THE INFLUENCE OF CALCIUM ON THE INHIBITION OF ARSENIC DESORPTION FROM TREATMENT RESIDUALS IN EXTREME ENVIRONMENTS

A Thesis

by

JULIANNA G. CAMACHO

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

December 2004

Major Subject: Civil Engineering

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Approved as to style and content by:

Timothy A. Kramer (Chair of Committee)	Bill Batchelor (Member)
Richard H. Loeppert (Member)	David V. Rosowsky (Head of Department)

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ABSTRACT

The Influence of Calcium on the Inhibition of
Arsenic Desorption from Treatment
Residuals in Extreme Environments. (December 2004)

Julianna G. Camacho, B.S., University of Puerto Rico
Chair of Advisory Committee: Dr. Timothy A. Kramer

One of the most toxic environmentally mobile compounds found in water is arsenic. It has been used as a pesticide to control insects, fungi, weeds and rodents since the early part of this century because of its high toxicity. Sorption of toxic metals onto a metal oxy-hydroxide is the most popular and practical arsenic removal method from contaminated water. Water treatment with oxy-hydroxides creates arsenic containing residuals, which are usually disposed of in landfills. To prevent leaching, stabilization of the solid residuals is required. It has been reported that calcium may inhibit arsenic desorption and/or benefit arsenic sorption. The objective of this investigation is to assess arsenic leaching in the presence of calcium and phosphate ions at extreme pH. Two hypotheses have been identified to explain the decrease in soluble arsenic in the presence of calcium. One explanation is that arsenic reacts with calcium to form calcium arsenic solids. The second hypothesis is that calcium affects the surface properties of the oxy-hydroxide solid in solution.

Results show that calcium enhances the removal by iron oxides and prevents the leaching of arsenic from the residuals. Isotherm experiments show that arsenic adsorption can be described as occurring on nonporous powders or powders with pore diameters larger than micro-pores. Physically, with increase in adsorbate concentration, second and more layers are completed until saturation when the numbers of adsorbed layers becomes infinite. Further, experimental data were fitted to a Brunauer, Emmett and Teller isotherm (BET) model which assumes the initial layer can act as substrate for further adsorption. Finally, calcium-arsenic and calcium-phosphate solids were predicted to be formed by Visual MINTEQ modeling program. Nevertheless, from the x-ray diffraction output calcium-arsenic or calcium-phosphate solids were not identified.

Because no calcium arsenate solids were found it was concluded that calcium affects the surface properties of the oxy-hydroxide solids in solution. Increasing the pH produces negative surface charge, which in turn increases repulsion between the negatively charged hydrated arsenate ions and the $Fe(OH)_3$ surface. Calcium's positive charge might neutralize this effect enhancing the sorption of arsenic onto the oxy-hydroxide. Also, it was concluded that the competition between arsenic and phosphate was reduced by the same mechanisms.

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INTRODUCTION

One of the most toxic environmentally mobile compounds found in water is arsenic (As). Discovered in 1649, this naturally occurring metal is rare in its pure form. Arsenic, due to its high toxicity, has been used as a pesticide to control insects, fungi, weeds and rodents since the early part of this century (DeSesso et al., As of 1993, regulation in the United States prohibited all uses of arsenic in pesticides and herbicides.

The United Nations stated that there are approximately 20 countries, including the United States, where groundwater arsenic contamination has been reported and that arsenic pollution of drinking water extracted from groundwater aquifers has become an immense problem throughout Southeast Asia (Viraraghavan et al., 1999). The arsenic contamination of the groundwater in Bangladesh is one of the largest environmental tragedies in the last century. The Ganges-Meghna-Brahmaputra aquifer, which is the sole drinking water source for approximately 110 million people from Bangladesh and West Bengal, India, is contaminated with arsenic (Smith et al., 2000). The EPA has determined that decades of emissions of arsenic and lead from the ASARCO copper and lead smelters into the El Paso community ambient air have resulted in contamination of the soil in residential areas in the city of El Paso. The EPA began its investigation to determine the extent of the contamination during the week of July 9, 2001. The study by the U.S. Environmental Protection Agency found that soil on the grounds of five El Paso district schools contained high levels of arsenic and lead. The study checked areas around the old Asarco American Eagle Brick. In Texas's Brazos valley, arsenic acid was

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

used to defoliate cotton plants before harvesting. Also, drinking water from private wells in the San Antonio and Nueces River watersheds in South Texas has been reported to contain higher concentrations of arsenic than deemed safe by the U.S. Environmental Protection Agency caused by natural geologic sources of arsenic located in the bedrock of these watersheds.

The effects on humans of drinking arsenic-contaminated water include skin lesions; gangrene; and bladder, kidney, skin, and lung cancer (Smedley and Kinniburgh, 2002). Arsenic is classified by the International Agency of Research on Cancer and the US EPA as a human carcinogen (EPA, 1998). The toxicity of arsenic can be altered by a change in oxidation state. The toxicity of arsenic decreases as it becomes more oxidized (Hughes, 2002). In its reduced state (As (III)) is more toxic and difficult to remove from water than in its oxidized form (As (V)).

The US EPA maximum concentration limit (effective in 2006) for arsenic in drinking water is 10 ppb. Sorption of arsenic onto a metal oxy-hydroxide is the most popular and practical removal method for treatment of contaminated waters (Wilkie and Hering, 1996). Adding salts of metals, such as iron and aluminum, to contaminated waters and hydrolyzing with sodium hydroxide or calcium hydroxide forms the oxy-hydroxide sorbents. These oxy-hydroxides are strong adsorbents for arsenic in water with neutral pH. The arsenic is absorbed to the oxy-hydroxide, which is then settled out of solution. The result is water treatment residuals with high arsenic concentration. These arsenic containing residuals are typically disposed of in landfills (Leist et al., 2000). To prevent arsenic leaching from the disposed residuals, stabilization of the solid is required. Several factors affect the solubility and sorption of arsenic, and thus its leaching potential. In solution, pH has a major effect on the sorption of arsenic compounds. Another major factor is the presence of other ions in solution. These ions can compete with arsenic for sites in the solids or they can enhance the sorption of the arsenic (Kim et al., 2003; Dutre and Vandecasteele, 1995). Generally, the charge of the ion present determines the effect of arsenic sorption and leaching.

It has been reported that calcium may inhibit arsenic desorption and/or benefit arsenic sorption (Bothe & Brown et al., 1999). Also, the ion that most readily competes for sorption sites with arsenic is phosphate ion. The objective of this investigation is to assess arsenic leaching in the presence of calcium and phosphate.

Previous work has shown that elevated pH induced by NaOH addition generates increased leaching of arsenic (Parks et al., 2003). According to Parks et al. this trend is consistent with basic surface complexation models described by Dzombak and Morel (1990).

$$\equiv FeOH + AsO_4^{3-} + 3H^+ \leftrightarrow \equiv FeH_2AsO_4 + H_2O$$

As the pH increases, the H^+ concentration decreases which shifts the equilibrium to the reactants increasing the As(V).

Also, elevated pH induced by $NaCO_3$ addition generates even greater leaching of arsenic (Parks et al., 2003). According to Parks et al., this trend is also consistent with basic surface complexation models described by Dzombak and Morel.

As the pH increases, the H^+ concentration decreases which shifts the equilibrium to the reactants increasing the As(V). Further, as the carbonate concentration increases the competition for arsenic sorption increased resulting in an increase in additional soluble arsenic concentration.

$$\equiv FeOH + CO_3^{2-} + 2H^+ \leftrightarrow \equiv FeOCOOH + H_2O$$

Parks et al. showed that at elevated pH induced by $Ca(OH)_2$ addition generated minor leaching of arsenic. It can thus be inferred that the presence of calcium enhanced the sorption of arsenic onto the iron oxy-hydroxide.

Preliminary experiments for the removal of arsenic were conducted in the presence of phosphate using different quantities of calcium (Wee, 2003). The results are shown in Figure 1.

Figure 1. Soluble Total As and Ca Concentrations by 0.1M Phosphate Extractions as a Function of Lime Addition at pH 8 (Wee, 2003)

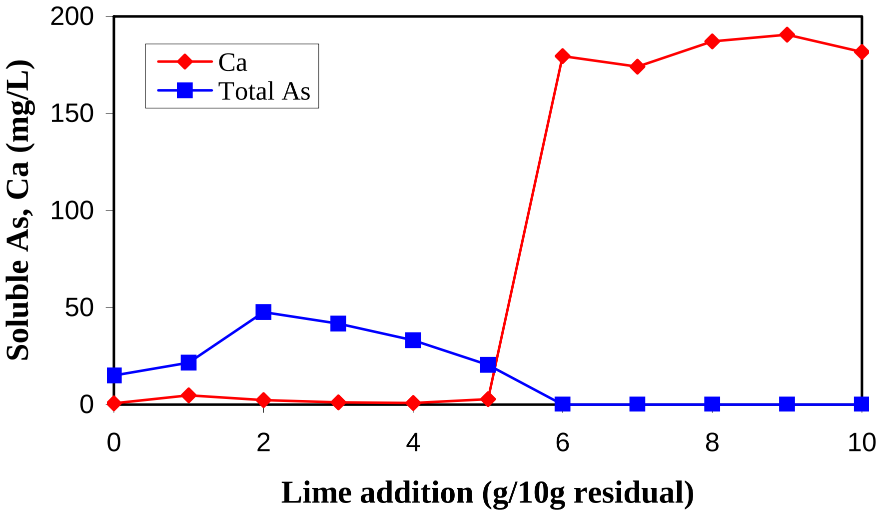


Figure 1 shows that the minimum lime addition that produces the best arsenic removal is 6 grams of lime or greater per 10 grams of dry residual. Other conclusions were drawn from the results of the preliminary experiments. In general, high pH favors arsenate desorption while low pH favors arsenite release. Nevertheless, desorption of arsenic from the iron oxy-hydroxides is minimal for both oxidation states of arsenic. However, the amount of arsenate desorbed was below detection limit at or below a pH of 8 for the iron residuals. Thus, the oxidation of arsenite to arsenate is highly desirable.

Also, while iron show increased desorption at higher pH for arsenate, calcium hydroxide actually lowers desorption. Thus, calcium addition with ferric chloride based coagulation may be the key to obtaining residuals that remain stable (resist leaching of arsenic) over a broad range of pH. When a competing ion is introduced in solution (i.e. phosphate) it significantly influences arsenic desorption of the iron-based residuals even in the presence of calcium. Finally, the metal salt-based residuals have a strong tendency to buffer the water and thus resist pH extremes. The iron residuals tend to maintain a neutral pH while the calcium residuals raise pH.

RESEARCH OBJECTIVES

The objective of this investigation is to assess arsenic leaching in the presence of enhancing (calcium) and competing (phosphate) ions at extreme pH. Two hypotheses have been identified to explain the decrease in soluble arsenic in the presence of calcium. One explanation is that arsenic reacts with calcium to form calcium arsenic solids. Calcium arsenic solids formation has been observed at pH>11.5 (Bothe & Brown, 1999; Parks et al., 2003). The second hypothesis is that calcium affects the surface properties of the oxy-hydroxide solid in solution. Increasing pH produces negative surface charge, which in turn increases repulsion between the negatively charged hydrated arsenate ions and the $Fe(OH)_3$ surface. Calcium's positive charge might neutralize this effect therefore enhancing the sorption of arsenic on to the oxy-hydroxide. While, the presence of a competing ion should increase the leaching of arsenic, the same hypotheses are expected to hold. To be exact, competition between arsenic and phosphate may be reduced by the same two hypotheses mechanisms. Calcium arsenic phosphate solids could be formed or calcium's positive charge might neutralize repulsion between the negatively charged phosphate ions and the $Fe(OH)_3$ surface.

This investigation will attempt to establish whether the decrease in arsenic leaching from iron oxy-hydroxides with calcium addition is due to calcium arsenic solid formation or a surface reaction with the residuals. Also, the decrease in arsenic phosphate competition, thus arsenic leaching from iron oxy-hydroxides, with calcium addition is due to calcium arsenic phosphate solid formation or a surface reaction with the residuals.

To establish the formation of calcium arsenic solids, tests will be conducted at different pH by adding calcium and iron salts to arsenic contaminated water. The precipitated solid is then analyzed with X-ray diffraction. Previous research has established that such solids do not form at pH<11.5. The solid-phase assemblages previously studied were:

$$\begin{array}{ll} Ca_4(OH)_2(AsO_4)_2 \bullet 4H_2O & Ca_3(AsO_4)_2 \bullet {}^{17}\!/_{4}\, H_2O \\ Ca_5(OH)_2(AsO_4)_3OH & Ca_3(AsO_4)_2 \bullet {}^{11}\!/_{3}\, H_2O \end{array}$$

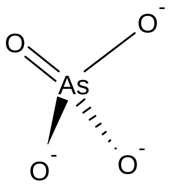
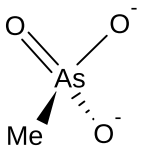
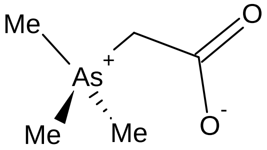
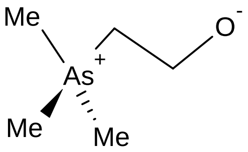
To attest that a surface reaction with the residuals is occurring, arsenic sorption test will be conducted. The data can be modeled by absorption isotherm equations, which can predict the amount of arsenic that can be removed at specific conditions and the shape of the isotherm will help describe the adsorption mechanism occurring.

Finally, the same work will be repeated in the presence of phosphate to test the two hypotheses in the presence of competing ions. The competing ion shown to cause the major impact in the leaching of arsenic from iron oxy-hydroxides is phosphate. The formation of phosphate calcium solid compounds will be explored and the mechanism of adsorption of arsenic in its presence studied.

ARSENIC IN DRINKING WATER

Arsenic is a metalloid found in water, soil, and air from natural and anthropogenic sources. It is the 51st most abundant element in the Earth's crust. Arsenic is usually found combined with one or more elements such as oxygen, hydrogen, chlorine, and sulfur and is referred to as inorganic arsenic. Over 150 arsenic-bearing minerals have been identified which occur mainly as sulphides and which are usually associated with ores containing copper, lead, zinc, gold and silver (Norman, 1998). When arsenic combines with carbon and hydrogen it is referred to as organic. In general the inorganic forms are more toxic. In water, inorganic arsenic is usually in two oxidation states, As (V) arsenate and As (III) arsenite. The more commonly known arsenic compounds are the anionic forms of arsenic acid and arsenous acid, respectively. Although the use of arsenical products such as pesticides and herbicides has decreased significantly in the last few decades, their use for wood preservation is still common (DeSesso et al., 1998). Chromate copper arsenate(V) and ammoniacial copper arsenite(III) are used in wood treatment as preservatives. Arsenic was a common pesticide used extensively in fruit production to control pH and eradicate the codling moth in orchards. Sodium arsenate is used to control fungi, which cause measles on grapes. Sodium arsenite and monomethyl arsenate are used as simple bulk weed killers, and arsenicals such as sodium arsenate and copper acetoarsenite ($Cu(CH_3COO)_2Cu(AsO_2)_2$) can be found in commercial household insecticides (Kartinen and Martin, 1999). Some common arseic-containing natural products are shown in Table 1.

Table 1. Structure of some common arsenic-containing natural products

Structure	**Name**
	Arsenate
	Methylarsenate
	Arseno-betaine
	Arseno-choline

Arsenic Toxicity

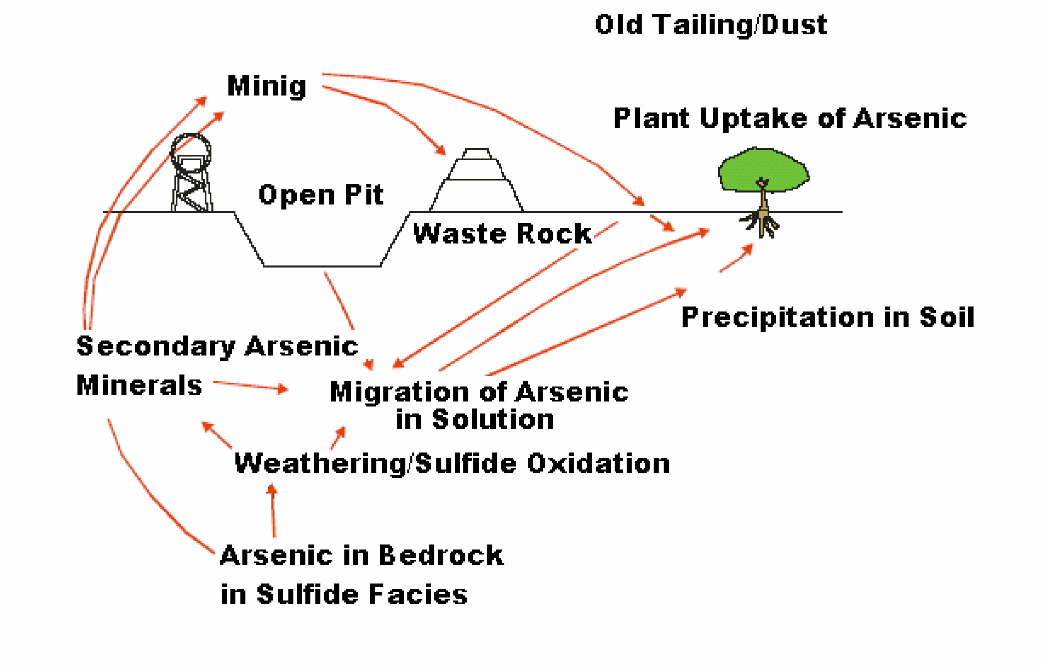
Arsenic is a known poison and carcinogen that has been shown to cause skin and lung cancer. High doses (more than 60 parts per million) of inorganic arsenic can cause damage to tissues including nerves, stomach, and skin, sometimes leading to death. Ingestion of low levels arsenic can also cause nausea, vomiting and diarrhea. It can also decrease production of red and white blood cells and produce abnormal heart rhythms. Some common problems in arsenic patients with arsenical skin lesions include intolerance to sunlight, burning sensation in the entire body, and respiratory problems. Drinking arsenic contaminated water for extended periods of time can result in arsenical symptoms such as melanosis, keratosis, gangrene, non-pitting edema, dorsum, squamous cell carcinoma, bladder cancer, and liver cancer (Hering, 1996).

The toxicity of arsenic can be altered by a change in oxidation state, chemical composition and solubility. The toxicity of arsenic decreases according to the reverse order of oxidation state; arsine > inorganic As (III) > organic As (III) > inorganic As (V) > organic As (V) > arsenous compounds. The metabolism of arsenic in an organism determines its toxic effects. Many mammalian species methylate inorganic arsenic including humans. Nevertheless, there is variation in the ability to methylate inorganic arsenic between species and among human populations (Fowler, 1983).

Arsenic Chemistry and Behavior

Arsenic is mobilized through natural processes such as weathering reactions, biological activity and volcanic emissions as well as through anthropogenic activities. Figure 2 shows the arsenic cycling in the environment. Most environmental arsenic problems are the result of mobilization under natural conditions. However, man has had an important additional impact through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants and the use of arsenic as an additive to livestock feed, particularly for poultry (DeSesso et al., 1998). Above all, mobilization of arsenic by industrial activities is more localized than by natural cycles. Excessive emissions by a single industrial activity can introduce arsenic into a geographic region at much greater mass flux than all of the natural processes combined (Fowler, 1983).

Figure 2. Arsenic Cycling in the Environment (Fowler, 1983)



Environmental Chemistry of Arsenic

The chemistry of arsenic is complicated due to its stability in four different oxidation states, +5, +3, 0 and –3, which are dependent upon redox conditions (Gupta & Chen, 1978). Arsenic primarily exists in the environment in its inorganic forms (oxidation states +3 and +5) or in its simple methylated forms. Arsenous acid (+3) and arsenic acid (+5) are water-soluble and can be present in a variety of forms (Norman, 1998). In solution, pH has a major effect on the solubility of arsenic compounds. In general, the higher the pH is the greater the arsenite (As III) solubility.

Arsenous acid (+3)

$$H_3AsO_3 \leftrightarrow H_2AsO_3^- + H_3O^+ \qquad pK_{a1} = 9.22$$

$$H_2AsO_3^- \leftrightarrow HAsO_3^{-2} + H_3O^+ \qquad pK_{a2} = 12.13$$

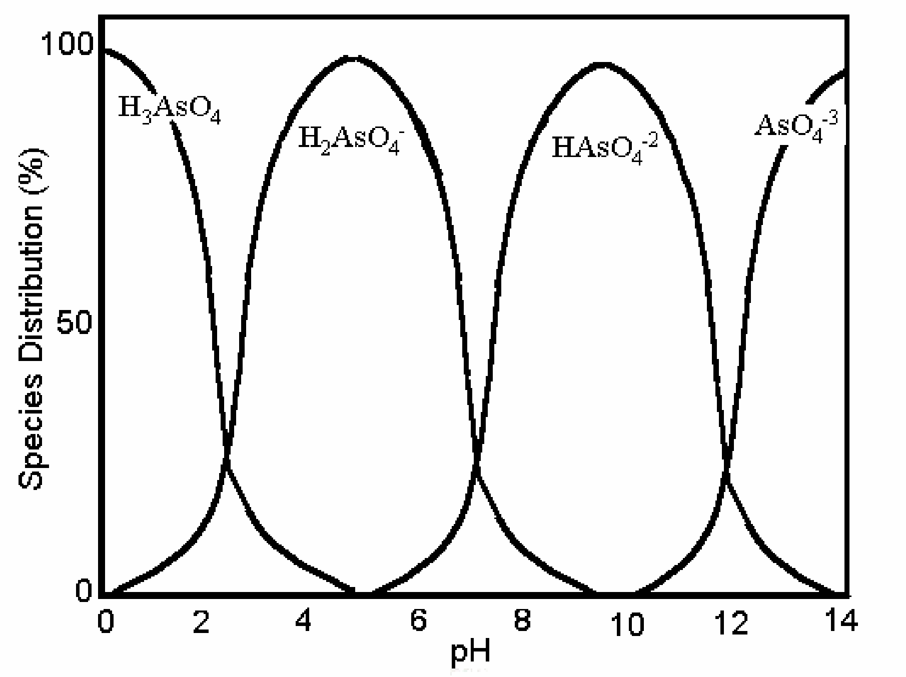
$$HAsO_3^{-2} \leftrightarrow AsO_3^{-3} + H_3O^+ \qquad pK_{a3} = 13.40$$

Arsenic acid (+5)

$$H_3AsO_4 + H_2O \leftrightarrow H_2AsO_4^- + H_3O^+ \qquad pK_{a1} = 2.20$$
$$H_2AsO_4^- + H_2O \leftrightarrow HAsO_4^{2-} + H_3O^+ \qquad pK_{a2} = 6.97$$
$$HAsO_4^{2-} + H_2O \leftrightarrow AsO_4^{3-} + H_3O^+ \qquad pK_{a3} = 11.53$$

The pK_as indicate that for non-complexed arsenic at environmental ranges of pH 4-8 arsenous acid (+3) (pK_{a1} = 9.22) is essentially not dissociated while arsenic acid (+5) (pK_{a1} = 2.20, pK_{a1} = 6.97) is almost all in some ionic form. Figure 3 shows the speciation of arsenic acid (+5) as a function of pH.

Figure 3. pC-pH Diagram for As(V)



As shown in Figure 3 the main species of non-complexed arsenic in solution are the ionic forms.

Aqueous arsenic concentration determination relies on the reduction potential at specific pH. The most common method of arsenic determination is hydride generation, where a powerful reductant is used to chemically react with the arsenic and the product of the reaction is used to determine the concentration. The species of arsenic that is determined depends on the pH of the reaction (Edwards et al., 1998). Table 2 shows some values for the reduction potential of arsenic.

Table 2. Standard aqueous reduction potentials at 25ºC

Reaction	**E^0v(V)**
$As + 3H^+ + 3e^- \leftrightarrow AsH_3$	-0.608
$As_2O_3 + 6H^+ + 6e^- \leftrightarrow 2As + 3H_2O$	0.234
$HAsO_2 + 3H^+ + 3e^- \leftrightarrow As + 2H_2O$	-0.248
$AsO_2^- + 2H_2O + 3e^- \leftrightarrow As + 4OH^-$	-0.68
$H_3AsO_4 + 2H^+ + 2e^- \leftrightarrow HAsO_2 + 2H_2O$	0.56
$AsO_4^{3-} + 2H_2O + 2e^- \leftrightarrow AsO_2^- + 4OH^-$	-0.71

Unlike arsenous acid, arsenic acid can be isolated in the solid state in hydrated forms. The crystalline compounds are often formulated as hydrates of As_2O_5. An important element of arsenic treatment from and environmental perspective is the solubility of any arsenic compounds that may be present. Some of the main arsenic compounds that may be present in a natural setting are shown in Table 3 with their solubility product. The principal species with which arsenic may combine are iron and calcium due to their abundance in the environment. The extremely low pKs imply total dissociation (Norman, 1998).

Table 3. Solubility products of selected arsenates

Compound	**pK_{sp}**
$Ca_3(AsO_4)_2$	6.8×10^{-19}
$Fe^{III}AsO_4$	5.7×10^{-21}
$Fe_3(AsO_4)_2$	5.2×10^{-26}

Arsenic Contaminated Water Treatment

Based on the EPA (EPA, 2002), the arsenic treatment technologies applicable to water are ion exchange, permeable reactive barriers, adsorption, membrane filtration, and precipitation/co-precipitation. Ion exchange has been used to treat groundwater and drinking water containing arsenic. Permeable reactive barriers (PRBs) are used to treat arsenic in groundwater at only a few sites. Although many candidate materials for the reactive portion of the barrier have been tested at bench scale, only zero valent iron and limestone have been used at full scale. Adsorption has been used to treat groundwater and drinking water containing arsenic. Membrane filtration can remove a wide range of contaminants from water. Precipitation/co-precipitation has been the most frequently used method to treat arsenic contaminated water, including groundwater, surface water, leachate, mine drainage, drinking water, and wastewater.

Precipitation/co-precipitation by coagulation and sorption of the toxic metals onto a metal oxy-hydroxide is the most popular and practical arsenic removal method from contaminated water. Adding salts of metals such as iron and aluminum to water at neutral or above neutral pH forms the oxy-hydroxide sorbents. Inclusion, adsorption, occlusion, solid-solution formation, or a combination of them can be the arsenic removal mechanism by coagulation with metal oxy-hydroxides (Benefield & Morgan, 1990).

These oxy-hydroxides are strong adsorbents for As (V) in pH neutral water. The treatment of water with these oxy-hydroxides creates arsenic containing residuals, which are later disposed of in landfills. To prevent arsenic leaching from the residuals, stabilization of the solid residuals is required. Several factors affect the solubility and sorption of arsenic, thus its leaching potential. In solution, pH has a major effect on the solubility of arsenic compounds.

Arsenic in Drinking Water Regulations

The arsenic standard for drinking water established by the World Health Organization in 1963 was 50 ppb; the guideline set in 1993 was 10 ppb. In the USA, the maximum contaminant level of arsenic in drinking water was 50 ppb, a level established in 1942 by the US Public Health Service. This is also the permissible level of arsenic in bottled water according to the US Code of Federal Regulations. However, it was proposed that the standard of 50 ppb had substantial increased risk of cancer and is not sufficiently protective of public health. The Environmental Protection Agency (EPA) was required by the Safe Drinking Water Act Amendments of 1996 to propose a new standard of arsenic by January 2000 and to finalize that regulation by January 2001. In 2002, Congress extended this deadline to June 22, 2001 and on October 31, 2001, the EPA affirmed the appropriateness of the MCL and reinstated 10 ppb as the new MCL for arsenic in drinking water. The new MCL effective date was February 22, 2002 and water systems must meet this standard by January 2006 (Wang and Wai, 2004; Federal Register, 2001).

IRON OXIDES AND HYDROXIDES

There are thirteen iron oxides, oxy-hydroxides and hydroxides. All iron oxides and hydroxides consist of iron, oxygen and/or hydroxide (OH^-). They differ in composition, valence of iron and crystalline structure. Iron oxides are widespread in nature present in soils, rocks, rivers, lakes, seafloor and air. (Schwertmann and Cornell, 1991)

Iron Oxide Synthesis

Formation of iron oxides in aqueous systems includes nucleation and crystal growth. Homogeneous nucleation occurs spontaneously in bulk solution when the supersaturation exceeds a critical value. Heterogeneous nucleation occurs when the presence of a solid phase reduces the free energy of nucleation and leads to an increase in rate of nucleation. Crystal growth consist of five main steps: diffusion of ions to the surface of the crystal, dehydration of ions at the surface, adsorption at the nucleus' surface, two-dimensional diffusion over the surface to an energetically more favorable position and one dimensional diffusion to a site where the ion is incorporates into the crystal (Schwertmann and Cornell, 1991).

One of the main means of synthesis of iron oxides is hydrolysis of solutions of Fe(III) salts. At very low pH, Fe^{3+} exists as $Fe(H_2O)_6^{3+}$. Hydrolysis involves the stepwise elimination of protons from the six water molecules that surround the central iron cation to form mono and binuclear species which interact further to produce species of higher nuclearity (Sylva, 1972). The polymeric species eventually precipitate. The degree of crystallinity of the precipitate depends on the reaction conditions. The two principal methods used to induce hydrolysis are heating the solution and the addition of base. As hydrolysis releases protons, the pH of the system falls.

Chemistry of Iron Oxides

The solubility of iron oxides is strongly influenced by pH because of the hydrolytic properties of both iron(II) and iron(III) aqueous species. The pH of the medium is important because the change in the oxidation sate of the ion produces changes in its hydrolytic behavior (Blesa et al., 2000). For example at pH 1 the stoichiometry is

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2 .$$

Alternatively, at pH> 7 the stoichiometry is

$$Fe^{2+} + O_2 + 3H_2O \rightarrow Fe(OH)_3 + HO_2^- + 2H^+ .$$

Table 4 shows some hydrolysis constants demonstrating the importance of pH on the species present in solution. Table 5 presents solubility constants indicating that different iron species have different solubility. Since the species present in solution depend on pH the solubility of iron is dependent on pH.

Table 4. Hydrolysis constant for iron(II) and iron(III) @ 25ºC

Equilibrium	**Log K_{so}**
$Fe(OH)_3$	3.42
α-FeOOH	-1.26
γ-FeOOH	2.50
α-Fe_2O_3	0.44
γ-Fe_2O_3	2.07
$Fe(OH)_2$	12.85
Fe_3O_4	36.08

Table 5. Solubility constant for iron(II) and iron(III) @25ºC

Equilibrium	**Log K$_a$**
$Fe^{2+} + H_2O \rightarrow FeOH^+ + H^+$	-9.33
$FeOH^+ + H_2O \rightarrow Fe(OH)_2(aq) + H^+$	-11.28
$Fe(OH)_2(aq) + H_2O \rightarrow Fe(OH)_3^-$	-8.84
$Fe^{3+} + H_2O \rightarrow FeOH^{2+} + H^+$	-2.19
$FeOH^{2+} + H_2O \rightarrow Fe(OH)_2^+ + H^+$	-3.48
$Fe(OH)_2^+ + 2H_2O \rightarrow Fe(OH)_4^- + 2H^+$	-16.78

Finally, the solubility of non-complex iron species is graphically depicted for two oxidation sates (II and III) in Figures 4 and 5.

Figure 4. Speciation of Fe(II) in Water @25ºC

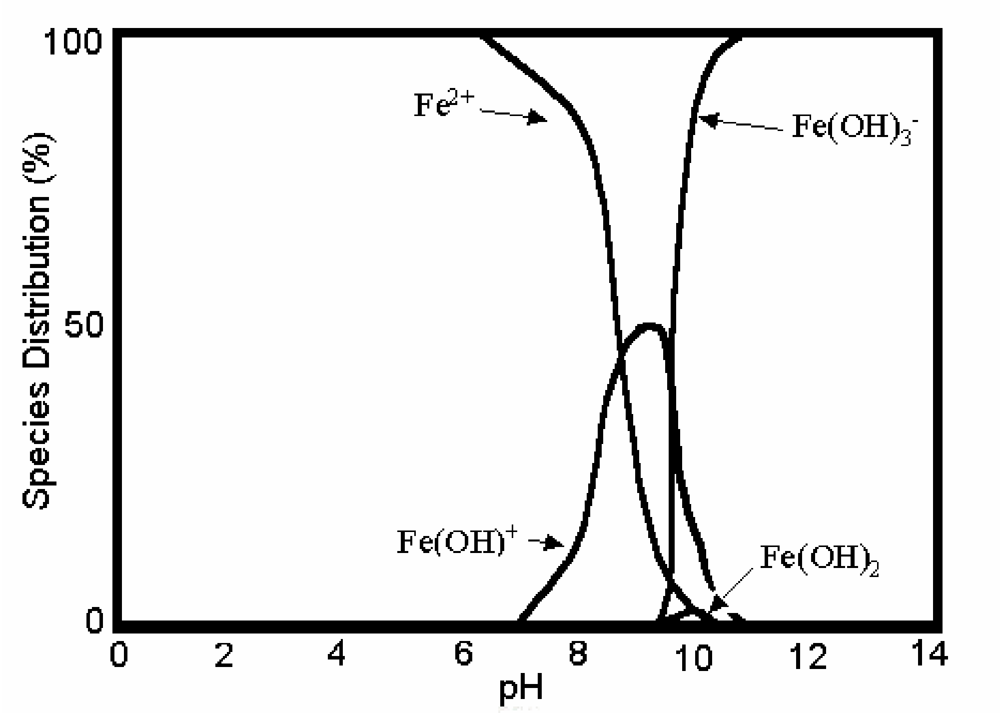
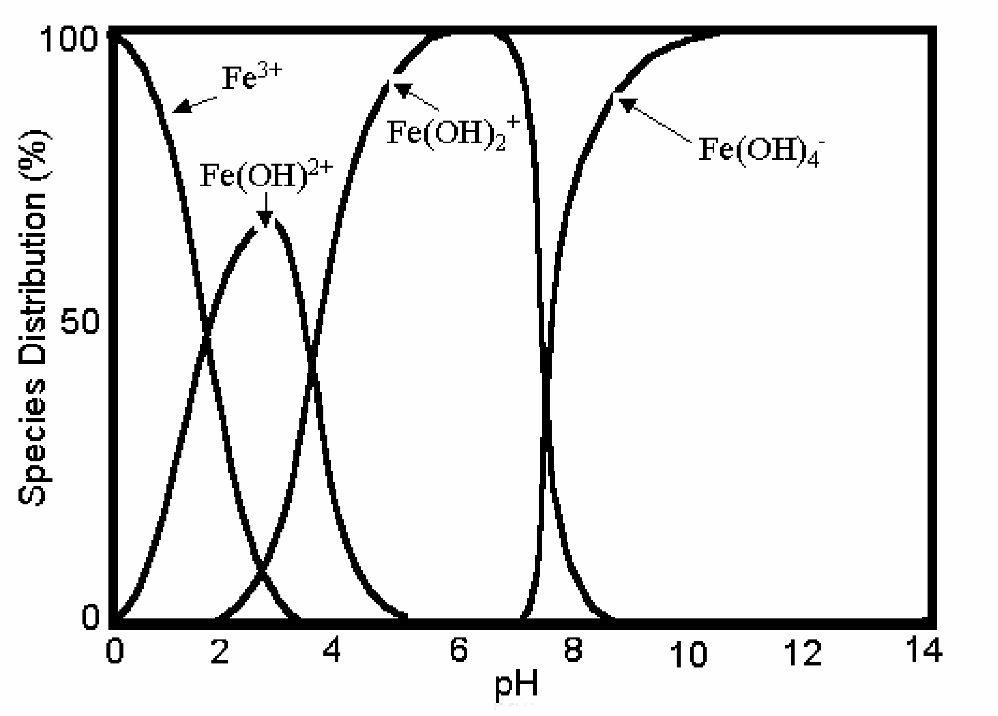


Figure 5. Speciation of Fe(III) in Water @ 25ºC



Adsorption on Iron Oxides and Hydroxides

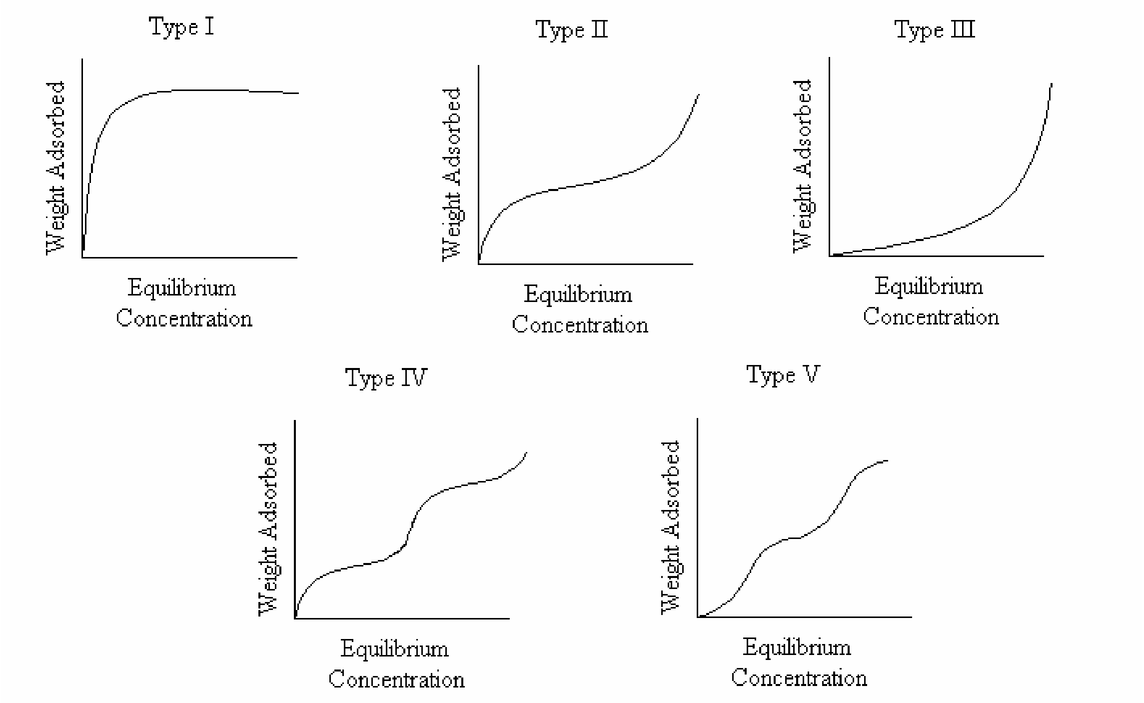
Metal ions form mixed complexes in solution, in which different ligands complete the metal ion coordination sphere. Surface complexes are in fact similar to these aqueous mixed-ligand complexes. Therefore metal complexes may sorb from solution in the same way as aqueous ions (Blesa et al., 1994).

Solutes present in the aqueous phase in contact with suspended oxide particles sorb on the interfacial region as a result of the changes in the activity coefficient brought about by interactions. When added to the electrostatic components, diverse adsorption isotherms result. Some of the most common applied adsorption isotherms equations are in Table 6. Also, the absorption mechanism can be classified into different types depending on isotherm behavior. As described by Lowell and Shields (1991), adsorption isotherms can be classified by one of five types classified by behavior and condition (Figure 6).

Table 6. Commonly applied adsorption isotherms

Name	**Equation**	**Applicability**
Langmuir	$q = \frac{Q_m b C_{eq}}{1 + b C_{eq}}$	Single-site chemical interaction of uncharged solute with no lateral interaction.
Freundlich	$q = k C_{eq}^{1/n}$	Multi site interaction
Frumkin	$\frac{q}{Q_{\max}} = \frac{K_{Fr} C_{eq} \exp\left(2\alpha q / Q_{\max} \right)}{1 + K_{Fr} C_{eq} \exp\left(2\alpha q / Q_{\max} \right)}$	Adsorption of laterally interacting chains onto single surface sites
Frumkin-Fowler-Guggenheim	$\frac{q}{Q_{\max}} = \frac{K_{FFG} C_{eq} \exp\left(\mathrm{F}^2 N_s q / CRTQ_{\max} \right)}{1 + K_{FFG} C_{eq} \exp\left(\mathrm{F}^2 N_s q / CRTQ_{\max} \right)}$	Single site chemical interaction of ions, under the influence of a macro potential
BET	$q = \frac{Q_M K_1 K_2 C_{eq}}{K_1 K_2 C_{eq} - K_2 \left(K_1 C_{eq} \right)^2 + C_{eq}^2 + K_1^2 - 2 K_1 C_{eq}}$	When the initial layer can act as substrate for further adsorption

Figure 6. Five Isotherm Classifications



Type I describes adsorption limited to a few molecular layers where the asymptotic approach to a limiting quantity indicates that all of the surface sites are occupied. Type II describes adsorption that occurs on nonporous powders or powders with pore diameters larger than micro-pores. The inflection point indicates the completion of the first adsorbed monolayer. With increase in adsorbate concentration, second and more layers are completed until at saturation the numbers of adsorbed layers becomes infinite. Type III describes isotherms in which as adsorption proceeds additional adsorption is facilitated due to the greater interaction between adsorbate-adsorbed later compared to the adsorbate interaction with the adsorbent surface. Type IV describes adsorption on to porous adsorbents with pores in the radius range of 15-

1000 angstroms. Type V describes adsorption similar to Type III but with pore in the radius range of 15-1000 angstroms (Lowell and Shiels, 1991).

Water Treatment with Ferric Salts

In the coagulation-flocculation process, ferric chloride or ferric sulfate is added and dissolved in water. Ferric hydroxide microflocs are formed rapidly. The water is then gently stirred for few minutes for agglomeration of microflocs into larger easy to settle the flocs. During this flocculation process several of the micro-particles and negatively charged ions are attached to the flocs by electrostatic attachment. Arsenic is also adsorbed onto coagulated flocs. As trivalent arsenic occurs in a zero valent form, it is not subject to significant removal. Oxidation of As (III) to As (V) is thus required as a pretreatment for efficient removal. Arsenic removal is dependent on pH and 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 (EPA, 2002) As (V) removal efficiency is normally greater than As (III) by coagulation with ferric salts.

LITERATURE REVIEW*

There are many theories as to why calcium could inhibit arsenic desorption and/or benefit arsenic sorption, however there is a considerable amount of disagreement among researchers. This phenomenon is partly due to the fact that sorption of inorganic ions is dependent on multiple factors. Experimental sorption data have been explained by empirical means such as partition coefficients, isotherm equations and conditional equilibr*ium sorption constants. However, sorption of inorganic ions on hydrous oxides is strongly dependent on solution conditions. Such conditions include pH, ionic strength, and the presence of competing ions (Dzombak and Morel, 1990). It is generally accepted is that As(V) is more easily adsorbed than As(III). Research has shown that the best way to remove arsenic from contaminated drinking water is to oxidize the arsenic to arsenate and use a Fe^{3+} based oxy-hydroxide as the sportive substrate.

Previous work has shown that elevated pH induced by NaOH addition generates greater leaching of arsenic (Parks et al., 1997). According to Parks et al. this trend is consistent with basic surface complexation models described by Dzombak and Morel (1990).

$$\equiv FeOH + AsO_4^{3-} + 3H^+ \leftrightarrow \equiv FeH_2AsO_4 + H_2O$$

As the pH increases, the H^+ concentration decreases which shifts the equilibrium to the reactants increasing the arsenic concentration.

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* Part of the data reported in this chapter is reprinted with permission from Characterization and Stabilization of Arsenic in Water Treatment Residuals, by H. Y. Wee, 2003, M.S. thesis, Texas A&M University.

Also, elevated pH induced by $NaCO_3$ addition generates even greater leaching of arsenic (Parks et al., 1997). Wilkie and Hering(1996) also observed an effect in the adsorption of arsenic in the presence of carbonate. According to Parks et al. (1997), this trend is also consistent with basic surface complexation models described by Dzombak and Morel (1990).

$$\equiv FeOH + CO_3^{2-} + 2H^+ \leftrightarrow \equiv FeOCOOH + H_2O$$

As the pH increases, the H^+ concentration decreases which shifts the equilibrium to the reactants increasing the arsenic concentration. Furthermore, as the carbonate concentration increases, the competition for arsenic sorption increased, resulting in an increase in additional soluble arsenic concentration.

Parks et al. (1997) has shown that elevated pH induced by $Ca(OH)_2$ addition resulted in minor leaching of arsenic. Furthermore, the amount of $Ca(OH)_2$ added did not appear to affect arsenic leaching. Two hypotheses have been identified to explain the decrease in soluble arsenic in the presence of calcium. One explanation is that arsenic reacts with calcium to form calcium arsenic solids. Calcium arsenic solids formation has been observed at pH>11.5 (Bothe & Brown, 1999; Parks et al., 1997). The second hypothesis is that calcium's positive charge affects the surface properties of the oxy-hydroxide solid. Elevated pH produces a negative surface charge, which in turn increases repulsion between the negatively charged arsenic ions and the $Fe(OH)_3$ surface. Calcium's positive charge might neutralize this effect, therefore enhancing the sorption of arsenic on to the oxy-hydroxide. Wilkie and Hering (1996) reported that, in the absence of calcium, as the pH increased above the point of zero charge of the iron oxy-hydroxide (about pH 8.1) the absorption of an anion on a negatively charged oxide surface becomes increasingly unfavorable. The adsorption of calcium results in a positive surface charge being maintained in this pH range, thus favoring anion adsorption.

Wilkie and Hering (1996) investigated the effect of competing negatively charged ion (SO_4^{2-}) and observed competition between the sulfate and the arsenic ions. Also, when arsenate/Fe residuals were tested for leaching in the presence of phosphate excessive leaching was found.

Sorption and Desorption Preliminary Studies

Wee (2003) obtained residuals by the removal of arsenic by co-precipitation/sorption using ferric chloride and sodium hydroxide addition. Ferric chloride was added in a 20:1 mole ratio to a 100 mg/L solution of either arsenate or arsenite. The extent of arsenite and arsenate removal for each sample composition was quantified, and the residuals were analyzed for iron and calcium content. Wee (2003) also conducted desorption studies consisting of TCLP, pH variance (4, 6, 8 and 10), and the presence of competing anions (i.e. phosphate). The extent of removal of both arsenite and arsenate is displayed in Tables 7 and 8.

Table 7. Arsenic removal efficiency without calcium addition

	As(III)	**As(V)**
Initial Concentration [μg/L]	100000	100000
Soluble Concentration [μg/L]	33	ND
Removal Efficiency [%]	**99.967**	**100**

Table 8. Arsenic(V) removal efficiency with and without calcium addition

	$FeCl_3$ + $Ca(OH)_2$	$FeCl_3$ + NaOH
Initial Concentration [μg/L]	100000	100000
Soluble Concentration [μg/L]	4.95	ND
Removal Efficiency [%]	**99.995**	**100**

Wee (2003) concluded that, in general, high pH favors arsenate desorption while low pH favors arsenite release, though desorption of arsenic from the iron oxy-hydroxides is minimal for both oxidation states of arsenic. However, the amount of arsenate desorbed was below detection limit at or below pH 8 for the iron residuals. Thus, the oxidation of arsenite to arsenate is highly desirable.

Wee (2003) also concluded that while iron shows increased arsenate desorption at higher pH, the addition of calcium carbonate actually lowers desorption. Thus, calcium addition with ferric chloride base coagulation may be the key to obtaining residuals that remain stable (resist leaching of arsenic) over a broad range of pH.

Wee (2003) showed that arsenic can be readily removed from contaminated water using relatively simple techniques. These processes are simple, robust, and easily incorporated into conventional water treatment or improved systems. However, they all produce residuals that can, under the appropriate circumstances, produce environmental problems upon disposal. For example, the addition of ferric chloride ($FeCl_3$) to waters with a variety of compositions containing arsenate has been shown by this research to consistently result in effluent water with arsenic content well below the MCL established by the USEPA. However, when the residuals are exposed to low levels of phosphate (1.3 mM) or a pH of greater than 8, substantial arsenic (V) is released and would contaminate the environment if improperly disposed. When a competing ion is introduced into solution (i.e. phosphate) it significantly influences desorption of iron-based residuals, even in the presence of calcium. Finally, the metal salt-based residuals have a strong tendency to buffer the water and thus resist pH extremes. The iron residuals tend to maintain a neutral pH while the calcium residuals raise pH.

Desorption Inhibition by Calcium Addition during Coagulation

When Wee (2003) tested arsenate/Fe residual samples by leaching in the presence of phosphate (1.3 mM), excessive leaching was found. However, it was also noted that the calcium carbonate residuals resisted leaching in the phosphate environment, which was found to be consistent with the literature. Therefore, calcium hydroxide addition to control pH rather than NaOH was used to form the residuals. Minimal leaching was found from the arsenate/Fe^{3+}/Ca^{2+} residuals with respect to phosphate competition and these data are presented in Tables 9-13 (Wee, 2003).

Table 9. Arsenic TCLP extraction data without calcium addition (mg As/kg dry solids) (Wee, 2003)

Time (hr)	0.5	1	2	4	8	18
As(III)	1.3	1.3	1.2	1.1	0.97	0.94
As(V)	0.011	0.011	0.008	BDL	BDL	BDL

Table 10. Arsenic desorption vs. pH without calcium addition (mg As/kg dry solids) (Wee, 2003)

	pH 4		**PH 6**		**PH 8**		**PH 10**	
	8 hr	24 hr	8 hr	24 hr	8 hr	24 hr	8 hr	24 hr
As(III)	25	26	13	15	7.7	8.6	9.4	9.7
As(V)	BDL	BDL	BDL	BDL	1.2	3.0	53	83

Table 11. As(V) desorption vs. pH (mg As/kg dry solids) (Wee, 2003)

pH	**4**	**6**	**8**	**10**
$FeCl_3 + Ca(OH)_2$	BDL	BDL	1.46	45.8
$FeCl_3$ + NaOH	BDL	BDL	2.95	82.5

Table 12. Arsenic desorption vs. pH in the presence of phosphate without calcium addition (mg As/kg dry solids) (Wee, 2003)

	pH 4		**pH 6**		**pH 8**		**pH 10**	
	8 hr	24 hr	8 hr	24 hr	8 hr	24 hr	8 hr	24 hr
As(III)	24	34	20	41	20	21	23	24
As(V)	220	120	52	50	40	36	31	220

Table 13. Arsenic desorption vs. pH in the presence of phosphate with and without calcium addition (mg As/kg dry solids) (Wee, 2003)

Time (hr)	**0.5**	**1**	**2**	**4**	**8**	**12**	**24**
$FeCl_3 + Ca(OH)_2$	0.305	0.269	0.210	0.150	0.210	0.507	0.150
$FeCl_3$ + NaOH	221	123	51.9	50.2	39.5	35.9	30.6

In Table 11 desorption versus pH is shown, and the results indicate the Fe/Ca system is much better at retaining arsenate than the Fe/Na mixture. In the phosphate study, 10 grams of the residuals sample was placed in 100 ml of solution containing 1.3 mM of phosphate and the liquid was extracted over a 24 hour period. In the Fe/Ca system, a very low amount of arsenate was released, and desorption was also improved at higher pH. Two possible hypotheses for this behavior can be identified. One is that the calcium is forming solid phase calcium phosphate, and the other is that the calcium is altering the surface chemistry of the iron oxy-hydroxide (Wee, 2003).

Stabilization Techniques

Wee (2003) examined the addition of lime (CaO), fly ash, ferrous sulfate, and ordinary Portland cement (OPC) as suitable solidification and stabilization compounds. Lime and OPC had a significant influence on minimizing arsenic leaching using the leachate solutions listed in Table 14. Lime had by far the greatest impact on reducing and eliminating the leaching of arsenic from the treatment residuals. These data are displayed in Figures 7 and 8, as well as Tables 14 and 15. Note that in Figure 7, the addition of excess lime eliminates arsenic leaching using the high pH phosphate leachate. The data of Figure 8 indicates that OPC has a minimal influence on the leaching of arsenic under worse case conditions. Wee (2003) believed that, over time, due to calcium reaction with CO_2 in the atmosphere, the amount of excess calcium needed to preserve the stability of the residuals could erode. Therefore, the addition of small amounts of OPC may be beneficial. Data for the mixed system appears in Tables 14 and 15 for both the GFH and alumina residuals samples.

Table 14. Extracted As, Fe, and Ca concentrations by TCLP #2 and 0.1M phosphate extraction depending on lime and OPC addition (Wee, 2003)

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

Figure 7. Soluble Total As and Ca Concentrations by 0.1M Phosphate Extractions as a Function of Lime Addition (Wee, 2003)

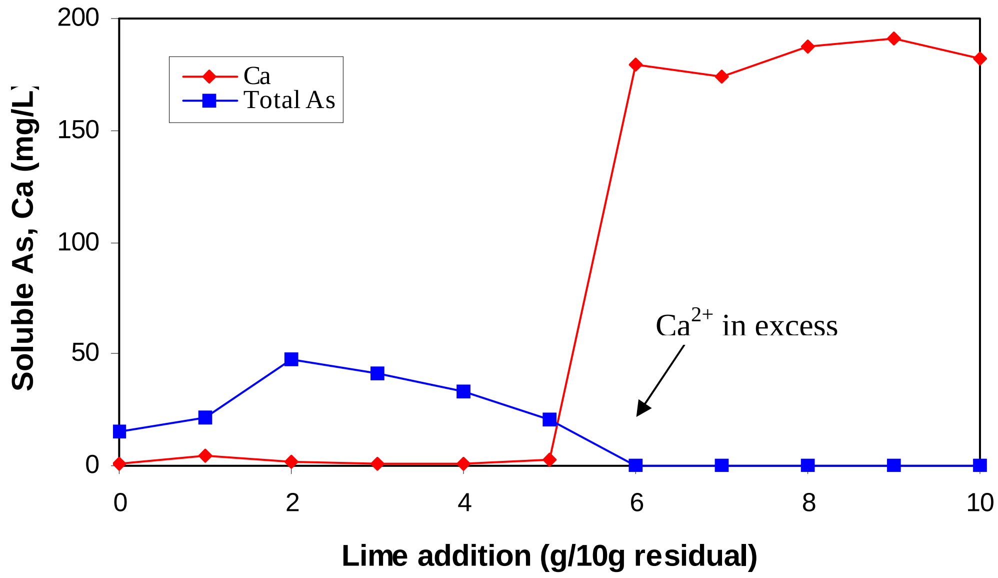


Figure 8. Soluble Total As and Ca Concentrations by 0.1 M Phosphate as a Function of OPC Addition (Wee, 2003)

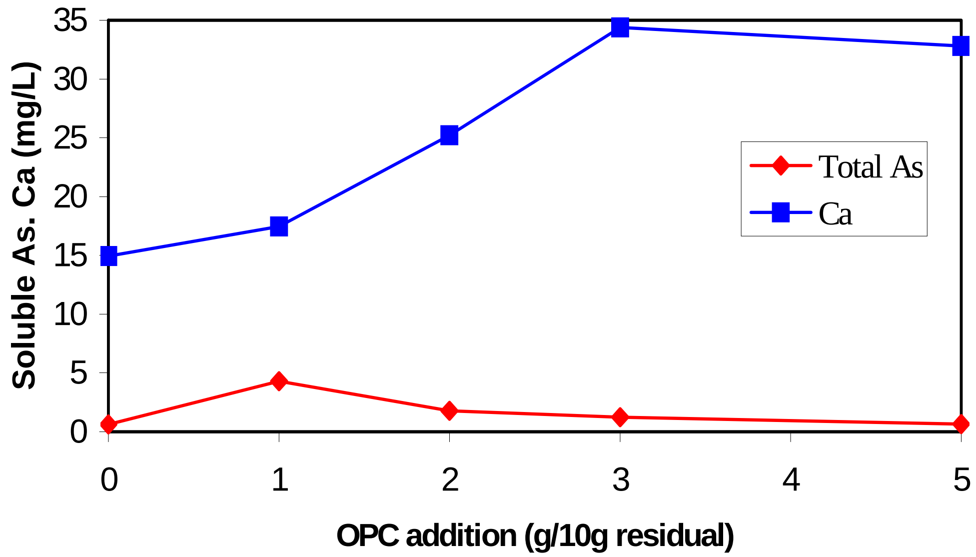


Table 15. Extracted As, Al, and Ca concentrations by toxic characteristic leaching procedure and phosphate extraction depending on lime and OPC addition (Wee, 2003)

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

Wee (2003) formulated several hypotheses as to why the addition of excess calcium would prove to be so influential in the elimination of arsenic leaching under all conditions tested in these experiments (including the presence of competing ions). These hypotheses were: solid phase calcium and phosphate compounds are formed, thus removing phosphate from competition for sorption sites on the metal oxy-hydroxides, the calcium improves surface charge properties of the metal oxy-hydroxide increasing the sorption of both arsenic and phosphate, and solid phase arsenic and calcium and solid phase calcium and phosphate compounds are formed thus reducing the aqueous concentration of both species.

EXPERIMENTAL METHODS

Synthetic Residuals Production

This section describes the method used to produce the synthetic residuals used in all experiments. Two types of residuals were used, iron based residuals and iron base residuals with calcium addition. The materials and apparatus used are described in Appendix A.

Synthetic Residuals Production

The ferrihydrite syntheses were conducted as described by Schwertmann and Cornell (1991) with slight modifications. $FeCl_3 \cdot 6H_2O$ and NaOH were added to deionized water, and the resulting suspension was adjusted to pH ~8. Then the mixture was allowed to settle and the supernate was decanted. The residuals were filtered using a 0.2 µm pore-size membrane, and the percent solids were determined for use in the production of calcium-containing residuals.

Synthetic Residuals Containing Calcium Production

The same procedure for ferrihydrite syntheses, with some modification, was used for the synthetic residuals containing calcium. Figure 1 shows the minimum lime addition that produces excess calcium and thus, expected to produce the best arsenic removal. This amount is 6 grams of lime per 10 grams of dry residual. Therefore, 16.61 g of $CaCl_2$ were added per 10 grams of dry residual suspended in deionized water and adjusted the pH to ~8.

Synthetic Wastewater Production

This section describes the method used to produce the synthetic wastewater used in all experiments. Arsenic and phosphate were present in the wastewater as the adsorption variables and nitrate was present as an ionic strength buffer. The materials and apparatus used are described in Appendix A.

Stock Solutions Production

The arsenic stock solution (2 g As(V)/L) was prepared using As_2O_5. Phosphate stock solution (0.133 M) was prepared using NaH_2PO_4. Nitrate stock solution (1 M) was prepared using $NaNO_3$. These solutions were used to create the synthetic wastewaters used in all experiments.

Arsenic Synthetic Wastewater Production

The arsenic wastewater had an initial As(V) concentration of 200 mg/L. For example, 20 mL of the arsenic stock solution and 20 mL of the nitrate stock solution were diluted to 2000 mL with deionized water. The nitrate is added in a concentration of 10 mM to control the ionic strength.

Arsenic-Phosphate Synthetic Wastewater Production

The arsenic-phosphate wastewater used in all experiments had an initial As(V) concentration of 200 mg/L and an initial PO_4^{3-} concentration of 1.33 mM (unless otherwise specified). For example, 20 mL of the arsenic stock solution, 20 mL of the phosphate stock solution and 20 mL of the nitrate stock solution were diluted to 2000 mL with deionized water. The nitrate was added in a concentration of 10 mM to control the ionic strength.

Arsenic Sorption Test

The arsenic sorption tests were conducted to determine the change in sorption with change in calcium content and presence of competing ions. The data will show sorption as a function of time for pH 8 and 11. The materials and apparatus used are described in Appendix A.

Arsenic Sorption Test Experiment

Desorption experiments were carried out using the synthetic residuals as sorption media in the presence of arsenic and phosphate wastewater. The residuals were mixed with the wastewater at a ratio of 1 to 20 mass to volume at pH of 8 and 11. The mixture was stirred in the orbital shaker for about 24 hours. Samples were taken at 0, 0.5, 1, 2, 4, 8, 12 and 24 hours by centrifuging for about 10 minutes at 3000 rpm and filtering the sample through a 0.2 µm pore-size membrane. The samples were analyzed for soluble arsenic using continues Hydride Generation with Atomic Absorption Spectroscopy (HG-AAS) and soluble phosphate using Ion Chromatography (IC). The analysis methods are described in Appendix B.

Arsenic Desorption Test

Arsenic desorption tests were carried out with synthetic residuals at pH of 8 and 11 to assess the possible reduction in desorption of arsenic with calcium addition and increase desorption in the presence of phosphate. The materials and apparatus used are described in Appendix A.

Arsenic Desorption Experiment

Desorption experiments were carried out using the residuals from the sorption experiments. The saturated residual was mixed with DI water at a ratio of 1 to 20 mass to volume at pH 8 and 11. The mixture was stirred in the orbital shaker for about 24 hours. Samples were taken at 0, 0.5, 1, 2, 4, 8, 12 and 24 hours by centrifuging the samples for about 10 minutes at 3000 rpm and filtering through a 0.2 μm membrane. The samples were analyzed for soluble arsenic using HG-AAS and phosphate. The analysis methods are described in Appendix B.

Arsenic Adsorption Isotherms

Arsenic sorption tests were conducted to determine the influence of calcium in arsenic sorption with change in residual amount. The data will show sorption as a function of residual mass for pH 8 and 11. The materials and apparatus used are described in Appendix A.

Arsenic Adsorption Test Experiment

Arsenic adsorption tests were carried out by mixing increasing amounts of synthetic residual to wastewater adjusting the pH to 8 and 11. The solution was then stirred in the orbital shaker for about 24 hour to reach equilibrium. To determine the aqueous concentration the solution was centrifuge for about 10 minutes at 3000 rpm. An aliquot was filtered through a 0.2 μm pore-size membrane and analyzed for soluble arsenic using HG-AAS. The analysis methods are described in Appendix B. This data was used to determine isotherm parameters in Excel for the Langmuir isotherm

$$q = \frac{Q_m b C_{eq}}{1 + b C_{eq}} \qquad [1]$$

the Freundlich isotherm

$$q = k C_{eq}^{1/n} \qquad [2]$$

the BET isotherm

$$q = \frac{Q_M K_1 K_2 C_{eq}}{K_1 K_2 C_{eq} - K_2 \left(K_1 C_{eq}\right)^2 + C_{eq}^2 + K_1^2 - 2 K_1 C_{eq}} \qquad [3]$$

Calcium Arsenic Solid Formation

This test was conducted to establish the formation of calcium arsenic solids at different pHs. Previous research has established that such solids do not form at pH<11.5. The solid-phase assemblages previously studied were:

$$Ca_4(OH)_2(AsO_4)_2 \bullet 4H_2O$$

$$Ca_5(OH)_2(AsO_4)_3 OH$$

$$Ca_3(AsO_4)_2 \bullet 11/3\, H_2O$$

$$Ca_3(AsO_4)_2 \bullet 17/4\, H_2O$$

The materials and apparatus used are described in Appendix A.

Calcium Arsenic Solid Formation Test

The synthetic residuals were mixed with the wastewater at pH 8 and 11 and subsequently stirred in an orbital shaker for about 24 hours. The solution was then centrifuged for about 10 minutes at 3000 rpm and filtered through a 0.2 μm pores-size membrane. The resulting solids were analyzed for calcium arsenic solids using X-ray diffraction. The specifications for the X-ray diffraction analysis are described in Appendix B. Also, the solutions were modeled using VMINTEQ to determine the possible solids formed.

RESULTS AND ANALYSIS

Synthetic Residuals Analysis

Table 16 presents the basic composition of the synthetic residuals used in all of the experiments.

Table 16. Composition of the synthetic residuals

	Calcium Concentration (g/g dry solids)	% Solids
Synthetic Residual	0	12
Synthetic Residual Containing Calcium	10	20

Arsenic Sorption Test

Arsenic sorption tests were conducted to determine the change in sorption in the presence of calcium as an absorption-enhancing ion and phosphate as a competing ion. The data shows sorption as a function of time for pH 8 and 11.

Arsenic Sorption at pH 8 and 11

Sorption of arsenic on to iron oxy-hydroxides is shown in Figures 9,10 and 11. The initial concentration of arsenic (As(V)) in the water was 200 mg/L. The effectiveness of arsenic removal with $FeCl_3$ treatment is evident, since within the first half hour the concentration of arsenic was reduced to ~50 μg/L and within 24 hours the concentration was reduced to ~10 μg/L. At both pH 8 and 11 the aqueous arsenic concentration was lower for the water treated in the presence of calcium. The data for the experiments conducted is shown in Tables 17, 18 and 19.

Table 17. Sorption of arsenic (V) at pH=8

Time (hr.)	**Iron oxide (μg/L)**	**Iron oxide with calcium (μg/L)**
0	200,000	200,000
0.5	16.0	17.7
1	11.5	6.8
2	5.9	1.6
4	3.2	0.9
8	2.5	1.4
12	5.2	0.7
24	1.6	-----

Figure 9 shows that the aqueous concentration of total arsenic in the presence of calcium was lower than that in the experiments without calcium. Although both experiments show a decrease in arsenic concentration to below that of the proposed MCL (10 ppb) (Table 17), the experiment conducted in the presence of calcium reached this level at ~1 hour, compared to ~2 hours for the experiment without calcium. Therefore calcium appears to reduce the time it takes for total arsenic concentrations to reach the MCL.

Figure 9. Sorption of Arsenic (V) at pH=8

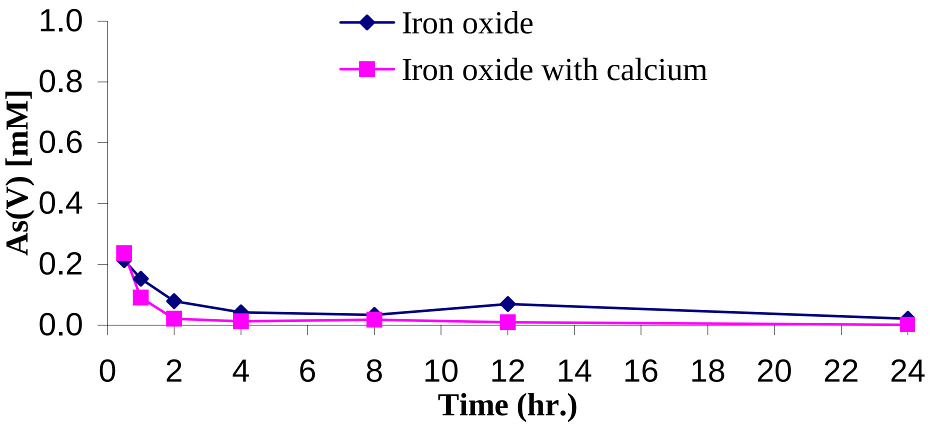


Table 18. Sorption of arsenic (V) at pH=11 (Experiment 1)

Time (hr.)	**$FeCl_3$ (μg/L)**	**$FeCl_3 + Ca(OH)_2$ (μg/L)**
0	200,000	200,000
0.5	47	19
1	40	16
2	27	19
4	19	11
8	15	7
12	12	6
24	7	1

Figure 10 shows that the aqueous concentration of arsenic in the presence of calcium was consistently lower than that in the experiments without calcium. Although both experiments showed a decrease in arsenic concentration to a value lower than that of the proposed MCL (10 ppb) (Table 18), the experiment conducted in the presence of calcium reached such level at ~8 hours, compared to ~24 hours for the experiment without calcium. That the third point in the experiment conducted in the presence of calcium could have some experimental error. Since the concentrations measured were so low, small experimental errors could have been magnified.

Figure 10. Sorption of Arsenic (V) at pH=11 (Experiment 1)

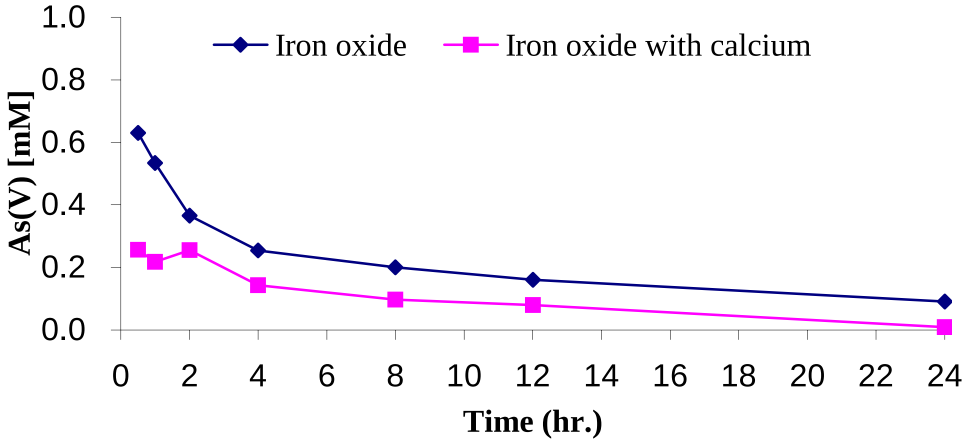
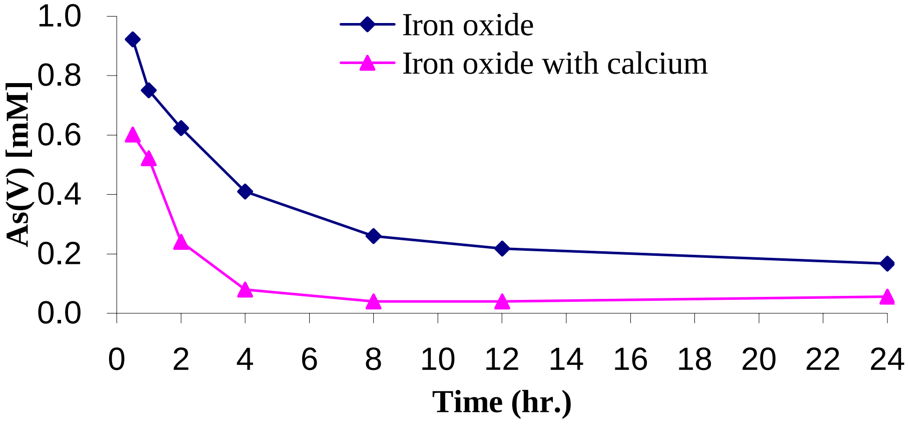


Table 19. Sorption of arsenic (V) at pH=11 (Experiment 2)

Time (hr.)	**$FeCl_3$ (µg/L)**	**$FeCl_3 + Ca(OH)_2$ (µg/L)**
0	200,000	200,000
0.5	69	45
1	56	39
2	47	18
4	31	10
8	19	6
12	16	3
24	13	4

The experiment shown in Figure 10 was repeated (Figure 11). Figure 11 shows the same trend as Figure 10 where the aqueous concentration of arsenic in the presence of calcium was consistently lowers than that in the experiments without calcium. In this case, a decrease in arsenic concentration to a value lower than that of the proposed MCL (10 ppb) was only found in the presence of calcium after ~8 hours.

Figure 11. Sorption of Arsenic (V) at pH=11 (Experiment 2)



The data presented in Figures 9-11 strongly suggest that the presence of calcium aids in the sorption (removal) of arsenate from water. In Figures 10 and 11, sorption at pH 11, this trend is more evident than in Figure 9, sorption at pH 8, suggesting that the sorption enhancement due to calcium addition increases with increase in pH.

Arsenic Sorption at pH 8 and 11 in the Presence of Phosphate

The sorption of arsenic on to iron oxy-hydroxides in the presence of phosphate is shown in Figures 12 and 13. Figure 12 shows sorption at pH 8. The initial concentration of phosphate in this experiment (13.3 mM) was 10 times higher than the concentration of the experiments conducted at pH 11 (1.33 mM) (shown in Figure 13). The difference in the concentrations of phosphate for the two experiments is that when the experiment was conducted with an initial phosphate concentration of 1.3 mM no effect was observed. This could be explained by the fact that pH 8 is closer to the point of zero charge (PZC) of the oxy-hydroxide (as shown in Figure 5). At the PZC repulsion between the iron oxyhydroxide and the negatively charged ions is less than at pH 11.

Therefore, the concentration of phosphate was increased to increase the competition of phosphate and arsenic. The initial concentration of arsenic (As(V)) in the water was 200 mg/L. In the presence of phosphate, the adsorption of arsenate in the presence of calcium was higher when comparing adsorption with and without calcium present. The data for the experiments conducted is shown in Tables 20 and 21.

Table 20. Sorption of arsenic (V) and phosphate at pH=8

Time (hr.)	**$FeCl_3$**		**$FeCl_3$ + $Ca(OH)_2$**	
	As (μg/L)	**PO_4^{3-} (mg/L)**	**As (μg/L)**	**PO_4^{3-} (mg/L)**
0	200,000	1456	200,000	1456
0.5	1239	1300	1135	845
1	1308	1204	1209	701
2	1467	1228	630	620
4	1363	1077	654	631
8	1289	1102	922	542
12	1304	973	957	519
24	513	1045	493	542

Figure 12 shows the same trend as was observed for the sorption of arsenic in the previous section, in which the aqueous concentration of arsenic in the presence calcium was consistently lower than that for the experiments without calcium. In this case, the arsenic concentration never reached the MCL (10 ppb), shown in Table 20. The final concentrations of dissolved arsenic (V) and phosphate were lower in the presence of calcium. Furthermore, the soluble phosphate concentration at 24 hours in the presence of calcium was half of that found in the absence of calcium.

Figure 12. Sorption of Arsenic and Phosphate at pH=8

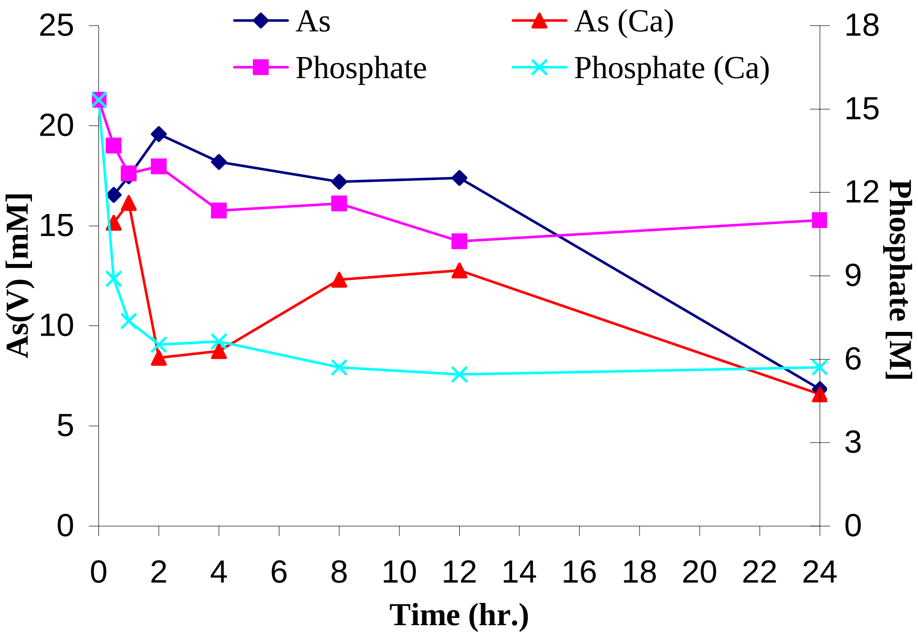
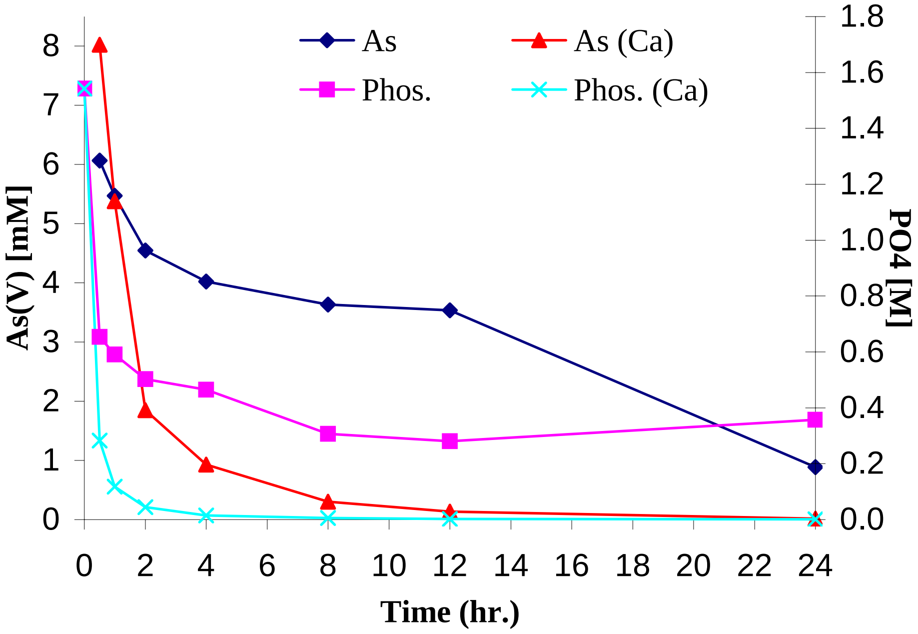


Figure 13 shows the same trend for the sorption of arsenic described in the previous section, in which the aqueous concentration of arsenic in the presence calcium was lower than that in the experiments without calcium. In this case, in the presence of calcium the arsenic concentration was lower than the MCL (10 ppb). The final concentration of both arsenic (V) and phosphate were lower in the experiment with calcium addition. Furthermore, the concentrations of both ions at 24 hours were lower at pH 11 than at ph 8. This trend could possibly be explained by the precipitation of calcium-containing solids as suggested by Parks et al. (2003) above pH 11, in the Calcium Arsenic Solids Formation section the solids found in these experiments will be described.

Table 21. Sorption of arsenic (V) and phosphate at pH=11

Time (hr.)	**$FeCl_3$**		**$FeCl_3$ + $Ca(OH)_2$**	
	As (μg/L)	**PO_4^{3-} (mg/L)**	**As (μg/L)**	**PO_4^{3-} (mg/L)**
0	200,000	146.50	200,000	146.50
0.5	454	62	601	27
1	410	56	403	11
2	341	48	139	4
4	301	44	70	1
8	272	29	23	1
12	265	27	10	0
24	67	34	1	0

Figure 13. Sorption of Arsenic (V) and Phosphate at pH=11



Arsenic Desorption Test

Arsenic desorption tests were carried out with the synthetic residuals at pH 8 and 11, to assess the possible reduction in desorption with calcium content and increased desorption in the presence of phosphate as described in the Arsenic Desorption Experiment section on page 34.

Arsenic Desorption at pH 8 and 11

Desorption of arsenic from the iron oxy-hydroxides is shown in Figures 13 and 14. The presence of calcium significantly reduced desorption of arsenic. The data for the experiments is shown in Tables 22 and 23.

Table 22. Desorption of arsenic (V) at pH=8

Time (hr.)	**$FeCl_3$ (μg/L)**	**$FeCl_3 + Ca(OH)_2$ (μg/L)**
0	0.00	0.00
0.5	1145	918
1	1153	691
2	1126	691
4	464	691
8	464	470
12	464	237
24	464	237

Figure 14 shows that the aqueous concentration of arsenic in the presence of calcium is lower than that in the experiments without calcium addition. After 24 hours the experiment conducted in the presence of calcium leached half the amount of arsenic than the experiment conducted without calcium leached. In both experiments, arsenic concentrations higher than the MCL were observed (Table 22). Also, both experiments indicate a trend in which the concentration of arsenic initially increased but then decreased to an equilibrium concentration. This behavior was unexpected and could be due to the formation of a solid phase.

Figure 14. Desorption of Arsenic (V) at pH=8

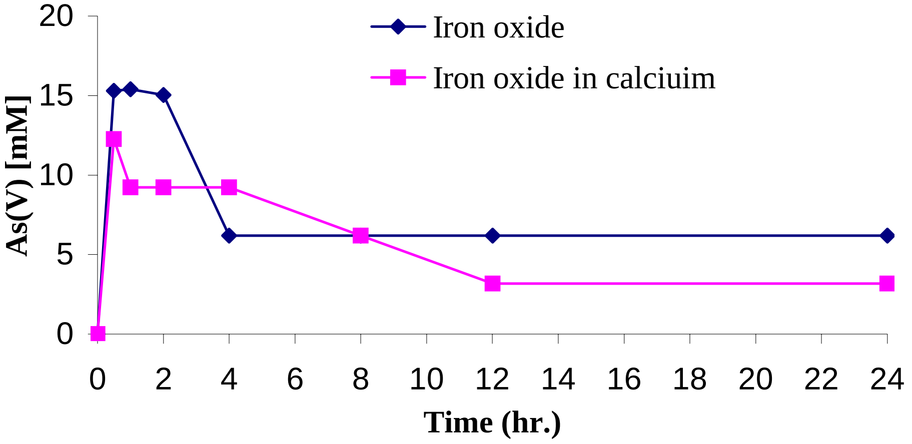
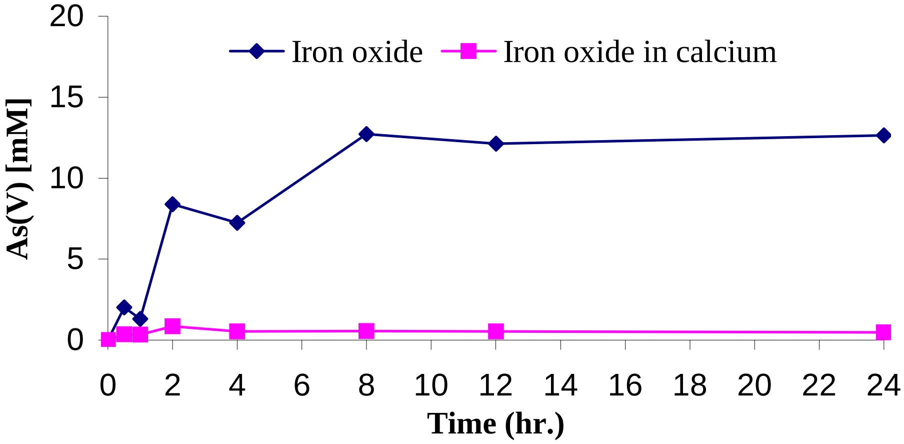


Table 23. Desorption of arsenic (V) at pH=11 by phosphate extraction

Time (hr.)	**$FeCl_3$ (µg/L)**	**$FeCl_3 + Ca(OH)_2$ (µg/L)**
0	0.00	0.00
0.5	15.14	2.63
1	9.82	2.58
2	62.91	6.36
4	54.28	4.03
8	95.27	4.14
12	90.80	4.00
24	94.64	3.59

The aqueous concentration of arsenic in the presence of calcium was lower than that without calcium (Figure 15). Both experiments showed arsenic concentrations higher than that of the MCL (Table 23). The experiment conducted in the presence of calcium indicated a lower amount of leached arsenic than the experiment conducted without calcium. The final concentration of both arsenic (V) and phosphate were lower in the presence of calcium. Furthermore, the concentration of both ions at 24 hours was lower at pH 11 as the previous experiments showed. Again, findings described by Parks et al. (2003) could explain the reduction in soluble arsenic concentration, by the formation of calcium arsenic solids that have reduced solubility in water. In the Calcium Arsenic Solids Formation section, page 70, the solids found in these experiments are identified and described.

Figure 15. Desorption of Arsenic (V) at pH=11



Arsenic Desorption at pH 8 and 11 in the Presence of Phosphate

Desorption of arsenic and phosphate from the iron oxy-hydroxides is shown in Figures 15 and 16. The presence of calcium reduced desorption of phosphate from the solid but did not significantly affect desorption of arsenic at pH 8. However, at pH 11, desorption of both arsenic and phosphates were reduced in the presence of calcium. The data for these experiments is shown in Tables 24 and 25. In the experiment conducted in the presence of calcium a lower amount of arsenic was leached than in the experiment conducted without calcium. The final concentrations of both arsenic (V) and phosphate were lower in the presence of calcium. Furthermore, the concentrations of both ions at 24 hours were lower at pH 11. Again, this result could be explained by the findings of Parks et al. (2003) in which calcium arsenic solids were found at pH above 11. The solids found in the current experiment will be identified and described.

Table 24. Desorption of arsenic (V) and phosphate at pH=8

Time (hr.)	**$FeCl_3$**		**$FeCl_3 + Ca(OH)_2$**	
	As (μg/L)	**PO_4^{3-} (mg/L)**	**As (μg/L)**	**PO_4^{3-} (mg/L)**
0	0.00	0.00	0.00	0.00
0.5	5.16	196.30	7.41	75.40
1	4.48	194.14	6.07	102.52
2	5.30	200.34	6.77	91.90
4	5.38	164.56	6.36	92.06
8	4.46	175.56	6.11	135.44
12	4.57	211.18	5.23	97.52
24	4.33	188.94	4.71	124.76

Figure 16 shows that the aqueous concentrations of both arsenic (V) and phosphate were similar in the presence of calcium and the absence of calcium. Both experiments showed arsenic concentrations lower than that of the MCL (Table 24).

Figure 17 shows that the concentration of aqueous arsenic in the presence of calcium was lower than that of the experiments without calcium. Both experiments showed arsenic concentrations higher than that of the MCL (Table 25).

Figure 16. Desorption of Arsenic (V) and Phosphate at pH=8

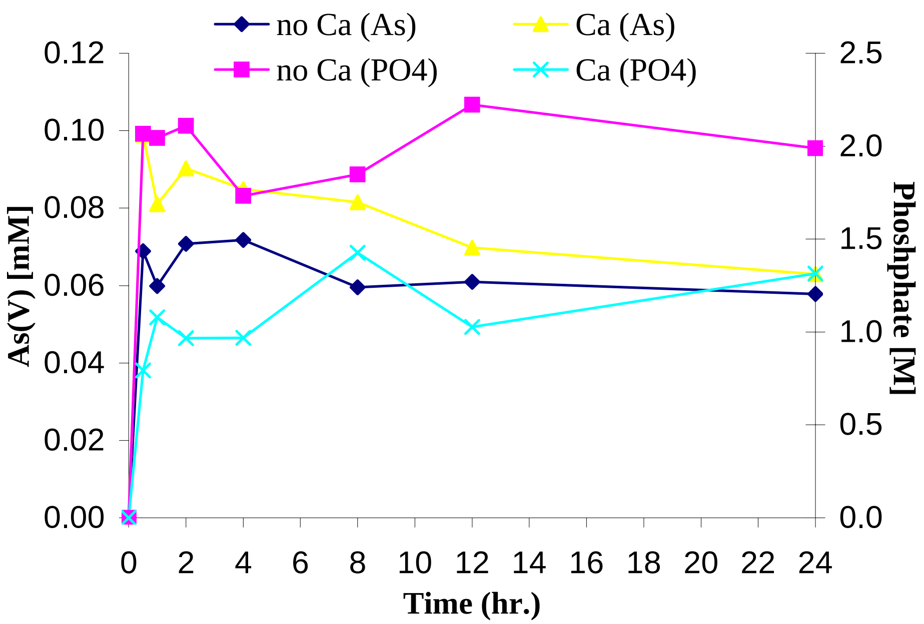
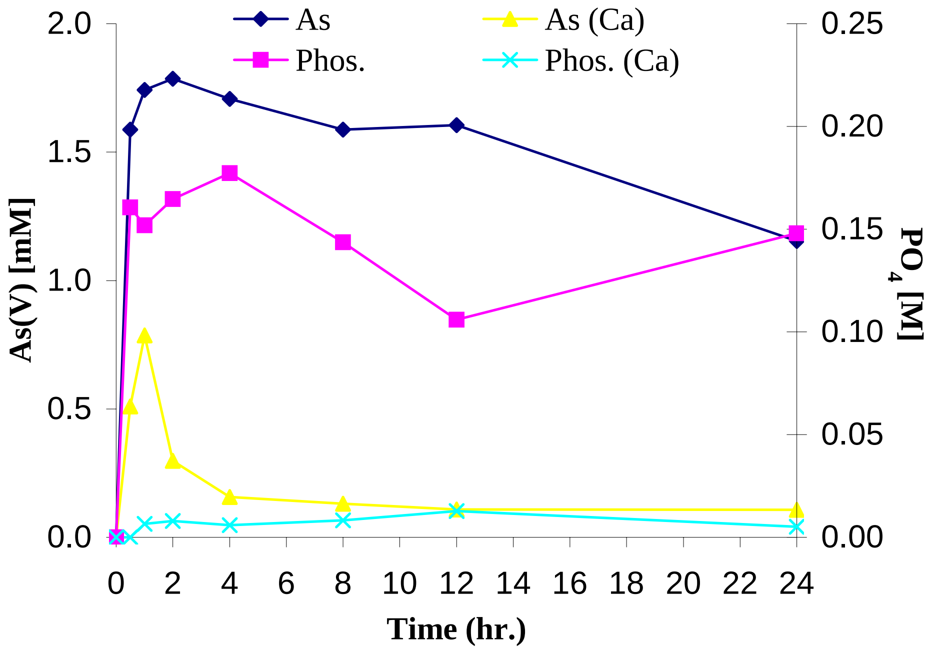


Table 25. Desorption of arsenic (V) and phosphate at pH=11

Time (hr.)	**FeCl$_3$**		**FeCl$_3$ + Ca(OH)$_2$**	
	As (μg/L)	**PO$_4^{3-}$ (mg/L)**	**As (μg/L)**	**PO$_4^{3-}$ (mg/L)**
0	0.00	0.00	0.00	0.00
0.5	118.95	15.26	38.16	0.00
1	130.50	14.43	58.90	0.62
2	133.82	15.64	22.34	0.75
4	127.93	16.83	11.75	0.57
8	118.97	13.63	9.83	0.79
12	120.24	10.05	8.11	1.22
24	86.42	14.06	8.00	0.49

Figure 17. Desorption of Arsenic (V) and Phosphate at pH=11



Arsenic Desorption at pH 11 by Phosphate Extraction

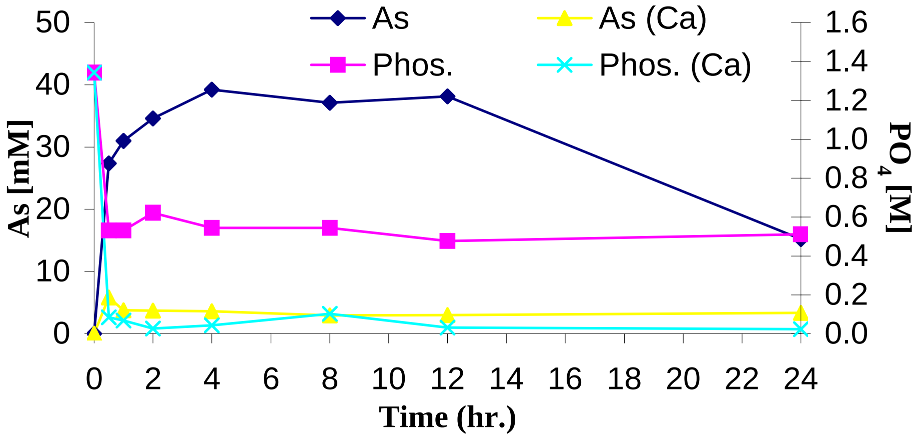
Desorption of arsenic from the iron oxy-hydroxides in the presence of phosphate is shown in Table 26 and Figure 18. The initial aqueous phosphate concentration was 1.3 mM. Since the phosphate concentration decreases form 1.3 mM and the arsenic concentration increase from zero, the aqueous phosphate concentration was sorbed while the arsenic in the solid was desorbed. In the presence of calcium, final aqueous concentrations of both arsenic and phosphate were less than those in the absence of calcium. Thus, phosphate was less soluble and less arsenic was desorbed in the presence of calcium.

Table 26. Desorption of arsenic (V) at pH=11

Time (hr.)	**$FeCl_3$**		**$FeCl_3 + Ca(OH)_2$**	
	As (μg/L)	**PO_4^{3-} (mg/L)**	**As (μg/L)**	**PO_4^{3-} (mg/L)**
0	0.00	127.46	0.00	127.46
0.5	2050.47	15.07	436.77	7.93
1	2320.08	50.38	282.96	6.45
2	2589.68	59.08	277.16	2.58
4	2939.18	51.75	268.45	4.04
8	2779.41	51.68	219.55	9.76
12	2859.29	45.33	225.56	2.92
24	1141.03	48.61	252.32	2.21

The data from the experiments where arsenic and phosphate were leached from the solid (Figure 17) and the data from the experiments where arsenic was leached in the presence of phosphate (Figure 18) show the same trend. The main difference is that the concentrations were generally larger in the extraction of arsenic by phosphate. This trend is probably due to the difference in phosphate concentrations. The amount of phosphate in the solid was less than the amount of phosphate in solution so the equilibrium concentration would be higher. The difference in phosphate concentration is due to the fact that sorption of wastewater containing 1.3 mM of phosphate was carried out in order to create solids contaminated with phosphate. As shown in the sorption experiments, not all of the aqueous phosphate was sorbed.

Figure 18. Extraction of Arsenic (V) by Phosphate at pH=11



Summary

Tables 27 and 28 show the concentrations of each ion on the solid at 24 hours for the sorption/desorption experiments. The concentration of arsenic on the solid was consistent for almost all experiments. Apparently ~35mg (0.45 mmol) of arsenic was sorbed by one gram of dry solid. The phosphate concentration varied with pH and calcium content. With the current data, it would be hard to determine the amount of phosphate that can be sorbed by one gram of dry solid because no experiments were conducted with any arsenic in solution. It is important to note that the total mmoles per gram of dry solid were variable for the experiments containing phosphate. A probable explanation is that the initial concentration of phosphate for the experiment conducted at pH 8 was ten times higher than that of the experiment conducted at pH 11; therefore more phosphate was available for solid formation and a different equilibrium was reached. Overall, more phosphate was sorbed in the presence of calcium.

Table 27. Sorption summary

		As (mmol/g dry solid)	**PO_4^{3-}** (mmol/g dry solid)	**Total** (mmol/g dry solid)
pH 8	No Ca	0.46	NA	0.46
	Ca	0.48	NA	0.48
pH 11	No Ca	0.45	NA	0.45
	Ca	0.48	NA	0.48
pH 8	No Ca	0.46	0.74	1.19
	Ca	0.74	1.70	2.17
pH 11	No Ca	0.46	0.20	0.66
	Ca	0.74	0.27	0.74
pH 11	No Ca	0.44	NA	0.44
	Ca	0.64	NA	0.64

Table 28. Desorption summary

		As (mmol/g dry solid)	**PO_4^{3-}** (mmol/g dry solid)	**Total** (mmol/g dry solid)
pH 8	No Ca	0.45	NA	0.45
	Ca	0.48	NA	0.48
pH 11	No Ca	0.45	NA	0.45
	Ca	0.48	NA	0.48
pH 8	No Ca	0.46	0.40	0.86
	Ca	0.74	1.47	1.94
pH 11	No Ca	0.46	0.17	0.63
	Ca	0.74	0.27	0.74
pH 11	No Ca	0.44	0.14	0.58
	Ca	0.64	0.32	0.95

Arsenic Adsorption Isotherms

Arsenic adsorption isotherms were obtained to determine the change in sorption with changes in amount of residual added. The data will show sorption as a function of residual concentration at pH 8 and 11. The data was also plotted as concentration sorbed as a function of equilibrium dissolve concentration in order to classify the isotherm by its behavior. Also, the data was fitted using Langmuir, Freundlich and BET isotherms. Langmuir isotherms represent single-site chemical interaction of uncharged solute with no lateral interaction. Freundlich represents multi site interaction in a heterogeneous solid. BET represents multilayer interaction when the initial layer acts as substrate for further adsorption.

Arsenic Adsorption Isotherm at pH 8

Figures 19 and 20 show the adsorption isotherm experimental data at pH 8 with and without the addition of calcium. The initial concentration of arsenic was 200 mg/L. The aqueous concentrations decreased as the amount of residual was increased. In the comparison of the data from the experiments in the presence of calcium and in the absence of calcium, no significant differences in the shapes of the isotherms were evident. Nevertheless, the equilibrium concentrations in the experiments with calcium addition tend to be about half of the equilibrium concentrations in the experiments without calcium addition at low residual concentrations. This data suggests that the presence of calcium aids in the sorption of arsenic on to the iron oxides.

Figure 19. Absorption Isotherm Experiment Data for Arsenic without Calcium Addition at pH 8

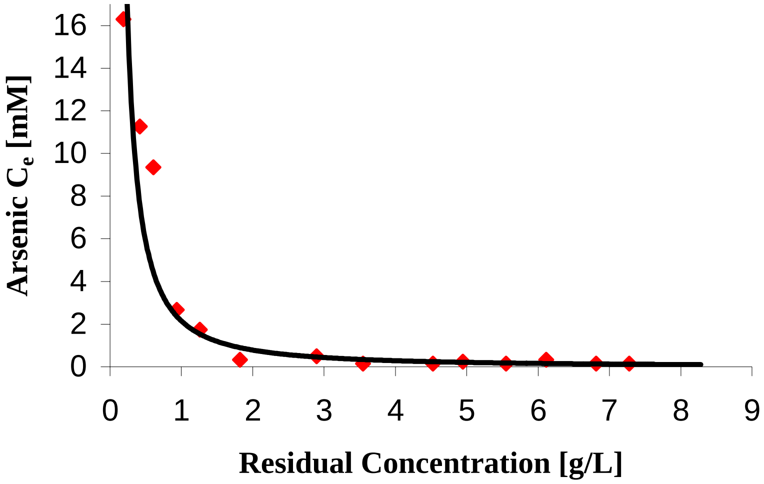
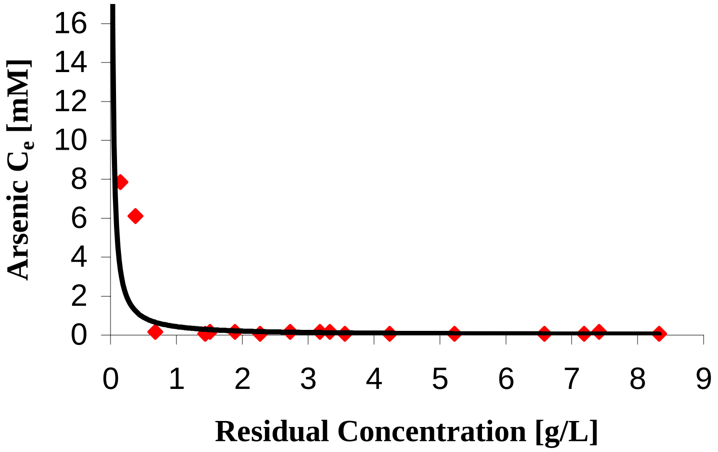


Figure 20. Absorption Isotherm Experiment Data for Arsenic with Calcium Addition at pH 8



The plots of arsenic concentration in equilibrium (24 hours) as a function of residuals solids concentration (Figure 19 and 20) have the same shape as Type II isotherms. Figure 21 shows the experiment without calcium addition. The shape of the graph is very similar to the trend of a Type II isotherm. If this classification were correct, the first monolayer would be expected to be filled at about 400 mg/g of arsenic sorbed or 800 µg/L of dissolved arsenic at equilibrium.

Figure 21. Absorption Isotherm for Arsenic without Calcium Addition at pH 8

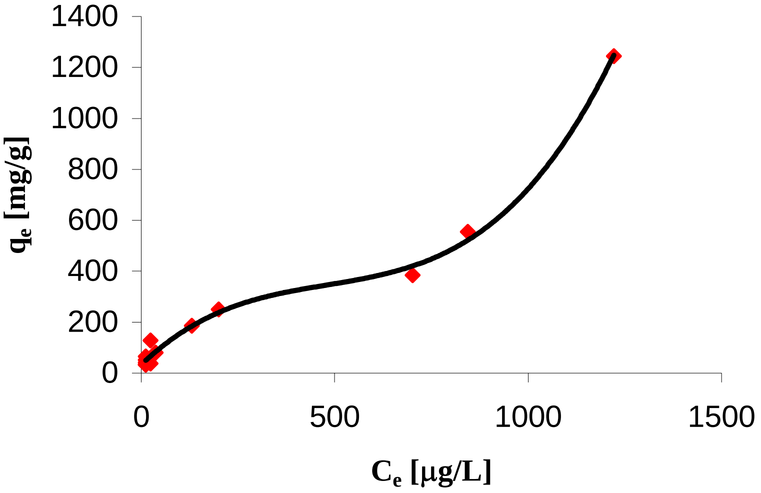
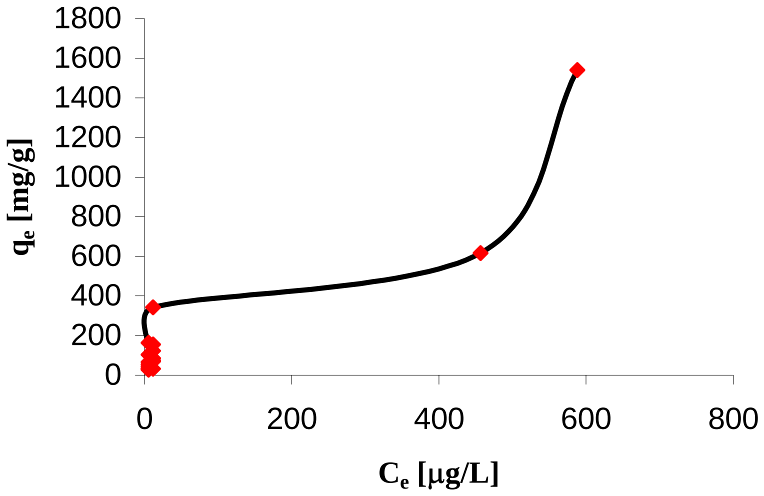


Figure 22 shows the results of the experiment with calcium addition. The shape of the graph is similar to the trend of a Type II isotherm. The main difference is the steep slope at low equilibrium concentrations in solutions. In this case, the first monolayer would be expected to be filled at about 600 mg/g of arsenic sorbed or 400 µg/L of dissolved arsenic at equilibrium.

Figure 22. Absorption Isotherm for Arsenic with Calcium Addition at pH 8



Fitting the data to a linearized Langmuir equation did not give a good coefficient of determination. Plotting the experimental data using the Langmuir equation at pH 8 with no calcium present did not give a good fit as the R^2 value is 0.7334, shown in Figure 23. As expected from Figure 21, at low adsorption concentrations the data appears to be linear shown by the boxed data in Figure 23. This relationship would be expected when one monolayer is being filled.

When only the data in the box is plotted, a better coefficient of determination of 0.9189 is found as shown in Figure 24. This trend suggests that the classification as Type II isotherm is correct, and the adsorption is not a single-site chemical interaction.

Figure 23. Linearized Langmuir Isotherm (No Calcium) at pH 8

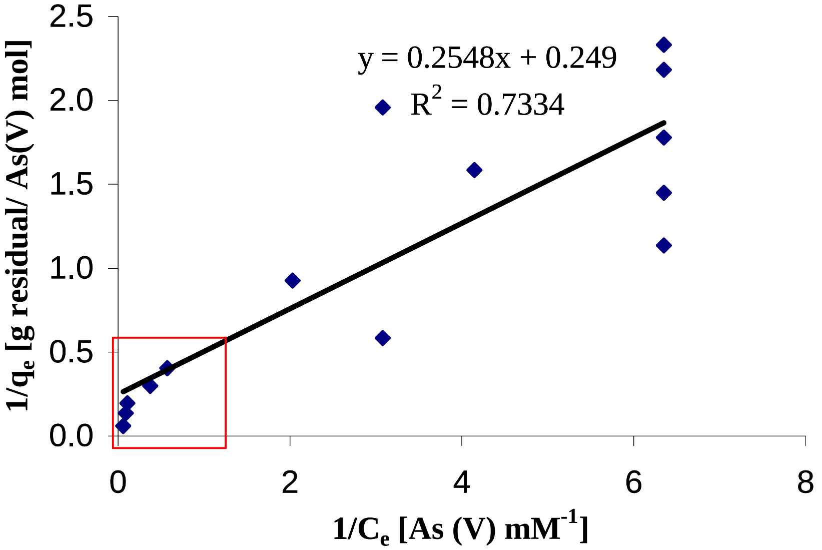
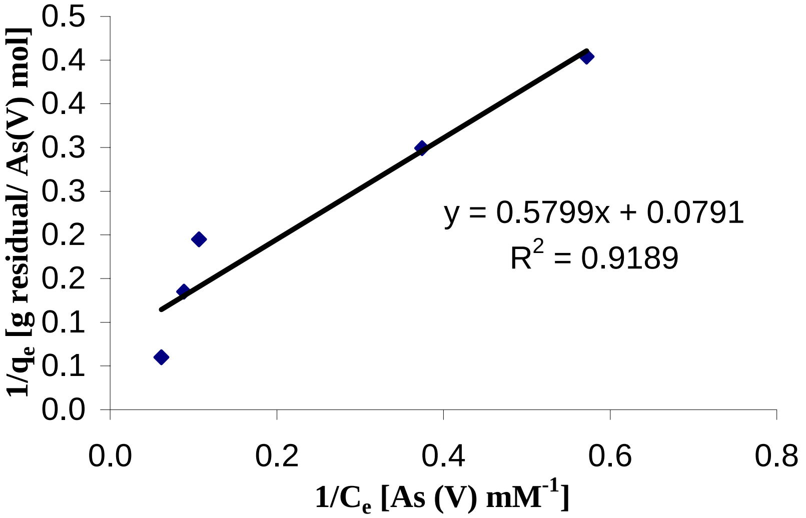
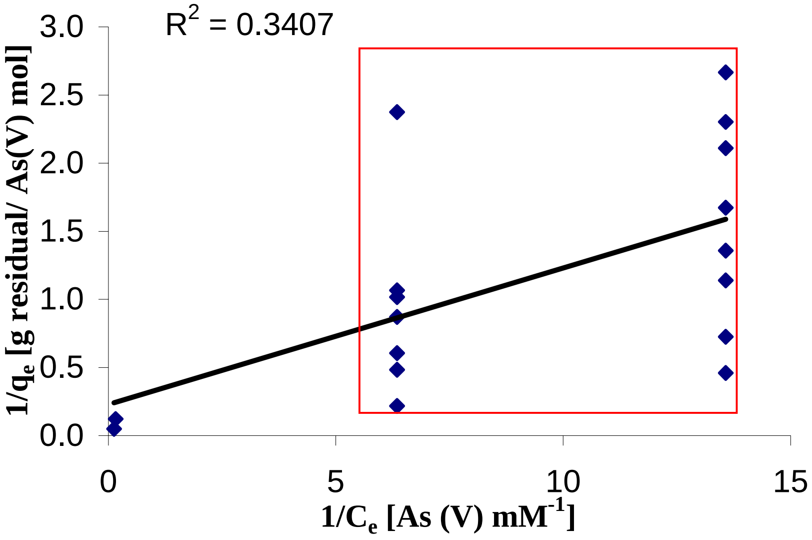


Figure 24. Linearized Langmuir Isotherm of Selected Points (No Calcium) at pH 8



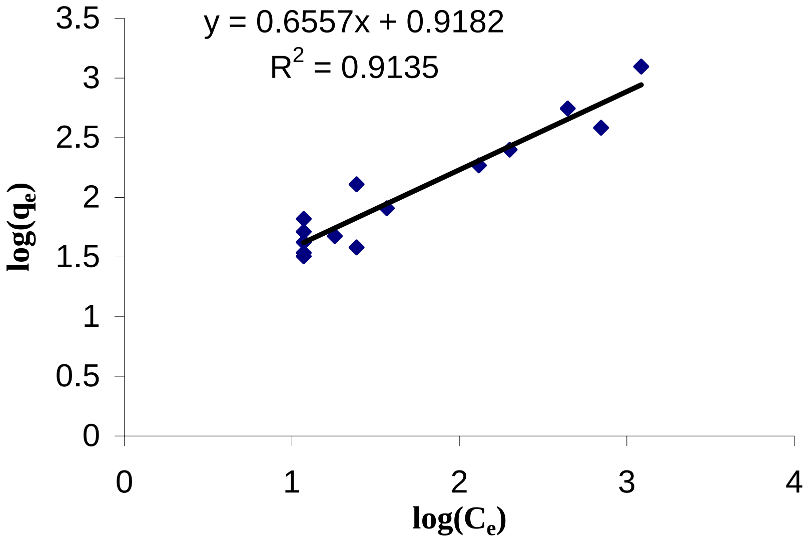
Plotting the experimental data using the Langmuir equation at pH 8 with calcium present did not give a good fit as the R^2 value is 0.3407 shown in Figure 25 for the boxed data points. Physically all this point ma represent the same adsorption. Since the linearized Langmuir equation is obtained by inverting the concentrations, small difference between values are amplified.

Figure 25. Linearized Langmuir Isotherm (with Calcium) at pH 8



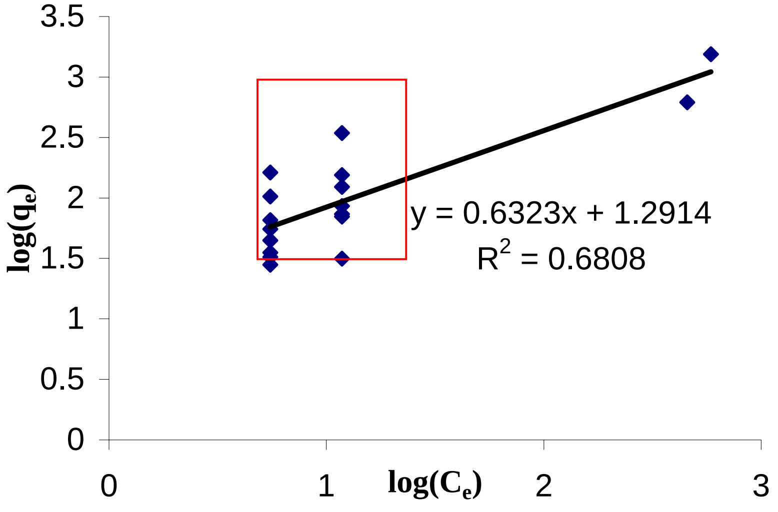
Fitting the data to a linearized Freundlich equation gave a better fit than the linearized Langmuir equation. This was expected since the residuals are solids formed relatively fast; therefore, it can be assumed that the surface is heterogeneous and amorphous with large pores which one of the assumptions used in the Freundlich isotherm. Plotting the experimental data using the Freundlich equation at pH 8 with no calcium present did gave a good fit, as the coefficient of determination is 0.9135 shown in Figure 26 suggesting multi site interaction in a heterogeneous solid.

Figure 26. Linearized Freundlich Isotherm (No Calcium) at pH 8



A plot of the experimental data for pH 8 with calcium present using the Freundlich equation gave a better fit than Langmuir but not as good as the Freundlich fit for the experiment with no calcium added as shown in Figure 27. The coefficient of determination was 0.6808. The boxed data in Figure 27 could represent the same adsorption point or could be the effect of solids formation. Furthermore, these points correspond to the boxed data in the Langmuir isotherm in Figure 25. In the Solids Formation Section the solids formed during this experiment will be identified.

Figure 27. Linearized Freundlich Isotherm (with Calcium) at pH 8



The BET parameters were determined by using the experimental data. Then the experimental data was compared to the BET model using the equation

$$q_e = \frac{Q_M K_1 K_2 C_{eq}}{K_1 K_2 C_{eq} - K_2 \left(K_1 C_{eq}\right)^2 + C_{eq}^2 + K_1^2 - 2K_1 C_{eq}} \qquad [4]$$

The difference was calculated and minimized by changing the parameters Q_M, K_1 and K_2 in the equation. The isotherm data and BET model at pH 8 with no calcium is shown in Figure 28, and the isotherm data and BET model at pH 8 with calcium is shown in Figure 29. The parameters for both BET models are shown in Table 29. The data used to construct the model are in Appendix C.

Table 29. BET parameter for the isotherm at pH 8

BET	No Ca	Ca
K_1	0.58	0.46
K_2	3.02	5.62
Q_M	1.09	1.79

As shown in Figures 28 and 29 the BET model overlaps significantly wit the experimental data for both experiments. The experimental data for the isotherm test conducted without calcium seems to have a better fit than for the experiment conducted with calcium. This data indicates that the adsorption mechanism is a multilayer interaction, where the initial layer acts as substrate for further adsorption.

Figure 28. BET Isotherm (No Calcium) at pH 8

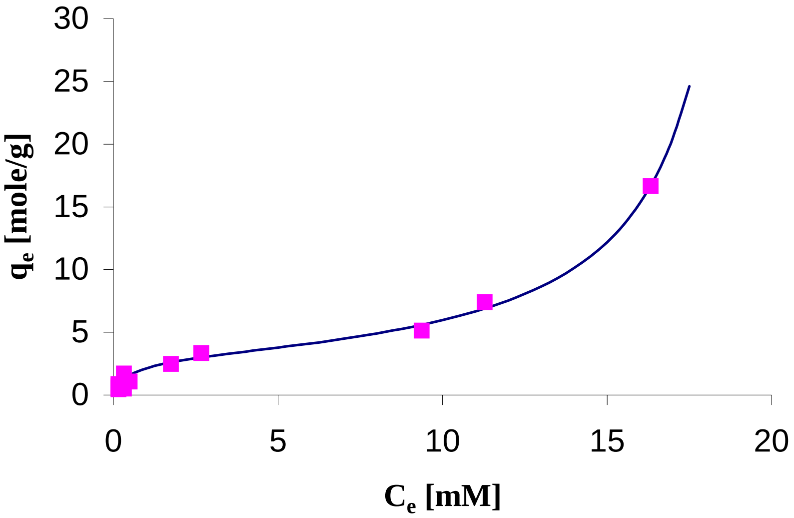
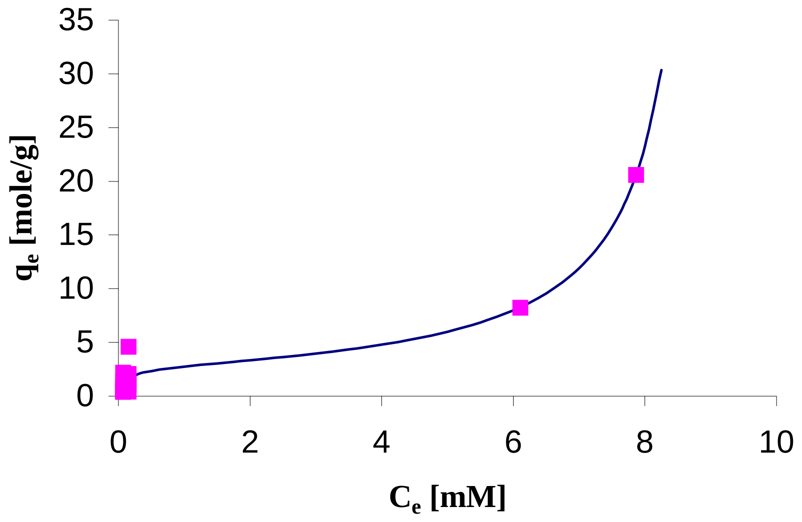


Figure 29. BET Isotherm (with Calcium) at pH 8



Arsenic Adsorption Isotherm at pH 11

Figures 30 and 31 show the adsorption isotherm experimental data at pH 11 with and without the addition of calcium. The initial concentration of arsenic was 200 mg/L. The aqueous concentrations decreased as the amount of residual added increased. Again, comparing the data from the experiment in the presence of calcium and in the absence of calcium no significant difference in the shape of the graph can be seen. Nevertheless, the equilibrium concentrations in the experiments with calcium addition tend to be about half of the equilibrium concentrations in the experiments without calcium addition at low residual concentrations. These data would further suggest that the presence of calcium aids in the sorption of arsenic on to the iron oxides.

Figure 30. Absorption Isotherm Experiment Data for Arsenic without Calcium Addition at pH 11

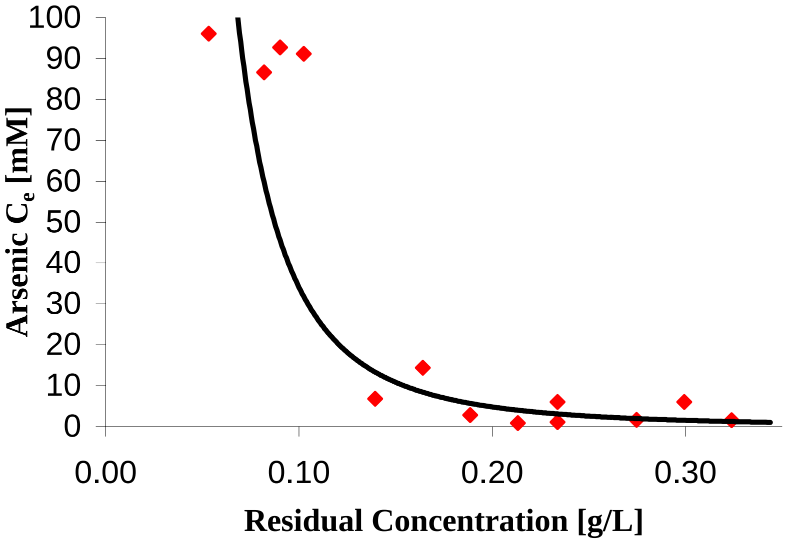
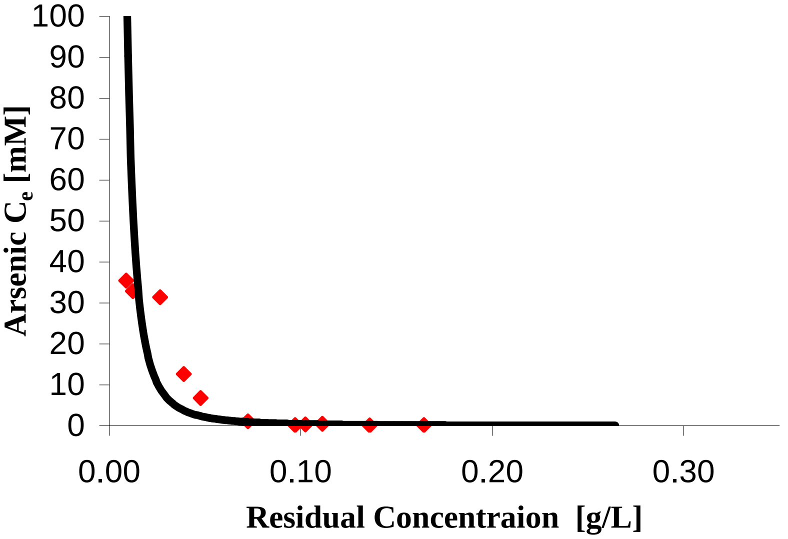


Figure 31. Absorption Isotherm Experiment Data for Arsenic with Calcium Addition at pH 11



The plots of concentration sorbed as a function of concentration in equilibrium have the same shape as Type II isotherms. Figure 32 shows the experiment without calcium addition. The shape of the graph is very similar to the trend of a Type II isotherm. If this classification were correct, the first monolayer would be expected to be filled at about 250 mg/g of arsenic sorbed or 6000 μg/L of dissolved arsenic at equilibrium. Figure 33 shows the experiment with calcium addition. The shape of the graph is also very similar to the trend of a Type II isotherm. In this case the first monolayer would be expected to be filled at about 1000 mg/g of arsenic sorbed or 2000 μg/L of dissolved arsenic at equilibrium.

Figure 32. Absorption Isotherm for Arsenic without Calcium Addition at pH 11

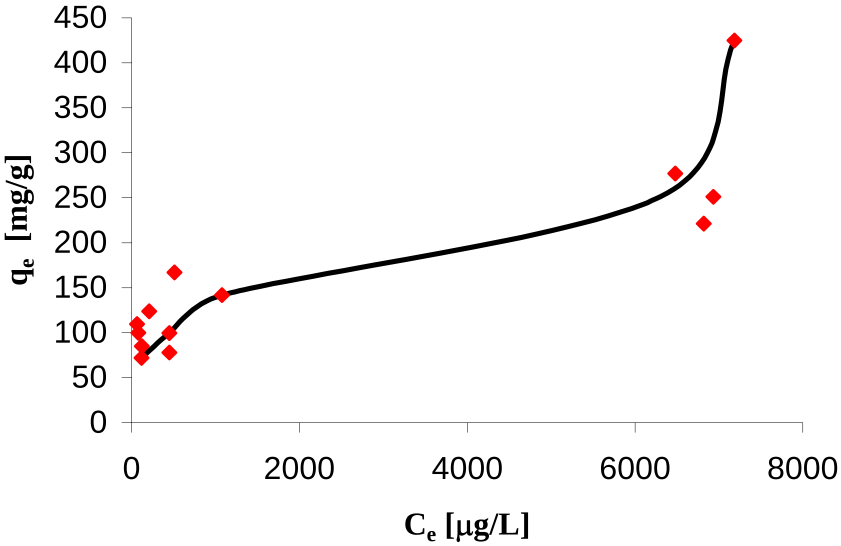
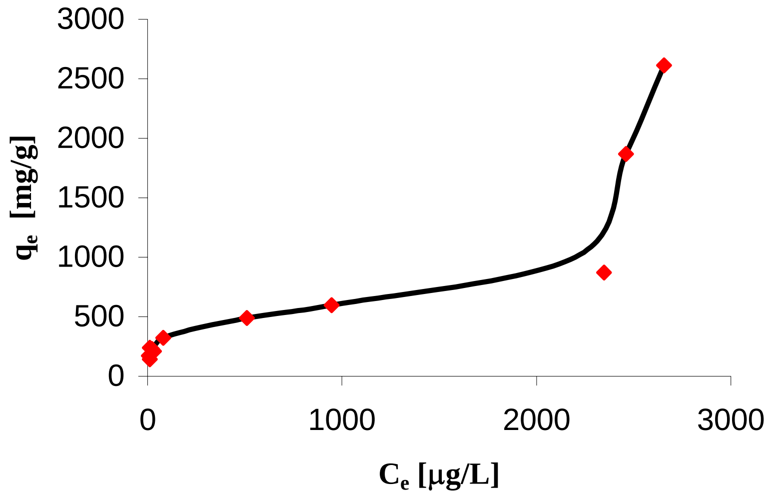
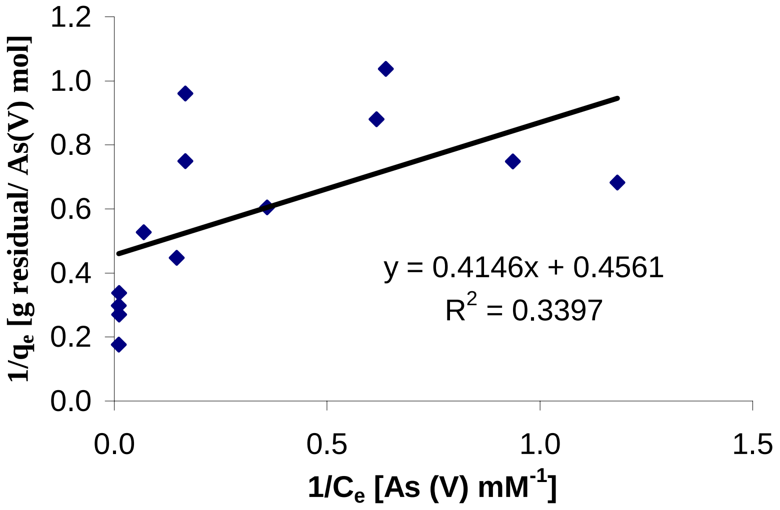


Figure 33. Absorption Isotherm for Arsenic with Calcium Addition at pH 11



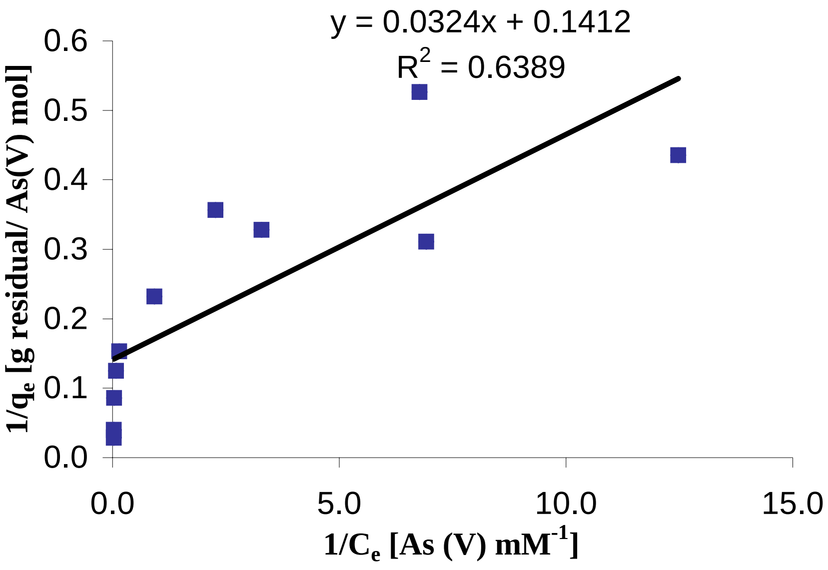
Fitting the data to a linearized Langmuir equation did not give a good coefficient of determination. Plotting the experimental data using the Langmuir equation at pH 11 with no calcium present did not give a good fit as the R^2 value is 0.3397, shown in Figure 34.

Figure 34. Linearized Langmuir Isotherm (No Calcium) at pH 11



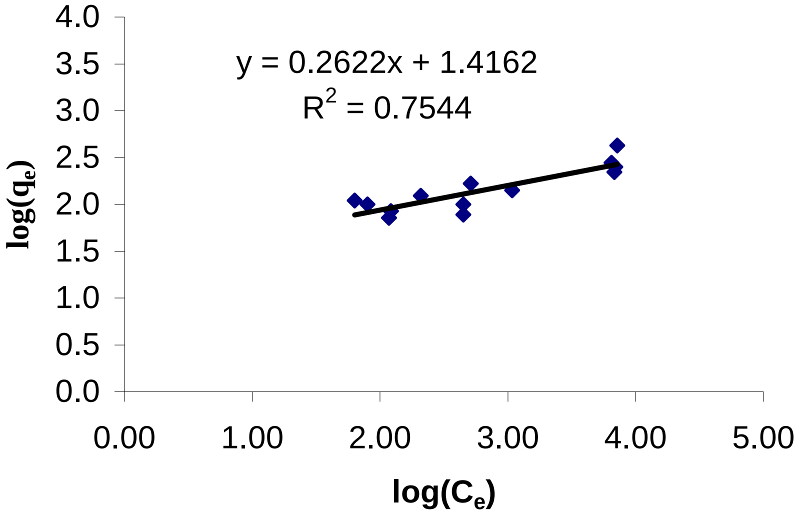
Plotting the experimental data using the Langmuir equation at pH 11 with calcium present did not give a good fit as the R^2 value is 0.6389 shown in Figure 35. Even though, the coefficient of determination is higher than that of the experiment with no calcium addition. The Langmuir plot indicates that the adsorption is not single site chemical interaction.

Figure 35. Linearized Langmuir Isotherm (with Calcium) at pH 11



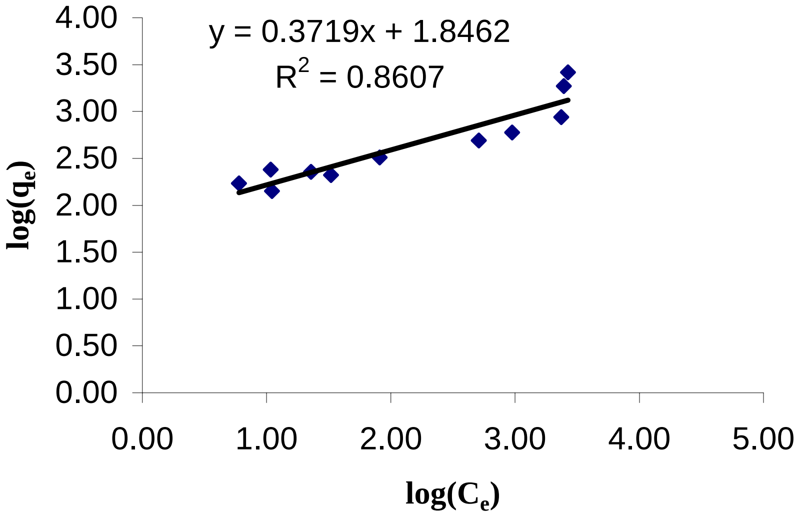
Fitting the data to a linearized Freundlich equation gave a better fit than the linearized Langmuir equation. Again, this was expected since the residuals are solids formed relatively fast. Plotting the experimental data using the Freundlich equation at pH 11 with no calcium present did gave a good fit, as the coefficient of determination is 0.7544 shown in Figure 36.

Figure 36. Linearized Freundlich Isotherm (No Calcium) at pH 11



Plotting the experimental data using the Freundlich equation at pH 11 with calcium present gave a better fit than Langmuir and the Freundlich fit for the experiment with no calcium added as shown in Figure 37. The coefficients of determinations suggest that the adsorption is closer to multi site interaction in a heterogeneous solid.

Figure 37. Linearized Freundlich Isotherm (with Calcium) at pH 11



The BET parameters were determined by using the experimental data. Then the experimental data was compared to the BET model. The isotherm data and BET model at pH 11 with no calcium is shown in Figure 38 and the isotherm data and BET model at pH 11 with calcium is shown in Figure 39. The parameters for both BET models are shown in Table 30. The data used to construct the model are in Appendix C.

Table 30. BET parameter for the isotherm at pH 11

BET	No Ca	Ca
K_1	0.04	0.06
K_2	590.32	589.99
Q_M	1.34	3.43

As shown in Figures 38 and 39 the BET model overlaps significantly with the experimental data for both experiments. The experimental data for the isotherm test conducted without calcium seems to have a better fit than the experiment conducted with calcium.

Figure 38. BET Isotherm (no Calcium) at pH 11

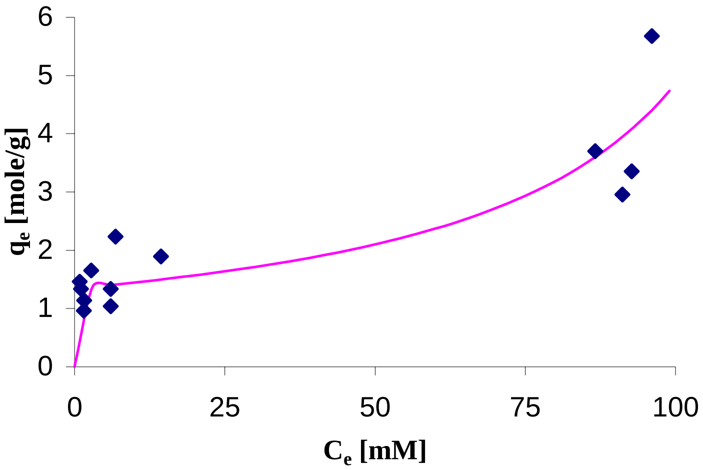
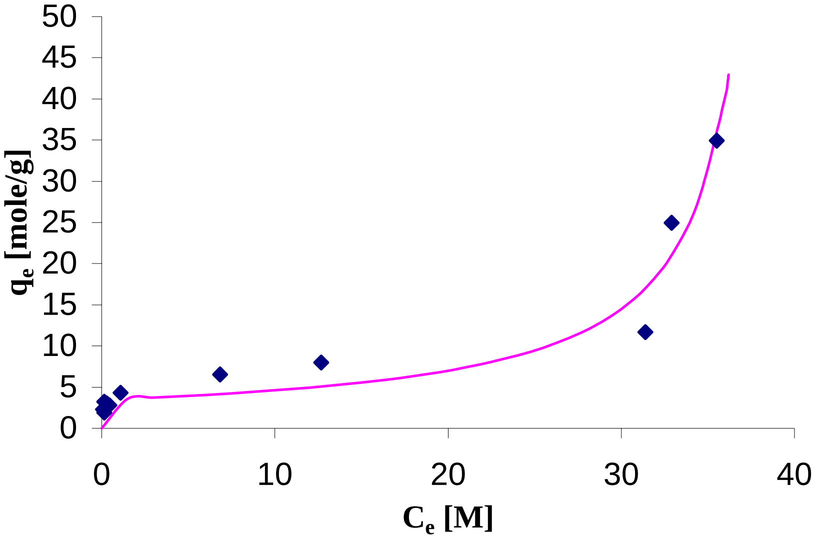


Figure 39. BET Isotherm (with Calcium) at pH 11



The adsorption data at pH 8 and 11 supports the classification of Type II adsorption and BET mechanism. These data would indicate that the adsorption mechanism is multilayer interaction where the initial layer acts as substrate for further adsorption.

Calcium Arsenic Solid Formation

This test was conducted to establish the formation of calcium arsenic solids and calcium phosphate solids at different pH values. Previous research has established that such solids form at pH>11.5. The formation of such solids was investigated at different pH values, since solid formation could explain the reduction in soluble arsenic and phosphate concentrations in the presence of calcium, and its effect on reducing the concentrations of arsenic in leachate from wastewater treatment residuals.

VIMITEQ Results

The solution conditions used for the sorption test were used as input for the simulation with VMINTEQ, to try to reproduce experimental conditions and determine what results could be expected from theoretical calculations based on thermodynamic models integrated in the computer program. The VMINTEQ calculations suggest that solid formation could have played a role in the reduced concentrations of soluble arsenic and phosphate. Tables 31-36 list the solids that VMINTEQ predicts to be formed. All the results from the model are shown in Appendix D.

Table 31. Solids formed in clean water with no calcium

Solid	Equilibrium amount (mol/l)
$Fe(OH)_{2.7}Cl_{0.3}$	2.00E-01

Table 32. Solids formed in clean water with calcium

Solid	Equilibrium amount (mol/l)
$Fe(OH)_{2.7}Cl_{0.3}$	2.00E-01

Comparison of the solids predicted at pH 8 and 11 (Tables 33 and 34) indicates that more calcium-arsenic solids would be expected at a higher pH than at a lower pH.

Table 33. Solids formed in arsenic wastewater with calcium at pH 8

Solid	Equilibrium amount (mol/l)
$Fe(OH)_{2.7}Cl_{0.3}$	2.00E-01
$Ca_3(AsO_4)_2 \cdot 4H_2O$	0.00080825

Table 34. Solids formed in arsenic wastewater with calcium at pH 11

Solid	Equilibrium amount (mol/l)
$Fe(OH)_{2.7}Cl_{0.3}$	2.00E-01
$Ca_3(AsO_4)_2 \cdot 4H_2O$	0.0013338

Comparison of the amount of solids predicted at pH 8 and 11 (Tables 35 and 36) indicates that more calcium-arsenic solids would be expected at a higher pH than at a lower pH but the amount of phosphate-calcium solids does not change.

Table 35. Solids formed in arsenic and phosphate wastewater with calcium at pH 8

Solid	Equilibrium amount (mol/l)
$Fe(OH)_{2.7}Cl_{0.3}$	2.00E-01
$Ca_3(PO_4)_2$ (beta)	6.65E-04
$Ca_3(AsO_4)_2 \cdot 4H_2O$	7.93E-04

Table 36. Solids formed in arsenic and phosphate wastewater with calcium at pH 11

Solid	Equilibrium amount (mol/l)
$Fe(OH)_{2.7}Cl_{0.3}$	2.00E-01
$Ca_3(PO_4)_2$ (beta)	6.65E-04
$Ca_3(AsO_4)_2 \cdot 4H_2O$	1.33E-03

X-ray Diffraction Results

The results from the XRD results are in Appendix E. Unfortunately, the results were inconclusive. The solids intended to be identified were not found in the XRD output. The output was compared to the spectra of calcium hydrogen arsenate hydrate, calcium hydrogen arsenate, calcium phosphate and calcium arsenate hydrate. The lack calcium-arsenic and calcium-phosphate solid in the XRD output does not conclusively indicate that they are not present. The results could be due to the lack of crystallinity of the solids. The residuals are solids formed in a relatively short period of time; therefore it is safe to assume the solids have amorphous surfaces. Another explanation is that the solids are not calcium-arsenic solids but iron-arsenic solids.

CONCLUSION

Summary

The data from the sorption experiments indicates that the presence of calcium aids in the sorption (removal) of arsenic from water. Since this trend is more evident at pH 11 than pH 8, the sorption enhancement due to calcium increases with pH. Even though the effect of calcium addition is more visible at pH 11 than 8 the overall concentration at pH 8 was lower than at pH 11 in the presence of calcium. This is to be expected from the description of arsenic sorption in past research.

The data from the desorption experiments indicate that the presence of calcium prevent the leaching of calcium from the residuals. For the desorption of arsenic at pH 8 the data show a trend were the concentration of arsenic increased but then decreased to what seems to be an equilibrium concentration. This behavior was unexpected and could be due to the formation of some kind of solid. Also, this trend is seen in the experiment conducted with and without calcium addition suggesting that if a solid is formed, it could be an arsenic iron solid or another kind of solid not the expected calcium-arsenic solids. Contrasting, the behavior of desorption of arsenic at pH 8, the desorption of arsenic at pH 11 was as expected. The calcium addition prevented the leaching of arsenic significantly. For the extraction of arsenic by phosphate the addition of calcium had a significant effect on the leaching of arsenic. Both, final arsenic concentration and final phosphate concentration were lower in the experiment with calcium addition.

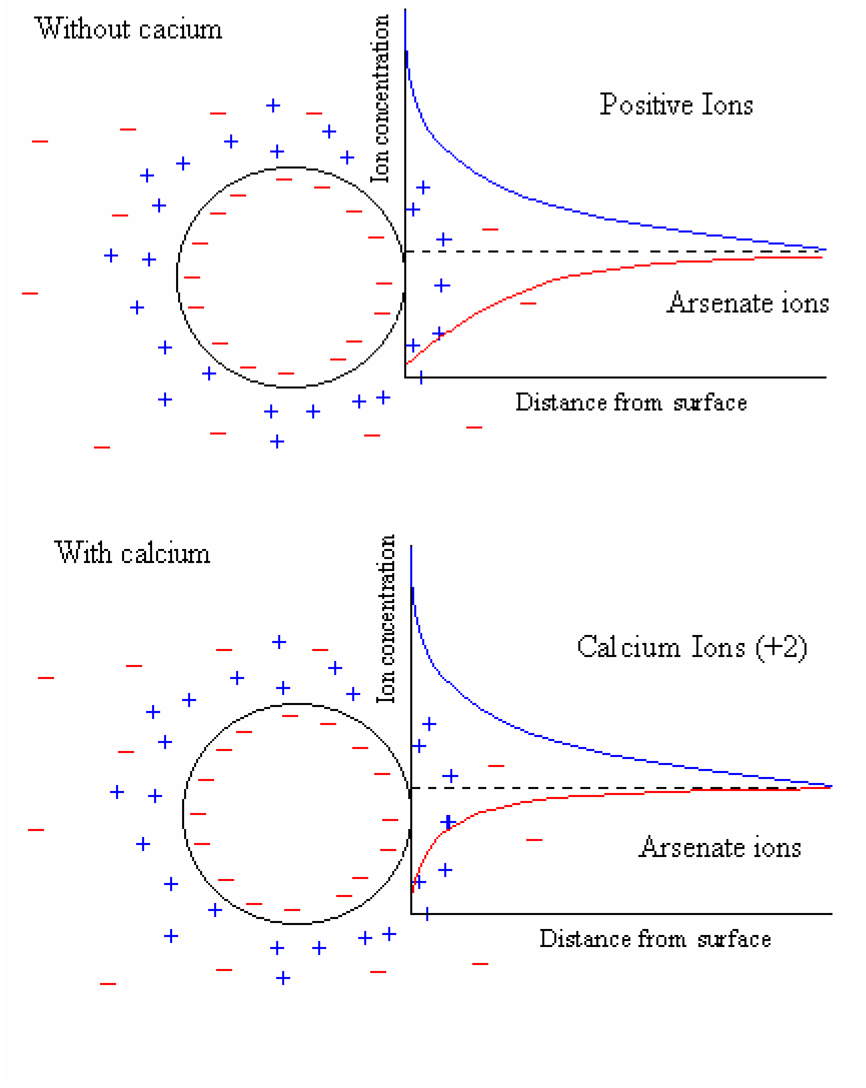
The isotherm experiments indicate that arsenic adsorption can be classified as Type II, which describes adsorption that occurs on nonporous powders or powders with pore diameters larger than micro-pores. Physically, with increase in adsorbate concentration, two or more layers are completed until at saturation the numbers of adsorbed layers becomes infinite. Further, experimental data were fitted to a BET model, which assumes the initial layer can act as substrate for further adsorption.

Finally, calcium-arsenic and calcium-phosphate solids were predicted to be formed by VMINTEQ. Nevertheless, from the XRD output calcium-arsenic or calcium-phosphate solids were not identified.

Conclusion

Because no calcium arsenate solids were found it was concluded that calcium affects the surface properties of the oxy-hydroxide solid in solution. Increasing pH produces negative surface charge, which in turn increases repulsion between the negatively charged hydrated arsenate ions and the $Fe(OH)_3$ surface. Calcium's positive charge might neutralize this effect therefore enhancing the sorption of arsenic on to the oxy-hydroxide. A diffuse ion atmosphere surrounds the negatively charged iron oxide. Positive ions (i.e. H^+, Ca^{2+}) are attracted to the iron oxide surface (Figure 40). Negative arsenic ions are repelled from the surface and their lowest concentration is closest to the iron oxide surface. As the distance from the iron oxide surface increases, the concentration of the arsenic ions increases (Figure 40). In the presence of calcium, this repulsion is decreased, allowing higher concentrations of arsenic ion to exist closer to the iron oxide surface. Also, it was concluded that the competition between arsenic and phosphate was reduced by the same mechanisms.

Figure 40. Schematic Drawing of Conclusion



Recommendations

To further understand the impact of calcium and competing ions on the leaching of arsenic from treatment residuals more experiments have to be conducted at different pH and initial concentrations of phosphate and arsenic. Also, all experiments should be replicated so that statistical analysis between the experiments conducted with and without calcium addition can be conducted. More important would be to model a variety of conditions and compare them with experimental data.

Also, isotherm experiments should be conducted with higher initial arsenic concentrations or smaller amounts of residual to obtain a larger equilibrium arsenic concentration and residual concentration range.

Finally, experiments should be conducted to further investigate solids formation with different ratios of calcium: iron: arsenic: phosphate and to identify solids formed by conducting more specific techniques. Also, it should be determined if more than calcium solids are formed.

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APPENDIX A

MATERIALS

Synthetic Residuals Production

This section describes the method used to produce the synthetic residuals used in all experiments.

Apparatus

a. pH meter
b. Stirring apparatus
c. Buchner funnel
d. Filter (0.2µm)
e. Laboratory balance

Reagents
a. $FeCl_3$- ACS Reagent Grade
b. NaOH- A.C.S. reagent grade, Fisher
c. $Ca(OH)_2$- ACS Reagent Grade
d. $CaCl_2$- ACS Reagent Grade

Synthetic Wastewater Production

This section describes the method used to produce the synthetic wastewater used in all experiments. Arsenic and phosphate were present in the wastewater as the absorption variables and nitrate was present as an ionic strength gauge.

Apparatus
a. 100 mL Volumetric Flask
b. 2000 mL Volumetric Flask
c. Laboratory balance

Reagents
a. AsO_5- ACS Reagent Grade
b. NaH_2PO_4- A.C.S. reagent grade, Fisher
c. $NaNO_3$- ACS Reagent Grade

Arsenic Sorption Test

Arsenic sorption test were conducted to determine the change in sorption with change in calcium content and presence of competing ions. The data show sorption as a function of time for pH 8 and 11.

Apparatus

a. pH meter
b. Centrifuge
c. Flame atomic absorption spectrometer (model name: Thermo Elemental, Solar M6 AA)
d. Continuous hydride generation system (model name: Thermo Elemental, VP90)
e. Capped polypropylene bottles
f. Laboratory balance
g. Orbital shaker
h. Filter (0.2 μm)

Reagents

a. Synthetic Residual Containing Calcium
b. HCl- A.C.S. reagent grade
c. NaOH- A.C.S. reagent grade
d. DI water

Arsenic Desorption Test

Arsenic desorption tests were carried out with synthetic residuals at pH of 8 and 11 to assess the possible reduction in desorption with calcium content and increase desorption in the presence of phosphate.

Apparatus

a. pH meter
b. Centrifuge
c. Flame atomic absorption spectrometer (model name: Thermo Elemental, Solar M6 AA)
d. Continuous hydride generation system (model name: Thermo Elemental, VP90)
e. Capped polypropylene bottles
f. Laboratory balance
g. Orbital shaker

Reagents

a. Synthetic Residual Containing Calcium and Arsenic
b. HCl- A.C.S. reagent grade
c. NaOH- A.C.S. reagent grade
d. DI water
a. HCl (1N)- ACS Reagent Grade
b. NaOH (1N) - ACS Reagent Grade

Arsenic Adsorption Isotherms

Arsenic sorption tests were conducted to determine the change in sorption with change residual amount. The data will show sorption as a function of residual mass for pH 8 and 11.

Apparatus

a. pH meter
b. Centrifuge
c. Flame atomic absorption spectrometer (model name: Thermo Elemental, Solar M6 AA)
d. Continuous hydride generation system (model name: Thermo Elemental, VP90)
e. Capped polypropylene bottles
f. Laboratory balance
g. Orbital shaker
h. Filter (0.2 μm)

Reagents

e. Synthetic Residual Containing Calcium
f. HCl- A.C.S. reagent grade
g. NaOH- A.C.S. reagent grade
h. DI water

Calcium Arsenic Solid Formation

This test was conducted to establish the formation of calcium arsenic solids at different pHs. Previous research has established that such solids do not form at pH<11.5. The solid-phase assemblages previously studied are:

$$Ca_4(OH)_2(AsO_4)_2 \bullet 4H_2O$$

$$Ca_5(OH)_2(AsO_4)_3OH$$

$$Ca_3(AsO_4)_2 \bullet {}^{11}\!\!/_{3}\,H_2O$$

$$Ca_3(AsO_4)_2 \bullet {}^{17}\!\!/_{4}\,H_2O$$

Apparatus

a. pH meter
b. Filter (0.2µm)
c. Capped polypropylene bottles
d. Buchner funnel
e. Laboratory balance
f. Orbital shaker

Reagents

a. Synthetic Residual Containing Calcium and Arsenic
b. HCl- A.C.S. reagent grade
c. NaOH- A.C.S. reagent grade
d. DI water

APPENDIX B

ANALYSIS METHODS

Continuous Hydride Generation with Atomic Absorption Spectroscopy

Analysis method used to determine soluble arsenic.

Reagents

a. As_2O_5- A.C.S. reagent grade, Aldrich
b. HCl- trace-metal grade, Fisher
c. $NaBH_4$- A.C.S. reagent grade, EM
d. NaOH- A.C.S. reagent grade, Fisher
e. DI water- ~18 conductivity
f. Air -AAS grade
g. C_2H_2 (acetylene gas) -AAS grade
h. Argon gas -AAS grade

Continuous Hydride Generation with Atomic Absorption Spectrometry

Continuous hydride generation with atomic absorption spectrometric method (HG/AAS) (Standard method 3114C) is employed to determine arsenic concentrations. Using a hydride generation system As (III) and As (V) can be converted to AsH_3 using the reducing agent sodium borohydride ($NaBH_4$).

$$NaBH_4 \rightarrow H^+ + Na + H_3B \ \ @ \ pH \downarrow \text{ Stable with NaOH}$$

$$As_2O_3 + BH_4^- + H^+ \rightarrow AsH_3 + H_3BO_4 + H_2O$$

Arsenic pentoxide is used to prepare arsenic stock solution As (V) following the standard method 3114B (APHA et al, 1998). Total arsenic analysis is conducted using hydrochloric acid. The reductant is sodium borohydride and is prepared for all analyses. The concentrations of analytical standards used are 0 (blank), 5, 15, 25, 50 and 100 μg/L. Arsenic standards are kept and used for one week after preparing. All arsenic samples are stored in a refrigerator (4°C) until analyzed. Arsenic analysis is conducted within 48 hours after collecting samples. Dilution of the arsenic standards and samples are carried out using deionized (DI) water. Table 37 contains the reagents and gases used for the analysis.

Table 37. Reagents and gases used for arsenic analysis

Hydrochloric 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
Stock solution	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 is a flame atomic absorption spectrometer (FLAAS) (model name: Thermo Elemental, Solar M6 AA) and a continuous hydride generation system (model name: Thermo Elemental, VP90) using the software package SOLAAR M. The operating parameters used are summarized in Table 38. Acceptance limit for the linear coefficient of calibration curve is $R^2 = 0.995$.

Table 38. Operating parameters for arsenic analysis using HG/AAS

Parameter	Description
Lamp	Hollow Cathode Lamp (HCL) Coded lamp supplied by Unicam Atomic Absorption
Gas pressure	Air (30 psi) and Acetylene (9 psi) for flame Argon (5 psi) for carrier gas

Table 38. Continued

Parameter	Description
Absorption 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
Signal	40 µg/L gives about 0.2 Abs

Ion Chromatography (IC)

Ion chromatography was used to determine the concentration of soluble phosphate. The equipment used was the Dionex DX-80 Ion Analyzer (DX-80). This equipment performs isocratic analysis using suppresses conductivity detection. Table 39 lists the anions that can be detected (in mg/L).

Table 39. List of anions that can be analyzed by Dionex DX-80 Ion Analyzer

Anion	Compound
F	Fluoride
Cl	Chloride
NO_2	Nitrite
Br	Bromide
NO_3	Nitrate
HPO_4	Phosphate
SO_4	Sulfate

APPENDIX C

BET ISOTHERM

Table 40. BET isotherm calculations no calcium pH 8

C_e Experimental [mM]	q_e Experimental [mol/g]	q BET [mol/g]	Error= $(q_e\text{-q BET})^2$
3122.10			
16.33	16.64	16.67	0.00
11.29	7.41	6.90	0.26
9.37	5.13	5.60	0.22
2.67	3.34	3.01	0.11
1.75	2.48	2.62	0.02
0.33	1.72	1.18	0.29
0.49	1.08	1.52	0.19
0.16	0.88	0.70	0.03
0.16	0.69	0.70	0.00
0.24	0.63	0.96	0.11
0.16	0.56	0.70	0.02
0.33	0.51	1.18	0.45
0.16	0.46	0.70	0.06
0.16	0.43	0.70	0.07
		Sum	1.83

Table 41. BET isotherm calculations with calcium pH 8

C_e Experimental [mM]	q_e Experimental [mol/g]	q BET [mol/g]	Error= $(q_e\text{-q BET})^2$
3122.1			
7.87	20.58	20.57	0
6.11	8.24	8.27	0
0.07	2.17	1.03	1.31
0.16	2.06	1.56	0.26
0.16	1.65	1.56	0.01
0.07	1.38	1.03	0.12
0.16	1.15	1.56	0.17

Table 41. Continued

C_e Experimental [mM]	q_e Experimental [mol/g]	q BET [mol/g]	Error= $(q_e\text{-q BET})^2$
0.16	0.98	1.56	0.33
0.16	0.94	1.56	0.38
0.07	0.88	1.03	0.02
0.07	0.74	1.03	0.08
0.07	0.6	1.03	0.18
0.07	0.47	1.03	0.3
0.07	0.43	1.03	0.35
0.16	0.42	1.56	1.29
0.07	0.38	1.03	0.42
		Sum	5.24

Table 42. BET isotherm calculations with no calcium pH 11

C_e Experimental [mM]	q_e Experimental [mol/g]	q BET [mol/g]	Error= $(q_e\text{-q BET})^2$
3122.10			
96.07	5.68	4.40	1.62
86.65	3.70	3.60	0.01
92.70	3.36	4.08	0.52
91.16	2.96	3.94	0.97
6.83	2.23	1.41	0.68
14.39	1.89	1.50	0.16
2.79	1.65	1.37	0.08
0.85	1.46	1.35	0.01
6.00	1.33	1.40	0.00
1.07	1.34	1.35	0.00
1.62	1.14	1.36	0.05
6.00	1.04	1.40	0.13
1.57	0.96	1.36	0.15
		Sum	4.39

Table 43. BET isotherm calculations with calcium pH 11

C_e Experimental [mM]	q_e Experimental [mol/g]	q BET [mol/g]	Error= $(q_e\text{-q BET})^2$
3122.10			
35.50	34.94	35.19	0.06
32.90	24.98	20.99	15.93
31.38	11.66	17.00	28.45
12.67	8.00	5.08	8.53
6.83	6.53	4.17	5.58
1.08	4.31	3.54	0.59
0.14	3.21	3.45	0.06
0.30	3.05	3.47	0.18
0.44	2.80	3.48	0.46
0.08	2.30	3.45	1.33
0.15	1.90	3.46	2.42
		Sum	63.59

APPENDIX D

VMINTEQ RESULTS

Table 44. Soluble speciation in clean water no calcium addition

	Concentration (mol/L)
Cl-1	4.83E-01
Fe(OH)2+	4.03E-15
Fe(OH)3 (aq)	3.67E-16
Fe(OH)4-	2.77E-15
Fe+3	4.46E-25
Fe2(OH)2+4	8.36E-36
Fe3(OH)4+5	9.24E-47
FeCl+2	1.00E-24
FeOH+2	2.22E-19
H+1	5.44E-09
Na+1	4.93E-01
NaCl (aq)	5.72E-02
NaOH (aq)	1.01E-06
OH-	3.41E-06

Table 45. Solids speciation in clean water no calcium addition

	Total Dissolved (molal)	% Dissolved	Total precipitated (molal)	% Precipitates
Cl^{-1}	5.40E-01	90	6.00E-02	10
Fe^{+3}	7.17E-15	0	2.00E-01	100
H^{+1}	-4.41E-06	100	0	0
Na^{+1}	5.50E-01	100	0	0

Table 46. Soluble speciation in clean water and calcium addition

	Concentration (mol/L)
Ca+2	7.45E-02
CaCl+	3.95E-02
CaOH+	1.57E-06

Table 46. Continued

	Concentration (mol/L)
Cl-1	6.56E-01
Fe(OH)2+	3.56E-15
Fe(OH)3 (aq)	3.13E-16
Fe(OH)4-	2.42E-15
Fe+3	3.19E-25
Fe2(OH)2+4	4.47E-36
Fe3(OH)4+5	3.49E-47
FeCl+2	1.15E-24
FeOH+2	1.82E-19
H+1	5.29E-09
Na+1	4.75E-01
NaCl (aq)	7.48E-02
NaOH (aq)	9.43E-07
OH-	3.29E-06

Table 47. Solids speciation in clean water and calcium addition

	Total Dissolved (molal)	% Dissolved	Total precipitated (molal)	% Precipitates
Ca^{+2}	1.14E-01	100	0	0
Cl^{-1}	7.70E-01	92.771	6.00E-02	7.229
Fe^{+3}	6.29E-15	0	2.00E-01	100
H^{+1}	-5.81E-06	100	0	0
Na^{+1}	5.50E-01	100	0	0

Table 48. Soluble speciation in arsenic wastewater and calcium addition @ pH 8

	Concentration (mol/L)
AsO4-3	1.32E-06
Ca(NO3)2	2.73E-11
Ca+2	7.24E-02
CaCl+	3.85E-02
CaNO3+	6.49E-04

Table 48. Continued

	Concentration (mol/L)
CaOH+	6.11E-07
Cl-1	6.55E-01
Fe(OH)2+	6.77E-15
Fe(OH)3 (aq)	2.37E-16
Fe(OH)4-	7.30E-16
Fe+3	3.81E-24
Fe2(OH)2+4	1.01E-34
Fe3(OH)4+5	1.49E-45
FeCl+2	1.38E-23
FeOH+2	8.67E-19
H+1	1.33E-08
H2AsO4-	3.95E-05
H3AsO4	4.37E-11
HAsO4-2	1.01E-03
Na+1	4.83E-01
NaCl (aq)	7.61E-02
NaNO3 (aq)	5.73E-04
NaOH (aq)	3.82E-07
NO3-1	8.78E-03
OH-	1.31E-06

Table 49. Solids speciation in arsenic wastewater and calcium addition @ pH 8

	Total Dissolved (molal)	% Dissolved	Total precipitated (molal)	% Precipitates
AsO_4^{-3}	1.05E-03	39.457	1.62E-03	60.543
Ca^{+2}	1.12E-01	97.873	2.42E-03	2.127
Cl^{-1}	7.70E-01	92.771	6.00E-02	7.229
Fe^{+3}	7.74E-15	0	2.00E-01	100
H^{+1}	1.09E-03	100	0	0
Na^{+1}	5.60E-01	100	0	0
NO_3^{-1}	1.00E-02	100	0	0

Table 50. Soluble speciation in arsenic wastewater and calcium addition @ pH 11

	Concentration (mol/L)
AsO4-3	1.37E-06
Ca(NO3)2	2.68E-11
Ca+2	7.11E-02
CaCl+	3.77E-02
CaNO3+	6.36E-04
CaOH+	5.98E-04
Cl-1	6.56E-01
Fe(OH)2+	5.38E-17
Fe(OH)3 (aq)	1.89E-15
Fe(OH)4-	5.80E-12
Fe+3	3.04E-32
Fe2(OH)2+4	6.43E-45
Fe3(OH)4+5	7.59E-58
FeCl+2	1.10E-31
FeOH+2	6.90E-24
H+1	1.33E-11
H2AsO4-	4.09E-11
H3AsO4	4.52E-20
HAsO4-2	1.05E-06
Na+1	4.83E-01
NaCl (aq)	7.61E-02
NaNO3 (aq)	5.73E-04
NaOH (aq)	3.82E-04
NO3-1	8.79E-03
OH-	1.31E-03

Table 51. Solids speciation in arsenic wastewater and calcium addition @ pH 11

	Total Dissolved (molal)	% Dissolved	Total precipitated (molal)	% precipitates
AsO_4^{-3}	2.42E-06	0.091	2.67E-03	99.909
Ca^{+2}	1.10E-01	96.49	4.00E-03	3.51
Cl^{-1}	7.70E-01	92.771	6.00E-02	7.229
Fe^{+3}	5.80E-12	0	2.00E-01	100
H^{+1}	-2.29E-03	100	0	0
Na^{+1}	5.60E-01	100	0	0
NO_3^{-1}	1.00E-02	100	0	0

Table 52. Soluble speciation in arsenic and phosphate wastewater and calcium addition @ pH 8

Compound	Concentration (mol/L)
AsO4-3	1.36E-06
Ca(NO3)2	2.68E-11
Ca+2	7.12E-02
CaCl+	3.78E-02
CaH2PO4+	2.54E-09
CaHPO4 (aq)	2.09E-07
CaNO3+	6.38E-04
CaOH+	6.00E-07
CaPO4-	8.76E-08
Cl-1	6.56E-01
Fe(OH)2+	6.77E-15
Fe(OH)3 (aq)	2.37E-16
Fe(OH)4-	7.30E-16
Fe+3	3.82E-24
Fe2(OH)2+4	1.01E-34
Fe3(OH)4+5	1.50E-45
FeCl+2	1.38E-23
FeH2PO4+2	6.55E-29
FeHPO4+	7.63E-23
FeOH+2	8.68E-19
H+1	1.33E-08
H2AsO4-	4.07E-05
H2PO4-	4.95E-09
H3AsO4	4.49E-11
H3PO4	4.43E-15
HAsO4-2	1.04E-03
HPO4-2	7.34E-08
Na+1	4.84E-01
Na2HPO4 (aq)	2.34E-08
Na2PO4-	6.86E-11
NaCl (aq)	7.63E-02
NaH2PO4 (aq)	2.29E-09
NaHPO4-	1.35E-07
NaNO3 (aq)	5.75E-04
NaOH (aq)	3.83E-07
NaPO4-2	3.04E-11
NO3-1	8.79E-03
OH-	1.31E-06
PO4-3	1.27E-11

Table 53. Solids speciation in arsenic and phosphate wastewater and calcium addition @ pH 8

	Total Dissolved (molal)	% Dissolved	Total precipitated (molal)	% precipitates
AsO_4^{-3}	1.08E-03	40.632	1.59E-03	59.368
Ca^{+2}	1.10E-01	96.165	4.37E-03	3.835
Cl^{-1}	7.70E-01	92.771	6.00E-02	7.229
Fe^{+3}	7.74E-15	0	2.00E-01	100
H^{+1}	1.12E-03	100	0	0
Na^{+1}	5.61E-01	100	0	0
NO_3^{-1}	1.00E-02	100	0	0
PO_4^{-3}	5.38E-07	0.04	1.33E-03	99.96

Table 54. Solids speciation in arsenic and phosphate wastewater and calcium addition @ pH 11

Compound	Concentration (mol/L)
AsO4-3	1.41E-06
Ca(NO3)2	2.63E-11
Ca+2	6.98E-02
CaCl+	3.70E-02
CaH2PO4+	2.57E-15
CaHPO4 (aq)	2.12E-10
CaNO3+	6.24E-04
CaOH+	5.87E-04
CaPO4-	8.87E-08
Cl-1	6.57E-01
Fe(OH)2+	5.38E-17
Fe(OH)3 (aq)	1.89E-15
Fe(OH)4-	5.80E-12
Fe+3	3.05E-32
Fe2(OH)2+4	6.47E-45
Fe3(OH)4+5	7.65E-58
FeCl+2	1.10E-31
FeH2PO4+2	5.39E-43
FeHPO4+	6.27E-34
FeOH+2	6.91E-24
H+1	1.33E-11
H2AsO4-	4.21E-11
H2PO4-	5.13E-15
H3AsO4	4.65E-20
H3PO4	4.58E-24
HAsO4-2	1.08E-06
HPO4-2	7.61E-11
Na+1	4.84E-01
Na2HPO4 (aq)	2.42E-11
Na2PO4-	7.08E-11
NaCl (aq)	7.63E-02
NaH2PO4 (aq)	2.37E-15
NaHPO4-	1.39E-10
NaNO3 (aq)	5.75E-04
NaOH (aq)	3.82E-04
NaPO4-2	3.15E-11
NO3-1	8.80E-03
OH-	1.31E-03
PO4-3	1.33E-11

Table 55. Soluble speciation in arsenic and phosphate wastewater and calcium addition @ pH 11

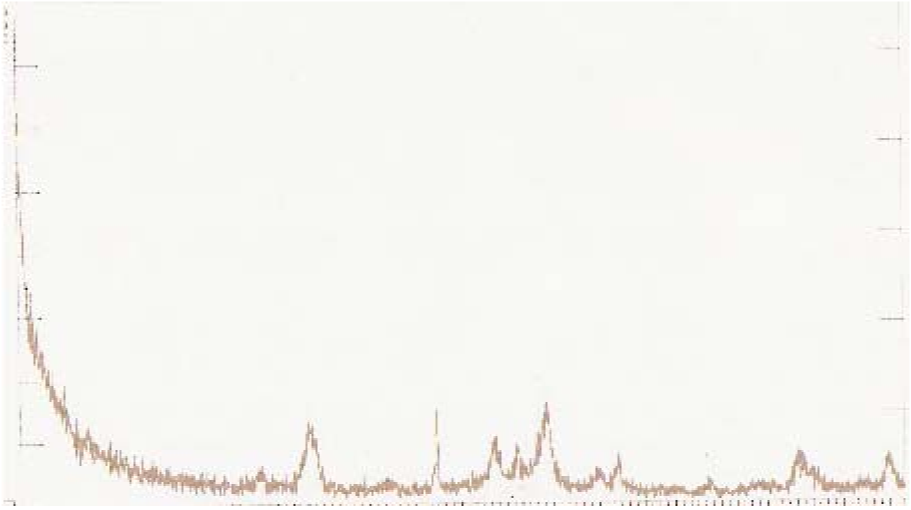
	Total Dissolved (molal)	% Dissolved	Total precipitated (molal)	% Precipitates
AsO_4^{-3}	2.49E-06	0.093	2.67E-03	99.907
Ca^{+2}	1.08E-01	94.74	6.00E-03	5.26
Cl^{-1}	7.70E-01	92.771	6.00E-02	7.229
Fe^{+3}	5.80E-12	0	2.00E-01	100
H^{+1}	-2.28E-03	100	0	0
Na^{+1}	5.61E-01	100	0	0
NO_3^{-1}	1.00E-02	100	0	0
PO_4^{-3}	8.92E-08	0.007	1.33E-03	99.993

APPENDIX E

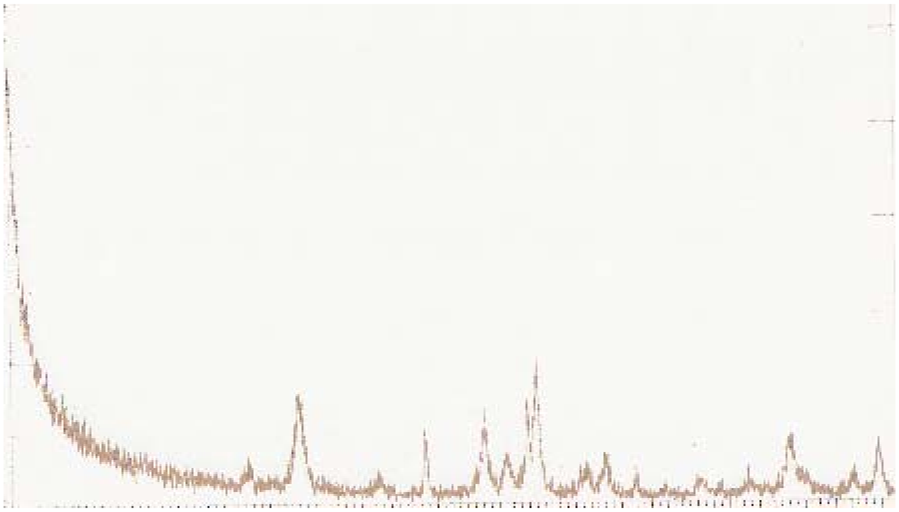
XRD RESULTS

The analysis was conducted with a scan interval of 2.1° to 60° at 2°/min or faster.

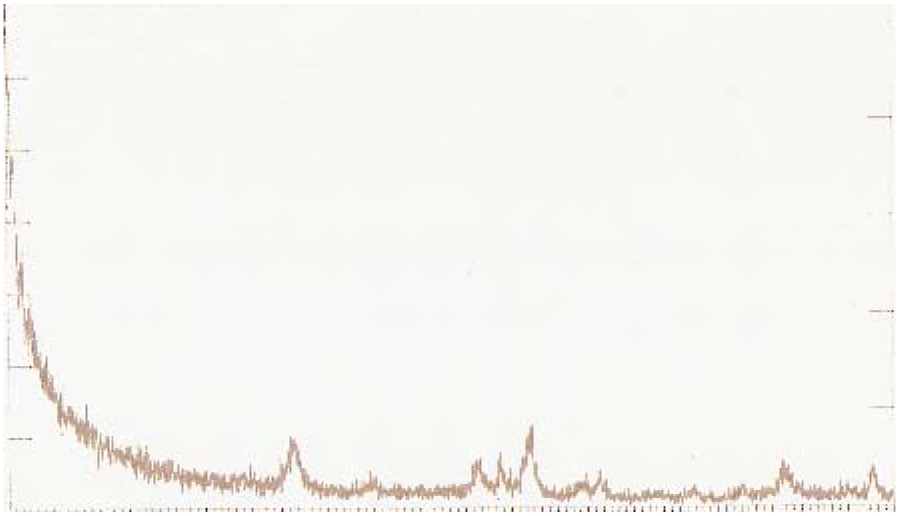
pH 8, 6:10 Ca:Fe mass ratio and $[As(V)]^0$=200mg/L



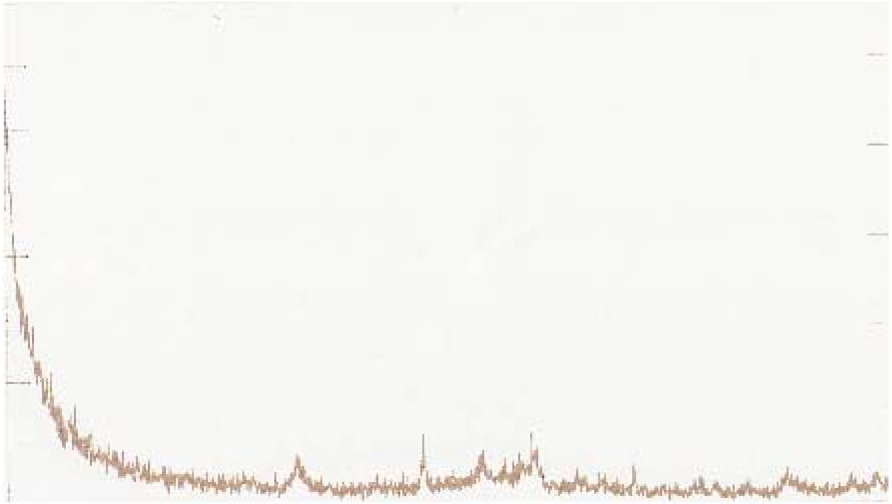
pH 11, 6:10 Ca:Fe mass ratio and $[As(V)]^0$=200mg/L



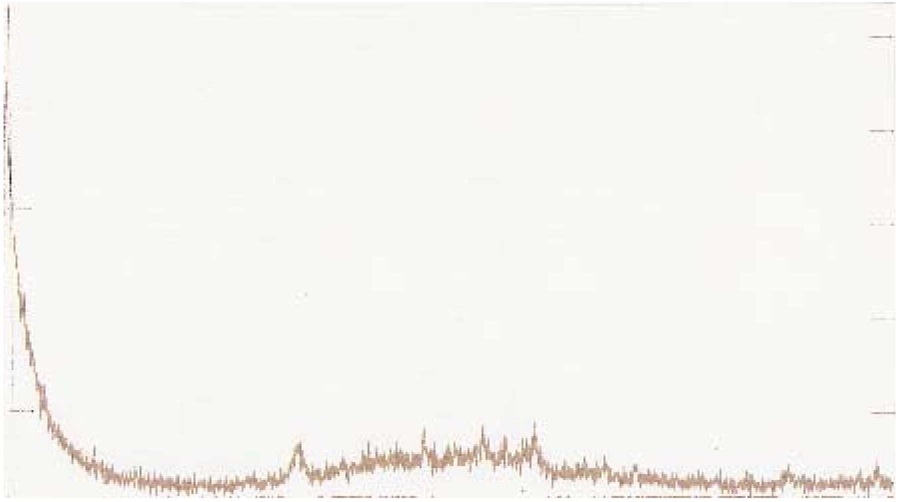
pH 8, 6:10 Ca:Fe mass ratio, [As(V)]^0=200mg/L and [PO$_4^{2-}$]^0=1.3mM



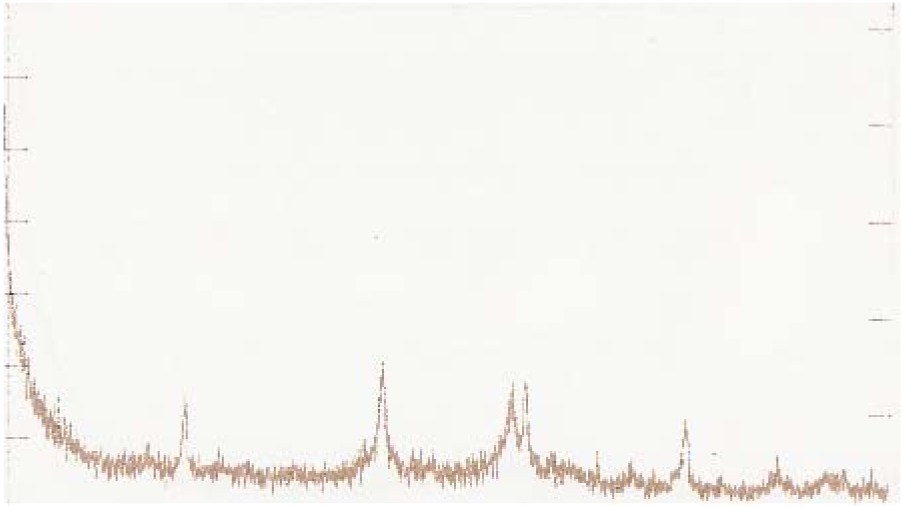
pH 11, 6:10 Ca:Fe mass ratio, [As(V)]^0=200mg/L and [PO$_4^{2-}$]^0=1.3mM



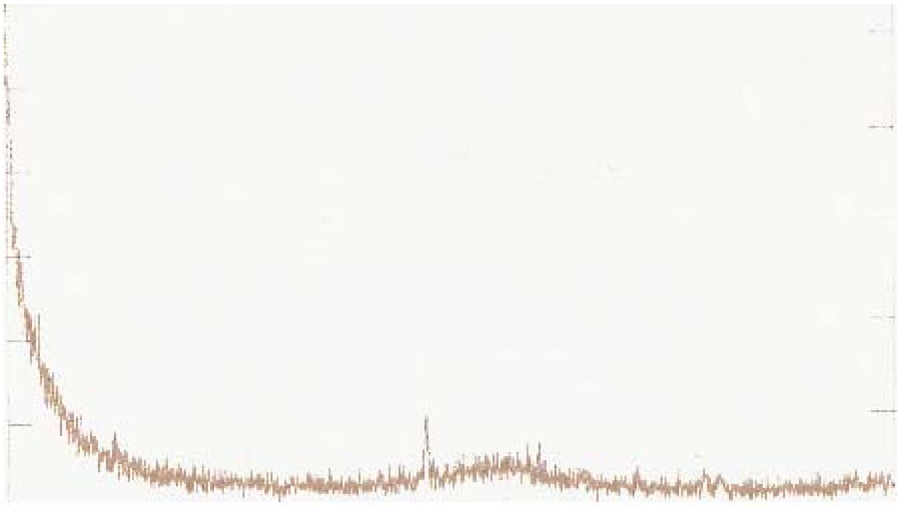
pH 11, 6:10 Ca:Fe mass ratio, $[As(V)]^0$=200mg/L and $[PO_4^{2-}]^0$=1.3mM



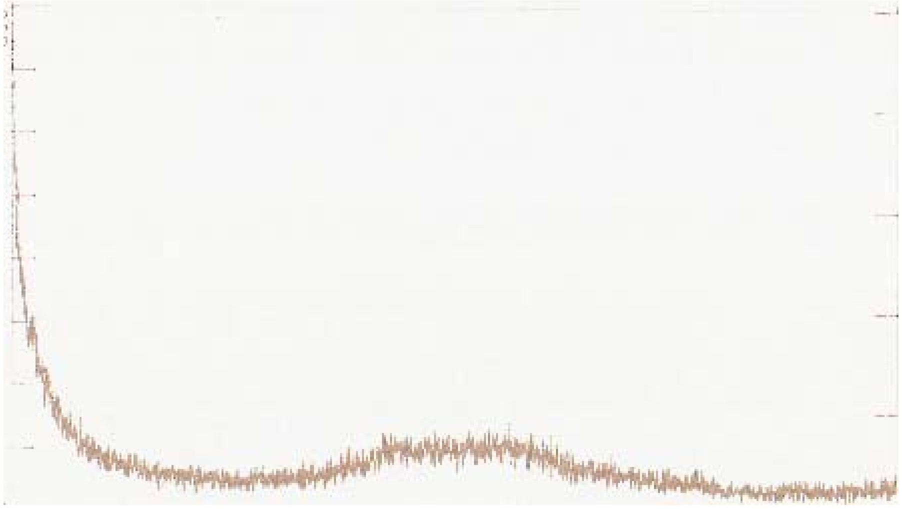
pH 7, 10:1 Ca:Fe mass ratio and $[As(V)]^0$=200mg/L



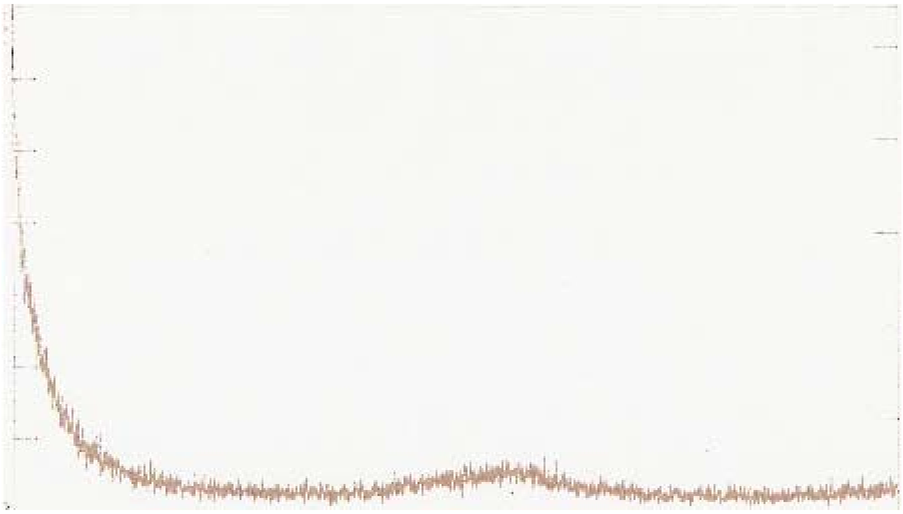
pH 8, 10:1 Ca:Fe mass ratio and [As(V)]^0=200mg/L



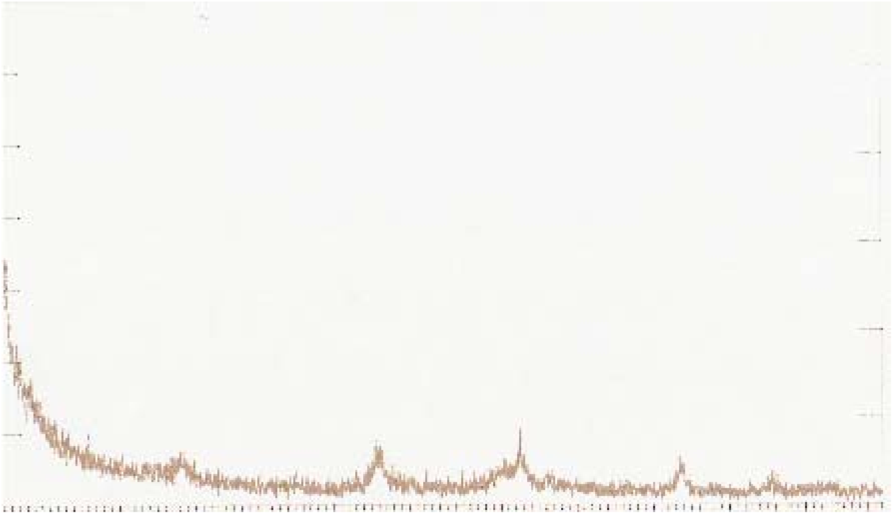
pH 8, 5:1 Ca:Fe mass ratio and [As(V)]^0=200mg/L



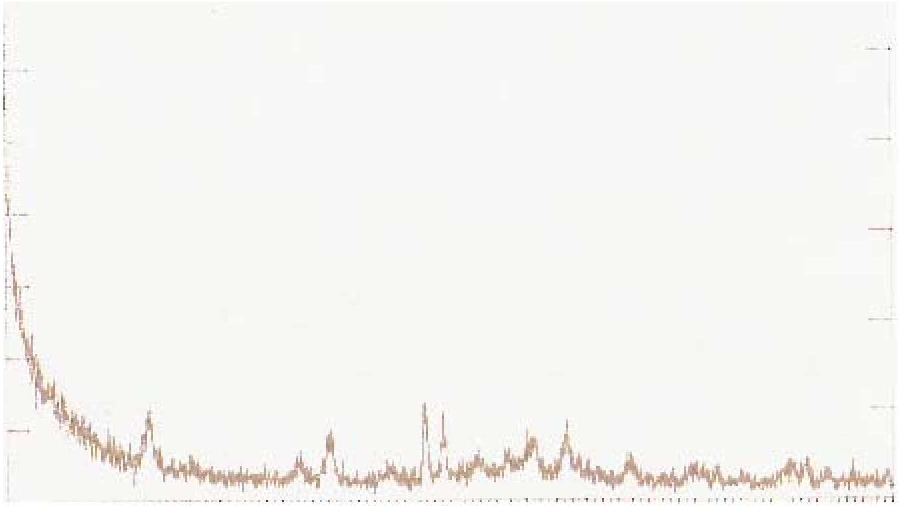
pH 8, 1:1 Ca:Fe mass ratio and $[As(V)]^0$=200mg/L



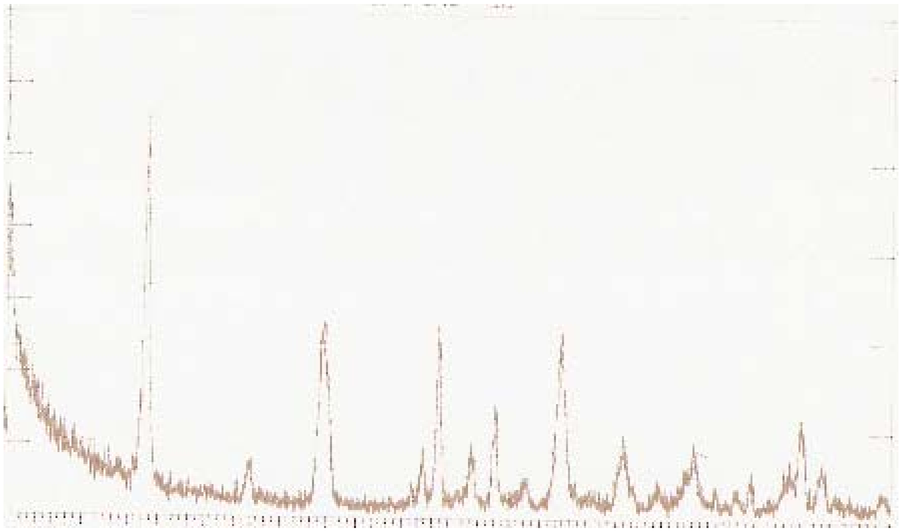
pH 10, 10:1 Ca:Fe mass ratio and $[As(V)]^0$=200mg/L



pH 11, 10:1 Ca:Fe mass ratio and $[As(V)]^0$=200mg/L



pH 12, 10:1 Ca:Fe mass ratio and $[As(V)]^0$=200mg/L



VITA

Julianna G. Camacho, daughter of Jorge Camacho and Alma Rodriguez, was born in San Juan, Puerto Rico. After graduating from high school, she enrolled and graduated with a B.S. in chemical engineering in May 2001 (cum laude) from the University of Puerto Rico-Mayagüez. She enrolled at Texas A&M University to obtain an M.S. degree in civil engineering in the field of environmental engineering. As a graduate research assistant, she conducted a study of the Texas A&M Brayton Fire School's wastewater treatment system. As a National Science Foundation intern at the Center for Advanced Engineering Fiber and Films (CAEFF), she worked within a multi-disciplinary research team. Her role within the project was to analyze filter samples acquired from the DuPont Corporation using optical microscopy and image analysis software to develop a particle size distribution function for computer modeling of polymer flow through rigid filtration media. As an undergraduate research assistant, she conducted research in chemical engineering. The project involved the optimization of proton exchange membrane fuel cell's performance by humidification control. She placed first at the 2000 AIChE National Student Poster Paper Competition in Los Angeles.

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