# FACTORS AFFECTING ARSENIC MOBILIZATION IN EXPERIMENTAL SUBSURFACE SYSTEMS

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# FACTORS AFFECTING ARSENIC MOBILIZATION IN EXPERIMENTAL SUBSURFACE SYSTEMS

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# FACTORS AFFECTING ARSENIC MOBILIZATION IN EXPERIMENTAL SUBSURFACE SYSTEMS

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# VITA

Tanja Radu, daughter of Biljana and Borivoj Jovanov, was born on June 25, 1977. in Vrsac, Socialist Federative Republic of Yugoslavia (today Republic of Serbia). In 1996, she graduated from gymnasium “Borislav Petrov – Braca” in Vrsac. After graduation, Tanja enrolled in the Polytechnic College in Belgrade and graduated in 2000 with the degree of Bachelor of Environmental Engineering. In May 2001, she decided to continue her education in the Department of Civil Engineering at Auburn University, Auburn, USA. Tanja obtained the Masters of Civil Engineering in 2005. In 2006 she joined the National Centre for Sensor Research, Dublin City University, Dublin, Ireland as a Research Assistant while completing her dissertation for the Department of Civil Engineering at Auburn University, Auburn, USA. Tanja will obtain the degree of Doctor of Philosophy from Auburn University in November 2007. She married Aleksandar Radu in June 2000.

# DISSERTATION ABSTRACT

# FACTORS AFFECTING ARSENIC MOBILIZATION IN EXPERIMENTAL SUBSURFACE SYSTEMS

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Elevated concentrations of arsenic (As) in groundwater is a widespread problem that affects millions of people around the world. Other than the adverse affects on human health, this problem often raises economic, social and political issues in the affected nations. Understanding processes that dictate the transport of As in the subsurface is the first step towards finding the solution of this problem.

Transport of As, hence its concentration in groundwater, is controlled by processes of adsorption/desorption, oxidation/reduction and reduction/dissolution and it depends on both physical (flow) and chemical (pH, presence of competing ions) conditions. Due to their abundance in natural systems, iron oxides are often used in laboratory experiments as a model media for studying processes of adsorption and desorption of As species. Oxides of manganese are used in As oxidation studies.

Although many conclusions can be drawn from batch experiments, creating simulated dynamic transport of As in experimental subsurface systems gives a great insight into transport processes and better simulate naturally occurring conditions.

Even though As(III) is often assumed to be more mobile than As(V), it was shown in laboratory experiments that under certain conditions, As(V) becomes more mobile. The presence of competing ions often influences As concentration in groundwater by competing for adsorptive sites on mineral surfaces, and/or desorbing previously adsorbed species and releasing them to the solution. The ability of phosphate to mobilize As was studied in column experiments. The presence of carbonate in groundwater is often associated with elevated As concentrations and is pointed to as one of the key factors controlling As distribution in subsurface. This is a topic of scientific dispute, as there are also researchers reporting no effect of carbonate presence. Using a novel experimental setup, it was shown that increased carbonate concentrations had relatively little effect on As(V) adsorption on iron oxide surfaces. Comparing the effects of carbonates and phosphates on mobilization of As(V), it was shown that carbonates mobilize less As(V) even when present in much higher concentration then phosphate.

Batch experiments often give important information about kinetic and adsorption processes. Using data obtained from batch experiments, an effort was made to scale batch parameters to column level. This resulted in the development of a numerical model that integrated transport and reactions of As during transport in the column. Validity of the model was confirmed by comparing model prediction with the experimentally obtained data. This showed that it was possible to achieve good scaling from batch to column scale and to predict transport of As in column scale experiments.

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Finally, I would like to dedicate this dissertation to my family who supported me and cheered for me trough the rough times. To my parents, Biljana and Borivoj Jovanov, for never losing faith in me. To my husband Aleksandar Radu for always being there for me, for his endless patience and love.

(The following section is a translation of the last paragraph to Serbian language)

Konačno, želim da posvetim ovu disertaciju mojoj porodici koja me je podržavala i navijala za mene tokom teških vremena. Mojim roditeljima, Biljani i Borivoju Jovanov, jer nikada nisu prestali da veruju u mene. Mom mužu Aleksandru Radu, jer je uvek bio uz mene, za njegovo beskrajno strpljenje i ljubav.

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# 1. GENERAL INTRODUCTION

## 1.1 Introduction

At the beginning of the twenty first century, clean drinking water is becoming one of the most valuable natural resources. In attempt to avoid waterborne diseases which easily spread in surface waters, many nations have turned to groundwater as their main source of drinking water. However, groundwater in many areas of the world is polluted by naturally high concentration of arsenic (As), a metalloid toxic for human health. In recent years, problems associated with As pollution have been recognized as a significant environmental problem. In most groundwaters, the background concentration of As is very low, less than 10 μg/l (WHO, 2003). However, the values of As in groundwater reported in literature vary by several orders of magnitude, where concentrations as high as 5000 μg/l occur naturally. These concentrations occur in variety of environments, from oxidizing to reducing environments, and in areas with active or past industrial, mining, or geothermal activity (WHO, 2003).

In subsurface environments, the major minerals which bind As species are oxides of iron, manganese and aluminum. Due to the abundance of these oxides in nature, studying their interactions with As is likely to provide a good insight into processes occurring in natural aquifers. Mobility of As in subsurface systems may be significantly affected by the presence of competing ions, through competition for adsorptive sites at mineral surfaces. The most common competing ions include phosphate, carbonate, silicate, and organic matter.

This dissertation examines the transport of As in experimentally simulated subsurface environments, and the factors affecting it. Special attention was paid to the effects of competing ions, changes in pH and the flow rate of systems, as well as the process of As oxidation.

## 1.2 Objectives

The main objective of this dissertation is to investigate the transport of As in experimental subsurface environments.

Specific research objectives include:

1. Studying the influence of pH, flow rate, and phosphate on the adsorption, desorption and mobilization of two As species that occur most often in the environment - As(III) and As(V). Showing how the above mentioned factors can promote or suppress mobility of As species.
2. Better understanding of the influence of dissolved carbonate on the adsorption, desorption and mobilization on As(III) and As(V). Comparison of the effect of carbonate and phosphate.
3. Obtaining a deeper insight into the process of As oxidation and adsorption by $MnO_2(s)$ by the use of batch and column experiments. Development of a scalable model for prediction of transport in dynamic system by using parameters obtained from batch experiments.

These objectives were met by a combination of laboratory work and mathematical modelling.

Although laboratory studies have limited ability to replicate environmental conditions, they are important for studying the fundamental mechanisms dictating the transport of species under consideration. Experimental work done was a combination of dynamic, column-based experiments and stirred, batch experiments. Synthetic Fe-oxide (goethite) coated sand and synthetic manganese oxide (pyrolusite) were used as porous experimental media, both are commonly occurring subsurface minerals. Flow through packed columns more closely simulates hydrodynamic conditions expected in the field. Column experiments played an important role in understanding the influence of various parameters on the transport of As in subsurface systems. Batch experiments provided important kinetic parameters. These parameters later played a key role in the development of a scalable model for As adsorption and oxidation.

Mobility of As species, As(III) and As(V), was studied through a set of experiments using both species and a variation of parameters: pH, flow rate and presence of phosphates. Parameters were adjusted in such a way as to promote the mobility of either As(III) or As(V). Phosphate was introduced with goal to study its effect on As mobilization and determine the degree of mobilization. This could have potentially strong implications in natural groundwater systems, where inflow of phosphate rich water can disturb the equilibrium between adsorbed As species and Fe-oxide surfaces and mobilize As causing its high concentration in solution phase.

The use of a novel system for introducing carbonate in column experiments gave a new insight into the relative effect of dissolved carbonate on the transport of As in subsurface systems, especially to its mobilization. The possibility of varying dissolved carbonate concentrations in the system, and especially pairing this effect to that of phosphate resulted in very interesting experimental conclusions. Introducing two competing ions makes the system more similar to natural groundwater, where numerous ions compete for the adsorption sites on mineral surfaces. Also, comparing the effects of two ions shows which ion has a predominant role in As mobilization.

The main objective in experiments with $MnO_2$(s) was to examine adsorption and oxidation of As. Due to very weak adsorptive capability of used $MnO_2$(s), it was especially challenging to understand and explain adsorption process on the surfaces of the mineral. Kinetic experiments helped in gaining insight in this process and obtaining key parameters describing the system. Speciation experiments played a key role in understanding distribution of As and Mn species. Distribution of As(III) and As(V) species was closely monitored throughout experiments. A conceptual model of the system was developed based on parameters obtained from the batch experiments and several assumptions. Mathematical modelling was used to develop a scalable model for predicting As adsorption and oxidation in column experiments.

## 1.3 Organization

The results of this investigation are presented in Chapters 3 through 5. Chapters 3 through 5 are similar to papers published previously by the author entitled “Transport of As(III) and As(V) in experimental subsurface systems”, (Radu et al., *ACS Symposium Series* 915; 91-103, 2005), “Effects of dissolved carbonate on arsenic adsorption and mobility” (Radu et. al., *Environmental Science and Technology,*39(20); 7875-7882, 2005) and “Development of a scalable model for predicting arsenic oxidation and adsorption at pyrolusite surfaces” (Radu et al. *Journal of Contaminant Hydrology*, in press).

Chapter 3 describes the influence of pH, flow rate, and phosphate on adsorption, desorption, and mobilization of As(III) and As(V) on synthetic goethite coated surfaces. Chapter 4 describes the effect of dissolved carbonate on As mobilization on goethite surfaces. This effect was also compared to that of phosphate. Chapter 5 describes the development of a scalable model for predicting distribution of As species on pyrolusite surfaces. Adsorption and oxidation of the species was examined on a batch and column scale. The results and implication of these investigations are summarized in Chapter 6. Also, possible areas for further research are recommended.

# 2. LITERATURE REVIEW

## 2.1 Introduction

Arsenic (As) is a metalloid found in soil, the atmosphere, natural waters and living organisms (Smith et al., 1998). Its elevated concentrations in drinking water pose a great risk to millions of people worldwide (Nordstrom, 2002), which has been called the largest mass poisoning of a population in history (Smith et al., 2000). For example, in Bangladesh only, it is estimated that between 35 and 77 million people are drinking water contaminated with As (Smith et al., 2000). Other affected countries include, but are not limited to: India, Argentina, Vietnam, Hungary, Romania, and Chile (Nordstrom, 2002; WHO, 2003). Awareness of the seriousness of the problem of poisoning by As contaminated groundwater was recognized relatively recently, in the late 1980s and early 1990s. Since this time, an extensive research in the area has been done, including both field and laboratory studies. Accordingly, the Environmental Protection Agency (EPA) recently revised the maximum contaminant level (MCL) standard of As to 10 μg/l from 50 μg/l (EPA, 2001).

Sources of As include both natural and anthropogenic sources. Arsenic occurs in more than 200 minerals, where it is most commonly present in a form of oxides and sulphides (Magalhaes, 2002; WHO, 2003). Some of the As bearing minerals include arsenopyrite (FeAsS), realgar (AsS), orpiment ($As_2S_3$), and arsenolite ($As_2O_3$) (Azcue and Nriagu, 1994). The As occurrence in minerals is often associated with the presence of the metals such as Pb, Ag, Cd, Sb, W, and Mo. The average concentration of As in the lithosphere is estimated to be 2 mg/kg (WHO, 2003). The concentration of airborne As is usually low (Wang and Mulligan, 2006), where volcanic activity, combustion of fossil fuels and industry are its major sources (WHO, 2003). The most common anthropogenic sources of As are industry (i.e. wood preservation), smelting and roasting of ores, mining, coal combustion, and agricultural use of fertilizers and pesticides (Smith et al., 1998; Aguilar et al., 2007). Both active and abandoned mining areas pose significant threat because of the presence soils highly polluted with As and heavy metals and the risk of spreading pollution to the surrounding areas or to groundwater, through processes such as acid mine drainage (Concas et al., 2006; Petaloti et al., 2006; Rapant et al., 2006; Wang and Mulligan, 2006; Aguilar et al., 2007). The greatest environmental concern about As is related to its presence in natural waters. In general, the presence of As in natural groundwater is usually associated with mineral deposits, mining waste, geothermal areas and the agricultural use of herbicides and pesticides (Smith et al., 1998).

Arsenic occurs in nature in both organic and inorganic forms. Organic forms include compounds such as monomethylarsonic (MMAA) acid and dimethylarsinic acid (DMAA). However, inorganic As species are the ones of the greatest environmental concern. Because of their solubility in water and high abundance and toxicity, As(V) and As(III) are the most important inorganic compounds. The equilbria reactions for arrsenous ($H_3AsO_3$) and arsenic ($H_3AsO_4$) acid are given by the following reactions (Smith et al., 1998):

Arsenous acid:

$$H_3AsO_3 + H_2O \leftrightarrow H_2AsO_3^- + H_3O^+ \quad \text{p}K_{a1} = 9.22 \qquad (2\text{-}1)$$

$$H_2AsO_3^- + H_2O \leftrightarrow HAsO_3^{-2} + H_3O^+ \quad \text{p}K_{a2} = 12.13 \qquad (2\text{-}2)$$

$$HAsO_3^{-2} + H_2O \leftrightarrow AsO_3^{-3} + H_3O^+ \quad \text{p}K_{a3} = 13.40 \qquad (2\text{-}3)$$

Arsenic acid:

$$H_3AsO_4 + H_2O \leftrightarrow H_2AsO_4^- + H_3O^+ \quad \text{p}K_{a1} = 2.20 \qquad (2\text{-}4)$$

$$H_2AsO_4^- + H_2O \leftrightarrow HAsO_4^{-2} + H_3O^+ \quad \text{p}K_{a2} = 6.97 \qquad (2\text{-}5)$$

$$HAsO_4^{-2} + H_2O \leftrightarrow AsO_4^{-3} + H_3O^+ \quad \text{p}K_{a3} = 11.53 \qquad (2\text{-}6)$$

Over the normal soil pH range, the most thermodynamically stable species are $H_2AsO_4^-$ and $HAsO_4^{2-}$ in the case of As(V), and $H_3AsO_3$ in the case of As(III). Speciation of As is additionally controlled by the redox (Eh) potential of the environment (Madhavan and Subramanian, 2006; Polizzotto et al., 2006) For example, reducing conditions enhance As mobilization (Beauchemin and Kwong, 2006). The importance of this is especially pronounced in wetlands areas, which have periodical changes between flooding and dry conditions. Reducing conditions occur during flooding periods and can mobilize As either by direct reduction of As(V) to more mobile As(III) species, or through dissolution of Fe oxides which then release adsorbed As (Wang et al., 2007). Alternatively, dry periods bring oxidizing conditions which favors the precipitation of dissolved species of Fe, Mn, and As (La Force et al., 2000). This is why the Eh-pH diagrams are often used to predict the presence and stability of As species under specific environmental conditions. An Eh-pH diagram for inorganic As is given at Figure 2-1.

At high Eh values characteristic for aerobic waters, inorganic arsenic acid or arsenate, $H_3AsO_4$ predominates at extremely low pH (<2); within a pH range of 2 to 11, it is replaced by $H_2AsO_4^-$,and $HAsO_4^{2-}$. Inorganic arsenous acid or arsenite, $H_3AsO_3$, exists at low pH and under mildly reduced conditions, but as the pH increases it is replaced by $H_2AsO_3^-$. Only after the pH exceeds 12, $HAsO_3^{2-}$ can be seen. Also, at the very low Eh, arsine ($AsH_3$) might be formed.

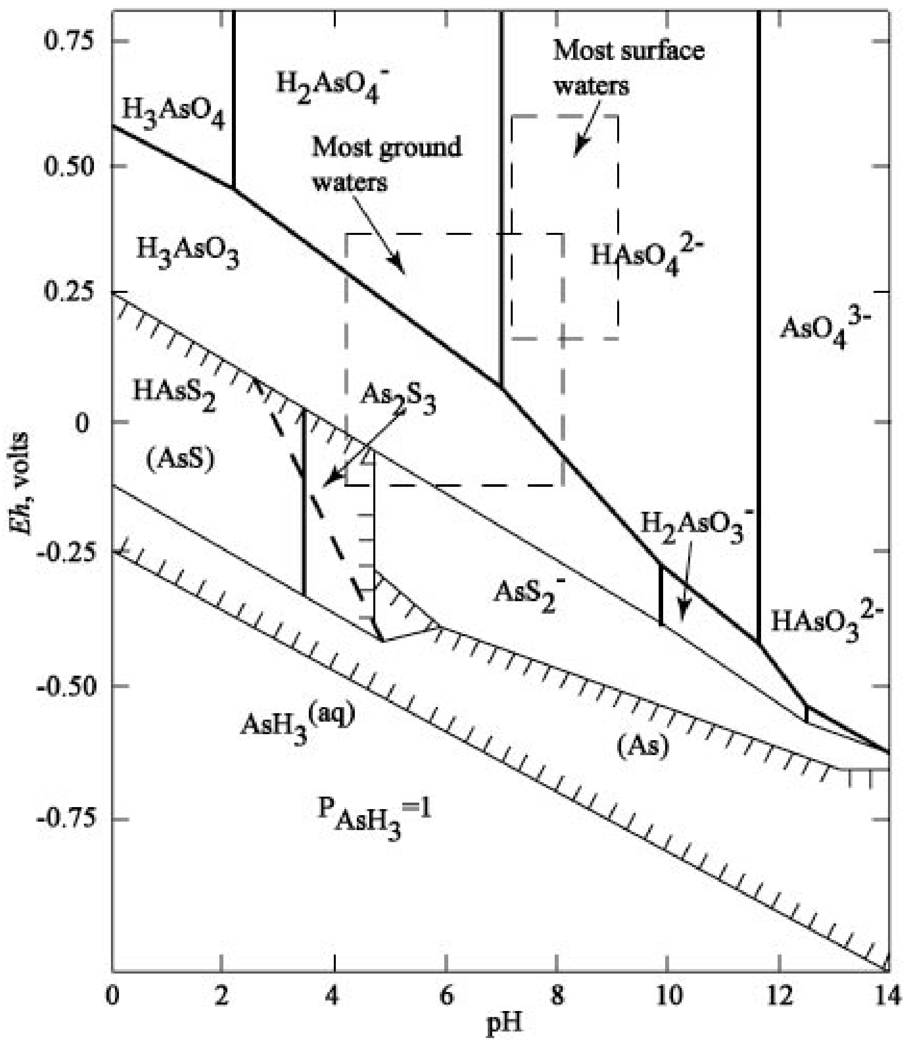


Figure 2-1 Eh-pH diagram for As at $25^{o}C$ and 1atm with total As $10^{-5}$ M and total sulfur at $10^{-3}$ M (source: Schnoor et al. (Schnoor, 1996))

Inorganic As species are more toxic than organic. Among the inorganic species, As(III) is estimated to be 60 times more toxic than As(V) (Ferguson and Gavis, 1972). The reason for this is As(III)'s ability to react with sulfhydryl groups in the body, which increases its residence time in the organism (Korte and Fernando, 1991; Chris Le et al., 2004). The most common pathway of human exposure to As is drinking contaminated water. Drinking As contaminated water is found to be significantly correlated with As in hair, nails and urine (Ahamed et al., 2006). The health effects of long term As exposure on humans include skin lesions, neurological effects, pulmonary disease, hypertension, cardiovascular disease, and occurrence of internal cancers such as bladder, kidney and lung cancer (Smith et al., 2000; Mead, 2005; Walvekar et al., 2007). However, difficulties in extrapolating As exposure studies from rodents to humans delayed the reduction of the As drinking water standard (Smith et al., 2002). Also, after issuing a new 10 μg/l MCL, EPA estimated that the total national cost for treatment, monitoring and reporting of As in drinking water will be $181 million (EPA, 2001). Some of the technologies used to remove As from drinking water include coagulation and filtration using aluminum sulfate, iron chloride and iron sulfate, lime softening, adsorption on activated alumina, and reverse osmosis (Edwards, 1994; EPA, 2000; Mondal et al., 2006).

## 2.2 Adsorption reactions

The most important processes controlling As concentration in groundwater include adsorption/desorption, precipitation/dissolution and oxidation/reduction. Arsenic in soils is usually associated with Fe and Al oxyhydroxide soil particles (Yang and Donahoe, 2007). Adsorption of As species and its affinity for metal oxide surfaces is a widely studied process where extensive research has been done and a variety of adsorbents have been examined. Most commonly, adsorption experiments involve Fe oxides such as goethite (Fendorf et al., 1997; Manning et al., 1998; O'Reilly et al., 2001; Zhao and Stanforth, 2001; Dixit and Hering, 2006) and ferrihydrite (Fuller et al., 1993; Raven et al., 1998). Also, there are reported experiments with Al adsorbents (Arai et al., 2001;

Halter and Pfeifer, 2001; Parks et al., 2003), Mn oxides (Bajpai and Chaudhuri, 1999; Chiu and Hering, 2000; Manning and Suarez, 2000), zero-valent Fe (Su and Puls Robert, 2004; Kanel et al., 2005; Kanel et al., 2006), or a combination of the above adsorbents (Kunzru and Chaudhuri, 2005).

The extended X-ray adsorption fine structure spectroscopy (EXAFS) method was used by many researchers to determine the type of the complexes that As builds at the surface of the iron oxide minerals (Waychunas et al., 1993; Fendorf et al., 1997; Manning et al., 1998; Arai et al., 2001; Farquhar et al., 2002; Sherman and Randall, 2003; Marcus et al., 2004). They have found inner sphere complexes involving monodentate, bidentate mononuclear and bidentate binuclear configurations. The monodentate configuration was found to be most unstable (Marcus et al., 2004) and the easiest to break. The type of bonds formed depends on As surface coverage where monodentate is favored at low coverage, while stronger bidentate complexes prevail at higher surface coverage (Waychunas et al., 1993). Waychunas et al. (Waychunas et al., 1993) concluded that as surface coverage increases, the fraction of monodentate bonds decreases. Similarly, As was proposed to form inner sphere bidentate binuclear complexes at the $MnO_2$ surfaces (O'Reilly et al., 2001).

Goethite ($\alpha$-FeOOH) is one of the most common iron oxides. It is characteristic of strongly weathered soils where it appears as a yellowish-brown coating on the soil particles (Bohn et al., 2001). The reactions between goethite surface and As species may be represented by the following equations (Hering et al., 1996; Dixit and Hering, 2003; Williams et al., 2003):

$$\equiv FeOH + AsO_4^{3-} + 3H^+ \rightarrow \equiv FeH_2AsO_4 + H_2O \qquad (2\text{-}7)$$

$$\equiv FeOH + AsO_3^{3-} + 3H^+ \rightarrow \equiv FeH_2AsO_3 + H_2O \qquad (2\text{-}8)$$

When both Fe- and Mn-oxides are present in soil, Fe, rather than Mn controls the total concentration and distribution of As (Deschamps et al., 2003; Marcus et al., 2004; Chen et al., 2006). Adsorption on $MnO_2$ (s) was found by many authors to be very weak (Driehaus et al., 1995; Scott and Morgan, 1995). Since $MnO_2$ (s) was found to be a very good oxidizing agent for As(III) and this oxidation happens during the equilibration time, Driehous et al. (Driehaus et al., 1995) found that As(III) and As(V) adsorb to the same extent on $MnO_2$. Because of its fast oxidation and rapid conversion of As(III) to As(V), very often only As(V) adsorption is considered. For example, Moore et al. (Moore et al., 1990) found that all adsorbed As on the surface of birnessite was in the form of As(V).

### 2.2.1 The effect of pH and point of zero charge

As mentioned above, pH has an effect on As speciation in nature. This has been widely studied and reported in literature (Hering et al., 1996; Singh et al., 1996; Raven et al., 1998; Dixit and Hering, 2003; Chen et al., 2006; Al-Abed et al., 2007) The adsorption pH dependence is usually examined in two ways: a) series of batch experiments to obtain adsorption isotherms, each at different, but constant pH or b) monitoring the change in adsorption with change in pH. The latter method is often referred to as an adsorption edge method. Total charge on the mineral surfaces considerably varies with changes in pH. The point of zero charge ($pH_{pzc}$) is the pH value at which positive and negative charges at the mineral surface are equal (Bohn et al., 2001). If the pH increases above this value, the surface becomes negatively charged. A decrease in pH would result in a positively charged surface. A primary driving force for the pH dependant adsorptive properties of minerals is the gain or loss of $H^+$ from the functional groups at the surface. This plays an important role in adsorption of As species, especially negatively charged As(V) species that predominate in natural groundwater. For example, positively charged surface (in the case when $pH<pH_{pzc}$ of mineral) would cause an electrostatic attraction of negatively charged As(V) species. This causes a generally lower adsorption of As(V) species at higher pH where weaker adsorption is caused by the repulsion by the negatively charged surface. On the other hand, As(III) is better adsorbed under higher pH conditions with its adsorption maximum reported to be at pH 9 (Fuller et al., 1993). In the pH range of natural waters, As(III) adsorption is attributed to chemical interactions through specific adsorption because of the lack of Coulombic interactions on the mineral surface. The $pH_{pzc}$ reported for goethite ranges from 7 to 9.5 (Gaboriaud and Ehrhardt, 2003), while for $MnO_2(s)$ it depends on the modification of the mineral and has values of 2.3, 2.8 and 6.4 for birnessite, cryptomelane, and pyrolusite, respectively (Oscarson et al., 1983).

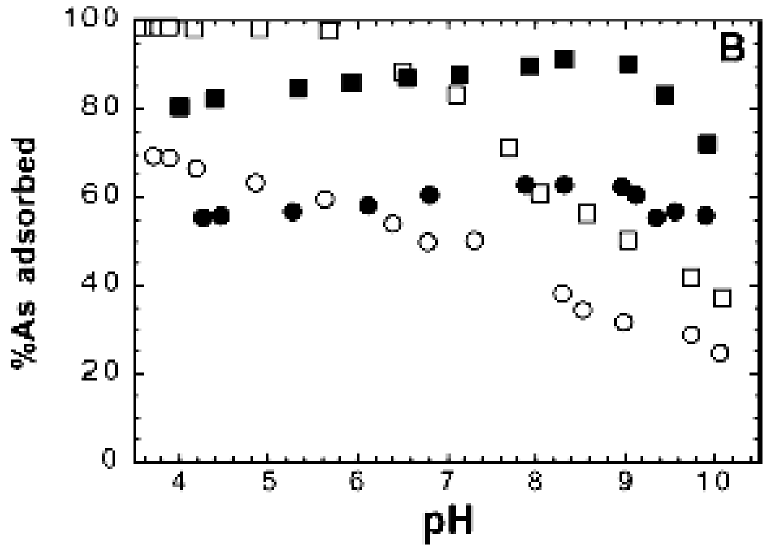


Figure 2-2 Comparison of As(V) (open symbols) and As(III) (closed symbols) adsorption edges on goethite. The total As concentrations shown are 100 µM (circles) and 50 µM (squares). Experimental conditions: 0.01 M $NaClO_4^-$, 0.5 g/l goethite (source: Dixit and Hering (Dixit and Hering, 2003))

### 2.2.2 The effect of the mineral surface properties

Properties of the mineral surface strongly influence adsorption of As species. One of its important characteristics directly affecting adsorption is the surface area of the mineral. This value greatly varies for different minerals. For example, goethite surface area is reported to range from 20 (Dixit and Hering, 2006) to 94 $m^2/g$ (Villalobos et al., 2001). On the other hand, hydrous ferric oxide has surface area up to 600 $m^2/g$ of mineral (Dzombak and Morel, 1990). A higher surface area generally provides higher adsorption. A property that determines surface area of any given material is its degree of crystalinity. Highly ordered crystalline structures such as goethite have lower surface area than amorphous ferrihydrite. Freshly precipitated metal oxides often have highly disordered structure that tends to transform to a more ordered one during the aging process. For example, the experiments of Fuller et al. (Fuller et al., 1993) showed that more As(V) adsorption occurred on the freshly precipitated ferrihydrite surface than on the aged surface. After the initial adsorption of As(V) on the surface, it was slowly released in to the solution as crystalline growth was taking place and causing desorption. Cornell and Schwertmann (Cornell et al., 1996) showed in their research that the surface area of ferrihydrate greatly decreases with aging, where initially high surface area of ~600 $m^2/g$ was reduced to 150 $m^2/g$ of aged product.

Its been reported that particle size of the adsorbent also plays an important role in the adsorption of As (Yang et al., 2006). For example, Singh et al. (Singh et al., 1996) observed in their study that a decrease of hematite particles from 200 to 100 μm caused an increased removal of As(V). This is directly caused by the increase of surface area of particles as their size decreased. Anawar et al. (Anawar et al., 2003) examined the correlation of size of natural Bangladesh sediments with As. They found a pronounced effect of the grain size, where As was always associated with a fine grain minerals. Arsenic concentration was found to be much higher in the fine particle fraction than in large particle fraction of the sediments. Similar conclusions were reported by Ruiz-Chanacho et al. (Ruiz-Chancho et al., 2007), in whose research high As concentrations were associated with the fraction of smaller particles, such as iron (hydro)oxides.

### 2.2.3 Adsorption kinetics

A long term adsorption rate experiments by several authors (Pierce and Moore, 1982; Fuller et al., 1993; Hering et al., 1996; Raven et al., 1998) indicate a two-phase adsorption pattern. The first phase is characterized by the fast initial uptake which is then followed by the much slower adsorption. Fuller at al. (Fuller et al., 1993) concluded in his research that initial rapid uptake was completed in <5 min., while slow adsorption continued for more than 192 hours. Similarly, in Williams et al.'s experiments (Williams et al., 2003) the rapid period of adsorption occurred for 24-48 hours followed by a slower process over a couple of weeks. The slower process might be caused by several factors such as formation of surface precipitate and diffusion to adsorption sites within colloidal aggregates (Fuller et al., 1993). Raven et al. (Raven et al., 1998) suggest in their experiments that adsorption on surface of ferrihydrite is a diffusion controlled process. They observed that initial fast phase was followed by the slow adsorption over the next 96 hours. In this case, adsorption kinetics was also influenced by the oxidation state of As species: at the lower pH (4.6) As(V) adsorption was considerably faster, while at pH (9.2) As(III) adsorbed faster.

Adsorption of As(V) species on $MnO_2$(s) oxides is very weak and it was often found to happen in time scale of minutes. For example, Driehous et al. (Driehaus et al., 1995) reported that only two minutes after the beginning of reaction, total As concentration remains the same in the solution.

### 2.2.4 Effect of competing ions

Very often high amounts of both organic and inorganic ligands are present in groundwater. Adsorption of As can be greatly affected by these ions, where competition for the adsorption sites on the surface of minerals can greatly change the amounts of As adsorbed. The most commonly studied competing ions for As include phosphate, carbonate, silicate, organic matter, and sulfate.

The phosphate effect on As adsorption is well documented (Jain and Loeppert, 2000; Zhao and Stanforth, 2001; Meng et al., 2002). The tri-protic $H_3PO_4$ has a pKa values of 2.1, 7.2, and 12.3 (Snoeyink and Jenkins, 1980) which are very close to that of As. Because of its similar chemistry to As, it has proven to be a significant competing ion. Its affinity towards minerals such as goethite (Nilsson et al., 1992), as well as very similar binding of phosphate and As(V) on goethite surfaces (Rietra et al., 1999) is previously reported. High phosphate concentrations are often observed in As contaminated groundwater such as Bangladesh where its concentration ranged from 0.2 to 3 mg P/l (Meng et al., 2001). Zhao et al. (Zhao and Stanforth, 2001) proposed that adsorption of both As and phosphate is a two phase process with initial rapid adsorption followed by the slower phase. When ions are added in high concentration, competition is observed and only ions adsorbed in the slower phase of adsorption can be desorbed. Williams et al. (Williams et al., 2003) concluded that phosphate is able to effectively compete for adsorption sites and it significantly decreases adsorption of As(V). In Meng et al.'s (Meng et al., 2002) experiments phosphate also was strongly competitive with As, significantly more competitive than ions such as silicate and bicarbonate.

Carbonate is often associated with high As concentrations in groundwater. For example, a range of 50-650 mg/l bicarbonate concentration was found in a groundwater of Bangladesh (Meng et al., 2001; Anawar et al., 2003). In the pH range of natural waters carbonate is mostly present as bicarbonate ($HCO_3^-$) which is caused by pKa values of $H_2CO_3$* of 6.3 and 10.3 (Snoeyink and Jenkins, 1980). In experiments examining carbonate adsorption on goethite, Villalobos et al. (Villalobos and Leckie, 2000) found that adsorption is highly pH dependant where maximum adsorption occurred between pH 6.5 and 7. There are rather confusing reports in the literature regarding the importance of carbonate competition with As for adsorption at the surface sites on the iron mineral surfaces. The effect observed in experimental studies ranges from major (Anawar et al., 2004), to intermediate (Holm, 2002; Su and Puls Robert, 2004), to minor (Hering et al., 1996; Raven et al., 1998; Meng et al., 2000). These reports address both aqueous and adsorbed As. In an examination of the competing effect of carbonate, silicate and sulfate, Meng et al. (Meng et al., 2000) concluded carbonate had a negligible effect on the removal by ferric chloride of both As(V) and As(III). Similarly, Fuller et al. (Fuller et al., 1993) concluded that the presence of carbonate had little effect on initial As(V) adsorption or its subsequent release. Williams et al.'s (Williams et al., 2003) research also supports the finding about no effect of carbonate on As(V) adsorption on goethite. However, a theoretical examination of displacement of adsorbed As with carbonate by Appelo et al. (Appelo et al., 2002) indicated that carbonate occupies sites on ferrihydrate surface which reduces available sites for As adsorption. This was proposed to be a major cause for elevated concentrations of As in groundwater of Bangladesh. Arai et al. (Arai et al., 2004) concluded via modeling that, when compared to a carbonate free system, As(V) adsorption on hematite was enhanced in presence of air equilibrated carbonate. However, this was not well supported with experimental data which showed no significant difference under carbonate-free and air equilibrated conditions.

Natural organic matter (in forms of humic and fulvic acid) is a product of natural decomposition of organic matter of animal and plant origin, and it is very complex combination of organic acids. There are numerous publications dealing with the phenomena of natural organic matter (NOM) and the effects of its presence on systems containing As species (Deschamps et al., 2003; Bauer and Blodau, 2006; Buschmann et al., 2006; Dobran and Zagury, 2006; Wang and Mulligan, 2006; Wang and Mulligan, 2006; Ko et al., 2007). NOM can affect As chemistry in several ways: serving as a competing ion for adsorption sites, forming aqueous complexes, or changing redox potential of site surfaces (Wang and Mulligan, 2006). Bauer et al. (Bauer and Blodau, 2006) identified competition of As and NOM for adsorption sites to be major mechanism of release of adsorbed As from solid phases. The NOM can also reduce As concentration and mobility by process of binding As, trough formation of aqueous As-NOM complexes (Buschmann et al., 2006).

Several researchers examined the effect of silicate on As adsorption (Jain and Loeppert, 2000; Meng et al., 2000; Meng et al., 2001; Anawar et al., 2003). It was concluded that silicate is a significant competitive ion for As.

The combined competitive effect of ions in concentrations typically found in Bangladesh groundwater was examined by Meng at al. (Meng et al., 2002). Major competing ions were phosphate, silicate and bicarbonate. It was shown that affinity of ions for surface sites decreased in the following order:

As(V)>phosphate>As(III)>silicate>bicarbonate. However, when a combination of any two or all three competing ions was introduced, the effect was more pronounced than with any ion alone. This shows the complexity of the problem where in natural groundwater systems where the distribution of As is controlled by a set of factors. Examining the effect of any single competing ion in laboratory studies helps in better understanding of As chemistry, but its occurrence in nature depends on the multiple interactions of the mineral surface, As, and various competing ions.

## 2.3 As mobilization

Mobilization is the key factor controlling As concentration in groundwater. Generally speaking, As in groundwater is controlled by two factors: a geochemical trigger necessary for its release from the sediments, and environmental conditions that allow As to remain in groundwater (i.e. not to be flushed or adsorbed to the sediments). There is a wide range of possible triggers for As release. Laboratory batch and columns studies might provide an important insight and better understanding of these processes.

As mentioned above, As(III) and As(V) exhibit different chemical behavior. While As(V) is generally assumed to be more strongly adsorbed, As(III) has a greater mobility with less affinity for adsorption on mineral surfaces. Masscheleyn et al. (Masscheleyn et al., 1991) showed that the reduction of As(V) to As(III) causes a significant release of As from the natural soil into the solution. The change in As speciation can be triggered by the redox changes in the environment, for example, when oxidizing environments become reducing. This change would reduce As(V) to As(III) and possibly cause its release into the groundwater. A cause for the environment to become reducing is a rapid accumulation and burial of sediments or flooding of soils.

Flooded areas such as alluvial aquifers and delta plains (such as Bengal delta plain) are often associated with high As concentrations (Anawar et al., 2003). Accumulated soil organic matter decomposes and uses up available dissolved oxygen. If the degree of the diffusion of surface oxygen to deeper layers of soil is slower than its consumption, oxygen becomes deficient. The use of all available oxygen is followed by the reduction of $Fe^{3+}$, Mn(IV), $NO_3^-$, $SO_4^{2-}$, and $CO_2$ (Bohn et al., 2001). The groundwater of As-affected areas in the world (such as Bangladesh) very often contains dissolved iron, ammonium, and low concentrations of dissolved oxygen, sulfate and nitrate indicative reducing conditions (Anawar et al., 2003).

Flushing of the aquifer is one of the important factors controlling As concentrations in groundwater. In a closed aquifer there is little flushing so different ions including As accumulate, often in high concentration, and are equilibrated with the solid phase. In aquifers with a more dynamic flushing As would be diluted with the natural flow and its concentration is unlikely to be as high. A rapid flow rate causes a shorter contact time between mineral surfaces and As species and this directly affects the amount of As desorbed. Also, it was suggested that the flow path of groundwater may influence its quality (Harvey et al., 2006). For example, flow paths leading to irrigation wells may have low concentrations of As due to rapid flushing of sediments. On the other hand, groundwater flow that is recharging from areas with oxidizing conditions may introduce oxidants able to immobilize dissolved As, therefore lowering As concentrations in groundwater. Darland et al. (Darland and Inskeep, 1997) demonstrated that pore water velocity plays an important role in the transport of As(V). The adsorption of As depends on kinetics, which is directly affected by the flow rate. An increase in pore water velocity caused more rapid As(V) breakthrough and less of its retention on the amorphous iron oxide. Similarly, in research of Singh et al. (Singh and Pant, 2006) adsorption of As(III) by activated alumina and iron oxide impregnated activated alumina decreased with an increase of pore water velocity.

Reduction of the surface area is caused by weathering of soils where amorphous mineral surfaces become more crystalline. If the surface area is reduced, adsorbed As species might be released into groundwater. The reduced number of available surface sites for adsorption will prevent released ions from re-adsorption on the surface.

Microbial metabolism of buried peat deposits is proposed to drive reductive dissolution of FeOOH(s) and release of adsorbed As species (McArthur et al., 2001; Varsanyi and Kovacs, 2006; Wang and Mulligan, 2006). This effect is especially pronounced in anoxic aquifers with abundant organic matter, such as in deltaic areas similar to that of Bangladesh. Also, Höhn et al. (Höhn et al., 2006) proposed that microbal reduction of As(V) is one of major driving forces in release of As(III) into groundwater of studied aquifer.

## 2.4 Oxidation reactions

As previously mentioned, As(III) is more toxic and harder to remove from groundwater. The oxidation of As(III) into As(V) makes removal significantly easier because of the higher affinity of As(V) for mineral surfaces.

While $MnO_2$(s) minerals are less abundant in nature when compared with Fe and Al oxides (Kent and Fox, 2004) and are relatively weak adsorbents of As (Driehaus et al., 1995; Scott and Morgan, 1995), they are very good oxidants of As(III). $MnO_2$(s) appears in nature in the form of three polymorphs of various crystalinity: birnessite (δ-$MnO_2$(s)), cryptomelane (α-$MnO_2$(s)) and pyrolusite (β-$MnO_2$(s)) (Oscarson et al., 1983). The oxidation on $MnO_2$ surfaces depends on the form of the mineral, where the least crystalline birnessite has shown to be the most efficient for As(III) oxidation.

The oxidation of As(III) results in release of As(V) and Mn(II) into the solution and it is proposed to follow the reaction (Nesbitt et al., 1998):

$$MnO_2(s) + H_3AsO_3 + 2H^+ \rightarrow Mn^{2+} + H_3AsO_4 + H_2O \qquad (2\text{-}9)$$

A decrease of As(III) from solution followed by the simultaneous increase of As(V) indicates that As(V) is the direct product of oxidation. This was reported to be a pH dependant process, with As(III) removal and As(V) production rates decreasing with a pH increase (Amirbahman et al., 2006). Very often, the formation of intermediate Mn(III) product is proposed so oxidation becomes a two-step reaction. In each of these steps one electron is transferred from Mn (IV) to As, first building Mn(III) and then, ultimately, Mn(II). Nesbit et al. (Nesbitt et al., 1998) reported that Mn(III) accumulates at the surface for 90 minutes and after that time it decreases and undergoes a reductive dissolution. Sparingly soluble Mn(III) accumulation at the surface causes a delay in the release of Mn(II) from the surface where it is expected that release of Mn(II) would be stoichiometricaly related to the As(III) oxidation in the ratio 1:1. However, the formation of the intermediate Mn(III) product might eventually cause release of Mn to exceed release in later phases of the product of oxidation, As(V) (Scott and Morgan, 1995). In addition, Chakavarty et al. (Chakravarty et al., 2002) reported that in natural ferruginous manganese ore ( a naturally occurring ore, containing pyrolusite, goethite and quartz), pyrolusite behaves in a similar manner as MnOOH(s) because of the presence of chemically bound moisture. Amirbahman et al. (Amirbahman et al., 2006) showed that Mn is directly responsible for As(III) oxidation by varying Mn concentrations, where the As(III) removal rate increased with increasing amounts of Mn.

Oxidation was often proposed to follow first order kinetics with the time scale of a few hours (Nesbitt et al., 1998; Manning and Suarez, 2000). It was found to be a biphasic process, with a rapid oxidation of As(III) followed by a continuous slow process. In the first phase of this process most of the As(V) was released into the solution (Moore et al., 1990). After a very short adsorption time (time scale of minutes), total As concentration remains constant while As(III) is further oxidized and As(V) is released in to solution for hours (Driehaus et al., 1995; Bajpai and Chaudhuri, 1999; Manning and Suarez, 2000). An increase of Mn oxide surfaces in soil causes an increase in As(III) oxidation (Bajpai and Chaudhuri, 1999). The differences in the rates of As(III) depletion (adsorption and oxidation) are attributed in the literature to the difference in crystalinity of $MnO_2$(s) minerals (Oscarson et al., 1983). However, Amirbahman et al. (Amirbahman et al., 2006) used an apparent second order model to describe the kinetics of the abiotic oxidation of As (III) by aquifer materials. They estimated two types of rate constants which conceptually represented oxidation at “slow” and “fast” sites.

Katsoyiannis et al. (Katsoyiannis et al., 2004) reported in their research that the abiotic rates of oxidation are slow to that of a biotic process. They proposed that the presence of bacteria plays an important role in the process of oxidation of As(III). Rhine et al. (Rhine et al., 2005) showed the ability of microbes to cycle and speciate As.

# 3. TRANSPORT OF As(III) AND As(V) IN EXPERIMENTAL SUBSURFACE SYSTEMS

## 3.1 Introduction

The presence of Fe oxides has a significant influence on the mobility of As in groundwater. Previous research has proven Fe oxides to be strong adsorbents for As (Fuller et al., 1993; Hering et al., 1996; Wilkie and Hering, 1996; Melitas and Farrell, 2002). The adsorption of As(III) and As(V) was reported to occur by forming monodentate and bidentate surface complexes between Fe oxides and As species (Fendorf et al., 1997). It is influenced by the type of Fe oxide and the oxidation state of the As species (Dixit and Hering, 2003). The adsorption of As on goethite is not an umber>57</rec-number><ref-type name="Journal Article">17</ref-author>Driehates) followed by a much slower phase of continued uptake for days (Fuller et al., 1993). Phosphate, often present in high concentrations relative to As in nature, is an effective competing ion for sites on the surface of the Fe minerals (Fuller et al., 1993). This is caused by its similar chemical behavior to that of the As species. Phosphate is available in As-contaminated agricultural areas due to the treatment of soils with fertilizers containing phosphate (Smith et al., 1998). The competing effect of phosphate ions is well known from previous research (Zhao and Stanforth, 2001).

However, most of the previous research done in this area was conducted in well mixed batch experiments (Dixit and Hering, 2003). In contrast, dynamic column experiments more accurately simulate a natural groundwater flow and therefore, are closer to the real situation in the field. Yet there has been limited research done with dynamic flow experiments (Greenleaf et al., 2003; Vaishya and Gupta, 2003; Williams et al., 2003). The objective of this study was to examine As(III)/As(V) interactions with Fe oxides in the dynamic environment of column experiments. The variables of main interest were pore water velocity, pH, and the presence of phosphate as a competing ion. The goal of this study was to investigate and compare the adsorption and mobility of As(III) and As(V) under various conditions in column experiments.

## 3.2 Materials and Methods

**Materials:** The adsorbent used in these experiments was synthetic goethite-coated sand. Goethite ($\alpha$-FeOOH) is a common coating material for subsurface particles (Bohn et al., 2001). The Fe-coated sand was prepared by air oxidation of $FeCl_2 \cdot 2H_2O$ in a suspension of medium quartz sand as described by Roden et al. (Roden et al., 2000). The extractable Fe was measured by extraction with dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960), and the sand had a Fe content of 75 ± 1 $\mu$M Fe per gram of sand, or 4200 mg Fe per kg of sand.

Arsenic solutions were prepared using reagent grade $NaAsO_2$ and $As_2O_5$. A constant ionic strength of 0.01 M was achieved by the addition of $NaNO_3$. The desired pH values of solutions were adjusted by the addition of HCl or NaOH. The phosphate solution was prepared by use of $NaH_2PO_4$.

The column experiments were performed at pH values of 4.5 and 9. In this pH range, the predominant As(III) species is neutral arsenous acid, $H_3AsO_3$ (pKa of 9.2), while the predominant As(V) species in the same pH range are $H_2AsO_4^-$ (pH<6.98) and $HAsO_4^{2-}$ (pH>6.98).

**Analytical methods:** Unfiltered aqueous samples were analyzed for total As concentration by atomic absorption spectrometry. Samples were analyzed within a few hours of sample collection. Separation of As(III) and As(V) species was obtained by use of an ion exchange column containing Dowex 1X 50-100 mesh CL Form resin (Ficklin, 1983). The As(V) species were adsorbed to the resin while As(III) passed through the resin column. The As concentration in the column inlet solution was checked prior to each experiment as well as after the end of the experiments. In the case of As(III) experiments, only solutions containing a minimum 95% of As(III) were used.

## 3.3 Experimental Setup

Columns were prepared using 2.4 g of Fe-coated sand dry-packed to a depth of 2.1 cm in a one-centimeter diameter glass tube. Solutions were pumped through the column using an Acuflow Series II high performance liquid chromatography pump. Effluent was collected using a Spectra/Chrom CF-1 Fraction Collector.

The variables examined in this study were pore water velocity, pH, and phosphate concentration. The column was pre-conditioned by pumping As-free 0.01 M $NaNO_3$ solution at a pH of 4.5 or 9 for 24 hours. After pre-conditioning, a solution containing $1.33\times10^{-5}$ M (1 mg/L) As in 0.01 M $NaNO_3$ at the same pH was introduced to the column (solution I in Figure 2-1). Next (solution II in Figure 2-1), an As-free 0.01 M $NaNO_3$ solution was pumped through the column. Finally, a $2.5 \times 10^{-4}$ M $NaH_2PO_4$ with 0.01 M $NaNO_3$ solution was introduced (solution III in Figure 2-1). Each of these solutions was pumped through for 700 pore volumes. The column pore volume was determined by direct physical measurement. The resulting column effluent breakthrough curves exhibited three distinct sections corresponding to the solutions being pumped through the column. The first stage (I) of the breakthrough curve represents the As that was initially eluted out of the system (i.e., the As that was not adsorbed to the sand at the end of the input pulse). The second stage (II) was the As that was desorbed from the system by the As-free 0.01 M $NaNO_3$ solution. The final stage (III) measured the As that was mobilized by phosphate.

To study the effect of different groundwater velocities, the pump rate was adjusted to achieve a pore water velocity of 0.23 cm/min (low velocity) and 2.3 cm/min (high velocity). To examine the effect of pH, experiments were performed at both pH 4.5 and 9, corresponding to the approximate pH range of natural soils (Bohn et al., 2001). Experiments were performed in duplicate.

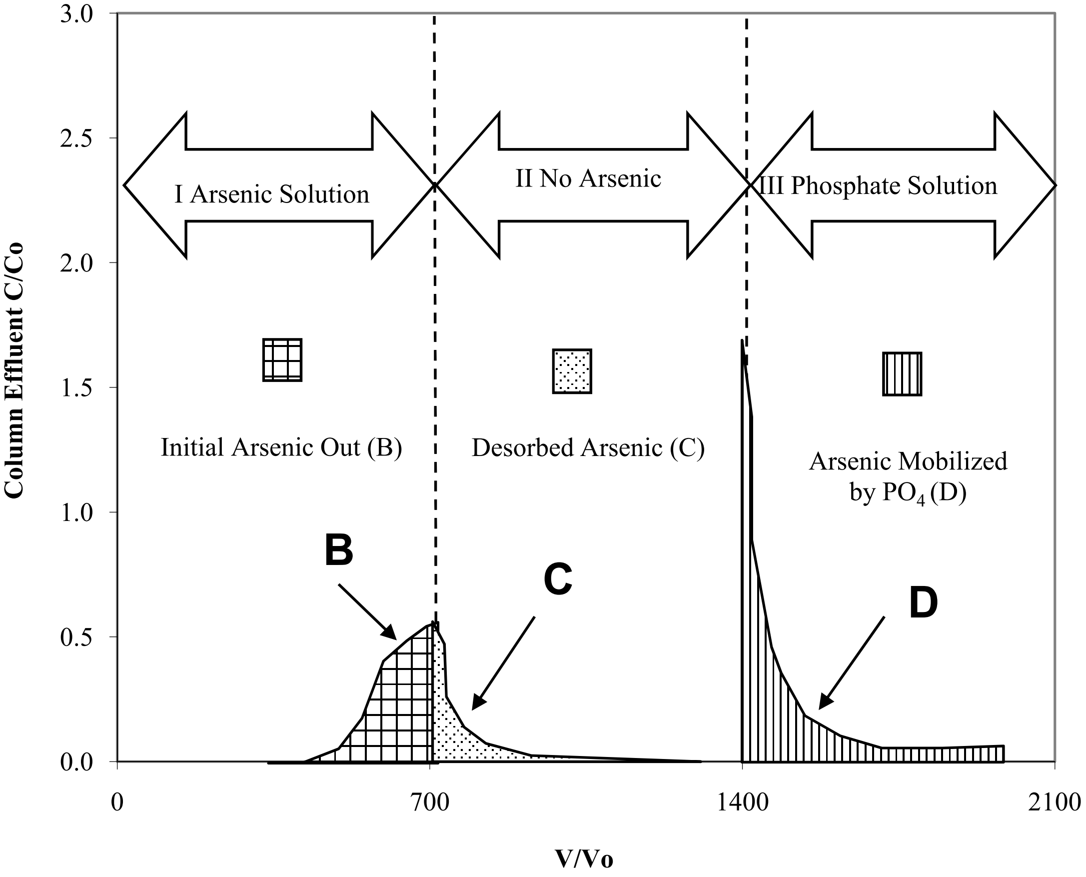


Figure 3-1. Schematic diagram of column outlet concentrations ($C/C_0$) as a function of pore volume: B- As effluent concentration (input amount minus amount adsorbed) in Phase I, C- amount desorbed in As-free solution (Phase II) and D – amount mobilized by phosphate addition (Phase III)

## 3.4 Quantitative Techniques for Column Comparisons

The experimental results were quantified by mass balances for the percentage of mass adsorbed, desorbed, and mobilized by phosphate as described below. These sections were constructed by integrating various portions of the effluent curves (Figure 3-1). The mass balances were performed on three sections (B, C, and D) of the effluent curve, and the following quantities were calculated:

% As Adsorbed = (A-B)/A *100% (3-1)

% As Desorbed = C/ (A-B) *100 % (3-2)

% As Mobilized w/$PO_4$ = D/ (A-B-C)*100% (3-3)

% Total As Recovered = (B+C+D)/A *100 % (3-4)

The part “A” (not shown on Figure 3-1) is the initial total As input to the column. A summary of the results is given in Table 3-1.

## 3.5 Results and Discussion

### 3.5.1 Effect of pore water velocity

**As (III):** At the pore water velocity of 0.23 cm/min, As(III) first broke through at about 200 pore volumes (Figure 3-2). Because of the decreased contact time between the solution and sand, it was expected that for high pore water velocity, the breakthrough curve would be shifted to the left, indicating less As(III) adsorbed with a more rapid initial breakthrough. Surprisingly, in the case of As(III) adsorption, the initial breakthrough occurred at approximately the same pore volumes for both pore water velocities. However, the influence of different pore water velocities on the breakthrough curve can be observed in the number of pore volumes necessary to reach a $C/C_0$ value of 1. The breakthrough curve at high velocity was more rapid, reaching a $C/C_0$ value of almost 1 after 700 pore volumes, while the lower velocity experiment had only reached a $C/C_0$ value of 0.8 after the same number of pore volumes. The percentage of adsorbed As(III) was calculated for both pore water velocities (Table 3-1). In the case of lower velocity, 47 ± 0.4% of the As(III) was adsorbed, while only 28 ± 10% was adsorbed in experiments at high velocity. This indicates that the pore water velocity and resulting contact time had a significant effect on As(III) adsorption in these experiments.

Table 3-1. Quantitative comparison of goethite coated sand experiments.

**As(III)**

| V(cm/min) | pH | % adsorbed | % desorbed | % mobilized | % recovered total |
|---|---|---|---|---|---|
| 0.23 | 4.5 | 47 ± 0.4 | 58 ± 17 | 68 ± 18 | 94 ± 8 |
| 2.30 | 4.5 | 28 ± 10 | 64 ± 10 | 100 ± 15 | 104 ± 4 |
| 0.23 | 9 | 59 ± 4 | 52 ± 4 | 61 ± 2 | 89 ± 2 |

**As(V)**

| V (cm/min) | pH | % adsorbed | % desorbed | % mobilized | % recovered total |
|---|---|---|---|---|---|
| 0.23 | 4.5 | 77 ± 7 | 13 ± 1 | 47 ± 2 | 64 ± 2 |
| 2.30 | 4.5 | 56 ± 5 | 17 ± 1 | 41 ± 2 | 73 ± 2 |
| 0.23 | 9 | 51 ± 5 | 24 ± 1 | 43 ± 2 | 78 ± 3 |

Calculation based on formulas (3-1), (3-2), (3-3), and (3-4), "±" represents standard deviation

The pore water velocity had no significant effect on As(III) desorption. There was 58 ± 17% of adsorbed As(III) desorbed at low velocity, while 64 ± 10% was desorbed at high velocity.

When introduced to the system, the phosphate ions initially replaced As(III) ions on the Fe coated sand, as indicated by the immediate peak in effluent As concentration. After this initial peak, the effluent concentrations rapidly decreased. The phosphate containing solution essentially flushed all of the remaining As(III) out of the system, resulting in essentially complete recovery of the As(III) introduced to the columns (Table 3-1).

**As (V):** The pore water velocity had an even more significant effect on As(V) adsorption (Figure 3-2). At 0.23 cm/min, As(V) first broke through ($C/C_o > 0.02$) at about 400 pore volumes, and at 700 pore volumes, $C/C_o$ was equal to 0.86. If adsorption equilibrium was not instantaneous, it would be expected that at a higher flow rate, the breakthrough curve would shift to the left because of the decreased time that the As(V) has in contact with the sand. This phenomenon was observed when the bulk velocity was increased to 2.3 cm/min. With a higher flow rate, initial breakthrough ($C/C_o > 0.02$) first occurred after only 300 pore volumes. The breakthrough curve also peaked more rapidly, reaching a $C/C_o$ value of 0.98 by 600 pore volumes. These experiments demonstrated that contact time has a significant effect on As(V) adsorption, transport, and breakthrough, causing less As(V) to adsorb to the sand at the higher flow rate. At the lower flow, 77 ± 7% of the input amount of As(V) adsorbed, while at high flow rate only 56 ± 5% was adsorbed.

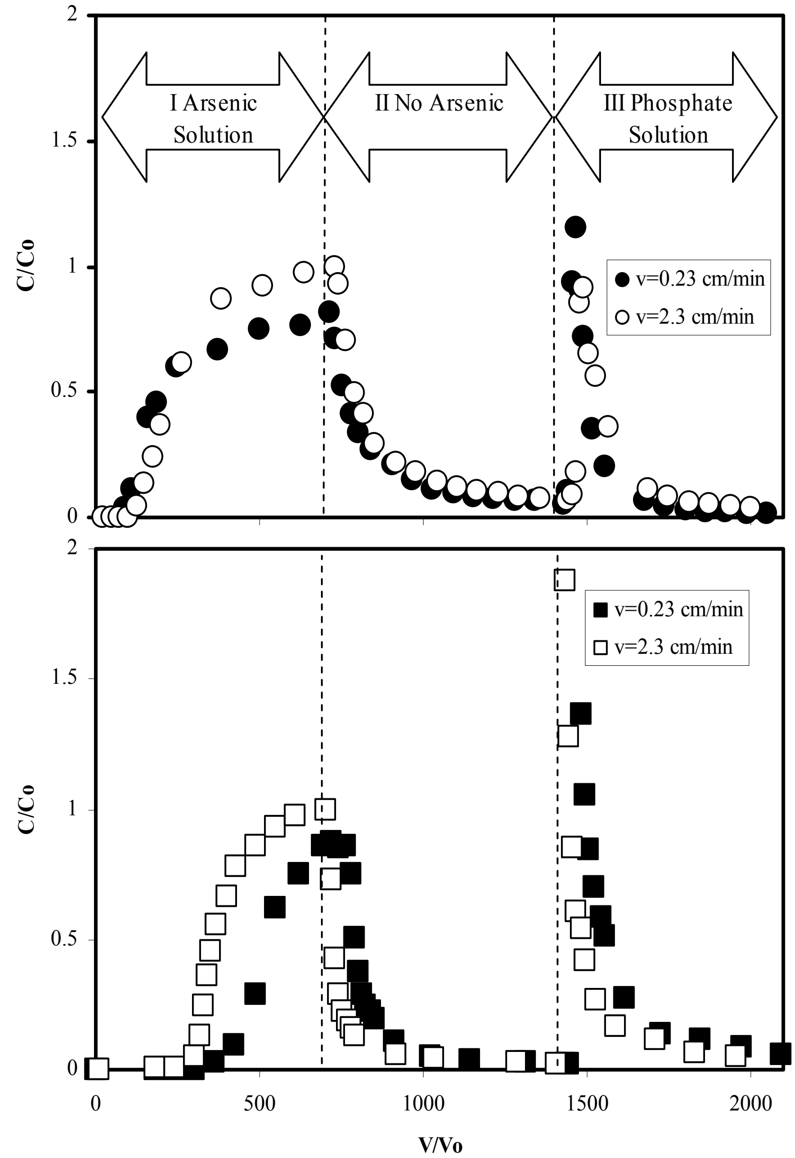


Figure 3-2 Breakthrough curves for As(III)(top) and As(V) (bottom) in a column of goethite coated sand; comparison of the pore water velocity effect, pH 4.5

Desorption also occurred more rapidly at the high pore water velocity. On a percentage basis, more As(V) was desorbed at the higher pore water velocity: 17 ± 1% versus 13 ± 1% for the lower pore water velocity. More As(V) was mobilized by phosphate ions at the lower flow rate than at the high flow rate because of the longer residence time. At the lower flow, 47 ± 2% of the remaining adsorbed As(V) was mobilized, while at the high rate, 41 ± 2% of the As was mobilized. For both pore water velocities, recoveries were less than 100%, 64 ± 2 for 0.23 cm/min and 73 ± 2 for 2.3 cm/min.

### 3.5.2 pH variation experiments

**As (III):** The As(III) breakthrough was much more rapid at pH 4.5 than at pH 9 (Figure 3-3). This result agrees with previously performed batch tests (not shown) which show that As(III) adsorption is favored at pH 9. The breakthrough curve at pH 9 reached a $C/C_0$ value of 1 after 700 pore volumes. The effluent concentration from the experiment performed at pH 4.5 did not reach this value. There was 48 ± 0.4% of As(III) adsorbed at pH 4.5, while 59 ± 4% was adsorbed at pH 9.

The desorption process was similar at both pH values. Figure 3-3 shows an initially higher concentration in the effluent at pH 9, which is consistent with the higher adsorbed As concentration at pH 9. However, there was no significant difference in the relative As desorption at these two pH values, 58 ± 17% desorbed at pH 4.5 compared with 52 ± 4% for pH 9.

Upon the addition of $2.5\times10^{-4}$ M phosphate, 68 ± 18% of the remaining As(III) was mobilized at pH 4.5 while 61 ± 2% mobilized at pH 9. The total recovery of As(III) in all experiments ranged from 89 to 100% .

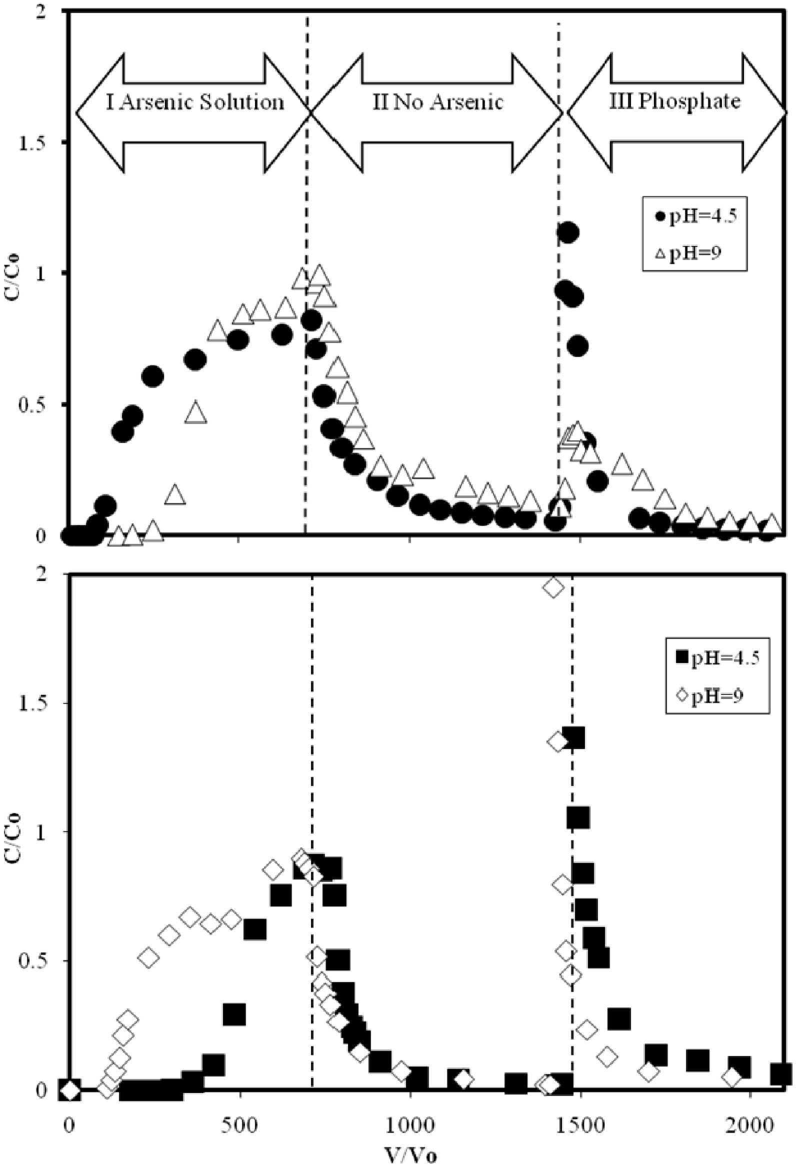


Figure 3-3 Breakthrough curves for As(III) )(top) and As(V) (bottom) in a column of goethite coated sand: comparison of the pH effect , v=0.23 cm/min

**As (V):** As(V) showed much more rapid breakthrough and greater mobility at pH 9, in contrast to As(III) which showed the opposite effect (Figure 3-3). At pH 9 the breakthrough curve was not as steep, and it had an intermediate leveling for the pore volume range of 300 to 500. Less As(V) was initially adsorbed at pH 9 (51 ± 5%) than at pH 4.5 (77 ± 7%). These results can be explained from the surface charge stand point. The $pH_{pzc}$ for goethite reported in literature varies between 7.0 and 9 (Gaboriaud and Ehrhardt, 2003). At low pH values such as pH 4.5, the goethite surface is positively charged. The increase in pH reflects a decrease in the number of protons in water, thus making the Fe surface more negatively charged. The As(V) ions were electrostatically repulsed by the negatively charged surface, and more As(V) remained in the aqueous phase. At the low pH the surface is positively charged, and it attracts $H_2AsO_4^-$ ions present in the solution at this pH (Raven et al., 1998). This is also the potential explanation for the lower recovery of As(V).

An increase in pH also had an effect on As(V) desorption in the sand. Approximately 24 ± 1% of the adsorbed As(V) was desorbed by the pH 9 solution, compared with only 13 ± 1% that was desorbed by the pH 4.5 solution. The phosphate solution at the lower pH was able to mobilize more As(V). In terms of mass, twice as much As(V) was mobilized by the pH 4.5 solution, but the actual percentage of mobilized As(V) calculated with respect to the initially adsorbed amount was very similar. At pH 4.5, 47 ± 2% of As(V) was mobilized compared with 43 ± 2% mobilized on pH 9. Total recovery of As(V) in all As(V) experiments mentioned above ranged from 64 to 78%. The lowest recovery corresponds to pH 4.5 where As(V) adsorption is strongest and therefore more of As(V) was retained on the sand and irreversibly adsorbed, even in the presence of phosphate.

## 3.6 Comparison of As(III) and As(V) data

A comparison of the collected experimental results between As(III) and As(V) is presented in Figure 3-4. The results confirm the greater mobility of As(III) at pH 4.5 while As(V) is more mobile at pH 9. On the other hand, As(III) has shown to be more readily desorbed in As-free solution than As(V) at both pH values. However, an interesting feature is observed in this part of the experiment. Although As(III) was more readily desorbed than As(V), a significant amount remained adsorbed even after 700 pore volumes of As-free solution. Moreover, the addition of phosphate ions easily mobilized both As(III) and As(V) ions. The addition of $2.5\mathrm{x}10^{-4}$ M of phosphate remobilized the remaining As(III) and a significant fraction of As(V). However, this amount of phosphate ions was insufficient to completely remobilize As(V), since approximately 25-30% of As(V) remained adsorbed at the end of the experiments.

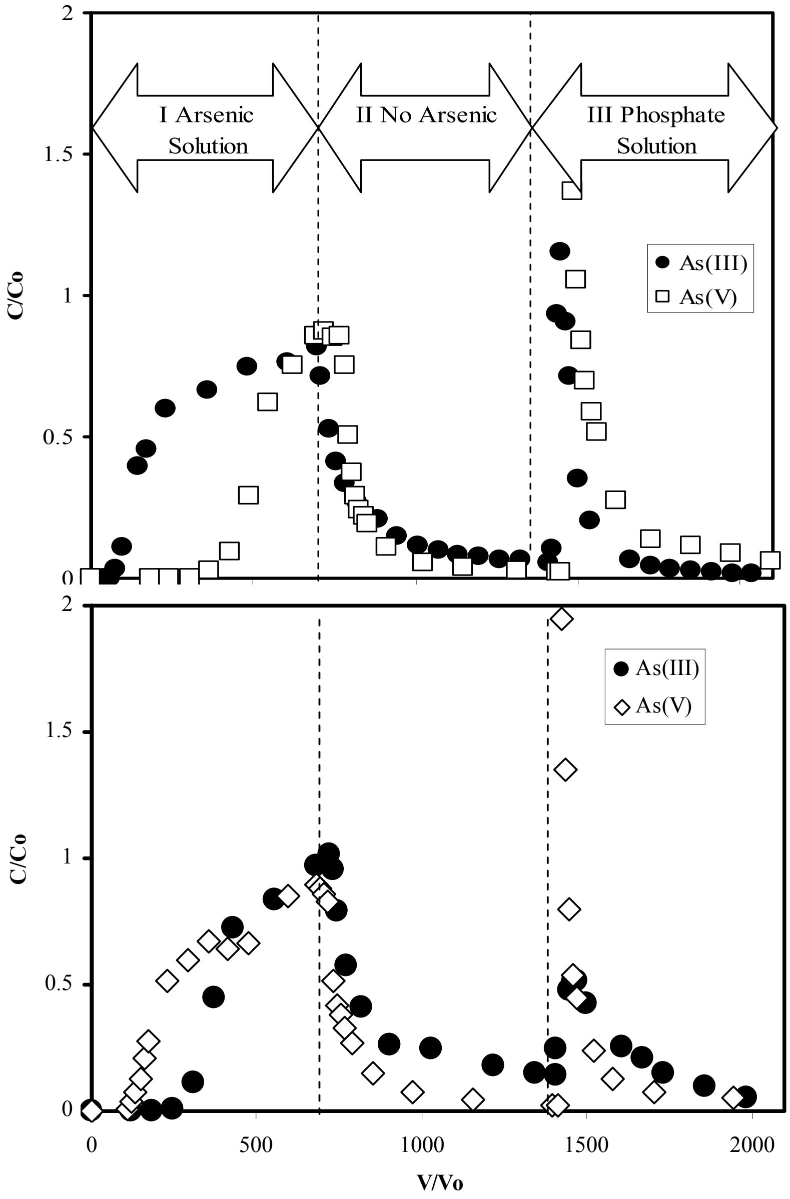


Figure 3-4 Comparison of the breakthrough curves for As(III)/ As(V) in a column of goethite coated sand – pH 4.5(top) and pH 9 (bottom), v=0.23 cm/min

## 3.7 Conclusions

As demonstrated in this study, As adsorption and transport is dynamic and complex. It depends on both physical (flow) and chemical parameters (pH and competing ions). In this study, we conclude that the adsorption of As species is a rate dependent process. In all cases, adsorption was significantly reduced in the case of high pore water velocity because of shorter contact time. The system was also highly dependent on the pH. Our findings agree with the conclusion of previous researchers that As(III) adsorption is favored at high pH, while As(V) is more strongly adsorbed at low pH (Wilkie and Hering, 1996). Overall As(III) exhibited higher mobility (weaker bonding) and was desorbed from the sand more easily.

Overall we can summarize the conclusions as follows:

(1) Both As(III) and As(V) exhibited rate dependent adsorption;

(2) As(III) was desorbed more readily than As(V) in As-free solution. However, a significant amount of both As(III) and As(V) remained adsorbed even after 700 pore volumes of As-free solution;

(3) $2.5 \times 10^{-4}$ M phosphate remobilized the remaining As(III) and a significant fraction of the As(V). However, approximately 25-35% of the As(V) was not recovered even in the presence of $2.5 \times 10^{-4}$ M phosphate;

(4) As(III) was less strongly adsorbed and more mobile at pH 4.5 than pH 9, while As(V) was less strongly adsorbed and more mobile at pH 9.

(5) The overall comparison of the examined parameters on the system indicates that the effect on mobility and recovery of As species increased in the order pH < pore water velocity < phosphate < oxidation state.

(6) Simple models (e.g., $K_D$) of contaminant transport will not work. In order to make an accurate model, one must consider many parameters including pore water velocity (i.e., kinetic effects), pH, the presence of the competing ions, and adsorption irreversibility. Efforts to model this data are ongoing.

# 4. THE EFFECTS OF DISSOLVED CARBONATE ON ARSENIC ADSORPTION AND MOBILITY

## 4.1 Introduction

Arsenic is one of the most challenging environmental problems today. Millions of people worldwide are exposed to naturally-occurring As-contaminated groundwater as their only source of drinking water (Nordstrom, 2002). In addition to its acute toxicity, long-term exposure to As potentially leads to a number of serious illnesses including skin, bladder, lung, and kidney cancer (Smith et al., 2000).

Arsenic occurs in nature in both organic and inorganic forms, the inorganic form typically being the most important one. The two inorganic oxidation states of highest environmental concern are arsenite (As(III)) and arsenate (As(V)). Arsenite predominates under reducing conditions, while As(V) predominates under oxidizing conditions (Smedley and Kinniburgh, 2002). Arsenate is known to strongly adsorb onto Fe minerals (Hering et al., 1996; Wilkie and Hering, 1996), with adsorption increasing with decreasing pH (Dixit and Hering, 2003).

The causes of extremely high levels of naturally-occurring As in groundwater in some areas of the world are still unknown, although several hypotheses have been formulated (Smedley and Kinniburgh, 2002). The processes controlling its concentration in groundwater are adsorption/desorption, precipitation/dissolution, and oxidation/reduction. The presence of minerals containing Fe, Mn, and Al thus play a significant role, as they are proven adsorbents of As. Adsorption may also be affected by pH, ionic strength, and the presence of other ions. The competitive effect of phosphate, for example, has been well studied (Zhao and Stanforth, 2001). Some of the proposed mechanisms that could trigger As release in groundwater are the reductive dissolution of Fe minerals bearing adsorbed As, the reduction of adsorbed As(V) and subsequent desorption of less strongly adsorbed As(III), and the oxidation of As-containing pyrite (Appelo et al., 2002).

The carbonate system in groundwater and subsurface systems also has the potential to influence As adsorption and mobility. The presence of dissolved carbonate may influence the adsorption of trace metals by competing for sites on mineral surfaces, forming carbonato-complexes which can either enhance or suppress adsorption, and forming precipitates (Villalobos et al., 2001). For example, Harvey et. al (Harvey et al., 2006) concluded that As mobility in Bangladesh is closely related to the recent inflow of carbon through either displacement by carbonate or organic-carbon driven Fe oxide reduction. In the pH range of most natural waters, dissolved carbonate is mostly present as $HCO_3^-$ which corresponds with $pK_a$ (T=298 K, I=0 M) values of $H_2CO_3^*$ of 6.3 and 10.3. A typical range of total carbonate in groundwater in the United States is 0.5-8 mM (Stumm and Morgan, 1996). Some of the sources of carbonate include the microbiological oxidation of dissolved organic matter and the weathering and dissolution of carbonate bearing minerals (Anawar et al., 2003). Measurements of carbonate adsorption in systems containing goethite ($\alpha$-FeOOH) indicated the maximum aqueous carbonate adsorption in systems closed to $CO_2(g)$ transfer occurs between pH 6 and 7, while in systems open to the atmosphere, adsorption continuously increased with pH (Villalobos and Leckie, 2000; Villalobos et al., 2003). Carbonate ions have shown to be a better leaching agent for adsorbed As (Kim et al., 2000; Anawar et al., 2003) than $HCO_3^-$. However, $HCO_3^-$ is typically the predominant carbonate species in groundwater and in experiments where the effect of carbonate is examined.

Villalobos et al. (Villalobos et al., 2001) examined the effect of carbonate on the adsorption of heavy metals onto goethite. Carbonate did not have an effect on the adsorption of Pb when present up to 1% $CO_2$ (g), but the adsorption of carbonate increased in the presence of Pb. A successful triple layer model (TLM) simulation was obtained when the presence of the ternary Pb-$CO_3$ surface complex was considered and its contribution increased with pH. Surface carbonate was controlled by this complex over most of the pH range studied. In the same research, reduced adsorption of Cr(VI) at low pH in the presence of carbonate was explained by the effects of surface competition and surface electrostatic repulsion, which was successfully simulated by the TLM. For U(VI), adsorption decreases at high pH values in systems open to $CO_2$(g), because of the appearance of strong aqueous carbonato complexes and their competition with surface sites for the binding of U(VI) (Villalobos et al., 2001; Barnett et al., 2002).

The displacement of adsorbed As with dissolved carbonate was recently examined theoretically by Appelo et al. (Appelo et al., 2002), and this mechanism was proposed to potentially be one of the major reasons for high As concentrations in groundwater. Appelo et al.'s modeling results concluded that the adsorption of carbonate would occupy about 70% of the total sites on the surface of ferrihydrite ($Fe_2O_3 \cdot H_2O(s)$) in the subsurface and therefore significantly reduce the adsorption of As. Appelo et al.

hypothesized that this mechanism may be responsible for the problem of As contaminated groundwater in Bangladesh since this water has a very high alkalinity related to the high $CO_2$(g) partial pressure. The mobilization of As by carbonate has been used to explain the occurrence of high levels of As in groundwaters in Bangladesh (Anawar et al., 2003; Anawar et al., 2004) and elsewhere (Garcia-Sanchez et al., 2005). Appelo et al.'s results, however, were not consistent with the experimental results of Meng et al. (Meng et al., 2000) who concluded that the presence of bicarbonate does not have an influence on the adsorption of either As(III) or As(V) on freshly-precipitated Fe oxyhydroxide. Fuller et al.'s (Fuller et al., 1993) data also supports Meng et al.'s findings. In Fuller et al.'s experiment with dissolved carbonate in equilibrium with air, its presence had little effect on either adsorption on ferrihydrite or the release of As(V). Similarly, carbonate had a minor effect on the extent of As(V) adsorption to an Fe oxide-containing soil in the experimental study of Williams et. al (Williams et al., 2003).

Arai et al. (Arai et al., 2004) concluded that steady-state As(V) adsorption on hematite actually increased in air-equilibrated ($P_{CO2} = 10^{-3.5}$ atm) as opposed to carbonate-free systems at pH 4, 6, and 8. The only time when the adsorption of As(V) decreased in the presence of $CO_2$(g) was the early stage (t<3 hr) of the air-equilibrated experiment at pH 8. Although "there is no straightforward explanation for enhanced As(V) adsorption on carbonate-adsorbed hematite surfaces" (Arai et al., 2004) they hypothesized that the observed increase in As(V) adsorption in the presence of carbonate was due to the difference in "shared charge" (valence state of the central atom divided by number of bonded oxygen atoms). Since the shared charge of $AsO_4^{3-}$ (1.25) has a value greater than that of $OH^-$ (1.0, carbonate-free solution) but smaller than that of $CO_3^{2-}$

(1.33, carbonate-equilibrated solution) it makes it easier for $AsO_4^{3-}$ to replace $CO_3^{2-}$ than an $OH^-$ group bound on the Fe surface. Therefore, carbonate enhances $AsO_4^{3-}$ adsorption. Although Arai et al. (Arai et al., 2004) showed via modeling that the presence of carbonate at high enough concentrations (e.g., 1% $CO_2(g)$) could theoretically decrease As(V) adsorption, their pseudo-equilibrium experimental data showed no significant difference in the adsorption of As(V) on hematite as a function of pH in the open air and carbonate-free systems after twenty-four hours.

An interesting possibility regarding the influence of carbonate on As adsorption was also proposed by Kim et al. (Kim et al., 2000). They hypothesized that sulfides (such as orpiment, $As_2S_3$) and sulfosalts, rather than pyrite, are sources of As in groundwater in southeast Michigan. They further suggest that As forms stable aqueous carbonato-complexes such as $As(CO_3)_2^-$, $As(CO_3)(OH)_2^-$, and $AsCO_3^+$, thereby dissolving minerals such as orpiment. Kim et al. (Kim et al., 2000) hypothesized that carbonation of As-sulfide minerals is the major process causing As leaching into groundwater. The As-carbonato complex may be subsequently converted to bicarbonate and As oxyanions, resulting in an elevated aqueous As concentration. However, this effect would presumably only be applicable to environments with significant sulfide-bound As.

The goal of our research was to examine the relative effect of dissolved carbonate on As adsorption/desorption on synthetic Fe oxide coated sand, particularly its potential effect on As(V) mobilization in the subsurface. Also, the comparison of the relative competitive effect of phosphate and carbonate was examined for a better understanding of their relative potential influence on high As concentrations in groundwater. Although most of the previous research on carbonate/As interactions on the mineral surface were done in batch experiments (Kim et al., 2000; Meng et al., 2000; Anawar et al., 2004), we have focused on column experiments that more closely resemble a natural dynamic subsurface system. Recent experimental results (Islam et al., 2004), which were consistent with thermodynamic predictions, have indicated that the reduction of As(V) to As(III) occurs subsequent to the reductive dissolution of Fe(III) oxides and the release of As(V) to solution. Accordingly, we have concentrated on the effect of carbonate on the adsorption of As(V) to Fe oxides, although an additional experiment was conducted with As(III) for comparison purposes.

## 4.2 Experimental section

**Materials.** A 1000 mg/L As(V) stock solution was prepared from reagent-grade As pentoxide ($As_2O_5$). The solutions used in this study were obtained by diluting this stock solution to the desired concentration. A constant ionic strength of 0.1 M was achieved by the addition of $NaNO_3$. The desired pH values of the solution were adjusted using NaOH and $CO_2$(g) as described below. MINTEQA2 (Allison et al., 1990) was used to determine the amount of NaOH required in order to obtain a system pH of 7.00 ± 0.1 for each $CO_2$(g) partial pressure. The phosphate solution was prepared by dilution of $2.5 \times 10^{-2}$ M stock solution of $Na_2HPO_4$. The water used in all experiments was double-deionized water prepared with a MILLI-Q system. All glassware and plastic ware were cleaned by soaking in a 0.01 M $HNO_3$ for a minimum of twenty-four hours, followed by several rinses with MILLI-Q water.

**Fe Oxide Coated Sand.** Synthetic Fe coated sand was used as the adsorbent in the column experiments. Crystalline Fe oxide minerals such as goethite (□-FeOOH) are a common coating material for subsurface particles that have been shown to adsorb As and influence As transport in the subsurface (Fendorf et al., 1997; Villalobos and Leckie, 2000; Bohn et al., 2001; Zhao and Stanforth, 2001). Similar coatings on quartz sands have been shown to control adsorption of metals to natural subsurface materials (Coston et al., 1995). The use of synthetic Fe oxide coated sand allowed us to more closely approximate real subsurface materials and flow conditions while still maintaining a chemically well-controlled system (e.g., no pre-adsorbed phosphate). The Fe oxide coated sand was prepared as described by Roden et al. (Roden et al., 2000), which involved the air oxidation of $FeCl_2 \bullet 2H_2O$ in a suspension of medium quartz sand. This method has been shown to produce goethite as the primary Fe phase with few crystalline impurities (Roden et al., 2000). After the complete oxidation of Fe(II), the sand was repeatedly rinsed with distilled water to remove all electrolytes and then freeze-dried. The Fe oxide coated sand had a DCB-extractable (crystalline plus amorphous) (Jackson et al., 1986) Fe content of 94.7 ± 2.6 □mol Fe / g sand and an AOD-extractable (amorphous) Fe content of c. 10% of this value. The surface area, as determined by $N_2$-BET method, was 1.25 $m^2/g$ of sand. This value corresponds to a specific surface area of 237 $m^2/g$ of Fe, based on the DCB-measured Fe content and separate determination of the surface area of the clean sand, which is consistent with c. 90% of the Fe in goethite (100 $m^2/g$ goethite) and c. 10% of the Fe in ferrihydrite (600 $m^2/g$ ferrihydrite).

**Partial Pressure Apparatus.** The partial pressure of $CO_2$(g) in aqueous solution was controlled using a gas proportioning flowmeter setup to combine predetermined flow rates of $CO_2$(g) and $N_2$(g) (Figure 4-1). A multitube flowmeter assembly using a three gas proportioner frame (Cole-Parmer A-03218-54) and tripod base (Cole-Parmer A-03218-59) was used as the base assembly for the apparatus. Two correlated, 150 millimeter flowtubes were used for controlling gas flow rates. Nitrogen gas was passed through a borosilicate flowtube with glass float and high flow rate (Cole-Parmer A-03217-21). Carbon dioxide gas was passed through a borosilicate flowtube with glass float and low flow rate (Cole Parmer A-03219-70). Gas flow rates were controlled using high-resolution metering valve cartridges. By utilizing various flow rates, the partial pressure of $CO_2$ (g) in aqueous solution was adjusted to $10^{-3.5}$ atm (air), $10^{-1.8}$ atm, (1.5% $CO_2$(g)), or $10^{-1.0}$ atm (10% $CO_2$(g)). For example, to create a $CO_2$(g) partial pressure of $10^{-1.0}$ atm, which equates to 10.0% $CO_2$(g) in the system, gas flow rates were adjusted to allow 90.0% $N_2$(g) and 10.0% $CO_2$(g) to bubble into solution. The equilibrium state of the solution was monitored by pH. For experiments with air, an aquarium pump was used to pump ambient air through the column rather the gas proportioning system.

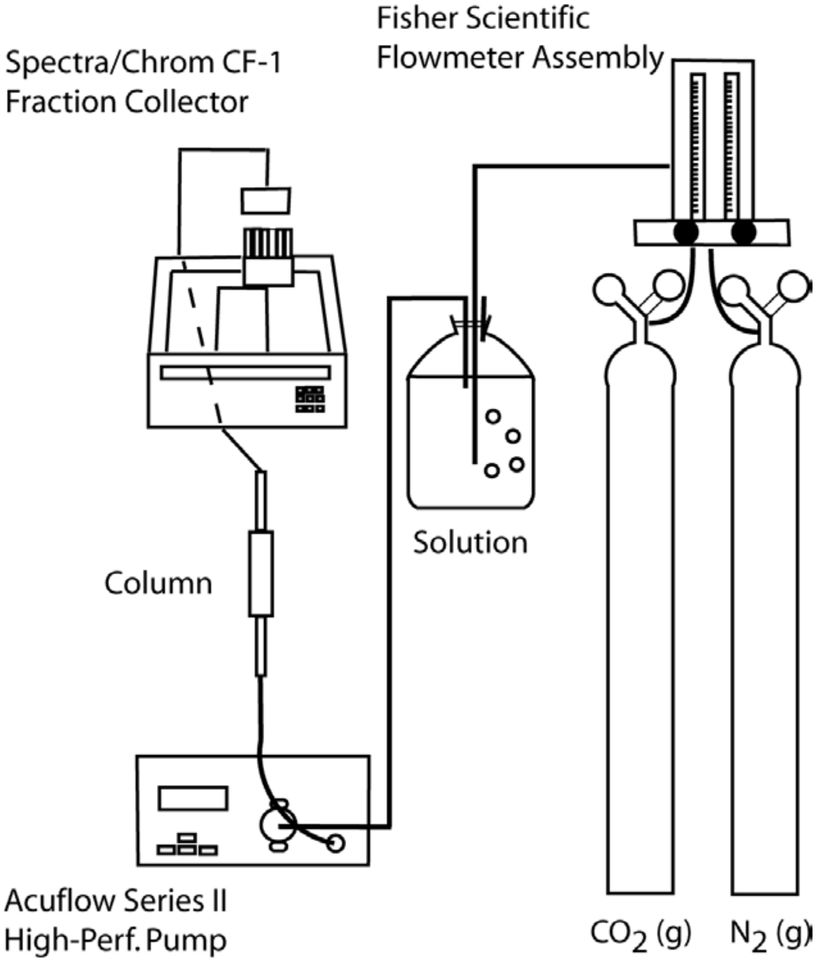


Figure 4-1 Schematic of partial pressure apparatus and column setup.

**Column Experiments.** Column experiments were conducted using the Fe oxide coated sand media described previously. One cm diameter glass columns were dry packed at room temperature with 3.17 g of Fe oxide coated sand to a depth of 2.5 cm. Solutions were pumped through the columns using an Acuflow Series II high performance liquid chromatography pump. Effluent was collected using a Spectra/Chrom CF-1 fraction collector and later analyzed for As concentration.

Analysis of break-through curves of non-reactive tracers from some of the columns (and numerous similar columns packed in an identical manner in our laboratory over the years) have shown our packing method to produce uniformly-packed columns free of preferential flow paths that could cause physical non-equilibrium. The columns were preconditioned by pumping an As-free solution of 0.1 M $NaNO_3$ equilibrated with the desired partial pressure of $CO_2$(g). Preconditioning of the column occurred for at least one hour prior to the start of the adsorption experiments. After preconditioning, three or (more typically) four solutions were sequentially pumped through the column.

Adsorption experiments were performed using a stock solution of 13.3 μM As(V) in a background solution of 0.1 M $NaNO_3$ to control ionic strength and NaOH to buffer the solution to pH 7 at the desired $CO_2$(g) partial pressure (Solution 1). The pH of the solution was maintained constant during the experiment at pH 7.00 ± 0.1. Carbon dioxide gas partial pressure ($P_{CO2}$) was adjusted to $10^{-3.5}$ atm (ambient air, 0.072 mM total carbonate), $10^{-1.8}$ atm (1.5%, 3.58 mM), or $10^{-1.0}$ atm (10.0%, 22.7 mM). The pH of the stock solution was monitored throughout the experiment to maintain the appropriate partial pressure conditions. Final pH measurements were taken at the effluent of the column during the experiment and were consistent to within ± 0.25 units of the initial pH. A total As concentration of 13.3 µM generally produced dissolved As concentration well within the range of typical As-contaminated groundwater of the Ganges delta (Anawar et al., 2003).

After approximately 850 pore volumes of As-containing Solution 1 were pumped through the column, an identical As-free background solution (Solution 2) was pumped through the column for a period of approximately 240 pore volumes to monitor As desorption. Solution 2 was also bubbled with $CO_2(g)$ to maintain the same partial pressure and pH as Solution 1. After Solution 2, a series of solutions were run through the column to determine the effects of anion competition on the mobilization of As. Solutions of $10^{-1.0}$ atm $CO_2(g)$ partial pressure (Solution 3) and/or a $2.5 \times 10^{-4}$ M $Na_2HPO_4$ solution (Solution 4) were used to determine the amount of adsorbed As that could be competitively mobilized from the Fe oxide-coated sand by carbonate and phosphate respectively. In the experiments where the initial $CO_2(g)$ pressure was already $10^{-1.0}$ atm, the introduction of the phosphate solution (Solution 4) immediately followed the As-free solution (Solution 2). The purpose of the phosphate solution was not to compare the effects of carbonate and phosphate on As adsorption and mobility under identical conditions (e.g., at the same concentrations) but to determine whether environmentally-relevant concentrations of total phosphate were more or less important than environmentally-relevant concentrations of carbonate in controlling As adsorption and mobility.

The resulting column effluent breakthrough curves exhibited four distinct sections corresponding to the solutions being pumped through the column (Figure 4-2).

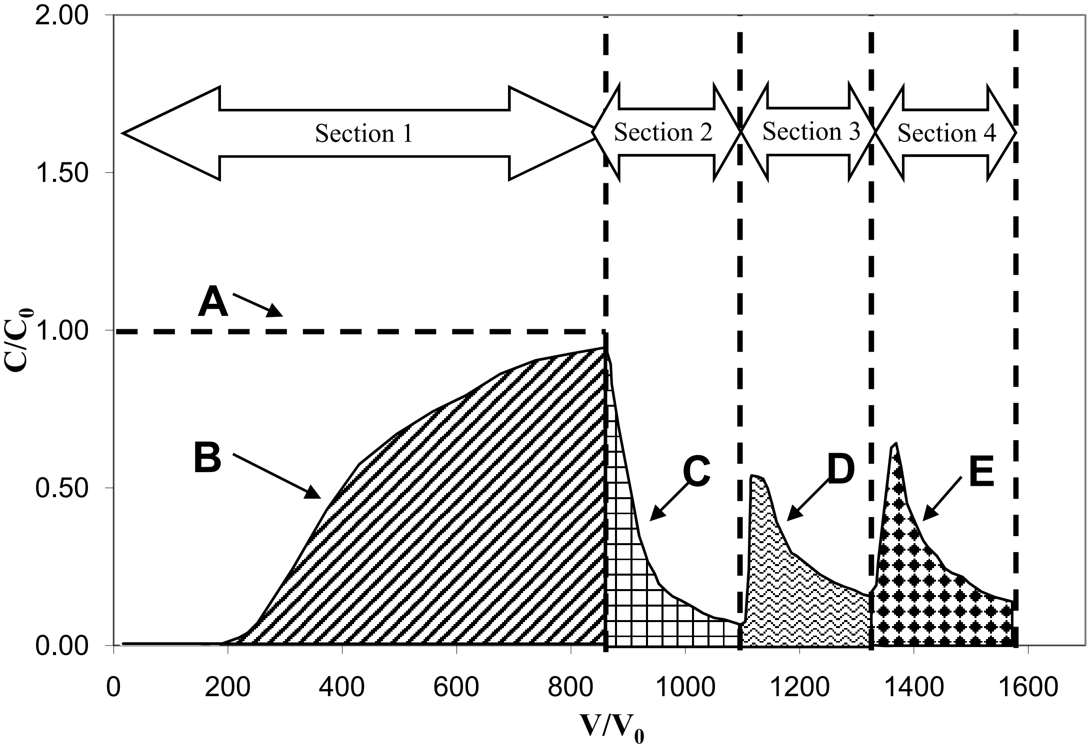


Figure 4-2 Schematic diagram of breakthrough curve used for calculating mass balance of As adsorbed (Section 1), desorbed (Section 2), mobilized by carbonate (Section 3), and mobilized by phosphate (Section 4).

The first stage (Section 1) of the breakthrough curve represents the As that was initially eluted out of the system (i.e., the As that was not adsorbed to the sand at the end of the input pulse of Solution 1). The second stage (Section 2) of the breakthrough curve is the As that was desorbed from the system by the identical As-free solution (Solution 2). The third and fourth stage (Section 3 and Section 4) of the breakthrough curve measured the As that was mobilized by carbonate (Solution 3) and phosphate (Solution 4), respectively. All solutions collected were weighed for volume determination and diluted for analysis. Samples were analyzed immediately following the experiment or refrigerated at 4°C until analysis.

To examine the potential kinetic effects, the experiment with $10^{-3.5}$ $CO_2$ (g) partial pressure was repeated at a 5x lower pore water velocity (1.7 cm/min compared to 8.5 cm/min for the rest of the experiments). Also, an additional column experiment was conducted with As(III) in lieu of As(V) at an initial partial pressure of $10^{-3.5}$ $CO_2$ (g) in an identical manner as described above except that the 1000 mg/L As(III) stock solution was prepared from reagent grade $NaAsO_2$. During the course of the experiment with As(III), random samples were analyzed by the method of Ficklin (Ficklin, 1983) to check for possible oxidation of As(III) to As(V). No oxidation of As(III) to As(V) was observed over the course of the experiment.

**Analytical Methods.** A Perkin Elmer HGA-600 Graphite Furnace and 3110 Perkin Elmer Atomic Absorption Spectrometer was used to analyze for total As concentration in the aqueous samples. The Atomic Absorption Spectrometer was equipped with an electrodeless discharge lamp (EDL), with the radiation source at a wavelength of 193.7 nm. Arsenic samples were injected into the graphite tube together with a palladium-magnesium nitrate matrix modifier. The instrument was calibrated prior to use by the five-point calibration method. Standards were tested periodically and each sample analyzed in duplicate in order to ensure accuracy of the analysis. The linear concentration range was below 1.3 μM and samples were diluted gravimetrically if needed. Samples were analyzed within a few hours of collection or refrigerated at 4°C until analysis.

**Quantitative Techniques for Column Comparisons.** The relative effects of carbonate and phosphate on As mobility were quantified by calculating mass balances for the percentage of mass adsorbed, desorbed, mobilized by carbonate, and mobilized by phosphate as described below. These sections were determined by graphically integrating sections of the effluent curves as shown on Figure 4-2. Mass balance calculations were performed on four sections (B-E) of the effluent curve by using the following formulas:

$$\%\text{ As Initially Adsorbed} = \frac{A-B}{A} * 100 \tag{3-1}$$

$$\%\text{ Adsorbed As Initially Desorbed} = \frac{C}{A-B} * 100 \tag{3-2}$$

$$\%\text{ Remaining As Mobilized with carbonate} = \frac{D}{A-B-C} * 100 \tag{3-3}$$

$$\%\text{ Remaining As Mobilized with phosphate} = \frac{E}{A-B-C-D} * 100 \tag{3-4}$$

$$\%\text{ Total As Recovered} = \frac{B+C+D+E}{A} * 100 \tag{3-5}$$

A summary of the mass balance results for all experimental conditions are given in Table 4-1. In order to quantify repeatability, most experiments were performed in duplicate or triplicate in which case a standard deviation was calculated (shown in the text as “±” the standard deviation).

Table 4-1.  Quantitative analysis of column experiments.

| Exp. # | Carbonate Concentration mM (% $CO_2$ (g)) | Pore Water Velocity (cm/min) | % As Initially Adsorbed | % Adsorbed As Initially Desorbed | % Remaining As Mobilized w/carbonate | % Remaining As Mobilized w/phosphate | % Total As Recovered |
|---|---|---|---|---|---|---|---|
| 1 | 0.074 (Atm) | 8.5 | 54 ± 3 | 11 ± 2 | 16 ± 2 | 20 ± 6 | 68 ± 4 |
| 2 | 3.5 (1.5) | 8.5 | 53 ± 1 | 13 ± 2 | 11 ± 0 | 18 ± 1 | 67 ± 0 |
| 3 | 23.6 (10) | 8.5 | 39 ± 1 | 21 ± 0 | – | 23 ± 2 | 76 ± 1 |
| 4 | 3.5 (1.5) | 1.7 | 62 | 12 | 12 | 20 | 62 |
| 5 | 0.074 (atm) | 8.5 | 50 ± 5 | 32 ± 3 | 48 ± 7 | 53 ± 5 | 91 ± 5 |

## 4.3 Results and discussion

**Column Experiments.** Experiments were conducted to measure the effects of carbonate on As(V) transport in a simulated subsurface environment. The effect of pore water velocity on As(V) transport was also examined, as the system was not in equilibrium. The range of total carbonate concentrations used in our experiments 0.072, 3.58 and 22.7 mM ($P_{CO2}$ of $10^{-3.5}$, $10^{-1.8}$, and $10^{-1.0}$ atm, respectively), roughly corresponds with carbonate concentrations found in the natural waters of Bangladesh by Anawar et al. (Anawar et al., 2003), the latter being twice the highest reported value. It is also comparable with the range of dissolved carbonate in groundwater in the United States of 0.5-8 mM (Stumm and Morgan, 1996). The neutral pH was chosen because it is within the pH range of natural groundwater in Bangladesh (Anawar et al., 2003), and carbonate adsorption in closed systems has been shown to reach a maximum in the pH range of 6.0-7.0 (Villalobos et al., 2003). Under our experimental conditions (pH 7), the predominant As(V) species were negatively charged $H_2AsO_4^-$ and $HAsO_4^{2-}$, while the predominant carbonate-containing species was $HCO_3^-$. For practical reasons, pore water velocities in our experiments greatly exceed those of the natural groundwaters (USGS, 2004). Since the reported equilibration time for the As(V)-goethite system has been reported to be twenty-four hours (Dixit and Hering, 2003), we assume that our system was not at equilibrium and we examined the effect of pore water velocity on As(V) transport accordingly.

The relative effects of carbonate concentration were evaluated by comparing experiments with $P_{CO2(g)}$ of $10^{-3.5}$, $10^{-1.8}$, and $10^{-1.0}$ atm and the results are presented in Figure 4-3

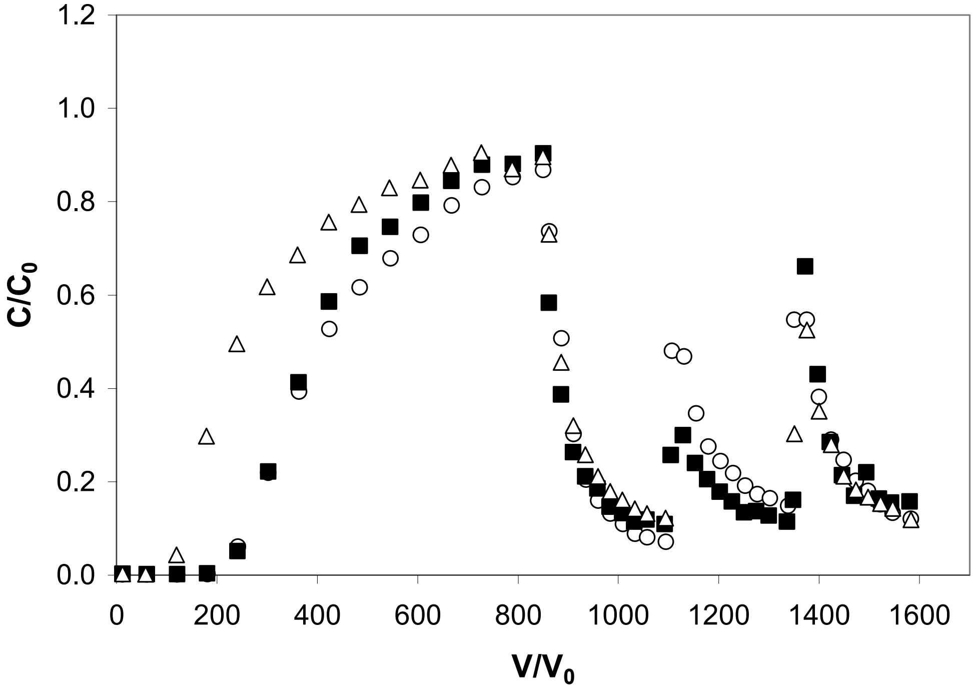


Figure 4-3 Effect of $10^{-3.5}$ atm (0.072 mM) (○), $10^{-1.8}$ atm (3.58 mM) (■), and $10^{-1.0}$ atm (22.7 mM) (Δ) $P_{CO2(g)}$ on As(V) adsorption with pore water velocity 8.5 cm/min and pH 7.0.

As previously mentioned, the breakthrough curve with an initial $CO_2$(g) partial pressure of $10^{-1.0}$ atm (22.7 mM carbonate) differ from the other two by the omission of Section 3 (mobilization by $10^{-1.0}$ atm) and therefore there is a break in that part of the graph on Figure 4-3. A relative quantitative comparison of the mass balance results from these three experiments is shown in the Table 4-1 (noted as Experiments 1, 2, and 3). The percent of As(V) initially adsorbed in Section 1 indicates no effect of carbonate between $10^{-3.5}$ and $10^{-1.8}$ atm of $CO_2(g)$ partial pressure, yielding 54 ± 3 % in the case $10^{-3.5}$ atm $CO_2(g)$ and 53 ± 1 % for $10^{-1.8}$ atm $CO_2(g)$, despite a fifty-fold increase in dissolved carbonate concentration. Only in the presence of $10^{-1.0}$ atm $CO_2(g)$, a >300-fold increase in dissolved carbonate, was there a slight decrease in initial As(V) adsorption to 39 ± 1 %. Comparison of the other sections, percent desorbed and percent mobilized by carbonate and phosphate also indicates that the presence of carbonate at partial pressures of $10^{-3.5}$ to $10^{-1.8}$ atm has a relatively negligible effect on As desorption and mobilization and just a slight effect in the case of $10^{-1.0}$ atm $CO_2(g)$. Increasing the $CO_2(g)$ partial pressure up to $10^{-1.0}$ atm in experiments 1 and 2 (Table 4-1) mobilized only 11-16% of the remaining adsorbed As (Section 3). Even after increasing the partial pressure of $CO_2(g)$ to $10^{-1.0}$ atm, which corresponds to a dissolved total carbonate concentration of 22.7 mM, a further 18-20% of the remaining adsorbed As could then be mobilized by only 0.25 mM total phosphate. Compared to a maximum initial aqueous As(V) concentration of only 13.3 μM, these results indicate that dissolved carbonate, even at extremely high concentrations, is not an effective competitive anion with As(V) under these conditions. The percent of recovered As(V) for these experiments is very similar, 68 ± 4 % for $10^{-3.5}$ atm, 67 ± 0 % for $10^{-1.8}$ atm, while in case of $10^{-1.0}$ atm carbonate there was a slightly higher recovery of 76 ± 1 %. Our findings are similar to those of Williams et. al (Williams et al., 2003), who find only a slight effect of carbonate on As(V) adsorption and that some adsorbed As(V) was not remobilized even in the presence of 0.25 mM phosphate. The initial breakthrough in the case of $10^{-1.0}$ atm $P_{CO2}$ occurred approximately fifty pore volumes earlier than in case of $10^{-3.5}$ atm and $10^{-1.8}$ atm carbonate suggesting a slight effect of high carbonate concentration on the adsorption and mobility of As(V). As mentioned before, experiments with $10^{-3.5}$ atm and $10^{-1.8}$ atm carbonate were almost identical, showing that at these carbonate concentrations, adsorption of As(V) would be almost unaffected by carbonate competition.

Sections 3 and 4 (mobilization by carbonate and phosphate), provide some interesting data with respect to the relative competitive effect of these two ions. Even though carbonate has been reported to be a good competitive adsorbent for As species, our results indicate that phosphate is much stronger and therefore, a much more significant competitive ion. In all of our experiments phosphate was introduced to the system after mobilization with $10^{-1.0}$ atm $CO_2(g)$ and still was able to recover a significantly higher amount of As(V) when compared to the amount mobilized by carbonate. Since the competitiveness of phosphate in all experiments was more pronounced, under the given experimental conditions and neutral pH, phosphate, rather than carbonate, would be the key factor controlling the concentration of As(V) in groundwater. The total phosphate concentration used in our experiments corresponds approximately to the high range of dissolved phosphate concentrations in groundwater of Bangladesh (Meng et al., 2001). The total (dissolved plus adsorbed) concentration of phosphate in Bangladesh is obviously higher than the dissolved concentration alone due to the typically strong adsorption of phosphate to Fe oxides (Zhao and Stanforth, 2001). The presence of fertilizer-derived phosphate has been mentioned as a possible contributing cause to elevated As concentrations in the Ganges delta of Bangladesh and West Bengal, India (Acharyya et al., 1999).

Equilibrium ($C/C_0$=1) was not reached in either of the experiments. The maximum value of $C/C_0$ reached was 0.95 which indicates that within Section 1 the adsorption capacity of the sand was not reached and that there were some unoccupied sites left after the As(V) input was stopped. Kinetic factors as well as thermodynamic parameters can affect the relative competition between As(V), total carbonate, and phosphate. The flow rates used in these experiments significantly exceeded those commonly found in the environment, which are usually difficult to duplicate in the laboratory due to practical constraints. To examine the potential effects of kinetics on the relative competition between As(V), total carbonate, and phosphate, experiment number 2 was repeated at a 5x slower pore water velocity.

The effect of the pore water velocity was examined by a comparison of experiments done at pore water velocities of 8.5 and 1.7 cm/min and the results are presented in Figure 4-4 and Table 4-1 (Experiments 2 and 4, respectively).

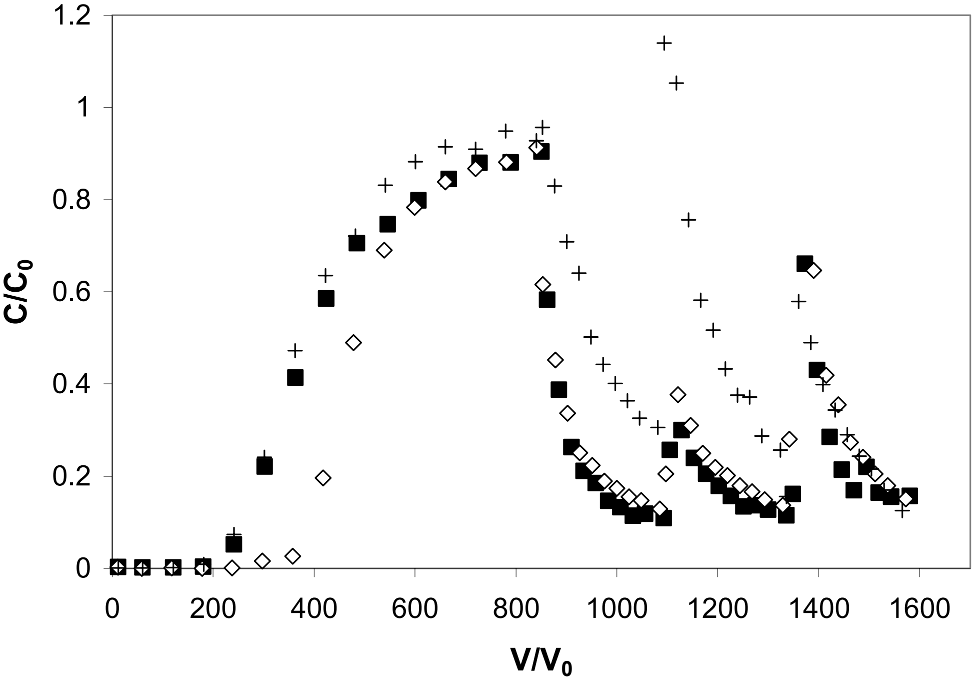


Figure 4-4 Effect of pore water velocity: high pore water velocity (8.5 cm/min) (■) and low pore water velocity (1.7 cm/min) (◊) on As(V) breakthrough curve with $10^{-1.8}$ atm $CO_2$ (g) (3.58 mM) and effect of $10^{-3.5}$ atm on As(III) adsorption (+) in the system at pH 7.0.

A slight difference is noticeable only in the adsorption section of the experiment where a low pore water velocity of 1.7 cm/min caused a higher percent of As(V) initially adsorbed, 62%, versus 53 ± 1 % adsorbed at a porewater velocity of 8.5 cm/min. The rest of the experimental sections yielded very similar results indicating little effect of the change in pore water velocity. The difference in the adsorption part can be explained by the longer As(V)-Fe oxide contact time, in the case of low pore velocity, allowing more As(V) to be adsorbed on the Fe oxide surface. In our previous work (Radu et al., 2004) we observed similar findings for the effect of pore water velocity on the adsorption of As species. Thus although there are indications of kinetic limitations in these experiments, these limitations applied equally to As(V), carbonate, and phosphate (they actually applied to a lesser extent to carbonate, as the column was preconditioned at the initial $CO_2$(g) partial pressure). Decreasing the pore water velocity by 5x actually allowed As(V) to adsorb to a greater extent in the presence of the $10^{-1.8}$ atm $P_{CO2}$. Thus we see no evidence of kinetic effects (e.g. due to an artificially high pore water velocity compared to natural groundwater) altering our conclusions about the relative competitiveness of As(V), carbonate, and phosphate.

Under reducing conditions common in some aquifers, As(V) may be reduced to As(III), potentially making the relative competition of As(III) and carbonate for Fe oxide surfaces an important process as well. To examine the effect of carbonate on As(III) adsorption and mobility, Experiment 1 was repeated with As(III) rather than As(V). The data for As(V) versus As(III) (Experiments 1 versus 5, Figure 4-4 and Table 4-1) indicates a relatively similar initial adsorption behavior, As(V) being adsorbed to a slightly greater extent than As(III) in Section 1 (54±3 versus 50±5%), which is consistent with a similar affinity of As(V) and As(III) for Fe oxides at pH 7 (Dixit and Hering, 2003). However, a comparison of the following three sections (desorption in As-free, carbonate, and phosphate solutions) shows an apparent greater adsorption reversibility and/or lability as evidenced by the relative amount of As(III) released in each corresponding section exceeding that of As(V) for the same experimental conditions. In the As-free solution (Section 2), 32±3% of the As(III) adsorbed at the end of the input pulse (Section 1) was desorbed in c. 240 pore volumes compared to only 11±2% of the

As(V) desorbed during the same period. Correspondingly, increasing the $CO_2$(g) to 10% mobilized 48±7% of the remaining As(III) compared to only 16±2% of the remaining As(V) remobilized under the same conditions. Thus increasing the partial pressure of $CO_2$(g) from $10^{-3.5}$ to 0.1 atm had a greater effect on mobilizing adsorbed As(III) than As(V). However, when 0.25 mM phosphate was introduced after the 10% $CO_2$(g) solution, it was able to mobilize even a greater relative amount (53±5%) of the remaining As(III) than did the 10% $CO_2$(g). This supports our previous conclusion about phosphate being a stronger competing ion when compared with carbonate. Thus although carbonate mobilized adsorbed As(III) to a greater extent than it mobilized adsorbed As(V) due to the more reversible/labile binding of As(III) to Fe oxides at pH 7 versus As(V), carbonate was still a less effective competitive ion than phosphate. The greater overall reversibility/lability of As(III) compared to As(V) is also evidenced by the greater overall experimental recovery of As(III) (91±5%) versus As(V) (68±4%) for these experiments. The relatively low overall recovery of the adsorbed As(V) indicates that in all experiments there was a certain amount of As(V) strongly, and at least kinetically, irreversibly bound on the Fe oxide surface. This As(V) could not be removed over the time scale of these experiments by desorption or mobilization by either carbonate or phosphate, which has previously been reported (Zhao and Stanforth, 2001; Williams et al., 2003; Radu et al., 2004).

**Implications.** Under the experimental conditions of this study, the presence of even large amounts of carbonate (over three orders of magnitude greater than the As(V) concentration) had a relatively small effect on the adsorption and mobility of As(V), at least in terms of the total amount of adsorbed As(V). Increasing the $CO_2$(g) partial pressure from atmospheric to 0.1 atm decreased the relative amount of As(V) adsorption during the initial phase of the experiment from 54±3 to only 39±1%. In addition, even very high carbonate concentrations were not able to effectively mobilize previously adsorbed As(V) as compared to a much lower phosphate concentration (just over one order of magnitude more than the As(V) concentration). The effects of high carbonate on As(III) mobilization were greater than the effects on As(V) mobilization, reflecting the greater reversibility/lability of As(III) bonding compared to As(V) bonding, which was also observed in As-free and phosphate-containing solutions. However, As(III) was still mobilized to a greater extent by 0.25 mM phosphate than by 23.6 mM carbonate. It should be noted, however, that mobilizing even relatively small amounts of As from the solid phase can produce large absolute As concentrations in the aqueous phase. For example, increasing the $CO_2$(g) partial pressure from atmospheric to 0.1 atm, while mobilizing only 16±2% of the adsorbed As(V) (Table 4-1, Experiment 1), increased the effluent As(V) concentration from c. 0.1 μM to a peak of c. 6 μM, which did not decrease all the way back to pre-0.1 atm levels even after c. 240 pore volumes.

As noted earlier there have been a wide range of reports regarding the importance of carbonate competition on As(V) adsorption to Fe oxides (the effect on As(III) has been less studied). Experimentally, the reported competitive effects have ranged from significant (Pantsar-Kallio and Manninen, 1997; Anawar et al., 2004), to intermediate (Su and Puls, 2001; Holm, 2002; Kanel et al., 2005), to minor (Fuller et al., 1993; Meng et al., 2000; Williams et al., 2003). As noted above, at least one reason for the reported differences could be due to whether the studies examined the effects of carbonate on adsorbed or aqueous As(V). In general, the most significant experimental effects

(Pantsar-Kallio and Manninen, 1997; Anawar et al., 2004) have been reported for very high carbonate concentrations (0.05-1 M), which are typically much higher than observed in most groundwaters. Consistent with the results reported herein, even those studies that have reported competitive effects generally report that they are less important than the competitive effects of other common anions such as phosphate and silicate (Meng et al., 2000; Su and Puls, 2001; Holm, 2002; Williams et al., 2003; Kanel et al., 2005).

Another interesting observation is that some of the reported competitive effects of carbonate on As(V) adsorption to Fe oxides have been as a result of modeling studies rather than experimental data. For example, our experimental results are also consistent with the recent experimental data of Arai et al. (Arai et al., 2004) where the "effects of dissolved carbonate on As(V) uptake were almost negligible" in pseudo-equilibrium adsorption experiments with hematite. However, our experimental results are not consistent with the theoretical calculations of Arai et al. (Arai et al., 2004), who predicted, but did not show experimentally, a competitive effect at 1% $CO_2(g)$. In their (Arai et al., 2004) model, the predicted competition was due to the theoretical effects of carbonate adsorption on the surface charge of hematite rather than direct competition with As(V) for surface sites. In contrast, Appelo et al. (Appelo et al., 2002) predicted significant competitive effects of carbonate on As(V) adsorption to goethite and ferrihydrite as a result of the large number of sites on the Fe oxide surface theoretically occupied by carbonate. However, even though our experimental ratio of total carbonate to total Fe is either in the range of or an order of magnitude higher than the modeled ratio of Appelo et al. (Appelo et al., 2002), we saw little evidence of competition from carbonate causing a significant effect on As(V) adsorption and mobility, at least as measured on the solid phase.

To the extent that the experimental and modeling results differ, one problem may lie in that the carbonate adsorption models used for these predictions have been largely calibrated from data in systems without As(V) (e.g., carbonate and Fe oxides but no As(V)) (Zachara et al., 1987; Villalobos and Leckie, 2000; Villalobos et al., 2001; Appelo et al., 2002). Arai et al. (Arai et al., 2004) did use experimental data from a multi-component system (As(V), carbonate, and Fe oxide) but the experimental data they used showed relatively little competitive effect. The competitive effect that Arai et al. (Arai et al., 2004) predicted occurred when they extrapolated their results outside the range of their experimental data. As recently discussed by Hiemstra et al. (Hiemstra and Van Riemsdijk, 1999; Hiemstra and Van Riemsdijk, 2002), it is relatively easy to describe the pH-dependent bonding of ions to oxide surfaces given a number of fitting parameters. However, it does not necessarily follow thermodynamically that models that correctly describe the pH-dependent adsorption in single component systems will properly predict the resulting interactions in multi-component systems. In particular, without some grounding in actual surface species, surface complexation adsorption models may not be able to predict adsorption outside the range of conditions that they were calibrated under. The results of recent in situ measurements of carbonate species adsorbed on Fe oxides reveal that the binding is complex (i.e., there are multiple species) (Bergar et al., 2005) and that the species are not entirely consistent with previous conceptual and modeling approaches (Hiemstra et al., 2004). Our results and the experimental results of others call into question the importance of carbonate in mobilizing As in typical natural groundwaters. A complete resolution of the differences between and among the often competing and contradictory experimental data and theoretical predictions may require additional equilibrium adsorption data in multicomponent (As(III/V)-carbonate-Fe oxide) systems and possibly different modeling approaches.

# 5. DEVELOPMENT OF A SCALABLE MODEL FOR PREDICTING ARSENIC TRANSPORT COUPLED WITH OXIDATION AND ADSORPTION REACTIONS

## 5.1 Introduction

Management of groundwater systems contaminated by various natural and anthropogenic arsenic (As) sources has been a major environmental problem that has received increased attention in recent years. Since As is a toxic metalloid, high concentrations of As in groundwater pose considerable risk to human health (Smith et al., 2000). Currently, there is considerable interest in understanding the processes that control As transport in contaminated groundwater systems (Zhang and Selim, 2006). Such an understanding can be used to design efficient methods to treat contaminated drinking water sources. Also, a fundamental understanding of the transport, adsorption and oxidation of As in groundwater systems will help better manage and mitigate the overall risks posed by As contamination.

The predominant forms of As in water and soil are inorganic, which can be present in the form of arsenate [As(V)] or arsenite [As(III)]. The toxicity of As depends on its chemical form and As(III) is the more toxic species (Chris Le et al., 2004). The presence of As in natural waters is controlled by adsorption, ion exchange, dissolution/ precipitation, and redox reactions. In general, As(III) tends to bind more weakly to soils compared to As(V) and hence is more soluble and difficult to remove from contaminated water (Edwards, 1994). Therefore, many research efforts have focused on oxidizing As(III) to the more easily removable As(V) (Wilkie and Hering, 1998; Katsoyiannis et al., 2004). The $MnO_2(s)$, a well known natural oxidizing agent, has often been used to oxidize As(III) to As(V) (Driehaus et al., 1995; Chiu and Hering, 2000; Manning et al., 2002).

Mn (hydr)oxides typically appear in natural soils in concentrations much lower than those of Fe and Al (hydr)oxides (Kent and Fox, 2004); however, $MnO_2(s)$ is an excellent oxidant, and it strongly influences As speciation. $MnO_2(s)$ can exist in nature in three polymorphic forms: birnessite ($\delta$-$MnO_2(s)$), cryptomelane ($\alpha$-$MnO_2(s)$) and pyrolusite ($\beta$-$MnO_2(s)$) (Oscarson et al., 1983). X-ray diffraction analysis indicates that both birnessite and cryptomelane have relatively poor crystalline structures and relatively high specific surface area, while pyrolusite has a highly ordered crystalline structure (Oscarson et al., 1983). The point of zero charge ($pH_{pzc}$) values reported for birnessite, cryptomelane and pyrolusite, are 2.3, 2.8 and 6.4, respectively (Oscarson et al., 1983). Therefore, pyrolusite would be positively charged below pH ~6.4, while both birnessite and cryptomelane would both be negatively charged over the entire pH range of natural waters. Pyrolusite can interact more strongly with As oxyanions compared to either birnessite or cryptomelane (Oscarson et al., 1983) hence it is a better adsorbent despite its highly crystalline structure and low surface area. Pyrolusite is commonly present in natural soils (Jardine and Taylor, 1995; Liakopoulos et al., 2001); therefore, it is an excellent choice for a fundamental experimental study involving As fate and transport in natural systems. Furthermore, the abundance of pyrolusite in natural manganese ores (Chakravarty et al., 2002) indicate the potential for using pyrolusite to develop low cost solutions for treating As contaminated drinking water (Anawar et al., 2003).

Researchers have used pyrolusite in column experiments to study its interactions with various environmental contaminants including Co(II)-EDTA complexes (Jardine and Taylor, 1995), Cr (Eary and Rai, 1987; Guha et al., 2001), Fe – CN complexes (Rennert et al., 2005), and Pu (Powell et al., 2006). Since the (hydr)oxides of Mn are widely distributed in soils and sediments as both discrete particles and as coatings on soil/sediment components (Oscarson et al., 1983), As is likely to interact with $MnO_2$(s) in natural environments. Ouvrard et al. (Ouvrard et al., 2002a; Ouvrard et al., 2002b) examined the diffusion-controlled adsorption of As(V) on a natural $MnO_2$(s). They reported that the reactive transport process was affected by nonlinear adsorption and intra-particle diffusion mechanisms.

Most of the $MnO_2$(s)-mediated As oxidation studies have focused on the oxidative ability of birnessite (Scott and Morgan, 1995; Manning et al., 2002; Tournassat et al., 2002), and only a limited amount of data is available for As(III) oxidation by pyrolusite minerals (Oscarson et al., 1983). Furthermore, nearly all the published work examined the oxidation of As(III) in batch experiments (Scott and Morgan, 1995; Manning et al., 2002) and only a few studies have used column experiments to examine the interactions between As and $MnO_2$(s) minerals in dynamic systems (Ouvrard et al., 2002a; Ouvrard et al., 2002b). More importantly, to the best of our knowledge, no one has addressed the issue of scaling batch-observed As adsorption and oxidation reaction parameters to predict the reactive transport scenarios in a column-scale system.

The overall aim of this research effort was to study the interactions of solid $MnO_2$ (pyrolusite) and As at a batch scale and use the knowledge to develop a scalable reactive transport model that can utilize batch-scale data to predict column-scale transport scenarios. Therefore, the objective of the first phase of this study was to complete batch experiments to evaluate the kinetics of As(III) oxidation using pyrolusite, and also characterize pyrolusite's ability to adsorb various As species. The objective of the second phase was to develop a column-scale reactive transport model using the reaction information obtained from the batch-scale experiments. The final objective was to complete a set of column experiments to test the predictive capability of the reactive transport model.

## 5.2 Experimental details

### 5.2.1 Materials and Methods

The 13 μM As stock solutions were prepared using $NaAsO_2$ (Fisher Scientific) for As(III) solutions, and $As_2O_5$ (Alfa Aesar) for the As(V) solutions. A constant ionic strength of 0.01 M was achieved by the addition of $NaNO_3$. The pH value was adjusted to 4.5 using HCl. In all experiments, ionic strength and pH were kept constant. This pH was chosen because it allowed us to maintain a relatively constant pH throughout the course of the experiments without the use of pH buffers that could potentially influence

As and/or $MnO_2$(s) chemistry. The water used in all experiments was double-deionized water passed through a MILLI-Q system.

The $MnO_2$(s) used in our experiments was a synthetic pyrolusite manufactured by J. T. Baker Inc. The powder X-ray diffraction method confirmed the modification of the oxide to be pyrolusite. The column experiments were completed in a system packed with pure pyrolusite and various mixtures of quartz sand (Iota 6, Unimin) and pyrolusite. The Mn contents in three samples of pyrolusite-sand mixtures were determined by the acid digestion method (EPA, 1996) to ensure uniform mixing. The porosities of pure sand and pyrolusite were obtained by gravimetric analyses using a glass pycnometer.

Aqueous samples were analyzed for total As concentration by atomic absorption spectrometry using a Perkin Elmer HGA-600 Graphite Furnace and 3110 Perkin Elmer Atomic Absorption Spectrometer (AAS) with an electrodeless discharge lamp (EDL) as the radiation source at a wavelength of 193.7 nm. The same instrument was used for analyzing Mn concentrations with a wavelength of 279.5 nm and HCL lamp. All the samples were filtered prior to analysis with a 0.45 μm filter (Fisher Scientific). Mn samples were diluted, if required, prior to AAS analysis.

Separation of As(III) and As(V) species was obtained using an ion exchange column containing Dowex 1X 50-100 mesh $Cl^-$ form resin (Ficklin, 1983). The As(V) species were adsorbed to the resin while As(III) passed through the resin column. The inlet and outlet solutions were analyzed using AAS to estimate the concentration values of $As_{tot}$ and As(III), respectively. The concentration of As(V) was calculated as the difference between these two values. The As species concentrations in the column inlet solution were verified prior to each experiment and at the end of the experiments.

### 5.2.2 Batch experiments

Stock solutions of 13 μM of As(III) and As(V) were used for all batch experiments. The kinetics of As(III) oxidation was examined in four separate experiments with 13 μM As(III) and 0.25, 0.5, 2.0, and 10.0 g/l of $MnO_2$(s), while As(III) and As (V) adsorption kinetic experiments were performed with 100 g/l of $MnO_2$(s). Experimental vials were shaken and samples were taken at selected time intervals. The As(V) adsorption isotherm was evaluated from the data collected from batch adsorption experiments. One gram of $MnO_2$(s) was allowed to equilibrate with a liter of As(V) solutions at various concentrations. After 48 h of shaking, the contents of the vials were filtered and analyzed for As concentration**.**

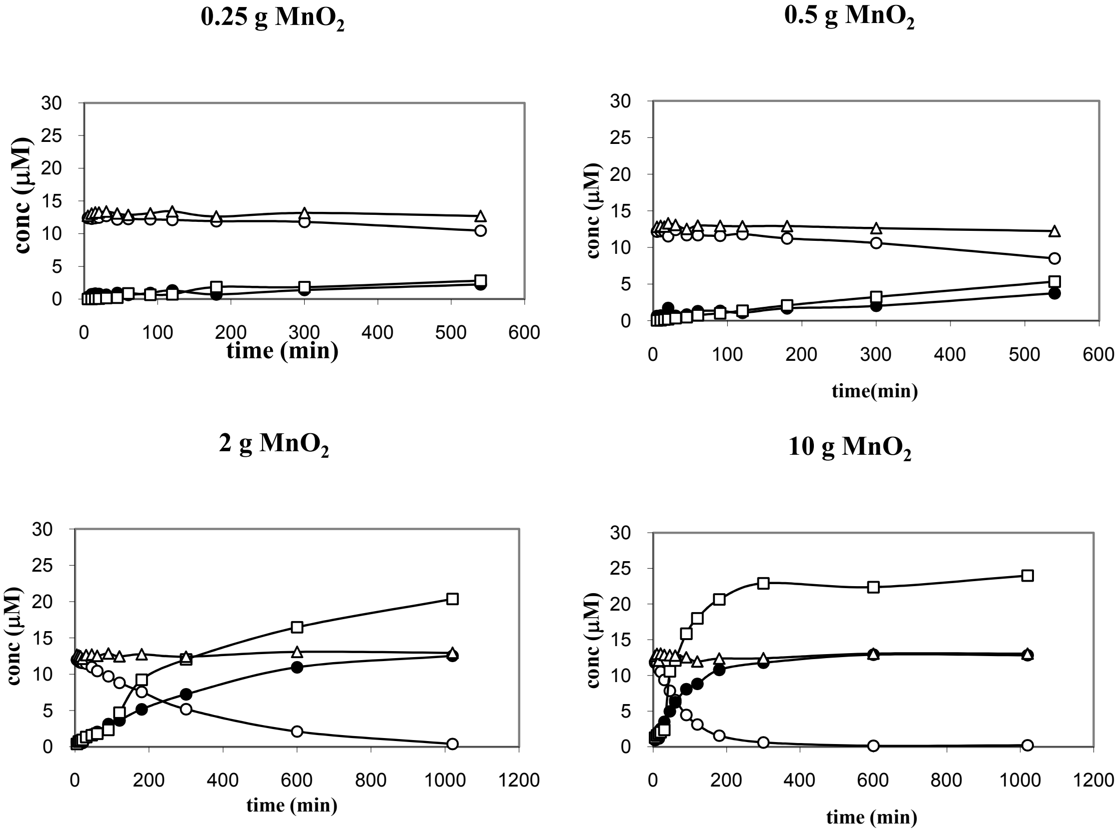
### 5.2.3 Column Experiments

Various combinations of sand and pyrolusite were dry-packed in a 7 cm long and 1 cm diameter glass column. Columns were packed with either pure pyrolusite or with a sand-pyrolusite mixture. Previous experiments in our laboratory (results not shown) had indicated that the adsorption of As on the sand (Iota 6, Unimin quartz sand) used in our columns was negligible. The columns were oriented vertically and solutions were introduced from the bottom up at a constant flow rate at the ambient temperature ≈ 22-23°C. All the inlet solutions were open to the atmosphere. Solutions were pumped through the column using an Acuflow Series II high performance liquid chromatography pump. The column was pre-conditioned to remove trapped air by pumping As-free, 0.01 M $NaNO_3$ solution with a pH of 4.5 for 24 hours. Later, a solution containing 13 μM As(III) or As(V) was pumped through the column for 35 pore volumes. Effluent was collected using a Spectra/Chrom CF-1 Fraction Collector and later analyzed to estimate As concentration levels.

## 5.3 Results of batch experiments

### 5.3.1 Oxidation of As(III) by $MnO_2$(s)

The observed concentrations of As and Mn species in the batch kinetic experiments conducted using various doses of $MnO_2$(s) are presented in Figure 5-1. In all these batch experiments, as the As(III) concentration decreased with time an equivalent amount of As(V) appeared in the solution; the total As concentration remained constant in all the experiments. This clearly indicates that the decrease of As(III) in solution is caused by the direct oxidation process which converted As(III) to As(V). Furthermore, since the total amount of As in the solution remained constant over the time, there was negligible adsorption of either As(III) or As(V) on the $MnO_2$(s). This data also indicated close to an one-to-one ratio between As(III) depletion and As(V) release. Scott and Morgan (Scott and Morgan, 1995) made similar observations in their experimental study where adsorption of the oxidation product As(V) onto the $MnO_2$ surface (birnessite) was minimal. The observed half life of As(III) decay in our experiments ranged from 2 days in the 0.25 g/l $MnO_2$(s) experiments to 1 hour in the 10 g/l of $MnO_2$(s) experiments.


0.25 g $MnO_2$

0.5 g $MnO_2$

2 g $MnO_2$

10 g $MnO_2$

Figure 5-1 Experimental behavior of the As (III) (○), As(V) (●), $As_{tot}$ (Δ), and Mn(II) (□) in the batch experiment containing 0.25, 0.5, 2, and 10 g/l of $MnO_2$(s) in 13 µM As(III) solution, pH=4.5 and 0.01 M $NaNO_3$

$$MnO_2(s)+H_3AsO_3+2H^+ \rightarrow Mn^{2+}+H_3AsO_4+H_2O \tag{5-1}$$

We also assumed that the oxidation of As(III) and the subsequent release of the reaction products As(V) and Mn(II) will follow the multi-step reaction model proposed by Scott and Morgan (Scott and Morgan, 1995). In this model, the first step involves the formation of an inner-sphere surface complex where As(III) diffuses into oxidative sites and displaces surface-bound $OH^-$ and $H_2O$ via ligand substitution and binds to the oxide metal ion. The second step is the transfer of two electrons from As(III) to the surface. In the third and fourth steps, the surface-bound oxidized As(V) and the reduced metal Mn(II) are released into the solution. In the above process, the total number of reactive surface sites will remain constant as the result of the formation of a new site when the reduced Mn(II) is released and the near-surface Mn-O group is protonated (Scott and Morgan, 1995). Since oxidation is assumed to follow Equation (5-1), As(III) and Mn(IV) must react on a molar basis and the Mn(II) concentration is expected to be close to that of As(V). To release each Mn(II) atom, two electrons should be transferred from As(III) to Mn(IV) at the surface of the mineral. We have studied the oxidation of As(III) by exposing different amount of $MnO_2$(s) to the As solution of constant concentration. In experiments with the lower $MnO_2$(s) concentration levels (0.25 g/l) the amount of Mn(II) released corresponded to As(V) level or slightly exceeded it. However, in experiments with higher $MnO_2$(s) concentration (2 and 10 g/l), we noticed that the concentration of aqueous Mn(II) exceeded the As(V) level. The release of Mn(II) into the solution directly depended on the initial $MnO_2$(s) loading level. In all four experiments the initial release of Mn(II) followed the trend of As(V) release. However, in the experiment with 2 g/l of $MnO_2$(s) a difference in released Mn(II) relative to As(V) could be observed at approximately 180 min, while in the case of 10 g/l of $MnO_2$(s) the excess of released

Mn(II) was observed at approximately 30 min. We hypothesize that the presence of Mn(III) sites at the surface of the mineral as the reason for this observation. Note that Mn(III) sites would only require one electron to reduce and release Mn(II) into the solution. The reduction of Mn(III) would cause the Mn(II) concentration to exceed the concentration of aqueous As(V). This would also change the ratio of As to Mn from the initially expected 1:1 to the value closer to 1:2 since for the release of one Mn(II) only one electron will be required. This effect is more noticeable at higher $MnO_2$(s) loading because of the abundance of $MnO_2$(s) sites. Scott and Morgan (Scott and Morgan, 1995) made similar observations and they hypothesized that the Mn(II) release exceeded that of As(V) because of the difference between the assumed +IV oxidation state of the Mn surface and its "real" average value. They postulated that during the synthesis of the $MnO_2$(s) particles, some of Mn may have been reduced below the +IV oxidation state to the +III or +II oxidation states. The computed apparent oxidation state for their systems were +3.6 and +3.42. In the published literature, Kanungo and Mahapatra (Kanungo and Mahapatra, 1989) reported an average oxidation state of 3.62 for a similar system.

As(III) oxidation by $MnO_2$(s) is commonly represented by a (pseudo-) first-order kinetic expression of the form (Oscarson et al., 1983; Thanabalasingam and Pickering, 1986; Scott and Morgan, 1995):

$$\frac{d[As(III)]}{dt} = -k_{obs}[As(III)] \tag{5-2}$$

where $k_{obs}$ is the observed first-order rate constant. Based on Equation (5-2), the dependence of logarithmic values of As(III) concentration versus time can be expressed as:

$$\ln[As(III)] = \ln[As(III)]_0 - k_{obs}t \qquad (5\text{-}3)$$

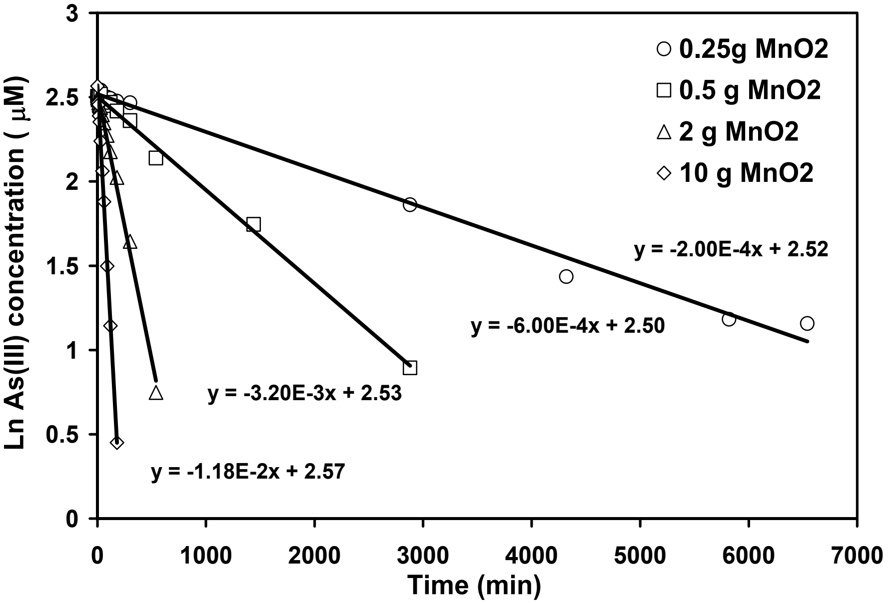


Figure 5-2 Linearized plots of As (III) depletion data

In Figure 5-2, we plot logarithmic values of observed As(III) concentration with respect to time for all four kinetic runs. The data show a linear variation with respect to time, indicating first-order dependence with respect to As(III) concentration. The slope of the lines shown in Figure 5-2 represents the observed oxidation rate constants ($k_{obs}$). Interestingly, the absolute magnitude of $k_{obs}$ clearly increases with an increase in the amount of $MnO_2$(s). This indicates that the observed first-order rate constant depends on the amount of $MnO_2(s)$ in the system. To further examine this dependence, we plotted the observed oxidation rate constant as a function of the amount of $MnO_2(s)$ in the system (see Figure 5-3). A linear dependence was once again observed, indicating that $k_{obs}$ can be related to $MnO_2(s)$ concentration using the expression:

$$k_{obs} = k[MnO_2(s)] \tag{5-4}$$

where k is a second order oxidation rate constant and its value was estimated to be 0.0012 $lg^{-1}min^{-1}$ (with the regression coefficient value of 0.99). From Equations (5-2) and (5-4), the As(III) oxidation kinetics can be expressed as the following second order reaction:

$$\frac{d[As(III)]}{dt} = -k[As(III)][MnO_2(s)] \tag{5-5}$$

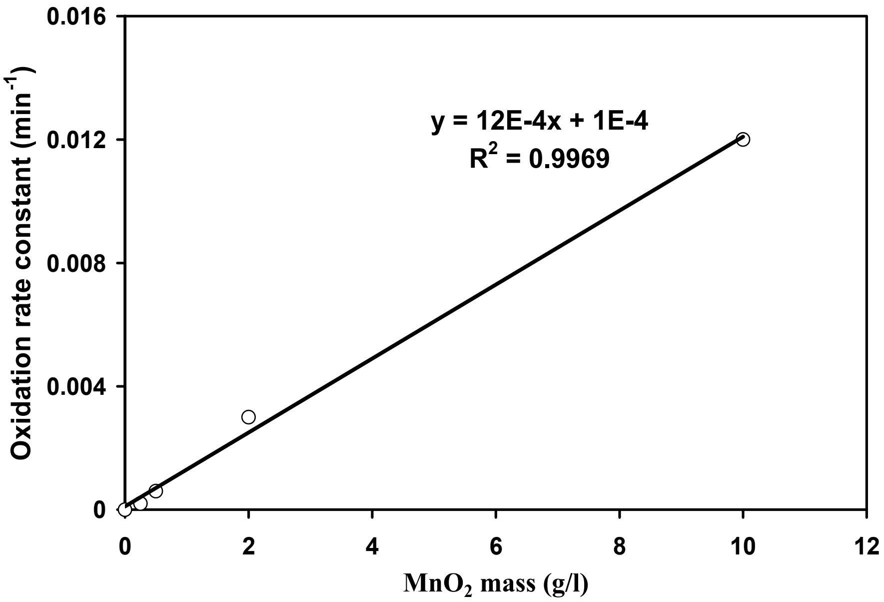


Figure 5-3 Linear relationship between first-order oxidation rate constant and $MnO_2(s)$ mass

Recently, Amirbahman et al. (Amirbahman et al., 2006) used a similar second order model to describe the kinetics of the abiotic oxidation of As (III) by natural soils. It should be noted that the second order kinetic equation (5-5) is more versatile than the commonly-used pseudo-first-order model (Equation 5-2) since it can be used to describe the reaction rate systems involving different solid-to-solution ratios and different Mn contents. Therefore, it has the inherent potential to scale the reaction information from a batch-scale system, which typically involves a low solid-to-solution ratio, to a column-scale system that involves a very high solid-to-solution ratio.

### 5.3.2 Adsorption of As(III) and As(V) by $MnO_2$(s)

The adsorption of As(V) onto $MnO_2$ minerals has been previously observed (Hering et al., 1996; Chiu and Hering, 2000; Ouvrard et al., 2002a). However, the adsorption of As(III) onto manganese oxides consisting predominantly of Mn(IV) has not been observed yet (Amirbahman et al., 2006). The oxidation kinetic experiments reported in the previous section indicated negligible adsorption of both forms of As species. This is because the solid-solution-ratio used in these experiments were relatively low (ranging from 0.25 to 10 g of $MnO_2$ per liter) and hence very little surface sites were available for adsorption. Note that in all the oxidation experiments the total As remained a constant (see Figure 5-1) indicating that adsorption was not important. However, the amount of surface-active oxidation sites were sufficient to oxidize As(III) to As(V).

We completed adsorption kinetic experiments using 10 g of $MnO_2$(s) in 100 ml of As(V) solution (note that this experiment had ten times the highest solid-to-solution ratio used in previous oxidation experiments). Figure 5-4 shows the adsorption kinetics of As(V) onto $MnO_2$(s), which is found to be a very fast reaction. We repeated these experiments and found that both forms of As species partitioned to the solid phase to a similar extent at the pH value of 4.5 (results not shown). Other preliminary experiments also indicated that the overall adsorption potential of the pyrolusite surface was relatively small when compared to its oxidation potential. Our finding was similar to that of other researchers who also concluded that As adsorption by $MnO_2$(s) exhibited very fast kinetics, with the total As concentration remaining constant after about 2 minutes, whereas As(III) continue to be oxidized for a long time (Driehaus et al., 1995; Tournassat et al., 2002). Based on these observations and based on the literature information that indicated As(III) adsorption onto $MnO_2$(s) has not been observed (Amirbahman et al., 2006), we hypothesized that our $MnO_2$(s) system consists of oxidative sites and adsorption (which are non-oxidative) sites. The oxidative sites are renewable and they rapidly oxidize As(III) and release As(V) to the solution through the mechanism postulated by Scott and Morgan (Scott and Morgan, 1995), which was summarized in the previous section. The adsorption sites are finite and they only adsorb As(V) ions.

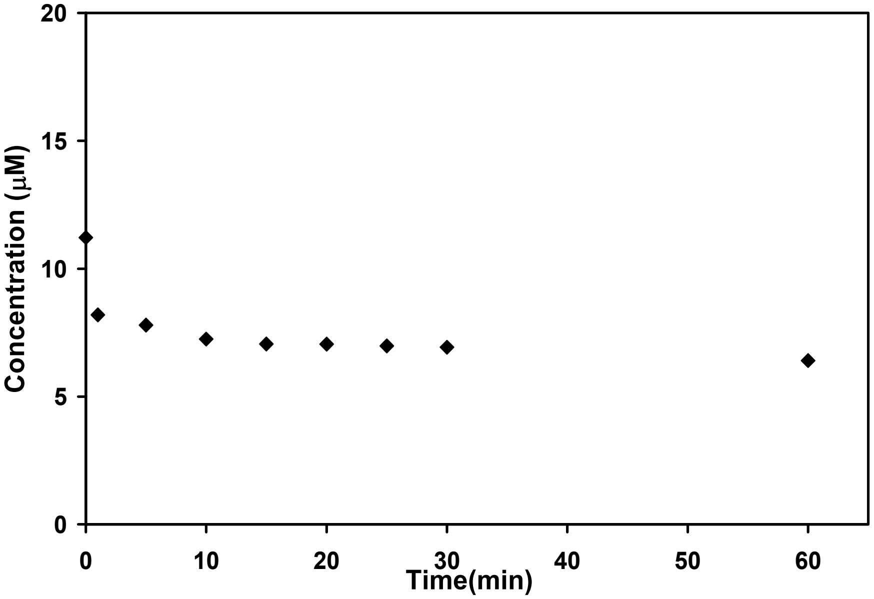


Figure 5-4 Kinetics of As(V) adsorption reaction (completed using 13 μM As(V) at 10 g of $MnO_2$(s) in 100 ml of solution, at pH 4.5 and I=0.01 M $NaNO_3$)

To quantify the amount of As(V) adsorption sites, we completed a set of batch adsorption experiments using different initial As(V) concentrations. We then fitted the Langmuir isotherm model to the As(V) adsorption data and the results are shown in Figure 5-5. In the Langmuir model the adsorbed concentration is related to the aqueous concentration by the following equation:

$$q = \frac{K_l q_{\max} As(V)}{1 + K_l As(V)} \tag{5-6}$$

Where $K_l$ is the Langmuir constant, which is a measure of the strength of adsorption, and $q_{max}$ is the maximum adsorptive capacity, a measure of the total amount of adsorption site per mass of the adsorbate. The value of $K_l$ of our system (I=0.01M, pH=4.5) was estimated to be 2.025 $l\mu mol^{-1}$, and the maximum adsorptive capacity was estimated to be 0.053 μmol As/g. Such a low value of adsorptive capacity explains why our oxidation kinetic data (shown in Figure 5-1), did not show any adsorption effects. The amount of As available in these kinetic experiments was close to three orders of magnitude higher than the adsorption capacity of $MnO_2(s)$ present in the system. Hence, our kinetic experiments were relatively insensitive to adsorption.

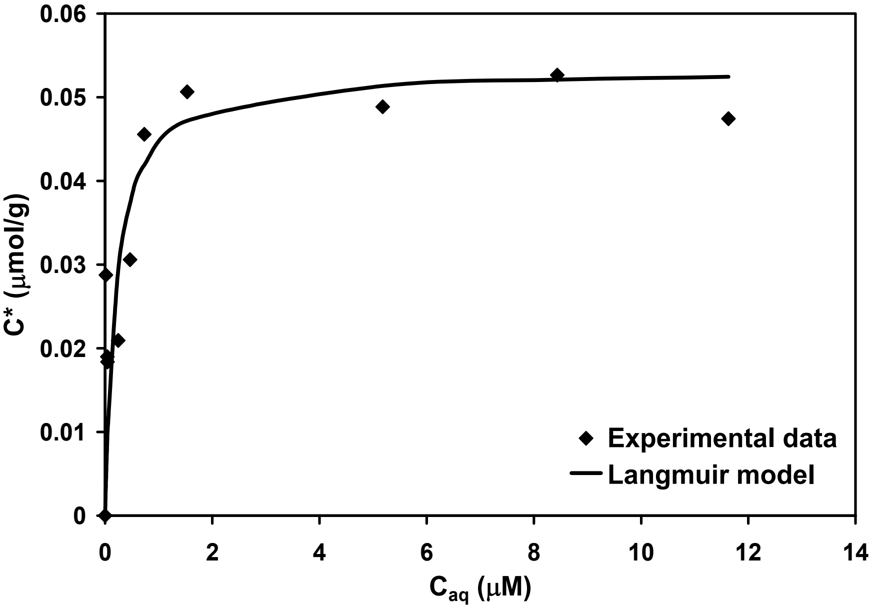


Figure 5-5 As(V) adsorption isotherm (completed using 1 g/l of $MnO_2$(s) and various initial As(V) aqueous concentrations, pH 4.5 and I=0.01 $NaNO_3$)

## 5.4 Development of a scaled reactive transport model

The batch experiments enabled us to determine the key reaction parameters needed for developing a model for predicting the fate and transport of As in a dynamic column-scale reactor. The modeling efforts included the development of a conceptual model, which was derived from the findings of the batch experiments, development of an approach to scale the batch parameters to column scale, and development of a numerical model to couple the adsorption and reaction mechanisms with contaminant transport. The integrated numerical model was then used to predict the behavior of As transport in a column. To check the validity of the reactive transport model, the experimental observations were compared with model results.

This work was completed in collaboration with a Master student Anjani Kumar (Kumar, 2006) who developed the numerical model.

### 5.4.1 Conceptual model

Figure 5-6 illustrates a conceptual model for predicting the reactive transport of As in a $MnO_2$-containing column. This conceptual model was postulated based on the results obtained from the batch experiments. As shown in the figure, two types of sites are assumed to be present on the surface of $MnO_2(s)$ particles: 1) renewable oxidation sites, which mediate the kinetically-controlled reaction that oxidizes As(III) to As(V); and 2) non-renewable (fixed amount of) equilibrium adsorption sites which can only adsorb As(V) ions (Kumar, 2006). Our adsorption experiments showed that the maximum adsorption capacity (at I=0.01M, pH=4.5) of the system (total amount of sites) is 0.053 μmol of As/g of $MnO_2(s)$.

Conceptually, the fate and transport of As(III) within a saturated column can be described as follows: 1) As(III) enters the column and is partially or fully oxidized to As(V); 2) As(V) is then adsorbed onto the $MnO_2(s)$ grains; this step continues until the adsorption capacity is fully exhausted; and 3) the portion of As(III) not oxidized as well as the portion of As(V) not adsorbed are transported further into the column (Kumar, 2006).

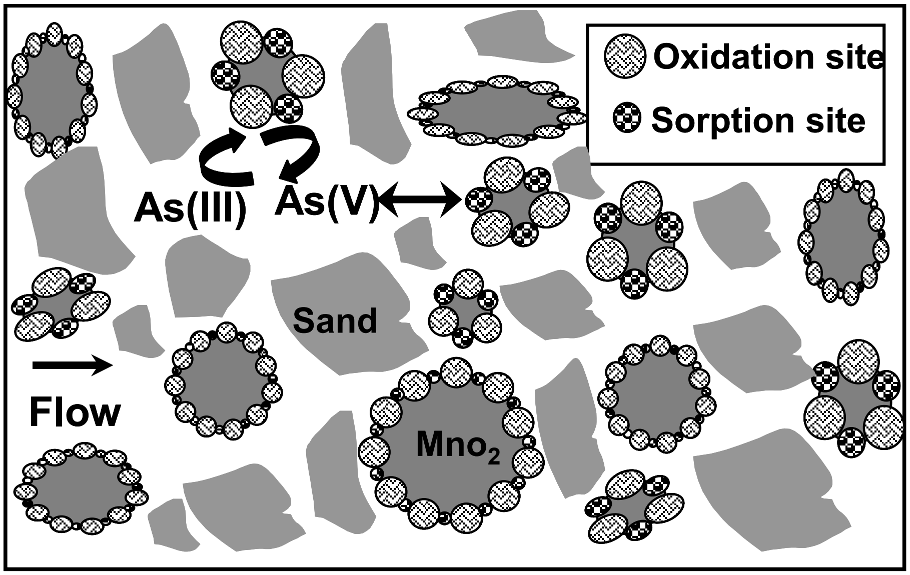


Figure 5-6 Conceptual model of the reactive transport system considered in
5.this study

A detailed discussion of development of the reactive transport model is given in Kumar (Kumar, 2006).

### 5.4.3 Reactive Transport Simulations and the Design of Column Experiments

Column-scale numerical simulations were completed to simulate multiple hypothetical experimental scenarios. From these numerical experiments (Kumar, 2006), the following reactive transport scenarios were selected for further testing in the laboratory.

**a)** ***Reactive transport in a column packed with an extremely high level of $MnO_2(s)$**:* This column was assumed to contain 100% of pure $MnO_2$ solids. This extremely high $MnO_2(s)$ content system was selected to study the reactive transport under the maximum extent of oxidation and adsorption. Two types of experiments were conducted with the input solution containing either As(III) (designated as Exp A) or As(V) (designated as Exp B).

**b)** ***Reactive transport in a column packed with a medium level of $MnO_2(s)$***. This column was constructed to contain 50% (by wt.) of $MnO_2(s)$ and 50% sand (Iota 6, Unimin quartz sand). This medium-level $MnO_2(s)$-content system was selected to study transport in a moderately reactive system. As(III)-containing solution was flushed through these columns to determine how the change in sand-$MnO_2(s)$ ratio will affect the oxidation and adsorption capacity of the column. This experiment is designated as Exp C.

**c)** ***Reactive transport in a column packed with an extremely low level of $MnO_2(s)$:*** Since in all of the above experiments the numerical model predicted complete oxidation of As(III) to As(V), we designed a low $MnO_2(s)$-content experiment to study As(III) transport in a low-level of reactivity system. The $MnO_2(s)$ content was designed sufficiently low to guarantee only partial oxidization of the influent As(III) solution. The results of this study is expected to test the ability of our transport model to predict As(III) transport under partial oxidation conditions. This experiment is designated as Exp D.

Three experimental columns of length 7 cm and diameter 1 cm, containing the selected levels of $MnO_2(s)$-sand mixture, were used to test the three reactive transport scenarios discussed above. The extremely high $MnO_2(s)$ system was packed with 12.9 grams of pyrolusite minerals, the medium level $MnO_2(s)$ system was packed with a 50%

pyrolusite-sand mixture containing 5.3 grams of $MnO_2$(s) and 5.3 grams of sand. The extremely low $MnO_2$(s) system was packed with 0.37 grams of $MnO_2$(s) and 8.2 grams of sand. A constant flow rate of 0.3 ml/min was used in all the column experiments. The As(III) or As(V) concentration in the influent solutions was 13 μM. Other details of the column experiments are summarized in Table 5-1. The estimated values of $MnO_2$(s) concentration (the values of “f $\square_c$”) in the high, medium and low $MnO_2$(s)-content experimental systems are: 2.35, 0.96 and 0.067 gram/cm$^3$, respectively (note: these concentration values are expressed in terms of the bulk volume).

Table 5-1. Summary of transport parameters

| Parameter | Value |
|---|---|
| Inlet As conc. (μM) | 13 |
| $MnO_2$ column porosity | 0.54 |
| Sand porosity | 0.425 |
| Porosity of 50% $MnO_2$ column | 0.472 |
| Column height (cm) | 7 |
| Column diameter (cm) | 1 |
| Flow rate (ml/min) | 0.3 |
| Longitudinal dispersivity (cm) | 1.0 |
| $K_l$ (lμmol$^{-1}$) | 2.025 |
| k (lg$^{-1}$min$^{-1}$) | 0.0012 |
| $q_{max}$ (μmol As/g of $MnO_2$(s)) | 0.053 |

## 5.5 Results and discussion of column data

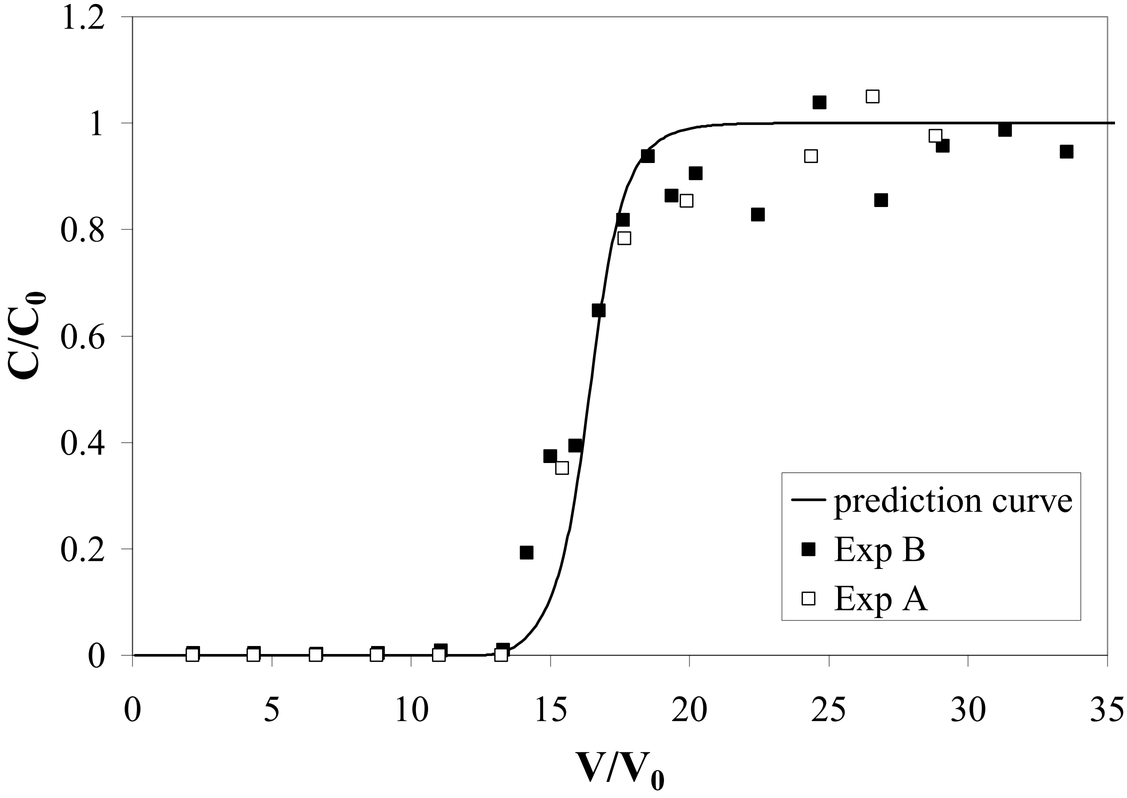


Figure 5-7 Comparison of the observed and model-predicted As breakthrough profiles for experiments A and B (data shown are $As_{tot}$, which is identical to As(V) due to complete oxidation within the high $MnO_2$(s) columns).

As(III) and As(V) breakthrough data from columns that were packed with 100% pyrolusite (Exp A and Exp B) are compared with the model prediction in Figure 5-7. Based on the batch data, one can predict complete oxidation of As(III) in the 100% $MnO_2$(s) column. This would imply that the breakthrough results from the As(III) experiment (Exp A) would closely follow the results from the As(V) experiment (Exp B).

Figure 5-7 depicts Exp A and Exp B results along with the theoretical model results. Due to complete oxidation, the breakthrough data from Exp A closely matches the data from Exp B. Complete oxidation of As(III) was further verified using the speciation analysis of the outlet solution which indicated the concentration of $As_{tot}$ was equal to As(V) (data not shown). Numerical model predictions closely predicted the number of pore volumes after which the breakthrough would occur. Experimental breakthrough has occurred around 16.5, while numerical model predicted value was 17.4 pore volumes. To predict the observed spread around the breakthrough front required a dispersivity value of 1 cm (it is important to note that the value of dispersivity was the only parameter that needed calibration). However, tracer transport experiments completed in the column indicated a dispersivity value of 1 to 2 mm (close to the grain size value). The simulation of the reactive transport front required a relatively high dispersivity value, which is about an order of magnitude higher than the values estimated from the tracer tests. This indicates that dispersion due to physical heterogeneities in this column was low (in the 1 mm range); however the reactive fronts were affected by pore-scale chemical heterogeneities which contributed to further spreading. This additional spreading effect, which is caused by chemical heterogeneities, adds new complexities to the physical-heterogeneity-related dispersion problem and it needs further investigation.

In Figure 5-8, the results of As(III) transport through the column with 50 % $MnO_2$(s) (Exp C) are compared against model predictions. Speciation analysis was performed on the outlet solution to verify the complete extent of oxidation. The analysis indicated that As(III) was fully oxidized since only As(V) was detected in the effluent solution. Therefore, the total As breakthrough profile depicted on Figure 5-8 was identical to the As (V) profile. Predictions based on the numerical model for $As_{tot}$ corresponded well with the experimental results. Furthermore, the experimentally obtained number of pore volume where breakthrough occurred is 8.9. Interestingly, the number of pore volumes after which the breakthrough occurred in Exp C was found to be approximately half the number of pore volumes required in Exp A and Exp B. This indicates that the level adsorption scales almost linearly with the amount of $MnO_2(s)$ present in the system.

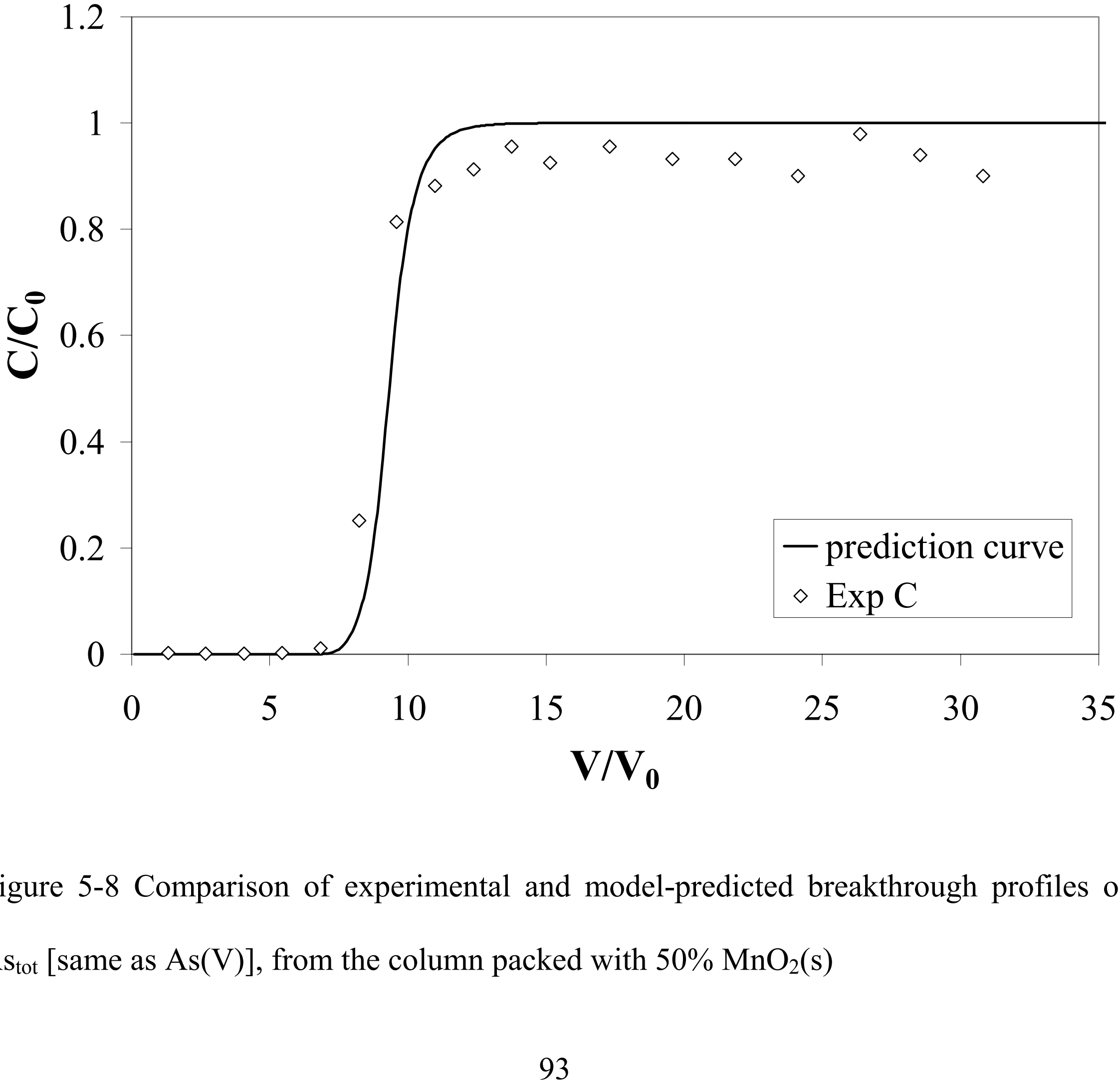


Figure 5-8 Comparison of experimental and model-predicted breakthrough profiles of $As_{tot}$ [same as As(V)], from the column packed with 50% $MnO_2(s)$

In the experiments with 100% and 50% of $MnO_2$(s), due to complete oxidation of As(III) to As(V), the total As concentration observed in the breakthrough was identical to the As(V) profile. The numerical model predicted this effect; the simulation results predict that As(III) will be completely oxidized to As(V) within the column.

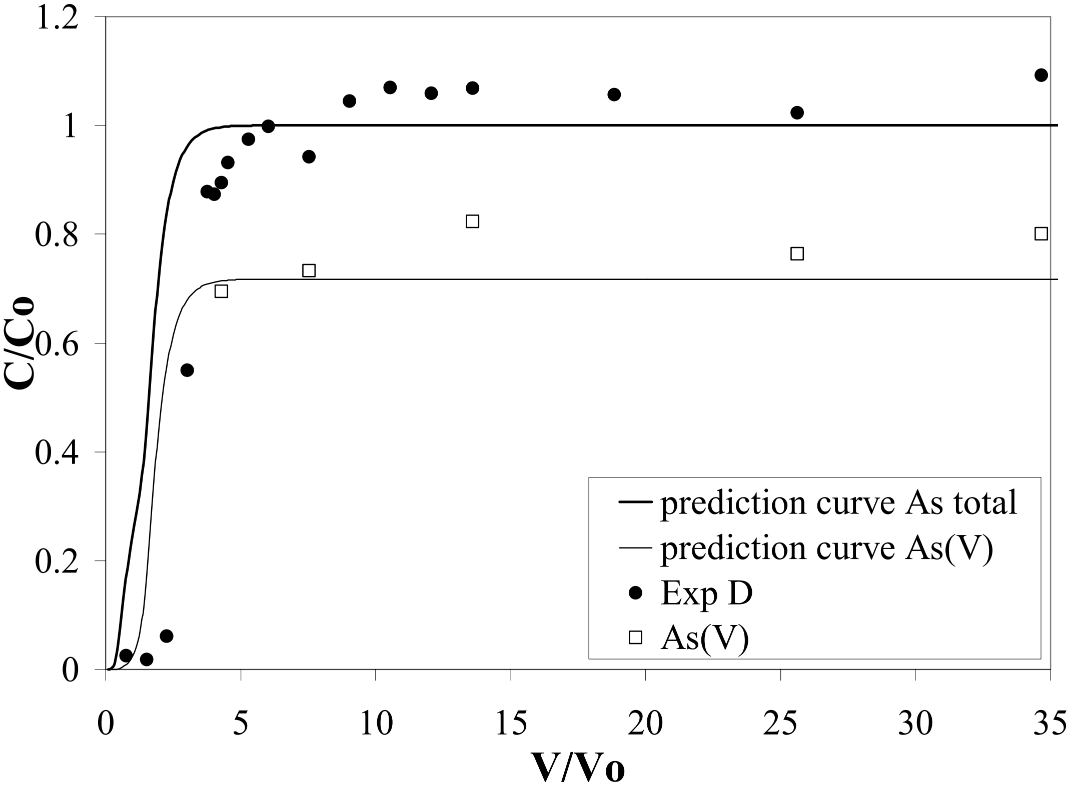


Figure 5-9 Comparison of experimental and model-predicted $As_{tot}$(●) and As(V) (□) breakthrough profiles from the Exp-D column packed with extremely low $MnO_2$(s)

The third experiment was designed to study the reactive transport under partial oxidation conditions. The goal here was to test the model's ability to accurately predict As(III) oxidation kinetics coupled with adsorption reactions. Figure 5-9 presents the breakthrough profiles from the column containing a low amount of $MnO_2$(s) (Exp D). The figure shows the observed profiles of $As_{tot}$ and As(V) are in good correspondence with model predictions. In this case, the experimentally obtained fraction of As(V) was 0.78, indicating partial oxidation of As (III). The model predicted value of this fraction was 0.77, which corresponded well with the experimental value. In all our experiments the oxidation of As(III) by $MnO_2$(s) grains continued even after the adsorption capacity was fully exhausted, which is consistent with the conceptual model we adopted in the study.

## 5.6 Summary and conclusions

We studied the oxidation of As(III) and the adsorption of As(III) and As(V) by synthetic pyrolusite [β-$MnO_2$(s)]. Batch experiments were completed to develop the reaction kinetics and adsorption isotherms for the As-$MnO_2$(s) system. The reaction information developed from the batch-scale data was integrated into a reactive transport model to perform column-scale transport predictions. Based on the batch results we conclude that the commonly used pseudo-first-order reaction kinetic model neglects the scaling effects with respect to the $MnO_2$(s) concentration. A second-order kinetic model that explicitly included a $MnO_2$(s) concentration term is a more appropriate model to describe As oxidation reaction with pyrolusite minerals. The adsorption of As on

$MnO_2$(s) follows the Langmuir isotherm with an adsorption capacity of 0.053 μmol of As/g of $MnO_2$(s) at I = 0.01M and pH=4.5. The second order oxidation reaction kinetics and the Langmuir isotherm model, which we derived from the batch-scale data, were coupled to a transport model to predict column-scale reactive transport. The results from the scaled reactive transport model accurately predicted the breakthrough profiles observed in multiple column experiments. Therefore, we conclude that the oxidation and adsorption reaction information obtained from batch-scale experiments are valuable data and, if appropriately scaled, they can describe column-scale reactive transport.

# 6. SUMMARY, IMPLICATIONS AND RECOMMENDATIONS

This dissertation has contributed to a better understanding of As chemistry and its transport through a simulated subsurface systems. Examination of the adsorption and oxidation on Fe- and Mn minerals, as well as the influence of phosphate and carbonate, provides a better insight into the complex mechanism of As mobility in the environment.

## 6.1 Summary

The following section consists of paraphrased abstracts, as listed at page ix of this dissertation.

The goal of the study described in Chapter 3 was to investigate the adsorption and transport of As(III) and As(V) in columns with Fe-coated sand. The experiments were conducted to examine the effect of pH, pore water velocity, and phosphate on As(III)/As(V) mobility. Both As(III) and As(V) exhibited rate-dependent adsorption in the columns. An increase in pH led to a significant increase in As(III) adsorption (decreased mobility) but decreased As(V) adsorption (increased mobility). As(III) was desorbed more readily than As(V) in As-free solution. The competing effect of phosphate was examined by introducing phosphate solution to the column with adsorbed As(III)/As(V). Phosphate mobilized both adsorbed As(III) and As(V), but some As(V) remained immobile even in the presence of phosphate. In general, but not under all circumstances, As(III) adsorbed less and was more mobile than As(V). The effect of the examined parameters on mobility and recovery of As species increased in the order pH < pore water velocity < phosphate < oxidation state.

The effects of high aqueous carbonate concentrations on As mobility and transport in the subsurface using synthetic Fe oxide-coated sand column experiments were described in Chapter 4. Elevated aqueous carbonate concentrations in groundwater have been studied and linked, by some authors, to increased aqueous As concentrations in natural waters. This study found that increasing carbonate concentrations had relatively little effect on As(V) adsorption to the Fe oxide-coated sand surface at pH 7. The adsorption of As(V) decreased marginally when the $CO_2$ (g) partial pressure increased from $10^{-3.5}$ atm to $10^{-1.8}$ atm, despite a fifty-fold increase in total dissolved carbonate (0.072 mM to 3.58 mM). Increasing the $CO_2$(g) partial pressure to $10^{-1.0}$ atm resulted in only a slight decrease in As(V) adsorption and increase in mobility, despite a >300-fold increase in total dissolved carbonate (to 22.7 mM). When compared to phosphate, a known competitive anion, carbonate mobilized less adsorbed As(V) than was mobilized by phosphate, even when present in much higher concentrations than phosphate. This was also true for an experiment with lower pore water velocity and an experiment where As(III) was introduced instead of As(V). Experiments lead to conclusion that while carbonate anions do compete with As for adsorption to Fe oxide-coated sand, the competitive effect is relatively small in regards to the total concentration of adsorbed As and the potential competitive effects of phosphate.

The Chapter 5 describes the effort made to better understand As adsorption and oxidation on $MnO_2$(s) surfaces. Understanding the fundamentals of As adsorption and oxidation reactions is critical for predicting its transport dynamics in groundwater systems. Batch experiments were completed to study the interactions of As with a common $MnO_2$(s) mineral, pyrolusite. The reaction kinetics and adsorption isotherm developed from the batch experiments were integrated into a scalable reactive transport model to facilitate column-scale transport predictions. A set of column experiments was then completed to test the predictive capability of the reactive transport model. The batch results indicated that the commonly used pseudo-first order kinetics for As(III) oxidation reaction neglects the scaling effects with respect to the $MnO_2$(s) concentration. A second order kinetic equation that explicitly includes $MnO_2$(s) concentration dependence is a more appropriate kinetic model to describe As oxidation by $MnO_2$(s) minerals. The As adsorption reaction follows the Langmuir isotherm with the adsorption capacity of 0.053 □mol of As(V)/g of $MnO_2$(s) at the tested conditions. The knowledge gained from the batch experiments was used to develop a conceptual model for describing As reactive transport at a column scale. The proposed conceptual model was integrated within a reactive transport code that accurately predicted the breakthrough profiles observed in multiple column experiments. The kinetic and adsorption process details obtained from the batch experiments were valuable data for scaling to predict the column- scale reactive transport of As in $MnO_2$(s)-containing sand columns.

## 6.2 Implications and recommendations

This dissertation investigated transport and behavior of As species in experimental subsurface systems. Special attention was focused on influence of factors that may trigger mobilization of As, as well as its chemical changes. Results of these experiments are expected to have strong implications in natural groundwater systems.

Mobilization of As from subsurface sediments is still not a well understood phenomena. Numerous factors may trigger release of As from the surface of a mineral to the solution phase. This can directly influence the quality of groundwater, which is used as a source of drinking water in many countries. Natural field conditions are very complex. They are influenced by a wide range of parameters. There are multiple simultaneous interactions between solid and liquid phases of subsurface materials (ion-ion, ion-mineral surface), as well as influence of factors such as change in pH, change in redox potential, sudden inflow of competitive ion- rich water, change of flow rate in the aquifer, weathering, etc. Simulating these conditions in the laboratory would be very difficult, if not impossible. However, isolating the effects of each particular parameter may give us a better insight into processes in subsurface, and their relative overall importance. Identifying key parameters controlling chemistry in the subsurface environment can not only help us better understand these systems, but also get us closer to predicting behavior of species and outcome of possible change of parameters in nature.

Changes in the flow rate in natural systems may be triggered by several factors, including flooding/draughts and pumping water from aquifers. These incidents may disturb solid to solution ratio of subsurface sediments and groundwater. The column experiments with variation of flow rate showed that higher flow rates cause less As adsorption on the surface of goethite coated sand. Also, the desorption rate increased with increasing flow rate. This may be directly compared to a situation of flooding the area with As rich minerals. Inflow of As-free water may cause desorption of As from the minerals and increase its concentration in groundwater. Release of even small amount of As into the groundwater may cause large absolute As concentrations in the aqueous phase. For example, it was estimated that complete mineral dissolution and desorption of As from sediments containing 1 mg/kg of As would result in concentration of 3000-6000 μg As/l in groundwater (WHO, 2003). On the other hand, slow flow of groundwater may provide more contact time between dissolved As and surface of minerals, causing more As adsorption, hence less As in solution phase. Even though natural groundwater flows at much slower rate than the ones simulated in the experiments, relative comparison of the effect of "fast" and "slow" flow can be useful in overall understanding of this effect, and predicting behavior of As in the case of sudden change in flow rate of groundwater. It also may serve as an explanation of high As concentrations in water in some areas that use groundwater as a source of drinking water. Pumping water from the aquifer may cause a surge of water coming from farther parts of the aquifer, causing desorption of As adsorbed at the subsurface minerals.

Inflow of fresh water in an aquifer may often bring water rich in various ions, which can then directly affect As chemistry in groundwater. These ions may compete for adsorption sites on the mineral surfaces causing less As adsorption, or promoting mobilization of the previously adsorbed As. In some instances presence of ions is proposed to enhance As adsorption. Ions examined in this dissertation are phosphate and carbonate, two commonly occurring ions in natural systems. It was interesting not only to analyze behavior and interactions of these ions with As species, but also to compare a relative effect of each ion, when both are present in As rich systems. The second scenario is closer to the real situation in nature, where various ions are present at the same time, and are competing for adsorption sites.

Phosphates occur in subsurface environment in the form of phosphate rocks. There are many additional sources of phosphates in natural systems, including soluble phosphate fertilizers and release through processes of excretion and decay of living organisms. Also, soil weathering slowly leaches phosphates from the soil. In the experiments, phosphate proved to be a competing ion when introduced to goethite packed column where As was previously adsorbed. Mobilization of adsorbed As was enhanced at lower pH for As(III), and higher pH for As(V). This also shows the complexity of the problem, where a set of environmental conditions dictate chemical behavior of species. It is also interesting to point out that phosphate couldn’t mobilize entire amount of previously adsorbed As, as there was a fraction of As that remained adsorbed on the goethite surface after the course of experiment. Being commonly present in natural groundwater often in high concentrations, and closely associated with absorbents such as $Fe^{3+}$ and $Al^{3+}$, phosphate ions may be one of the important parameters controlling As distribution in subsurface systems.

Sources of dissolved carbonate include the weathering and dissolution of carbonate bearing minerals and the microbiological oxidation of dissolved organic matter. Even though some authors propose that carbonates play a key role in mobilization of As, experimental results indicated a negligible effect. A slight effect was noticed only in the case of a significant increase of carbonate concentration. However, this increase in concentration is not likely to be found in natural systems (twice the highest reported value), as carbonate usually occurs in lower levels. Also, chosen experimental conditions (pH=7.00) favor carbonate adsorption on goethite, which should provide maximal competitive effect of this ion. This also serves as proof that the presence of carbonates does not affect As(V) chemistry, where even extremely high levels of carbonate could not produce a significant effect on As(V) adsorption/desorption under experimental conditions used. In the simulation of more reducing conditions, As(III) was introduced to the system. The effect of carbonate was slightly more pronounced, where, when compared to As(V), less As(III) was initially adsorbed, and more was later desorbed by increasing carbonate concentration showing higher overall recovery of the more mobile As(III) species.

It is interesting to compare the effects of two competitive ions, phosphate and carbonate, on As mobilization. Experiments described in Chapter 3 showed very strong competitive effects of phosphate ions. However, only presence of both phosphate and carbonate in the same system can give a deeper insight into the relative importance of these ions. In experiments described in Chapter 4, carbonate was introduced in extremely high concentrations to achieve its maximum potential of desorbing As. However, even when much lower concentrations of phosphate (compared to that of carbonate) was introduced after carbonate, it was able to further desorb As. This indicated a stronger competitive effect of the phosphate. These findings provide a better understanding of the complex problem of interactions between As and various competing ions with goethite surface. Isolating the effects of carbonate and phosphate only, it was possible to quantify the relative importance of these ions. This scenario is one step closer to the real life situation, where the presence of many ions and different surface types, influenced by many factors (flow, pH) finally determine the concentration of As in groundwater.

Under reducing conditions, As exists in a more toxic and more mobile form- As(III). Examination of oxidation of As(III) by $MnO_2$(s) in experimental conditions provided some interesting conclusions. A thorough understanding of processes on the surface of $MnO_2$(s) was achieved by a combination of batch and column experiments. It was concluded that distribution of As depends on both As and $MnO_2$(s) concentration. Using parameters obtained from the batch experiments, a numerical model for prediction of distribution of As species was developed. This served as an ultimate proof of validity of obtained parameters and assumptions used in development of the conceptual model. Scaling of batch data to a column scale is a promising way of predicting concentrations of contaminants in a dynamic system. This can be achieved by detailed examination of the properties of solid media. Prediction of oxidation may be an interesting and useful tool in designing water treatment systems, where there is a need for converting As(III) into less toxic and easier to remove As(V) species.

Knowledge gained from the experiments described in Chapter 5 would also be beneficial in the development of future models for the prediction of distributions of various contaminants.

Based on the results from Chapter 4, it can be concluded that very often there is a discrepancy between the experimental data and theoretical model predictions. This indicates a need for additional work in this field, where more than one component competes for the adsorptive sites. The data for single component systems, even though useful in development of models, should be replaced by equilibrium adsorption data with multiple component included, such as As(III), As(V), goethite surface, and carbonate species. Similar may be said for the system containing phosphate as a competing ion, where multi component data would give more information than the data describing only interaction of a single component with the mineral surface (i.e. phosphate-goethite, As-goethite).

Further development of the concepts presented in this dissertation would result not only in a deeper understanding of the problematic of As contamination, but it would also lead closer to the development of efficient techniques for As removal from contaminated groundwater. For example, using knowledge gained from experiments described in Chapters 3 and 5, pairing of the goethite coated sand and $MnO_2$(s) into one system for As removal, would provide an efficient removal media. The $MnO_2$(s) minerals, even though not very good adsorbents, have a great potential to oxidize As(III) to less toxic As(V). Furthermore, it was shown in Chapter 5 that oxidative sites on the surface of $MnO_2$(s) are renewable, which would provide for long term efficiency of the oxidation process. On the other hand, goethite coated sand was shown to be a very good adsorbent of As species (as described in Chapter 3). By manipulating parameters such as the flow rate and pH of contaminated water (as described in Chapter 3), it would be possible to develop an ideal set of conditions for As removal. The use of this kind of system would be especially beneficial in areas where groundwater is contaminated with high concentrations of As(III). Furthermore, the performance of such a system would be predictable by the use of models such as one described in the Chapter 5, where good characterization of the solid media can provide parameters necessary for accurate prediction of As distribution in the outlet solution.

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