ASSESSMENT OF THE EFFECTS OF SOIL AMENDMENTS ON THE LEACHING

OF LEAD AND ARSENIC FROM CONTAMINATED SOIL

Except where reference is made to the work of others, the work described in this thesis is my own or was done in collaboration with my advisory committee. This thesis does not include proprietary or classified information.

_____

Yu Wang

Certificate of Approval:

_____	_____
Dongye Zhao Associate Professor Civil Engineering	Mark O. Barnett, Chair Associate Professor Civil Engineering
_____	_____
T. Prabhakar Clement Associate Professor Civil Engineering	Stephen L. McFarland Acting Dean Graduate School

ASSESSMENT OF THE EFFECTS OF SOIL AMENDMENTS ON THE LEACHING OF LEAD AND ARSENIC FROM CONTAMINATED SOIL

Yu Wang

A Thesis

Submitted to

the Graduate Faculty of

Auburn University

in Partial Fulfillment of the

Requirements for the

Degree of

Master of Science

Auburn, AL
December 15, 2006

ASSESSMENT OF THE EFFECTS OF SOIL AMENDMENTS ON THE LEACHING OF LEAD AND ARSENIC FROM CONTAMINATED SOIL

Yu Wang

_____
Signature of Author

_____
Date of Graduation

THESIS ABSTRACT

ASSESSMENT OF THE EFFECTS OF SOIL AMENDMENTS ON THE LEACHING OF LEAD AND ARSENIC FROM CONTAMINATED SOIL

Yu Wang

Master of Science, December 15, 2006
(B.S., Nanjing University, 1999)

99 Typed Pages

Directed by Mark O. Barnett

Lead has a long history in the life of human beings. Unfortunately, only recently did people start to realize that lead is a toxin. Because of increasing human activity, soil lead pollution has become a serious environmental problem. Phosphorus is an important amendment for the *in situ* immobilization of lead in contaminated soils. To evaluate the effect of phosphorous on the bioaccessibility of lead in contaminated soil, a Physiologically Based Extraction Test (PBET) was used in this thesis research.

Three kinds of lead contaminated solids were used in the *in situ* immobilization test. In the *in situ* process, enough phosphate was added to form chloropyromorphite (the least soluble lead-phosphate salt). In the PBET process, chloropyromorphite was oversaturated in the PBET supernatant for lead-contaminated soil, potentially indicating that it could

precipitate from the PBET solution itself, resulting in an experimental artifact. To better understand the lead reactions occurring in the process, the formation of chloropyromorphite was studied in HCl- and HNO_3- based PBET solution. In the presence of phosphate, lead was not efficiently removed from the PBET solution under either homogeneous or heterogeneous conditions. In homogeneous chloropyromorphite formation tests under different conditions, the lead solubility in the PBET solution was generally greater than predicted for chloropyromorphite. The results indicate that the PBET is an acceptable method to evaluate the bioaccessibility of lead contaminated soils that are treated by phosphate amendments, as almost no lead precipitation occurred in the PBET process.

Arsenic (As) is a toxic metalloid that has caused widespread soil contamination problems. While various iron-based amendments have been studied for immobilizing As in contaminated soils, the feasibility of stabilized iron-based nanoparticles has not been reported. This study investigated the effectiveness of using three types of iron-based nanoparticles, including zero-valent iron (ZVI), ferrous sulfide (FeS), and magnetite (Fe_3O_4), for the immobilization of arsenic in two kind contaminated soils.

Different Fe/As molar ratio (5:1 ~100:1) and treatment times (3 and 7 days) were conducted to evaluate the effect of these nanoparticles. Higher amounts of iron particles were more effective in reducing As bioaccessibility and leachability. In addition, magnetite nanoparticles generally worked a little better than FeS and ZVI nanoparticles in reducing the bioaccessibility. For two different types of soils, treatment was more effective on the soil with the lowest iron content and highest As concentration. These results suggest that the immobilization of As and reduction of As bioaccessibility in soil

by adding iron-base nanoscale particles maybe an effective method to remediate As contaminated soils.

ACKNOWLEDGEMENTS

The author would like to acknowledge the excellent instruction, support, and guidance of his advisor, Dr. Mark O. Barnett and his co-advisor Dr. Dongye Zhao. Additional thanks to Dr. Prabhakar Clement for his instruction, knowledge, and support during the author's term at Auburn University. The author would like to thank Jinling Zhuang for technical assistance in the environmental laboratory at Auburn University. Thanks to Dr. Daniel E. Giammar in the Civil and Environmental Engineering Department at Washington University at St. Louis for the instruction during the author's visiting term. Thanks also to Thomas Albrecht-Schmitt in the Chemistry Department at Auburn University for the powder X-ray diffractometer measurements. The author would also like to thank his loving wife Jie Gao for her support and understanding, as well as his parents, Shusen Wang and Yingli Wan for their encouragement during the author's term at Auburn University.

Style manual or journal used *Guide to Preparation and Submission of Theses and Dissertations*

Computer software used:

Microsoft Office XP: Excel, PowerPoint, Word,

Endnote 7.0

Visual MINTEQ 2.40

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Lead and Human Beings

Lead is the heaviest member of the carbon family (Group □) with a molecular weight of 207.20. Lead has such a long history in the life of human beings that its first use can be dated back to ancient Egypt (3400 B.C.) [1]. Unfortunately, only recently did people start to realize that lead is a neurotoxin that can harm the brains and nervous systems of young children temporarily or permanently [2]. High amounts of lead ingestion are also fatal for adult [2]. Some researchers even attributed the fall of Rome to lead poisoning [2]. Nowadays lead is being used in many industrial products, such as lead-acid batteries used by cars, lead solder which is used to seal cans, and as a metal alloy which is used for military (e. g. bullets and shells) [2]. Because of its multiple use, lead has many pathways to enter human body and damage human health. Generally, people can get lead in their body under the following three circumstances: "1) ingest objects covered with lead; 2) ingest paint chips or soils that contain lead; 3) breathe in lead dust" [3].

1.2 Lead in the Soil Environment

The abundance of lead in the Earth's crust ranges from 0.0013% to 0.002% [2]. Almost no pure lead element exists on the earth [4], and all pure lead came from human

activities. In nature, galena (PbS) is the most common ore of lead minerals [5]. Other solid forms of lead are anglesite, or lead sulfate ($PbSO_4$); cerussite, or lead carbonate ($PbCO_3$); and mimetite ($PbCl_2 \cdot Pb_3(AsO_4)_2$) [4].

Lead is an reactive metal and can form many compounds with other elements. The increasing impacts of human activities have caused large quantities of lead to be released into the environment, especially into the soil environment. After entering soil, lead will then cause soil pollution. Different target criteria have been set to define soil pollution. The lead limit was established at 400 ppm (residential) and 750 ppm (industrial) for human health criteria; for the ecological receptor criteria, the lead limit was 740 ppm (mammalian) and 40.5 ppm (avian) [6]. According to report of Salatas et al., lead was the main pollutant at DOD (Department of Defense) sites [6]. Therefore, some data for lead soil pollution were published, and different methods to clean lead-contaminated soil were studied. Cao et al. reported that lead concentrations in soils in Florida fire ranges increased due to the weathering of lead bullets [7, 8].

There are two ways to remediate lead soil pollution, one is a "capping strategy", and the other is *in situ* immobilization.

1.3 *In situ* Lead Immobilization with Phosphorus

Phosphorus is an important amendment for *in situ* lead immobilization in contaminated soil, and most remediation techniques use phosphate [9-20]. It has been suggested that phosphate minerals, such as phosphate rock and apatite, can significantly reduce lead bioavailability in lead contaminated soils [4]. For example, Ma et al. studied *in situ* immobilization of lead with apatite ($Ca_5(PO_4)_3OH(s)$) as an amendment and

showed reduction of lead bioavailability by phosphate amendment [21]. Ruby et al. used *in situ* formation of lead phosphate in soils as a method to immobilize lead [22]. The phosphate amendment method was shown to be the most cost-effective option for reducing the leaching and bioavailability potential of soil phase lead [23].

Researcher observed that lead and phosphate could form precipitates very easily and quickly in the aqueous phase. In 1932, Jowett and Price measured the solubility of two kinds of lead phosphate salts, $Pb_3(PO_4)_2$ and $PbHPO_4$ [24]. Their study demonstrated that chloropyromorphite ($Pb_5(PO_4)_3Cl(s)$) is the main constituent in the formation of solids or minerals [24]. Previous research has revealed that chloropyromorphite formation and stability of lead are the most important mechanisms [25-27]. Thus, the formation of solid Pb-PO_4 complexes (especially for chloropyromorphite) in lead contaminated soils is considered as a final step in many remediation strategies [4].

Hettiarachchi and Pierzynski and Cotter-Howells et al. studied lead phosphate formation in soils, and proposed that phosphate amendments could induce further pyromorphite ($Pb_5(PO_4)_3X(s)$, where X can be Cl^-, OH^-, or Br^-) formation [4, 28]. Chloropyromorphite plays an important role in the immobilization process because it is least soluble among all the lead phosphate minerals, which is the most desired characteristics for lead immobilization amendment [4]. Direct evidence for the formation of pyromorphite in lead-contaminated soils with P amendment has been reported [29, 30].

1. 4 Chloropyromorphite Formation and Dissolution

For soil remediation, the chloropyromorphite formation is an important step in lead immobilization. Because of the importance of chloropyromorphite in the *in situ* lead soil remediation, most previous studies for chloropyromorphite formation were done under heterogeneous conditions [22, 26, 31]. Other solid lead species could also be transformed to chloropyromorphite by a dissolution-precipitation mechanism to immobilize soluble soil Pb *in situ* by simply adding phosphate or phosphate salt to the soil. Cotter et al. observed chloropyromorphite formation with soil lead and added phosphate [28], and Laperche et al. studied the effect of amendment apatite on soil lead and chloropyromorphite formation [30, 32]. Zhang and Ryan reported the formation of chloropyromorphite from galena in the presence of hydroxyapatite, and attributed this result to hydroxyapatite dissolution and consequent phosphate release. [29].

This reaction primarily occurs under heterogeneous conditions, though the solubility of both Pb and P could affect the effectiveness of P-induced Pb remediation [33]. The main factor in the remediation is soil pH. Cao et al. and Yang et al. concluded that low pH will lead to rapid chloropyromorphite formation [15, 19]. Zhang et al studied the chloropyromorphite formation on the surface of goethite, and showed that chloropyromorphite can even be formed from adsorbed lead [34].

Odyakov and Zhizhina studied chloropyromorphite formation under homogenous conditions by adding Pb^{2+} into $H_2PO_4^-$ and Cl^- system, and their results showed that at their experimental pH (3.0 - 6.0), the reaction was very quick [35]. They concluded that the ratio of $H_2PO_4^-$ and Pb^{2+} in precipitation crystals will change with different aqueous reactant ratio. Scheckel et al. conducted similar experiment in soft-drinks (phosphoric

acid) and observed significant lead removal during the first several minutes [36]. XRD result and SEM photo of chloropyromorphite precipitation were further used to provide direct evidence for chloropyromorphite formation [36, 37]. Figure 1.1 is the XRD pattern of standard chloropyromorphite.

Effects of the presence of different cations and anions on the pyromorphite formation were also studied. Anions (NO_3^-, Cl^-, F^-, SO_4^{2-}, and CO_3^{2-}) can increase the pyromorphite formation while cations (Al, Cd, Cu, Fe(II), Ni, and Zn) will inhibit the process [38, 39]. Dissolved organic matter can affect chloropyromorphite formation, and this is explained by Pb complexation [40]. Organic matter inhibited the formation of chloropyromorphite at pH 3 and 4, but showed no effect at pH 5, 6 and 7 [41]. Besides, organic coating around the nuclei of chloropyromorphite may inhibit the reaction as well [41]. The study done by Martinez et al. indicated that lead will be over-saturated in some aqueous phases [20, 42, 43].

Previous studies [5, 8, 19, 44-46] observed a quick kinetic formation of chloropyromorphite by the reaction of lead and phosphate. In addition, the reverse reaction - dissolution of chloropyromorphite, was also studied under different conditions. The effect of pH on solubility of chloropyromorphite has been investigated [47]. Increasing pH was associated with a decreasing lead uptake, indicating positive effect on lead remediation effectiveness. On the other hand, low pH results in no obvious remediation effect. However, this result conflicts with some other studies [15, 19], where low pH was related to the increase in both formation and dissolution rates of chloropyromorphite. The formation of chloropyromorphite or hydroxypyromorphite were barely observed in alkaline condition [48].

1.5 Bioaccessibility and Bioavailability of Lead

Bioaccessibility and bioavailability are two important aspects of contaminated soils and sediments. In 2002, the National Research Council published the report "Bioavailability of contaminants in soils and sediments: processes, tools, and applications" which defined the word "bioavailability" [49]. Hettiarachchi and Pierzynski referred bioavailability to "the portion of a substance or element in soil that is available for absorption into living organisms, such as humans, animals, or plants" [4, 23]. In the review paper written by Ruby et al., bioaccessibility was also defined as "the fraction that is soluble in the gastrointestinal environment and is available for adsorption". [50].

In general, there are currently two methods to assess bioavailability and bioaccessibility respectively: one is *in vivo* (conducted with living animals), and the other is *in vitro* (conducted outside the living organism in the laboratory) [4, 23]. The well known Physiologically Based Extraction Test (PBET) has been proposed to quickly measure bioaccessibility [51].

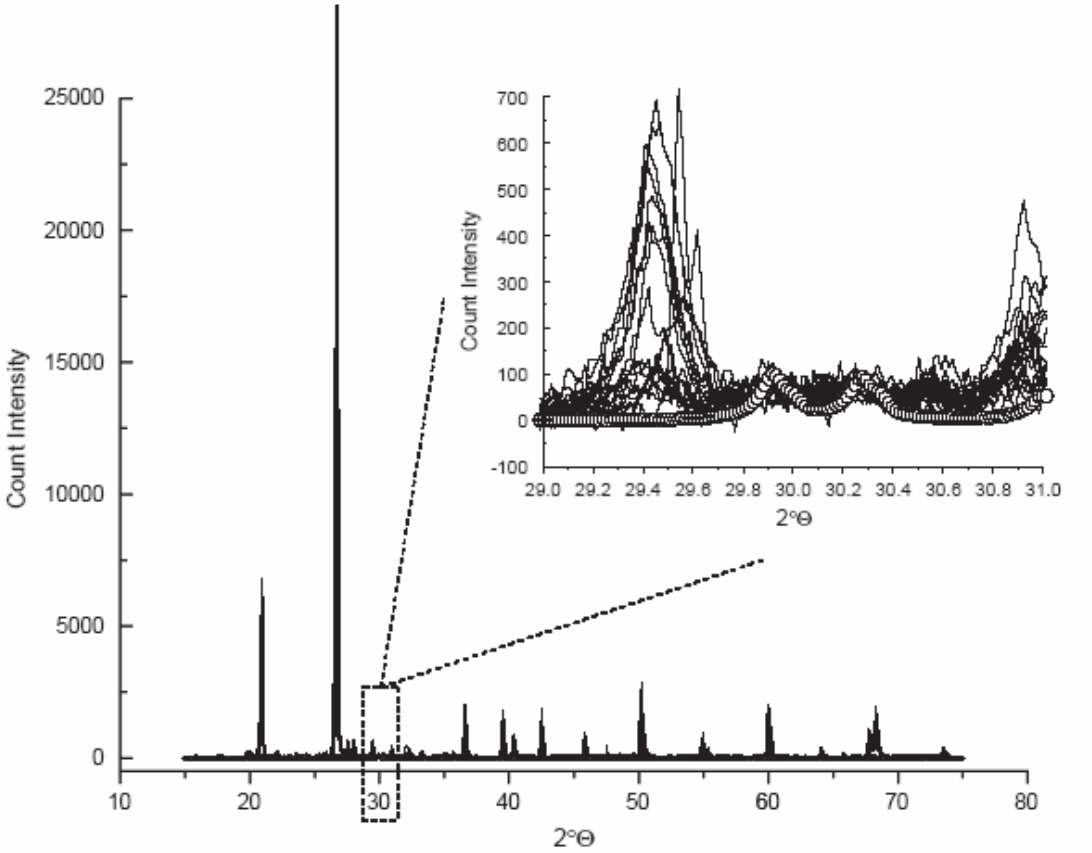

Figure 1.1 XRD Patterns for Amended Soil. The Curve consisting of Circles Represents a 1% Diluted Chloropyromorphite Standard. [52]

1.6 Physiologically Based Extraction Test

In early 1990s, the relationship between lead content and lead uptake by human was studied, and work was published on the geochemistry of lead in a simulated stomach environment [53, 54]. In 1996, Ruby et al. first brought up the idea of "Physiologically Based Extraction Test" (PBET) [51]. It is "an in vitro test system for predicting the bioavailability of metals from a solid matrix and incorporates gastrointestinal tract parameters representative of a human (including stomach and small intestinal pH and chemistry, soil-to-solution ratio, stomach mixing, and stomach emptying rates)" [51]. Basically, the PBET is used to simulate in vivo processes for Pb and As bioavailability in order to estimate the changes induced by soil amendments [4, 23]. In that report, Ruby et al. [51] specified that the absolute bioavailability of Pb is the fraction of ingested Pb that is absorbed into systemic circulation. The idea of PBET excited many environmental scientists since the PBET is such a simple chemical procedure that it could potentially replace the complicated animal experiments, such as immature swine and rat feeding studies.

After developing the PBET, Ruby et al. studied the relationship between the PBET test and traditional animal test. They compared the results of the PBET extraction with data from a Sprague-Dawley rat model and found that there is a linear correlation between in vitro estimated bioaccessibility and in vivo measured relative bioavailability [23, 51]. Pu et al. evaluated the relationship between the rat model and PBET model for assessing toxicity from soil for phenanthrene [55]. Oliver et al. observed a significant positive relationship between in vitro measurements of Pb in dust and blood Pb level of children [56]. Recently, Marschner compared the soil lead in vitro bioaccessibility and in

vivo bioavailability and concluded that there is a correlation between intestine bioaccessibility and in vivo bioavailability [57].

Several control factors, is very important in PBET, and can affect the extraction results, such as pH, temperature, and stomach mixing and emptying rates [60]. Based on the Ruby et al.'s PBET extraction method [51], some modified methods were designed to simulate the human GI tract by different researchers [55, 58, 59] (Table 1.2). In this thesis, we report results from a modified, streamlined version of the PBET extraction [60, 61].

1.7 Objectives

The objective of this study was to determine whether or not reductions in Pb bioaccessibility when adding P amendments to soil were occurring *in situ* or as an experimental artifact in the PBET itself. Amendments (KH_2PO_4) were applied *in situ* to lead contaminated soils, and the immobilization of lead in the amendment process was monitored. The formation of chloropyromorphite was studied in the PBET process, and the lead immobilization rate was evaluated in PBET solution under different conditions. In addition, the dissolution of chloropyromorphite was studied to examine the lead release rate in PBET solution.

Table 1.1 Summary of parameters which used by different PBET [58]

Parameter	PBET model [51]	PBET [60-62]	In Vitro model [56]	PBET [63]	PBET (used in this study)
Target organism	human	human	human	human	human
pH	1.3, 2.5 and 4.0	1.5	1.3	2.2	2.3
Na^+	none	none	none	none	none
Cl^-	none	0.406 M	0.1 M	Near 0.25M	0.242 M
Glycine	none	0.4 M	none	0.4M	0.4 M
Pepsin	1.0%	none	0.1%	none	none
Citrate	0.05%	none	1.0%	none	none
Malate	0.05%	none	0.1%	none	none
Lactic acid	0.5%	none	none	none	none
Acetic acid	0.5%	none	none	none	none
Fluid solution	40 mL	10 mL	140 mL	35 mL	100 mL
Amount of soil	0.4g	0.1g	10 g	3.5 g	1g
Temperature	37℃	37℃	37℃	37 ℃	37℃
Food added	none	none	none	none	none
Extraction time	60 mins	60 mins	120 mins	60mins	60 mins
Soil/solution ratio	1/160	1/100	1/14	1/10	1/100

1.8 Organization

The organization of this thesis follows the guidelines of a publication style thesis as outlined in the *Guide to Preparation and Submission of Theses and Dissertations* printed by the Auburn University Graduate School.. The results of the investigation are provided in chapter two and chapter three of this thesis, which are prepared as two draft manuscripts for journal submission.

CHAPTER II

ASSESSMENT PBET PROCEDURE FOR PHOSPHATE AMENDMENT LEAD-CONTAMINATED SOIL SAMPLES

2.1 Introduction

The ingestion of soils is typically the major human-health risk pathway, especially to children's health, at lead (Pb)-contaminated sites. As such, the *in situ* immobilization of Pb in contaminated soils is a potentially cost-effective way to reduce the risk of Pb-contaminated soils. Accordingly, *in situ* soil remediation of lead via phosphate amendments to transfer lead to insoluble phosphate minerals has been extensively studied [5, 15, 19, 22, 26, 44-46, 64].

Among the lead phosphate minerals, chloropyromorphite [$Pb_5(PO_4)_3Cl(s)$] is the least soluble and therefore the most important lead phosphate mineral in soil lead remediation [4]. Cotter-Howells [28] studied lead phosphate formation in soils, and proposed that phosphate amendments could induce further chloropyromorphite formation. Direct evidence for the formation of chloropyromorphite in lead contaminated soils with P amendment has been reported [30, 31, 65]. From the published literature [31, 33, 34, 42, 47, 66, 67], all Pb sources and minerals including anglesite [$PbSO_4(s)$], cerrusite [$PbCO_3(s)$] and Pb adsorbed on goethite, can be transformed to chloropyromorphite under the right conditions. Odyakov and Zhizhina [35] studied the formation of chloropyromorphite in aqueous phase, and they concluded the formation is very quick

and the ratio of $H_2PO_4^-$ and Pb^{2+} in precipitation crystal can change in different aqueous reactant ratio. Scheckel and Ryan [36] studied the formation of chloropyromorphite in soft-drink (phosphoric acid) and found most lead removal happened in the first several minutes. Other studies [21, 29, 38, 39, 68] showed that the reaction rate of chloropyromorphite formation was kinetically rapid from dissolved lead and other phosphate sources in a heterogeneous system.

The method used to assess the bioavailability of lead in soil is an important issue. The bioavailability of Pb has been estimated using the physiologically based extraction test (PBET) [5, 45, 51], an in vitro leachability test that was designed to mimic the solubility-limiting conditions in a child's digestive tract. For lead (Pb), the results of the in vitro PBET have been shown to be linearly correlated with results from an in vivo Sprague-Dawley rat model ($r^2 = 0.93$) [51].

However, Scheckel et al. [69] warned that the results of a sequential extraction test of identical materials were compromised by the rapid formation chloropyromorphite in the extraction procedure itself. Scheckel et al. [52] also warned of the possibility of experimental artifacts confounding the results of soil amendment experiments when assessing their effectiveness with extraction tests like the PBET.

The objective of this study was to evaluate the potential formation of chloropyromorphite in soil as an experimental artifact during the PBET extraction tests. Phosphate amendments were added to three different kinds of Pb-containing solids, and the concentration of Pb, phosphate and potassium (K^+, a tracer) were measured during the PBET process. The saturation indices of chloropyromorphite and other minerals were

monitored along with Pb removal in the PBET solution and various control solutions as a function of time during the process.

2. 2 Methods and Materials

2. 2. 1 Materials

All chemicals employed in this study were analytical grade or above and obtained from Fisher Scientific (Pittsburgh, PA), and all solutions were prepared with deionized water (18 MΩ·cm) from an ion exchange apparatus. Experiments were conducted on a Pb-contaminated soil collected from the field and on two solid materials spiked with Pb in the laboratory. The Pb-contaminated soil sample was collected from a small-arms firing range in east-central Alabama. An uncontaminated sample of the same type of soil was collected within a few hundred meters of the firing range. Both of these soil samples were ground and sieved to less than 250 μm. The uncontaminated soil sample and a sample of pure quartz sand were spiked with a small volume of concentrated $Pb(NO_3)_2$ solution to a 1:10 g solid per mL of 10^{-3} M $CaCl_2$ solution sufficient to achieve a target solid-phase Pb concentration of 1000 mg kg^{-1}. A small volume of 1 M NaOH solution was added to the soil/sand slurry at the same time as the Pb spike to neutralize the acid added with the Pb spike. After 48 hr of mixing, the soil/sand suspensions were centrifuged and the supernatant was decanted. The decanted supernatants were filtered through a 0.45-μm membrane filter, and the concentration of Pb in the filtrate was measured. After rinsing by pure water three times, the soil/sand was then dried. The total Pb recovery for the Pb-spiked soil and sand were 100±10%. The concentration of Pb in the Pb-contaminated

soil, the Pb-spiked soil, and the Pb-spiked sand were 3900, 700, and 780 mg kg^{-1}, respectively.

2. 2. 2 Amendments

A 2.0 gram sample of each of the three solid materials was weighed and placed in a 20 mL HDPE bottle. A phosphate amendment [potassium dihydrogen phosphate, $KH_2PO_4(s)$] was added to each to achieve a total P content of 0% (unamended control) and 5% by mass. The soil and amendments were dry mixed for five minutes. Then 0%, 30%, 100%, or 500% (e.g., 5 mL water per 1 g solid) deionized water was to each material. The samples without free-standing water (0% and 30% moisture) were aged immediately for seven days as described below. The samples with free-standing water (100% and 500% moisture) were shaken for four hours. After the shaking process, the samples with 100% and 500% moisture were centrifuged and the supernatant was decanted and filtered using a 0.45 µm syringe filter. The wet solid samples were then placed in an oven at approximately 70 ºC for four hours to evaporate additional moisture to achieve a moisture content of 30%. All samples were then aged in a covered apparatus receiving a constant flow of 100% relative humidity air. After seven days, the samples were removed from the aging apparatus and air-dried for 24 hours and then oven dried at 55 ºC for 24 hours. The concentration of lead, phosphate and potassium in the supernatant of the 100% and 500% moisture samples were measured as described below.

2. 2. 3 PBET Extractions

The bioaccessibility of lead in the solid materials was monitored by a modified streamlined version of the PBET method. The PBET extraction solution was made using

a 0.4 M glycine solution adjusted to a pH of 2.3 with concentrated HCl. The solution pH was adjusted at a temperature of 37 ± 2 ºC using a pH meter calibrated with buffer solutions adjusted to 37 ± 2 ºC. A 0.1 gram soil sample, 1:100 solid to solution ratio, which has previously been shown to be consistent with a 1.0 g sample at the same solid to solution ratio , was used for running the PBET. During the 1-hour extraction, the water temperature in the bath was maintained at body temperature (37±2 ºC). The samples were removed at 60 minutes, centrifuged and filtered. Finally Pb, K and P concentration in the PBET supernatant were analyzed as described below. A NIST soil sample was run as QA/QC control at the same time.

2. 2. 4 Additional Wet Chemical Experiments

A series of homogeneous (solution phase only) and heterogenous (both solid and solution phase) wet chemistry experiments were conducted to better understand the dynamics of chloropyromorphite formation and dissolution. These experiments were conducted using a variety of sources and concentration of Pb (II) and P and auxillary chemicals (to adjust ionic strength and pH) and the aqueous concentrations of Pb and P were monitored over time as described below. Many of these experiments were conducted at room temperature (~22 ºC) rather than body temperature (37 ºC) as in the PBET solution so that the results would be more directly comparable to thermodynamic calculations, where the majority of the data is tabulated at 25 ºC. Tests were conducted to simulate the aqueous conditions in the PBET test in the absence of a solid phase.

In addition to the standard PBET chemical solution, 16.1 mM aqueous phosphate and 241 μM Pb(II) via the addition of 0.25 mL 676.2 mM KH_2PO_4 and 0.25 mL 10.12 mM

$Pb(NO_3)_2$ were added to the PBET solution. These P and Pb concentrations were equivalent to the total (dissolved plus solid) amount of phosphate and Pb in 10 mL of PBET extraction solution of a 6400 mg/kg Pb-contaminated soil plus a 5% P amendment. Because Cl^- is a constituent of chloropyromorphite, both HCl-based and HNO_3- based (using HNO_3 in place of HCl) PBET solutions were made. The glycine concentration was maintained at 0.4 M in both, but the final Cl- concentration of HCl-based PBET solution was 0.242 M and NO_3^- concentration in HNO_3-based PBET solution was 0.236 M. In addition, 0.4, 0.1, 0.01, 0.001 M glycine solution were made with 0.2 M NaCl and 0.3, 0.2, 0.1, 0.01, 0.001 M glycine with 0.2 M NaCl solution were adjusted pH to 2.3 with same method used to make the PBET solution. Also, pH 2.3 (NaCl/HCl), 4.5 (CH_3COONa/ CH_3COOH), 7.0 (Pipe/NaOH) buffer solution with 0.2 M NaCl PBET solutions were tested.

Batch experiments were conducted at 37 ºC (310 K) and room temperature, ~22 ºC (295 K). Additional solutions of just 241 μM Pb (II) and 16.1 mM $H_2PO_4^-$ were added in these solutions and DI water, respectively. A white precipitate was observed immediately in most solutions except PBET and 0.3, 0.2, 0.1 M glycine (pH=2.3). Each sample was shaken for 10 min, 20 min, 30 min, 45 min, 60 min, 2 hour, 4 hour, 8 hour, 12 hour, 24 hour, 2 day, 3 day, 4 day, 5 day, and 7 day, respectively. After shaking, the samples were opened, and an aliquot of the supernatant was withdrawn and immediately filtered with a 0.45 μm syringe filter, and the pH of the remaining solution was immediately measured with a pH meter and combination electrode. The filtrate was used to measure the aqueous chloride, phosphate and lead concentrations. After 1 hour of shaking, 0.1 g sand was added into PBET solution as potential precipitation nuclei. Pb, Cl, P concentration were

measured after adding the nuclei. All saturation indexes for chloropyromorphite in solution were calculated with Visual MINTEQ [70].

2. 2. 5 Heterogenous Chloropyromorphite Formation Test

0.254 g Phosphate Rock (about 19% P, equivalent to 0.0156 M P) was added into 10 ml PBET solution as P source with 241 μM Pb concentration, and the sample was shaken 1 hour at 37ºC. The samples were shaken for 1 hour, then centrifuged and filtered and the final Pb concentration was measured.

2. 2. 6 Chloropyromorphite Synthesis and Dissolution Test

Precipitation of various aged samples of chloropyromorphite was carried out in HDPE bottle similar to the method described by Scheckel and Ryan [47]. A solution of 0.25 M $Pb(NO_3)_2$, 0.15 M KH_2PO_4 and 0.1 M NaCl were mixed at room temperature (~22 ºC) and aged three days with the pH controlled at 7.0 by additional NaOH while purging with nitrogen. The aged material was collected by centrifugation and washed 5 times with DI water to remove excess lead, phosphate, and chloride. After washing, the chloropyromorphite was air-dried. Dissolution experiments were carried out in batch method with 0.1 g chloropyromorphite shaken with 10 mL PBET solution with 0 or 0.0161 M phosphate.

2. 2. 7 Measurements

Aqueous lead concentrations were measured with a flame Atomic Absorption Spectrometer (SpectrAA 220FS, Varian). Phosphate and chloride concentrations were

measured with an ion chromatograph (Model DX-120, AS14 column, Dionex, Sunnyvale, CA).

2. 3 Results and Discussions

2. 3. 1 Effects of Soil Moisture on Amendment Addition

Since the amendment we used in this study, potassium dihydrogen phosphate, KH_2PO_4 is relatively soluble in the aqueous phase, it will dissolve and release phosphate ions quickly in soil solution . There are a series of steps required for phosphate amendments to reduce lead bioaccessibility. First phosphate and/or Pb must dissolve into the aqueous phase, the transport media for the reactants. Secondly, phosphate, Cl, and Pb(II) must collide and react (in one step or a series of steps), resulting in the formation of chloropyromorphite. Other lead minerals will transfer to chloropyromorphite quickly in the presence of aqueous phosphate [32]. In our experiments where KH_2PO_4(s) was added to dry Pb-contaminated solids in the presence or absence of varying amounts of soil moisture, the rate controlling step of phosphate entering the aqueous phase is the water content of sample. In experiments with free-standing water (100% and 500%) moisture, the water content was sufficient to rapidly dissolve and mix the dissolution products throughout the solution. In experiments without any moisture, the formation of chloropyromorphite would necessarily be limited because of the absence of a transport media and the resulting lack of contact between Cl, Pb (II), and PO_4-containing molecules and ions. The amendment with 30% moisture corresponds to an intermediate condition of soil moisture condition with no free-standing water [71], typical of field amendment applications (e.g., at Joplin, MO, the amendments were hand applied to tilled

soil and then rototilled into the soil). Soil moisture experiments were conducted to evaluate the effect of water content on reducing bioaccessibility, and whether the increasing water content can reduce the bioaccessibility of lead in soil.

In order to determine the progress of different reactions in the amendment and PBET process, concentrations of lead, potassium (as a tracer to monitor amendment dissolution) and phosphate were monitored in PBET solution and, where possible, the supernatant of the soil solution (100% and 500% moisture only).

The K measurements in the initial soil solution for the samples with free-standing water (supernatant of 100%, 500%) indicated that KH_2PO_4 was rapidly dissolved in the 100% and 500% moisture. After 4 hours, the amount of K released to the soil solution ranged from 34.0-89.0% for the 100% moisture sample and from 47-88.1% for 500% moisture sample. In contrast, only 6.7 - 19% of the phosphate appeared in the supernatant of the 100% and 500% moisture samples respectively. This phenomena indicates either incongruent dissolution (more K than P dissolved), or, more likely, the greater reactivity of phosphate with the solid phase compared to K^+. In either case, at the end of the 4 hour period, there was ample P available to react with the Pb on a stoichiometric basis.

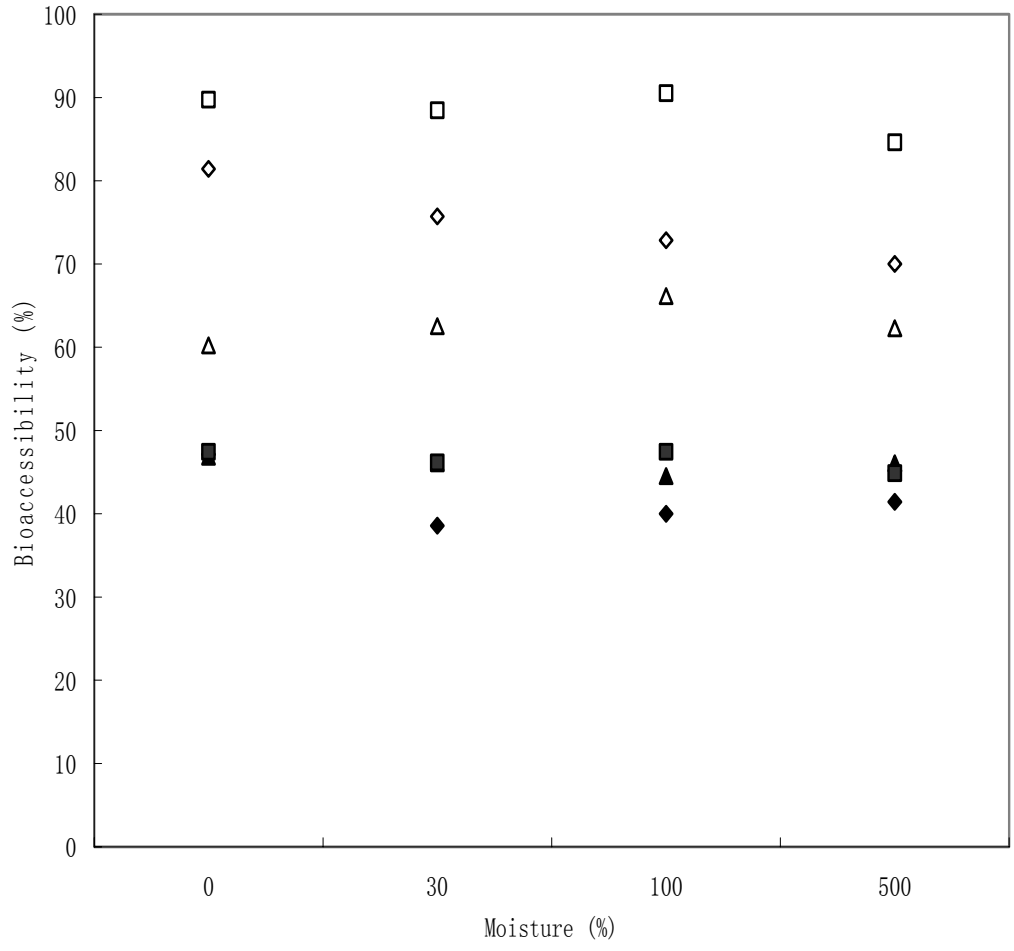

Figure 2. 1 Effect of initial moisture content on the resulting bioaccessibility of amended (closed symbol) and unamended (control, open symbol) Pb-spiked soil (diamonds), Pb-contaminated soil (triangles), and Pb-spiked sand (squares) (T = 37 ºC).

Figure 2.1 shows the bioaccessibility of the control (no phosphate added) and amended samples after seven days of aging as a function of the initial moisture content. For all samples and all moisture contents, the control (unamended, open symbols) samples exhibited higher bioaccessibility than the amended samples, indicating that the addition of phosphate to the samples markedly reduced their bioaccessibility. In addition, for the unamended samples, for all moisture contents, the bioaccessibility increased in the order expected (i.e., weathered soil has lower bioaccessibility than spiked soil and spiked soil has lower bioaccessibility than spiked sand). The bioaccessibility of the unamended Pb-contaminated soil and Pb-spiked sand was relatively independent of initial soil moisture content. However, the bioaccessibility of the Pb-spiked soil decreased as initial moisture content increased, potentially reflecting the impact of additional moisture on the aging of soils spiked with labile metals. In contrast, all three materials at all soil moistures exhibited relatively consistent bioaccessibility, indicating that the phosphate source was likely controlling the bioaccessibility of Pb for all amended samples, regardless of Pb source or moisture added with the amendment.

2. 3. 2 Lead and Phosphate in the PBET

Since the initial soil moisture content did not markedly affect the resulting lead bioaccessibility in the amended samples, we were concerned that the observed reduction in Pb bioaccessibility may have been occurring in the PBET solution itself instead of *in situ* [52, 69], at least for the 0% moisture sample. To further understand the dynamics occurring in the PBET solution, we monitored the aqueous Pb, P, and K concentrations for these samples in PBET supernatant versus time over the nominally one hour

extraction. The concentration profiles for the Pb-contaminated soil are shown in Figure 2.2 (a, b, c). For all four initial moisture contents and all three kinds of solid media (the concentration profiles for the Pb-spiked soil and Pb-spiked sand were similar and are not shown), as the extraction time increased, the concentration of Pb, K, and P increased until reaching an approximately constant concentration. The K concentrations reached an approximately constant concentration within ~10 mins. Mass balance calculations of the K decanted in the original soil solution (100% and 500% initial moisture content only) and the K in the PBET indicated that all of the original KH_2PO_4(s) amendment had been completely solubilized within at least the first ten minutes in the PBET solution.

In contrast, the Pb and P concentrations did not reach a constant concentration until approximately 20-30 minutes. This delay relative to K indicates either slower release into the PBET solution or reactions in addition to simple dissolution occurring in the PBET. For the sample that didn't receive any initial moisture with the KH_2PO_4(s), this delay in the concentration of P relative to K almost certainly indicates additional reactions of P other than simple dissolution.

Mass balance calculations were performed on aqueous phosphate measurements in PBET solution, by subtracting the phosphate concentration in the control samples (no P amendment) sample and phosphate removed with the decanted supernatant (for the 100% and 500% moisture only). The corrected phosphate percent in PBET of total amendment was near 15% for the two soil samples and near 25% for the Pb-spiked sand, indicating greater phosphate attraction for the soil than for the sand.

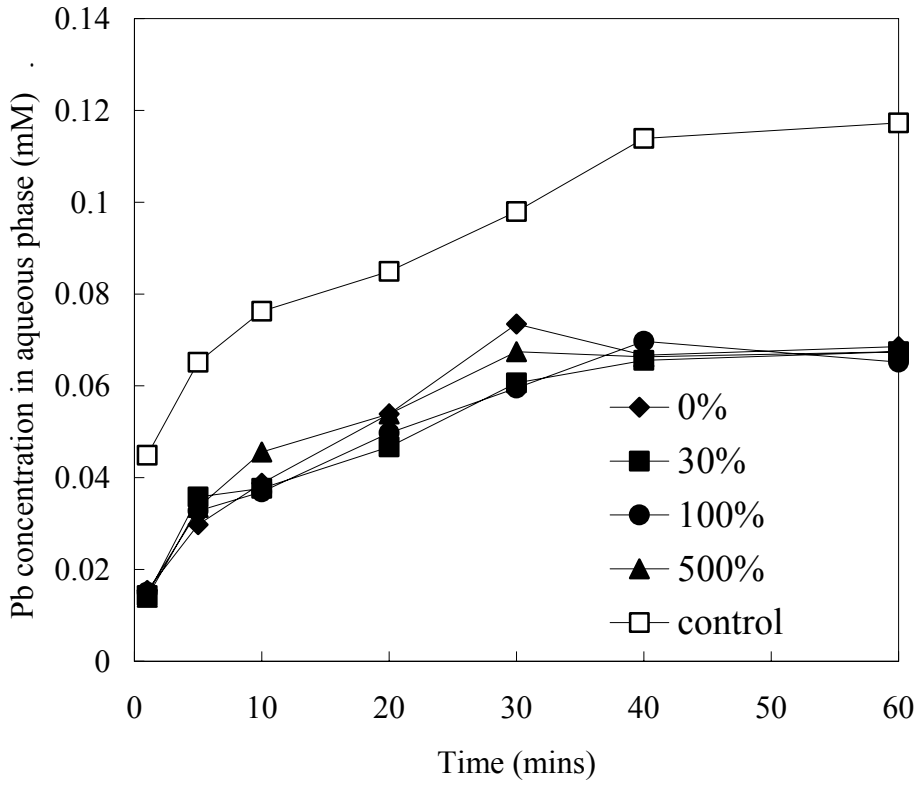

Figure 2.2 (a) Concentration of dissolved Pb during the PBET extraction of the Pb-contaminated soil (T = 37 ºC). Unamended (open symbol, 30% moisture) and amended (closed symbol) results at various initial moisture contents shown.

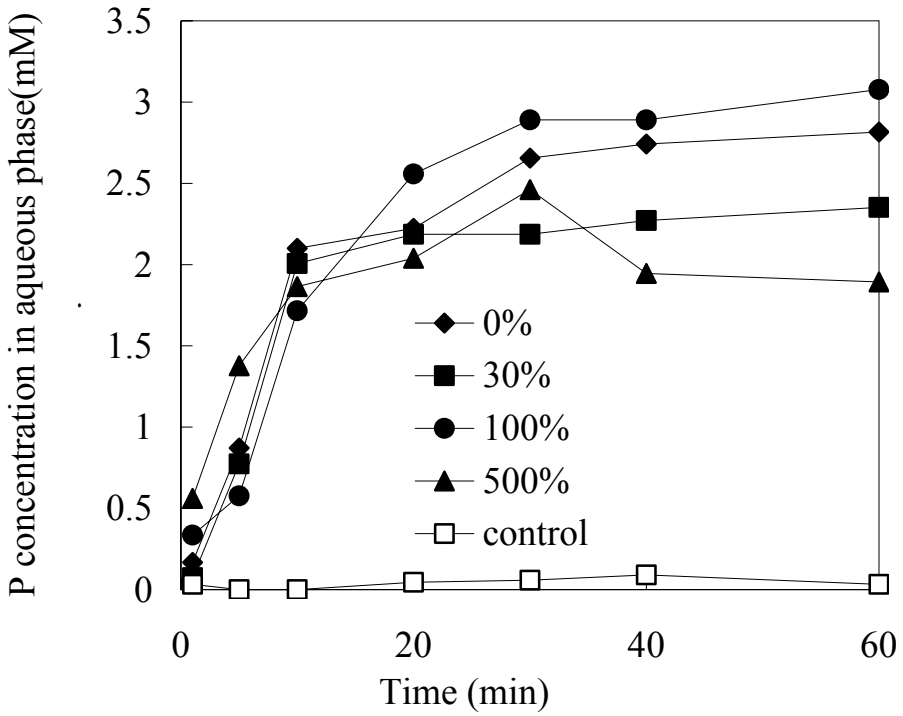

Figure 2.2 (b) Concentration of dissolved P during the PBET extraction of the Pb-contaminated soil (T = 37 ºC). Unamended (open symbol, 30% moisture) and amended (closed symbol) results at various initial moisture contents shown.

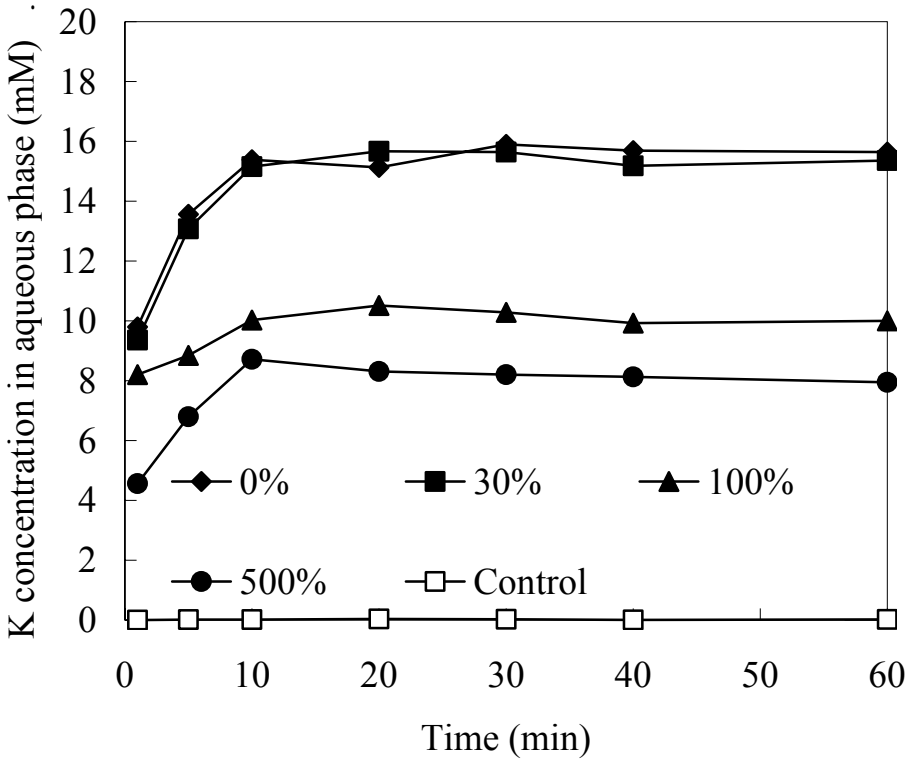

Figure 2.2 (c) Concentration of dissolved K during the PBET extraction of the Pb-contaminated soil (T = 37 ºC). Unamended (open symbol, 30% moisture) and amended (closed symbol) results at various initial moisture contents shown.

All moisture samples resulted in an initially low Pb concentration followed by a slow increase to a steady-state Pb concentration. The concentration of Pb reached a constant value in 30-40 minutes, indicating either slower release than P or additional reactions not involving aqueous P after the P concentration had reached steady-state. The saturation indices of lead minerals for all the solid sample and all sampling time (0, 10, 20, 30, 45, 60 minutes) were calculated with the different Pb, P, Cl concentration by Visual MINTEQ. For the Pb-spiked soil and the Pb-spiked sand, the saturation indices of all Pb- and P-containing solids were all well below 0, with the saturation indices of chloropyromorphite ranging from -2.99 to -1.45. It indicates that no potential lead mineral precipitation in the PBET solution for these two solids. However, for the Pb-contaminated soil, the final chloropyromorphite SI for all points were above 0, ranging from 0.56 to 1.11. The SI of all other Pb- and P-containing minerals were all well below -2.0. Thus thermodynamically, no known pure Pb- or P-containing solids could be controlling the solubility, and thus the bioaccessibility, of Pb for the Pb-spiked soil and sand, and only chloropyromorphite could be controlling the bioaccessibility of the Pb-contaminated soil.

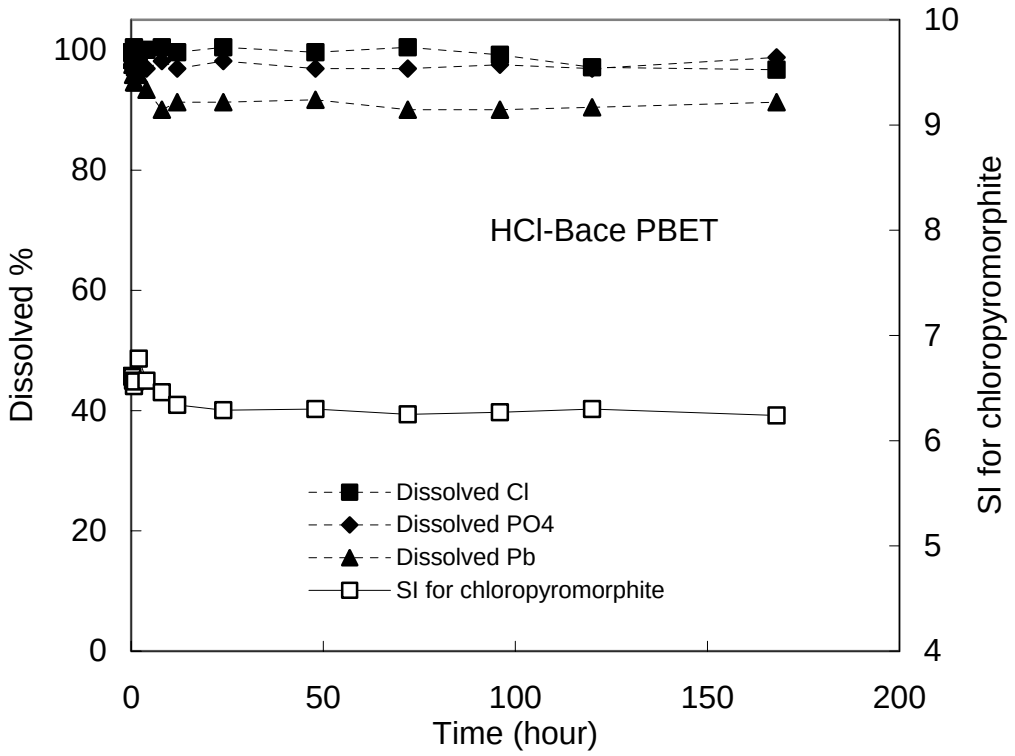

Figure 2. 3(a) Saturation indices and percentage of added Pb(II) and P in the dissolved phase as a function of aging time for HCl-based PBET solutions (~22 ºC). Initial P concentration was 0.0161 M, Cl^- concentration was 0.242 M, and Pb concentration was 0.000241 M.

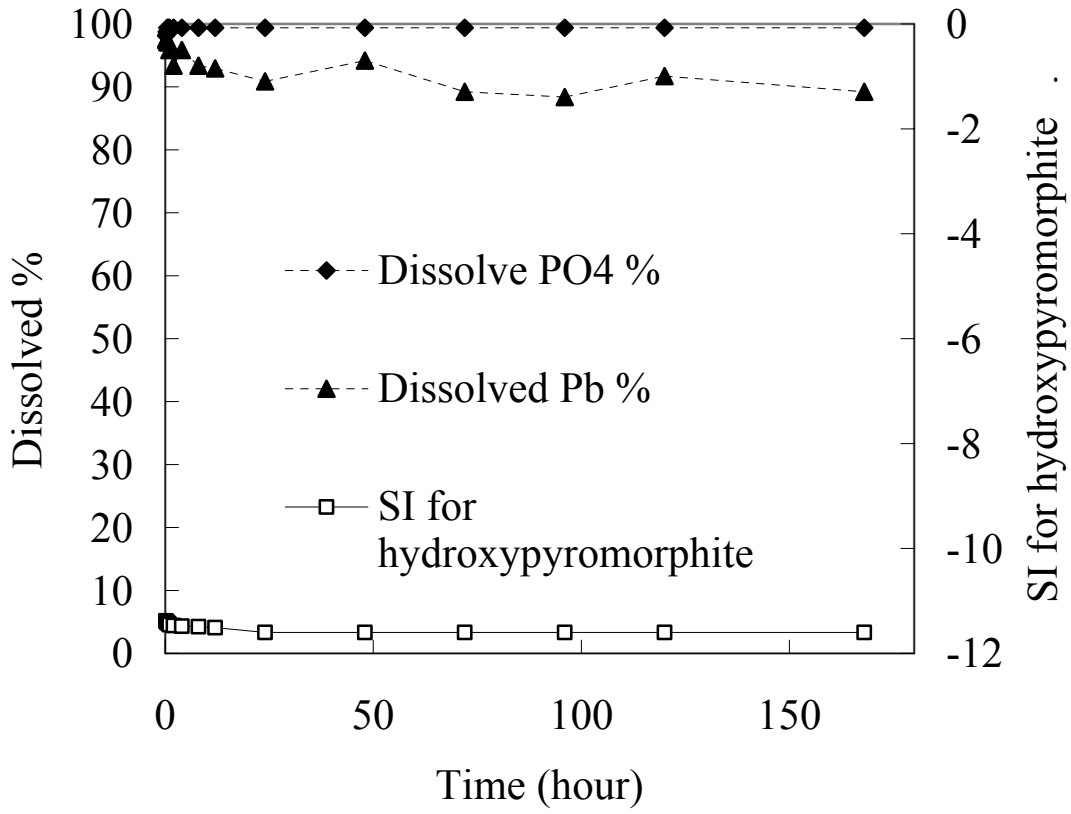

Figure 2. 3(b) Saturation indices and percentage of added Pb(II) and P in the dissolved phase as a function of aging time for HNO_3-based PBET solutions (~22 ºC). Initial P concentration was 0.0161 M, Cl^- concentration was 0.242 M, and Pb concentration was 0.000241 M.

2. 3. 3 Homogeneous Chloropyromorphite Formation Test in PBET

The concentrations of Pb and P in the PBET solutions indicated that, regardless of the amount of moisture added initially with the P amendment, the Pb concentration reached a constant concentration before the end of the PBET. However, the wide range of resulting SI values did not suggest that the samples had consistently reached equilibrium with respect to chloropyromorphite, the thermodynamically stable solid phase. To better understand the potential reactions occurring between lead and phosphate in the PBET, a homogenous test (i.e., no solid present) was performed to measure the reaction of lead and phosphate in two kinds of PBET solution, both at 37 ºC, the normal PBET temperature, and at 25 ºC in an effort to more accurately model the data thermodynamically. In addition, although the PBET protocol specifies the use of HCl as a stomach acid simulation, we conducted additional experiments with HNO_3 rather than HCl, as Cl is a potential reactant with Pb and P in the formation of chloropyromorphite in the PBET solution. Finally, the experiment at 25 was conducted for up to seven days to see where the reactions would end up. Under the normal PBET conditions (HCl, 1 hour extraction, 37 ºC) less than 5% of the Pb was removed from the PBET solution (not shown), clearly indicating the homogeneous precipitation of chloropyromorphite from the PBET was not occurring, at least not to the extent predicted thermodynamically. Similarly very little Pb (<10%, Fig. 2. 3a) was removed from the normal PBET solution at 25 ºC, even after seven days. In addition, replacing the HCl in the PBET solution with HNO_3 resulted in almost exactly the same degree of Pb removal (c. 10%, Fig. 2. 3b), even after seven days. At the end of the experiment shown in Fig. 2. 3a, the calculated SI for chloropyromorphite was 6.49, extremely oversaturated with respect to

chloropyromorphite. In fact, these solutions were initially close to saturation with respect to $PbHPO_4$(s), with SI values ranging of -0.72 and 0.61 respectively. Over the seven day period, approximately the same degree of Pb removal occurred in both solutions, decreasing the SI for $PbHPO_4$(s) to -0.76 and -0.66 respectively. The final SI for chloropyromorphite in the HCl-based PBET solution was 6.49, indicating that the solution was significantly supersaturated with respect to chloropyromorphite, even after seven days. In an attempt to potentially increase the reaction rate, pure quartz sand was added as a precipitation nuclei to some samples after 1 hour aging time, however, no difference was observed. It sum, this information clearly indicates the precipitation kinetics of this reaction are slow with comparison other chloropyromorphite formation test in homogeneous condition [35, 36].

The difference between our study and Odyakov and Zhizhina's [35] is the glycine concentration and pH. Prior works studied the complexation reaction of Pb ion and glycine [72-74]. Pb ion was easy to form complexes with high concentration glycine at low pH. Table 2.1 is the reaction and constant in the PBET solution. So a series of homogeneous chloropyromorphite formation experiments with different pH and glycine concentrations were conducted to explain the phenomena.

Table 2.1 Reactions Included in PBET Modeling (25 ºC, I= 0.1, from VM)

Chemical	Reaction	Log K
Chloropyromorphite ($Pb_5(PO_4)_3Cl$, s)	$5Pb^{2+} + 3PO_4^{3-} + Cl^- \rightarrow Pb_5(PO_4)_3Cl$	-84.4
Hydroxylpyromorphite ($Pb_5(PO_4)_3OH$, s)	$5Pb^{2+} + 3PO_4^{3-} + OH^- \rightarrow Pb_5(PO_4)_3OH$	-76.8
$Pb(OH)_2$(s)	$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2$	8.15
$Pb_3(PO_4)_2$(s)	$3Pb^{2+} + 2PO_4^{3-} \rightarrow Pb_3(PO_4)_2$	-43.53
$PbHPO_4$(s)	$Pb^{2+} + H_2PO_4^- \rightarrow PbHPO_4 + H^+$	-23.8
PbH-(glycine)$^{2+}$	$Pb^{2+} + H^+ + glycine^- \rightarrow$ PbH-(glycine)$^{2+}$	11.7
Pb-(glycine)$^+$	$Pb^{2+} + glycine^- \rightarrow$ Pb-(glycine)$^+$	5.25
$Pb(glycine)_2$	$Pb^{2+} + 2glycine^- \rightarrow Pb\text{-}(glycine)_2$	8.35
$Pb(H\text{-}glycine)_2^{2+}$	$Pb^{2+} + 2H^+ + 2glycine^- \rightarrow Pb(H\text{-}glycine)_2^{2+}$	21.3
H-glycine	$H^+ + glycine^- \rightarrow H\text{-}glycine$	9.77
H_2-glycine	$H^+ + H\text{-}glycine \rightarrow H_2\text{-}glycine^+$	12.24
$PbCl^+$	$Pb^{2+} + Cl^- \rightarrow PbCl^+$	1.67
$PbCl_2$	$Pb^{2+} + 2Cl^- \rightarrow PbCl_2$	1.89
$PbCl_3^-$	$Pb^{2+} + 3Cl^- \rightarrow PbCl_3^-$	1.91
$PbCl_4^{2-}$	$Pb^{2+} + 4Cl^- \rightarrow PbCl_4^{2-}$	1.81

2. 3. 4 Homogeneous Chloropyromorphite Formation Test in Different Condition

Other precipitation tests were performed with different pH (2.3, 4.5 and 7.0) buffer solution and different glycine concentration (0.4, 0.3, 0.2, 0.1, 0.01 and 0.001M) with or without adjusting pH to 2.3. Precipitation tests were performed in three pH buffers (2.3, 4.5 and 7.0). An interesting visual observation was noted when the Pb solution was added to the solution with P. A white precipitate formed immediately in two kinds of buffer solution (pH 4.5 and 7.0), similar with Scheckel et al.'s result in soft-drink, compare to that nothing was observed in PBET solution. The pHs in solution were monitored during the reaction, and they were kept close to the original value. From the Pb concentration versus time curves (Figure 2. 4), it seem that the reaction is very quick and above 90% Pb precipitate in the first hour. For different glycine concentration solution but without adjusting pH samples, the same white precipitations were observed. The Pb concentration dropped quickly (Figure 2. 5) in different glycine concentration solution. The pH of all of these solutions, however, remained >3.9.

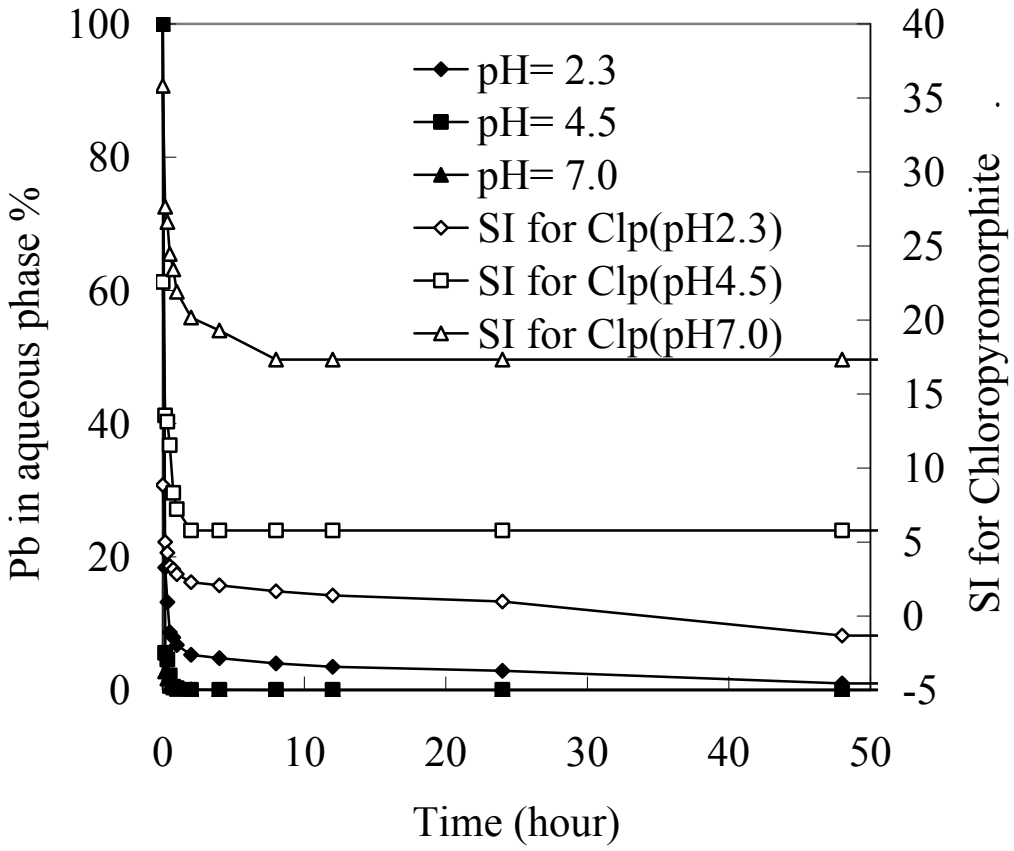

Figure 2. 4 Percentage of dissolved lead versus time in different pH buffer solutions (pH 2.3, 4.5, 7.0; 0.2 M NaCl; 22 ºC). No glycine in the solution. Initial P concentration was 0.0161 M, and Pb concentration was 0.000241 M. Total Cl^- was 0.2 M.

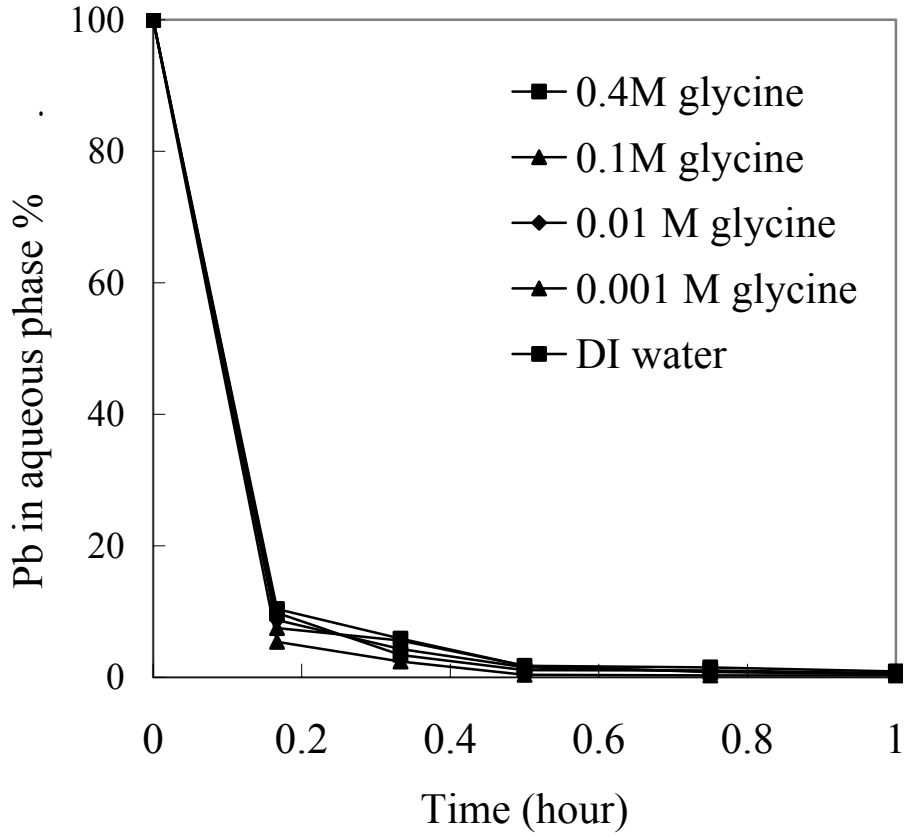

Figure 2. 5 Percentage of dissolved lead versus time in different glycine solutions (pH 3.9-6.8; 0.2 M NaCl; 22 ºC). Initial P concentration was 0.0161 M, and Pb concentration was 0.000241 M. After 1 hour, the concentration didn't change appreciably over the next 7 days.

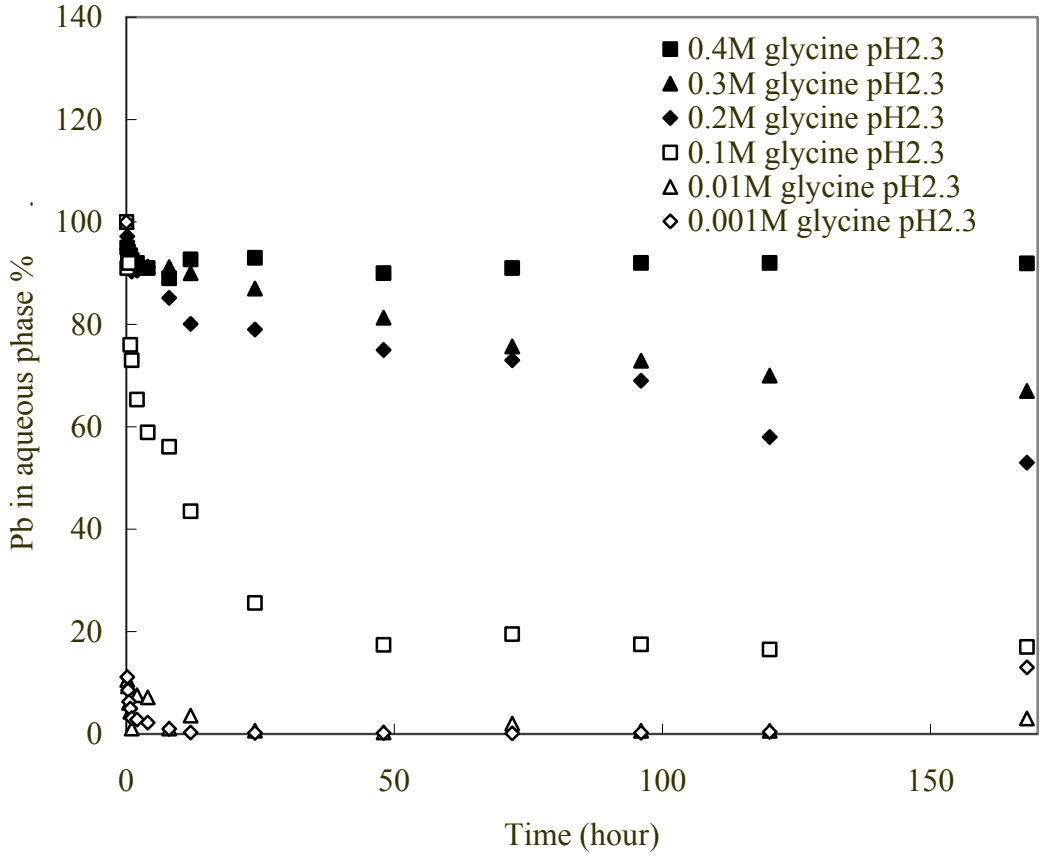

Figure 2. 6 (a) Percentage of dissolved lead versus time (7 days) in the presence of different glycine concentrations solution (T=~22 ºC, pH=2.3). Initial P concentration was 0.0161 M, Cl^- concentration was 0.242 M, and Pb concentration was 0.000241 M.

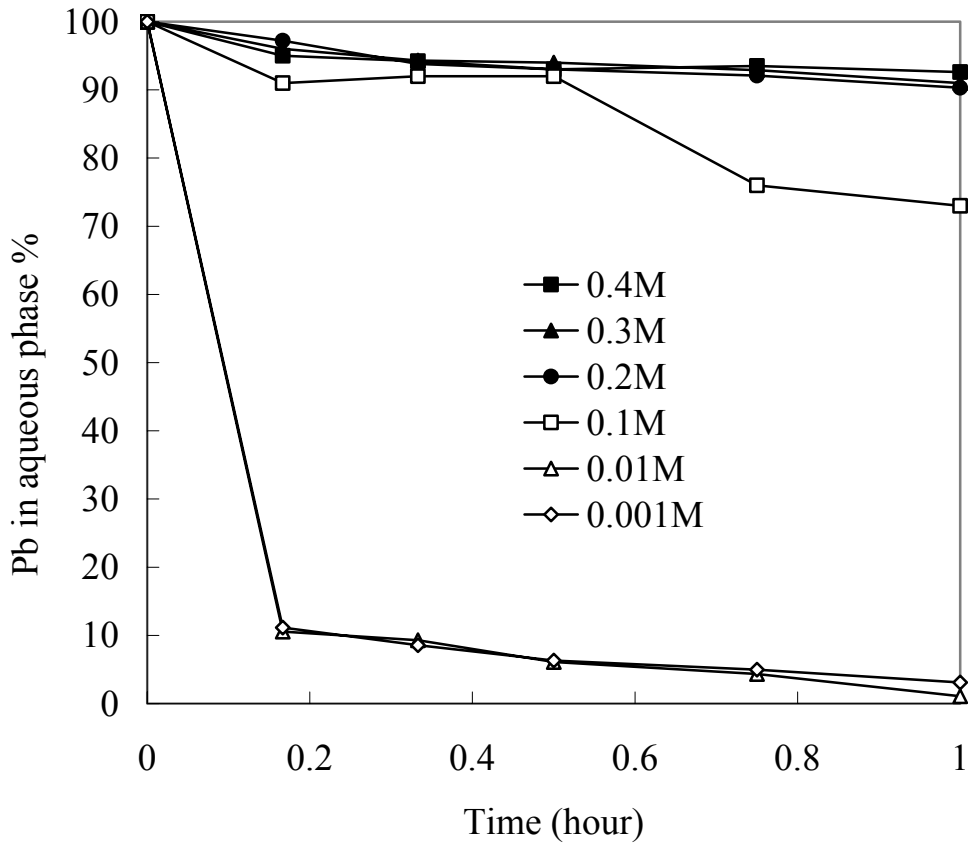

Figure 2. 6 (b) Percentage of dissolved lead versus time (1 hour) in the presence of different glycine concentrations solution (T=~22 ºC, pH=2.3). Initial P concentration was 0.0161 M, Cl^- concentration was 0.242 M, and Pb concentration was 0.000241 M. .

The experiments above show that neither low pH, the presence of glycine, nor ionic strength along interferes with the bulk precipitation of chloropyromorphite. However, as demonstrated in Figure 2. 6, at pH 2.3, as the concentration of glycine increases, the rate of precipitation of chloropyromorphite decreases dramatically. In the presence of only 0.001 and 0.01 M glycine, the Pb concentration dropped very rapidly (<15 min) and had dropped to less than 5% of its initial concentration within one hour. However, when the glycine concentration was increased to 0.1 M, the white precipitate was not observed after just 1 hour, at which time there was still near 70% Pb for 0.1 M and >90% Pb for 0.2 and 0.3 M in the solution.

The saturation index of chloropyromorphite in 0.1 M glycine solution before reaction was 7.8, and after 7 days reaction the saturation index of chloropyromorphite in 0.1 M glycine is 3.95. And the saturation index of chloropyromorphite in 0.4 M glycine solution before reaction was 6.7, and after 7 days reaction the saturation index of chloropyromorphite in 0.4 M glycine is 6.49. It seems that the high concentration glycine will block the precipitation in low pH and keep the solution over-saturated.

2. 3. 5 Heterogeneous Chloropyromorphite Formation

Rock phosphate was added into Pb-PBET solution as a P source. Figure 2. 7 is the aqueous lead percent in PBET solution after adding the rock phosphate. After 1 hour aging at 37 ºC, 89.1% Pb was still in aqueous phase, this phenomenon indicate in heterogeneous condition, the transformation reaction of lead to solid phase in the present of phosphate in PBET environment is slow, only 11% Pb was transfer to solid phase . This illuminates that the lead removal reaction (chloropyromorphite formation) is slow in

PBET solution under both homogenous and heterogeneous conditions. Based on the results from heterogeneous and homogeneous condition, we propose that the high concentration of glycine will block the reaction among Pb^{2+}, Cl^- and PO_4^{3-}, because chloropyromorphite formation is a multi-ion compound, glycine can affect the collision of ions.

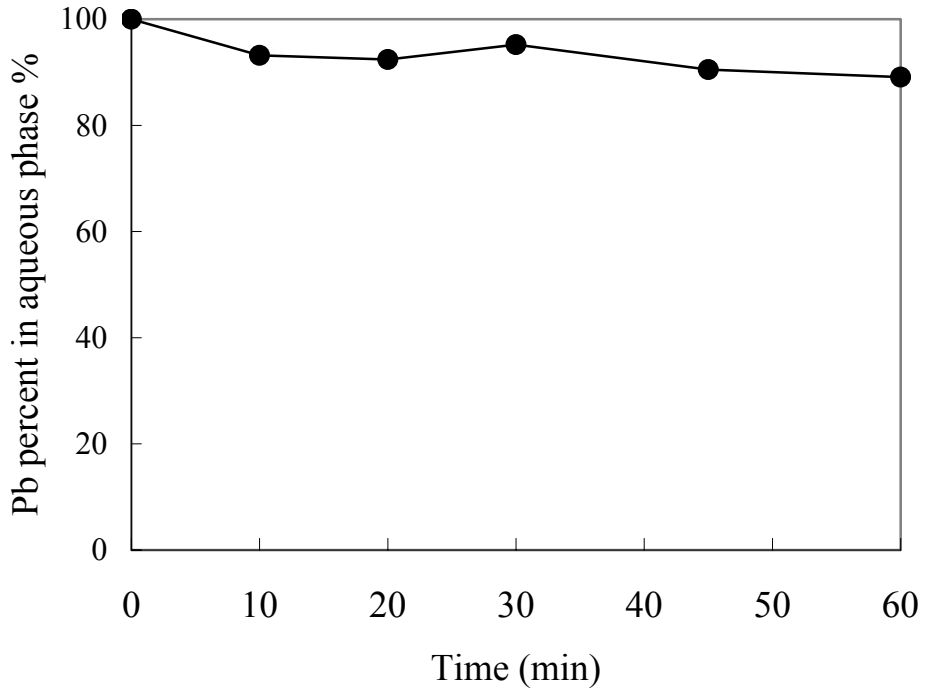

Figure 2. 7 Percentage of Pb in aqueous phase vs. time with solid phosphate rock added to the PBET solution (37 ºC). Total Pb in PBET solution was 0.000241M and total P concentration was similar 0.0161M.

2. 3. 6 Chloropyromorphite Dissolution

Figure 2. 8 show the Pb^{2+} concentration change during the dissolution of chloropyromorphite in 1 hour. In the present of P, only 0.3% Pb of chloropyromorphite dissolved from solid. This rate of dissolution was slower than Scheckel and Ryan's result [47]. The other hand, the saturation indices of chloropyromorphite of the PBET solution during 1 hour were 5.168~5.81 without P and 6.34~7.04 for with P. It seems that chloropyromorphite is over-saturated in the PBET solution. Although Pb solubility sometimes does not conform to thermodynamic predictions, this specific observation, the apparent supersaturation of chloropyromorphite, has been noted in a number of other studies. For example, adding phosphate and chloride to soil reduced Pb solubility but not to the level predicted thermodynamically, suggesting potential inaccuracies in the thermodynamic data [41, 75]. Martínez et al. continually observed dissolved Pb^{2+} activity in suspension one to two orders of magnitude higher than predicted thermodynamically, even in samples aged up to three years, which was consistent with several other published data sets. Perhaps most relevantly, Lang and Kaupenjohann consistently observed solutions apparently oversaturated with respect to chloropyromorphite, particularly at low pH in the presence of organic ligands, which they potentially attributed to kinetic limitations, colloids, and crystallization inhibition. Whatever the cause, our data clearly do not support the formation of chloropyromorphite in PBET solution.

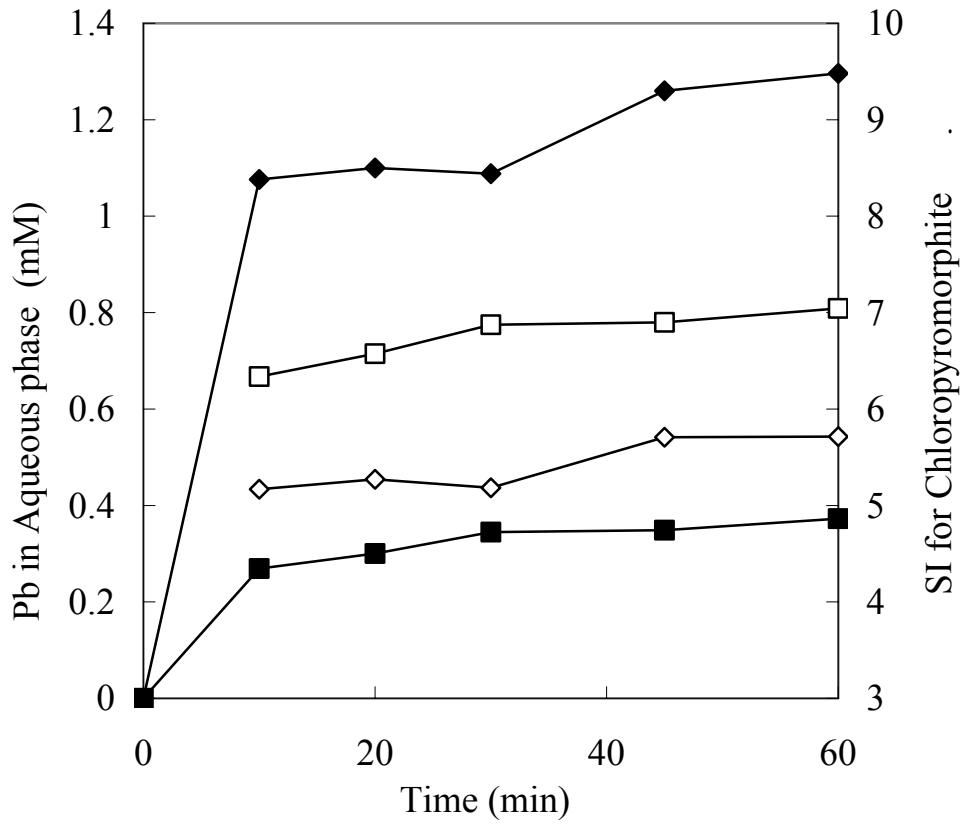

Figure 2.8 Pb release chloropyromorphite in the PBET as a function of time (37ºC). 0.1 g chloropyromorphite was added into 10 ml PBET solution with 0.0161M phosphate (■) and without phosphate (◆). Saturation indices were calculated by visual MINTEQ with P (□) and without P (◇)

2. 3. 7 Conclusion

In the PBET process for the three amended solids, the concentration of K^+, Pb^{2+} and $H_2PO_4^-$ increased in the one hour PBET time. For both Pb-spiked soil and Pb-spiked sand, the saturation indices of lead-phosphate minerals were below 0. This result indicated no potential lead mineral precipitation in the PBET solution for these two solids. However, for Pb-contaminated soil, due to the high initial soil Pb concentration, after 10 minutes in the PBET process, the SI for all points were above 0 (0.56-1.12). These numbers indicated that the PBET solutions were oversaturated.

In the homogeneous chloropyromorphite formation test in PBET solution, under the normal PBET conditions (HCl, 1 hour extraction, 37 ºC) less than 5% of the Pb was removed from the aqueous phase, clearly indicating that the homogeneous precipitation of chloropyromorphite from the PBET was not occurring to any significant extent. Under heterogeneous conditions, after one hour aging at 37 ºC, 89.1% Pb was still in aqueous phase. It showed that the transformation reaction of lead to solid phase was very slow in the present of phosphate in PBET solution.

These results illuminate that the lead removal reaction (chloropyromorphite formation) is very slow in PBET solution under both homogenous and heterogeneous conditions. Based on this conclusion, we speculate that high concentrations of glycine may block the reaction among Pb^{2+}, Cl^- and PO_4^{3-} by affecting the collision of ions since chloropyromorphite formation involves multiple ions. This result also indicates that the immobilization of lead occurs more under *in situ* conditions than in the PBET process.

CHAPTER Ⅲ

IN SITU SOIL IMMOBILIZATION OF ARSENIC BY NANOSCALE ZERO-VALENT IRON, FERROUS SULFIDE (FeS), MAGNETITE (Fe_3O_4) PARTICLES

3. 1 Introduction

Arsenic in soils and groundwater results from natural sources (e.g. natural geochemical reactions) as well as anthropogenic activities, such as mining, discharges of industrial wastes, military activities, and application of agricultural pesticides. Arsenic is ranked the second most common inorganic pollutant in the U.S. superfund sites [76]. Arsenic contaminated soils, sediments and waste slurry are major sources of arsenic in food and water. To mitigate the toxic effect on human health, the maximum contaminant level (MCL) for arsenic in drinking water was lowered from the previous 50 ppb to 10 ppb, effective in January 2006.

Arsenic is a redox active element, with *As*(V) or (III) being the two most common stable oxidation states in soils [77]. In general, inorganic arsenic is more toxic than organic arsenic [78], and arsenic in soils is less bioavailable and less bioaccessible than arsenic in water due to soil adsorption effect [79].

Arsenate can strongly interact with soils, especially, iron (hydr)oxides. Adsorption of arsenate by iron (hydr)oxides have been widely studied [80-88]. These studies have focused on the adsorption and surface complexation of arsenic on the amorphous and

crystalline iron oxide structures, such as ferrihydrite and goethite. The complexation between arsenate and iron (hydr)oxide surfaces has been known to be inner-sphere surface complexation as either mono-dentate core sharing, bi-dentate core sharing, or bi-dentate edge sharing complexes [80, 89].

Laboratory-scale and field-scale studies have been reported on *in situ* remediation of *As*-contaminated groundwater by zero-valent iron (ZVI) [90-92] and iron oxides [93]. They observed that ZVI can reduce the concentration of *As* in aqueous phase. Recently, nanoscale iron-based media (such as zero-valent iron) have been studied for potential uses in environmental remediation [94-96]. Because of the small particle size, large surface area, and high reactivity, these nanoscale materials have showed great potential for treatment of contaminated soil and groundwater [97-99]. Cumbal and Sengupta [100] studied arsenic removal from water by hydrated iron oxides nanoparticles loaded on polymer-matrix, and the immobilized nanoscale iron oxides displayed high sorption capacity for both arsenite and arsenate. For the arsenic removal in groundwater by iron-based nanoparticles, surface adsorption appears to an important mechanism [101]. Compared to commercial iron powder or granular iron particles, ZVI nanoparticles offer much faster sorption kinetics and are more deliverable in the subsurface. Consequently, iron nanoparticles hold great potential to immobilize arsenic *in situ* in contaminated soil and groundwater [94].

However, because of the high reactivity and inter-particle interactions, ZVI nanoparticles tend to agglomerate rapidly, resulting in the formation of much large (>microscale) particles and loss of reactivity and soil mobility. To prevent iron nanoparticle agglomeration, various particle stabilization strategies were reported [102-

104]. He and Zhao [104] reported a new method for synthesizing stabilized iron nanoparticles by using some low-cost and environmentally benign starch and cellulose as a stabilizer. The stabilized nanoparticles displayed much improved physical stability, soil mobility, and reactivity compared to non-stabilized iron particles.

To quantify relative *As* mobility and leachability in soil, two operationally defined measures, bioaccessibility and TCLP (toxicity characteristic leaching procedure) leachability, have been commonly used. Bioaccessibility is quantified by a physiologically based extraction test (PBET), which mimics the conditions in human stomach and essentially reflects *in vivo* accessibility of *As* [50]. TCLP is an EPA-defined standard method for measuring extractability of various chemicals from solid wastes. Earlier, a number of researchers [105-107] used TCLP tests to evaluate the leachability of *As* in contaminated soils.

Akhter et al. [107] concluded that higher iron content in soil reduces the leachability of arsenic. Yang et al. [62] observed that high iron content reduced the bioaccessibility of arsenic in soil.

The objective of this study was to test the effectiveness of stabilized nanoparticles for reducing the bioaccessibility and TCLP leachability of arsenic in soils. Three types (ZVI, FeS, and Fe_3O_4) of stabilized nanoparticles were prepared using a water-soluble starch as a stabilizer, and then used for treating two representative soils in batch experiments. Effects of the *Fe*-to-*As* molar ratio were examined on the treatment effectiveness.

3. 2 Materials and Method

3. 2. 1 Materials

All chemicals used in this study were of analytical grade or above, and were obtained from Fisher Scientific (Pittsburgh, PA). All solutions were prepared with deionized water (18 MΩ·cm).

An *As*-contaminated sandy soil (*As* concentration: 315 mg/kg and denoted as WAOS) was collected from Washington Orchard, an orchard contaminated from application of *As*-based pesticides. In addition, a relatively clean clay soil was collected near a small police firing range in east-central, Alabama, USA. Both soils were first fractionated using standard sieves, and soil fractions of <250 μm were used in all experiments.

The WAOS soil has an iron content of nearly 5.24% and a soil pH of 6.75. The range soil has a higher iron content soil (12.2%) and a soil pH of 4.83. For subsequent testing, the range soil was first spiked with arsenic following the procedures by Yang et al. [62], resulting in an arsenic concentration of 89 mg/Kg.

3. 2. 2 Preparation of Nanoparticles

The method developed by [104] He and Zhao was adopted for preparing ZVI Nanoparticles. In brief, a water-soluble starch (Alfa Aesar, Wall Hill, MA) was used as a stabilizer in the preparation. The preparation was carried out in a 250 mL flask. Before use, deionized (DI) water and starch solution were purged with N_2 for 2 h to remove dissolved oxygen (DO). $FeCl_3$ stock solution was added to a starch solution (2.4%) through a buret, to give a final Fe concentration of 2.35 g/L and a starch concentration of 1.2%. The final pH was 8.1. Then, Fe^{3+} was reduced to Fe^0 using stoichiometric amounts

of sodium borohydride (equation 3.1). To ensure efficient use of the reducing agent BH_4^-, the reactor system was operated in the absence of DO. The flask was shaken via hands during the reaction.

$$Fe(H_6O_3)^{3+} + 3\ BH_4^- + 3\ H_2O \rightarrow Fe^0 + 10\ (0.5)H_2 + 3\ B(OH)_3 \qquad (3.1)$$

A method used by Si et al. [108] was modified for synthesizing magnetite (Fe_3O_4) nanoparticles. First, 50 mL of an aqueous solution of $FeCl_2 \cdot 4H_2O$ (5.0 g/L as Fe) was added dropwise to a 50 mL aqueous solution of 2.55% (w/v) starch solution under continuous shaking. The mixture was shaken for 30 minutes to allow for formation Fe^{2+}-starch complex. Then, the pH of the solution was then increased slowly to 11 by adding 0.5 M NaOH solution. The reaction mixture was subsequently aged for 1 h with constant shaking, give a final Fe concentration of 2.35 g/L and a starch concentration of 1.2%. (equation 3.2).

$$6\ Fe^{2+} + O_2 + 12\ OH^- \rightarrow 2\ Fe_3O_4 + 6\ H_2O \qquad (3.2)$$

The method by Xu and Akins [109] for preparing CdS nanoparticles was modified for preparing our starch-stabilized FeS nanoparticles. First, deionized water and starch solution (3.6%) were purged with pure nitrogen to remove the dissolved oxygen. The, $FeCl_2$ solution was prepared and added into starch solution to form Fe-starch complex (Fe: 3.525g/L, Starch: 1.8% (w/v)). Na_2S solution (4.03g/L as S) was added dropwisely to Fe-starch solution to form the FeS nano-particles, give a final Fe concentration 2.35g/L and 1.2% starch concentration. Final pH was 6.8. Equation 3.3 gives is the reaction stoichiometry.

$$FeCl_2 + Na_2S \rightarrow FeS + 2\,NaCl \quad (3.3)$$

3. 2. 3 Treatments for As-Contaminated Soils

A series of soil treatment tests were performed in 15 mL centrifuge tubes (Fisher, polypropylene tube), where 2 g of two kinds of an *As*-laden soils sample was mixed with a nanoscale particles (Fe_3O_4, FeS, or NVI) suspension. To test the effect of iron dosage on arsenic immobilization effectiveness, the range of *Fe*:*As* molar ratio (5:1, 10:1, 25:1, 50:1, 75:1, 100:1) was tested. In all cases, the soil-to-solution ration was either 1g: 2mL solid-aqueous ratio (for *Fe:As* molar ratio of 5:1, 10:1, or 25:1) or and 1g: 10mL solid-water ratio (for *Fe:As* molar ratio of 50:1, 75:1, 100:1). In addition, control tests were carried out in parallel with 2 g of a soil with 4 mL and 10 mL, respectively, of 1.2% starch solution. After the mixtures were shaken thoroughly for 5 minutes, the tubes were placed on a rotator for 3 days or 7 days. After the treatments, all samples were centrifuged with 6000 g force (Fisher, Accuspri 400 centrifuger). Arsenic and iron concentrations in the supernatants were monitored after centrifuging. Upon removal of the supernatant, each soil sample was oven-dried at 70°C for one day. 0.1 g of treated soils was sampled and used for PBET, 0.5 g for TCLP tests, and 1.0 g for soil pH measurements. To ensure data quality, all tests were performed in duplicates.

3. 2. 4 TCLP and PBET Extraction Test

The bioaccessibility of lead was monitored by a modified PBET method [61, 62]. PBET extraction solution was made using a 0.4 M glycine solution adjusted to a pH of 1.5 using HCl solution. In each PBET test, 0.1 gram of a soil sample is mixed with 10 mL

of the extraction solution, i.e. a, 1:100 solid-to-solution ratio of 1:100. During the 1-h extraction, water temperature was maintained at body temperature (37±2 °C) with a water bath. After the extraction, the samples were centrifuged at 1000 g force. The supernatant was then filtered using 0.45μm filter (Fisher, DISPNR 25mm 0.45μm filter), and then analyzed for arsenic extracted. To ensure QA/QC, NIST soil samples were also subjected to the same procedure.

TCLP tests were performed to evaluate the leaching potential of arsenic in the untreated and treated *As*-contaminated soils following the US. EPA protocol (Method SW-846). In brief, 0.5 g of an air-dried soil sample was mixed with the TCLP extraction solution at a solid-to-liquid ratio of 1:20. The mixtures were placed on a rotating shaker operated at 30 rpm. After 18 hours of extraction, the samples were centrifuged at 1000 g force, and the supernatants were separated by 0.45 μm filter. The soluble arsenic concentration in the filtrate was analyzed with AAS.

3. 2. 5 Analytical Method

Aqueous samples were diluted as necessary and analyzed for aqueous *As* and *Fe* concentrations. A graphite-furnace atomic absorption spectrometer (GFAA) was used to analyze *As* concentration. Aqueous *Fe* concentrations in samples were analyzed using a flame atomic adsorption spectrometer (FLAA). Solution pH was measured with a pH meter (Thermo Orion, pH meter 410).

3. 3 Results and Discussion

3. 3. 1 Treatment Effects on Soil Chemistry

As mentioned earlier, treated soil samples were first centrifuged. To ensure mass balances for both the nanoparticles and arsenic in the systems, total Fe and *As* in the supernatants were also analyzed. For the range soil samples treated with the three nanoparticles, iron concentration was less than 1% of total Fe amount added, and arsenic concentration was less than 0.5% total arsenic initially in the soils. These observations indicated that upon the high speed centrifuging, virtually all of the nanoparticles were removed from the aqueous phase. For the WAOS soil samples, 0.1-1.1% of total iron and 1.1-2.4% of arsenic stayed in the supernatant when treated with Fe_3O_4 nanoparticles, whereas 1.5-2.6% of total iron and 0.9-2.7% of arsenic remained in the supernatants with nanoscale NVI particles; and 1.3-3.9% of total iron and 0.3-2.7% arsenic were in the supernatants with FeS nanoparticles. These results again indicated that most of iron treatments were removed from the solution.

The soil pH was also measured after the treatments. All results were showed in Table 3.1. For two type's soils, pHs of control samples were similar with the initial soil pH, and after NVI and FeS Nanoparticles treatments, the soil pHs didn't change. However, because Fe_3O_4 nanoparticles solution has a high pH (~11), the pH of soil samples increase a little after nanoscale Fe_3O_4 particles treatment.

Table 3.1 pH Change for Different Molar ratio Treatments

Fe/As molar ratio	Initial pH	Control samples* (0)	5	10	25	50	75	100
WAOS-NVI*	6.75	6.73-6.89	6.74	6.71	6.73	6.82	6.79	6.89
WAOS-Fe_3O_4			7.03	7.15	7.17	7.19	7.26	7.37
WAOS-FeS			6.64	6.71	6.67	6.78	6.86	6.95
As-spiked-NVI	4.83	4.83-4.93	4.78	4.86	4.82	4.91	4.89	5.02
As-spiked-Fe_3O_4			4.96	5.03	5.04	5.12	5.17	5.35
As-spiked-FeS			4.81	4.91	4.89	4.87	4.94	5.03

*Control samples: for different soil/solution ratio and starch solution.
*WAOS-NVI: It is WAOS soil and NVI treatment.

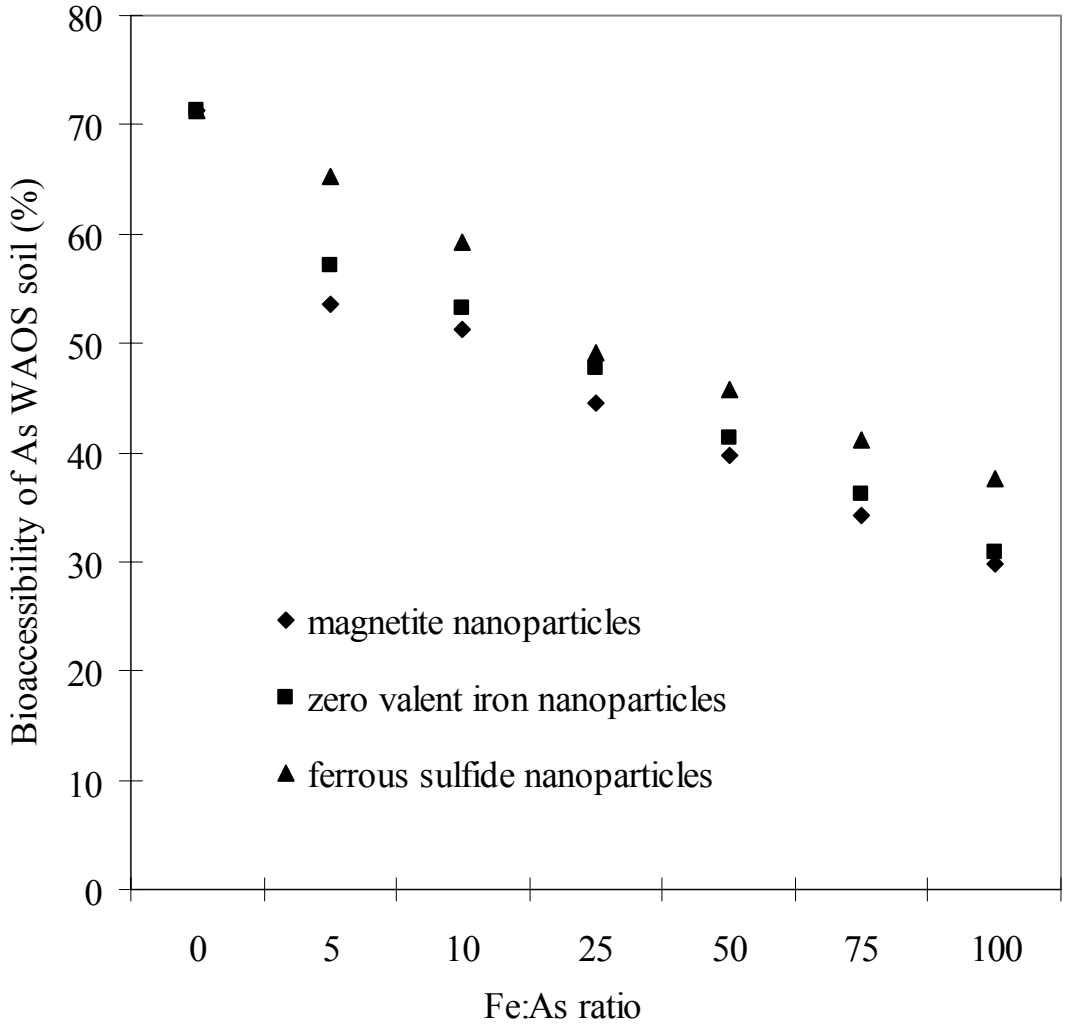

Figure 3. 1 Comparison of As bioaccessibility (PBET) of WAOS soil sample by different Fe/As ratio iron based nanoparticles treatments.

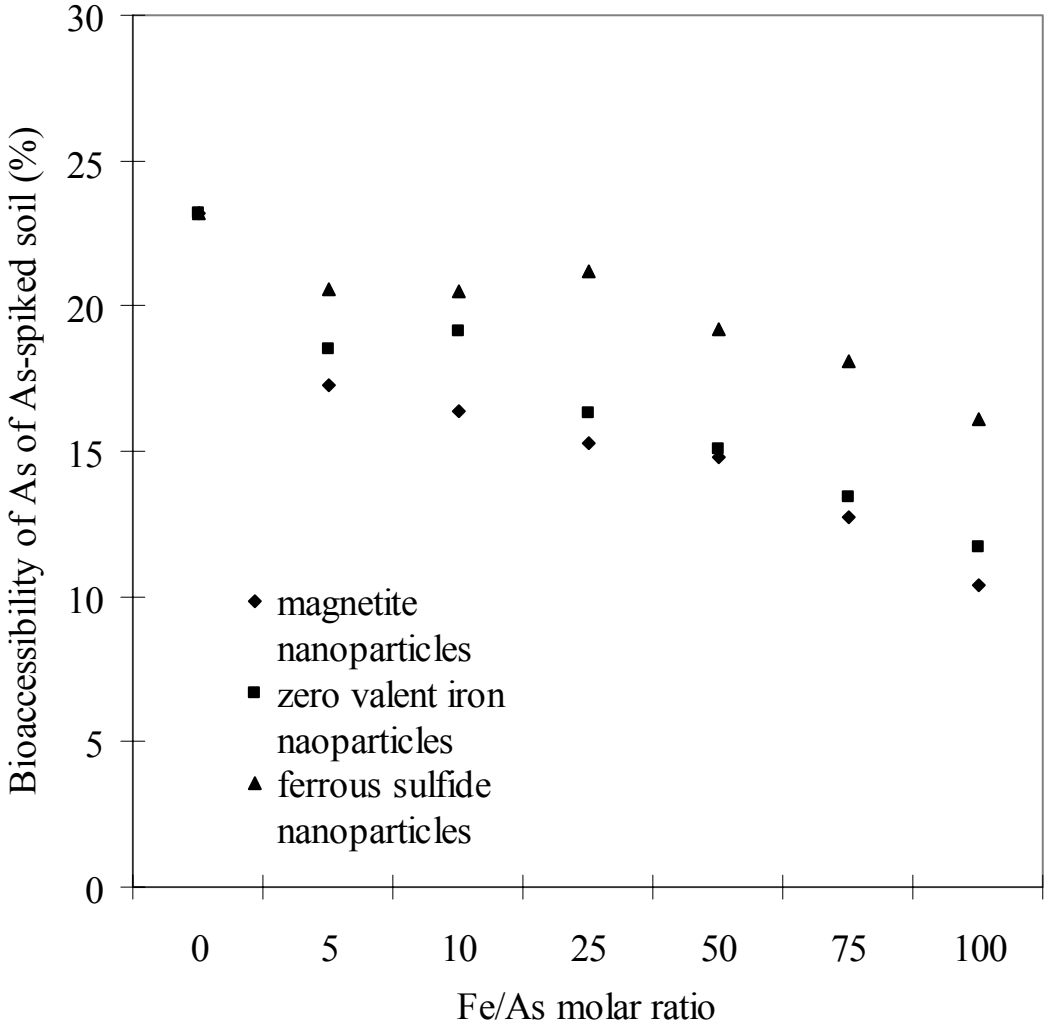

Figure 3. 2 Comparison of As bioaccessibility (PBET) of As-spiked soil sample by different Fe/As ratio iron based nanoparticles treatments.

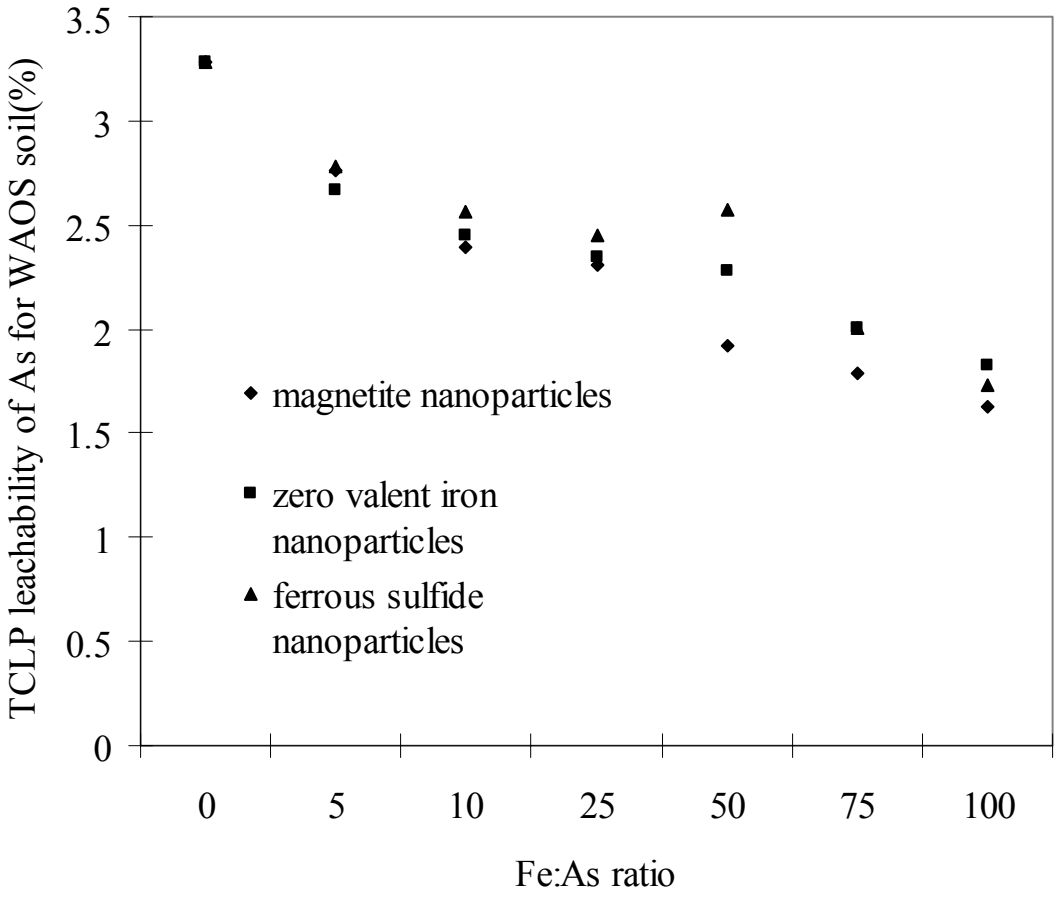

Figure 3.3 Comparison of As TCLP leachability of WAOS soil samples by different Fe/As ratio iron based nanoparticles treatments.

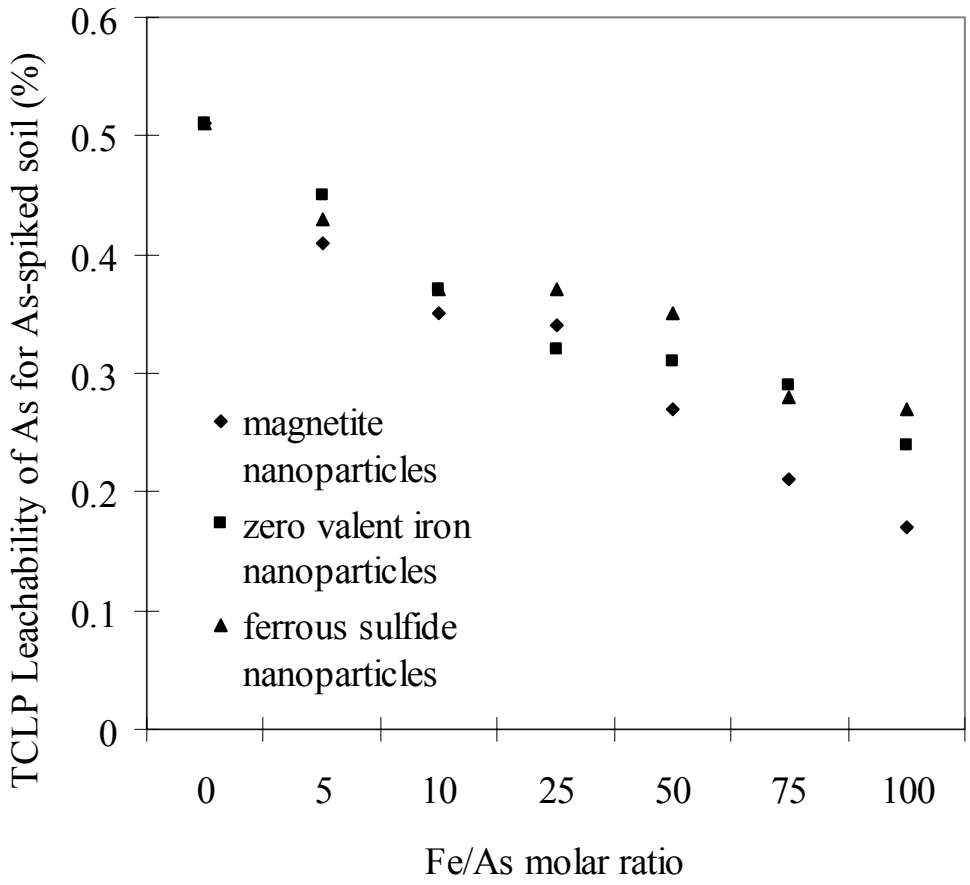

Figure 3. 4 Comparison of As TCLP leachability of As-spiked soil samples by different Fe/As ratio iron based nanoparticles treatments.

3. 3. 2 Reduction of PBET Bioaccessibility

The PBET-based bioaccessibility of arsenic for WAOS soil samples were measured after the treatments, and is given in Figure 3.1. Figure 3.1 shows that with the increasing *Fe/As* molar ratio, the bioaccessibility decreased progressively. After three days of the treatments, the bioaccessibility of *As* decreased from an initial 71.3±3.1% to 29.8±3.1%, 30.9±3.2%, 37.6±1.2% for *Fe/As* ratio 100:1 Fe_3O_4, NVI, FeS nanoparticles, respectively. Earlier, Subacz [110] studied the reduction of bioaccessibility of the same soil with *Fe/As* ratio 100:1 $FeCl_3$ amendment, and the bioaccessibility decreased to 33% after treatment. Compare to Subacz's result, magnetite nanoparticles treatment appears a little better (29.8% vs. 33%) than normal iron amendments.

For the As-spiked soil, similar results were observed (Figure 3.2). After three days of the treatments, the bioaccessibility of *As* decreased from an initial 23.2±2.8% to 10.4±1.5%, 11.7±1.4%, 16.1±0.8% for *Fe/As* ratio 100:1 Fe_3O_4, NVI, FeS nanoparticles, respectively. For the two soils, Fe_3O_4 nanoparticles appear to be most effective for *As* immobilization. The better performance of Fe_3O_4 nanoparticles treatment is at least partially due to the elevated soil pH upon the treatment. Earlier, Yang et al. [62] reported that bioaccessibility decreases with increasing soil pH. The treatment was more effective for the range soil, which has a >2 times greater iron content. Yang et al. [62] concluded that bioaccessibility of soil arsenic decrease with increasing iron content. Akhter et al. [107] also studied relationship between TCLP leachability of *As*-contaminated soils and iron content, and he correlated the leachability of *As* in soils and with iron content.

3.3.3 Reduction of TCLP Leachability

The initial TCLP leachability for both of the soils was quite low. The results were showed by Figure 3.3 and 3. 4. TCLP leachability is the *As* percent in the leachate vs. the total *As* content. The initial TCLP leachability for the untreated range soil was 0.51% and 3.28% for the untreated WAOS soil. This result was in accord with those reported by Akhter et al. [107], they studied *As*-contaminated soil from industrial sites. No TCLP leachates showed arsenic concentrations as high as 5 mg/L, which is the EPA benchmark value for a hazardous waste. When treated at the 100 *Fe/As* ratio, the leachability of arsenic in the WAOS soils decreased from the initial 3.28±0.78% to 1.63±0.16%, 1.83±0.06%, 1.73±0.17% by Fe_3O_4, NVI, FeS nanoparticles, respectively; whereas the leachability for the range soil decreased from the initial 0.51±0.11% to 0.17±0.04%, 0.24±0.03%, 0.27±0.04% by Fe_3O_4, NVI, FeS nanoparticles, respectively. For both soils, the *As* leachability was the lowest when Fe_3O_4 nanoparticles were applied. Miller et al. also observed that *As* in TCLP liquid was reduced for an *As*-contaminated soil from 1.42 to 0.26 mg/L by adding iron treatments (added $FeSO_4$) [105].

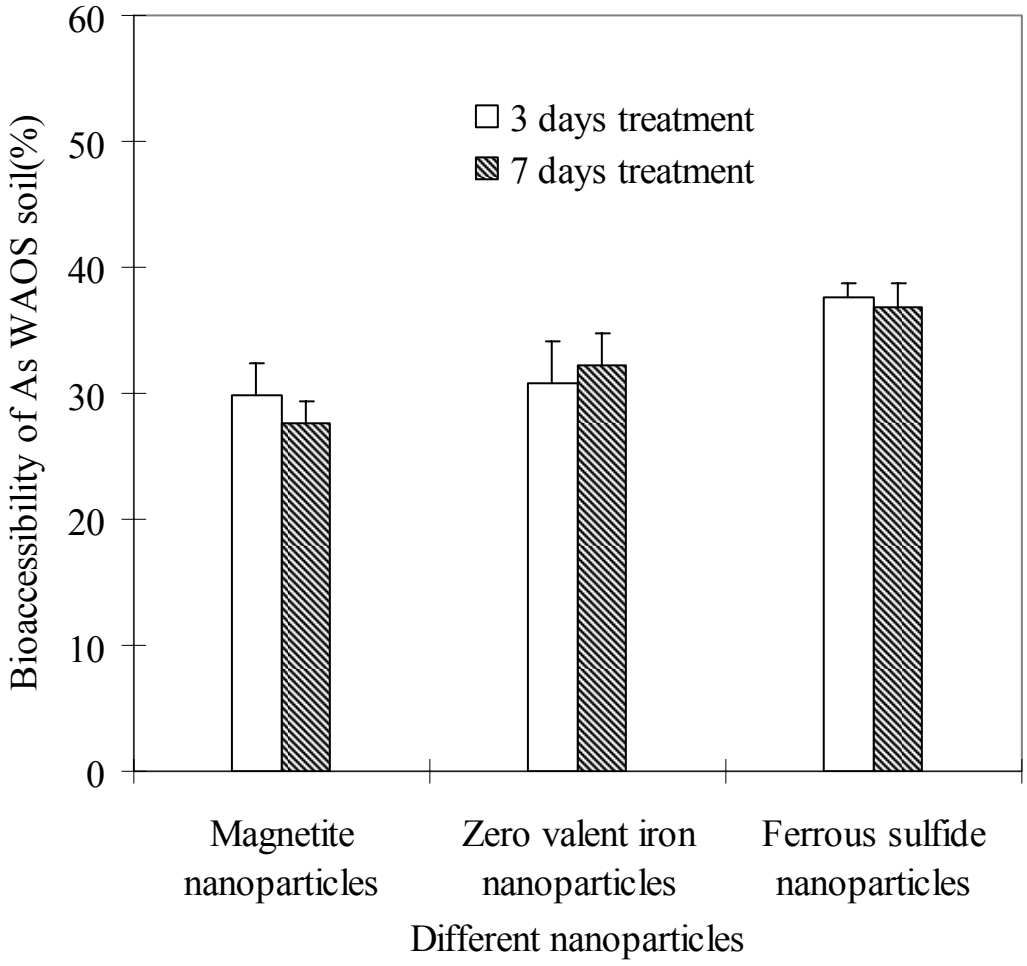

Figure 3. 5 Comparison of As bioaccessibility of WAOS soil samples for 3 and 7days treatment by different iron based nanoparticles

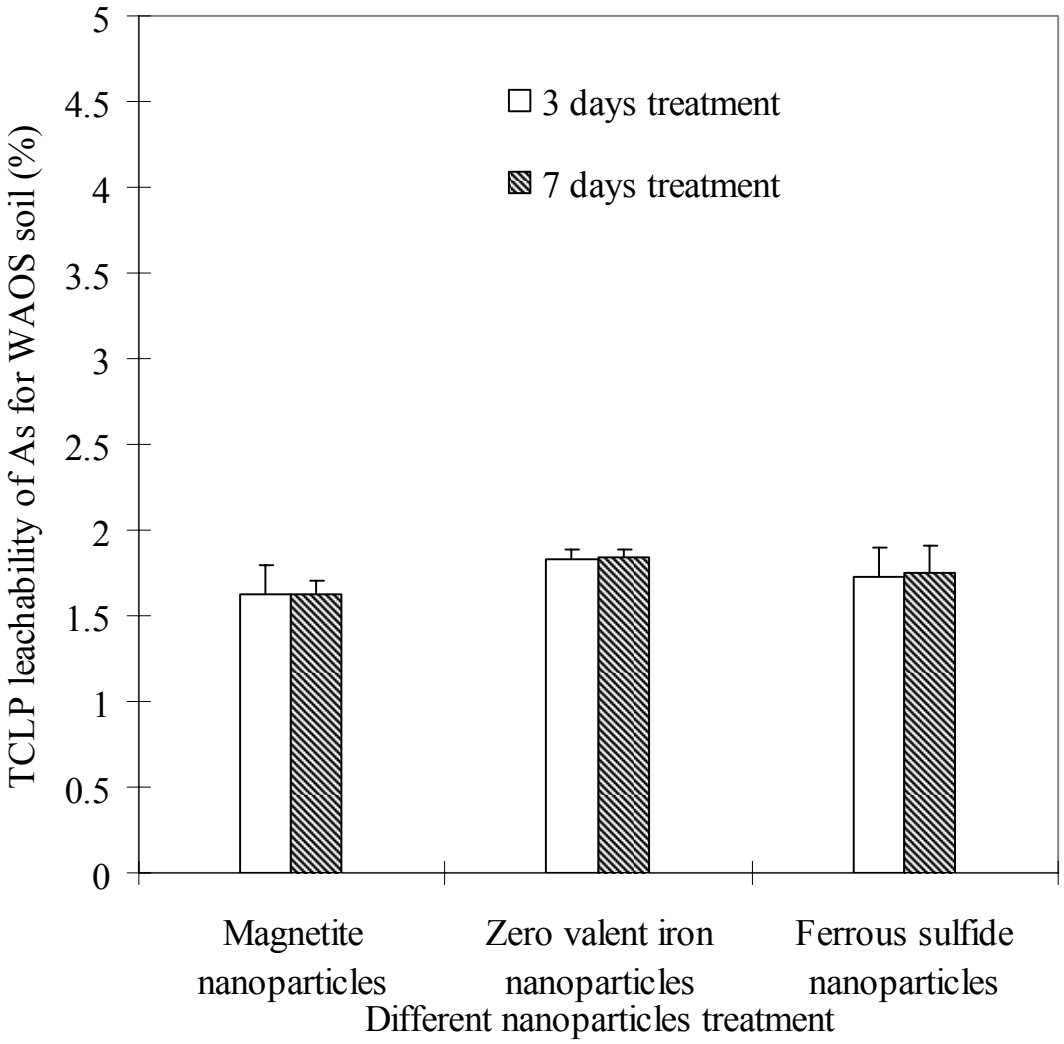

Figure 3. 6 Comparison of As leachability of WAOS soil samples for 3 and 7days treatment by different iron based nanoparticles

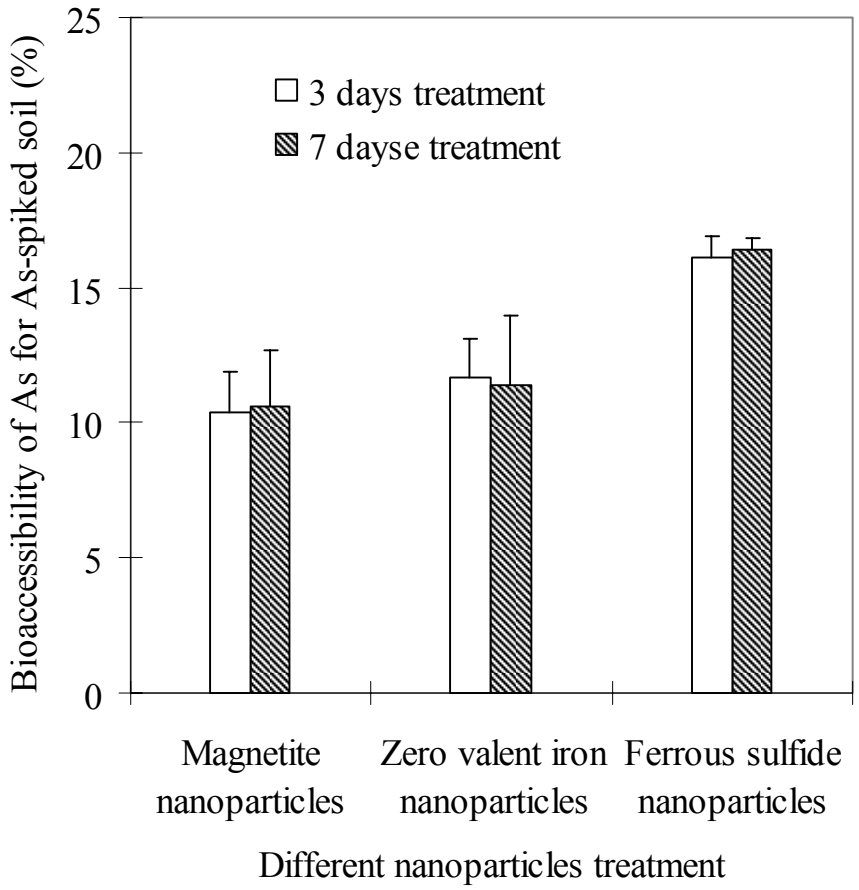

Figure 3. 7 Comparison of As bioaccessibility of As-spiked soil samples for 3 and 7days treatment by different iron based nanoparticles

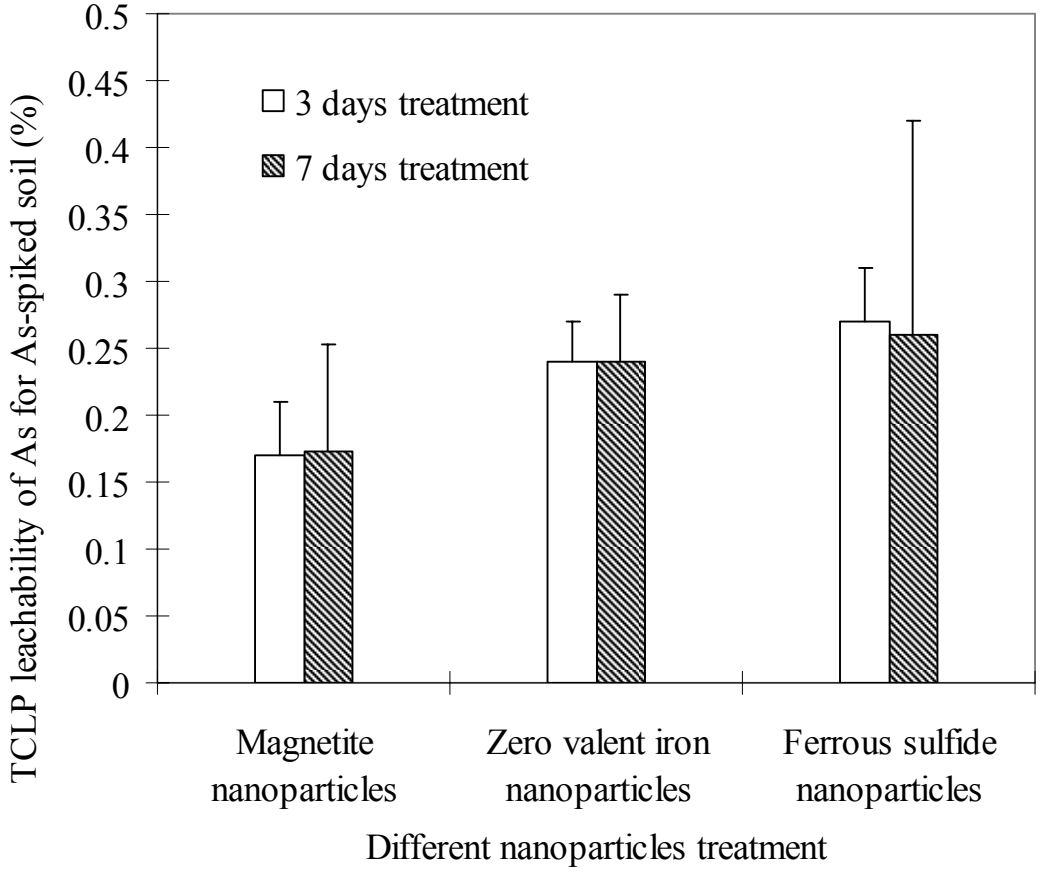

Figure 3. 8 Comparison of As leachability of As-spiked soil samples for 3 and 7days treatment by different iron based nanoparticles

3. 3. 4 Effect of Treatment Time

Figure 3.5 -3.8 compares the TCLP and PBET results when the soils were treated for 3 days and 7 days. From these figures, the bioaccessibility and leachability of *As* for 100:1 *Fe/As* molar ratio by 3 or 7 days treatment are comparable. A student t-test revealed no significant difference between the results from the two treatment times. Earlier, Subacz (2004) observed that the bioaccessibility of contaminated soils when amended with $FeCl_3$ for 3 days and 7days differed significantly. These results suggest that the stabilized nanoparticles offer rather fast mass transfer and reaction kinetics. Most of adsorption of arsenate occurred in one hour for nano zero valent iron groundwater treatments (Kanel et al. 2006). And the *As* adsorption reaction on nanoscale NVI were more quick than on micron ZVI.

3. 3. 5 Mechanisms of Arsenic Immobilization by Iron-based Nanoparticles

The mechanisms for arsenic sorption by iron oxides have been studied extensively [85, 86, 88, 93]. Waychunas et al. [111] described the adsorption mechanism of nanoscale iron oxides in soils and sediments, they concluded that nanoscale iron oxides have bigger surface area than microscale iron oxides to occur surface complexation reaction. Gao and Mucci stated that surface complexation is the main reaction mechanism for arsenic uptake by iron oxides (equations 3.4-3.8), [112].

$$>FeOH + H^+ \rightarrow >FeOH_2^+ \quad (3.4)$$

$$>FeOH \rightarrow >FeO^- + H^+ \quad (3.5)$$

$$>FeOH + H_2AsO_4^- \rightarrow >FeAsO_4^{2-} + H^+ + H_2O \quad (3.6)$$

$$>FeOH + H_2AsO_4^- \rightarrow >FeAsO_4H^- + H_2O \quad (3.7)$$

$$>FeOH + H_2AsO_4^- + H^+ \rightarrow >FeAsO_4^{2-}H_2 + H_2O \quad (3.8)$$

Previous work reported that zero-valent iron nanoparticles react with both contaminants and dissolved oxygen as well as water [103]. After the oxidation of zerovalent iron, an iron oxides layer forms at the surface of zero-valent iron particles, whereas some Fe^{2+} or Fe^{3+} ions can release into the aqueous phase. Cornell and Schwertmann [113] proposed that iron oxides form a passivation of the surface if the surface sites become saturated with iron oxides (equation 3.9-3.12). Arsenic, both arsenite and arsenate can be adsorbed on the surface of iron oxide [90-92]. Jegadeesan et al. [94] also proposed adsorption of arsenic on the corroded iron surface is the main mechanism of arsenite removal by nanoscale NVI from groundwater. Nanoscale zero-valent iron has a structure which 19% were in zero valent state with a coat of 81% iron oxides [101]. Kanel et al. also confirmed that nanoscale zero-valent iron and arsenate forms an inner-sphere surface complexation, 99% arsenate was adsorbed by nanoscale zero-valent iron in one hour. Bang et al. [114] claimed that arsenic can also be removed by Fe^0 through reducing arsenite and arsenate to zerovalent arsenic, which is insoluble in water.

$$Fe^0 + 2\ H_2O \rightarrow Fe^{2+} + H_2\ (g) + 2\ OH^- \quad (3.9)$$

$$4\ Fe^{2+} + 4H_2O + O_2 \rightarrow 4\ Fe^{3+} + 8\ OH^- \quad (3.10)$$

$$Fe^{2+} - e \rightarrow Fe^{3+} \quad (3.11)$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \quad (3.12)$$

Arsenic concentrations typically decrease under anoxic conditions by sulfide minerals [115]. Arsenic sorption on FeS was studied by [116] with X-ray absorption spectroscopy. They proposed eqn (3.13) as the main reaction for arsenite removal by FeS, which was supported by their XRD results. Nanoscale FeS particles have greater surface area, the sorption of arsenic on FeS nanoparticles can explain the immobilization of arsenic.

$$3FeS + H_3AsO_3 \rightarrow FeS_2 + FeAsS + Fe(OH)_3 \quad (3.13)$$

3. 4 Conclusion

The results of this investigation suggest that iron-based nanoparticles can be added to soils to decrease *As* bioaccessibility, leachability and the potential of bioavailability. The starch-stabilized nanoparticles were found effective to reduce both TCLP-leachability and PBET-bioaccessibility of *As* in *As*-contaminated soils. The bioaccessibility and leachability decrease with increasing *Fe/As* molar ratio. After three days treatments, the bioaccessibility of *As* decreased from an initial 71.3±3.1% to 29.8±3.1%, 30.9±3.2%, 37.6±1.2% for *Fe/As* ratio 100:1 Fe_3O_4, NVI, FeS nanoparticles, respectively, and for the 100 *Fe/As* ratio, the leachability of arsenic of in a range soil decreased from an initial 0.51±0.11% to 0.17±0.04%, 0.24±0.03%, 0.27±0.04% by Fe_3O_4, NVI, FeS Nanoparticles, respectively. Fe_3O_4 nanoparticles worked better than the other two nanoparticles in reducing the bioaccessibility and leachability. No significant difference in the effectiveness was evident between 3 days and 7 days treatments. Compare to two

soils, the treatment was more effective for the range soil which has much lower iron content. These results suggest that stabilized nanoparticles may serve as alternative media for in situ immobilization of arsenic in soils, especially soils with high *As* concentration and low Fe content.

CHAPTER IV

CONCLUSIONS

Conclusion

In Chapter 2 of this study, the Pb bioaccessibility of three types of Pb-contaminated solids was reduced by the use of phosphate amendment KH_2PO_4 (potassium dihydrogen phosphate) regardless of the initial moisture contents. Rapid potassium release into supernatants indicated that the amendment KH_2PO_4 dissolved and released potassium as well as phosphate ions quickly in free water (moisture) during soil remediation process. It also showed that there was enough phosphate in the *in situ* process to form lead-phosphate salt.

In the PBET process for the three amended solids, the concentration of K^+, Pb^{2+} and $H_2PO_4^-$ increased in the one hour PBET time. For both Pb-spiked soil and Pb-spiked sand, the saturation indices of lead-phosphate minerals were below 0 (saturation indices of chloropyromorphite ranged from -2.99 to -1.45; saturation indices of hydroxypyromorphite ranged from -21.58 to -20.05; saturation indices of $PbHPO_4$ ranged from -2.91 to -2.49). This result indicated no potential lead mineral precipitation in the PBET solution for these two solids. However, for the Pb-contaminated soil, due to the high initial soil Pb concentration, after 10 minutes in the PBET, the SI for all points were

above 0 (0.56-1.12). These numbers indicated that the PBET solutions were oversaturated.

In the homogeneous chloropyromorphite formation test in PBET solution, under the normal PBET condition (HCl, 1 hour extraction, 37 ºC) less than 5% of the Pb was removed from the aqueous phase, indicating that the homogeneous precipitation of chloropyromorphite from the PBET was not occurring to any significant extent. Similarly, even after seven days, very little Pb (10%) was removed from the normal PBET solution at 25 ºC, and the SI for chloropyromorphite was 6.49. In the HNO_3- based PBET solution, Pb removal was also less than 10% after seven days. For homogeneous chloropyromorphite formation experiments under different conditions, lead solubility was also greater than predicted for chloropyromorphite in most solutions. Under heterogeneous conditions, after one hour aging at 37 ºC, 89.1% Pb was still in aqueous phase. It showed that the transformation reaction of lead to solid phase was very slow in the present of phosphate in PBET solution.

These results illuminate that the lead removal reaction (chloropyromorphite formation) is very slow in PBET solution under both homogenous and heterogeneous conditions. Based on this conclusion, we speculate that high concentrations of glycine may block the reaction among Pb^{2+}, Cl^- and PO_4^{3-} by affecting the collision of ions since chloropyromorphite formation involves multiple ions. This result also indicates that the immobilization of lead occurs more under *in situ* conditions than in the PBET process.

Further research work is needed to monitor chloropyromorphite formation in amended soils by methods to definitively prove metal speciation (e. g. XAS, XRD). We also found lead solubility was greater than predicted for chloropyromorphite in the PBET condition,

suggesting further studies should be conducted at different pH values (e. g. 4.0 and 7.0) to indentify the cause for the higher than predicted solubility of lead in PBET solution. The ion activity products of chloropyromorphite should be calculated with equilibrium Pb^{2+}, Cl^- and $H_2PO_4^-$ concentrations at different pH conditions in PBET solutions, to compare the data to the reported K_{SO} of chloropyromorphite.

In the chapter 3 of this study, iron based nanoparticles were added to soils in order to reduce arsenic bioaccessibility and leachability. Using a soluble starch as stabilizer, most iron based nanoparticles attached to the solid phase after three days of treatment. Nanoparticles treatments were effective in reducing the bioaccessibility and leachability of arsenic from contaminated soils. As bioaccessibility and leachability decreased with increasing iron content. Among the three types of nanoparticles (100:1 Fe/As molar ratio) tested, the bioaccessibility and leachability of magnetite (Fe_3O_4) nanoparticle-treated soils were lower than the other two nanoparticle treatments, ferrous sulfide (FeS) and zero-valent iron (ZVI). No significant difference between three days and seven days of treatment was observed, indicating that most immobilization occur during first three days.

With regard to comparison between two soil types, treatment was more effective on the lower iron content, a high arsenic concentration soil. These results suggest that such laboratory-scale testing may be worthwhile, especially at sites that have high arsenic concentrations and low Fe contents. Further investigation is needed to understand the mechanism of arsenic immobilization by FeS and ZVI. The potential immobilization of arsenite by nanoscale iron based particles should also be investigated.

REFERENCES

1. Lead., http://www.chemistryexplained.com/elements/L-P/Lead.html (verified Jun. 21st. 2006).
2. Mielke, H.W., Lead in the inner cities. American scientist, 1999. 87: p. 62-77.
3. Lead in soil, http://www.epa.gov/lead/pubs/leadinfo.htm#facts.
4. Hettiarachchi, G.M. and G.M. Pierzynski, Soil lead bioavailability and in situ remediation of lead-contaminated soils: A review. Environmental progress, 2004. 23(1): p. 78-93.
5. Hettiarachchi, G.M., G.M. Pierzynski, and M.D. Ransom, In situ stabilization of soil lead using phosphorus. Journal of Environmental Quality, 2001. 30(4): p. 1214-1221.
6. Salatas, J.H., Y.W. Lowney, R.A. Pastorok, R.R. Nelson, and M.V. Ruby, Metals that drive health-based remedial decisions for soils at U.S. department of defense sites. Human and ecological risk assessment, 2004. 10: p. 983-997.
7. Cao, X., L.Q. Ma, M. Chen, D.W.J. Hardison, and W.G. Harris, Weathering of lead bullets and their environmental effects at outdoor shooting ranges. Journal of Environmental Quality, 2003. 32: p. 526-534.

8. Cao, X., L.Q. Ma, M. Chen, D.W. Hardison, and W.G. Harris, Lead transformation and distribution in the soils of shooting ranges in Florida, USA. The Science of the Total environment, 2003. 307: p. 179-189.

9. Zhu, Y.G., S.B. Chen, and J.C. Yang, Effects of soil amendments on lead uptake by two vegetable crops from a lead-contaminated soil from Anhui, China. Environment International, 2004. 30(3): p. 351-356.

10. Heinz, G.H., D.J. Hoffman, and D.J. Audet, Phosphorus amendment reduces bioavailability of lead to mallards ingesting contaminated sediments. Archives of Environmental contamination and toxicology, 2004. 46: p. 534-541.

11. Cao, X., L.Q. Ma, D.R. Rhue, and C.S. Appel, Mechanisms of lead, copper, and zinc retention by phosphate rock. Environmental pollution, 2004. 131: p. 435-444.

12. Brown, S., R. Chaney, J. Hallfrisch, J.A. Ryan, and W.R. Berti, In situ soil treatments to reduce the Phyto- and bioaccessibility of lead, zinc, and cadmium. Journal of Environmental Quality, 2004. 33: p. 522-531.

13. Seaman, J.C., J.M. Hutchison, B.P. Jackson, and V.M. Vulava, In situ treatment of metals in contaminated soils with phytate. Journal of Environmental Quality, 2003. 32: p. 153-161.

14. Melamed, R., X. Cao, M. Chen, and L.Q. Ma, Field assessment of lead immobilization in a contaminated soil after phosphate application. The Science of the Total Environment, 2003. 305: p. 117-127.

15. Cao, R.X., L.Q. Ma, M. Chen, S.P. Singh, and W.G. Harris, Phosphate-induced metal immobilization in a contaminated site. Environmental Pollution, 2003. 122(1): p. 19-28.

16. Hettiarachchi, G.M. and G.M. Pierzynski, In situ stabilization of soil lead using phosphorus and manganese oxide: influence of plant growth. Journal of Environmental Quality, 2002. 31: p. 564-572.

17. Geebelen, W., J. Vangronsveld, D.C. Adriano, R. Carleer, and C. H., Amendment-induced immobilization of lead in a lead-spiked soil: evidence from phytotoxicity studies. Water, air, and soil pollution, 2002. 140: p. 262-177.

18. Cao, X., L.Q. Ma, M. Chen, S.P. Singh, and W.G. Harris, Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. Environmental Science & Technology, 2002. 36(24): p. 5296-5304.

19. Yang, J., D.E. Mosby, S.W. Casteel, and R.W. Blanchar, Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. Environmental Science & Technology, 2001. 35(17): p. 3553-3559.

20. Stanforth, R. and J. Qiu, Effect of phosphate treatment on the solubility of lead in contaminated soil. Environmental Geology, 2001. 41(1-2): p. 1-10.

21. Ma, Q., S. Traina, and T. Logan, In situ lead immobilization by apatite. Environmental Science & Technology, 1993. 27: p. 1803-1810.

22. Ruby, M.V., A. Davis, and A. Nicholson, In-Situ Formation of Lead Phosphates in Soils as a Method to Immobilize Lead. Environmental Science & Technology, 1994. 28(4): p. 646-654.

23. Moseley, R.A., Decreasing lead bioaccessibility in soils with phosphate amendments. Thesis of Auburn University, 2006.

24. Jowett, M. and H.I. Price, Solubilities of the phosphates of lead. Transition Faraday Society, 1932. 28: p. 668-681.

25. Sauve, S. and M. Mcbride, Lead phosphate solubility in water and soil suspensions. Environmental Science & Technology, 1998. 32: p. 388-393.

26. Ma, Q.Y., Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environmental Science & Technology, 1995. 29: p. 1118-1126.

27. Zhang, P.C., J.A. Ryan, and J. Yang, In vitro soil Pb solubility in the presence of hydroxyapatite. Environmental Science & Technology, 1998. 32(18): p. 2763-2768.

28. CotterHowells, J., Lead phosphate formation in soils. Environmental Pollution, 1996. 93(1): p. 9-16.

29. Zhang, P.C. and J.A. Ryan, Formation of chloropyromorphite from galena (PbS) in the presence of hydroxyapatite. Environmental Science & Technology, 1999. 33(4): p. 618-624.

30. Laperche, V., S.J. Traina, P. Gaddam, and T.J. Logan, Chemical and mineralogical characterizations of Pb in a contaminated soil: Reactions with synthetic apatite. Environmental Science & Technology, 1996. 30: p. 3321-3326.

31. Ryan, J.A., P.C. Zhang, D. Hesterberg, J. Chou, and D.E. Sayers, Formation of chloropyromorphite in a lead-contaminated soil amended with hydroxyapatite. Environmental Science & Technology, 2001. 35(18): p. 3798-3803.

32. Laperche, V., T.J. Logan, P. Gaddam, and S.J. Traina, Effect of apatite amendments on plant uptake of lead from contaminated soil. Environmental Science & Technology, 1997. 31(10): p. 2745-2753.

33. Zhang, P.C. and J.A. Ryan, Formation of pyromorphite in anglesite hydroxyapatite suspensions under varying pH conditions. Environmental Science & Technology, 1998. 32(21): p. 3318-3324.

34. Zhang, P.C., J.A. Ryan, and L.T. Bryndzia, Pyromorphite formation from goethite adsorbed lead. Environmental Science & Technology, 1997. 31(9): p. 2673-2678.

35. Odyakov, V.F. and E.G. Zhizhina, A potentiometric study of precipitation in the (Pb^{2+}-H_2PO^4-Cl^-) system. Russian journal of inorganic chemistry, 2005. 50(6): p. 1051-1055.

36. Scheckel, K.G. and J.A. Ryan, In vitro formation of pyromorphite via reaction of Pb sources with soft-drink phosphoric acid. Science of the Total Environment, 2003. 302(1-3): p. 253-265.

37. Hopwood, J.D., R.J. Davey, M.O. Jones, R.G. Pritchard, P.T. Cardew, and A. Booth, Development of chloropyromorphite coating for lead water pipes. Journal of Materials Chemistry, 2002. 12: p. 1717-1723.

38. Ma, Q.Y., S.J. Traina, T.J. Logan, and J.A. Ryan, Effects of Aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. Environmental Science & Technology, 1994. 28: p. 1219-1228.

39. Ma, Q.Y., T.J. Logan, and S.J. Traina, Effects of NO_3^-, Cl^-, F^-, SO_4^{2-}, and CO_3^{2-} on Pb^{2+} immobilization by hydroxiapatite. Environmental Science & Technology, 1994. 28: p. 408-418.

40. Ma, L.Q.Y., Factors influencing the effectiveness and stability of aqueous lead immobilization by hydroxyapatite. Journal of Environmental Quality, 1996. 25: p. 1420-1429.

41. Lang, F. and M.K. Kaupenjohann, Effect of dissolved organic matter on the precipitation and mobility of the lead compound chloropyromorphite in solution. European journal of soil science, 2003. 54: p. 139-147.

42. Zhang, P.C. and J.A. Ryan, Transformation of Pb(II) from cerrusite to chloropyromorphite in the presence of hydroxyapatite under varying conditions of pH. Environmental Science & Technology, 1999. 33(4): p. 625-630.

43. Martinez, C.E., A.R. Jacobson, and M.B. McBride, Lead phosphate minerals: Solubility and dissolution by model and natural ligands. Environmental Science & Technology, 2004. 38(21): p. 5584-5590.

44. Chen, M., L.Q. Ma, S.P. Singh, R.X. Cao, and R. Melamed, Field demonstration of in situ immobilization of soil Pb using P amendments. Advances in Environmental Research, 2003. 8(1): p. 93-102.

45. Hettiarachchi, G.M., G.M. Pierzynski, and M.D. Ransom, In situ stabilization of soil lead using phosphorus and manganese oxide. Environmental Science & Technology, 2000. 34(21): p. 4614-4619.

46. Tang, X.Y., Y.G. Zhu, S.B. Chen, L.L. Tang, and X.P. Chen, Assessment of the effectiveness of different phosphorus fertilizers to remediate Pb-contaminated soil using in vitro test. Environment International, 2004. 30(4): p. 531-537.

47. Scheckel, K.G. and J.A. Ryan, Effects of aging and pH on dissolution kinetics and stability of chloropyromorphite. Environmental Science & Technology, 2002. 36(10): p. 2198-2204.

48. Essington, M.E., J.E. Foss, and Y. Roh, The soil mineralogy of lead at Horace's villa. Soil science society of American journal, 2004. 68: p. 979-993.

49. Council, N.R., Bioavailability of contaminants in soils and sediments: process, tools, and applications. National Academies Press: Washington, DC, 2002.

50. Ruby, M.V., R. Schoof, W. Barattin, M. Goldade, G. Post, M. Harnois, D.E. Mosby, S.W. Casteel, W. Berti, M. Carpenter, D. Edwards, D. Cragin, and W. Chappell, Advances in evaluating the oral bioavailability of inorganics in soil for Use in human health risk assessment. Environmental Science & Technology, 1999. 33(21): p. 3697-3705.

51. Ruby, M.V., A. Davis, R. Schoof, S. Eberle, and C.M. Sellstone, Estimation of lead and Arsenic bioavailability using a physiologically based extraction test. Environmental Science & Technology, 1996. 30: p. 422-430.

52. Scheckel, K.G., J.A. Ryan, D. Allen, and N.V. Lescano, Determining speciation of Pb in phosphate-amended soils: Method limitations. Science of the Total Environment, 2005. 350(1-3): p. 261-272.

53. Davis, A., M.V. Ruby, and P.D. Bergstrom, Bioavailability of arsenic and lead in soils from the butte, montana, mining distaict. Environmental Science & Technology, 1992. 26(3): p. 461-468.

54. Ruby, M.V., A. Davis, J.H. Kempton, J.W. Drexler, and P.D. Bergstrom, Lead bioavailability: Dissolution kinetics under simulated gastric conditions. Environmental Science & Technology, 1992. 26: p. 1242-1248.

55. Pu, X., L.S. Lee, R.E. Galinsky, and C.G. P., Evaluation of a rat model versus a physiologically based extraction test for assessing phenanthrene bioavailability from soils. Toxicological Sciences, 2004. 79(1): p. 10-17.

56. Oliver, D.P., M.J. Mclaughlin, R. Naidu, L.H. Smith, E.J. Maynard, and I.C. Calder, measuring Pb bioavailability from household dusts using an in vitro model. Environmental Science & Technology, 1999. 33: p. 4434-4439.

57. Marschner, B., P. Welge, A. Hack, J. Wittsiepe, and M. Wilhelm, Comparison of soil Pb in vitro bioaccessibility and in vivo bioavailability with Pb pools from a sequential soil extraction. Environmental Science & Technology, 2006. 40: p. 2812-2818.

58. Furman, O., D.G. Strawn, G.H. Heinz, and B. Williams, Risk assessment test for lead bioaccessibility to waterfowl in mine-impacted soils. Journal of Environmental Quality, 2006. 35: p. 450-458.

59. Sonmez, O. and G.M. Pierzynski, Phosphorus and manganese oxides effects on soil lead bioaccessibility: PBET and TCLP. Water, air, and soil pollution, 2005. 166: p. 3-16.

60. Yang, J.K., M.O. Barnett, P.M. Jardine, and S.C. Brooks, Factors controlling the bioaccessibility of arsenic(□) and lead(□) in soil. Soil and sediment contamination, 2003. 12(2): p. 165-179.

61. Yang, J.K., M.O. Barnett, J. Zhuang, S.E. Fendorf, and P.M. Jardine, Adsorption, oxidation, and bioaccessibility of As(□) in soils. Environmental Science & Technology, 2005. 39: p. 7102-7110.

62. Yang, J.K., M.O. Barnett, P.M. Jardine, N.T. Basta, and S.W. Casteel, Adsorption, sequestration, and bioaccessibility of As(□) in soils. Environmental Science & Technology, 2002. 36: p. 4562-4569.

63. Geebelen, W., D.C. Adriano, D. van der Lelie, M. Mench, R. Carleer, H. Clijsters, and J. Vangronsveld, Selected bioavailability assays to test the efficacy of amendment-induced immobilization of lead in soils. Plant and Soil, 2003. 249(1): p. 217-228.

64. Arnich, N., M.C. Lanhers, F. Laurensot, R. Podor, A. Montiel, and D. Burnel, In vitro and in vivo studies of lead immobilization by synthetic hydroxyapatite. Environmental Pollution, 2003. 124(1): p. 139-149.

65. Scheckel, K.G. and J.A. Ryan, Spectroscopic speciation and quantification of lead in phosphate-amended soils. Journal of Environmental Quality, 2004. 33(4): p. 1288-1295.

66. Ponizovskii, A.A. and E.V. Mironenko, Mechanisms of lead(II) sorption in soils. Eurasian Soil Science, 2001. 34(4): p. 371-381.

67. Manecki, M., P.A. Maurice, and S.J. Traina, Kinetics of aqueous Pb reaction with apatites. Soil Science, 2000. 165(12): p. 920-933.

68. Xu, Y. and F.W. Schwartz, Lead immobilization by hydroxyapatite in aqueous solution. Journal of Contaminant Hydrology, 1994. 15: p. 187-206.

69. Scheckel, K.G., C.A. Impellitteri, J.A. Ryan, and T. McEvoy, Assessment of a sequential extraction procedure for perturbed lead-contaminated samples with and without phosphorus amendments. Environmental Science & Technology, 2003. 37(9): p. 1892-1898.

70. Gustaffsson, J.P., http://www.lwr.kth.se/english/oursoftware/vminteq/ (verified Jan. 21st. 2006).

71. Reedy, R.C. and B.R. Scanlon, Soil Water content monitoring using electromagnetic induction. the Journal of Geotechnical and Geoenvironmental Engineering, 2003. 129: p. 1028-1039.

72. Maeda, M., Y. Tanaka, and G. Nakagawa, Potentiometric investigation of complex formation of lead(II) with glycine and DL-alanine. Journal of inorganic nuclear chemistry, 1979. 41: p. 705-709.

73. Khayat, Y., M. Cromer-Morin, and J.P. Scharff, Stability constants for lead(II) complexes of glycine, serine, aspartic acid and glycyl-L-leucine. Journal of inorganic nuclear chemistry, 1979. 41: p. 1496-1498.

74. Berggren, J., O. Bortin, and S. Gobom, A potentiometric study on the complex formation of the lead(□)-glycine system. Acta Chemica Scandinavica A, 1988. 42: p. 685-690.

75. Martinez, C.E., A.R. Jacobson, and M.B. Mcbride, Lead phosphate minerals: Solubility and Dissolution by Model and nature ligands. Environmental Science & Technology, 2004. 38: p. 5584-5590.

76. Davis, A., D. Sherwin, R. Ditmars, and K.A. Hoenke, An analysis of soil arsenic records of decision. Environmental Science & Technology, 2001. 35: p. 2401-2406.

77. Fendorf, S., M.J.L. Force, and G. Li, Temporal Changes in Soil Partitioning and Bioaccessibility of Arsenic, Chromium, and Lead. Journal of Environmental Quality, 2004. 33: p. 2049-2055.

78. Smith, E. and R. Naidu, Arsenic in the soil environment: A review. Advances in Agronomy, 1998. 64: p. 149-195.

79. Davis, A., M.V. Ruby, M. Bloom, and R. Schoof, Mineralogic constraints on the bioavailability of arsenic in smelter-impacted soil. Environmental Science & Technology, 1996. 30(2): p. 392-399.

80. Sherman, D.M. and S.R. Randall, Surface complexation of arsenie(V) to iron(III) (hydr)oxides: Structural mechanism from ab initio molecular geometries and EXAFS spectroscopy. Geochimica et Cosmochimica Acta, 2003. 67(22): p. 4223-4230.

81. Dixit, S. and J.G. Hering, Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environmental Science & Technology, 2003. 37(18): p. 4182-4189.

82. Ford, R.G., Rates of hydrous ferric oxide crystallization and the influence on coprecipitated arsenate. Environmental Science and Technology, 2002. 36(11): p. 2459-2463.

83. Jain, A., K.P. Raven, and L. Richardh, Arsenite and arsenate adsorption on ferrihydrite: Surface charge reduction and net OH- release stoichiometry. Environmental Science & Technology, 1999. 33(8): p. 1179-1184.

84. Grossl, P.R., M. Eick, and D.L. Sparks, Arsenate and chromate retention mechanisms on goethite .2. Kinetic evaluation using a pressure-jump relaxation technique. Environmental Science & Technology, 1997. 31(2): p. 321-326.

85. Waychunas, G.A. and J.A. Fuller, Geometry of sorbed arsenate on ferrihydrite and crystalline FeOOH: Re-evaluation of EXAFS results for topological factors in predicting sorbate geometry, and evidence for monodentate complexes. Geochimica et Cosmochimica Acta, 1995. 59(17): p. 3655-3661.

86. Manceau, A., The mechanism of anion adsorption on iron oxides - evidence for the bonding of arsensate tetrahedra on free Fe(O,OH) edges. Geochimica et Cosmochimica Acta, 1995. 59(17): p. 3647-3653.

87. Fuller, C.C. and J.A. Dadis, Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. Geochimica et Cosmochimica Acta, 1993. 57(10): p. 2271-2282.

88. Waychunas, G.A. and B.A. Rea, Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochimica et Cosmochimica Acta, 1993. 57(10): p. 2251-2269.

89. Beak, D.G., N.T. Basta, K.G. Scheckel, and S.J. Traina, Bioaccessibility of Arsenic(V) bound to ferrihydrite using a simulated gastrointestinal system. Environmental Science & Technology, 2006. 40: p. 1364-1370.

90. Nikolaidis, N.P., G.M. Dobbs, and J.A. Lackovic, Arsenic removal by zero-valent iron: field, laboratory and modeling studies. Water research, 2003. 37: p. 1417-1425.

91. Su, C. and R.W. Plus, Arsenate and arsenite removal by zerovalent iron : effects of phosphate, silicate, chromate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. Environmental science & technology, 2001. 35: p. 4562-4568.

92. Su, C. and R.W. Puls, Arsenate and arsenite removal by zerovalent iron : kinetics, redox transformation, and implications for in situ groundwater remediation. Environmental science & technology, 2001. 35: p. 1487-1942.

93. Fendorf, S., M.J. Eick, P. Grossl, and D.L. Sparks, Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. Environmental science & technology, 1997. 31: p. 315-320.

94. Jegadeesan, G., K. Mondal, and S.B. Lalvani, Arsenate remediation using nanosized modified zerovalent iron particles. Environmental progress, 2005. 24: p. 289-296.

95. Huber, D.L., Synthesis, properties, and application of iron nanoparticles. Small, 2005. 1: p. 482-501.

96. Zhang, W., Nanoscale iron particles for environmental remediation: An overview. Journal of nanoparticles research, 2003. 5: p. 323-332.

97. Yang, G.C.C. and H.-L. Lee, Chemical reduction of nitrate by nanosized iron: kinetics and pathways. Water research, 2005. 39: p. 884-894.

98. Chen, S.-s., H.-d. Hsu, and C.-w. Li, A new method to produce nanoscale iron for nitrate removal. Journal of nanoparticle research, 2005. 6: p. 639-647.

99. Joo, S.H., A.J. Feitz, and T.D. Waite, Oxidative degradation of the carbothioate herbicide, molinate, using nanoscale zero-valent iron. Environmental science & technology, 2004. 38: p. 2242-2247.

100. Cumbal, L. and A.K. Sengupta, Arsenic Removal Using Polymer-Supported Hydrated Iron(III) Oxide Nanoparticles: Role of Donnan Membrane Effect. Environmental Science & Technology, 2005. 39: p. 6508-6515.

101. Kanel, S.R., J.-m. Greneche, and H. Choi, Arsenic(□) removal from groundwater using nanoscale zero-valent iron as a colloidal reative barrier material. Environmental science & technology, 2006. 40: p. 2045-2050.

102. Raveendran, P., J. Fu, and S.L. Wallen, Complete Grenn Synthesis and Stablization of Metal Nanoparticles. J. Am. Chem. Soc., 2003. 125: p. 13940-13941.

103. Ponder, S.M., J.G. Darab, J. Bucher, and D. Gaulder, Surface chemistry and electrochemistry of supported zerovalent iron nanoparticles in the remediation of aqueous metal contaminants. Chemical Material, 2001. 13: p. 479-486.

104. He, F. and D. Zhao, Preparation and characterization of a new class of starch-stabilized bimetallic nonaparticles for degradation of chlorinated hydrocarbons in water. Environmental science & technology, 2005. 39: p. 3314-3320.

105. Miller, J., H. Akhter, F.K. Cartledge, and M. Mclearn, Treatment of arsenic-contaminated soils □: Treatability study and remediation. Journal of environmental engineering, 2000. 126: p. 1004-1012.

106. Jing, C., S. Liu, M. Patel, and X. Meng, Arsenic leachability in water treatment adsorbents. Environmental Science & Technology, 2005. 39: p. 5481-5487.

107. Akhter, H., F.K. Cartledge, J. Miller, and M. Mclearn, Treatment of Arsenic-contaminated soils □: soil characterization. Journal of environmental engineering, 2000. 126: p. 999-1003.

108. Si, S., A. Kotal, T.K. Mandal, S. Giri, H. Nakamura, and T. Kohara, Size-controlled synthesis of magnetic nanoparticles in the presence of polyelectrolytes. Chemical Material, 2004. 16: p. 3489-3496.

109. Xu, W. and D.L. Akins, Reverse micellar synthesis of CdS nanoparticles and self-assembly into a superlattice. Materials Letters, 2004. 58: p. 2623-2626.

110. Subacz, J.L., Decreasing arsenic bioaccessibility with iron amendments. Thesis of Auburn University, 2004.

111. Waychunas, G.A., C.S. Kim, and J.F. Banfield, Nanoparticulate iron oxide minerals in soils and sediments: unique properties and contaminant scavenging mechanisms. Journal of nanoparticle research, 2005. 7: p. 409-433.

112. Gao, Y. and A. Mucci, Individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater. Chemical geology, 2003. 199: p. 91-109.

113. Cornell, R.M. and U. Schwertmann, Iron oxides. Wiley-vch. New York. 1996.

114. Bang, S., M.D. Johnson, G.P. Korfiatis, and X. Meng, Chemical reactions between arsenic and zero-valent iron in water. Water Research, 2005. 39: p. 763-770.

115. Bostick, B.C., C. Chen, and S. Fendorf, Arsenic retention mechanisms within estuarine sediments of Pescadero, CA. Environmental Science & Technology, 2004. 38: p. 3299-3304.

116. Bostick, B.C. and S. Fendorf, Arsenic sorption on troilite (FeS) and pyrite (FeS2). Geochimica et cosmochimica Acta, 2003. 67: p. 909-921.