

**GEOCHEMICAL CONTROLS ON ARSENIC AND PHOSPHORUS  
IN NATURAL AND ENGINEERED SYSTEMS**

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## ABSTRACT

This thesis elucidates fundamental reactions that can control concentrations of arsenic and phosphate in water sources. High levels of arsenic or phosphorus have significant implications for the environment-- arsenic is extremely toxic to humans while phosphorus can cause eutrophication.

Initial work focused on arsenic solids that might exert geochemical control on soluble arsenic. Formation of proposed iron, barium, copper and zinc-arsenic solids were systematically examined under realistic environmental conditions. Thermodynamically favored copper, ferrous and barium solids did not form under circumstances of significance to drinking water sources. However, sorption of arsenic to iron, zinc and copper solids was discovered to be very significant, depending on the pH and solids age.

Given the established importance of sorption in arsenic and phosphate chemistry, two key constituents (silica and sulfide) implicated in mobilization of sorbed arsenic or phosphate were examined in detail. The addition of silica, which competes with arsenate or phosphate for sorption sites on  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  hydroxides, caused release of 0-30% sorbed As and P at pHs between 7.0 and 8.5. Reaction of sulfide with  $\text{Fe}(\text{OH})_3$  led to instantaneous release of 50-95% of sorbed As and P through a reductive dissolution mechanism. This instantaneous release was slowly reversed as orpiment ( $\text{As}_2\text{S}_3$ ) and vivianite [ $\text{Fe}_3(\text{PO}_4)_2$ ] slowly precipitated, but under other circumstances, these solids would not be expected to form. Modeling results suggest that arsenic and phosphate concentrations could either increase or decrease in response to reaction between  $\text{Fe}(\text{OH})_3$  and sulfides, thereby reconciling literature reports that seemed to contradict one another.

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## AUTHOR'S PREFACE

This work is presented in three chapters written in Virginia Tech manuscript format. Each chapter is a manuscript that has been submitted for publication to *Environmental Science & Technology*. Chapter I, "Geochemical control of aqueous arsenic by iron, barium, and copper solids," examines the significance of various metal-arsenic solids commonly found in natural and engineered systems. Results of that work focused attention on mechanisms of phosphate and arsenic release from  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  solids. Chapter II, "Silica and sulfide induced release of phosphorus sorbed to  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ " examined how two common chemical constituents could increase, or decrease, concentrations of soluble phosphate found in engineered and natural systems. Chapter III, "Silica and sulfide induced release of arsenic sorbed to  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ ," is complementary to Chapter II and builds on its key findings, but focuses on the more complicated system containing arsenic.

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## CHAPTER I

### GEO-CHEMICAL CONTROL OF AQUEOUS ARSENIC BY IRON, BARIUM, ZINC AND COPPER SOLIDS

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**Abstract.** It is commonly accepted that particulate arsenic in water is associated with colloidal iron. In some circumstances, however, significant particulate arsenic is present when zinc and copper containing colloids are present, but when iron colloids are absent. This study examined arsenic (V) behavior in solutions containing iron, barium, copper and zinc under realistic environmental conditions (e.g., pH = 7,  $\mu\text{-}10^{-3}$  M, T=20° C) and metal concentrations. In systems with ferrous iron, the thermodynamically favored solid  $\text{Fe}_3(\text{AsO}_4)_2$  did not form under conditions commonly encountered in the environment. Barium arsenate solids were confirmed as very soluble, with a  $K_{\text{sp}}$  value for  $\text{BaHAsO}_4$  of  $10^{-3.92\pm 0.11}$ , and are not likely to control arsenic concentrations at the ppb level. Arsenate did not appear to form specific solids with copper or zinc, but was strongly sorbed to the surfaces of the metal hydroxides, with observed maximum sorption densities around 0.2:1 (As:Cu). The extent of adsorption to copper and zinc solids was a strong function of solution pH and solids age.

#### Introduction

Arsenic, a naturally occurring carcinogen, has been closely examined in recent years from the perspective of speciation and transport in both natural and engineered systems (1). Occurrence of arsenic in drinking water supplies is of particular concern—a recent National Academy of Sciences review suggested that the current drinking water standard of 50 ppb could result in an excess lifetime cancer risk of 1% (2). The United States Environmental Protection Agency (USEPA) recently proposed an order of magnitude reduction in the drinking water maximum contaminant level to better protect public health.

In the environment, arsenic might be present within at least 320 different arsenic containing minerals, or sorbed/co-precipitated to other solids (3). Extensive studies on pure mineral forms

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(4-7) and solids which sorb arsenic (8-10) suggest arsenic precipitation by ferrous or barium as an important geochemical control. In fact, for nearly a half a century barium was thought (11,12) to be a key control on arsenic solubility in natural systems, but later work (5,6) indicated that this was not the case. Most recent attention has been focused on geochemical control via iron with relatively little attention given to other metals.

It has been strongly suggested that arsenic associates with other metals such as copper. For example, American Smelting and Refining Company (ASARCO) finds 80% of their arsenic associated with copper ore (13). Furthermore, extraction techniques used on synthetic smelter waste streams show 20% of the arsenic is incorporated into some type of copper containing solids (14). As noted by Welch *et al.* (15), improved understanding of arsenic occurrence will result from a thorough re-examination of thermodynamic data and by defining the elemental composition of arsenic containing solids found in environmental systems. This work attempts to do so for a few key metals.

## **Methods**

Precipitation experiments were designed to simulate conditions that may be encountered in natural or engineered systems but favor, through use of high yet reasonable metal concentrations, formation of a metal arsenic solid precipitate. For the one case where a metal arsenic solid was formed, both precipitation and dissolution experiments were used to verify the solid's solubility product ( $K_{sp}$ ). Solids were identified by measuring the stoichiometry of the soluble metal and arsenic loss from solution while also accounting for the amount of acid or base added to solution. The basic experimental setup used a covered 2-L solution at  $20 \pm 0.5^\circ\text{C}$  that was stirred constantly (by means of a shaker table or stir plate set at  $\geq 200$  rpm) in an HDPE bottle. Solutions were prepared with distilled-deionized water (subsequently polished with a  $0.2 \mu\text{m}$  pore-size filter) and purged with nitrogen gas for at least 5 minutes at a pH of about 5.5.

In several instances arsenic sorption to preformed metal hydroxides was also examined. For experiments with cupric,  $\text{Cu}(\text{OH})_2$  was formed by precipitation at pH 7.0, followed by aging the

solution for a specified time period as denoted in the text. Thereafter, arsenic was titrated into solution, pH adjusted, and a reaction time of 15 minutes allowed before sampling. ZnO solids used in sorption experiments were obtained directly from Fisher Scientific.

All stock solutions were made from reagent grade chemicals ( $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$ , ZnO,  $\text{NaNO}_3$ ) and preserved with 1%  $\text{HNO}_3$ . pH was adjusted as necessary (to  $\pm 0.1$  pH units of desired level) using  $\text{HNO}_3$  or NaOH, and samples were collected by filtration through a 0.45  $\mu\text{m}$  pore-size nylon filter. Collected samples were immediately acidified to 1%  $\text{HNO}_3$ . pH and elemental concentrations for different experiments varied between 5-9 and  $10^{-6}$ - $10^{-3}$  M, respectively (Table 1). pH was measured by a standard glass membrane probe and metals were quantified on an ICP emission spectrometer.

All equilibrium constants were corrected to zero ionic strength using the Debye-Hückel equation and corrected to 20°C using the Van't Hoff relationship (16). Acid dissociation constants for arsenic were taken from Stumm and Morgan. (17). Finally, a comparison of four different sorption models (linear, Langmuir, surface complexation with and without electrostatic correction) for natural arsenic partitioning with iron solids was made based on field data from Tenmile Creek, Montana using a sampling protocol as defined by Edwards *et al.* (18).

## Results

Experimental results are divided into three sections. First, the role of iron in aqueous arsenic chemistry was examined using both field and lab data. After re-examining arsenic solubility in systems with barium, the effect of copper on arsenate was studied.

*Iron-arsenic:* It has been observed that iron makes up a sizeable fraction of suspended particulate matter in water environments (19-21) and has a great affinity for arsenic (22-24). To examine this natural partitioning, various isotherm models were used for particulate iron using survey data collected in the National Arsenic Occurrence Survey (25) and a separate sampling trip to Tenmile Creek. For samples that contained more than 0.05 mg/L particulate iron, the arsenic surface complexation model proposed by Belzile and Tessier (26) could predict about 80% of the variation in measured sorbed arsenic concentrations based on pH, total arsenic concentration, and the total solids iron concentration for these data (Figure 1). Thus, the

conventional wisdom that particulate arsenic is associated with iron hydroxides seems valid in many systems.

However, 15% of the samples collected in the National Arsenic Occurrence Survey had between 0.3- 4 ppb particulate As and very low levels of particulate iron (< 2 ppb). Furthermore, the observed arsenic:iron molar ratio of greater than 0.5 in these solids was not consistent with expected sorption densities for iron hydroxides (~0.2). Interestingly, though iron was absent in these samples, particulate copper and zinc were present at significant levels (3-50 ppb). This raised the possibility that specific iron-arsenic solids, such as  $\text{Fe}_3(\text{AsO}_4)_2$  were present, or that arsenic was forming precipitates or sorbing to solids that did not contain iron. Results from other field surveys are consistent with this hypothesis (27, 28).

With respect to specific iron arsenic solids, ferrous iron has been suggested to form a highly insoluble precipitate with arsenate (Table 2). When examining arsenate removal from a solution highly supersaturated with respect to the proposed ferrous-arsenic solid, no reduced iron-arsenic solid formed for up to a 12 hours. After 12 hours, ferrous was changed to ferric as evidenced by precipitation in the control solution without arsenic, presumably by oxygen diffusion from the atmosphere through the HDPE container walls, or by entry during sampling. In either case, subsequent precipitation of fresh ferric hydroxide resulted in significant losses of arsenic (> 75% of total arsenic). Final sorption densities (As/Fe) at the end of one week approached 0.2, a value commonly associated with arsenic sorption onto iron hydroxides (10). Thus, ferrous arsenate did not form over short time periods in this experiment, and it does not seem to be a likely explanation for the observed high levels of particulate arsenic relative to particulate iron observed in some samples. This caused us to examine the possibility that barium arsenate solids were forming in our natural system samples.

*Barium-arsenic:* A very high solubility was determined for the barium-arsenic solid (Table 2), high enough to disregard barium as exerting any type of geochemical control in most natural systems where arsenic is typically found in the microgram per liter range. Extreme conditions (e.g. temperature, availability of other cations, pH) might enable a barium-arsenic solid to

precipitate, but for a pH of 7 and temperature of 20°C, a fraction of a gram per liter of both elements is present at equilibrium with the solid (Table 2).

Dominance of the  $\text{HAsO}_4^{2-}$  species (over  $\text{AsO}_4^{3-}$ ) at circa neutral pHs favored the formation of the  $\text{BaHAsO}_4$  solid over the  $\text{Ba}_3(\text{AsO}_4)_2$  solid. Some data at the higher alkaline pH conditions initially indicated the possibility of a mixed system (i.e., both 1:1 and 3:2 solids present) as the solutions were in the process of precipitating the solids. However, at equilibrium the 1:1 (Ba:As) solid appeared to be the most dominant at pH 7, 9, and 11. A  $K_{\text{sp}}$  value for the 3:2 solid was reported only to give an estimate of the magnitude (i.e. highly soluble solid) and should not be taken as an exact value.

Previous work has shown that two barium-arsenic solids exist (5,6). XRD analysis by Essington suggested the 1:1 solid's presence at neutral pH, while Robins conducted further work to determine a  $K_{\text{sp}}$  value. Work herein arrived at solid molar ratio of  $0.99 \pm 0.07$  after seven separate precipitation and dissolution experiments ranging in pH from 7 to 11. Precipitation of the 1:1 solid should remove one mole of hydrogen ions from the system, and observed measurements were consistent with this ( $r^2$  of actual vs. predicted acid consumption was 0.75 and 0.89 for the precipitation and dissolution reactions, respectively). Though all wet chemistry data was consistent with  $\text{BaHAsO}_4$ , the XRD pattern did not match the database pattern (29) possibly due to the existence of more than one crystalline form of the  $\text{BaHAsO}_4$  solid. Essington (5) also was unable to exactly match the reference pattern for the other barium-arsenic solid,  $\text{Ba}_3(\text{AsO}_4)_2$ . In agreement with Robins (6) and Essington (5), these findings indicated that barium-arsenic compounds are highly unlikely to form under natural conditions in drinking water sources. Thus, attention was focused towards other possible elements that might control arsenic solubility.

*Copper-arsenic:* Copper-arsenic solids have received relatively little attention as a geochemical control on trace arsenic.  $K_{\text{sp}}$  values in the literature (Table 2) predict  $\text{Cu}_3(\text{AsO}_4)_2$  might form with as little as 50  $\mu\text{g/L}$  arsenic near neutral pHs. Initial experiments attempted to form this

solid directly with subsequent work focused on arsenic behavior at lower levels of arsenic and copper.

Precipitation of a copper-arsenic containing solid occurred immediately following chemical addition (Figure 2). However, observed stoichiometry of removal, As:Cu of 0.3:1, disagreed with  $\text{Cu}_3(\text{AsO}_4)_2$ . Consideration of a possible 0.33:1 solid ( $\text{Cu}_3\text{AsO}_4(\text{OH})_3$ ) was also inconsistent with base consumption, which was 2 moles of  $\text{OH}^-$  consumed per mole of  $\text{Cu}^{2+}$  precipitated consistent with  $\text{Cu}(\text{OH})_2$  (s). Additional experiments with an ion specific electrode further confirmed that no soluble complexes were forming between copper and arsenic (Figure 3). Overall, these results indicate that arsenate does not interact directly with free cupric, via formation of a specific solid or significant complexes, but that the arsenate is removed by sorption to cupric hydroxide solid analogous to the situation with ferric.

Copper solids might be a significant control on soluble/solid arsenic speciation in the environment. For example, in a simple titration experiment comparing arsenic removal capabilities between copper and iron solids, copper was shown to quantitatively remove  $50\mu\text{g/L}$  arsenate with addition of  $1.6\text{ mg/L}$  cupric ion at pH 7. Further experiments demonstrated that sorption to copper hydroxide was a strong function of the solution pH and age of the solid (Figure 4). This is similar to the finding of Misra and Tiwari (8) that at an alkaline pH, much less arsenic sorbed onto iron solids, while Fuller *et al.* (10) and Goldberg (30) noted that aged iron solids sorb less arsenic. It was also interesting to note that the aging process of  $\text{Cu}(\text{OH})_2$  to tenorite was significantly decreased if arsenate was sorbed in significant quantities, assuming that a visual change from a blue to brown solid are indicative. That is, the typical transition from fresh copper hydroxide ( $\text{Cu}(\text{OH})_2$ ) to tenorite ( $\text{CuO}$ ) occurs in less than a day (31). In this study, fresh copper solids with sorbed arsenate retained a blue green color for at least one year.

In the copper system, the decrease in surface area with solid aging (32) might be as important if not more so than pH in determining arsenic sorption (Figure 4). For example, arsenate sorption is about 30% lower at pH 9.0 than at pH 7.0 for fresh  $\text{Cu}(\text{OH})_2$  solids, as would be expected based on competition from hydroxide; however, maximum sorption densities of arsenate onto aged  $\text{Cu}(\text{OH})_2$  was 40% less than for fresh solids at pH 7.0, and 90% less at pH 9. Although data

do not allow an unambiguous comparison, cupric hydroxide seems to be more strongly influenced by aging than iron solids in the Fuller *et al.* work (10).

### **Practical implications**

Interest in arsenic has increased recently as epidemiological data show that concentrations in the part per billion range can result in various types of cancer. Consumption of arsenic containing water is a key source of arsenic exposure for humans (1), and its effective removal has recently become a high priority. In terms of the coagulation process, use of copper to facilitate arsenic removal is not likely due to its elevated costs as compared with iron, the fact that there is a U.S. EPA action limit of 1.3 mg/L of soluble copper in drinking water, and problems with copper in sludge. However, arsenic would be expected to sorb strongly to  $\text{Cu}(\text{OH})_2$  scale on copper plumbing, and possibly concentrated in a manner that could be of human health concern. In support of this idea, a case study of arsenic contamination in a rural community's drinking water found arsenic at high concentrations on the wall of copper plumbing (33). These arsenic containing solids detach from the wall sporadically and contaminate the water-- in some cases as much as 5 mg/L arsenic was present in consumers drinking water, compared to the source water concentration of only 0.007 mg/L. Such levels of arsenic pose an acute health concern, although the water would be considered unpalatable to consumers due to the obvious copper levels as well. In any case, considering the broad use of copper and zinc in drinking water pipes, further work is necessary to better understand their interaction with arsenic and resulting implications for human exposure to arsenic.

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Table 1 - Experimental conditions tested. (x → y notation represents lowest concentration to highest concentration with approximately 10 incremental steps in between.)

**Precipitation**

**experiments:**

System elements	[metal] <sub>total</sub>	[As] <sub>total</sub>	pH
Ba-As	0.5 mg/L	0.8 mg/L	7
	500	500	7
	300 → 600	328	5, 9, 11
	300	328 → 488	5, 9, 11
Cu <sup>2+</sup> -As	6.4	2.3	7, 5.6
Fe <sup>2+</sup> -As	5.6	0.8	5
	5.6	0.8	6
Cu <sup>2+</sup> -As	0.1 → 5.1	.05	7
	0.1	0.05 → 1.0	7
Fe <sup>3+</sup> -As	0.1 → 5.5	0.05	7
	0.1	0.05 → 1.2	7

**Sorption**

**experiments:**

Solid	[metal] <sub>total</sub>	[As] <sub>total</sub>	
Cu(OH) <sub>2</sub> (s)	35 mg/L	0.05 → 200 mg/L	7, 9
CuO (s)	35	0.05 → 200	7, 9
ZnO (s)	35	0.1 → 150	9

Table 2- Possible arsenic solids of geochemical concern, and predicted equilibrium levels of arsenic following dissolution in distilled water at pH 7.0. Constants in bold italics were collected in this study.

<b>Solid</b>	<b>Equilibrium constant <math>K_{sp}</math>, @ <math>\mu=0</math>, T=25°C, pH=7.0</b>	<b>Equilibrium arsenic concentration (mg/L)</b>
BaHAsO <sub>4</sub>	$10^{-4.70}$ (6)	420
	$10^{-22.45}$ (5)	0.35
	<b><i><math>10^{-3.92}</math> (this study)</i></b>	<b><i>1000</i></b>
Ba <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	$10^{-14.82}$ (6)	5800
	$10^{-18.08}$ (5)	1100
	$10^{-50.10}$ (34)	0.0005
	<b><i><math>10^{-21.57}</math></i></b>	<b><i>88</i></b>
Cu <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	$10^{-34.74}$ (11)	0.72
	$10^{-55.12}$ (34)	0.59
	$10^{-37.85}$ (7)	0.17
	<b><i>no Cu-As solid formed</i></b>	----
Fe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub>	$10^{-21}$ (35)	$10^{5.4}$
	$10^{-41}$ (36)	23
	<b><i>no Fe<sup>II</sup>-As solid formed</i></b>	----
FeAsO <sub>4</sub>	$10^{-20.20}$ (34)	23
	$10^{-21.7}$ (4)	4.1
	<b><i>confirmed As sorption at low total As levels (ppb range)</i></b>	----

Table 3- Possible arsenic sorbing solids of geochemical concern. Data in bold italics collected in this study and determined by Langmuir fit to sorption data. Data in standard italics collected in coprecipitation experiments.

Proposed sorption product	Sorption coefficients		
	Maximum sorption density, $T_{\max}$ (M As/M Metal)	(mg As/g metal)	Equilibrium constant, $K_{\text{ads}}$ (L/mg)
Fe(OH) <sub>3</sub> (s)-As	0.1:1 (33,36)	134	
	0.19:1 coprecipitated, pH=7.5 (10)	255	
	0.10:1 coprecipitated, pH=7.5 (10)	134	
	<i>0.21:1 formed in-situ, pH=5</i>	<i>280</i>	
	<i>0.31:1 formed in-situ, pH=6</i>	<i>420</i>	
Cu(OH) <sub>2</sub> (s)-As	0.23:1 (33)	271	
	<b><i>0.22:1 0.5 hrs age, pH=7</i></b>	<b><i>263</i></b>	<b><i>0.24</i></b>
	<b><i>0.16:1 0.5 hrs age, pH=9</i></b>	<b><i>192</i></b>	<b><i>0.41</i></b>
	<b><i>0.14:1 1 day age, pH=7</i></b>	<b><i>169</i></b>	<b><i>0.37</i></b>
	<b><i>0.01:1 1 day age, pH=9</i></b>	<b><i>10</i></b>	<b><i>0.11</i></b>
ZnO(s)-As	no reported sorption densities		
	<b><i>0.12:1 aged solid, pH=9</i></b>	<b><i>140</i></b>	<b><i>0.46</i></b>

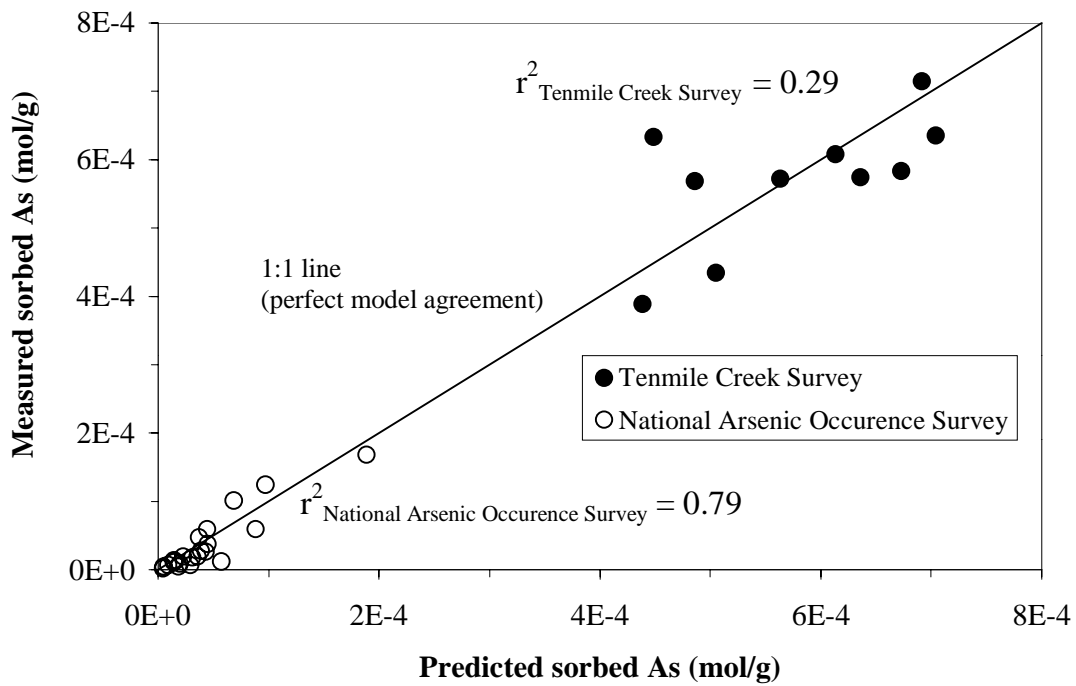


Figure 1- Application of Belzile and Tessier (3) model in predicting arsenic speciation in certain natural systems. Best fit was obtained when electrostatic corrections were not considered.

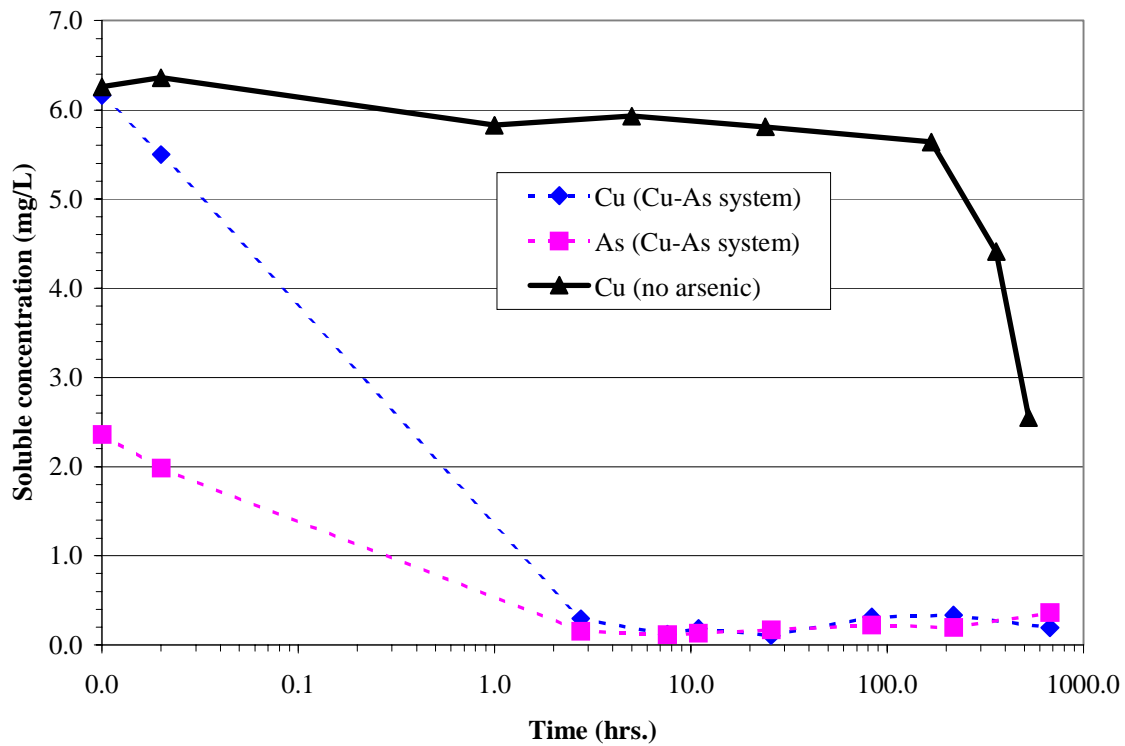


Figure 2- Soluble metal copper removal in a system with and without arsenic (pH=7,  $\mu=10^{-2.7}$  M, T=20°C).

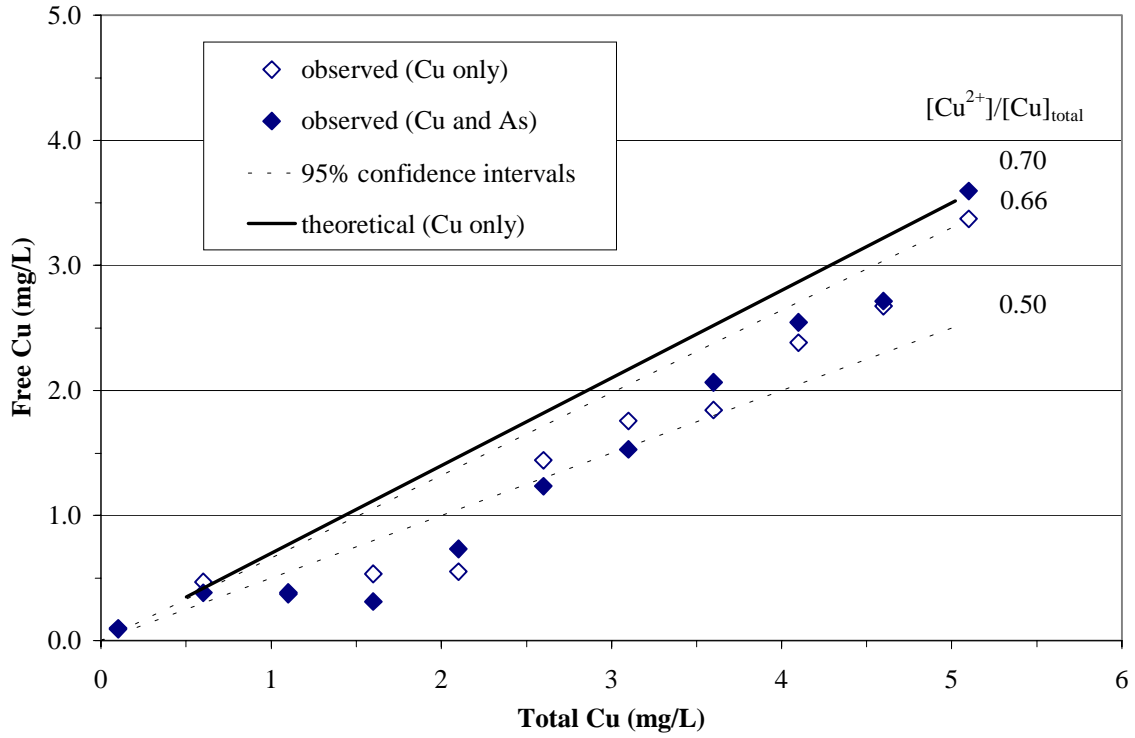


Figure 3- Free copper as determined by an ion specific electrode during titration of a 50  $\mu\text{g/L}$  arsenic solution ( $\text{pH}=7$ ,  $\mu=10^{-2.7}\text{M}$ ,  $T=20^\circ\text{C}$ ).

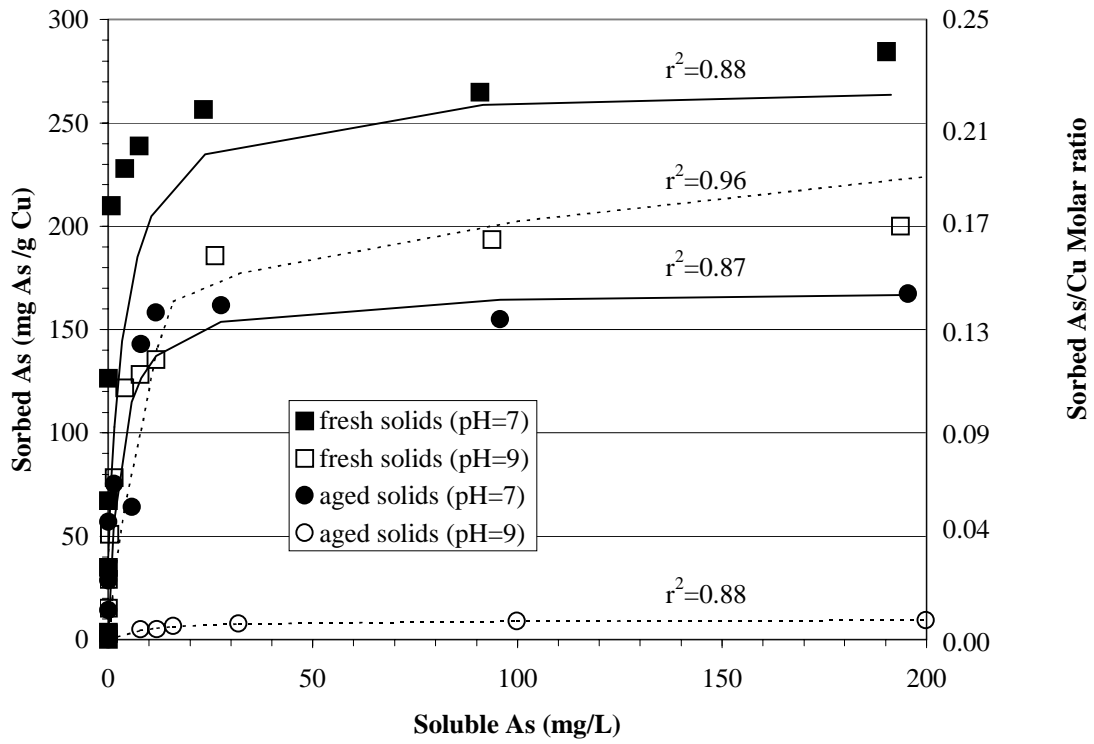


Figure 4- Effect of copper solid aging on sorption characteristics for arsenate ( $\mu=10^{-2.7}$ M,  $T=20^{\circ}\text{C}$ ).



## CHAPTER II

### SILICA AND SULFIDE INDUCED RELEASE OF PHOSPHORUS SORBED TO $\text{Fe}(\text{OH})_3$ AND $\text{Al}(\text{OH})_3$

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**Abstract.** Partitioning of P between soluble and solid phases is of importance in ecological systems. This work examined mobilization of sorbed phosphorus from Al and Fe hydroxides upon addition of silica and  $\text{H}_2\text{S}$  in well defined laboratory experiments. Silica competes with phosphate for surface sites, and if pH was increased from 7.0 to 8.5 in the presence of silica, as much as 30% of the sorbed P was released in 24 hours. Sulfide addition had a nearly insignificant impact on phosphate sorbed to aluminum hydroxide, but caused almost instantaneous release of nearly 100% of phosphate sorbed to iron hydroxide by reductive dissolution. Because the released phosphate could be re-precipitated by ferrous iron as vivianite, the equilibrium concentration of soluble phosphate can either increase or decrease upon reaction of sulfide with  $\text{Fe}(\text{OH})_3$  dependent on the P: $\text{Fe}(\text{OH})_3$  ratio, solution pH, total concentration of sulfide, silica concentration and other factors.

#### Introduction

Phosphorus chemistry has received considerable attention over the years due to its established importance as a limiting nutrient (1, 2). Excessive phosphorus can cause eutrophication which eventually results in a loss of plant and animal diversity, increased water temperatures, depletion of dissolved oxygen, and degraded water qualities in terms of odors and disinfection by-products (3, 4). Recent findings suggest over half of America's estuarine systems are moderately to highly eutrophied (5).

Sediments are acknowledged to play a key role in the uptake (immobilization) and release (mobilization) of phosphorus to natural waters (6). A variety of chemical/physical controls have been proposed to control P mobilization from sediments (7-10).

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Competition between phosphate and other species such as  $\text{AsO}_4^{3-}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  for surface sites on metal hydroxides has been extensively examined (11-14), but relatively little emphasis has been focused on the potential significance of competition from Si. A handful of field studies (9, 15, 16), beginning as early as the 1920s (17) noted P mobilization from sediments upon Si addition but laboratory confirmation of the phenomena is lacking. Due to analytical limitations this earlier work was also unable to detect low level releases of P which can be of importance in P limited ecosystems.

The redox state of sediments is also noted to control phosphate partitioning (18-22), but cause and effect relationships are rarely established due to the inherent complexity of sediments and microbial populations. The general finding of these studies is that under anaerobic conditions P is mobilized with bacteria either: dissolving  $\text{Fe}(\text{OH})_3$  solids directly (dissimilatory reducing bacteria, DIRB), producing by-products (e.g.  $\text{S}^{2-}$  from sulfate-reducing bacteria, SRB) that dissolve the oxide solids, or releasing internal P originally bound as ATP (poly-P bacteria). The net result is that organic matter settled on lake bottoms undergoes decomposition (22), depleting oxygen and lowering the redox potential causing reduction of iron oxides from ferric iron ( $\text{Fe}^{3+}$ ) to the more soluble ferrous iron ( $\text{Fe}^{2+}$ ), and releasing previously sorbed P. Considering these complex release mechanisms, it is not surprising to see conflicting observations in field studies. While one system might show low soluble  $\text{SO}_4^{2-}$  levels accompanying high soluble P levels (23), the converse of this (high  $\text{SO}_4^{2-}$  accompanying high P) can be found elsewhere (8, 11, 24).

Interestingly, while laboratory studies have examined sorption of P on synthetic Fe and Al oxides (25, 26) and numerous studies have correlated P release with bacterial activity (18-22), no studies have examined the release of phosphate sorbed to iron due to direct reaction with sulfides. This reaction is believed to be partly responsible for the levels of P observed under some circumstances. This work is designed to examine aspects of P mobilization upon addition of sulfide and Si in well defined lab conditions.

## **Methods**

The general experimental approach was to prepare aluminum and iron hydroxide solids with P sorbed on the surface followed by a chemical change including raising pH, adding  $\text{SiO}_2$ , or

adding  $S^{2-}$  and measuring the system response. To prepare the  $Al(OH)_3$  or  $Fe(OH)_3$  solids, distilled deionized water (polished with 0.2  $\mu m$  pore-size filter) was purged with  $N_2$  gas for 15 minutes at a pH of 5.5.  $AlCl_3$  or  $FeCl_3$  salts were added to solution to give a final concentration of 0.00179 M metal (48 mg/L Al or 100 mg/L Fe) and base was added simultaneously to give a pH of 7.0 which was maintained over 24 hours while stirring at 300 rpm in a high density polypropylene (HDPE) capped container. A concentrated stock solution of  $Na_2HPO_4$  was then added to the pre-formed solids and allowed to react for 24 hours while maintaining a pH of  $7.0 \pm 0.3$  giving final soluble P concentrations of 5-100  $\mu g/L$ . Consistent with our own kinetic studies, Bolan *et al.* (27) determined that P sorption onto Fe and Al oxides was at pseudo-equilibrium after 24 hours. Cases where P was not added at 24 hours is explicitly noted in the text.

The systems with P sorbed to metal hydroxides were then spiked various solutions. Depending on the circumstance, this included concentrated reagent grade stock solutions of NaCl and  $Na_2SO_4$ . The  $SiO_2$  was dosed from an unacidified 8,000 mg/L  $SiO_2$  stock solution at a pH of 12.0 as was sulfide ( $\sim 10 g/L S^{2-}$ ) made up directly from  $NaHS \cdot xH_2O$  a few hours before use. In the case of sulfide and silica dosing, tendencies to change pH were neutralized by concurrent dosing of predetermined amounts of HCl or NaOH. Samples were drawn with HDPE syringes, filtered through 0.45  $\mu m$  pore-size nylon filters and immediately acidified with concentrated HCl to 1% (v/v). All experiments, with the exception of the initial precipitation of solids, were conducted in a glove box purged initially (and every hour thereafter) with 99.998% pure  $N_2$  gas. All solutions were purged with  $N_2$  gas for 15 minutes before being brought into the glove box.

Al, Fe, P, and S were quantified by inductively coupled plasma atomic emission spectrometry (ICP-AES) according to Standard Method #3120B (28). Sulfide and ferrous were measured according to Standard Method# and pH was measured using a standard glass membrane probe. The temperature in all systems was  $23 \pm 2^\circ C$ .

## Results

*Role of Si in P mobilization:* Without addition of either silica or sulfide 0.2 to 3.5% of the P was soluble in systems with Al or Fe oxides at pH 7.0 or 8.5 (Figure 1, 2). Significant P release was observed after spiking of Si to systems where P was sorbed to synthetic Al or Fe oxides. For example, at pH 7.0 as much as 30% of the sorbed P was released when Al solids were exposed to 100 ppm SiO<sub>2</sub> (Figure 2), while a still significant release of P (6% or 100 ppb) occurred at lower, more typical Si levels (20 ppm SiO<sub>2</sub>)

It is well known that P sorption to oxides decreases at higher pH (29) and not surprisingly when the pH was raised from 7.0 to 8.5 in the Fe system with 0 mg/L SiO<sub>2</sub>, about 3% of the P was mobilized (Figure 1). The combined effect of higher silica and higher pH was much greater than the simple addition of both effects. Mobilization due to 100 mg/L Si spike resulted in 8% P, but raising pH to 8.5 and adding 100 mg/L SiO<sub>2</sub> mobilized 26% of the P. While pH and Si effects on P sorption have been studied independently, their combined effect has not been documented. By raising the pH and Si concentration, formation of polymeric Si is likely promoted (1), and these polymers have been shown by Taylor (30) to have much higher affinity for soluble Al. This work indicates these polymers can also cause mobilization of P.

*Role of S<sup>2-</sup> in P mobilization:* Sulfide addition to systems where P was sorbed to Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> solids generally resulted in P mobilization, although in the case of Al(OH)<sub>3</sub> the release was relatively small (Figure 2). Since Al<sup>3+</sup> cannot be reduced by S<sup>2-</sup> and there are no known P-S solids, any P released must be due to competitive effects. At a given level of SiO<sub>2</sub> about 100 µg/L P was released upon addition of 70 mg/L S<sup>2-</sup> (Figure 2). Ionic strength changes or competition from SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> also induced the same or a lower level P release (Figure 3), consistent with understanding that P sorbs quite strongly to oxides (31) and changes in ionic strength only slightly influence sorption (32). While Rydin (33) observed nearly 100% P mobilization from a wastewater treatment plant aluminum sludge and attributed the release to low redox potentials (-60 mV), potential alone cannot explain mechanistically why the P was mobilized. First, experiments in this study using sulfide which has at least twice the reducing potential of dithionite (S<sub>2</sub>O<sub>4</sub><sup>2-</sup>) used by Rydin induced no significant P release (~5%) was observed here. Secondly, when the same dose (1.4 g/L Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) as used by Rydin was applied

to the Al-P system here, at most 5% of the P was released in the first 24 hours. The two fold increase in ionic strength upon  $\text{Na}_2\text{S}_2\text{O}_4$  addition most likely caused this slight mobilization of P. Therefore, the release observed by Rydin might better be explained by some other mechanism (e.g. sludge sorbents besides Al which are releasing the P) rather than redox state or competition by  $\text{S}_2\text{O}_4^{2-}$ .

In marked contrast to the small changes observed in the system with  $\text{Al}(\text{OH})_3$ , the spiking of sulfide to systems where P was sorbed to  $\text{Fe}(\text{OH})_3$  led to release of greater than 70% of sorbed P in just 4 minutes when silica was absent (Figure 4). The rapid release of P was accompanied by a rapid release of  $\text{Fe}^{2+}$ , consistent with reductive dissolution of  $\text{Fe}(\text{OH})_3$  solids, the kinetics of which have been detailed (33, 34) and were evidenced by nearly instantaneous (<10 seconds) changes in amorphous the orange-reddish  $\text{Fe}(\text{OH})_3$  solid to a dark black solid with a distinct crystalline XRD pattern (Figure 5).

After formation of the black solid, soluble P levels decreased steadily due to precipitation of  $\text{Fe}_3(\text{PO}_4)_2$  (s). Interestingly, as was the case in early experiments, if soluble P had been measured after 24 hours no P release would have been detected and the conclusion would be that sulfides have minimal impacts on P mobilization. From XRD analysis, samples aged at 1 and 24 hours showed little change in solids' composition (Table 1). Roughly two thirds of the peak positions, defined by net intensities greater than 10 counts per second, matched with sulfur and  $\text{Fe}_3(\text{PO}_4)_2$  pattern for both the 1 and 24 hour solids. The remaining one third could not be identified.

Excess ferrous in the system after the sulfide spike (~10 mg/L) caused soluble P levels to drop to near zero (2  $\mu\text{g}/\text{L}$ ) in the presence or absence of Si, consistent with predictions based on existing  $K_{\text{sp}}$ 's for this solid. When present at 100 mg/L,  $\text{SiO}_2$  slowed down precipitation of vivianite, while it increased the amount of P initially released and persistence of detectable P in solution.. This is expected due to the strong complexation capability of Si which solubilized nearly 50 mg/L more iron (data not shown) than the system without iron after the initial  $\text{S}^{2-}$  spike.

*Modeling S<sup>2-</sup> induced P mobilization:* To consider the possible implications of sulfide induced P release from Fe(OH)<sub>3</sub> under a range of circumstances, a conceptual model was developed consistent with the earlier experimental observations (Figure 6). The model assumes that three solids might be present at equilibrium including Fe(OH)<sub>3</sub>, FeS, and Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Phosphate can be removed from the water only by formation of surface complexes with Fe(OH)<sub>3</sub> or by precipitation as vivianite but not by sorption onto FeS (18, 36). The conceptualization begins by assuming that all iron is present as Fe(OH)<sub>3</sub>, and based on the total P, pH and established surface complexation models (37), P is either soluble or sorbed onto the Fe(OH)<sub>3</sub>, consistent with observations of oxic environments (6, 38, 39). The system then responds to dosing different levels of S<sup>2-</sup>, or to production of a certain cumulative S<sup>2-</sup> concentration by bacteria, through a hypothesized sulfide reaction sequence of 1) reductive dissolution of Fe(OH)<sub>3</sub> by S<sup>2-</sup> with S<sup>0</sup> as an end product, 2) precipitation of S<sup>2-</sup> as FeS, and 3) eventual increases in S<sup>2-</sup> concentration in solution. The end product, elemental sulfur, of the oxidation of S<sup>2-</sup> was confirmed by XRD patterns, visual observation of white/yellow precipitate during the experiment, and observations by researchers elsewhere (33, 40). However, the sequence of S<sup>2-</sup> reactions needs additional quantitative study, but it is at least qualitatively consistent with the experimental observations discussed earlier. After considering these sulfide reactions, the equilibrium concentration and distribution of Fe and P species is predicted using MINEQL+ software (citation needed).

The model predicted that, as increasing concentrations of S<sup>2-</sup> react with the Fe(OH)<sub>3</sub> solids, the dominant forms of P change from sorbed species to precipitated vivianite, and finally end up 100% soluble if all iron is converted to FeS. In our own experiments, dosing of 70 mg/L S<sup>2-</sup> immediately produced between 70-100% soluble P, which is consistent with the model response at > 85 mg/L S<sup>2-</sup> dosed. In 24 hours however our results show gradually precipitation of P, presumably as vivianite. In spite of this new equilibrium with lower P levels, the model was still consistent at this new equilibrium if it was considered that 1) total sulfide in the system decreased with time 2) vivianite precipitation is kinetically limited. First, the model predicts a decrease in total sulfides would lead to a reduction in soluble P due to vivianite formation. Control experiments where sulfides were dosed into water at pH 7.0 showed that degassing over 24 hours resulted in a 15-25% reduction of the initial 70 mg/L sulfide dose. Degassing was quite

likely as the system was uncapped for half an hour during the 24 hour experiment in order to collect samples and adjust pH.

The second criteria that would reconcile experimental results with the model is the possibility that vivianite precipitates slowly. Indirect evidence of slow kinetics using the saturation index ( $\log Q/K_{sp}$ ) showed that the system was initially supersaturated 4 orders of magnitude with respect to vivianite in the first hours but then moved towards equilibrium with time. The slow kinetics theory was tested by creating a system with similar  $Fe^{2+}$  and P levels as observed in sulfide experiment but without sulfide. In this experiment with 3 mg/L P and 6 mg/L  $Fe^{2+}$ , 33% of the P precipitated in 24 hours. Silica, added at 60 mg/L  $SiO_2$ , retarded the precipitation of vivianite so that no significant losses (<5%) of P occurred in 24 hours. Similar inferences between silica and vivianite formation were observed in the sulfide experiment (Figure 4). Thus, due to degassing of sulfide and slow kinetics of vivianite formation, the equilibrium condition in the lab experiment moved progressively towards lower soluble P, exactly as predicted by the model.

Interestingly, the model conceptualization predicts that the qualitative response of soluble P to  $S^{2-}$  dosing depends on the initial equilibrium value of P (i. e. the ratio of  $P:Fe(OH)_3$ ) (Figure 7). At low pH and equilibrium P, initial sulfide releases P while at higher pH and equilibrium P, P is immobilized. For example, it was determined that above 200  $\mu g/L$  equilibrium P in the presence of 100 mg/L Fe at pH 7.0 (8 ppm curve is representative for “high” initial P levels), soluble P initially decreases in response to dosing up to 25 mg/L  $S^{2-}$  (or 25 mg/L cumulative  $S^{2-}$  production by bacteria), due to vivianite precipitation. At 50  $\mu g/L$  (or less) soluble P, however, a slight increase in P release is initially predicted, until vivianite solubility is exceeded and P decreases thereafter in response to sulfide doses. While this initial increase in P was less than 0.2% at 2.5  $\mu g/L$  initial soluble P and pH 7.0, lowering the pH to 6.0 and starting with 2.5  $\mu g/L$  soluble P resulted in 3.1% of the P being released. Other water quality factors besides pH (e.g. temperature, ionic strength) which limit vivianite formation would induce similar responses. Of course, if very high levels of  $S^{2-}$  are produced, all of the P is destined to be released.

While field evidence has shown that P can be mobilized upon onset of anoxic conditions (18, 19), the speed, magnitude, and mechanism behind P release has not been documented. Additionally, the non-linear behavior of soluble P with time (kinetic issue) or with varying total sulfide dosages (equilibrium issue), though observed by Willett (35) in field experiments, has not been examined. Using the model shown here, one can understand why the response of soluble P can vary so dramatically in natural systems (8, 23, 24). Changes in pH, total P in the system, or amount of sulfides present can result in soluble P levels that range from microgram to milligram per liter levels. While microbial activity can explain P mobilization phenomena in some cases, work here shows that release and mobilization due solely to sulfide interactions can also be significant.

### **Practical Implications**

Recent research has indicated that controlling P release from lake sediments, using whole lake aeration, is a hit or miss proposition (41). While sulfate has been linked to the likelihood of success (8, 42), sulfide, a product of sulfate reducing bacteria, can reverse the success of P removal and release significant amounts of sorbed P from Fe(OH)<sub>3</sub> surfaces. Al(OH)<sub>3</sub> surfaces, while not susceptible to S<sup>2-</sup> induced releases, desorb considerably more P than Fe(OH)<sub>3</sub> surfaces when Si is present. Thus, the type of sediment to which P is bound will be important in determining P release in response to changing water quality. In engineered systems, P removal by iron and aluminum sludges at wastewater treatment plants could be reversed under reducing conditions (43) (e.g. anaerobic digester units) or the removal efficiency compromised by the presence Si. Conversely, knowing that P sorption to Al(OH)<sub>3</sub> solids is unaffected by redox changes could be put to beneficial use by controlling P levels in lakes. Adding alum in this case would provide a consistent sink for P regardless of redox state or sulfate levels (44).

Finally, with respect to field analysis, sulfides can be the primary mechanism behind P release or immobilization yet their presence would not be detected. The direct reaction of S<sup>2-</sup> with Fe(OH)<sub>3</sub> observed in this work shows that P can be released nearly instantaneous at significant levels. According to the model presented here, S<sup>2-</sup> is not detectable in the water until all the Fe(OH)<sub>3</sub> has been consumed and Fe<sup>2+</sup> has precipitated as FeS even though reactions with S<sup>2-</sup> are responsible



for the P behavior that is observed. Thus, even if reductive dissolution by sulfides caused P mobilization from sediments, it should not be expected that sulfides would be detectable in the water.

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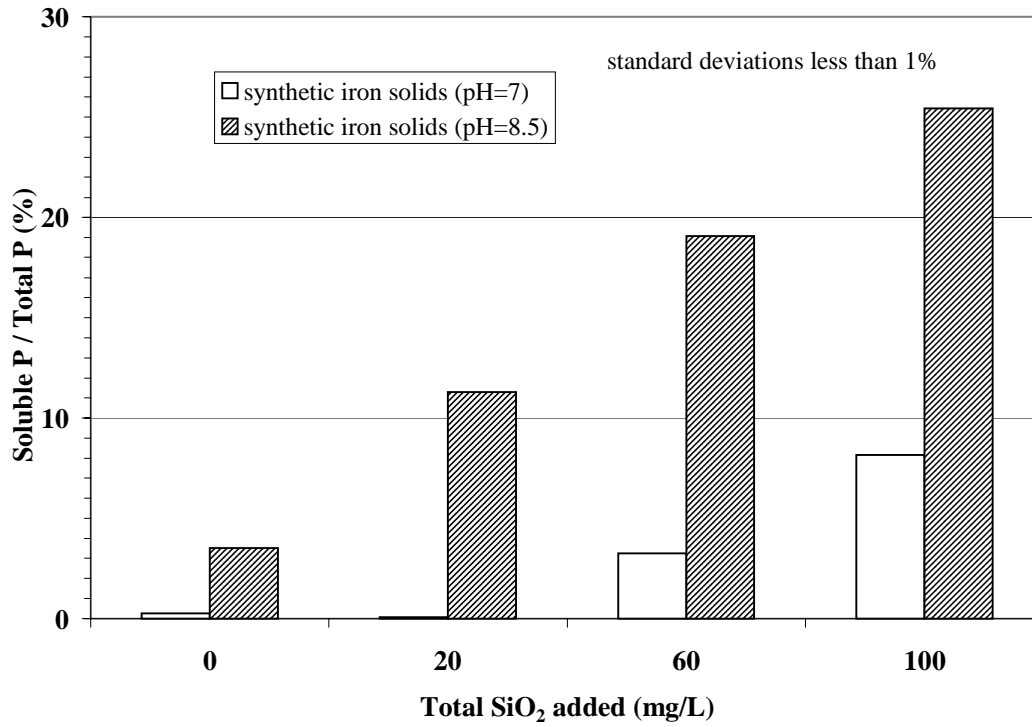


Figure 1- P mobilization from synthetic iron solids and natural sediments (solid's age=1 day,  $[\text{Fe}]_{\text{total}} = 100 \text{ mg/L}$ ,  $[\text{P}]_{\text{total-synthetic}} = 3 \text{ mg/L}$ ,  $\mu=0.005 \text{ M}$ )

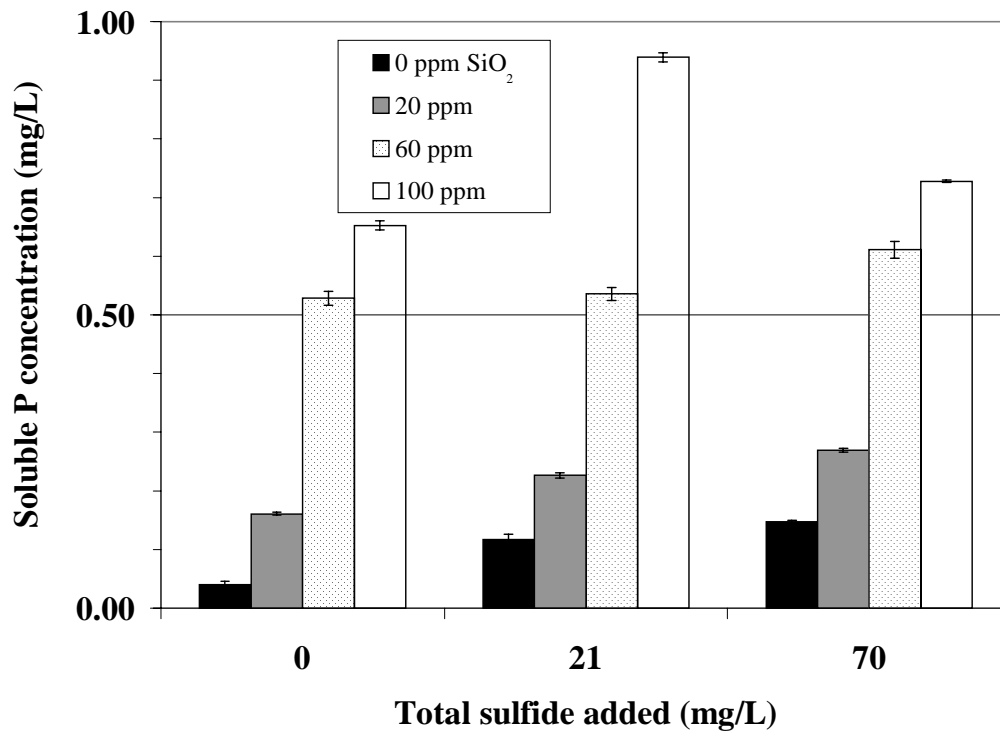


Figure 2- P mobilization from synthetic Al solids during SiO<sub>2</sub> addition (no sulfide) or during addition of combination SiO<sub>2</sub> and sulfide (pH=7.0, [P]<sub>total</sub>=2 mg/L, solid's age=21 days)

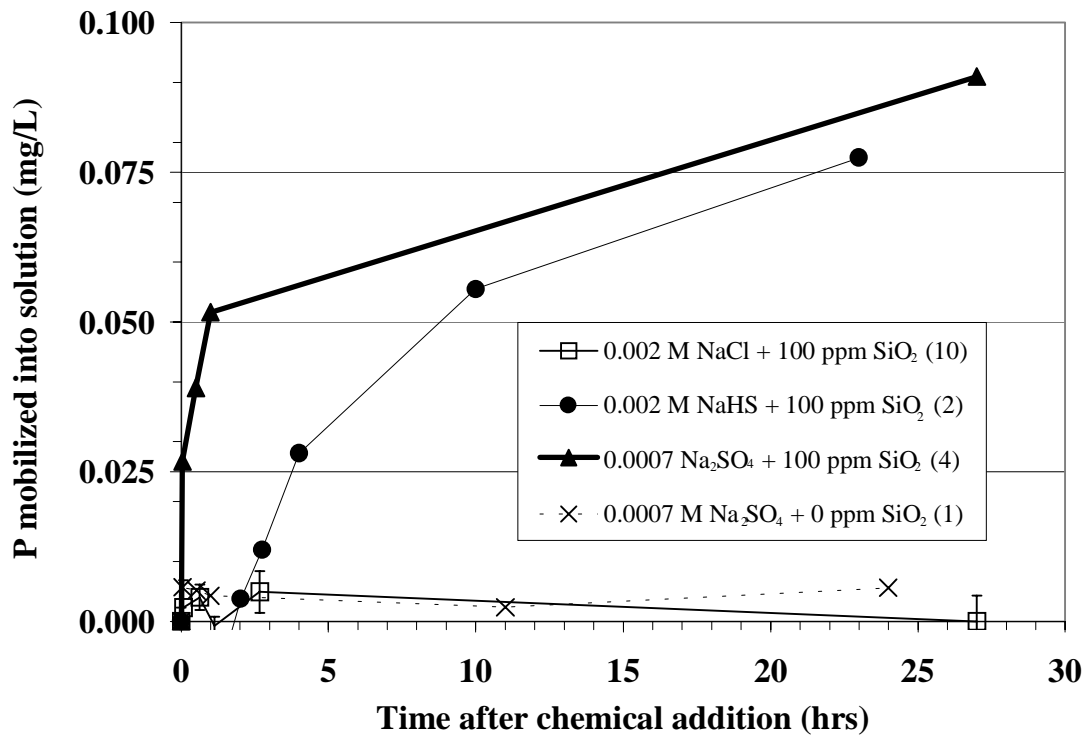


Figure 3- Kinetics of P mobilization from Al solids in response to various ions (pH=7.0, [P]<sub>total</sub>=2.25 mg/L, solid's age in days given in parenthesis)

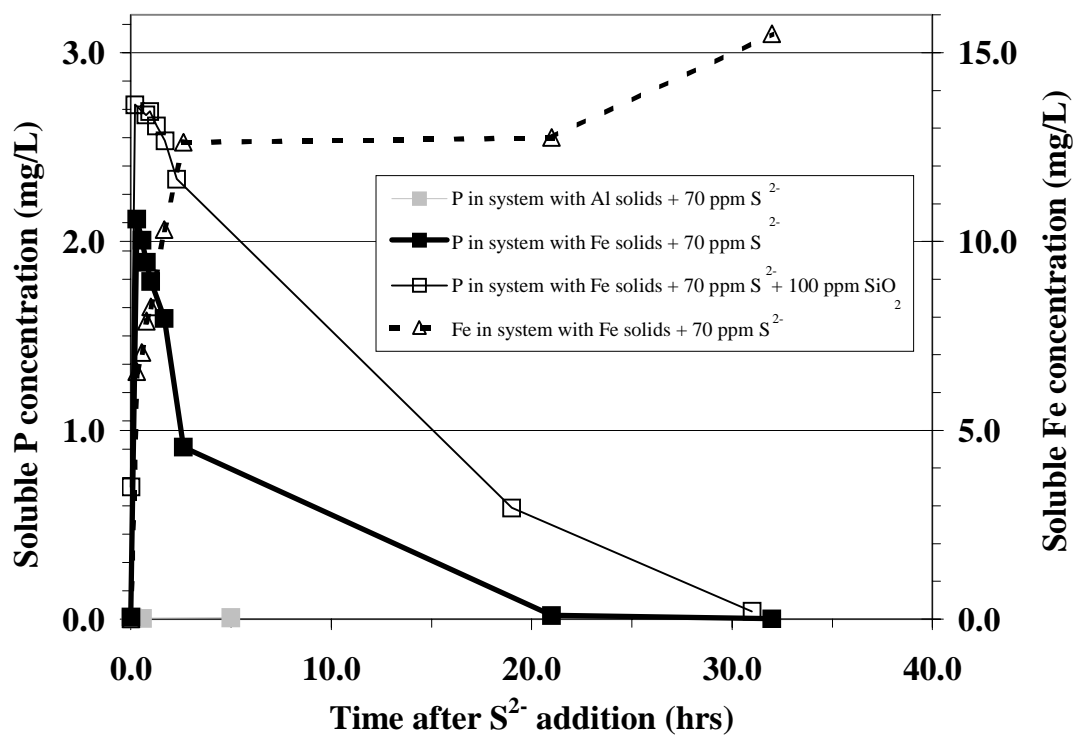


Figure 4- Kinetics of P mobilization from  $Fe(OH)_3$  solids upon spike with 70 mg/L sulfide (pH=7.0,  $[P]_{total} = 3.0$  mg/L,  $[Fe]_{total} = 100$  mg/L).



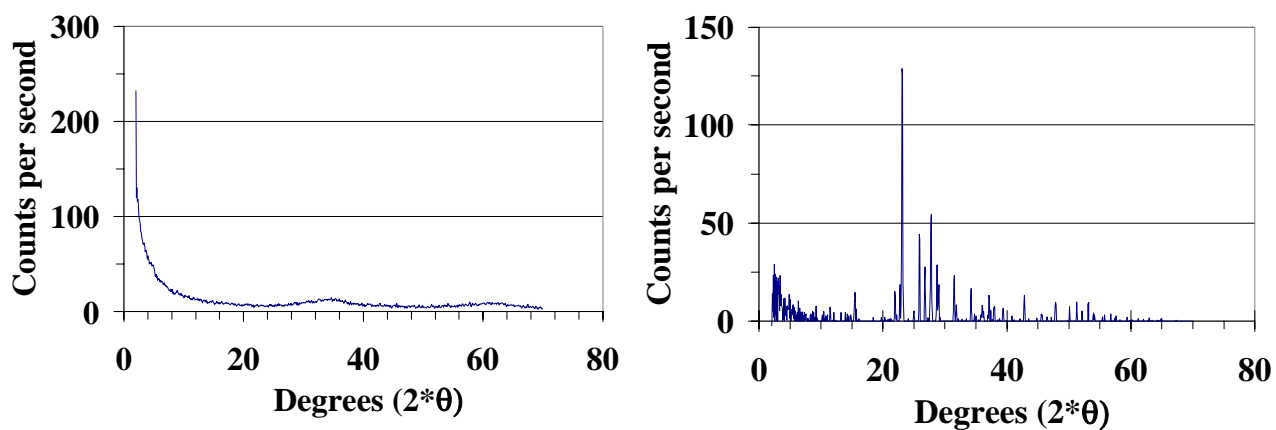
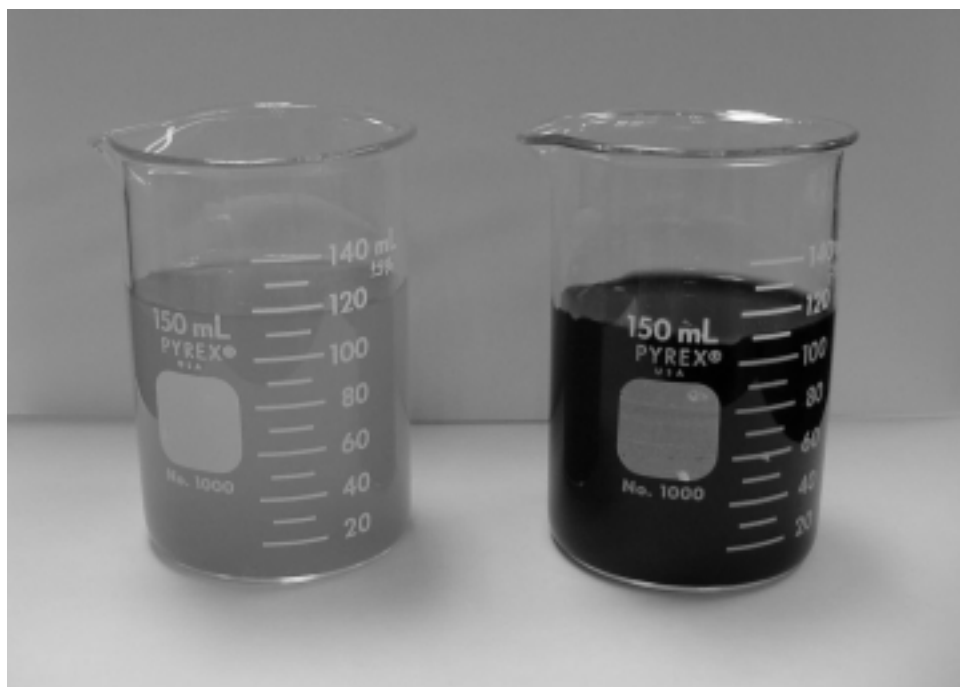


Figure 5- Color change and corresponding XRD patterns observed when a solution of  $Fe(OH)_3$  (left) was spiked with 70 mg/L  $S^{2-}$  (right).

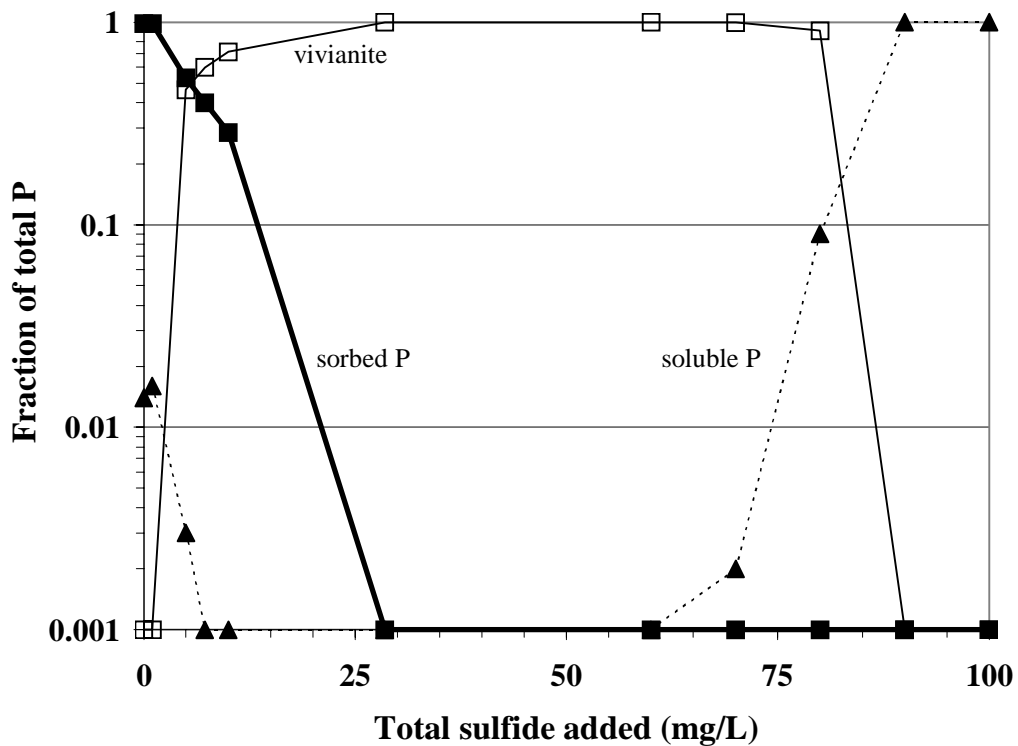


Figure 6- Model predictions for the equilibrium phosphate speciation in response to indicated sulfide dose (pH=7.0,  $\mu=0.01$  M, T=25° C,  $[\text{Fe}]_{\text{total}}=100$  mg/L,  $[\text{P}]_{\text{total}}=3.6$  mg/L,  $[\text{P}]_{\text{soluble initially}}= 50$   $\mu\text{g/L}$ , assumes  $\text{S}^{2-} \rightarrow \text{S}^0$  during reductive dissolution). If sulfate was the exclusive end product, the system would reach 0 sorbed P at 7.2 mg/L  $\text{S}^{2-}$  instead of 28.5 mg/L  $\text{S}^{2-}$ , and the x-axis would be adjusted accordingly by a constant 21.3 units.

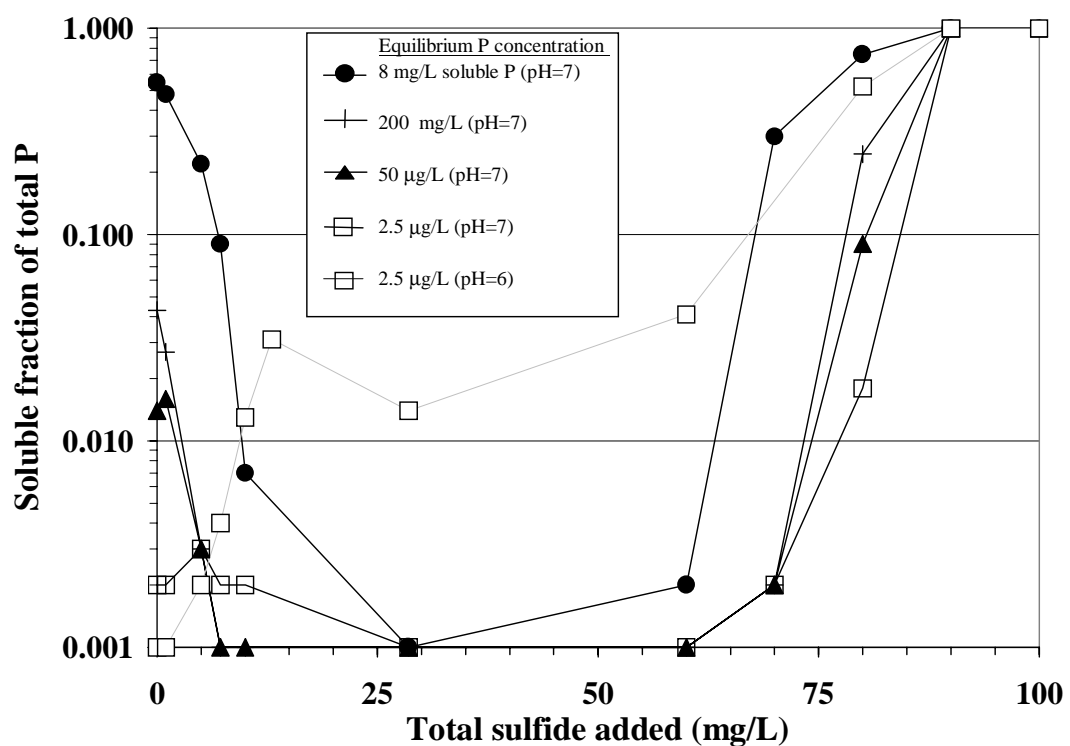


Figure 7- Model predictions for the response of soluble P to increased doses of sulfide at 100 mg/L initial  $\text{Fe}(\text{OH})_3$  (pH=7.0,  $\mu=0.01$  M,  $T=25^\circ\text{C}$ , assumes  $\text{S}^{2-} \rightarrow \text{S}^0$  during reductive dissolution). Y-axis values truncated at 0.001.

Table A1– XRD results for solids collected before and after sulfide addition to systems with and without P presorbed onto Fe(OH)<sub>3</sub> solids.

Solids' description	Solids present (Joint Committee on Powder Diffraction Standards file #)
<b>#1</b> <ul style="list-style-type: none"> <li>reddish- orange, easily filterable</li> <li>collected before S<sup>2-</sup> spike</li> <li>P present</li> </ul>	amorphous iron hydroxide (no crystalline pattern)
<b>#2</b> <ul style="list-style-type: none"> <li>dark black, colloidal</li> <li>collected 3 days after S<sup>2-</sup> spike</li> <li>no P present</li> </ul>	S (8-247)
<b>#3</b> <ul style="list-style-type: none"> <li>dark black, colloidal</li> <li>collected 1 hour after S<sup>2-</sup> spike</li> <li>P present</li> </ul>	S (8-247) , Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (37-481), 8 undefined peaks > 10 cps
<b>#4</b> <ul style="list-style-type: none"> <li>same as #3 but collected 24 hours after S<sup>2-</sup> spike</li> </ul>	S (8-247) , Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (37-481)., 6 underfined peaks > 10 cps

## CHAPTER III

### SILICA AND SULFIDE INDUCED RELEASE OF ARSENIC SORBED TO $\text{Fe}(\text{OH})_3$ AND $\text{Al}(\text{OH})_3$

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**Abstract** Partitioning of arsenic between soluble and solid phases is of critical importance in natural and engineered systems. This work examined mobilization of sorbed arsenic from Al and Fe hydroxides after addition of silica and  $\text{HS}^-$  in a controlled laboratory environment. Silica competes with arsenic for surface sites, and if pH was increased from 7.0 to 8.5 in the presence of silica, as much as 25% of the sorbed arsenic was released to the water in 24 hours. Sulfide did not strongly induce arsenic release from aluminum hydroxide, but released about 50% of the arsenic by nearly instantaneous reductive dissolution of the fresh  $\text{Fe}(\text{OH})_3$ . At the high levels of sulfide and arsenic tested in this work, released arsenic was re-precipitated, possibly as orpiment ( $\text{As}_2\text{S}_3$ ), but its formation could be kinetically limited at ppb arsenic levels of significance to human health. A simple model conceptualization for sulfide induced release of arsenic sorbed to  $\text{Fe}(\text{OH})_3$  was formulated which was consistent with many experimental observations, and that highlights the importance of better understanding the sequence of redox reactions between sulfide and arsenate sorbed to iron hydroxides.

#### Introduction

Arsenic in drinking water has aroused concern for human health in places around the world. Whether the route of infection is by inhalation (1, 2), ingestion (1, 3), or skin contact, arsenic can lead to serious health consequences at relatively low dosages. In fact, recent epidemiological evidence has prompted the USEPA to lower the current drinking water standard for arsenic from 50 to 10  $\mu\text{g}/\text{L}$  (4). Currently, 40 million people in Bangladesh and West Bengal (5) along with millions in the United States (6) and Argentina (7) are at risk for arsenic poisoning. In light of this, understanding arsenic speciation and solid-liquid chemical interactions are of prime importance not only for the applied sciences (e.g. water treatment engineering) but also geochemistry (e.g. understanding arsenic mobilization). With at least 320 different solid phases

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for arsenic (8) and numerous soluble complexes (9-12), soluble arsenic levels can be found in the environment ranging from trace levels to those that are acutely toxic.

Chemical factors known to release solid phase arsenic include: raising pH (13), competing anions (14, 15), redox potential of the system (16, 17), complexation of the sorbent (18), and age/degree of crystallinity of sorbent (13). Though no published data exist specifically for arsenic mobilization due to Si, early studies found that 25-50% of the sorption capacity of chemically similar phosphate was decreased when Si was added (19, 20). Evidence that Si sorbs to iron oxides, and hinders subsequent sorption by As, has been reported by other researchers (21-24), but no studies have examined As release from oxides by changes in Si concentration.

Fluctuating redox potentials in Bangladesh/West Bengal are believed responsible for high arsenic levels measured in these groundwaters (25). Both arsenic release (17, 26-28) and immobilization (29, 30) under anaerobic conditions have been observed. Sulfate-reducing bacteria (SRB), dissimilatory iron-reducing bacteria (DIRB), and dissimilatory arsenate-reducing bacteria (DAsRB) are all implicated in mobilizing sorbed arsenic (31-34), but the degree to which each plays a role is questionable (29). The importance sulfide production by SRB in mobilizing or immobilizing arsenic is unquestioned, even if the key reactions between sulfide and arsenate sorbed to iron have not been well defined in the laboratory. The goal of this work is to better understand how silica and sulfide can cause release of arsenate sorbed to iron and aluminum hydroxide.

## **Methods**

The general experimental approach was to prepare aluminum and iron hydroxide solids with arsenic sorbed on the surface, followed by a chemical change including raising pH, adding SiO<sub>2</sub>, or adding S<sup>2-</sup> and observing arsenic release. Solids were prepared and samples analyzed for soluble constituents as described in Davis and Edwards (35). A concentrated stock solution of Na<sub>2</sub>HAsO<sub>4</sub>\*7H<sub>2</sub>O was then added to the pre-formed solids and allowed to react for 24 hours while maintaining a pH of 7.0 ± 0.3, giving final soluble arsenic concentrations of 5-150 µg/L as noted in experiments. Cases where solids were aged longer than 24 hours before arsenic addition are noted in the text. The system was then spiked with concentrated reagent grade stock

solutions of SiO<sub>2</sub>, and then 24 hours later, with sulfide. The system response was then monitored.

## Results

*Role of Si in arsenic mobilization:* A significant release of arsenic was observed after spiking Si to systems where arsenic was sorbed to Al(OH)<sub>3</sub> or Fe(OH)<sub>3</sub>. Arsenic mobilization from 15 day old iron solids at 100 mg/L SiO<sub>2</sub> and pH 7.0 represented 25% (1.7 mg/L) of the total (Figure 1). As much as 50% (1.9 mg/L) of the sorbed arsenic was released if Al solids were exposed to 100 mg/L SiO<sub>2</sub> (Figure 2), while enough arsenic (>50 µg/L) was released at lower and more typical levels (20 mg/L SiO<sub>2</sub>) to be of concern relative to drinking water regulations and public health.

As mentioned earlier (35), previous studies examining Si induced phosphate release from soil (19, 20, 36) did not isolate effects of silica addition and pH. In this work at pH 7.0, for Fe(OH)<sub>3</sub> solid aged two days, raising the pH to 8.5 alone or adding 60 mg/L SiO<sub>2</sub> caused about 1% of the arsenic to be released (Figure 1). However, raising pH and adding 60 mg/L SiO<sub>2</sub> released 18% of the sorbed arsenic, confirming the previously described synergistic impact of the two parameters on arsenic sorption (24). Viewed from another perspective, a given amount of Si is about 14 times more effective at mobilizing arsenic at pH 8.5 than at 7.0. More arsenic was also released from solids that had aged longer. Silica added to Fe solids (Figure 1) aged 15 days before Si addition released 5 times as much arsenic compared to solids aged 2 days, presumably because of the lower surface area of the sorbent with aging and increased competition for sorption sites. The above observations regarding Si induced arsenic release are expected based on recent understanding of competitive sorption effects, even if they never have been studied explicitly in the lab (21-24).

*Role of S<sup>2-</sup> in arsenic mobilization:* Sulfide addition might compete with arsenate for sorption sites on Fe(OH)<sub>3</sub> and Al(OH)<sub>3</sub> as was observed above for Si. In addition, the sulfide has the potential to reduce As<sup>5+</sup> (in solution or sorbed to the surface) to As<sup>3+</sup> and form As<sub>2</sub>S<sub>3</sub> (orpiment) solids. When Fe(OH)<sub>3</sub> is present, added sulfide can also reductively dissolve the sorbent with concurrent release of Fe<sup>+2</sup>, and cause precipitation of FeAsS (arsenopyrite) or FeS.

Sulfide addition to the Al system immobilized significant amounts of arsenic, presumably by formation of orpiment, if the initial soluble arsenate concentration was above about 0.1 mg/L due to competition from Si (Figure 2). In the absence of Si, when initial arsenate was about 0.1 mg/L, only slight changes in soluble arsenic were observed when sulfide was dosed. The final levels of arsenic when 70 mg/L sulfide was dosed is consistent with formation of an  $\text{As}_2\text{S}_3$  type solid, with equilibrium soluble arsenic concentrations of about 0.1 mg/L.

Results from the Fe system were much more complex since both the sorbent  $[\text{Fe}(\text{OH})_3]$  and sorbate ( $\text{As}^{5+}$ ) can be reduced. After the 70 mg/L  $\text{S}^{2-}$  spike, the solution color turned from orange-red to black within 10 seconds, and the first measurement made 4 minutes after the  $\text{S}^{2-}$  spike revealed that nearly 50% of the arsenic had been mobilized (Figure 3). Soluble iron levels also rose to 12 mg/L Fe, of which 70-88% was in the reduced form ( $\text{Fe}^{2+}$ ) as determined colorimetrically. This is consistent with previous research that demonstrated the rapid transformation of oxidized iron to  $\text{FeS}(\text{s})$  in less than a minute (37). Twenty-eight hours after the  $\text{S}^{2-}$  spike, arsenic levels decreased back to  $\sim 100 \mu\text{g/L}$ , a value observed before the spike. Interestingly, if no data had been taken between 0 and 24 hours, it would have been concluded that the added  $\text{S}^{2-}$  had no impact on arsenic concentrations in this system.

Arsenic precipitation in response to sulfide dosing occurred in some cases in both the Al and Fe oxide systems. This immobilization of arsenic was hypothesized to occur through slow  $\text{As}_2\text{S}_3$  (orpiment) precipitation after arsenate had been reduced to arsenite. While arsenopyrite ( $\text{FeAsS}$ ) might have been present to some degree, the fact that: 1) arsenic was precipitated by sulfide in the aluminum system to a the same final level as was observed in the iron system (Figure 4,5), 2) field data has shown  $\text{FeAsS}$  formation is highly variable/unpredictable (38), 3) XRD patterns did not identify  $\text{FeAsS}$ , and 4) calculations suggest that supersaturation with respect to  $\text{FeAsS}(\text{s})$  was not exceeded support the idea that most arsenic was precipitated as an As-S solid (e.g.  $\text{As}_2\text{S}_3$ ). Though equilibrium arsenic levels in this work ( $\sim 100 \mu\text{g/L}$ ) are higher than predicted if  $\text{As}_2\text{S}_3(\text{s})$  was present and controlling arsenic solubility, similar observations of higher than expected arsenic in water relative to existing equilibrium have been made in field studies (16). However, direct evidence for  $\text{As}_2\text{S}_3(\text{s})$  by XRD analysis was not obtained, possibly due to the extremely strong signal from  $\text{S}^0$  in samples after sulfide addition.



To test the hypothesis that relatively slow orpiment formation caused the decreasing soluble arsenic concentrations in Figure 3, a series of experiments was conducted in which different levels of sulfide (1-70 mg/L  $S^{2-}$ ) were dosed to solutions containing only 3.5 mg/L arsenate (Figure 4). At a sulfide dose of 70 mg/L, more than 97% of the arsenic was precipitated in 3 minutes, but at a sulfide dose of 10 mg/L no significant arsenic precipitation occurred in 24 hours even though the system was supersaturated by 17 orders of magnitude with respect to  $As_2S_3$  (s). At a 30 mg/L sulfide dose, 84% of the arsenic was precipitated in 7 hours. In the experiment described in Figure 3, the theoretical sulfide concentration immediately following sulfide addition might range from a few mg/L sulfide up to tens of mg/L depending on the extent of  $Fe^{3+}$  reduction and  $Fe^{2+}$  precipitation (Table A1)—thus, the gradual decrease in arsenic over 24 hours shown in Figure 3 would be expected.

Evidence of significant arsenic sulfide complex formation (9, 10) and a more soluble  $K_{sp}$  ( $10^{-115.71}$ ) for  $As_2S_3$  (10) has been reported, but data collected for conditions in this work did not support those results. Most significantly, spiking increasing concentrations of  $S^{2-}$  to systems containing As-sulfide precipitates did not cause higher soluble arsenic, as would be expected if the solutions were at equilibrium with respect to the arsenic sulfide complexes (Figure A2 and Table A3). For the range of pHs (5.5-8.0), As levels (3.5- 7.0 mg/L), and  $S^{2-}$  levels (21 and 70 mg/L) tested in this work, the final equilibrium levels of arsenic favor were more consistent with the traditional  $K_{sp}$  value of  $10^{-127.8}$  for orpiment (39), rather than  $10^{-115.71}$  (10).

*Modeling  $S^{2-}$  induced arsenic mobilization:* A model conceptualization was developed that is consistent with the experimental observations of this study. The initial assumption is that soluble arsenate is in equilibrium with sorbed species on  $Fe(OH)_3$ . Increasing amounts of  $S^{2-}$  are then titrated into the system, and the equilibrium speciation of arsenic is calculated. It was necessary to make two sets of assumptions regarding sulfur chemistry including hierarchy of  $S^{2-}$  reactions and end products of  $S^{2-}$  oxidation. First,  $S^{2-}$  was assumed to react by ferric reduction, arsenate reduction and then  $FeS$  or  $As_2S_3$  (s) formation in sequence. The assumption that ferric reduction occurs first is supported by Zobrist *et al.* (34) who observed ferric reduction occurred were nearly twice as fast as arsenate reduction. In addition, the chemical potential (or driving force) for ferric reduction by  $S^{2-}$  is almost twice as great as for arsenate. Secondly,  $S^{2-}$  was assumed to

be oxidized to  $S^0$  during redox reactions. This is consistent with the measurements of  $S^0$  in the solids immediately after  $S^{2-}$  reactions, although other end products undoubtedly form and to the extent they did, less  $S^{2-}$  would be required to achieve a given level of response to sulfide in Figure 5. For example, if  $S^0$  is the end product, 31 mg/L  $S^{2-}$  is required to completely reduce  $Fe(OH)_3$  and arsenate, whereas 7.5 mg/L would be required if  $SO_4^{2-}$  was the exclusive end product (Table A1).

The model predicts that at low levels of  $S^{2-}$ , arsenic would be controlled by the concentration of  $Fe(OH)_3$  remaining, while at high levels of  $S^{2-}$ , arsenic would be precipitated by orpiment (Figure 5). This leads to a predicted initial release of arsenic when lower concentrations of sulfides react with iron hydroxides, eventually followed by arsenic precipitation after further sulfide additions. If a different reaction sequence is assumed, for example, if sulfide first reacted to convert arsenate to arsenite followed by precipitation of orpiment, a significant fraction of the arsenic would never be mobilized in response to increasing sulfide. Likewise, if the required degree of orpiment supersaturation is insufficient to initiate precipitation, as was observed in experiments in this work, it is possible that orpiment would never form, causing soluble arsenic to remain mobilized in response to increasing sulfide in sediments or soils. The sequence of redox reactions between sulfide and arsenate sorbed to various forms of  $Fe(OH)_3$ , as well as precipitation kinetics of various As-S solids, is deserving of additional study.

### **Acknowledgements**

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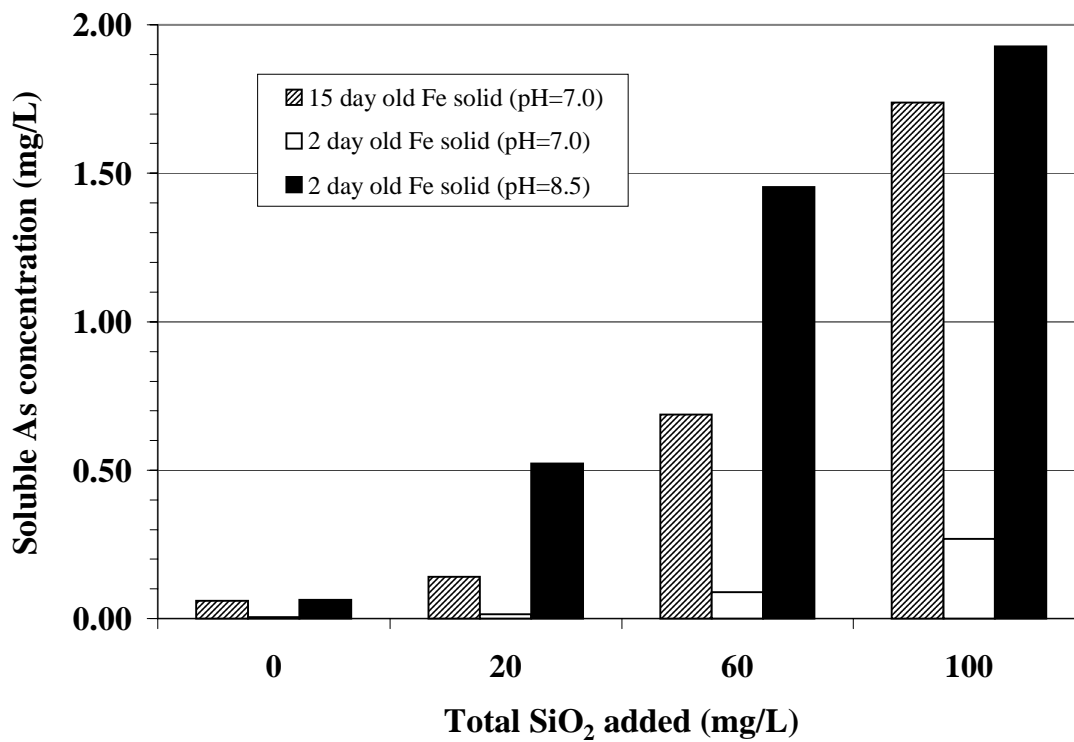


Figure 1- As mobilization from synthetic Fe(OH)<sub>3</sub> in the presence of silica ([Fe]<sub>total</sub>= 100 mg/L, [As]<sub>total</sub> = 7.2 mg/L,  $\mu=0.005$  M)

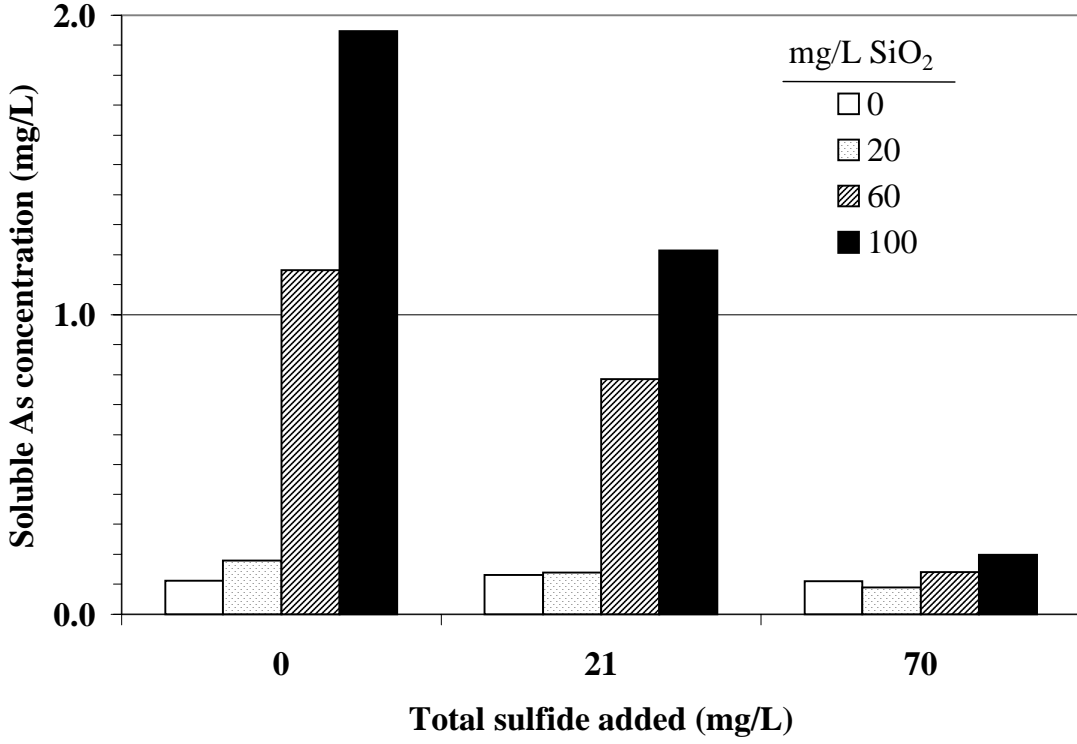


Figure 2- Combined silica and sulfide effects on arsenic mobilization from synthetic Al oxides ([Al]<sub>total</sub> = 48 mg/L, [As]<sub>total</sub> = 3.5 mg/L, pH=7.0,  $\mu$ =0.005-0.015 M, solid's age=15 days)

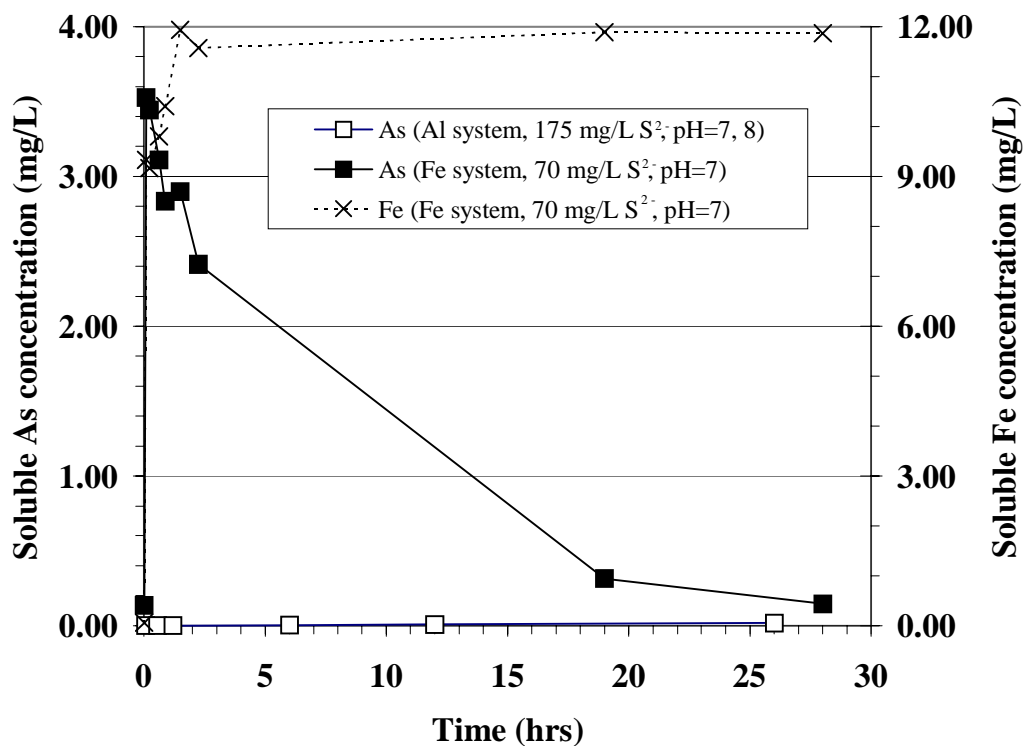


Figure 3- Kinetics of arsenic mobilization and reprecipitation from  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  solids in the presence of sulfide ( $[\text{As}]_{\text{total Al system}} = 3.5 \text{ mg/L}$ ,  $[\text{As}]_{\text{total Fe system}} = 7.2 \text{ mg/L}$ ,  $\mu = 0.007 \text{ M}$ )



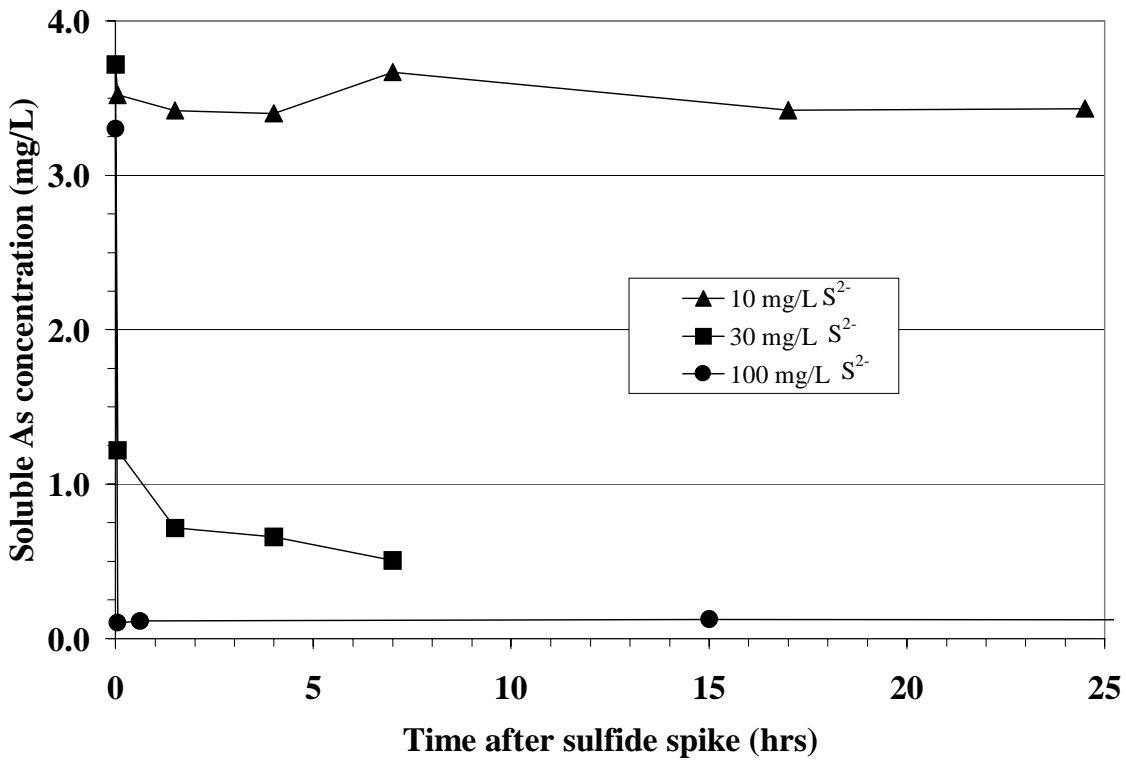


Figure 4- Arsenic immobilization as  $As_2S_3$  (s) with time at various degrees of supersaturation.

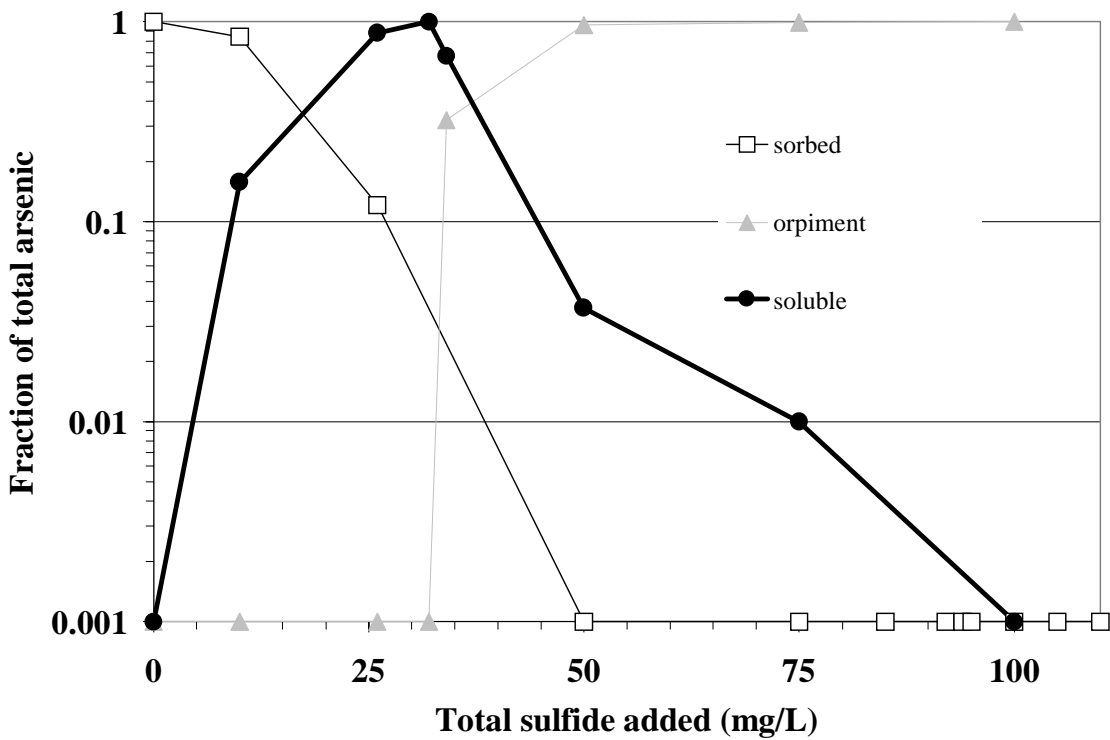


Figure 5- Equilibrium predictions for an iron-arsenic system with various levels of sulfide ( $[As]_{total} = 4.82$  mg/L,  $[Fe]_{total} = 100$  mg/L, pH=7.0,  $[Na^+] = 230$  mg/L,  $[CO_3^{2-}]_{total} = 0$ ,  $T = 25^\circ C$ , pH=7.0, assumes  $S^{2-} \rightarrow S^0$  during reductive dissolution unless noted, surface area<sub>ferric hydroxide</sub> =  $600$  m<sup>2</sup>/g). For  $S^{2-} \rightarrow SO_4^{2-}$  soluble curve shifts left 25 x-units.

Table A1- Key reactions and considerations used to model arsenate mobilization from Fe(OH)<sub>3</sub> solids at increasing sulfides levels.

Potential sinks for added sulfide	$S^{2-} \rightarrow S^0$ (2 e <sup>-</sup> transfer)	$S^{2-} \rightarrow SO_4^{2-}$ (8 e <sup>-</sup> transfer)
reduction of Fe <sup>3+</sup> to Fe <sup>2+</sup>	29 mg/L	7
reduction of As <sup>5+</sup> to As <sup>3+</sup>	2	0.5
precipitation of FeS (s)	57	57
precipitation of As <sub>2</sub> S <sub>3</sub> (s)	3	3

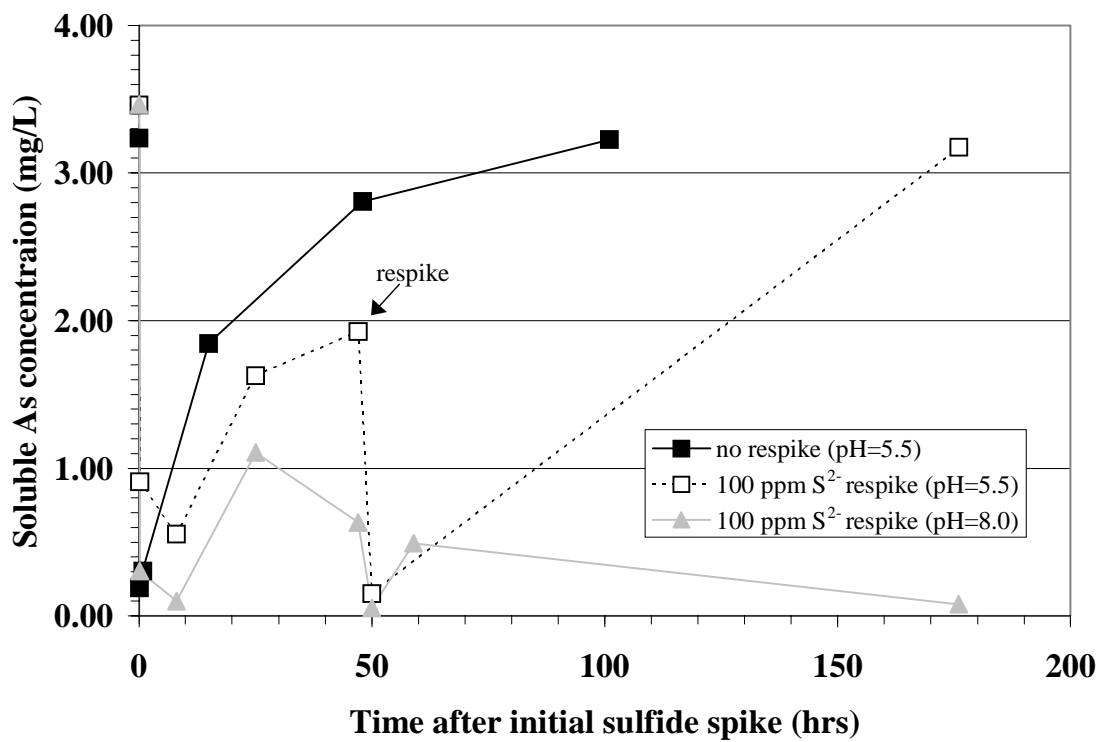


Figure A2- Arsenic precipitation in the absence of Al, Fe, or Si ( $[As]_{total} = 3.5 \text{ mg/L}$ ,  $[S^{2-}]_{initial \text{ spike}} = 70 \text{ mg/L}$ ,  $\mu=0.01 \text{ M}$ )

Table A3- Key reactions considered for the complexation of arsenic by sulfide (38, 39).

Reaction	Reported equilibrium constant
$\text{As}_2\text{S}_3 (\text{s}) + 6 \text{H}_2\text{O} \leftrightarrow 9 \text{H}^+ + 2 \text{AsO}_3^{3-} + 3 \text{HS}^-$	$K_{\text{sp}} = 10^{-115.71}$
$14 \text{H}^+ + 3 \text{AsO}_3^{3-} + 6 \text{HS}^- \leftrightarrow \text{H}_2\text{As}_3\text{S}_6^- + 9 \text{H}_2\text{O}$	$K = 10^{177.17}$
$13 \text{H}^+ + 6 \text{HS}^- + 3 \text{AsO}_3^{3-} \leftrightarrow \text{HAs}_3\text{S}_6^{2-} + 9 \text{H}_2\text{O}$	$K = 10^{170.61}$

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