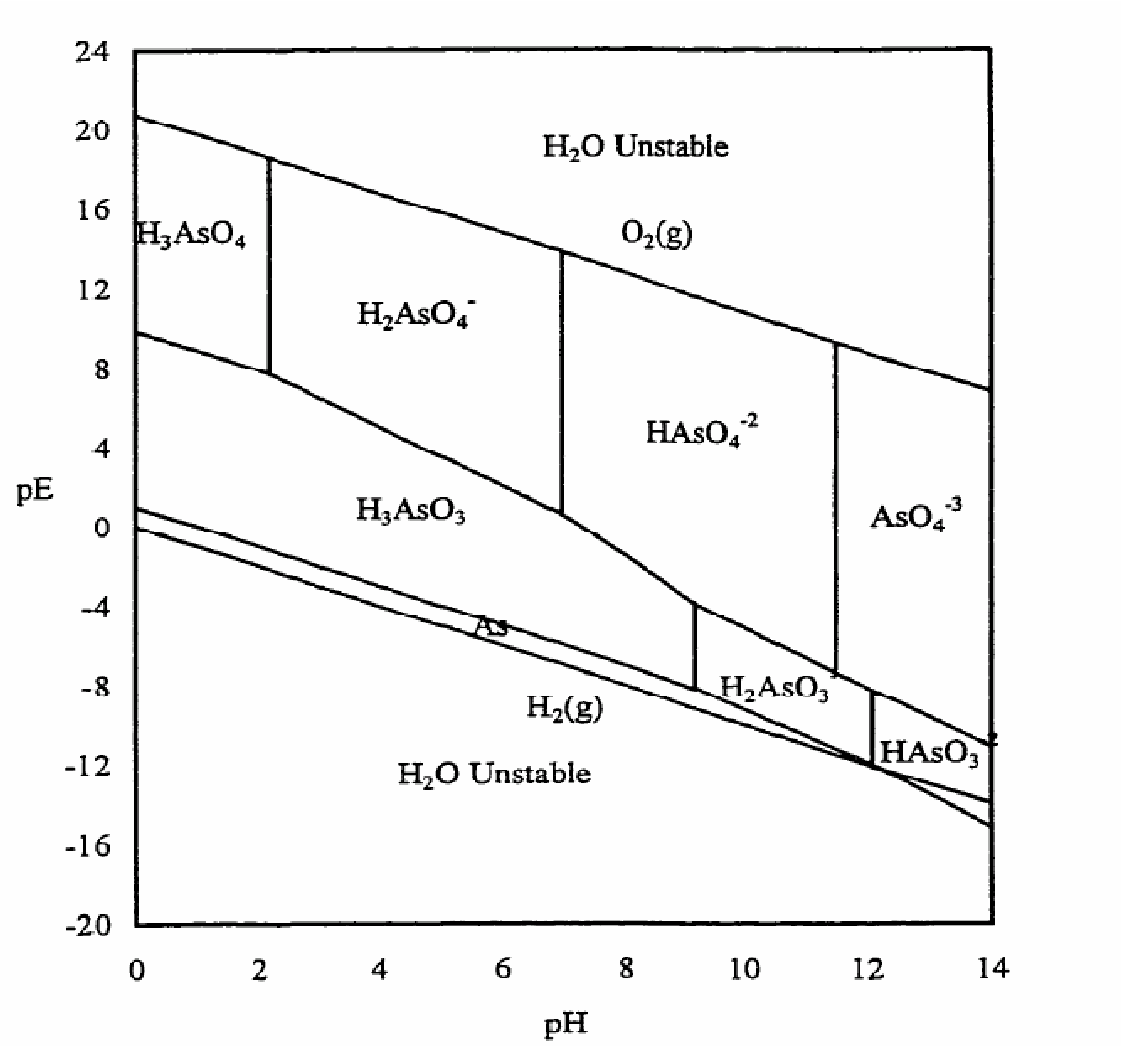
2.1.2 Effect of pH and Eh on the Distribution of Arsenic Species

The distribution and mobility of dissolved arsenic species are dependent on the pH and redox potential (Eh) conditions. The pH and Eh relationship is very important in understanding arsenic removal from water, arsenic immobilization/stabilization on solid phases as well as the distribution of arsenic species in water. Figure 2.2 illustrates the effect of pH and Eh (or pE) on major arsenic species at equilibrium conditions (Welch et al, 1988).

As shown in Figure 2.2, As(V) species are dominant under oxidizing conditions and As(III) is thermodynamically stable under mildly reducing conditions (Masscheleyn et al, 1991; Cherry et al, 1979). Normally, the Eh values of surface water and ground water are high and low, respectively. Thus, As(V) is more likely to occur in surface waters and As(III) tends to occur more frequently in ground waters.

As(III) is more mobile because it is present as a neutral form at the pH of most natural environments ($<$ pH 9) so it is less strongly adsorbed on mineral surfaces (Korte & Fernando, 1991). Meng et al (2001) pointed out that three redox zones can be divided according to the arsenic mobility: “an adsorption zone at $pe > 0$, a mobilization (transition) zone at $–4.0 < pe < 0$, and a reductive fixation zone at $pe < -4.0$”. Arsenic mobility is the greatest in the mobilization zone due to the reduction of ferric oxyhydroxides, main adsorbents for arsenic, to ferrous iron and As(V) to As(III). The three redox zones (oxidizing, mildly reducing, and very reducing) for arsenic mobility like the above were also suggested by several investigators (Carbonell-Barrachina et al, 1999; Masscheleyn et al, 1991).

FIGURE 2.2 pE/pH diagram for the As-H_2O system at 25°C



Source: Welch et al, 1988

Figure 2.2 is useful to understand the many complicated reactions related to arsenic, but it does not consider several other important factors. For example, the effects of coexisting solutes such as iron, aluminum, phosphates, silicates, carbonates, organic arsenic, and biotic redox reactions are not considered. The assumption of equilibrium at a low temperature is also oversimplified.

Several field investigations demonstrated that the pE/pH diagram for arsenic were oversimplified or were not accurately described (Williams et al, 1996; Korte & Fernando, 1991; Cullen & Reimer, 1989). As(III) and As(V) are detected in both oxidizing (e.g., surface waters) and reducing (e.g., groundwaters) environments. Several researchers explaine that the control of redox reactions, kinetically slow, might result in this disagreement (Peterson & Carpenter, 1983; Andreae, 1981). As(III) may be precipitated with sulfides at low Eh and iron oxyhydroxides would remove both As(III) and As(V) in oxidizing conditions. Therefore, under the coexistence of oxidized sulfur and reduced iron simultaneously, a substantial concentration of soluble arsenic can be present (Korte & Fernando, 1991).

Table 2.1 shows approximate values for the pK_a of inorganic arsenic species. It is concluded that ionization steps of As(III) and As(V) are significantly different. At normal natural pH environments (pH 4-9), $HAsO_4^{2-}$ and $H_2AsO_4^-$ are the dominant species for As(V) and $H_3AsO_3^0$ is for As(III) (Sadiq, 1997). Based on the data of Table 2.1, the mole fraction of total dissolved As(III) and As(V) as a function of pH can be drawn as shown in Figure 2.3.

TABLE 2.1 The pK_a values of inorganic arsenic species

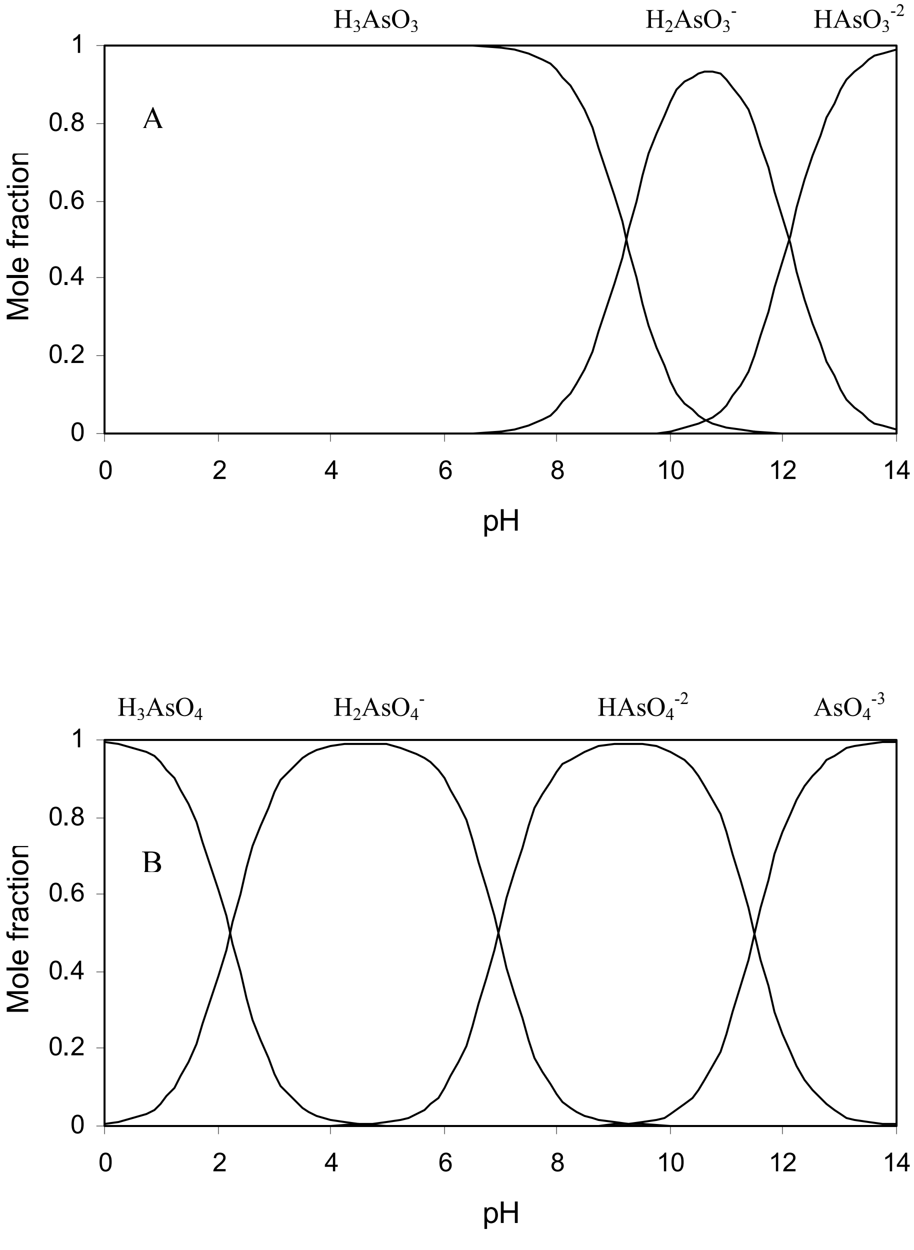
Arsenic species	pK_1	pK_2	PK_3
As(III): Arsenites	9.2	12.1	-
As(V): Arsenates	2.2	6.96	11.5

Source: Cherry et al, 1979

2.1.3 Toxicity

As(III) and As(V) are the most common toxic forms of inorganic arsenic present in drinking water. Biologically, As(III) is generally recognized to be more toxic than As(V) (Knowles & Benson, 1983). To humans, arsenite is about 60 times more toxic than arsenate (Ferguson & Gavis, 1972). When taken by humans and animals, inorganic As(V) is transformed to As(III), followed by methylation to monomethyl arsenic (MMA) and dimethyl arsenic (DMA) which are much less toxic forms (Jain & Ali, 2000). The toxicity order of arsenic species is arsenite > arsenate > MMA > DMA.

FIGURE 2.3 Mole fraction of total dissolved As as a function of pH in water at 25°C: (A) As(III), and (B) As(V)



2.2 TECHNOLOGIES TO REMOVE ARSENIC FROM WATER

Numerous treatment technologies have been developed and applied to arsenic removal from various contaminated waters. Based on the two references (USEPA, 2002; Amy et al, 2000), commonly used and applied treatment technologies have been selected and summarized in Table 2.2.

TABLE 2.2 The commonly applied technologies for arsenic removal from water

Technology	Brief description
Precipitative processes	Coagulation, enhanced coagulation, and lime softening are included this category. Metal hydroxides such as ferric salts, alum, and lime are used as precipitants. Preoxidation of As(III) to As(V) might be needed. Affecting factors on performance are precipitant type and dosage, arsenic oxidation state, pH, and competing compounds.
Membrane processes	Nanofiltration (NF) and reverse osmosis (RO) membranes can be the only membranes applied due to the low molecular weight of the arsenic species. Generation of a large volume of residuals is expected. The presence of solids and colloids, oxidation state of arsenic, pH, and temperature can be the factors affecting the removal performance.
Adsorptive processes	The typical adsorbents are activated alumina (AA), activated carbon (AC), and iron-based adsorbents such as, granular ferric hydroxide (GFH), and iron oxide-coated sand (IOCS). Each adsorbent has different conditions for arsenic removal. Currently, the most effective adsorbent is AA. Factors such as pH, oxidation state of arsenic, competing ions, and empty bed contact time (EBCT) have effects on the removal efficiency.
Ion Exchange	Strong base resins have been typically used. Important factors affecting performance are pH, competing ions, resin type, alkalinity, and arsenic oxidation state.

2.2.1 Coagulation with Ferric Salts

Coagulation (also called, precipitation/coprecipitation) with metal oxyhydroxides is the most effective, frequently used, and practical existing technology for arsenic removal (USEPA, 2002) and thus, this removal method is only selected and reviewed in this section. Ferric salts (e.g., ferric chloride), alum, and calcium are commonly employed as a coagulant. Currently, arsenic is treated by ferric oxyhydroxides via surface complexation at many water treatment plants (WTPs).

Dissolved colloidal or suspended contaminants are transformed to insoluble solids by the addition of ferric salts. Inclusion, adsorption, occlusion, solid-solution formation, or a combination of them can be the arsenic removal mechanism by coagulation with metal oxyhydroxides (Benefield & Morgan, 1990). Coagulation and adsorption studies with ferric salts and alum were conducted and very similar results of the two studies were observed (Hering & Elimelech, 1996). Therefore, it is inferred that the main controlling mechanism of arsenic removal by coagulation is adsorption.

The main factors affecting arsenic removal by coagulation are arsenic oxidation state, pH, coagulant dosage, and the presence of other inorganic solutes (USEPA, 2002; Hering & Elimelech, 1996). As(V) removal efficiency is normally greater than As(III) by coagulation with ferric salts. The effect of the pH range of 4 to 9 on As(V) removal in coagulation is insignificant, but As(III) removal is very much dependent on pH (Hering et al, 1996). In general, arsenic removal efficiencies can be improved with increased coagulant dosages (Cheng, et al, 1994; Edwards, 1994; Gulledge & O'Conner, 1973).

Hering et al (1996) examined the effects of sulfate and calcium on the arsenic removal. The results indicated that As(III) was much more poorly removed than As(V) at $pH < 7$ in the presence of sulfate and at high pH, removal efficiency of As(V) was increased in the presence of calcium. Competitive adsorption of As(V) and phosphate on iron minerals has been reported (Hongshao & Stanforth, 2001; Jain & Loeppert, 2000).

2.3 ARSENIC STABILIZATION TECHNOLOGIES IN RESIDUALS

2.3.1 Characterization of Arsenic Contained Residuals

Very little work has been conducted on the characterization and stabilization of arsenic containing residuals. Amy et al (2000) investigated arsenic leachability in various water treatment plant (WTP) residuals by the toxicity characteristic leaching procedure (TCLP). The results showed that the arsenic concentration in the residuals generated from WTPs was vastly different and soluble arsenic concentrations in the leachates also varied depending on residuals. However, the concentrations of arsenic in the leachates were not over the limit of 100 times of maximum contaminant level (MCL) for arsenic. Thus, the landfill disposal alternative was recommend for arsenic containing WTP residuals. However, arsenic residuals should be treated to avoid the possibility of leaching prior to disposal.

2.3.2 Toxicity Characteristics Leaching Procedure (TCLP)

The Toxicity Characteristics Leaching Procedure (TCLP), a regulatory test, is employed to determine whether a particular contaminant can be disposed in a landfill (USEPA, 1992). Evaluation of stabilization techniques has been broadly conducted using the TCLP method (LaGrega et al, 1994). In the TCLP method, target solid materials are crushed to small size, mixing with an extraction liquid, and agitated in a rotary reactor for 18 hours. Subsequently, insoluble and soluble phases are separated through a filter (USEPA, 1992). However, it was reported that TCLP would not be a suitable leaching test to predict the release of contaminants (oxoanion-forming elements) from municipal solid wastes (Hooper et al, 1998). Loeppert et al (2003) suggested that arsenic leaching could be higher than those predicted by the TCLP test.

2.3.3 Solidification and Stabilization (S/S)

USEPA (2002) introduced several treatment technologies for arsenic in soils and wastes: solidification and stabilization (S/S), vitrification, soil washing/acid extraction, pyrometallurgical recovery, and in situ soil flushing. S/S has been widely applied to arsenic treatment (immobilization) in soils (Miller, 1996; Voigt et al, 1996), industrial wastes (Fuessle & Taylor, 2000; Palfy et al, 1999; Yaziz et al, 1999; Dutre & Vandecasteele, 1998; Dutre & Vandecasteele, 1995), and residuals (Kameswari et al, 2001; Roy et al, 1992). In practice, only solidification and stabilization can be applicable to arsenic treatment in WTP residuals. Arsenic behavior in soils and wastes are similar to residuals since both are solid-phase media. Therefore, S/S processes can be utilized for arsenic immobilization in residuals.

Through physical and chemical means by S/S, hazardous substances and contaminants are stabilized within harden structures and will not be released. In general, S/S is designed to achieve one or more of the followings: (a) to improve the handling and physical characteristics of wastes, (b) to decrease the surface area of waste mass, (c) to limit the solubility of hazardous contaminants, and (d) to detoxify contained contaminants (LaGrega et al, 1994).

Several additives (binders) may be employed in the stabilization processes. Commonly used additives are cement (typically ordinary Portland cement (OPC)), lime, pozzolans such as, fly ash, slag, and kiln dust, and organically modified clays (LaGrega et al, 1994). The following materials have frequently been used as binders and reagents for the stabilization of arsenic tainted soils and wastes: Portland cement, lime, ferrous sulfate, ferric salts, and fly ash.

Portland cement. Cement is the most frequently used binder for solidification/stabilization for arsenic (USEPA, 2002). Type I ordinary Portland cement (OPC) typically consists of about 50% of tricalcium silicate ($3CaO\bullet SiO_2$), about 25% of dicalcium silicate ($2CaO\bullet SiO_2$), about 10% of tricalcium alminate ($3CaO\bullet Al_2O_3$), about 10% of tetraccalcium aluminoferrite ($4CaO\bullet Al_2O_3FeO_3$), and 5% other oxides by weight basis (Conner, 1993). Tricalcium silicate and dicalcium silicate of hydration can be expressed by the following reactions (Taylor, 1997):

$$2(3CaO\bullet SiO_2) + 6H_2O \rightarrow 3CaO\bullet 2SiO_2\bullet 3H_2O + 3Ca(OH)_2 \tag{2.1}$$

$$2(2CaO\bullet SiO_2) + 4H_2O \rightarrow 3CaO\bullet 2SiO_2\bullet 3H_2O + 3Ca(OH)_2 \tag{2.2}$$

It takes around 1 year to complete 95 to 98% of cement hydration. Calcium silicate hydrate (C-S-H) and portlandite ($Ca(OH)_2$) are the two main products of cement hydration. C-S-H represents about 60 to 70%, $Ca(OH)_2$ about 20 to 25%, and the other solid phases account for about 5 to 15% of the cement hydrates (Glasser, 1993).

Lime. Lime (calcium oxide, CaO) has been used as a material to stabilize arsenic contaminated wastes, residuals, and soils (Kim et al, 2003; Kameswari et al, 2001; Bothe & Brown, 1999; Dutre & Vandecasteele, 1998). The calcium arsenate precipitates ($Ca_4(OH)_2(AsO_4)_2\bullet 4H_2O$, $Ca_5(AsO_4)_3OH$, and $Ca_3(AsO_4)_2\bullet 2H_2O$) are generated as stable compounds for As(V) immobilization (Bothe & Brown, 1999). Dutre & Vandecasteele (1998) added cement and calcium to minimize the arsenic leaching in industrial wastes containing arsenic in high concentrations. They explained that the main reason why arsenic concentration in the leachate was lowered enormously was that $CaHAsO_3$, a stable and less soluble calcium-arsenic compound, was formed. Kim et al (2003) studied the stabilization of arsenic in mine tailings using iron. The results indicated that lower arsenic concentration in the leachate at a pH range of 3 to 6 was observed when $Ca(OH)_2$ rather than NaOH was used for pH adjustment. When higher initial Fe(III) concentration was added, this trend was more obvious. However, the solidified solids treated by lime only will decompose slowly when exposed to atmospheric CO_2 to form $CaCO_3$ and soluble arsenic species (Riveros et al, 2001).

Ferrous sulfate. The addition of a ferrous sulfate ($FeSO_4 \bullet 4H_2O$) solution to arsenic contaminated solids produces ferric arsenate ($FeAsO_4$), an insoluble compound or ferric hydroxide ($Fe(OH)_3$) precipitates which adsorb arsenic. However, the ferric arsenate generation mechanism by ferrous iron has not been well documented (Voigt et al, 1996). Sandesara (1978) recommended the use of ferrous sulfate rather than ferric sulfate due to the interferences with the curing of the cement. Indeed, ferrous sulfate has been employed for large-scale remediation of arsenic contaminated sites (USEPA, 1998; Miller, 1996). Sulfate can adversely influence the solids characteristics of wastes/cement matrices. Sulfate ions can results in ettringite formation, which causes the development of cracks in solidified solids (Taylor, 1997).

Ferric salts. Kim et al (2003) used ferric and ferrous salts to stabilize arsenic in mine tailings and concluded that the effectiveness of ferric sulfate is better than that of ferrous sulfate. However, ferrous S/S was recommended due to the greater solubility of ferrous hydroxide as compared to ferric hydroxide and the generation of larger molecule of ferric hydroxy-arsenic complex than ferrous arsenic compounds (Fuessle & Taylor, 2000).

Fly ash. Fly ash as an additive has been employed with other binders such as cement and lime (Kameswari et al, 2001; Fuessle & Taylor, 2000). Akhter et al (1997) tested solidifiation/stabilization of arsenic treated using various sets of binders over a period of four years. The performance of the combination of OPC and fly ash (Class F) was significantly lowered and the leached arsenic concentration of OPC and fly ash matrix became progressively greater over time.

2.4 ARSENIC ANALYSIS

Currently, arsenic analytical techniques for quantification as described in the Standard Methods (APHA et al, 1998) are

- Electrothermal Atomic Absorption Spectrometry – Standard Method 3113B
- Hydride Generation/Atomic Absorption Spectrometry (HG/AAS) – Standard Method 3114B and 3114C
- Inductively Coupled Plasma (ICP) Method – Standard Method 3120B
- Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) Method – Standard Method 3125B

Thus, furnace atomic absorption spectrometry (FAAS), HG/AAS, ICP, or ICP/MS is required to analyze arsenic concentration in waters. Affordable instruments in most water treatment plants and laboratories are FAAS and HG/AAS when comparing the prices of equipment and supplies. In this section, arsenic analysis by hydride generation with atomic absorption spectrometry (HG/AAS) is described in detail. In particular, the three standard curve method for arsenic speciation is illustrated.

2.4.1 Arsenic Analysis by Hydride Generation

The inorganic arsenic forms (As(V) and As(III)) must be converted (reduced) to arsine (AsH_3) to be analyzed by HG/AAS. A mixture of sodium borohydride ($NaBH_4$) and HCl is employed as reducing agents to generate AsH_3 from As(V) or As(III) (Hering & Elimelech, 1996; Korte & Fernando, 1991; Schmidt & Royer, 1973).

As(V) is first reduced to As(III), followed by transformation to AsH_3 (called two electron reduction), but As(III) can be directly reduced to AsH_3. Therefore, the reduction rate of As(V) is slower than that of As(III). This difference in kinetic reactions is more obvious at high pH. Thus, reduction rate is slower at high pH than at low pH. By controlling the pH of the reaction solution, inorganic arsenic speciation can be achieved (Aggett & Aspell, 1976; Braman & Foreback, 1973).

From the difference of reduction kinetics of As(III) versus As(V), two different approaches can be employed for arsenic analysis in As(III) and As(V) mixture systems. First, As(V) is prereduced with a prereductant such as potassium iodide (KI) or L-cysteine to overcome the incomplete generation of AsH_3 from As(V) by $NaBH_4$. However, the concentrations of both As(III) and As(V) cannot be determined by this approach. The second approach is “the three standard curve method” that can amend the difference of reduction kinetics and finally allows for the speciation of As(III) and As(V) (Loeppert & Biswas, Unpublished).

2.4.2 Three Standard Curve Method for Arsenic Speciation

The three standard curve method for inorganic arsenic speciation was prepared and developed by Loeppert & Biswas (Unpublished). The description of the theory and the procedure is summarized in this section.

Theory. The analytical absorbance (A) of a mixture of As(III) and As(V) by hydride generation with atomic absorption spectrophotometry (HG/AAS) is equal to the absorbance attributable to each As(III) and As(V). Thus, at pH 6.5 or pH 1.0 can be expressed by:

$$A_{6.5} = A_{As(III),pH6.5} + A_{As(V),pH6.5} \tag{2.3}$$

$$A_{1.0} = A_{As(III),pH1.0} + A_{As(V),pH1.0} \tag{2.4}$$

The slope of the standard curve is written by:

$$\text{Slope} = \frac{\text{absorbance}}{\text{concentration}} = \frac{A}{C} \tag{2.5}$$

FIGURE 2.4 Example for the relationship of slop versus concentration and absorbance

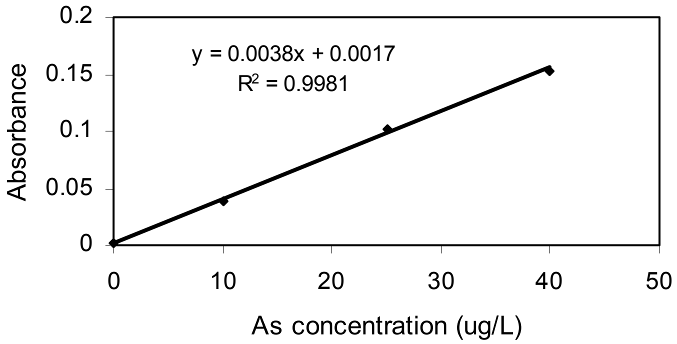


Figure 2.4 is one of the examples, which show the relationship of standard concentration versus absorbance. Equation 2.5 can be substituted into equations 2.3 and 2.4 and arsine formation from As(V) is zero at pH6.5. Therefore, equations 2.3 and 2.4 can be simplified to,

$$A_{6.5} = aC_{As(III)} \tag{2.6}$$

$$A_{1.0} = cC_{As(III)} + dC_{As(V)} \tag{2.7}$$

where, a = slope of As(III) standard curve at pH 6.5

c = slope of As(III) standard curve at pH 1.0

d = slope of As(V) standard curve at pH 1.0

Equations 2.6 and 2.7 can be further modified to:

$$C_{As(III)} = \frac{A_{6.5}}{a} \tag{2.8}$$

$$C_{As(V)} = \frac{\{[A_{1.0} - c(C_{As(III)})\}}{d} \quad (2.9)$$

Each As(III) and As(V) concentration can be determined by equations 2.8 and 2.9, respectively, and total As concentration is the sum of As(III) and As(V) concentrations.

Procedure. Primary As(III) and As(V) stock solutions (1 g/L) should be prepared from As_2O_3 and As_2O_5 (or $Na_2HAsO_4 \bullet H_2O$), respectively. The detailed preparation procedure is in Standard Method 3114B (APHA et al, 1998). The secondary stock solution (10 mg/L) is prepared by the dilution of the primary stock solution. Analytical standard solutions are prepared using the secondary stock solutions. The concentrations can be 0 (blank), 5, 10, 20, 40 μg/L. The reagents used are summarized in Table 2.3. Concentration of each reagent can be altered depending on the analytical instrument. The sample/acid, reductant, and carrier gas flow rates should be determined by preliminary tests for each specific analytical instrument.

TABLE 2.3 Reagents used for arsenic analysis

Parameter	Value
Borohydride concentration	1.5% (m/v) $NaBH_4$ in 0.5% NaOH
Phosphate buffer	0.2 M NaH_2PO_4 (monobasic), pH 3.0 adjusted by phosphoric acid
HCl concentration	5.0 M

Analysis with the mixture of borohydride solution and phosphate buffer corresponds to the reaction of pH 6.5 and the reaction from mixture of borohydride and HCl solutions is referred to the reaction of pH 1.0. It is possible to accurately analyze the As(III), As(V), and total As concentration from the three standard method. First, (i) As(III) standards and samples should be analyzed with the mixture of borohydride solution and phosphate buffer. From the As(III) standard calibration curve, the concentration of each sample can be calculated using the equation 2.8. Subsequently, (ii) As(III) and As(V) standards and samples (the same as those used in (i)) are subject to analyze with a mixture of borohydride and HCl solutions. The two calibration curves for As(III) and As(V) standards are obtained. Using the equation 2.9, As(V) concentration of each sample can be also determined. Total As concentration is the sum of As(III) and As(V) concentrations. Basically, three standard curves, As(III) standard curve obtained from analysis with a mixture of borohydride solution and phosphate buffer, and As(III) and As(V) standard curves obtained from analysis with a mixture of borohydride and HCl solutions, will be gained from this analysis.

CHAPTER III

MATERIALS AND METHODS

3.1 ANALYSIS

In this section, arsenic analysis and speciation and Fe, Al, Ca, and Mn analyses were described. Atomic absorption spectrometry (AAS) was the main instrument employed for the analyses.

3.1.1 Arsenic Analysis and Speciation

Continuous hydride generation with the atomic absorption spectrometric method (HG/AAS) (Standard method 3114, APHA et al, 1998) was employed to determine arsenic concentrations. Preparation of arsenic stock solutions for As(III) and As(V) from arsenic trioxide, As_2O_3 (Fisher, A.C.S. reagent grade), and arsenic pentoxide, As_2O_5 (Aldrich), respectively, were followed using the standard method 3114B (APHA et al, 1998). For the speciation of inorganic As(III) and As(V), the three standard curve method was used as described in Chapter 2. First, As(III) concentration was determined using a phosphate buffer and then As(III) and As(V) mixed analysis was conducted using hydrochloric acid. The reductant (sodium borohydride) was freshly prepared at every analysis. The concentrations of analytical standards used were 0 (blank), 5, 10, 20, and 40 μg/L. Arsenic standards were kept and used for one week after preparing. All arsenic samples were stored in a refrigerator (4°C) until analyzed. Arsenic analysis was conducted within 48 hours after collecting samples. Dilution of arsenic standards and samples were carried out using distilled (DI) water. The detailed information of reagents and gases used for arsenic analysis were summarized in Table 3.1. Figure 3.1 shows the schematic diagram of a continuous hydride generation system.

TABLE 3.1 Reagents and gases used for arsenic analysis

Hdrochloric acid:	5M HCl, diluted from conc. HCl, trace-metal grade, Fisher
Borohydride reagent:	1.5% (m/v) $NaBH_4$ (sodium borohydride), A.C.S. reagent grade, EM 0.5% (m/v) NaOH (sodium hydroxide), A.C.S. reagent grade, Fisher
Phosphate buffer:	0.2 M NaH_2PO_4 (monobasic) (sodium phosphate), A.C.S. reagent grade, EM pH 3.0 adjusted by H_3PO_4 (phosphoric acid), trace-metal grade, EM
Stock solutions:	1 g/L $As_2O_{3(s)}$, A.C.S. reagent grade, Fisher 1 g/L $As_2O_{5(s)}$, A.C.S. reagent grade, Aldrich
Gases:	Air (AAS grade), C_2H_2 (acetylene), Argon gas.

The apparatus used for the arsenic analysis was a flame atomic absorption spectrometer (FLAAS) (model name: Thermo Elemental, Solar M6 AA) and a continuous hydride generation system (model name: Thermo Elemental, VP90). The operating parameters used are summarized in Table 3.2. Using software package, called SOLAAR M, installed in the controlling computer, all analysis procedures and parameters can be controlled and monitored. Also, the software can draw the calibration curve of standard solutions and automatically calculate the concentration of each measurement sample. Acceptance limit for the linear coefficient of calibration curve was $R^2 = 0.995$.

FIGURE 3.1 Schematic diagram of a continuous hydride generation system

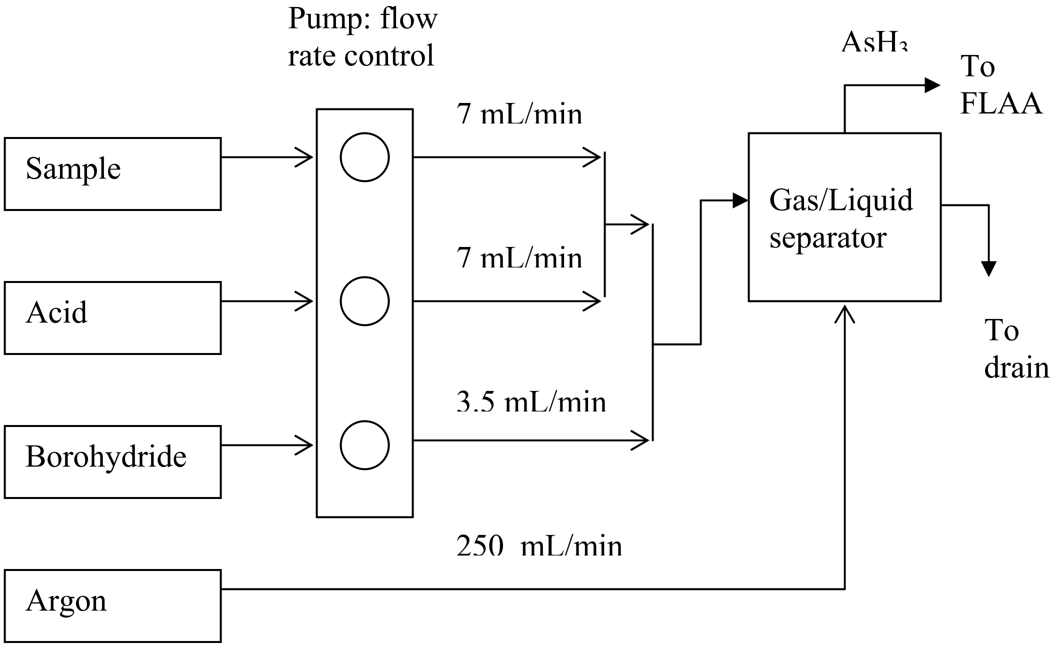


TABLE 3.2 Operating parameters for arsenic analysis using HG/AAS

Parameter	Description
Element:	As
Lamp:	Hollow Cathode Lamp (HCL) Coded lamp supplied by Unicam Atomic Absorption
Pressure of gases:	Air (30 psi) and Acetylene (9 psi) for flame Argon (5 psi) for carrier gas
Wavelength:	193.7 nm
Bandpass:	0.5 nm
Measurement time:	3 seconds
Number of measurement:	3 times (fast resamples)
Carrier gas (argon) flow:	250 mL/min
Background correction:	No
Signal:	40 µg/L gives about 0.2 Abs

3.1.2 Other Elemental Analyses

Methods for analysis of total iron, aluminum, calcium, and manganese are summarized in Table 3.3. All analytical standards of the four elements were prepared with DI water from stock solutions (Spex), repectively. Analyses of these elements were completed within three days after collecting samples. Acceptance limit for the calibration curve for the standards was $R^2 = 0.995$.

TABLE 3.3 Parameters for other elemental analyses

Fe	Method: Range of standards: Wavelength: Bandpass:	Direct Air-Acetylene Flame method, standard method 3111B, (APHA, AWWA, and WEF, 1998) 0 (blank), 1, 2.5, and 5 mg/L 248.3 nm 0.2 nm
Al	Method: Range of standards: Wavelength: Bandpass:	Direct Nitrous Oxide-Acetylene Flame method, standard method 3111D, (APHA, AWWA, and WEF, 1998) 0, 5, 10, and 20 mg/L 309.3 nm 0.5 nm
Ca	Method: Range of standards: Wavelength: Bandpass:	Direct Nitrous Oxide-Acetylene Flame method, standard method 3111D, (APHA, AWWA, and WEF, 1998) 0, 0.5, 1, and 1.5 mg/L 422.7 nm 0.5 nm
Mn	Method: Range of standards: Wavelength: Bandpass:	Direct Air-Acetylene Flame method, standard method 3111B, (APHA, AWWA, and WEF, 1998) 0, 0.5, 1, and 2 mg/L 279.5 nm 0.2 nm

3.2 CHARACTERIZATION TESTS OF FIELD RESIDUALS

3.2.1 Residual Handling

Three residuals samples from water treatment plants and three residuals samples from pilot plants were utilized as target materials in this study. Free liquid in residuals were removed by air-drying for the characterization studies (Kameswari et al, 2001). Each residual was placed in a clean vinyl-coated paper and dried under laboratory conditions for 24 hours. Subsequently, air-dried residuals were crushed, passed through a 2 mm sieve and mixed well to produce homogeneous conditions and minimize errors. Polyethylene bottles were used to contain the residuals.

3.2.2 General Physical and Chemical Tests

Solid content. Standard method 2540B (APHA et al, 1998) was used to determine total solids in each residual. Some (around 10 g) of each residual was taken and dried in an oven at 105°C for 24 hours. Calculation for the percent of dry solids is conducted using equation 3.1.

$$\text{Percent of dry solids (\%)} = \frac{(\text{C} - \text{B})}{\text{A}} \times 100 \qquad (3.1)$$

where, A = weight of raw waste (g)

B = weight of evaporating dish (g)

C = weight of dried waste + evaporating dish (g)

Acid digestion. Acid digestion of sediments, sludges, and solis, (USEPA method 3050B, USEPA, 1992) was used to establish the initial concentration of total arsenic, total iron, aluminum, calcium, and manganese in each residual. One gram (dry weight) of the sample was placed in a digestion vessel on a hot plate and digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). Each digested result was filtered using a filter paper and diluted with DI water to make a final volume of 100 mL. Analyses were conducted for total As, total Fe, Al, Ca, and Mn using the atomic absorption spectrometry (AAS).

pH measurement. Soil and waste pH, (USEPA method 9045C, USEPA, 1992) was employed to determine the pH of each residual. Twenty grams (dry weight) of a residual was completely mixed with 20 mL of DI water for 20 minutes, and the pH of the suspension was measured.

3.2.3 Toxicity Characteristic Leaching Procedure

Toxicity characteristic leaching procedure (TCLP) (USEPA 1311, USEPA, 1992) was conducted on all of the samples using the accepted and regulated protocol. Two TCLP extraction fluids were used: fluid #1 (0.1 M acetic acid & 0.064 M NaOH, pH 4.93) and fluid #2 (0.1M acetic acid, pH 2.88). However, fluid #1 is basically employed for acidic wastes and fluid #2 for basic ones. Ten grams of air-dried residual was mixed with 200 mL of leachant (liquid to solid weight ratio of 20:1) due to the small amounts of sample available. Sample and liquid mixture were placed in a polyethylene bottle and put into a rotary agitation apparatus and reaction of the leaching test was continuously run for 24 hours instead of 18 at room temperature (22±2°C). After the reaction, solid and liquid was separated using a 0.2 μm pore-size filter. The filtrate is defined as the TCLP extract. The pH of each extract was measured and recorded. All experiments were conducted in duplicate. All extracts were kept under refrigeration (4°C) until analyzed. Arsenic concentration and speciation were analyzed by hydride generation with atomic absorption spectrometry (HG/AAS). Iron, aluminum, and calcium concentrations were also determined using flame atomic absorption spectrometry (FLAAS).

3.2.4 Competitive Desorption

Desorption versus phosphate. Based on previous work by the researchers, phosphate tends to compete with As(V) on the surface of the iron (oxy)hydroxides for sorption sites and thus, tends to leach the arsenic compounds. Ten grams of air-dried residual was mixed with 200 mL of DI water, 10 mM $NaNO_3$ as an ionic strength buffer, and 0.1 M $NaH_2PO_4 \bullet H_2O$ (EM, A.C.S. reagent grade) as a phosphate source. The pH of the leachant used was adjusted to 7 by the addition of HNO_3 or NaOH as needed. Leaching reactions subsequently were conducted for 24 hours at room temperature. All leaching suspensions were filtered through a 0.2 μm pore size membrane.

Desorption versus sulfate. 0.1 M Na_2SO_4 (Fisher, A.C.S. reagent grade) as a sulfate source was mixed with 10 g of air-dried residual. The other experimental conditions were the same as those of desorption versus phosphate.

Desorption versus chloride. These studies were conducted by the addition of 0.1 M NaCl (Fisher, A.C.S. reagent grade) to a solution of 10 g of air-dried residual, 200 mL of DI water, and 10 mM $NaNO_3$ as an ionic strength buffer. The other experimental conditions were the same as those of desorption versus phosphate.

3.2.5 Effect of pH on Arsenic Leaching

Ten grams of each residual sample was added to 200 mL of DI water with the pH adjusted by adding either NaOH or HNO_3 as needed to achieve the desired final pH. An ionic strength buffer, 10 mM of $NaNO_3$, was added to each mixture. A range of pH was investigated at 4, 6, 8, and 10. Sodium acetate ($NaCH_3COO$, 10 mM) (Fisher, A.C.S. reagent grade) was employed as a pH buffer for pH 4 and 6. Sodium bicarbonate ($NaHCO_3$, 10 mM) (Fisher, A.C.S. reagent grade) was also used as a pH buffer for pH 8 and 10. A mixture of the residuals and leachant was mixed in a polyethylene bottle and reacted by a rotary apparatus for 24 hours at room temperature (22±2°C). After the reaction was completed, leached suspensions were filtered through a 0.2 μm pore size membrane to separate solids and liquids. Arsenic speciation was determined using HG/AAS and total Fe, Al, and Ca concentrations were analyzed using FLAAS.

3.3 SOLIDIFICATION AND STABILIZATION (S/S) TECHNIQUES OF FIELD RESIDUALS

The general goals of this study were not only to analyze a variety of water treatment residuals containing arsenic, but also to develop suitable technical methods to immobilize the arsenic in the residuals.

Free liquid in the residuals was removed by air-drying for the solidification and stabilization (S/S) experiment (Kameswari et al, 2001). Air-dried residuals were crushed, passed through a 2 mm sieve and thoroughly mixed to produce homogeneous conditions and minimize errors. All S/S experiments were carried out on the basis of 10 g of air-dried residual. Added-water to residuals ratio was 0.5 to 1, depending on the amount of binder used. Residuals and binder(s) were mixed thoroughly by hand with an acid-washed glass bar before addition of the water. The sludge-binder mixture was placed in an acid-washed plastic cup and cured at room temperature for 7 days. After curing, all solidified samples were crushed to the particle size < 2 mm (using 2 mm sieve) and kept in polyethylene bottles separately until subjected to extraction tests. All experiments were performed in duplicate.

Based on the preliminary experiments, calcium hydroxide and ordinary Portland cement were selected as binders for S/S studies.

3.3.1 Addition of Lime Only

Quicklime (CaO, calcium oxide) is mainly employed for S/S in field scale applications due to economic aspects. Mixing CaO and water produces a slurry of $Ca(OH)_2$. This process is called slaking,

$$CaO + H_2O = Ca(OH)_2 + \text{heat} \tag{3.2}$$

which is an exothermic reaction. Great care must be taken when CaO is handled since high heat is generated (Davis & Cornwell, 1998). Due to this safety problem, hydrated lime ($Ca(OH)_2$) was used in this study. Similar results were obtained when $Ca(OH)_2$ was used instead of CaO for S/S of arsenic in waste (Dutre & Vandecasteele, 1995).

$Ca(OH)_2$ (EM, A.C.S. reagent grade) was investigated by adding increasing amounts (1 to 10g/10g of air-dried residual) to the residuals, respectively. After curing for 7 days, extraction tests were conducted to determine the optimum amount of lime added for the control of arsenic leaching.

3.3.2 Addition of OPC Only

Ordinary Portland cement (OPC) is usually used as a main material for cement-based stabilization. The OPC used in this study was supplied by the Quikrete Company.

Different ratios of cement to residual (weight basis) were used: 0.1, 0.2, 0.3, and 0.5. and the optimum amount of cement added determined.

3.3.3 Addition of Lime and OPC

Based on the amount of lime and OPC determined in steps ‘addition of cement only’ and ‘addition of OPC only’, the optimum amount of lime and OPC added were selected and added to each residual sample.

3.3.4 Extraction Tests

To examine the effectiveness of the S/S of each residual sample, extraction tests were performed. Untreated residuals and all solidified solids were subjected to two extraction tests: TCLP #2 (0.1 M acetic acid, pH = 2.88) extraction solution, and the worst-case arsenic leaching condition (0.1 M NaH_2PO_4, pH = 10). The liquid to solid weight ratio was 20: 200 mL of leachant and 10 g of air-dried residual (weight of binders added was ignored for the comparison of leaching of raw residual to that of a solidified solid). All solidified specimens were pulverized to the particle size < 2 mm. The extraction period was 24 hours for all extraction tests. Leaching reactions were conducted in polyethylene bottles by a rotary shaker. After extraction, the leached suspensions were filtered to separate liquid and solids with a 0.2 μm membrane filter. Arsenic speciation and Fe, Al, and Ca concentrations were determined according to the analytical methods described above. The variables used in the extraction tests and subsequent analyses conducted are summarized in Table 3.4.

TABLE 3.4 Extraction tests examined and subsequent analyses conducted

Parameter	Description
Types of leachant	(i) TCLP extraction #2 (0.1 M acetic acid, pH = 2.88) (ii) Phosphate extraction (0.1 M NaH_2PO_4, pH = 10)
Leachant-to-residual ratio	20:1 (200 mL: 10 g)
Surface area of residual	Particle size smaller than 2.00 mm
Extraction period	24 hours
Extraction vessel	Polyethylene bottle
Temperature	Room temperature (22±3°C)
Separation of liquid and solids	0.2-μm pore size membrane filter with syringe
Storage of samples	In a refrigerator (4°C)
Arsenic speciation	Using HG/AAS within 2 days after collecting samples
Fe, Al, Ca analyses	Using FLAAS with 3 days after collecting samples

CHAPTER IV

RESULTS AND DISCUSSION

4.1 CHARACTERIZATION OF THE FIELD RESIDUALS

Water treatment residuals used for this study were supplied by three water treatment plants and two pilot plants. Most arsenic containing residuals are generated from iron- or alum-based coagulation, adsorption (mainly by activated alumina), membrane filtration and lime-based softening. The water treatment plants supplying residuals were El Paso Water Utilities (El Paso, TX), Public Utilities Department of City of Billings (Billings, MT), and Helena Water Treatment Utilities (Helena, MT). The three water treatment residuals were named after their origin. The other three arsenic contaminated residual samples were two types of adsorption media from two pilot plants. These two adsorption media were utilized during pilot studies at Naval Air Station Fallon (NASF) (Fallon, NV) and CH2MHILL – El Paso (El Paso, TX) for arsenic removal from groundwater. The pilot plant residuals from NASF were a granular ferric hydroxide material (GFH) and CH2MHILL – El Paso supplied two different types of adsorption media, GFH and ALCAN FS50, an alumina based media. All the adsorption media were exhausted, which means arsenic concentration in the water going out of the adsorption column was above the MCL of 10 μg/L. The residuals from the pilot plants were named after the media type and origin.

Granular ferric hydroxide (GFH) is an emerging removal technology for arsenic by adsorption in fixed bed reactors (Driehaus et al, 1998). This technique combines the advantages of the coagulation-filtration process and the fixed bed adsorption such as activated alumina. The processing of this technology is simple and operation can be run without the need for pH adjustment or preoxidation (Simms et al, 2000). Therefore, an unskilled person can operate the water treatment system. The process may be an acceptable treatment alternative for small-scale systems.

ALCAN FS50 is activated alumina promoted with a proprietary additive engineered to accomplish enhanced arsenic removal (Alcan Chemicals, 1998). The arsenic adsorption capacity of ALCAN FS50 proved to be five times greater than unpromoted activated alumina.

The information of water treatment facilities and residual samples is summarized in Table 4.1.

TABLE 4.1 Information summary of water treatment facilities and residual samples

Residual	Type	Name of the facility
GFH – Fallon	GFH	Naval Air Station Fallon (NASF) – Fallon, NV
AA – El Paso	AA	CH2MHILL – El Paso, TX
GFH – El Paso	GFH	CH2MHILL – El Paso, TX
El Paso	Alum	El Paso Water Utilities – El Paso, TX
Billings	Ferric	Public Utilities Department – Billings, MT
Helena	Alum	Helena Water Treatment – Helena, MT

4.1.1 General Physical and Chemical Properties

Digestion results. The major elements, which can strongly influence the arsenic behavior (sorption, release, and oxidation) in residuals, are iron, aluminum, calcium and manganese (Sadiq, 1997). Therefore, the concentrations of these elements initially contained in each residual sample were determined by acid digestion. The concentrations of major metals obtained from the six residuals are shown in Table 4.2.

TABLE 4.2 Concentrations of major metals in residuals

Residual	Total As (mg/kg)	Total Fe (mg/kg)	Total Al (mg/kg)	Total Ca (mg/kg)	Total Mn (mg/kg)
GFH – Fallon	2680	521000	212	1510	741
AA – El Paso	33.2	20600	298000	5640	10.5
GFH – El Paso	2290	503000	993	5690	852
El Paso	15.3	24000	18100	35800	425
Billings	148	50000	30300	18400	713
Helena	402	20300	45800	1860	1350

As expected, the highly elevated concentrations of total arsenic and total iron in GFHs of the pilot plant studies were detected due to the high arsenic adsorption capacity and the adsorption media being made principally from ferric hydroxide. From Table 4.2, the content of arsenic in the GFH was greater than that in the AA on the basis of weight. Chemicals added typically vary in water treatment facilities. Therefore, it is hard to find solid relationships between the arsenic removal type of media and digestion results. A high portion of Fe, Al, and Ca were found in the residuals from the water treatment plants.

Results of pH and solid content. The pH and solid content of each air-dried residual is shown in Table 4.3. Water treatment residuals are usually dewatered prior to disposing into a landfill. Commonly used dewatering processes for water treatment residuals are air-drying and mechanical dewatering (Hsieh & Raghu, 1997). The most typical air-drying types are sand drying beds and lagoons. Belt filter presses, centrifuges, pressure filter presses, and vacuum filters are the mechanical dewatering devices.

TABLE 4.3 pH and solid content of residuals

Residual	pH	Solid content (%)
GFH – Fallon	7.27	69.1
AA – El Paso	7.55	83.6
GFH – El Paso	7.85	67.9
El Paso	7.85	96.5
Billings	7.44	91.9
Helena	7.93	80.9

It is critical to know the pH to predict arsenic behavior in a residual because arsenic adsorption and release reactions are very pH dependent. The pH values of the residual samples were measured according to the USEPA method 9045C (USEPA, 1992). However, the values are only estimates. All of the pH values of residuals were found to be around neutral (between 7 and 8).

4.1.2 TCLP Analysis

The field residuals were subjected two types of leaching solutions for the toxicity characteristics leaching procedure (TCLP). TCLP extraction solution #1 (pH=4.93) is designed for acidic solid wastes and TCLP extraction solution #2 (pH=2.88) is for basic ones. However, TCLP #1 and TCLP #2 were used for all residuals because pH values for residuals obtained were around neutral. Results of TCLP #1 and TCLP #2 are presented in Table 4.4 and Table 4.5, respectively.

TABLE 4.4 Results of TCLP extraction solution #1

Residual	Final pH	As(III) (mg/kg)	As(V) (mg/kg)	Fe (mg/kg)	Al (mg/kg)	Ca (mg/kg)
GFH – Fallon	5.44	< 0.02	0.37	< 1	< 20	1070
AA – El Paso	5.18	0.10	0.07	0.60	157	5340
GFH – El Paso	5.14	0.29	0.15	< 1	< 20	8410
El Paso	6.61	0.06	0.24	< 1	< 20	11100
Billings	5.94	0.31	0.79	3.12	< 20	8530
Helena	5.48	2.49	6.13	47.8	151	817

As(III) and As(V) concentrations in the extracted solutions were both higher with TCLP #2 than with TCLP #1, except the GFH – El Paso in which leached As(V) concentration decreased. As(III) was the major As species of total soluble As in AA – El Paso and GFH – El Paso residuals even though redox status of the system of mixed TCLP extraction and residuals was generally assumed to be oxidizing. It is thought that the main reason why the results were obtained is that AA and GFH media were utilized during pilot plant studies in El Paso for arsenic removal from groundwater and thus, it is assumed they contained much larger portion of As(III). However, As(V) was the dominant As species released in the other residuals. When higher As was released in a residual, higher concentration of a soluble major adsorbent, such as Fe or Al hydroxide, was observed. Therefore, it is concluded that As desorption behavior is controlled by Fe or Al hydroxides. Soluble Ca concentration was high in al residuals through both TCLP tests because the solubility of $Ca(OH)_2$ and $CaCO_3$ is high at low pH. Mn concentrations of the residuals were relatively lower than other elements (ref. Table 4.2) and Mn concentrations in the leachates were very low. Thus, measurement of Mn concentration was not conducted in further tests. The final pH of each extract was lower for TCLP #2 than TCLP #1 as expected.

TABLE 4.5 Results of TCLP extraction solution #2

Residual	Final pH	As(III) (mg/kg)	As(V) (mg/kg)	Fe (mg/kg)	Al (mg/kg)	Ca (mg/kg)
GFH – Fallon	3.50	< 0.02	0.62	132	< 20	1447
AA – El Paso	4.01	0.16	< 0.02	6.38	3611	3521
GFH – El Paso	3.76	0.33	< 0.02	2.83	< 20	5821
El Paso	4.93	0.07	0.20	286	< 20	28510
Billings	4.30	0.72	1.74	3409	203	12300
Helena	3.97	4.97	14.2	919	4511	877

From these data, it is concluded that pH is critical for the release of As, Fe, Al, and Ca. In oxidized systems, the solubility, adsorption and movement of arsenic (As(III) and As(V) both) is controlled predominantly by adsorption reactions with oxide minerals such as Fe and Al oxides (Loeppert et al, 2003; Sadiq, 1997; Masscheleyn et al, 1991; Artiola et al, 1990). At low pH (3-5), solubility of the Fe and Al oxides increases and thus, the concentration of inorganic arsenic released in the leachates is expected to be also increased. However, maximum As(V) adsorption on Fe and Al hydroxides is usually achieved at low pH (4-5) (Raven et al, 1998; Anderson et al, 1976). Therefore, it is considered that arsenic leaching might be underestimated through the use of TCLP.

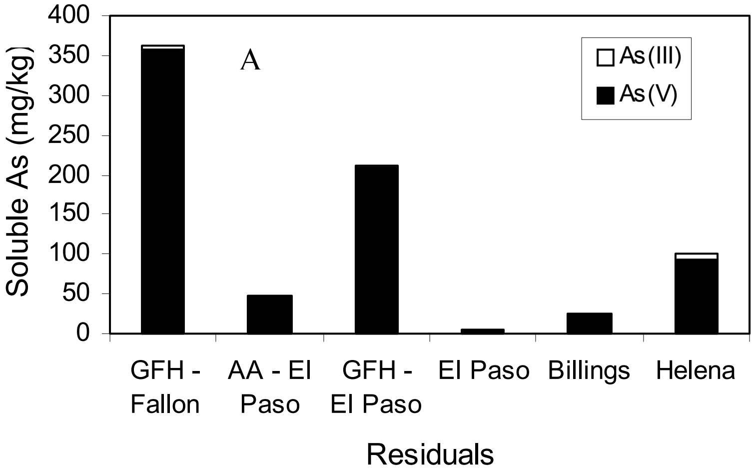
Ca may precipitate As in the form of calcium arsenate at high pH. However, as shown in Tables 4.4 and 4.5, released Ca concentrations were significant due to the low pH of the leachates. Ca carbonates are soluble and unstable at low pH conditions and consequently, they play a minor role for arsenic solubility in acidic residuals (Sadiq, 1997).

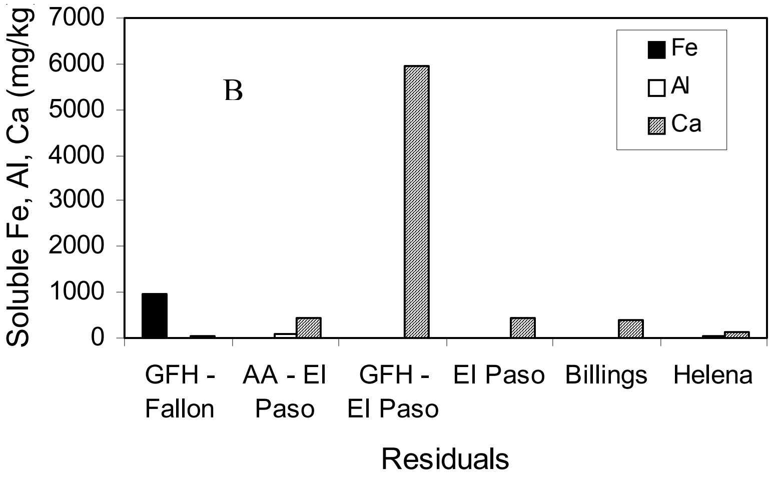
4.1.3 Competitive Desorption Analysis

Competitive desorption with phosphate. The mobilization of bound arsenic on adsorbents such as Fe and Al hydroxides is strongly influenced by the presence of ligands that can compete with arsenic for surface sorption sites. In particular, phosphate tends to compete with As(V) for sorption sites on the surface of the metal hydroxide (equation 4.1) and thus, tends to extract the As(V) compounds (Loeppert et al, 2003; Hongshao & Stanforth, 2001; Hiemstra & Riemsdijk, 1999; Hingston et al, 1971).

$$\text{Fe-oxide-AsO}_4\text{H} + \text{HPO}_4^{2-} \rightarrow \text{Fe-oxide-PO}_4\text{H} + \text{HAsO}_4^{2-} \quad (4.1)$$

FIGURE 4.1 Competitive desorption with phosphate: (A) soluble As concentration, and (B) soluble Fe, Al, and Ca concentrations





The adsorption behavior of phosphate and As(III) are very different, and a significantly higher concentration of bound As(III) compared to As(V) was observed on iron minerals in the presence of 0.1 M sodium phosphate (Jackson & Miller, 2000; Jain & Loeppert, 2000). These studies indicated that there might be specific sites for As(III) on the iron oxide minerals.

Figure 4.1 presents the soluble concentrations of As(III) and As(V) (a) and soluble concentrations of Fe, Al, and Ca (b) released by the competition with phosphate. As noted, extraction solutions were adjusted to pH 7 and the final pH values after 24 hours of reaction were between 7.2 and 7.6. The results indicated that As(V) was the dominant arsenic species extracted by phosphate. GFH – Fallon and GFH – El Paso residuals contained high concentration of total arsenic (ref. Table 4.2) and thus, the concentration of As(V) released in the two residuals was much higher than that in the other residuals. It was very difficult to find a reason to explain why much higher soluble Ca concentration was observed in GFH – El Paso residual. Arsenic concentrations extracted by the phosphate competition on Fe oxide minerals usually increase at low and high pH conditions (Loeppert et al, 2003). Therefore, it is expected that higher As concentration would be released at low and high pH than the leached As concentration obtained in this study.

Competitive desorption with sulfate and chloride. The results of arsenic leaching in the presence of sulfate and chloride are shown in Figure 4.2. Any supporting data in which the presence of sulfate ions can influence the release of As were not found.

However, it was reported that As(III) and As(V) adsorption was decreased in the presence of sulfate, and this trend was more obvious at lower pH (Wilkie & Hering, 1996). It is concluded that the effect of sulfate on As desorption is minor even though it can influence adversely on As sorption. Any relationships for the release of arsenic and the presence of chloride were also not observed in Figure 4.3. The amount of As released in the presence of sulfate and chloride was much lower than that in the presence of phosphate when comparing Figures 4.1 to 4.2 and Figures 4.1 to 4.3.

FIGURE 4.2 Competitive desorption with sulfate: soluble As concentration

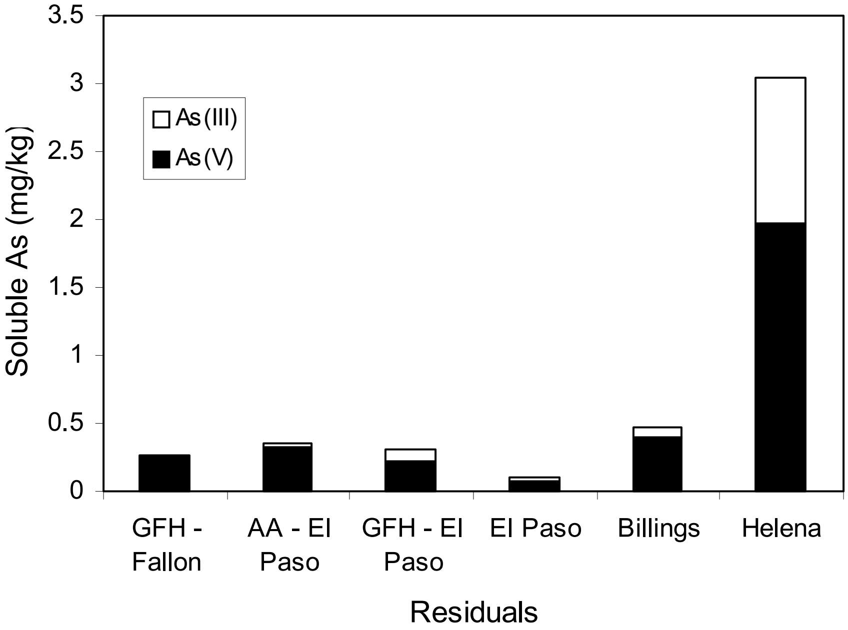
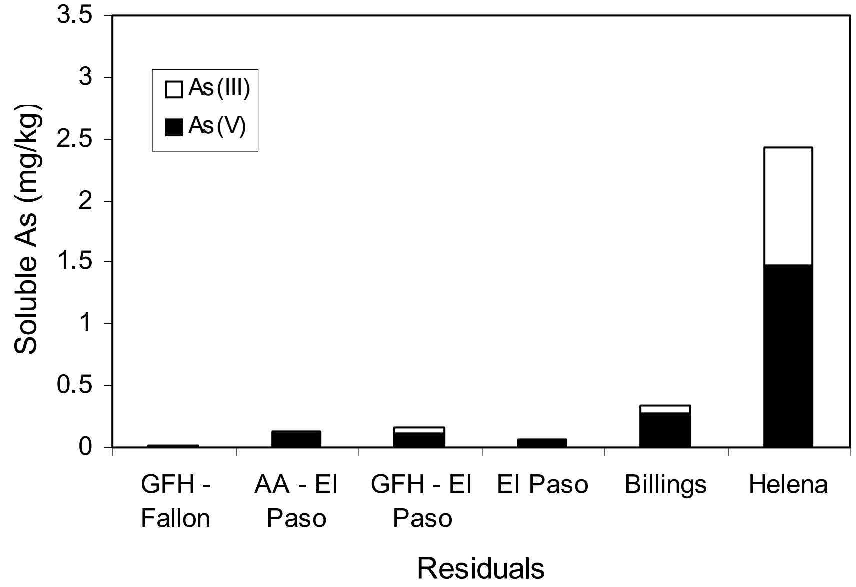


FIGURE 4.3 Competitive desorption with chloride: soluble As concentration



4.1.4 Effect of pH on Arsenic Leaching Analysis

Figure 4.4 shows the soluble As(III) and As(V) concentration and Tables 4.6, 4.7, and 4.8 present the influence of pH on leached Fe, Al, and Ca concentrations, respectively. Soluble arsenic and the other major metal (Fe, Al, and Ca) concentrations depended on the pH of the system.

FIGURE 4.4 Effect of pH on arsenic leaching: (A) As(III), and (B) As(V)

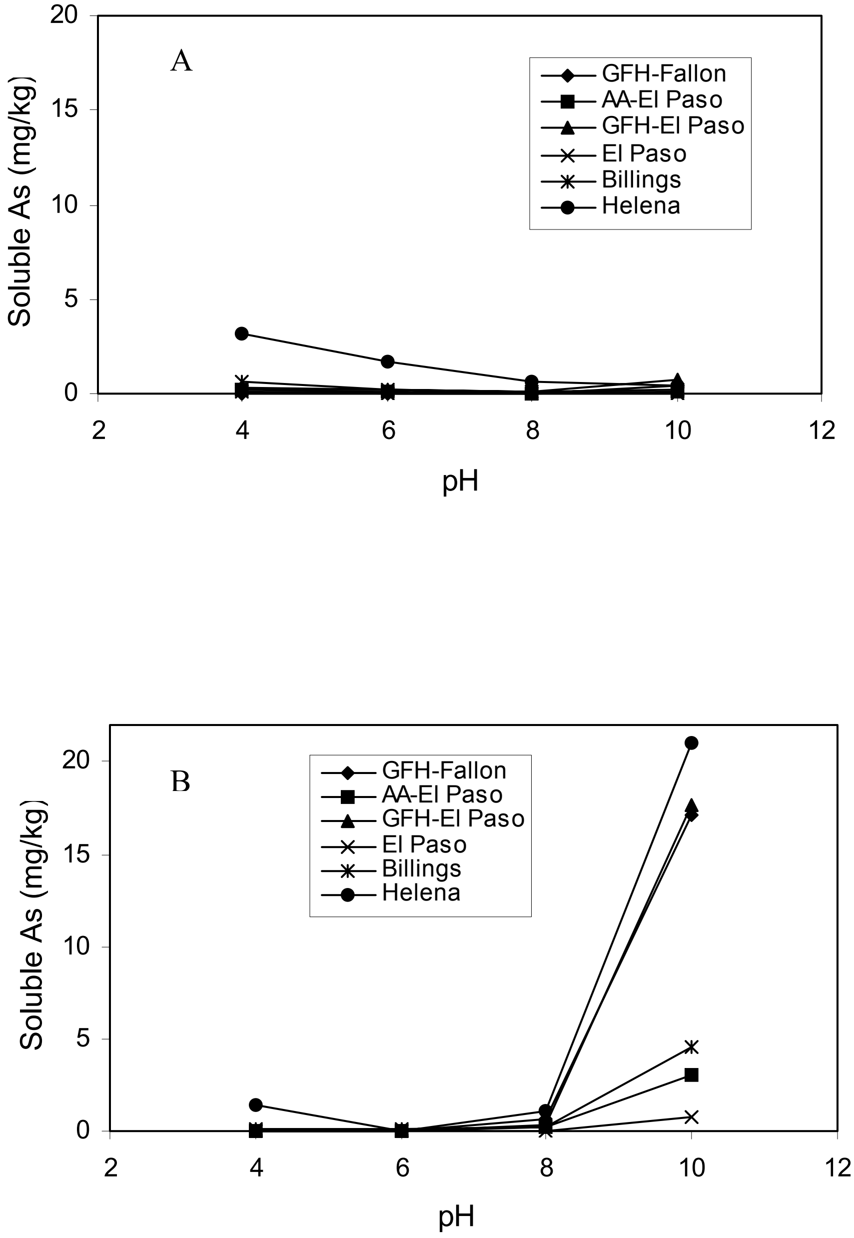


TABLE 4.6 Effect of pH on leaching: Fe

pH	GFH – Fallon (mg/kg)	AA – El Paso (mg/kg)	GFH – El Paso (mg/kg)	El Paso (mg/kg)	Billings (mg/kg)	Helena (mg/kg)
4	< 1	< 1	< 1	1572	2262	504
6	< 1	< 1	< 1	< 1	< 1	4
8	< 1	< 1	< 1	< 1	< 1	< 1
10	457	< 1	1356	< 1	< 1	12

TABLE 4.7 Effect of pH on leaching: Al

pH	GFH – Fallon (mg/kg)	AA – El Paso (mg/kg)	GFH – El Paso (mg/kg)	El Paso (mg/kg)	Billings (mg/kg)	Helena (mg/kg)
4	< 20	1143	< 20	85	304	1669
6	< 20	< 20	< 20	< 20	< 20	< 20
8	< 20	< 20	< 20	< 20	< 20	< 20
10	< 20	72	< 20	< 20	36	658

TABLE 4.8 Effect of pH on leaching: Ca

pH	GFH – Fallon (mg/kg)	AA – El Paso (mg/kg)	GFH – El Paso (mg/kg)	El Paso (mg/kg)	Billings (mg/kg)	Helena (mg/kg)
4	1636	7434	9421	31487	13263	1054
6	684	4299	6757	25344	4925	510
8	16	959	944	432	755	183
10	10	108	179	133	112	100

Higher arsenic concentrations were observed at low and high pH (4 and 10). As(III) concentrations were highest at pH 4, and soluble As(V) concentrations were highest at pH 10. The maximum adsorption for As(V) and As(III) usually occurs around pH 5 and around 9, respectively. Results of soluble Fe and Al concentrations were similar to those of arsenic. Interestingly, higher leached Fe and As(V) concentrations in GFH – Fallon and GFH – El Paso residuals were observed simultaneously at pH 10 because dissolution of Fe hydroxides occurred and, subsequently, As(V) was released. Higher soluble Al concentrations were observed at pH 4 than at low pH 10. Leached Ca concentrations were substantially increased as pH decreased due to the increase of Ca solubility. The results obtained in this study were very similar to those of other investigators (Carbonell-Barrachina et al, 1999; Masscheleyn et al, 1991)

The As(III) and As(V) desorption trends can be explained by the dissolution of Fe and Al hydroxides (i.e., increase of solubility) and the charge of arsenic species. The solubility diagrams of the Fe hydroxides as a function of pH are shown in Figure 4.5, which was constructed based on the hydrolysis constants in Table 4.9. Activity coefficients for the species were ignored, so activities and concentrations were assumed to be equal.

In the Table 4.9, $^*\beta$ is the hydrolysis constant. For the general reaction,

$$M + iHL = ML_i + iH^+ \tag{4.2}$$

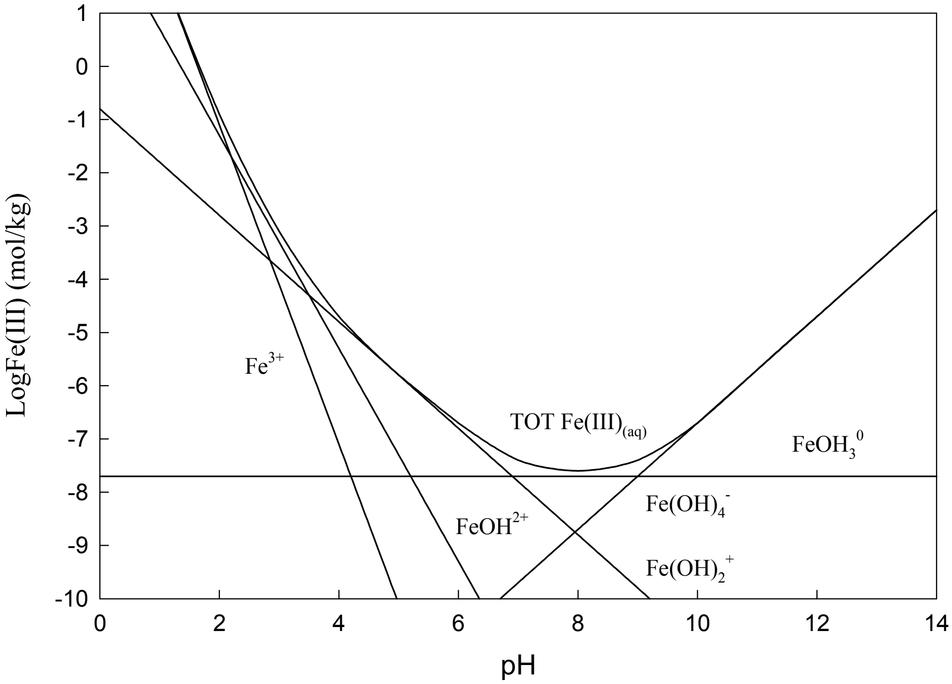
where, M = metal, and L = ligand.

$$^{*}\beta_i = \frac{[ML_i][H^+]^i}{[M][HL]^i} \tag{4.3}$$

TABLE 4.9 The hydrolysis constants for the Fe hydroxides (Langmuir, 1997b)

Reaction	$-\log{}^{*}\beta_i$
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	2.19
$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	5.67
$Fe^{3+} + 3H_2O = Fe(OH)_3^0 + 3H^+$	12.56
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	21.6

FIGURE 4.5 Solubility of amorphous $Fe(OH)_3$, $K_{sp} = 10^{-37.1}$, as a function of pH at 25°C



The solubility of Al hydroxide as a function of pH (Figure 4.6) was drawn using the same method used for the solubility of Fe hydroxide. Hydrolysis constants are summarized in Table 4.10.

The phenomenon of the increase in solubility of the solids, such as Fe and Al hydroxides, at low and high pHs is termed amphoteric behavior. By the amphoteric behavior, the solids are dissolved to form cationic species at low pH and to form anionic species at high pH (Langmuir, 1997b).

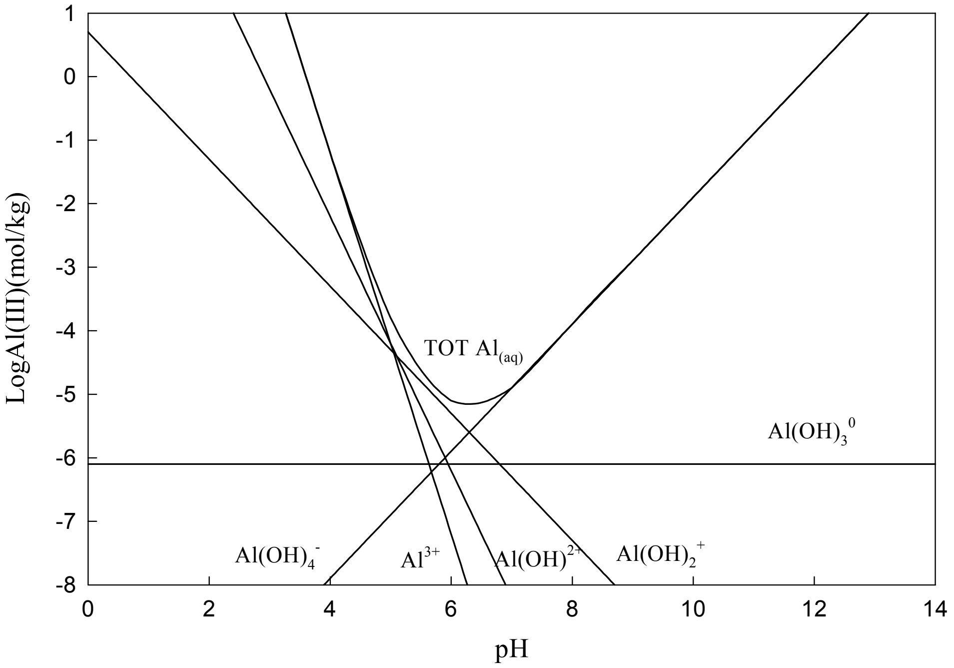
TABLE 4.10 The hydrolysis constants for the Al hydroxides (Langmuir, 1997b)

Reaction	$-\log{}^*\beta_i$
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	5
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$	10.1
$Al^{3+} + 3H_2O = Al(OH)_3^0 + 3H^+$	16.9
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$	22.7

An equation for the H^+ enhanced dissolution reaction can be expressed as in equation 4.4 (Loeppert et al, 2003). This equation basically describes the formation of cationic species by the dissolution of metal hydroxides.

$$\text{M-oxide-}AsO_4 + H^+ \rightarrow M^{3+} + H_2O + As_{aq} \qquad (4.4)$$

FIGURE 4.6 Solubility of amorphous $Al(OH)_3$, $K_{sp} = 10^{-31.2}$, as a function of pH at 25°C



During the dissolution of Fe and Al hydroxides, surface arsenic species can also be dissolved. At pH 4, the predominant As(III) species is $H_3AsO_3^0$, which has a neutral charge. The surfaces of Fe and Al hydroxides are positively charge at low pH (equation 4.4) and the charge of dominant As(III) species, which is neutral. Therefore, the dissolution of metal hydroxides, and at pH 4, positively charged surfaces of metal hydroxides and a neutral charge of dominant As(III) species facilitate the release of bound arsenic, and readsorption of leached As(III) cannot readily occur. At pH 4, the prevalent species for As(V) is $H_2AsO_4^-$, which can be easily adsorbed onto the metal hydroxides. Therefore, soluble As(V) concentration in the leachate was lower than that of As(III) at low pH (pH 4).

At high pH, anionic species of Fe and Al hydroxides are increased by the OH^- enhanced dissolution process, which can be expressed as in equation 4.5 (Loeppert et al, 2003; Jackson & Miller, 2000).

$$\text{M-oxide-AsO}_4 + \text{OH}^- \rightarrow \text{M-(OH)}_4^- + \text{As}_{aq} \qquad (4.5)$$

The surfaces of Fe and Al hydroxides are negatively charged at high pH. Therefore, the increasingly negative surface potential with increasing pH makes for unfavorable conditions for the adsorption of anionic arsenic species such as $HAsO_4^{-2}$ for As(V) and H_3AsO_3 and $H_2AsO_3^-$ for As(III) at pH 10. Finally, arsenic ions are leached from the sorption sites. In brief, the increasing negative surface charge of the metal hydroxides with increasing pH promote the desorption of As(V). The neutrally and negatively charged species of As(III) are predominant at pH 10 and thus, As(III) should be released due to repulsion from the negatively charged surface of metal hydroxides. It is expected that, at pH 10, the reason why leached As(III) concentrations were less than As(V) might be the lower concentrations of As(III) contained in the residuals and the presence of neutrally charged species of As(III).

At neutral pH (pH 6 and 8), the released arsenic concentrations and soluble Fe and Al concentrations were very low due to the insolubility of the Fe and Al hydroxides and the predominant arsenic species. When the disposal of the arsenic tainted residuals is planned without any post-treatment such as S/S, the neutral pH condition of the system should be maintained to minimize arsenic solubility and mobilization.

4.2. SOLIDIFICATION AND STABILIZATION OF FIELD RESIDUALS

The residuals employed for solidification and stabilization (S/S) treatment were GFH – Fallon and AA – El Paso. The selection criteria were arsenic concentration and the available amount of residual. In this section, GFH – Fallon was noted as GFH and AA – El Paso as AA. Lime (hydrated lime, $Ca(OH)_2$) and ordinary Portland cement (OPC) were utilized as binders for S/S. TCLP extraction solution #2 (0.1 M acetic acid, pH = 2.88), noted as TCLP #2, and phosphate solution (0.1 M NaH_2PO_4, pH=10), noted as 0.1M phosphate, were used for the extraction studies.

4.2.1 Addition of Lime Only

Granular Ferric Hydroxide (GFH). In the first step for the optimization of the solidification and stabilization (S/S) procedure, $Ca(OH)_2$ was added to the residual in 1 g increment per 10 g of air-dried residual and the solidified materials were cured for 7 days under laboratory conditions. The effects of lime addition on arsenic leaching of GFH are shown in Table 4.11 and Table 4.12.

TABLE 4.11 Extracted As, Fe, and Ca concentrations and final pH by TCLP #2 depending on lime addition: GFH

Lime addition (g)	As(III) (μg/L)	As(V) (μg/L)	Fe (mg/L)	Ca (mg/L)	Final pH
0	< 1	23	2	56	3.53
1	< 1	9	< 0.05	1616	6.30
2	< 1	4	< 0.05	1574	8.36
3	< 1	3	< 0.05	1574	11.08
4	< 1	3	< 0.05	1923	11.09
5	< 1	2	< 0.05	1816	11.22
6	< 1	2	< 0.05	2014	11.28
7	< 1	1	< 0.05	1970	11.32
8	< 1	2	< 0.05	1880	11.35
9	< 1	2	< 0.05	1987	11.37
10	< 1	1	< 0.05	2076	11.38

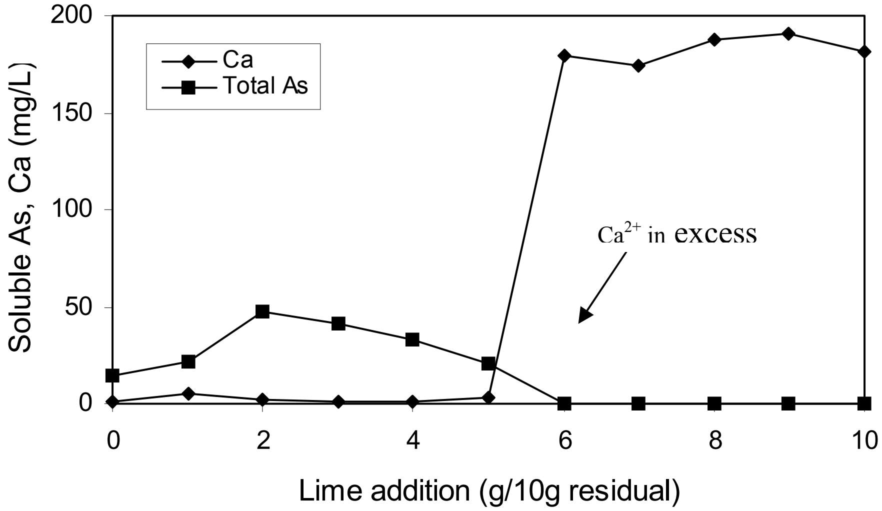
As shown in Table 4.11, leached arsenic concentrations were very low by the extraction test of TCLP #2 (pH=2.88). Therefore, it was almost impossible to find any effect of lime addition on arsenic leaching. However, the effect of lime addition was obvious when solidified materials were subject to a 0.1 M phosphate extraction solution (pH=10). The final pH of leachate by phosphate extraction was in the range of 10.2 to 13.2 depending on the lime addition. The soluble total As and Ca concentrations in the leachate by phosphate extraction as a function of lime addition is drawn in Figure 4.7.

TABLE 4.12 Extracted As, Fe, and Ca concentrations and final pH by 0.1 M phosphate depending on lime addition: GFH

Lime addition (g)	As(III) (μg/L)	As(V) (μg/L)	Fe (mg/L)	Ca (mg/L)	Final pH
0	150	14783	3	1	9.17
1	321	21354	< 0.05	5	10.24
2	529	47047	< 0.05	2	11.80
3	422	41271	< 0.05	1	12.72
4	362	32776	< 0.05	1	12.95
5	210	20286	< 0.05	3	13.01
6	< 1	5	< 0.05	180	13.11
7	< 1	1	< 0.05	174	13.15
8	< 1	1	< 0.05	187	13.15
9	< 1	1	< 0.05	191	13.16
10	< 1	1	< 0.05	182	13.17

The leached arsenic concentrations when compared to the no addition of lime (untreated GFH) increased when 1 to 5 g of lime was added. The behavior may be explained in that the pH values of the treatment increased with increasing lime addition, which might have made for unfavorable conditions for As(V) adsorption. However, soluble arsenic concentrations in the leachate were reduced when 6 g of lime was added. From the lime addition of 6 to 10 g, desorbed arsenic concentrations were not detected. At the range of 6 to 10 g of lime addition, excessive calcium, which did not join in any reactions, was found.

FIGURE 4.7 Soluble total As and Ca concentrations by 0.1M phosphate extraction as function of lime addition: GFH



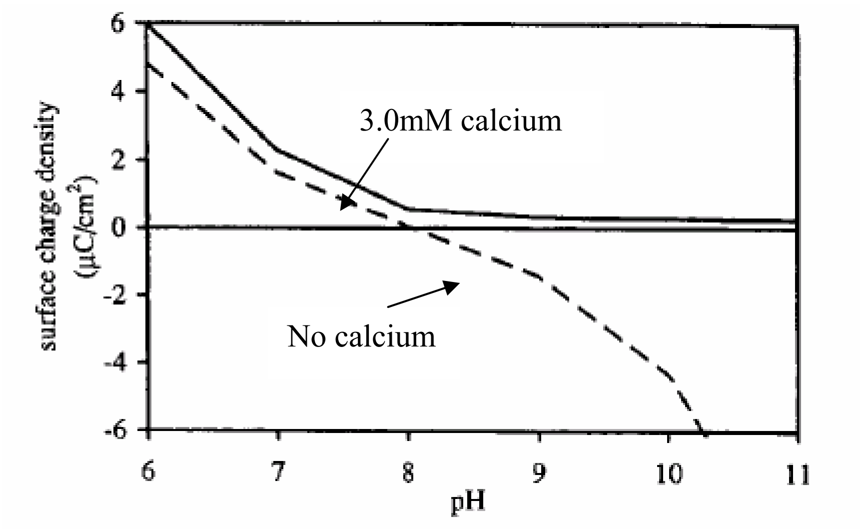
There are three possible explanations for the results observed in Table 4.12. The first is that phosphate in the extraction solution was precipitated with the lime (Marani et al, 1997) or with calcite ($CaCO_3$) (Donnert & Salecker, 1999). In wastewater treatment, lime has been frequently used to remove phosphorous. During the curing for 7 days, lime can react with atmospheric CO_2 and calcite ($CaCO_3$) generation might be possible. The pK values for phosphate are 2.2 for pK_1, 7.2 for pK_2, and 12.4 for pK_3. Thus, PO_4^{3-} is the predominant species of phosphate ions due to the high pH in the suspensions. $Ca_4H(PO_4)_3$ and /or $Ca_5(PO_4)_3OH$ could be generated as precipitated forms even though this should be determined by X-ray diffraction analysis. It appears that this explanation is likely. However, at high pH, the release of As(V) and Fe should be substantial, but the results obtained did not follow this expected trend. In brief, little or very low concentrations of As(V) and Fe were observed in the leachates even though the system pH was over 12. However, the removal of phosphate by precipitation should not be discounted.

The second explanation is that calcium-iron-arsenic compounds were generated by calcium hydration during the 7-day curing period. The final pH of leachates was very high. Thus, iron hydroxides are supposed to be dissolved as $Fe(OH)_4^-$. However, no soluble iron was detected. It is expected that calcium could play a critical role to prevent the iron leaching by the formation of calcium-iron compounds (Wilkie & Hering, 1996). Therefore, the bound arsenic on the surface of the iron hydroxides was not extracted due to the formation of calcium-iron compounds and maintenance of positive surfaces even though pH of the system was over 12. Wilkie & Hering (1996) suggested the cooperative effect of calcium on the adsorption of As(V) at high pH. According to their description, the adsorption of Ca^{2+} onto iron hydroxides resulted in a positive surface charge of the adsorbents in the high pH range. Thus, this made for favorable conditions for As(V) adsorption. The change of surface charge on Fe hydroxides in the presence or absence of calcium is illustrated in Figure 4.7. The suggested surface ractions for the complexation of Fe hydroxide and calcium and intrinsic adsorption constants (Schecher & McAvoy, 1994) are :

$$\equiv Fe^{w}OH + Ca^{2+} = \equiv Fe^{w}OCa^{+} + H^{+} \qquad \text{Log } K^{int} = -5.85 \qquad (4.6)$$

$$\equiv Fe^{s}OH + Ca^{2+} = \equiv Fe^{s}OHCa^{2+} \qquad \text{Log } K^{int} = 4.97 \qquad (4.7)$$

FIGURE 4.8 Surface charge density of Fe hydroxide as affected by calcium: Model predictions for TOT Fe = 50 μM in 0.01 M $NaNO_3$



Source: Wilkie & Hering, 1996

The cooperative effect of calcium was found in the phosphate adsorption on goethite in seawater, i.e. the enhancement of phosphate adsorption was observed in the presence of calcium at high pH (Hawke et al, 1989). The cooperative effect of calcium also has a drawback to be applied to the solidification with lime, because the effect was observed when both $Ca(OH)_2$ and Fe hydroxides were added together to remove As(V). In the systems studied in this research, lime was mixed with the GFH that already contained arsenic compounds. Therefore, it is not clear what portion of calcium was bound on the surface of the GFH with 7 days of curing time. The chemistry of the phosphate extraction system for GFH residuals solidified by lime is complex. Therefore, a variety of experiments, analyses and supporting data are absolutely required in order to obtain an explanation.

The last reason for the reduction of soluble arsenic concentration in the leachate is from the formation of less soluble calcium-arsenic compounds at high pH: calcium arsenate ($Ca_4(OH)_2(AsO_4)_2 \bullet 4H_2O$ and $Ca_4(AsO_4)_3OH$) or calcium arsenite ($CaHAsO_3$) (Kameswari et al, 2001; Bothe & Brown, 1999; Dutre & Vandecasteele, 1995). Solubility of iron hydroxides increases with the increase of system pH. Thus, the possibility of arsenic leaching was extended. However, calcium hydroxide solubility is low at high pH so calcium might precipitate with the arsenic and form less soluble calcium-arsenic compounds. This explanation is expected to be the most feasible one to interpret Figure 4.7. Bothe & Brown (1999) studied the effects of phosphate on the possible release of As(V) solidified with lime. They reported the control of solution phase composition by arsenate apatite ($Ca_5(AsO_4)_3OH$) in the suspensions containing phosphate, the formation of arsenate apatite at the expense of phosphate apatite ($Ca_5(PO_4)_3OH$), and no observation of solid solution transition between $Ca_5(AsO_4)_3OH$ and $Ca_5(PO_4)_3OH$ under the ambient conditions.

Activated Alumina (AA). The solidification/stabilization (S/S) of AA with the addition of lime only was also carried out, and S/S procedures, curing, and extraction tests were applied as those to GFH. Tables 4.13 and 4.14 present the soluble As(III), As(V), Al, and Ca concentrations and final pHs in leachates by TCLP #2 extraction and 0.1 M phosphate extraction, respectively. In general, very low concentrations of As(III) and As(V) were leached by the TCLP as shown in Table 4.13. Therefore, the extraction method is not suitable to show the effects of lime addition for the reduction of arsenic leaching.

TABLE 4.13 Extracted As, Al, and Ca concentrations and final pH by TCLP #2 depending on lime addition: AA

Lime addition (g)	As(III) (µg/L)	As(V) (µg/L)	Al (mg/L)	Ca (mg/L)	Final pH
0	12	1	101	166	4.12
1	3	4	1	1932	6.19
2	< 1	3	10	1776	10.20
3	< 1	1	2	2074	12.03
4	< 1	< 1	1	2742	12.37
5	< 1	< 1	1	2738	12.39
6	< 1	< 1	1	2395	12.41
7	< 1	< 1	1	2360	12.42
8	< 1	< 1	2	2768	12.46
9	< 1	< 1	2	2331	12.49
10	< 1	< 1	2	2326	12.50

As(V) was the predominant species of released arsenic due to the very high pH. Arsenic leaching increased as the amount of lime added was increased from 1 to 3, slowly reduced when 4 and 5 g of lime was added, and finally rapidly dropped when 6 and 7 g of lime was added. The arsenic leaching trend for AA was similar to that for GFH. The tendency of leached Al concentrations followed that of arsenic as shown in Table 4.14. This trend was obviously different than that of leached Fe concentrations, which were not detected for GFH. The tendency of Ca concentrations detected in leachates was opposite to that of arsenic. It is expected that excessive amounts of Ca, which were not used for arsenic stabilization and dissolved in solution, were detected.

TABLE 4.14 Extracted As, Al, and Ca concentrations and final pH by 0.1 M phosphate depending on lime addition: AA

Lime addition (g)	As(III) (µg/L)	As(V) (µg/L)	Al (mg/L)	Ca (mg/L)	Final pH
0	10	1491	1	6	9.10
1	10	2106	12	4	10.29
2	4	2193	301	4	10.09
3	4	2766	360	7	12.50
4	2	1775	426	12	12.67
5	1	950	349	1	12.76
6	< 1	93	65	10	12.81
7	< 1	< 1	4	148	12.87
8	< 1	4	5	161	12.91
9	< 1	< 1	4	167	12.94
10	< 1	< 1	4	176	12.96

It is suggested that the main mechanism for the prevention of arsenic leaching from AA was the precipitation of arsenic with lime, which generated stable calcium-arsenic compounds.

4.2.2 Addition of OPC Only

Granular Ferric Hydroxide (GFH). Ordinary Portland cement (OPC) is commonly employed as a binder for cement-based solidification and stabilization (S/S). In this study, OPC was mixed at 1, 2, 3, and 5 g with 10 g of residual to determine the effects of OPC addition on arsenic leaching. The leached As(III), As(V), Fe, and Ca concentrations and final pH in leachates by TCLP and 0.1 M phosphate leaching tests are shown in Tables 4.15 and 4.16, respectively.

TABLE 4.15 Extracted As, Fe, and Ca concentrations and final pH by TCLP #2 depending on OPC addition: GFH

OPC addition (g)	As(III) (μg/L)	As(V) (μg/L)	Fe (mg/L)	Ca (mg/L)	Final pH
0	< 1	23	2	56	3.53
1	< 1	7	< 0.05	1517	6.20
2	< 1	13	< 0.05	1587	7.26
3	< 1	32	< 0.05	1533	8.74
5	< 1	17	< 0.05	1518	11.05

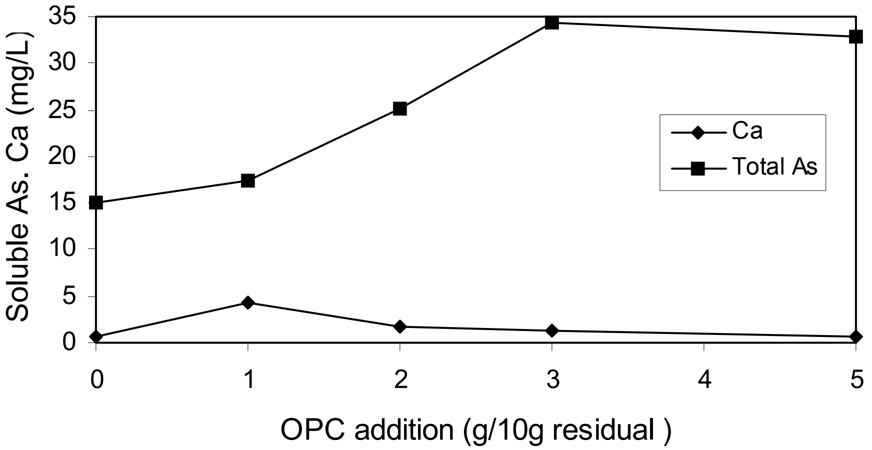
The arsenic concentrations detected in the leachates by the TCLP test were very low. The Ca concentrations found were relatively constant. Therefore, it is thought that calcium might not play any role in arsenic immobilization due to the presence of very low soluble arsenic concentrations. A relationship between arsenic leaching and OPC addition was not evident.

In the phosphate leaching study, it was obvious that OPC addition did not present a positive influence on arsenic immobilization as shown in Table 4.16. The results might be explained by two reasons: the available amount of Ca and pH. About 20 to 25% of $Ca(OH)_2$ from OPC by weight is normally generated from cement hydration (Glasser, 1993). Therefore, the available amount of calcium, which can precipitate arsenic and form stable calcium-arsenic compounds, was absolutely lower when compared to the results of lime addition. Thus, the released arsenic concentrations were considerable. To overcome this problem, higher amount of OPC would be required. As shown in Table 4.16, the final pH of leachates was high and this made for an unfavorable condition for As(V) adsorption. The relationship of total As concentration released and OPC addition is described in Figure 4.9.

TABLE 4.16 Extracted As, Fe, and Ca concentrations and final pH by 0.1 M phosphate depending on OPC addition: GFH

OPC addition (g)	As(III) (μg/L)	As(V) (μg/L)	Fe (mg/L)	Ca (mg/L)	Final pH
0	150	14783	3	1	9.17
1	199	17257	< 0.05	4	10.10
2	226	24970	< 0.05	2	10.83
3	325	34043	< 0.05	1	11.71
5	297	32510	< 0.05	1	12.65

FIGURE 4.9 Soluble total As and Ca concentrations by 0.1 M phosphate as function of OPC addition: GFH



Activated Alumina (AA). The results of S/S with the addition of OPC only for AA are shown in Tables 4.17 and 4.18. The TCLP extraction test did not demonstrate any effects of OPC addition on arsenic leaching; the same as for GFH.

TABLE 4.17 Extracted As, Al, and Ca concentrations and final pH by TCLP #2 depending on OPC addition: AA

OPC addition (g)	As(III) (μg/L)	As(V) (μg/L)	Al (mg/L)	Ca (mg/L)	Final pH
0	12	1	101	166	4.12
1	3	1	1	1601	5.96
2	1	7	1	1731	7.03
3	< 1	11	1	1782	10.25
5	< 1	2	1	1845	11.17

The main reason for the high soluble As(V) concentrations detected in the leachates is that the concentration of calcium in the system was not high enough.

TABLE 4.18 Extracted As, Al, and Ca concentrations and final pH by 0.1 M phosphate depending on OPC addition: AA

OPC addition (g)	As(III) (μg/L)	As(V) (μg/L)	Al (mg/L)	Ca (mg/L)	Final pH
0	10	1491	1	6	9.08
1	9	2040	1	3	10.08
2	10	3304	2	3	10.89
3	12	2309	9	2	11.62
5	8	2352	41	1	12.46

From the S/S study with the addition of OPC only to GFH and AA, it is suggested that OPC may not contribute positively to the immobilization of arsenic in residuals (Dutre & Vandecasteele, 1995). However, OPC should be used to improve the handling and the physical characteristics of the residuals (LaGrega et al, 1994).

4.2.3 Addition of Lime and OPC

Granular Ferric Hydroxide (GFH). Six grams of lime and 3 and 5 g of OPC were selected based on the addition of lime only and OPC only studies and added to 10 g of residual. The results of TCLP and phosphate leaching tests are shown in Table 4.19. Two sets of binder-residual mixtures (6 g of lime + 3 g of OPC and 6 g of lime + 5 g of OPC) gave very similar results for arsenic leaching as expected.

TABLE 4.19 Extracted As, Fe, and Ca concentrations by TCLP #2 and 0.1M phosphate extraction depending on lime and OPC addition: GFH

TCLP	Lime (g)	OPC (g)	As(III) (μg/L)	As(V) (μg/L)	Fe (mg/L)	Ca (mg/L)
	6	3	< 0.1	4	0.1	5162
	6	5	< 0.1	3	0.1	1202
Phosphate	**Lime (g)**	**OPC (g)**	**As(III) (μg/L)**	**As(V) (μg/L)**	**Fe (mg/L)**	**Ca (mg/L)**
	6	3	< 0.1	18	< 0.05	151
	6	5	< 0.1	24	< 0.05	127

When comparing the above results with those for the addition of lime only, there were no statistical differences for arsenic immobilization. However, the addition of lime only for the S/S of arsenic containing residuals has a problem because calcium-arsenic compounds may decompose slowly when exposed to atmospheric CO_2 (Riveros et al, 2001). The generally accepted equation for the reaction is

$$Ca_3(AsO_4)_2 + 3CO_2 + 3H_2O \rightarrow 3CaCO_3 + 2H_3ASO_4 \tag{4.8}$$

Therefore, any barriers which can block contact between the calcium-arsenic compounds and atmospheric CO_2 will be necessary for the management of arsenic immobilization in the residuals for a long period of time.

Activated Alumina (AA). Four sets of binder-residual mixtures were chosen based on the addition of lime only and OPC only studies. The results of the S/S with lime and OPC for AA are shown in Table 4.20.

From the above studies, it is suggested that the arsenic in the residuals can be successfully immobilized by the addition of lime and OPC. However, aging extraction tests for long time periods (e.g. over one year) are obviously necessary to demonstrate the efficiency of the stabilization of arsenic in water treatment residuals by lime and OPC addition.

TABLE 4.20 Extracted As, Al, and Ca concentrations by TCLP and phosphate extraction depending on lime and OPC addition: AA

TCLP	Lime (g)	OPC (g)	As(III) (μg/L)	As(V) (μg/L)	Al (mg/L)	Ca (mg/L)
	6	3	< 1	< 1	2	2086
	6	5	< 1	< 1	3	2064
	7	3	< 1	< 1	2	2143
	7	5	< 1	< 1	3	2179
Phosphate	**Lime (g)**	**OPC (g)**	**As(III) (μg/L)**	**As(V) (μg/L)**	**Al (mg/L)**	**Ca (mg/L)**
	6	3	< 1	1	7	139
	6	5	< 1	1	7	143
	7	3	< 1	1	8	141
	7	5	< 1	< 1	6	150

CHAPTER V

SUMMARY AND CONCLUSIONS

5.1 CHARACTERIZATION OF FIELD RESIDUALS

The arsenic leaching in water treatment residuals by the toxicity characteristic leaching test (TCLP) was underestimated due to the pH of the leachates, which are favorable for As(V) adsorption. The pH values in the leachates for TCLP extraction solutions #1 and #2 were 5.1 to 6.6 and 3.5 to 4.9 depending on the residual types, respectively. The released arsenic concentrations by TCLP #2 were generally higher than those by TCLP #1.

The presence of phosphate could produce an unfavorable condition for the binding of arsenic onto the adsorbents. The extracted As(V) concentrations by phosphate competition were substantial for each of the water treatment residuals. The effects of sulfate and chloride were negligible.

The pH values of the leachates were the most important factor in controlling arsenic behavior in the residuals. High concentrations of arsenic released were detected at low and high pH due to the increase in solubility of adsorbents such as Fe and Al hydroxides and the predominant arsenic species at that pH range.

The results obtained suggest that maintaining neutral pH in the environment for the residuals and minimizing the influent of arsenic competing ions such as phosphate are very important to enhance the stability of arsenic when arsenic containing residuals are disposed into a landfill without post-treatment.

5.2. SOLIDIFICATION AND STABILIZATION OF FIELD RESIDUALS

The reduction of arsenic concentration in the leachate can be obtained by the addition of lime to the residuals due to the formation of less soluble and stable calcium arsenic compounds. In practical aspects, solidified materials treated only by lime are not stable for the long term since the buffering effects of lime are decreased by dissolution and carbonation when exposed to atmospheric CO_2. Therefore, it is suggested that cement should be added with the lime in order to prevent and minimize the arsenic leaching over the long term.

It is thought that the immobilization of arsenic in residuals can be achieved through the formation of less soluble calcium arsenic compounds using lime and cement. Therefore, solidification and stabilization (S/S) techniques with lime and cement can be successfully applied to the immobilization of elevated arsenic concentrations in water treatment residuals.

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