EFFECT OF CALCIUM ON ARSENIC RELEASE FROM FERRIC AND ALUM SLUDGES AND LAGOONS

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ABSTRACT

The dewatering of arsenic-containing residuals is a process that has received little study in the past. Arsenic that has been removed from water by sorption to ferric or aluminum hydroxides can accumulate in residuals to concentrations many times higher than in the source water. The first part of this study evaluates the effectiveness of lime conditioning as a method for immobilizing this arsenic. As the pH is increased with addition of caustic soda or soda ash, soluble arsenic concentration increases dramatically. However, as the pH is increased with lime, very little arsenic is released back into the water. On the basis of previous research this phenomenon might be attributed to the formation of a calcium arsenate solid. However, this study indicates it is more likely that the soluble calcium neutralizes the negative surface charge on the hydroxide solids at high pH and enhances arsenic sorption compared to when calcium was absent.

In many cases arsenic-containing residuals are stored in lagoons and allowed to reside there for months or even years. Many parameters may affect the soluble arsenic concentration and speciation in these lagoons. The second portion of this study gives some baseline conditions for these lagoons, both with and without microbial activity and biological organic matter. In these practical situations it appears that lime can assist in keeping arsenic sorbed to the solids and prevent its release to the environment.

ACKNOWLEDGEMENTS

I am grateful for the opportunity to work under the direction of my advisors, Dr. John Novak and Dr. Marc Edwards, and for the tremendous support, guidance, and insight they have offered me. Additionally, I would like to thank all the members of my research group for their laboratory assistance, advice, and friendship.

Finally, special thanks go to my family and to my wife, Mary, who has provided me with love and encouragement every step of the way.

AUTHOR'S PREFACE

This work is presented in the Virginia Tech manuscript format. Each chapter is a separate manuscript formatted for journal submission.

Both chapters deal with ways in which calcium can influence arsenic release. In Chapter I an intensive bench scale study of calcium's effect on ferric and aluminum hydroxide residuals and possible mechanisms of interaction are discussed. A study of calcium's effect on ferric and aluminum hydroxide residuals under lagoon conditions is described in Chapter II. This research was supported by the AWWA Research Foundation.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

EFFECT OF CALCIUM ON ARSENIC RELEASE FROM FERRIC AND ALUM SLUDGES

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The dewatering of arsenic-containing residuals is a process that has received little study in the past. Arsenic that has been removed from water by sorption to ferric or aluminum hydroxides can accumulate in residuals to concentrations many times higher than in the source water. This study evaluates the effectiveness of lime conditioning as a method for immobilizing this arsenic. As the pH is increased with addition of caustic soda or soda ash, soluble arsenic concentration increases dramatically as is expected. However, if the pH is increased with lime, very little arsenic is released back into the water. On the basis of previous research this phenomenon might be attributed to the formation of a calcium arsenate solid. However, this study indicates it is more likely that the soluble calcium neutralizes the negative surface charge on the hydroxide solids at high pH and enhances arsenic sorption compared to when calcium was absent.

INTRODUCTION

Background. Arsenic has long been recognized as a human health concern. It is known to cause skin cancer and has been linked to liver, lung, bladder, and kidney cancer (Smith et al, 1992). Currently, the maximum contaminant level (MCL) for arsenic in public drinking water is 50 μg/L. At this level as many as 13 in 1000 people could die from arsenic-induced cancer based on a lifetime consumption of 1 liter per day (Smith et al, 1992).

The 1996 Safe Drinking Water Act required the EPA to revise the 50 μg/L MCL to a value more protective of human health by January 2001. The purpose of the new standard was to maximize the benefits to human health (by reduction of cancer risks) at a cost that can be justified by the benefits. A new standard was released in January 2001

that requires public water supplies to meet an arsenic MCL of 10 µg/L by 2006; however, the rule's effective date has been delayed numerous times.

Once the revised arsenic MCL is in place it is also likely that stricter regulations will be implemented for the disposal of arsenic-containing residuals. Dewatering is an important step in the disposal of drinking water treatment plant residuals. A more effective dewatering process will result in smaller volumes of residuals for disposal. Significant amounts of lime are sometimes used to aid in the conditioning of sludges, especially alum sludge, for dewatering. The pH is often raised into the 10 to 11 range. This can affect not only arsenic speciation but also arsenic solubility. Traditionally it has been thought that as the pH increases, the soluble arsenic concentration will also increase. Other researchers, however, have shown that as the pH is increased using lime, a calcium arsenate solid is formed under certain conditions; thus resulting in a decrease in soluble arsenic (Bothe and Brown, 1999).

Objectives. Little data is available that quantifies what occurs during lime conditioning. This study will quantify the amount of arsenic that will leach from arsenic-laden sludge obtained from two coagulation facilities utilizing various lime dosage rates. The goal is to determine the impact of lime conditioning on arsenic solubility. The mechanism(s) by which arsenic is sorbed or released from sludge solids is also clarified in the context of the data from this study.

MATERIALS AND METHODS

Sludge Sources. Sludge for all experiments was obtained from two sources: the Los Angeles Department of Water and Power and the City of Great Falls, Montana. These treatment plants have relatively high levels of arsenic in their source waters and both use coagulation in their process trains. The City of Los Angeles uses ferric chloride as their coagulant while the City of Great Falls uses alum.

Preliminary Tests. Each sludge was evaluated for solids content using standard method 2540G. Each sludge was also acid-digested per standard method 3030E so that the initial arsenic, iron, and aluminum present could be determined (*Standard Methods*, 1998).

Chemical Conditioning Test Protocol. Nano-pure water was added to each sludge sample such that a final solids concentration of 2% was obtained. Samples were prepared in 250 mL polyethylene bottles by adding an appropriate amount of wet sludge and diluting with nano-pure water to a final volume of approximately 125 mL. Calcium hydroxide (lime), sodium hydroxide (caustic soda), or sodium carbonate (soda ash) was added to individual bottles in varying amounts. The desired range of lime concentrations ranged from 0% to 20% by dry weight. Caustic or soda ash was added to other samples so that pH effects could be observed with and without the presence of calcium.

The initial pH was determined with a Corning 313 pH meter. Samples were then placed on an orbital shaker and allowed to react for 30 minutes. The final pH was then determined and the sample was filtered through a 0.45 micron pore size nylon disposable filter. The filter cake was divided into two parts for the subsequent analysis by the TCLP (Toxicity Characteristic Leaching Procedure) or California WET (Waste Extraction Test) procedure.

TCLP / CaWET Protocol. To fulfill the requirements of AWWARF Project RFP 2659 the filter cakes from the samples to which lime was added were subjected to the TCLP and the California WET tests. The TCLP test was performed per EPA Method 1311 with the following exception: the sample weight was less than 25 grams and a corresponding lower amount of extraction fluid was used. This test combines waste with acetic acid to simulate worst-case conditions that might be found in landfills. Its purpose is to determine if waste can safely be placed in landfills without fear of contaminating the groundwater.

Similarly, the California Waste Extraction Test was performed per the California Department of Toxic Substances Control Hazardous Material Laboratory SOP 910 except a lesser amount of sample was also used as in the TCLP test.   This test is more aggressive than the TCLP because it combines waste with citric acid for a longer reaction time. The citric acid is a chelating agent and usually extracts greater amounts of metals than the TCLP (Hooper et al, 1998). This chelation of iron results in the solubilization of arsenic that was sorbed to the iron.

Calcium Arsenate Solid Formation Test. A 500 mL solution containing calcium chloride and sodium arsenate was prepared. The final concentration was targeted to be 825 mg/L calcium and 2000 µg/L arsenic. These values were selected as they were the highest concentrations observed during the preliminary lime dosing tests. The solution was divided into six (6) aliquots and the pH of each was adjusted using 1 M sodium hydroxide to <8, 9, 10, 11, 12, and 12.5. Each aliquot was placed on an orbital shaker and allowed to react for 30 minutes. Part of each sample was then filtered through a 0.45 micron pore size nylon disposable filter while the remainder was filtered through a 0.025 micron pore size nylon disposable filter. The latter was performed to determine if any small colloidal sized particles were forming under these conditions.

Divalent Cation Theory Test. A 2% solid by weight solution was prepared from the City of Los Angeles ferric sludge. Thirty mL aliquots were taken and the pH was adjusted to 10.0 +/- 0.2 using 1 M sodium hydroxide. Each aliquot was dosed with varying amounts of calcium or magnesium, placed on an orbital shaker for 30 minutes, and then filtered through a 0.45 micron pore size nylon disposable filter. The test was then repeated at pH 11.

Analysis. All samples were analyzed for arsenic, iron, aluminum, calcium, and magnesium, as appropriate, on a JY Ultima Inductive Coupled Plasma – Emission Spectroscopy (ICP-ES) according to standard method 3120B using continuous hydride generation (*Standard Methods*, 1998).

QA / QC. A blank sample was evaluated in conjunction with each test to determine if the reagents used affected the concentration of any element of concern. A matrix 'spike and recovery' was also performed at random on at least 10% of the samples.

Arsenic concentrations in all blanks were below the instrument's detectable limit. Matrix 'spike and recoveries' were performed by adding 200 ppb arsenic to the sample.

4

Recoveries ranged between 85% and 115% in most cases, indicating little matrix interference.

Several replicates of the chemical conditioning tests were performed during the course of this study. Poor recoveries obtained during QA/QC, however, indicated that results of these tests were not sufficiently accurate for citation of data in this report. However, these replicate experiments did show the same general trends for other data collected and presented in this report that passed QA/QC criteria.

RESULTS AND DISCUSSION

Results are organized into two sections. The first is a discussion of the arsenic leachability data obtained from the sludge chemical conditioning tests. In the second section, theories are examined to explain why soluble arsenic concentrations decrease with increasing pH if calcium is present in solution.

Chemical Conditioning Tests

Caustic soda, soda ash, and lime were each evaluated as to their effect on arsenic leachability from ferric and alum sludges over a range of pH values.

Caustic Soda. Each sludge was treated with caustic soda over the pH range encountered with lime treatment. This test was performed to determine whether the observed arsenic release was solely due to a pH effect, i.e. hydroxide concentration. Soluble arsenic increased dramatically as the pH was increased with caustic soda (Figure 1-1). The same trends were observed for both the ferric and aluminum sludges. As much as 30% (w/w) of the available arsenic was leached from the ferric sludge at pH 11.6 when no lime (calcium) was present. This trend is consistent with the expectation based on surface complexation (Dzombak and Morel, 1990);

$$\equiv FeOH + AsO_4^{3-} + 3H^+ \leftrightarrow \equiv FeH_2AsO_4 + H_2O \qquad \text{(Equation 1)}$$
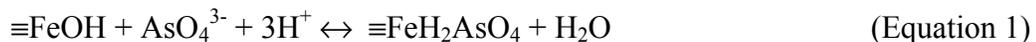
(where $\equiv$ represents a surface site).

As the pH is raised, the hydrogen ion concentration decreases, shifting equilibrium towards the reactants and releasing arsenate to solution.

5

Soda Ash. Each sludge was also treated with soda ash over the pH range encountered with lime treatment. This test was performed to determine the combined effect of pH and carbonate on arsenate release. The same trends were observed as with the caustic soda, but in a few cases the extra carbonate appeared to increase arsenic leaching. A maximum pH of 10.3 was obtained with soda ash for both ferric chloride and alum sludge sources. Soluble arsenic increased dramatically as the pH was increased (Figure 1-1). As much as 12% of the available arsenic was leached from the ferric sludge at pH 10.3 when soda ash was present. This also is consistent with the expectation based on the competition from hydroxide mentioned above, as well as extra competition from carbonate (Villalobos and Leckie, 2001);

$$\equiv FeOH + CO_3{}^{2-} + 2H^+ \leftrightarrow \ \equiv FeOCOOH + H_2O \qquad \text{(Equation 2)}$$
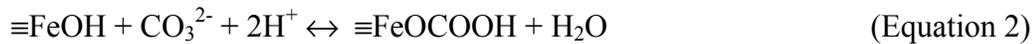
An increase in the carbonate concentration yields the expectation that soluble arsenic concentrations would increase when soda ash is used.

Lime. The data from the lime addition tests yielded some surprising results considering the previous simplistic argument. For the ferric hydroxide sludge the leachate arsenic concentration appeared to peak at a lime dose of approximately 5% (wt/wt) or a pH of 11 (Figure 1-2) and with only 0.55% (wt/wt) of the arsenic leached. By comparison, caustic soda and soda ash addition result in much higher soluble concentrations and an increased soluble arsenic concentration as pH increases. The lime data show the idea of more soluble arsenic leaching as pH increases is not always correct. This appears to be attributable to the increased calcium in the water associated with the use of lime as will be discussed later. Other data from the ferric sludge testing is summarized in Table 1-1.

The aluminum hydroxide sludge treated with lime showed a constant level of leaching and an abrupt increase in soluble arsenic at a lime dose of 20% or a pH of 10 (Figure 1-2). This phenomenon can be explained by looking at the solubility of aluminum. At high pH values, the solubility of aluminum increases dramatically. This is borne out by the data from this experiment. At a pH of 10.2 the soluble aluminum concentration rose to 93 ppm. At this pH, approximately 4% of the total aluminum was in the soluble form (Table 1-2). Since the arsenic was initially sorbed to the aluminum

6

hydroxide solid, as more aluminum is dissolved it can be expected that the soluble arsenic concentration will also increase.

TCLP and California WET results are shown in Tables 1-3 and 1-4. The amount of lime dosed did not seem to affect the final concentrations. At very high lime doses (ca 20%) there was a small decrease in the arsenic concentration. The ferric sludge results ranged from 0.006 to 0.018 for the TCLP and 10.9 to 14.3 ppm for the California WET. The alum sludge results ranged from 0.024 to 0.070 ppm for the TCLP and 6.5 to 8.8 ppm for the California WET. Since the regulatory limit is 5 ppm for both the TCLP and California WET procedures, each sludge passed the TCLP test but failed the California WET test for all lime doses.

Possible Reasons for Reduced Arsenic Leaching in the Presence of Calcium

Two hypotheses were formulated as to why soluble arsenic decreases with increasing pH in the presence of calcium as opposed to when only hydroxide and/or carbonate is present. The first hypothesis is that arsenic is reacting with the calcium to form a calcium arsenate solid (Bothe and Brown, 1999). The second theory is that calcium is somehow enhancing the surface adsorption of arsenic onto the solids in solution. Each of these hypotheses was investigated.

Calcium Arsenate Solid Formation. Formation of calcium arsenate solids has been observed by some researchers at high pH (Bothe and Brown, 1999). To examine whether formation of this solid could explain the results of this work, an experiment was conducted with 825 ppm calcium and 2000 ppb arsenic in solution with no sludge present over the pH range encountered in the previous chemical conditioning tests. Figure 1-3 graphically illustrates that a calcium arsenate solid did not form at a pH below 11.5. At pHs of 12 and 12.5 a calcium arsenate solid may be forming and/or the arsenic may be sorbing to lime that did not dissolve. The calcium and arsenic are not precipitating from solution in a stoichiometric amount and therefore, there could be more than one mechanism responsible.

Divalent Cation Theory. Since there was no calcium arsenate solid forming up to pH 12, the next hypothesis was that the calcium must be impacting the surface properties of ferric hydroxide solids impacting sorption. As the pH increases, the surface charge of ferric or aluminum hydroxide solids will become more negative. Since arsenic is naturally present in its anionic form (i.e. arsenate or arsenite), repulsion would result between the arsenic and the ferric hydroxide solid, resulting in less sorption. Calcium might neutralize this negative surface charge and allow the arsenic to remain sorbed to the ferric hydroxide solids.

To test this hypothesis, various amounts of calcium (as calcium chloride, not lime) or magnesium (as magnesium chloride) were dosed to a fixed amount of ferric hydroxide sludge. Magnesium was used as another representative divalent cation, but one that could not form calcium arsenate. Figure 1-4(a) shows the results obtained when the pH was held at 10. There is very good agreement between the amount of arsenic leached versus the molar amount of either calcium or magnesium remaining in solution, or in other words addition of either calcium or magnesium yield a similar outcome. The same test was also conducted at pH 11. Results for calcium are shown in Figure 1-4(b). Due to the insolubility of magnesium hydroxide at this pH magnesium data are not provided, but the trend for calcium is similar to that observed at pH 10.

Having established that divalent cations enhance the arsenic sorption to ferric hydroxide sludge at high pH, an explanation for this result was sought. The first idea is that cations can reduce the electrostatic repulsion for negatively charged arsenate and thereby retain arsenic on the surface. The second theory is that the divalent cation actually sorbs to the ferric hydroxide surface (Dzombak and Morel, 1990);

$$\equiv FeOH + Ca^{2+} \leftrightarrow \equiv FeOHCa^{2+} \qquad \text{(Equation 3)}$$

$$\equiv FeOH + Ca^{2+} \leftrightarrow \equiv FeOCa^{+} + H^{+} \qquad \text{(Equation 4)}$$
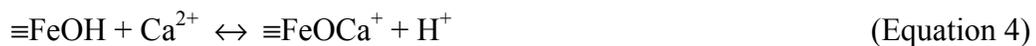
This sorbed calcium might provide a better site to which negatively charged arsenate might sorb. It has been shown that calcium adsorbs to ferric hydroxide surfaces in appreciable amounts at high pH (Smith, 2001). A mass balance on calcium was performed for each lime dose experiment and the amount of particulate calcium was calculated for data in this work. The ratio of particulate calcium to iron as a function of

pH is graphically shown in Figure 1-5, and indicates considerable partitioning of calcium to the solid phase. Since a molar ratio of 0.25 is considered to be the maximum amount of calcium that can sorb to a ferric hydroxide surface, it is readily apparent that a significant portion of the surface is covered with calcium above about pH 11 (Dzombak and Morel, 1990).

Diffuse Layer Compression. A model based on Chen et al. (2001) was used to evaluate the data at both pH 10 and 11 (Figure 1-6) (Chen, 2001). This model utilizes parameters such as ionic strength, pH, total arsenic, and total iron to estimate the percentage of arsenic that will be sorbed to a fresh iron surface. The role of calcium in the model is to shield repulsive forces between sorbed arsenic and no consideration is given to sorbed calcium species. The goal of using the model was to determine the extent to which trends in the data could be predicted based only on calcium involvement in the electrical double layer. The modeling proceeded as follows. First, the model was calibrated by selecting a total quantity of iron surface sites in the system without lime so that the model prediction of arsenic sorption matched the initial value actually present. The calibration was needed because no procedure can readily quantify the actual site density present for this real sample. Soluble calcium concentrations in each experiment were then entered into the model to obtain a prediction of the change in arsenic sorption. There is good agreement between the actual data and the model at these test conditions (Figure 1-6). The model, however, does not predict or explain the increased arsenic sorption at higher pH values (above 11). As noted earlier, there was evidence that lime or other calcium solid phases were also forming at these pH values and it is possible that arsenic was sorbing to these solids.

During this portion of the study no speciation of arsenic was performed and, therefore, it is impossible to ascertain whether the soluble arsenic was present as arsenate or arsenite. It was assumed in the above modeling that all arsenic was present as arsenate (As(V)) since no effort was made to keep the sludge in an anaerobic or anoxic environment. Since the sludge was of unknown age however, some reduction of arsenate could have taken place over time. Figure 1-7 illustrates modeling results that show the

speciation of arsenic and the amount of calcium in solution are both critical in determining sorption efficiency. The results indicate that increasing calcium content in the ferric hydroxide/water solution increases arsenate sorption but decreases arsenite sorption. This phenomenon could explain the modeling results described above and shown in Figure 1-6. If a portion of the arsenic were present as arsenite the model would predict less overall sorption resulting in an upward shift in the model curves shown in the figure. This shift would allow the model to provide a better fit to the actual data at higher levels of calcium.

Summary

Calcium present in water from lime or that is naturally present in 'hard' water appears to be a practical and viable method for immobilizing arsenic sorbed to ferric hydroxide and aluminum hydroxide solids. Ferric sludges do appear to retain their sorbed arsenic to a greater extent than alum sludges at the higher pH values encountered with lime use, probably due to the increased solubility of aluminum at these high pH values. Surface complexation modeling also appears to be a good method to determine the appropriate level of soluble calcium required to minimize arsenic release.

CONCLUSIONS

- Arsenic release from ferric hydroxide sludge increases with increasing pH in the absence of calcium.

- Arsenic release from alum sludge also increases with increasing pH even in the presence of calcium. Calcium does reduce the effect, however, when compared to increasing the pH with either caustic soda or soda ash.

- Lime has little effect on the TCLP or California WET values for both ferric and alum sludges, possibly due to the low pH of these tests.

- The reduction in arsenic leachability at higher pH values is most likely due to the divalent cation effect of calcium and not to the formation of a calcium arsenate solid.

10

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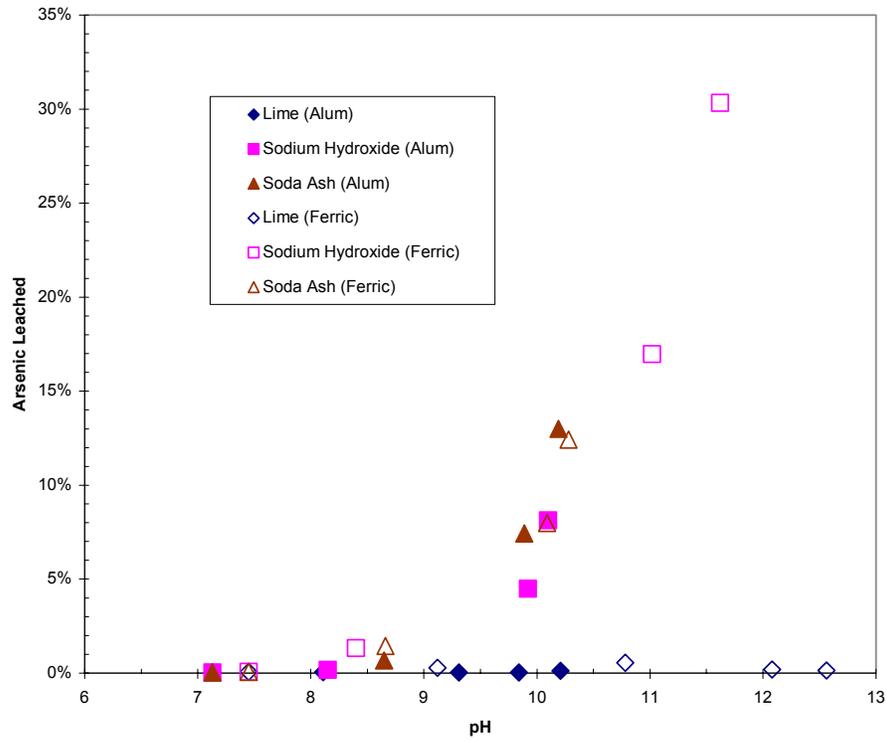
Figure 1-1: Effect of Lime, Sodium Hydroxide, and Soda Ash on Arsenic Leachability from Ferric and Alum Sludges.
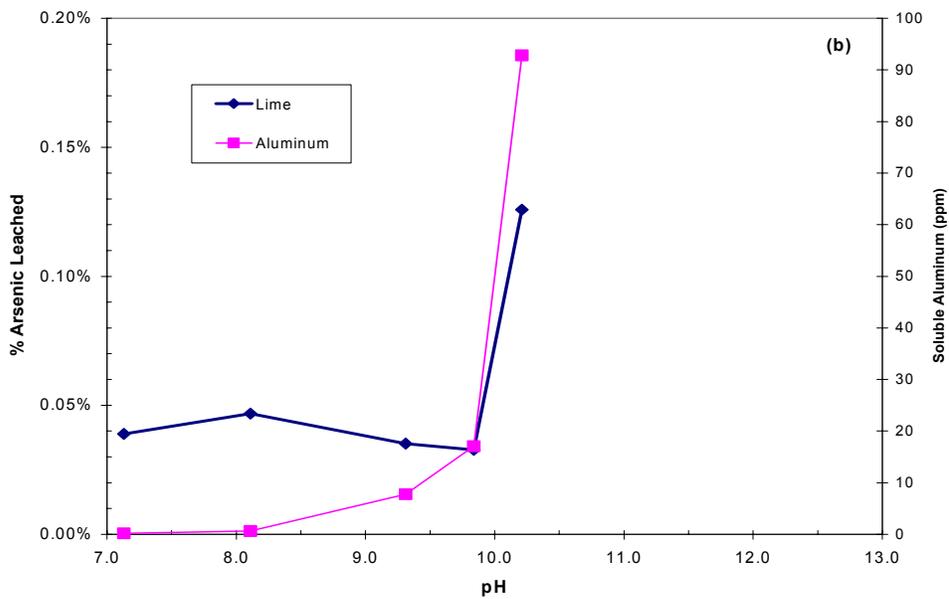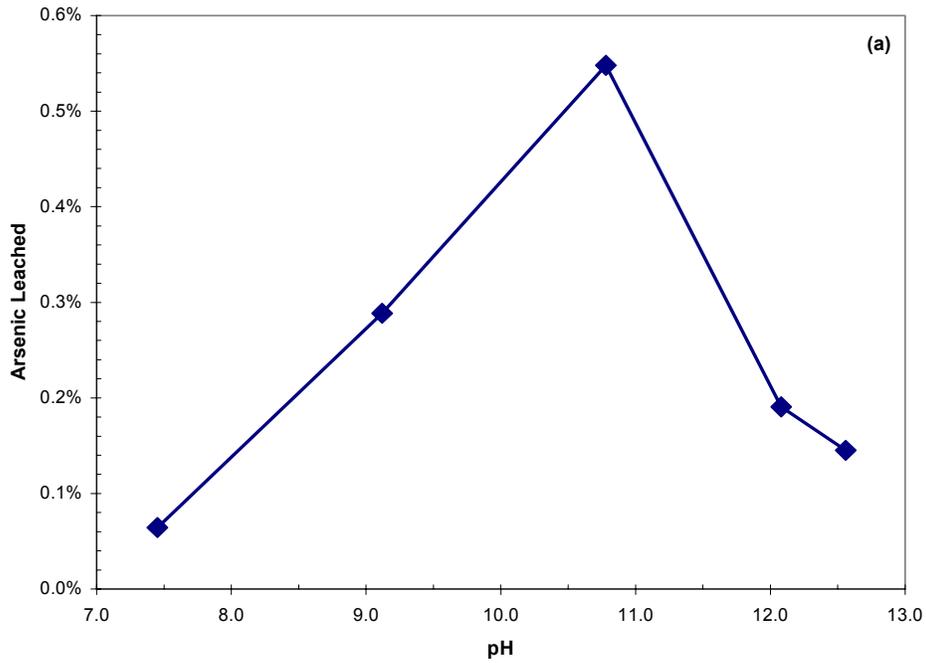
Figure 1-2: Effect of Lime on Arsenic Leachability.

(a) ferric hydroxide sludge from City of Los Angeles; (b) alum sludge from City of Great Falls (Note: this is same data as in Figure 1-1 shown on a different scale.)

Table 1-1: Lime Effects on Sludge from Ferric Coagulation WTP: Leachate Concentration Data

Leachate Concentrations

Lime % (dry w/w)	pH	Arsenic (ppb)	Iron (ppm)	Aluminum (ppm)	Calcium (ppm)	% As Leached
0.00%	7.5	9.6	0.004	0.017	3.7	0.064%
1.39%	9.1	42	0.014	0.077	23	0.289%
4.41%	10.8	82	0.003	0.268	47	0.548%
9.13%	12.1	29	0.002	0.915	291	0.190%
18.48%	12.6	21	0.010	1.252	500	0.145%

Table 1-2: Lime Effects on Sludge from Alum Coagulation WTP: Leachate Concentration Data

Leachate Concentrations

Lime % (dry w/w)	pH	Arsenic (ppb)	Iron (ppm)	Aluminum (ppm)	Calcium (ppm)	% As Leached
0.00%	7.1	5.3	ND	0.15	27	0.039%
1.38%	8.1	6.4	ND	0.62	39	0.047%
5.35%	9.3	4.8	ND	7.8	30	0.035%
9.82%	9.8	4.5	ND	17	38	0.033%
19.58%	10.2	17	ND	93	117	0.126%

Table 1-3: Lime Effects on Sludge from Ferric Coagulation WTP: TCLP and CaWET Data

Lime % (dry w/w)	pH	TCLP (ppm As)	CA WET (ppm As)
0.00%	7.5	0.006	11.6
1.39%	9.1	0.006	14.3
4.41%	10.8	0.018	13.6
9.13%	12.1	0.014	13.1
18.48%	12.6	0.010	10.9

Table 1-4: Lime Effects on Sludge from Alum Coagulation WTP: TCLP and CaWET Data

Lime % (dry w/w)	pH	TCLP (ppm As)	CA WET (ppm As)
0.00%	7.1	0.031	8.8
1.38%	8.1	0.070	7.7
5.35%	9.3	0.050	7.9
9.82%	9.8	0.037	8.0
19.58%	10.2	0.024	6.5
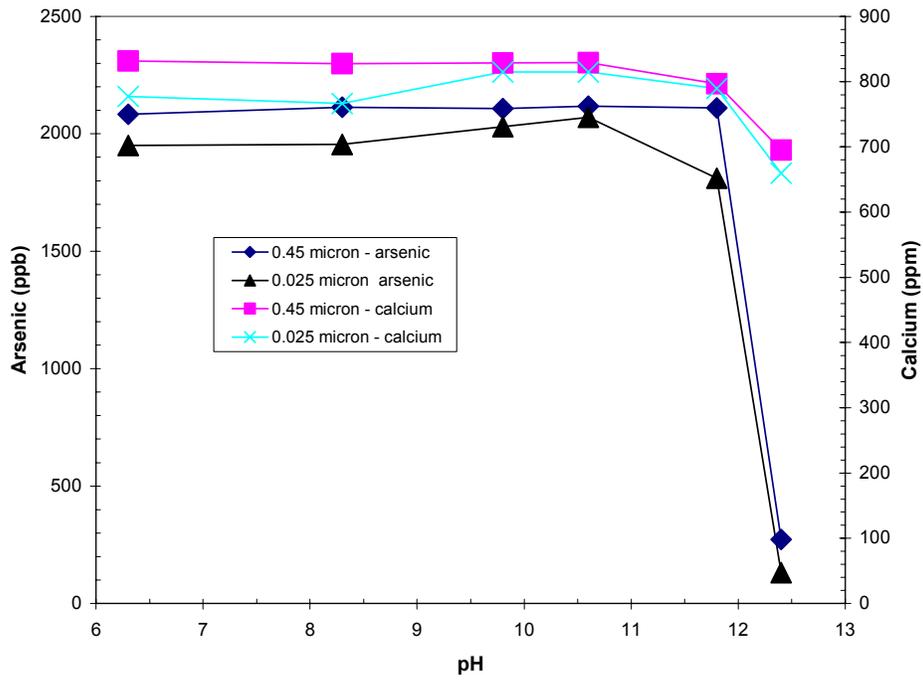
Figure 1-3: Calcium Arsenate Solid Formation Test.

Data indicates precipitation does not occur until pH 11.5. Even above this pH calcium and arsenic do not precipitate stoichiometrically.
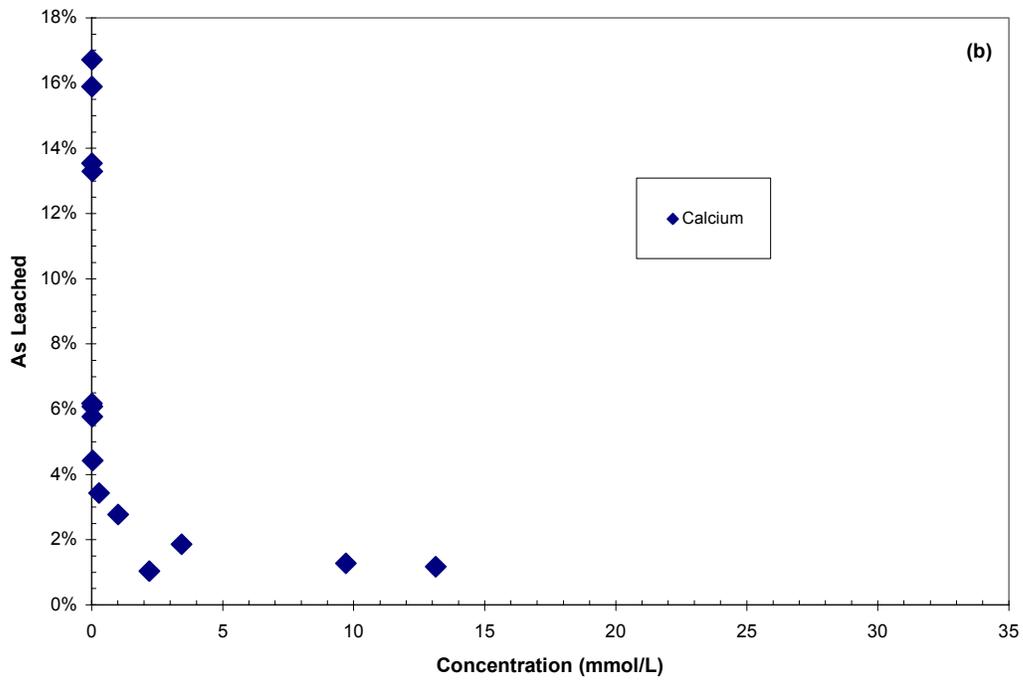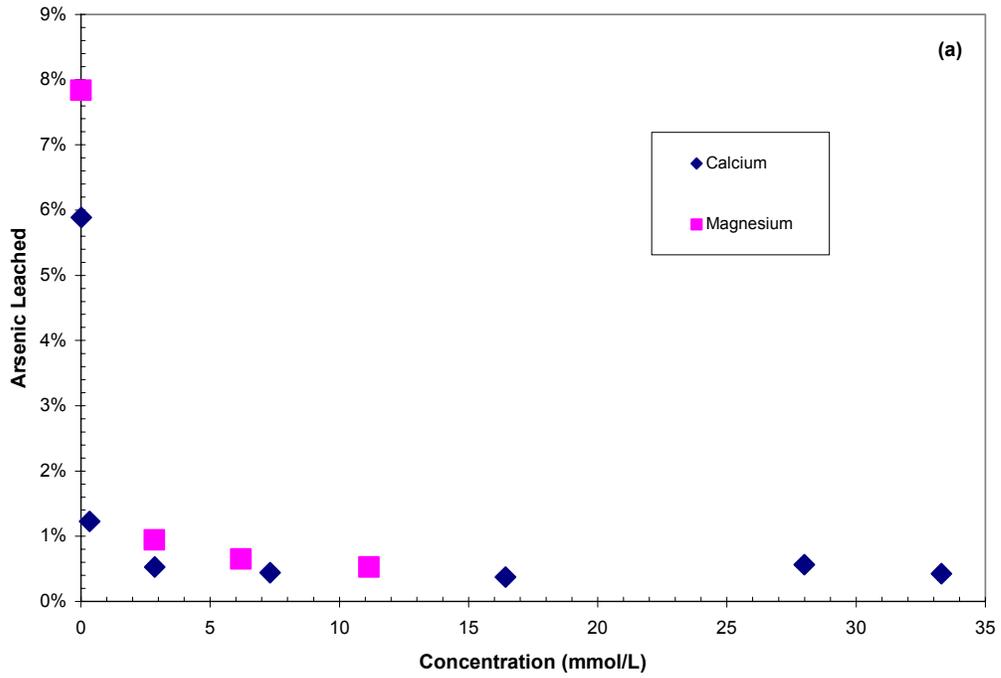
Figure 1-4: Divalent Cation Test.

(a) pH 10; (b) pH 11
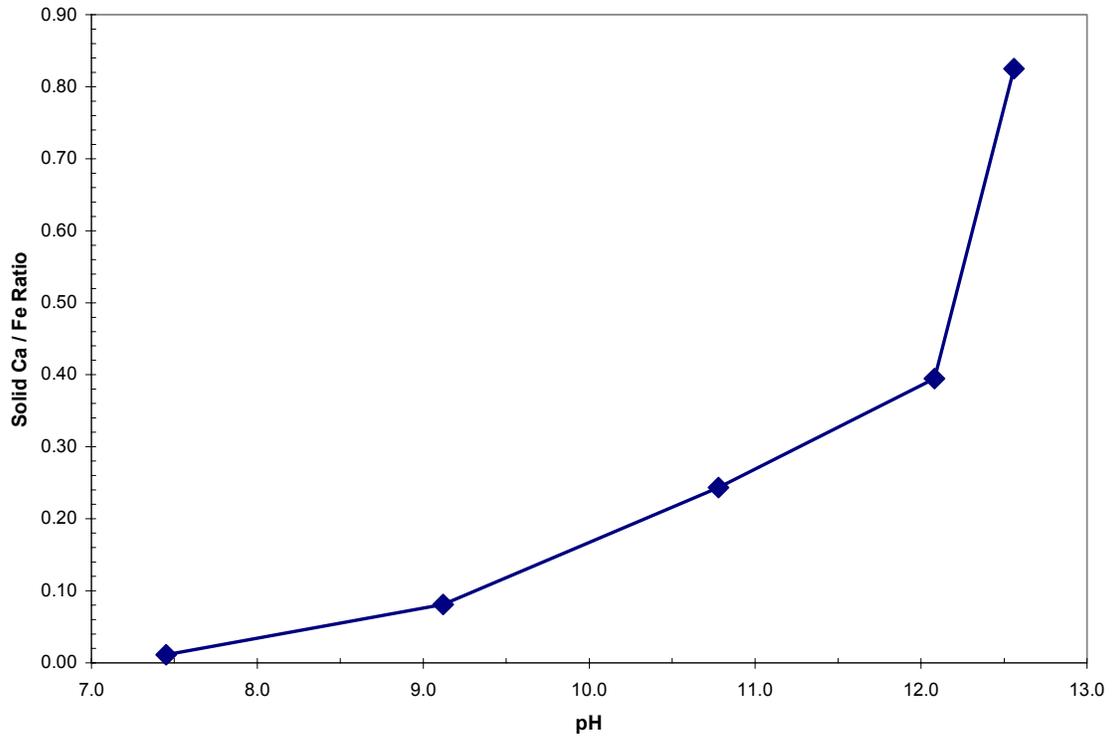
Figure 1-5: Particulate Calcium: Particulate Iron Molar Ratio v. pH
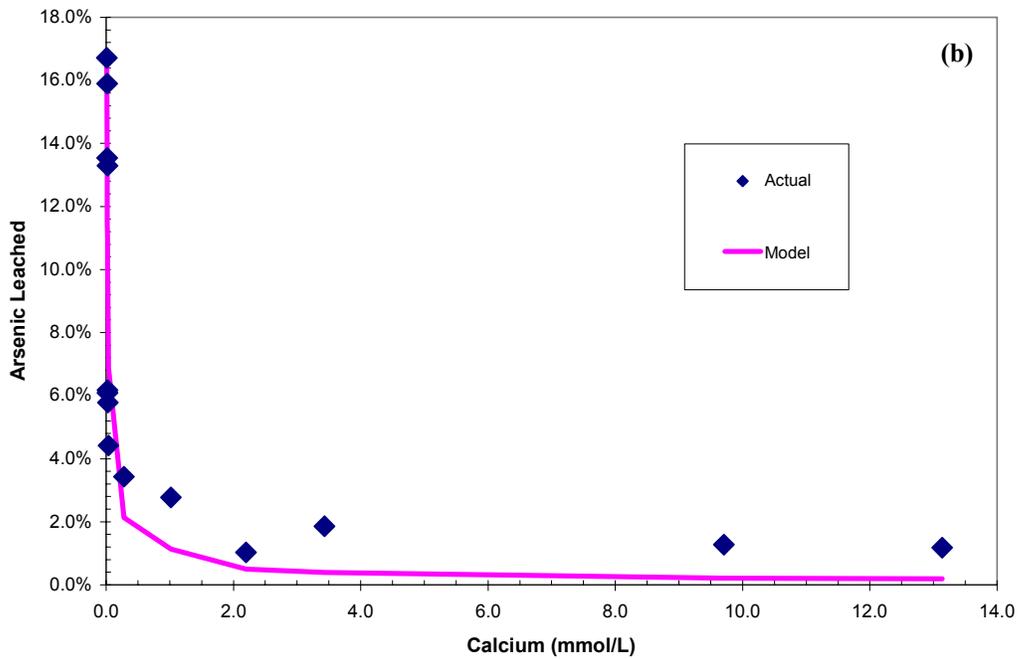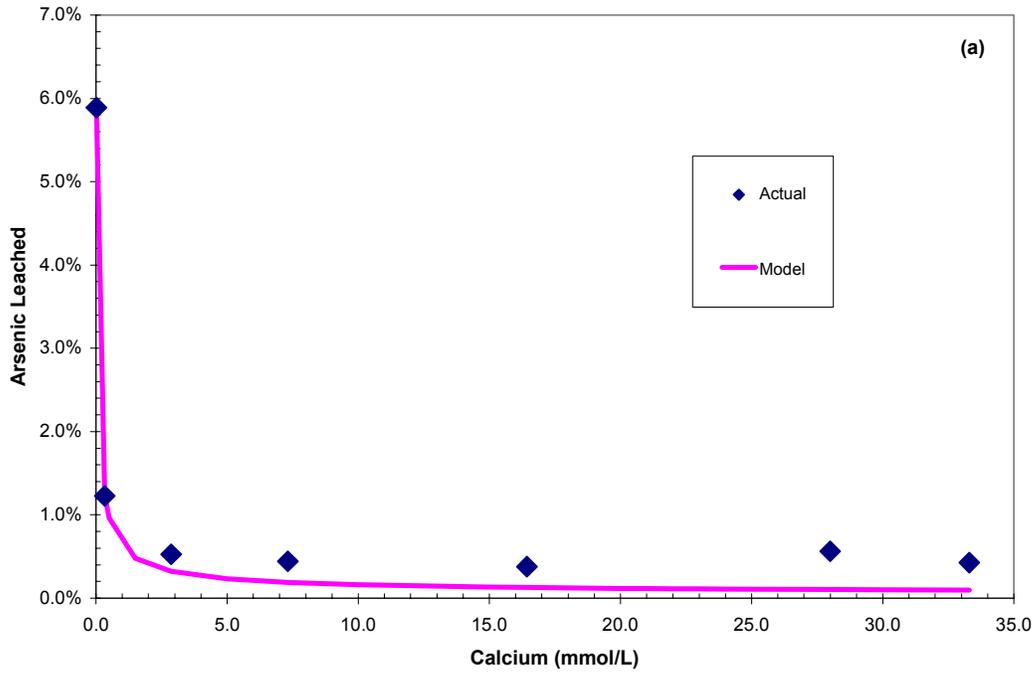
Figure 1-6: Surface Complexation Model.

(a) pH = 10; (b) pH = 11

19
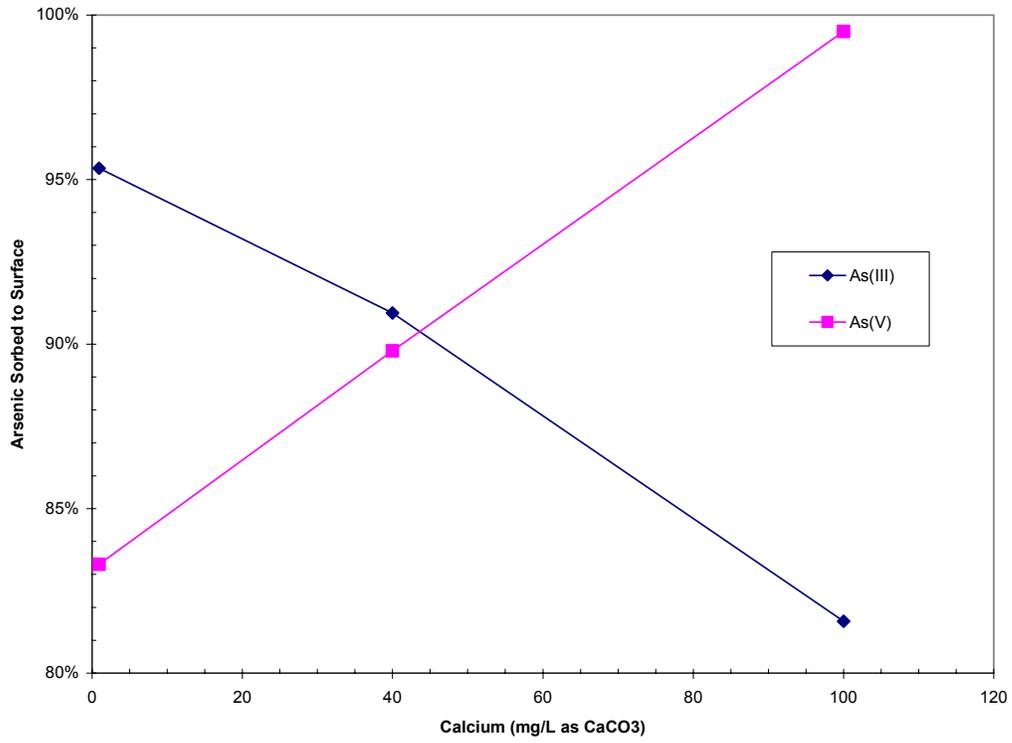
Figure 1-7: As(V) and As(III) vs. Calcium at pH 11 Modeling Results

Note: Total iron sites available = 56.4 mM; total arsenic in system = 0.194 mM

CHAPTER II

SOLUBLE ARSENIC CHARACTERISTICS IN LAGOONS OF FERRIC CHLORIDE AND ALUM COAGULATION WATER TREATMENT PLANTS

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The disposal of arsenic-containing wastes will receive more attention once the new arsenic MCL goes into effect. Arsenic that has been removed from water by sorption to ferric or aluminum hydroxides can accumulate in residuals to concentrations many times higher than in the source water. In many cases these residuals are stored in for months or even years. Many parameters may affect the soluble arsenic concentration and speciation in these lagoons. This study gives some baseline results for these lagoons, both with and without microbial activity and biological organic matter. It is also shown that lime can assist in keeping the arsenic sorbed to the solids and prevent release into the water.

INTRODUCTION

Arsenic has long been recognized as a human health concern. It is known to cause skin cancer and has been linked to liver, lung, bladder, and kidney cancer (Smith et al, 1992). Currently, the maximum contaminant level (MCL) for arsenic in public drinking water is 50 µg/L. At this level as many as 13 in 1000 people could die from arsenic-induced cancer based on a lifetime consumption of 1 liter per day (Smith et al, 1992).

The 1996 Safe Drinking Water Act required the EPA to revise the 50 µg/L MCL to a value more protective of human health by January 2001. The purpose of the new standard was to maximize the benefits to human health (by reduction of cancer risks) at a cost that can be justified by the benefits. A new standard was released in January 2001 that requires public water supplies to meet an arsenic MCL of 10 µg/L by 2006, however the rule's effective date has been delayed numerous times.

Once the revised arsenic MCL is in place it is also likely that stricter regulations will be implemented on the disposal of arsenic-containing residuals. Currently the limit

to dispose of waste in landfills is a Toxicity Characteristic Leaching Procedure (TCLP) value of 5 mg arsenic/L. This is 100 times the value of the current drinking water standard.

A common practice among water utilities is to place these residuals in lagoons and eventually allow the lagoons to dry and then ship the waste to a landfill for disposal. Currently, there are no regulations regarding the concentration of arsenic allowed in these lagoons – only that the TCLP of the waste that is hauled away is less than 5 mg/L. The water from these lagoons is normally pumped back into the treatment plant but in the case of unlined lagoons some of this water will find its way into the groundwater.

Many parameters have the potential of affecting the soluble arsenic concentration in storage lagoons, including pH, dissolved oxygen concentration, microbial activity, age of solids, and other trace metal concentrations to name a few. Previous research has shown that the speciation of arsenic is extremely important. Arsenic in its reduced form (As^{3+}) is much more toxic and much harder to remove from water than its oxidized form (As^{5+}) (Edwards, 1994). A recent study by Langner and Inskeep (2000), however, suggests that the reduction of As^{5+} plays a minor role in the solubilization of As^{5+} sorbed to ferric hydroxide.

This study will measure changes in soluble arsenic in lagoons at ferric chloride and alum coagulation water treatment plants. The goal is to determine the effect of biological organic matter on arsenic leaching, and what effect lime (calcium) has on the soluble arsenic concentration in these lagoons. The mechanism by which arsenic is sorbed or released from sludge solids is also discussed in the context of the data from this study.

MATERIALS AND METHODS

Sludge Sources. Sludge for all experiments was obtained from six sources: the Los Angeles Department of Water and Power; the City of Great Falls, Montana; the Indiana-American Water Company; the Lockwood Water Users Association; the City of Billings, Montana; and the City of Helena, Montana. These treatment plants have relatively high levels of arsenic in their source waters and all use coagulation in their

process trains. The City of Los Angeles, the Indiana-American Water Company, the Lockwood Water Users Association, and the City of Billings all use ferric chloride as their coagulant, while the City of Great Falls and the City of Helena both use alum.

Preliminary Tests.   Each sludge was evaluated for solids content using standard method 2540G. Each sludge was also acid-digested per standard method 3030E so that the initial arsenic, iron, and aluminum present could be determined (*Standard Methods*, 1998).

Ferric Lagoon Simulations.   Sludge from the four plants utilizing ferric chloride coagulant was received and divided into four 2-liter acid washed glass jars. The sludge in one jar was analyzed immediately for pH, dissolved oxygen, soluble arsenic, and soluble iron as follows: the sludge was separated into solid and liquid portions using a Whatman #41 filter (20-25 μm pore size). The liquid portion of the sludge was acid digested (EPA Method 3010) and analyzed with ICP-AES for total iron, aluminum, and arsenic. The other three jars were stored in the dark at a constant temperature of 20 °C to simulate lagoon storage. These jars were opened and analyzed at two, four, and six months. (Itle, 2001)

Ferric and Alum Lagoon Simulations with Biological Organic Matter.
Sludge from the City of Los Angeles was used for the ferric lagoon simulations and sludge from the City of Great Falls, Montana was used for the alum lagoon simulations. Three ferric lagoons and two alum lagoons were prepared in glass jars. Each lagoon held a total volume of 700 mL. Ferric sludge was added to three of these such that the solids concentration was 10%. Similarly, alum sludge was added to the other two such that the solids concentration was 6% (10% solids was extremely difficult to pour). Lime was added to two of the ferric lagoons such that the final concentration was 10% and 20% respectively (based on g lime/g dry solids). Lime was added to one of the alum lagoons for a final concentration of 10%. A third alum lagoon with 20% lime was not simulated due to the large amount of aluminum that would be dissolved at this pH. Activated sludge was obtained from the local wastewater treatment plant and used as a source of

23

biological organic matter (BOM). Approximately 10 mL was added to each lagoon.
Bactopeptone (500 mg/L), glucose (500 mg/L), and sodium sulfate (200 mg/L) were also
added to provide a source of food for the microbes. The jars were stored in the dark at a
constant temperature of 20 °C. Periodically, a 20 mL sample was withdrawn and
analyzed for pH and soluble arsenic, iron, aluminum, and calcium. At the end of the test
sulfide concentration was measured with a portable spectrophotometer. The speciation of
the arsenic was also determined at the end of the test according to the procedure given in
Edwards et al (1998).

Analysis. All samples were analyzed for arsenic, iron, aluminum, and calcium on
a JY Ultima Inductive Coupled Plasma – Emission Spectroscopy (ICP-ES) according to
standard method 3120B using continuous hydride generation (*Standard Methods*, 1998).

QA / QC. A blank sample was evaluated in conjunction with each test to
determine if the reagents used affected the concentration of any element of concern. A
matrix 'spike and recovery' was also performed at random on at least 10% of the
samples.

RESULTS AND DISCUSSION

Results are organized into two sections. The first section is a discussion of the
bench scale lagoons simulating lagoons at treatment plants that use ferric chloride as a
coagulant; specifically, the mechanism(s) that influence the soluble arsenic concentration
in these lagoons. In the second section the effect of lime addition to one of these lagoons,
as well as an alum plant lagoon, in the presence of BOM is discussed.

Ferric Lagoon Simulations

Four treatment plants that use ferric chloride as a coagulant were evaluated during
this study. Data from a companion thesis will be presented and modeled in an attempt to
identify possible mechanisms of arsenic dissolution from these ferric hydroxide sludges
(Itle, 2001).

Data and Observations. Dissolved oxygen in most cases was less than 1.0 mg/L and never exceeded 4.0 mg/L in any lagoon (Table 2-1). From these data it appears that an increase in the soluble iron concentration is associated with a corresponding increase in the soluble arsenic concentration (Figure 2-1). The change in soluble arsenic can also be plotted against the change in soluble iron (vs. initial concentration) (Figure 2-2) indicating that as more iron dissolves into the water, more arsenic is also made soluble. A strong correlation ($r^2 = 0.96$) appears if the Los Angeles data are eliminated, reasons for which will be discussed later (Figure 2-3).

One hypothesis to explain why soluble arsenic increases as the soluble iron increases is that dissolution of the iron hydroxide sorbent causes release of arsenic to the water. A model based on Chen et al. (see Appendix) was used to evaluate the data (Chen, 2001). This model utilizes parameters such as ionic strength, pH, total arsenic, and total iron to estimate the percentage of arsenic that will be sorbed to a fresh iron surface. The modeling proceeded as follows. First, the total quantity of iron that was not dissolved was estimated from the size of the bench scale lagoon, the amount of dry solids present, and the amount of iron per weight of dry solid. The undissolved concentration of iron and solution pH was entered for each lagoon at each sampling interval. Total arsenic availability was chosen by matching the initial amount of arsenic sorbed (i.e., a total arsenic concentration was chosen so that the predicted soluble arsenic matched the observed value). All arsenic was assumed to be in the pentavalent (As^{5+}) oxidation state at all times.

Table 2-2 shows the results of this modeling exercise. While there are many reasons why the model predictions may vary from field or laboratory data, the results suggest that the dissolution of iron cannot account for the increase of soluble arsenic. It retrospect this seems logical because only 0.4% of the iron sorbent was dissolved.

A second hypothesis is that the arsenic is converted to the reduced trivalent (As^{3+}) oxidation state in addition to dissolution of the iron hydroxide sorbent. Since As^{3+} sorbs less strongly to iron, this would release more arsenic to the water.

Modeling of this hypothesis was performed as before. Total arsenic was selected based on the soluble As^{5+} in the water. This time, however, the soluble arsenic was

assumed to be completely reduced to As^{3+} and a new equilibrium established. The model results for both Indiana and Lockwood overpredict the soluble arsenic (Table 2-3). This means that the experimentally observed releases could be explained if a fraction of the arsenic is still in the oxidized pentavalent state. The Billings modeling results indicate that much more arsenic (2 – 5 times) is soluble than would be predicted; however, the trend is correct. Thus, for these waters it seems possible that conversion of As(V) to As(III) could explain the results.

The Los Angeles modeling results require further explanation. The time zero soluble arsenic is extremely high (358 ppb). If the sludge is fresh then the soluble arsenic concentration should be close to the concentration in the plant effluent (e.g. see time zero soluble arsenic concentrations from the other plants). Since Los Angeles obviously does not supply water with 358 ppb arsenic, some arsenic must have leached from the solids before our analysis during transport to our lab.

There are several explanations for the model's inability to predict the elevated soluble arsenic concentrations at both Billings and Los Angeles. The model is only applicable to 'fresh' ferric hydroxide solids and 'aged' solids will have a lower surface area and a reduced number of surface sites (Dzombak and Morel, 1990). Less surface sites will mean fewer places for arsenic to sorb and therefore a higher arsenic concentration in solution. Another possible explanation is that the ferric iron may be transforming into ferrous iron and subsequently the ferrous iron combines with sulfide to produce a FeS solid. Although the iron is still in the solid phase FeS has a much lower sorption capacity as compared to ferric hydroxide and therefore more arsenic will be in solution (Davis, 2001). A third explanation may be that arsenic sulfide complexes could be forming as the lagoon environment becomes more reduced and complex formation would tend to increase arsenic leaching although other researchers did not find evidence that they formed (Davis, 2001).

Ferric and Alum Lagoon Simulations with BOM

It is widely known that the presence of bacterial activity and BOM lead to reducing conditions in a non-oxygenated environment. The effect of lime treatment on

various lagoons seeded with BOM is presented so that its viability as a treatment option can be evaluated.

Data and Observations. Samples from each lagoon were taken periodically. Concentrations of soluble arsenic, iron, aluminum, and calcium, as well as pH were determined throughout the study. Sulfide concentration was determined at the end of the study. Results are shown in Table 2-4 and Figure 2-4.

Ferric Lagoons. Three ferric hydroxide lagoons with 0%, 10%, and 20% lime were studied. Various trends were noted and will be discussed in turn.

pH: The pH of each lagoon was relatively constant over the course of the study.

Arsenic concentration: The soluble arsenic concentration in the 0% lime lagoon continued to increase as the test proceeded, while the arsenic in the 10% and 20% lime lagoons decreased slightly and then leveled off. It can also be noted that the soluble arsenic concentration decreased as the lime dose was increased.

Iron concentration: The soluble iron concentration in the 0% lime lagoon also continued to increase over the course of the test. The soluble iron in the other lagoons was fairly constant at a value similar to the initial concentration in the 0% lime lagoon.

Calcium concentration: The soluble calcium concentration in the 0% lime lagoon was fairly constant throughout the test. Calcium in the other lagoons decreased during the test. This was probably due to lime or calcium carbonate precipitation.

Sulfide concentration: The sulfide concentration was fairly low for the 0% and 10% lime lagoons (0.066 mg/L and 0.025 mg/L respectively). The 20% lime lagoon, however, had a relatively high sulfide concentration of 0.22 mg/L and a noticeable rotten egg odor.

Additionally, tests were conducted to determine the speciation of the soluble arsenic in each lagoon at the end of the test. The arsenic in the ferric lagoon with 0% lime was 100% As^{3+} at the end of the test. The lagoon with 10% lime had 49% As^{3+} and 51% As^{5+}. The lagoon with 20% lime had 64% As^{3+} and 36% As^{5+}. These results are not surprising since it was expected that the reduction of As^{5+} would be less when lime was present since the high pH might reduce bacterial activity. It was unexpected,

27

however, that the fraction of reduced arsenic would be slightly higher in the 20% lime lagoon versus the 10% lime lagoon and that sulfides were present in appreciable amount in the 20% lime lagoon. At this time we have no logical explanation for this occurrence. The presence of sulfide might suggest that the precipitation of orpiment (As_2S_3) is controlling arsenic solubility. At these levels of sulfide, however, there should be no arsenite in solution based on available constants.

As noted in the earlier bench scale lagoon tests, part of the reason arsenic is released as the soluble iron concentration is increased could be that arsenic is reduced to the trivalent oxidation state. This is exactly what was observed in this test as well. In the 0% lime lagoon where 100% of the arsenic is in the trivalent oxidation state, the soluble arsenic continued to increase as the test proceeded. On the other hand, in the 10% and 20% lime lagoons where the soluble iron concentration was fairly constant, the soluble arsenic concentration also remained fairly constant. We think that this is due to the lessened microbial activity in these lagoons; i.e. curtailed microbial activity means less arsenic is being reduced to the trivalent oxidation state.

Alum Lagoons. Two aluminum hydroxide lagoons with 0% and 10% lime were studied. Various trends were noted and will be discussed in turn.

pH: The pH of the 0% lime lagoon increased while the pH of the 10% lime lagoon decreased slightly during the course of the test.

Arsenic concentration: The soluble arsenic concentration in both lagoons continued to increase as the test proceeded.

Aluminum concentration: The soluble aluminum concentration in the 0% lime lagoon was relatively constant over the course of the test. The soluble aluminum in the 10% lime lagoon was extremely high at the outset of the test but began decreasing and continued to decrease throughout the test.

Calcium concentration: The soluble calcium concentration was fairly constant throughout the test in both lagoons.

28

Sulfide concentration: The sulfide concentration was extremely high in both the 0% and 10% lime lagoons (1.150 mg/L and 1.024 mg/L respectively). Both lagoons had a very noticeable sulfide odor.

Tests were also conducted to determine the speciation of the soluble arsenic in each of these lagoons. The arsenic in the alum lagoon with 0% lime was 60% As^{3+} and 40% As^{5+} at the end of the test. The lagoon with 10% lime had 39% As^{3+} and 61% As^{5+}.

No surface complexation models are currently available for aluminum hydroxide solids. However, it seems logical to assume that the increase in soluble arsenic corresponds to the reduction of arsenic from the pentavalent to the trivalent oxidation state. It is somewhat unexpected that in the 10% lime lagoon, the soluble arsenic is fairly low (19 ppb) at the outset of the test even though the soluble aluminum is quite high (88 ppm). This undoubtedly signifies that the dissolution of the aluminum hydroxide solid does not cause an increase in soluble arsenic. This might be expected, since only 0.2% of the total aluminum hydroxide solid sorbent in this sample had dissolved.

CONCLUSIONS

- Arsenic release in lagoons appears to be triggered partly by the reduction of arsenate to arsenite and not by the dissolution of iron.

- Lime addition reduces the amount of arsenic in solution when biological organic matter is present for both ferric and alum lagoons even though arsenic is being reduced from As(V) to As(III).

ACKNOWLEDGEMENT

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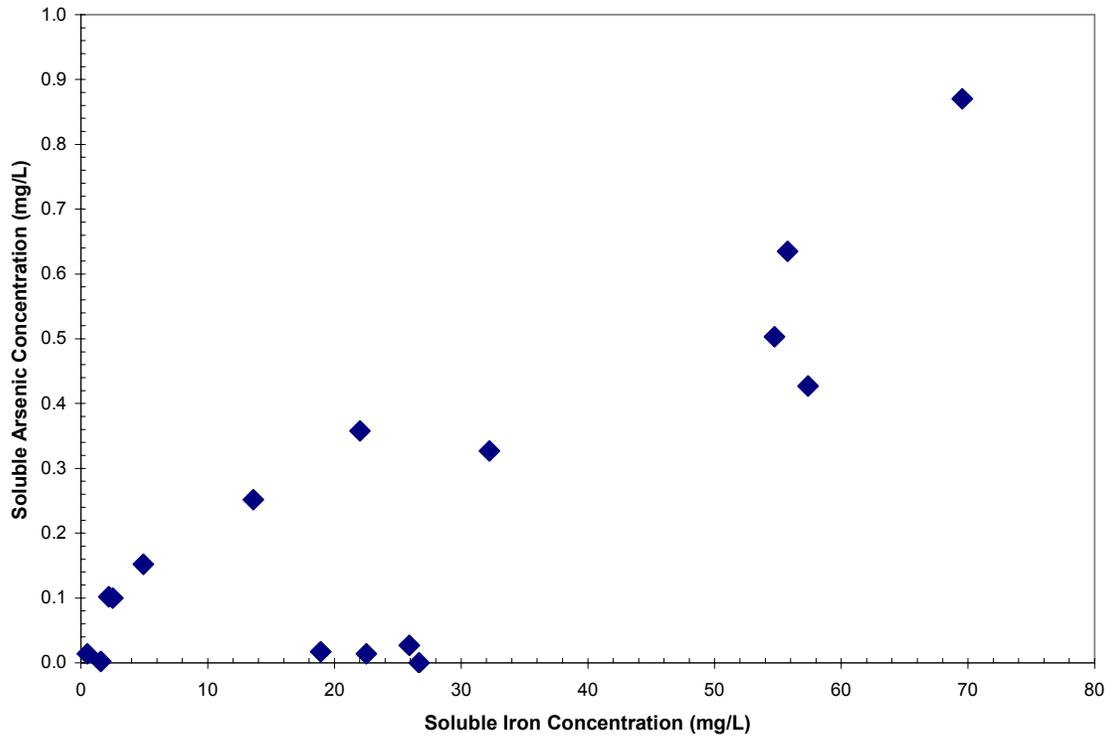
Figure 2-1: Soluble Arsenic v. Soluble Iron

Data from 6 month bench scale lagoon study on sludge from four ferric chloride coagulation water treatment plants
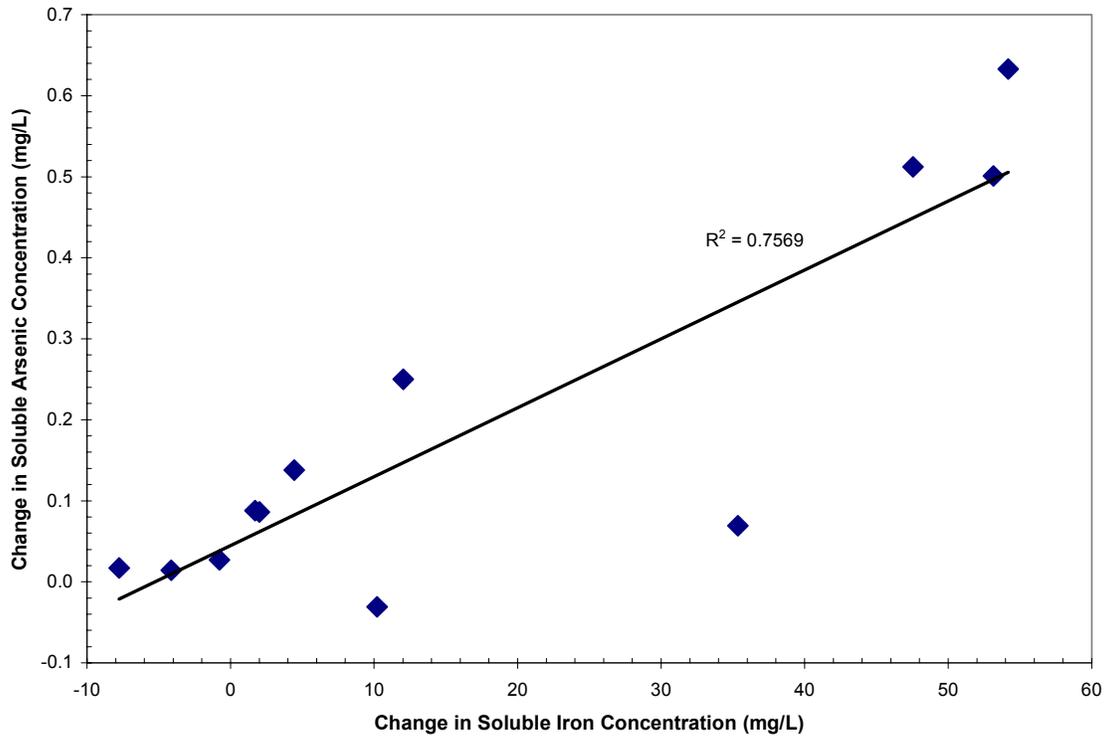
Figure 2-2: Change in Soluble Arsenic v. Change in Soluble Iron

Data from 6 month bench scale lagoon study on sludge from four ferric chloride coagulation water treatment plants
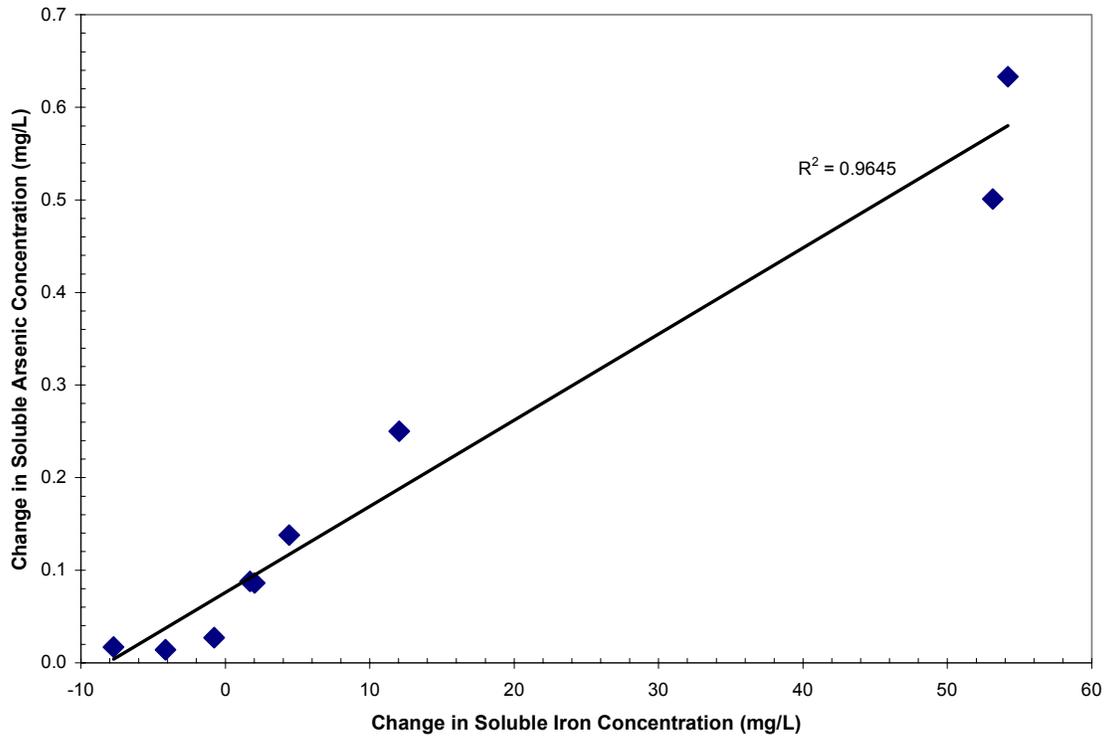
Figure 2-3: Change in Soluble Arsenic v. Change in Soluble Iron (excl. Los Angeles)

Data from 6 month bench scale lagoon study on sludge from three ferric chloride coagulation water treatment plants
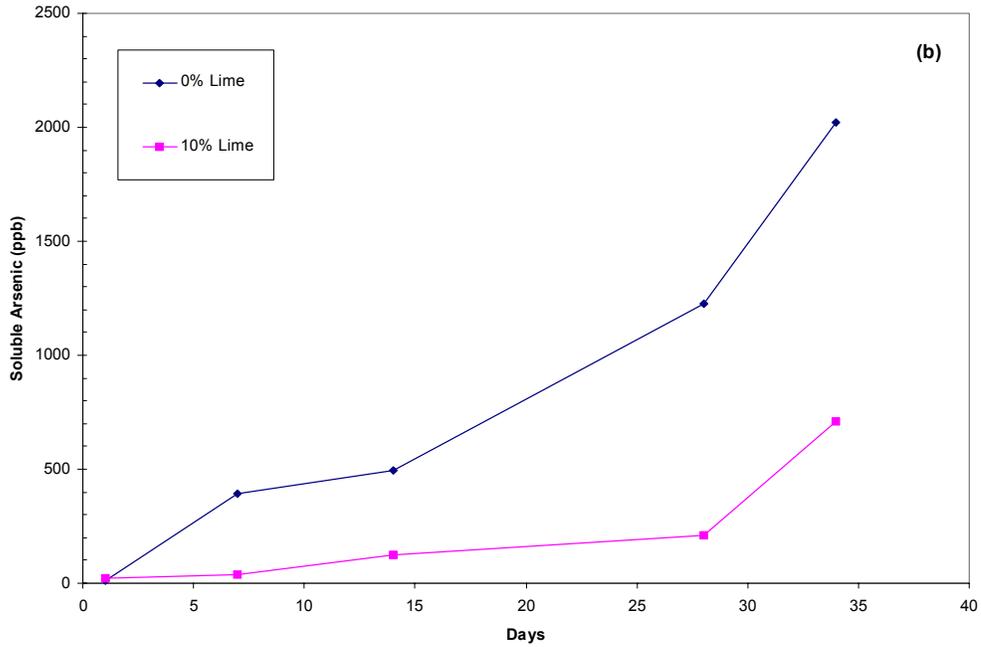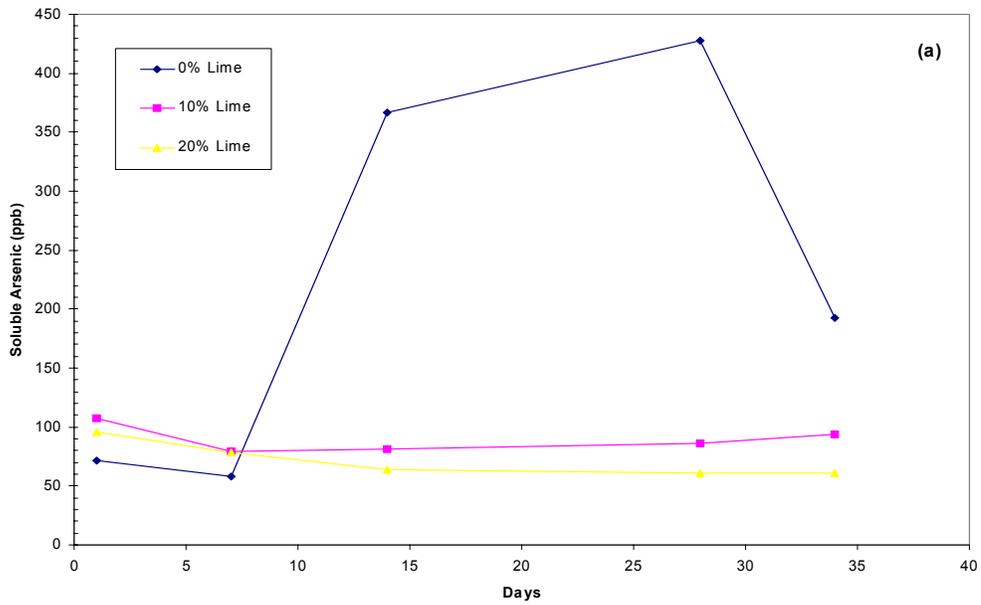
Figure 2-4: Soluble Arsenic v. Time for Lagoons Dosed with BOM
(a) ferric; (b) alum

Table 2-1: Data from Bench Scale Lagoon Study

(sludge from four ferric chloride coagulation water treatment plants)

Plant	Time (months)	pH	Dissolved Oxygen (mg/L)	Soluble As (mg/L)	Soluble Fe (mg/L)
Billings	0	6.95	3.15	0.002	1.57
	2	7.20	1.30	0.503	54.72
	4	7.11	0.70	0.635	55.76
	6	7.12	0.60	0.252	13.60
Indiana	0	7.20	4.00	0.014	0.50
	2	7.05	2.30	0.102	2.20
	4	7.03	1.00	0.100	2.52
	6	6.92	0.70	0.152	4.93
Lockwood	0	7.18	1.15	0.000	26.67
	2	7.44	0.50	0.027	25.90
	4	7.16	0.50	0.017	18.92
	6	7.22	0.40	0.014	22.53
Los Angeles	0	7.18	1.20	0.358	22.01
	2	7.06	0.40	0.870	69.56
	4	7.05	0.40	0.427	57.37
	6	6.94	0.50	0.327	32.23

Table 2-2: Summary of Lagoon Data and Model Results: As(V) Model only

Lagoon	Time (months)	Soluble As (mg/L)	Model Predicted As (mg/L)
Billings	0	0.0020	
	2	0.5028	0.0051
	4	0.6347	0.0037
	6	0.2522	0.0037
Indiana	0	0.0142	
	2	0.1022	0.0082
	4	0.1001	0.0076
	6	0.1521	0.0052
Lockwood	0	0.0000	
	2	0.0266	0.0008
	4	0.0174	0.0003
	6	0.0136	0.0003
Los Angeles	0	0.3584	
	2	0.8704	0.2376
	4	0.4857	0.2277
	6	0.3266	0.1528

Table 2-3: Summary of Lagoon Data and Model Results: As(III) Model only

Lagoon	Time (months)	Soluble As (mg/L)	Model Predicted As (mg/L)
Billings	0	0.0020	
	2	0.5028	0.1152
	4	0.6347	0.1150
	6	0.2522	0.1146
Indiana	0	0.0142	
	2	0.1022	0.1308
	4	0.1001	0.1308
	6	0.1521	0.1306
Lockwood	0	0.0000	
	2	0.0266	0.0709
	4	0.0174	0.0704
	6	0.0136	0.0705
Los Angeles	0	0.3584	
	2	0.8704	0.1846
	4	0.4857	0.1844
	6	0.3266	0.1838

Table 2-4: Lagoon Study Data – Ferric/Alum Sludge Dosed with BOM

Lagoon	Lime Dose	Time (days)	pH	Arsenic (ppb)	Iron (ppm)	Aluminum (ppm)	Calcium (ppm)	Sulfide (ppm)
Ferric	0%	1	7.25	72.1	0.19	0.09	15.2	
		7	7.23	57.8	7.54	0.16	35.7	
		14	7.35	367.1	17.98	0.19	42.3	
		28	7.20	427.3	21.37	0.22	44.3	
		34	7.91	192.7	0.45	0.17	38.9	0.066
Ferric	10%	1	12.02	107.3	0.29	1.52	647.2	
		7	12.28	79.8	0.52	1.46	579.6	
		14	12.20	80.9	0.34	1.64	485.4	
		28	12.01	86.4	0.30	1.55	459.5	
		34	11.88	93.5	0.38	1.47	393.3	0.025
Ferric	20%	1	12.01	95.4	0.23	1.63	710.2	
		7	12.46	78.3	0.51	1.65	681.7	
		14	12.50	64.0	0.34	1.96	593.1	
		28	12.4	60.5	0.29	1.89	583.8	
		34	12.34	60.8	0.49	1.95	517.4	0.220
Alum	0%	1	6.50	12.4	-0.01	0.21	40.7	
		7	7.17	390.4	0.01	0.41	129.2	
		14	7.51	497.3	0.03	0.46	109.9	
		28	7.35	1227.7	-0.01	0.42	98.7	
		34	8.17	2020.0	0.18	0.36	89.4	1.150
Alum	10%	1	9.75	19.1	-0.01	87.58	75.9	
		7	9.83	36.9	0.00	24.80	86.0	
		14	9.10	126.3	0.00	6.08	60.9	
		28	8.49	211.7	-0.01	1.05	78.3	
		34	8.42	709.0	-0.01	1.41	71.5	1.024

APPENDIX

CHAPTER V

PREDICTING ARSENIC REMOVAL BY FERRIC HYDROXIDES IN THE PRESENCE OF SILICA, NATURAL ORGANIC MATTER, AND SULFATE

Hsiao-wen Chen, Christina C. Davis, and Marc Edwards

Abstract. Surface complexation modeling was examined for prediction of arsenate, natural organic matter, and silica removal by ferric hydroxides. Estimation of surface potential and the predicted effect of hardness, natural organic matter, silica, and sulfate on arsenate removal were also addressed. The model accurately predicted arsenate removal in synthetic and natural water by adsorption or coagulation under a range of circumstances. Accurate modeling of arsenic removal in the presence of silica may require explicit consideration of both monomeric and dimeric silica species. Natural organic matter and silica are predicted to significantly reduce arsenate removal by competition, development of anionic surface charge, and hindered flocculation when surface potential is unfavorable. An accurate surface complexation model could be a powerful tool for projecting coagulation performance for a number of contaminants.

INTRODUCTION

Due to the adverse health effect of arsenic, the United States Environmental Protection Agency (USEPA) established a Maximum Contaminant Level (MCL) of 0.01 mg/L for total arsenic in drinking water (*1*). USEPA also identified modified coagulation/filtration as one of the best available technologies for arsenate (As[V]) removal. Currently water utilities use jar tests to determine coagulation conditions such as pH and coagulant dose. This trial-and-error practice is inefficient, especially when multiple water quality goals are to be achieved. An alternative is to project coagulation conditions with a model. Because adsorption and sedimentation are the main mechanisms of coagulation, an ideal model should be able to accomplish the following

- accurate prediction of arsenic adsorption,

- response to raw water quality variation, and

- estimation of floc stability, i.e., particle charge.

Several studies have utilized models to fit arsenic adsorption or coagulation data (*2-7*). Some of them found that simplified Langmuir isotherms could characterize arsenic removal (*3,5*). Although this model was very useful in a wide range of water systems, its drawbacks include a limited pH range of application, an inability to directly account for competition from other anions, and an inability to predict surface charge.

Dzombak and Morel (*8*) extensively examined the use of the diffuse layer surface complexation model to describe adsorption of solutes onto oxide surfaces with specific surface sites as a chemical reaction. This model also accounted for nonspecific electrostatic interactions. Following Dzombak and Morel's example, Hering et al. (*3*) evaluated the applicability of the surface complexation model (SCM) to arsenic removal by ferric chloride via adsorption and coagulation in the presence of calcium, sulfate, and phosphate. They concluded that adsorption processes were significant in governing arsenic removal during coagulation, and that the application of the SCM to natural water was limited partly due to the interference of natural organic matter (NOM). No attempt was made to correct for surface charge effects in this study.

In addition to arsenic, the SCM was also used to estimate adsorption of NOM (*9*), silica (*6,7,10-12*), and sulfate (*3,10,11,13,14*). Meng et al. (*7*) suggested that silica adsorption significantly reduced As[V] adsorption not only by competing for surface sites but also by reducing the surface potential. Swedlund and Webster (*6*) assessed the effect of silica on arsenic adsorption in synthetic water as well as thermal bore water. Although their SCM properly predicted arsenic removal from synthetic water containing no silica,

it underestimated the effect of silica in the synthetic water and the thermal bore water from pH 6-8. One possible reason was that their SCM excluded any polymeric silica species, which was acknowledged to be inconsistent with the authors' own data regarding the importance of silica species on the iron surface.

This study includes calibration of an SCM with laboratory adsorption data and its application to predict As[V] removal under a range of circumstances. The goal is to assess the limitations and potential of the SCM in predicting arsenic removal in the presence of competing ions.

METHODS

Experiments

Laboratory experiments were conducted to investigate the adsorption of As[V], silica, and NOM onto the surface of preformed amorphous ferric hydroxide ($Fe(OH)_{3(a)}$) under various conditions at 20ºC (Table 5-1). Plasticware was used to eliminate silica leaching from glassware. Fresh $Fe(OH)_{3(a)}$ was prepared by raising the pH of a ferric chloride stock to 6.0. An As[V] stock and a silica stock were prepared from $Na_2HAsO_4 \cdot 7H_2O_{(s)}$ and $Na_2SiO_{3(s)}$, respectively. The NOM used for this study was isolated from natural water bodies in Colorado, U. S. A. (*9*). After $Fe(OH)_{(a)}$ was aged for 12-16 hours, it was added to As[V], silica, and/or NOM solutions. The pH was immediately adjusted to target values and maintained within $\pm$ 0.15 pH units during a reaction period of 1.5 hours. Subsequently, an aliquot of each adsorption sample solution was passed through a 0.45µm-pore-size nitrocellulose or nylon filter. The adsorption sample solutions and the filtrates were analyzed for Fe, Si, and As with Inductive

Coupled Plasma - Emission Spectroscopy (ICP-ES) and for total organic carbon with a total organic carbon analyzer. The zeta potential of solids in silica adsorption samples was also measured. Details of material preparation and experimental procedures were described in Davis (*12*).

TABLE 5-1 Adsorption experiment conditions

pH	Fe (mg/L)	As[V] ($\mu g/L$)	NOM (mg C/L)	Silica (mg SiO_2/L)
5.00, 6.00, 7.25, 8.50, 9.50	10	62, 71	7.0, 7.4	0.0, 0.5, 5.0, 9.9, 20, 30, 50

Surface Complexation Model Calibration

The SCM used for model calibration consisted of surface complexation reactions for As[V] modified from Dzombak and Morel (*8*), for silica described in Davis (*12*), and for NOM by Chen and Edwards (*9*) (Table 5-2). Natural organic matter was assumed to be organic acids with discrete acidity constants and was denoted "H_2A^{n-}". Both monomeric and dimeric silica species in the aqueous phase as well as on the surface were included in the model.

Results of laboratory adsorption experiments were used to calibrate the model. Model inputs included pH, electrolyte concentrations, total concentrations of Fe, As[V], organic carbon, and silica. The mass law and mass balance equations and the electrostatic terms were then solved for the concentration of each species with Microsoft

Visual Basic$^{©}$ functions based on the bisection method (*15*). Characteristic parameters of

Fe(OH)$_{(a)}$ and NOM as well as the intrinsic adsorption constants were optimized with the

Microsoft Excel Solver$^{©}$ for a maximal coefficient of determination (r^2) to fit the

adsorption data.

TABLE 5-2 Equilibrium expressions for solution reactions and surface complexation reactions used for model calibration (See Appendix for denotations.)

Solution acid-base reactions

$\{OH^-\} = K_w\{H^+\}^{-1}$ $\qquad\qquad\qquad$ $K_w = 6.18 \times 10^{-15}$ at 20°C (*16*)

$\{HAsO_4^{2-}\} = K_{a2\_As5}\{H_2AsO_4^-\}\{H^+\}^{-1}$ $\qquad$ $K_{a2\_As5} = 10^{-6.96}$ (*8*)

$\{AsO_4^{3-}\} = K_{a2\_As5} K_{a3\_As5}\{H_2AsO_4^-\}\{H^+\}^{-2}$ $\qquad$ $K_{a3\_As5} = 10^{-11.50}$ (*8*)

$\{SiO(OH)_3^-\} = K_{a1\_Si}\{Si(OH)_4\}\{H^+\}^{-1}$ $\qquad\qquad$ $K_{a1\_Si} = 10^{-9.5}$ (*16*)

$\{HA^{(n+1)-}\} = K_{a1\_NOM}\{H_2A^{n-}\}\{H^+\}^{-1}$

Silica polymerization

$\{Si_2O_2(OH)_5^-\} = K_{poly\_Si}\{Si(OH)_4\}^2\{H^+\}^{-1}$ $\qquad$ $K_{poly,Si} = 10^{-5}$ (*17*)

Surface acid-base reactions

$[\equiv FeOH_2^+] = (K_{sa1}^{app})^{-1}[\equiv FeOH]\{H^+\}$ $K_{sa1}^{app} = K_{sa1}^{int} \cdot E_{-1}^{*}$

$[\equiv FeO^-] = (K_{sa2}^{app})[\equiv FeOH]\{H^+\}^{-1}$ $K_{sa2}^{app} = K_{sa2}^{int} \cdot E_{-1}$

As[V] adsorption

$[\equiv FeH_2AsO_4] = K_{sL1\_As5}^{app} [\equiv FeOH]\{H_2AsO_4^-\}\{H^+\}$ $K_{sL1\_As5}^{app} = K_{sL1\_As5}^{int}$

$[\equiv FeHAsO_4^-] = K_{sL2\_As5}^{app} [\equiv FeOH]\{H_2AsO_4^-\}$ $K_{sL2\_As5}^{app} = K_{sL2\_As5}^{int} \cdot E_{-1}$

Silica adsorption

$[\equiv FeSiO(OH)_3] = K_{sL1\_1Si}^{app} [\equiv FeOH]\{Si(OH)_4\}$ $K_{sL1\_1Si}^{app} = K_{sL1\_1Si}^{int}$

$[\equiv FeSiO_2(OH)_2^-] = K_{sL2\_1Si}^{app} [\equiv FeOH]\{Si(OH)_4\}\{H^+\}^{-1}$ $K_{sL2\_1Si}^{app} = K_{sL2\_1Si}^{int} \cdot E_{-1}$

$[\equiv FeSi_2O_2(OH)_5] = K_{sL1\_2Si}^{app} K_{poly\_Si} [\equiv FeOH]\{Si(OH)_4\}^2$ $K_{sL1\_2Si}^{app} = K_{sL1\_2Si}^{int}$

$[\equiv FeSi_2O_3(OH)_4^-] = K_{sL2\_2Si}^{app} K_{poly\_Si} [\equiv FeOH]\{Si(OH)_4\}^2\{H^+\}^{-1}$ $K_{sL2\_2Si}^{app} =$

$K_{sL2\_2Si}^{int} \cdot E_{-1}$

NOM adsorption

$[\equiv FeHA^{n-}] = K_{sL1\_NOM}^{app} [\equiv FeOH]\{H_2A^{n-}\}$ $K_{sL1\_NOM}^{app} = K_{sL1\_NOM}^{int} \cdot E_{-n}$

$[\equiv FeA^{(n+1)-}] = K_{sL2\_NOM}^{app} [\equiv FeOH]\{H_2A^{n-}\}\{H^+\}^{-1}$ $K_{sL2\_NOM}^{app} = K_{sL2\_NOM}^{int} \cdot E_{-(n+1)}$

$_*$ $E_{-i} = \exp\left(\dfrac{iF\Psi}{RT}\right)$, $i = 1$, n, or n+1

RESULTS AND DISCUSSION

Model Calibration

The SCM with the optimal values of the fitting parameters (Table 5-3) properly

predicted adsorption of As[V], silica, and NOM (Figure 5-1). Because surface potential

cannot be measured, zeta potential measurements were used to evaluate the relative

accuracy of surface potential predictions. While there is no established relationship

between surface potential and zeta potential, they should share the same sign, and the

magnitude of zeta potential should be less than that of surface potential. The surface

potential predicted by the SCM satisfied these criteria and reasonably matched the

measured zeta potential (Figure 5-2).

**TABLE 5-3 Values of surface complexation model constants optimal for
experimental data (See Appendix for denotations.)**

$Fe(OH)_{3(a)}$ parameters

f_s (mol sites/mol Fe)	A_s (m^2/g)	K_{sa1}^{int}	K_{sa2}^{int}
0.247	6924	5.13×10^{-8}	1.17×10^{-9}

NOM parameters

n	HOCC (mg C/mol H_2A^{n-})	K_{a1_NOM}
0.44	9.70×10^4	9.00×10^{-3}

As[V] and NOM adsorption constants

	K_{sL1}	K_{sL2}	r^2
As[V]	1.51×10^{15}	1.30×10^7	0.942
NOM	1.53×10^{10}	6.68×10^3	0.928

Silica adsorption constants

K_{sL1_1Si}	K_{sL2_1Si}	K_{sL1_2Si}	K_{sL2_2Si}	r^2
$< 1.90 \times 10^1$	$< 1.97 \times 10^{-7}$	9.50×10^{11}	3.90×10^5	0.873
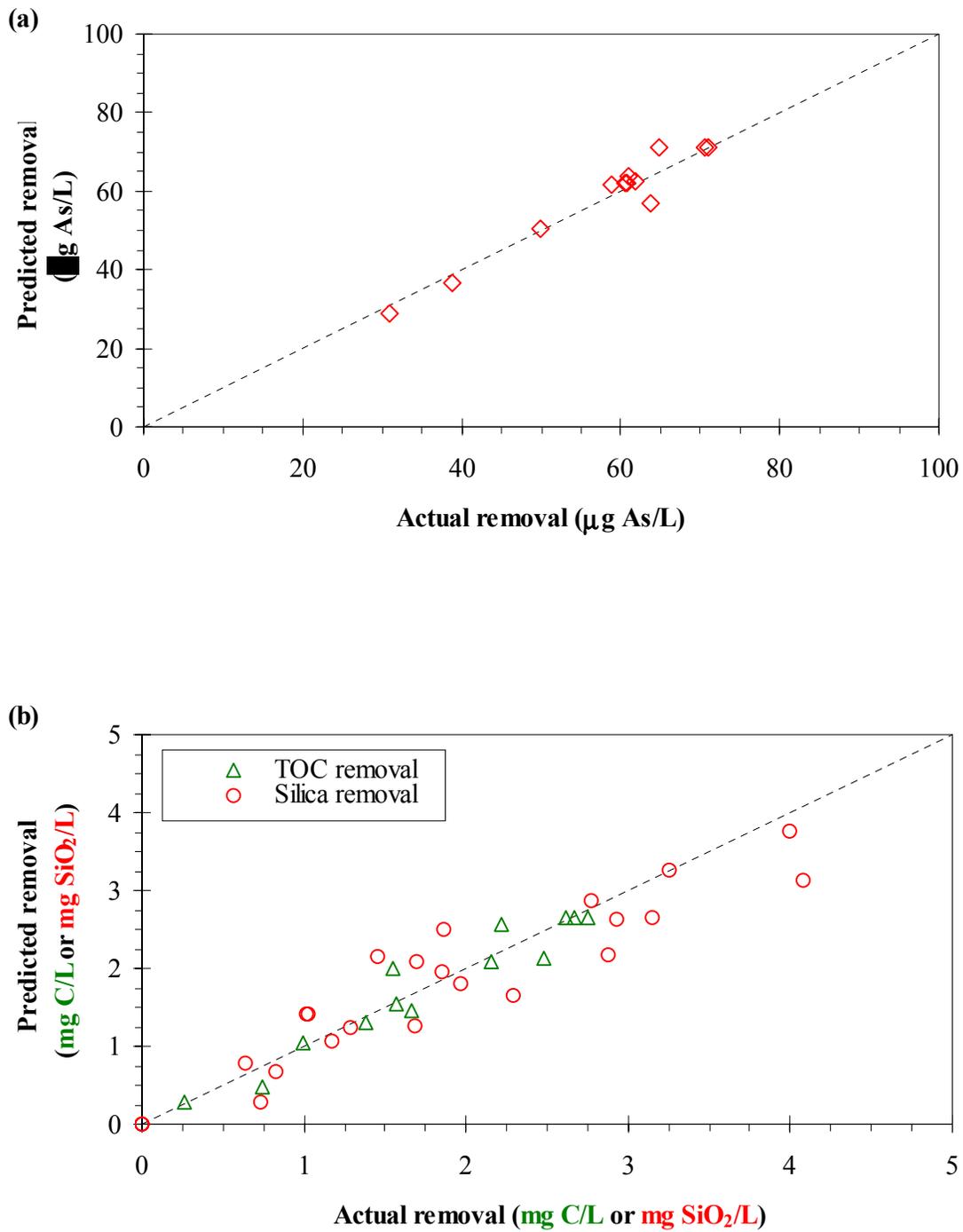
FIGURE 5-1 Surface complexation modeling of the adsorption of (a) As[V] and (b) NOM and silica onto ferric hydroxides.
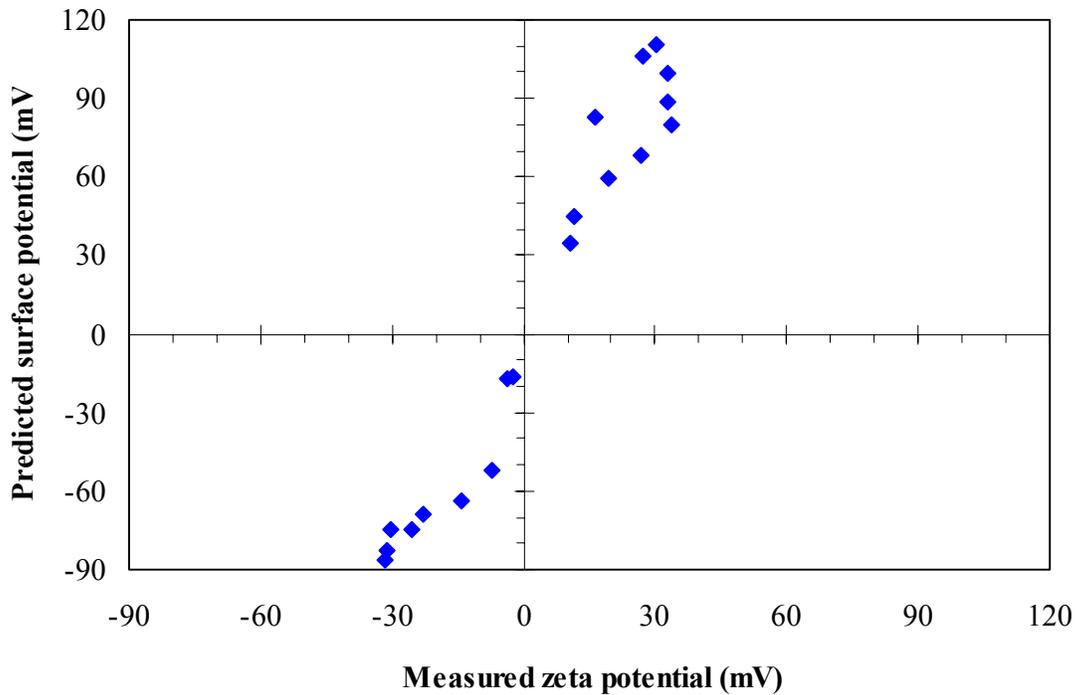
FIGURE 5-2 Surface potential for silica adsorption onto ferric hydroxides predicted by the surface complexation model versus measured zeta potential.

Model Validation

After the SCM was proven to properly predict the surface potential and the

adsorption of As[V], silica, and NOM, it was evaluated for its applicability to modeling

coagulation. In the literature, inconsistent conclusions have been drawn on the

controlling factor of arsenic removal by coagulation. McNeill and Edwards (*5*) examined

data of arsenic removal by coagulation at numerous water utilities and found that the

removal in water containing less than 5 mg/L of silica depended mainly on the coagulant

dose when pH was below 7.8 (Figure 5-3). In contrast, a pilot test showed that pH was

critical to removing arsenic by coagulation-filtration in water in Albuquerque, New

Mexico, which contained 51 mg/L of silica (Figure 5-4) (*18-21*).
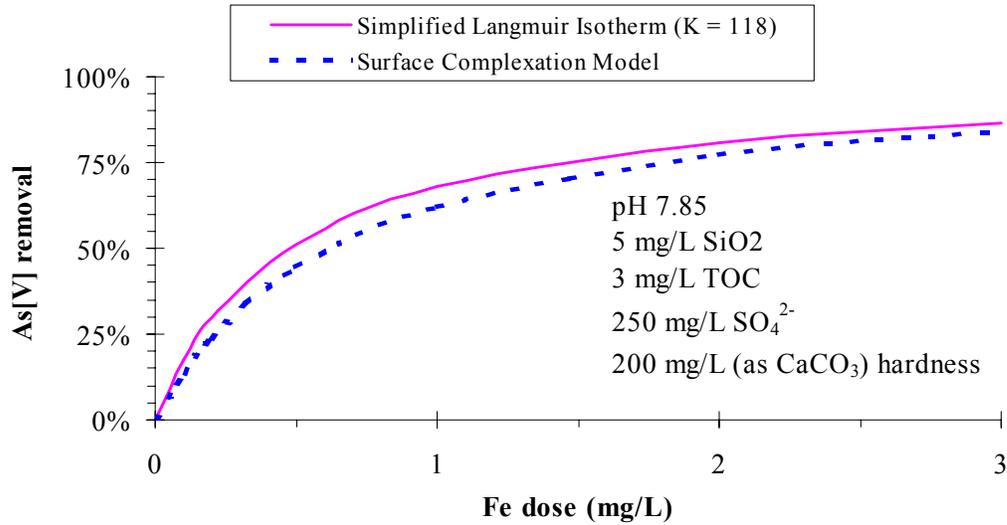
FIGURE 5-3 Comparison of As[V] removal predictions by a simplified Langmuir
isotherm (*5*) and by the surface complexation model calibrated with
adsorption data presented in this work.
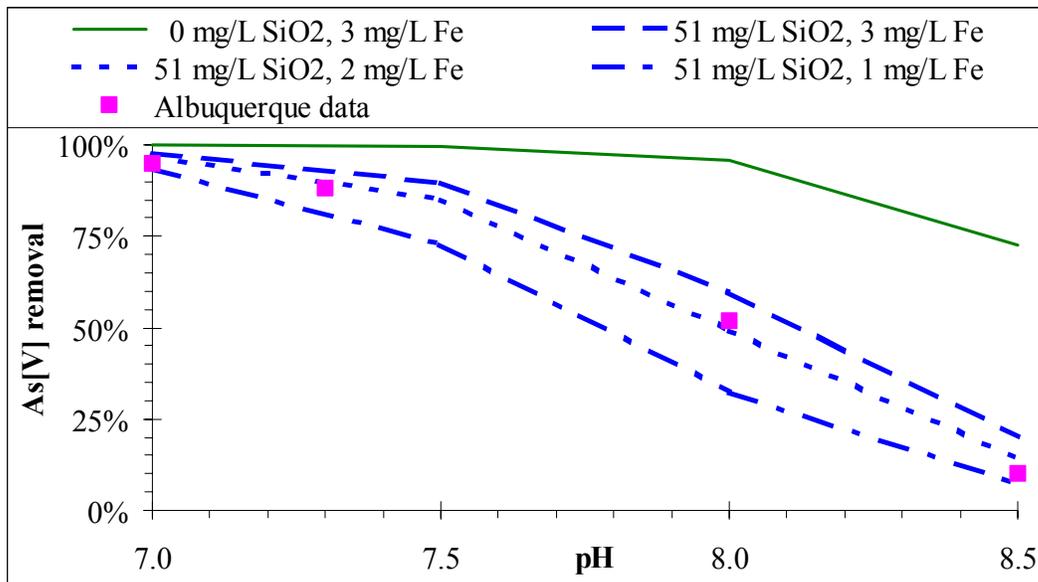
FIGURE 5-4 Arsenate removal by coagulation-microfiltration in an Albuquerque pilot
study. The water contained 51 mg/L of silica, and the coagulant dose was
1-3 mg/L as Fe. The lines represent SCM predictions.

50

McNeill and Edwards (*5*) successfully used a simplified Langmuir isotherm to characterize arsenic removal under the aforementioned conditions. Although the SCM was not calibrated for the ferric hydroxides formed during coagulation, it predicted the same trend in arsenic removal as did the simplified isotherm (Figure 5-3). In the Albuquerque pilot study, 1-3 mg/L of Fe was dosed. The SCM was able to capture the removal-pH relationship when as much as 51 mg/L of silica was present (Figure 5-4).

The SCM predicted little dependence of arsenic removal on pH when pH was lower than 8 and there was no silica in the water (Figure 5-4), which agreed with the observation of McNeill and Edwards (*5*). It appeared that silica significantly affected arsenic removal. Swedlund and Webster (*6*) used an SCM accounting for only monomeric silica species. The As[V] and silica adsorption constants were optimized to fit their As[V] and silica adsorption data, respectively. These constants were subsequently used to estimate As[V] removal (108 mg SiO_2/L) was present (Scenario 1 in Figure 5-5a). The SCM presented in this work included both monomeric and dimeric silica species. It was modified to fit data over a wide pH range of 3-12 (Table 5-4). The As[V] and silica adsorption constants of the modified SCM were optimized to fit As[V] and silica adsorption data, respectively, in Swedlund and Webster (*6*). Inclusion of silica dimers in the model slightly improved prediction of arsenic removal in the presence of 1.8 mM of silica (Scenario 2 in Figure 5-5a). Note that the silica sorption density was up to 0.05 M Si/M Fe. Inclusion of silica dimers considerably improved model prediction of silica adsorption only when the silica sorption density was greater than 0.1 M Si/M Fe (Figure 5-5b).

When the silica adsorption constants were optimized to fit As[V] adsorption in the presence of 1.8 mM of silica, the predictions significantly improved (Scenarios 3 and 4 in Figure 5-5a). This suggested that there might be interaction between As[V] and silica.

TABLE 5-4 Additional and modified equilibrium expressions for solution reactions and surface complexation reactions for a wide pH range (See Appendix for denotations.)

Solution acid-base reactions

$$\{H_2AsO_4^-\} = K_{a1\_As5}\{H_3AsO_4\}\{H^+\}^{-1} \qquad\qquad K_{a1\_As5} = 10^{-2.24}\ (8)$$

$$\{HAsO_4^{2-}\} = K_{a1\_As5}\,K_{a2\_As5}\{H_3AsO_4\}\{H^+\}^{-2} \qquad\qquad K_{a2\_As5} = 10^{-6.96}\ (8)$$

$$\{AsO_4^{3-}\} = K_{a1\_As5}\,K_{a2\_As5}\,K_{a3\_As5}\{H_3AsO_4\}\{H^+\}^{-3} \qquad\qquad K_{a3\_As5} = 10^{-11.50}\ (8)$$

$$\{SiO_2(OH)_2^{2-}\} = K_{a1\_Si}\,K_{a2\_Si}\{Si(OH)_4\}\{H^+\}^{-2} \qquad\qquad K_{a2\_Si} = 10^{-12.6}\ (16)$$

As[V] adsorption

$$[\equiv FeH_2AsO_4] = K_{sL1\_As5}{}^{app}[\equiv FeOH]\{H_3AsO_4\} \quad K_{sL1\_As5}{}^{app} = K_{sL1\_As5}{}^{int}$$

$$[\equiv FeHAsO_4^-] = K_{sL2\_As5}{}^{app}[\equiv FeOH]\{H_3AsO_4\}\{H^+\}^{-1} \quad K_{sL2\_As5}{}^{app} = K_{sL2\_As5}{}^{int} \cdot E_{-1}{}^{*}$$

$$[\equiv FeAsO_4^{2-}] = K_{sL3\_As5}{}^{app}[\equiv FeOH]\{H_3AsO_4\}\{H^+\}^{-2} \quad K_{sL3\_As5}{}^{app} = K_{sL3\_As5}{}^{int} \cdot E_{-2}$$

$$[\equiv FeOHAsO_4^{3-}] = K_{sL4\_As5}{}^{app}[\equiv FeOH]\{H_3AsO_4\}\{H^+\}^{-3} \quad K_{sL4\_As5}{}^{app} = K_{sL4\_As5}{}^{int} \cdot E_{-3}$$

Silica adsorption

$$[\equiv FeSiO_3(OH)^{2-}] = K_{sL3\_1Si}{}^{app}[\equiv FeOH]\{Si(OH)_4\}\{H^+\}^{-2} \quad K_{sL3\_1Si}{}^{app} = K_{sL3\_1Si}{}^{int} \cdot E_{-2}$$

$$_{*}\quad E_{-i} = \exp\!\left(\frac{iF\Psi}{RT}\right), i = 1, 2, 3, n,\ \text{or}\ n+1$$
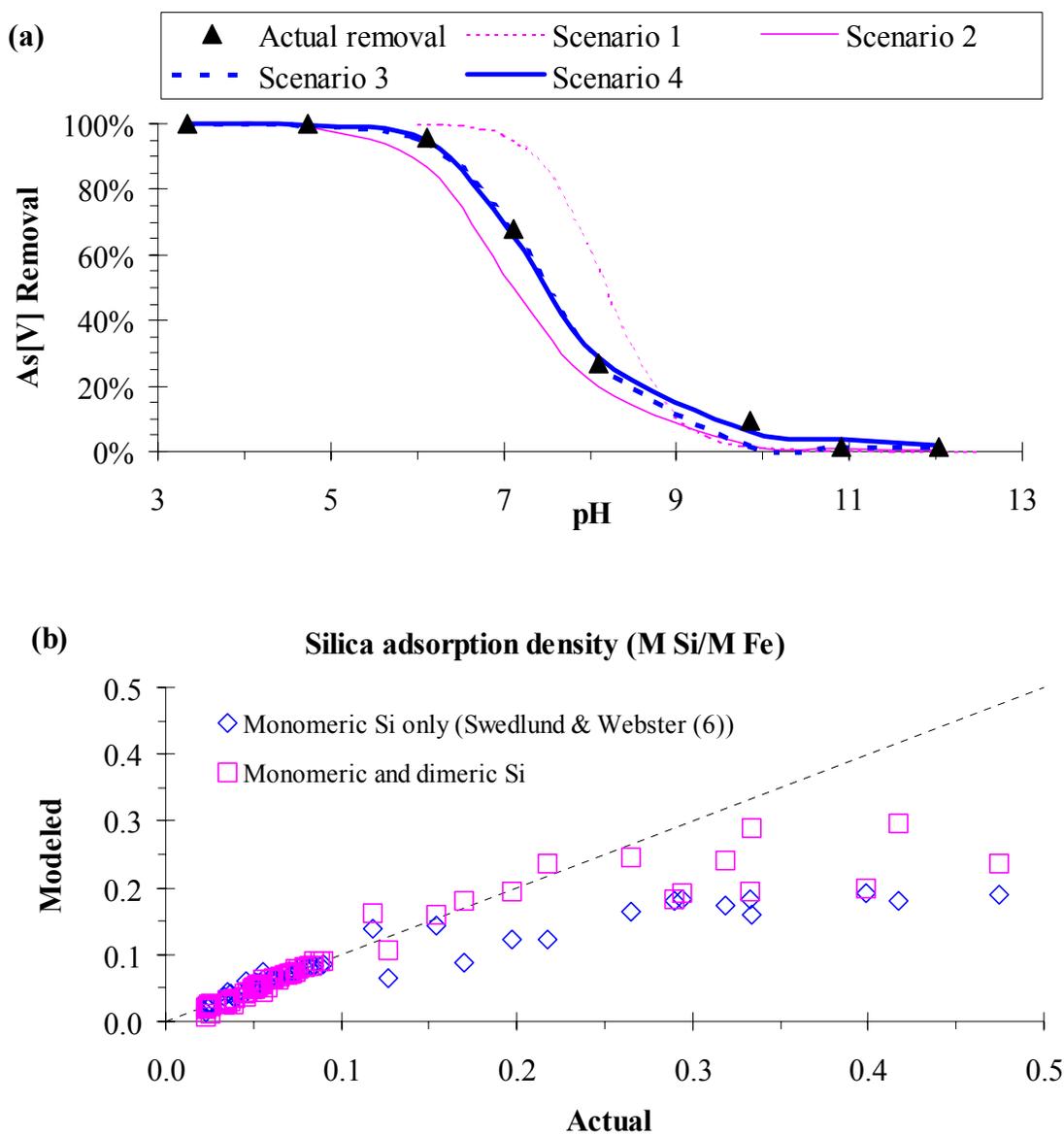
FIGURE 5-5 Comparison between adsorption prediction by a model including monomeric silica only and that by a model including both monomeric and dimeric silica. (a) Arsenic removal in the presence of 1.8 mM of silica. The data points represent actual removal in Swedlund and Webster (*6*). The lines represent model predictions: Scenario 1-prediction by Swedlund and Webster (*6*)-without silica dimers, adsorption constants optimized to fit individual single-adsorbate systems (As[V] or silica); Scenario 2-with silica dimers, adsorption constants optimized to fit individual single-adsorbate systems (As[V] or silica); Scenario 3-without silica dimers, silica adsorption constants optimized to fit As[V] adsorption in the presence of 1.8 mM of silica; Scenario 4-with silica dimers, silica adsorption constants optimized to fit As[V] adsorption in the presence of 1.8 mM of silica. (b) Modeled versus actual silica adsorption density.

<u>Model Projection</u>

The effect of silica, NOM, sulfate, and hardness on As[V] removal was examined using a water composition simulating the Albuquerque water: 51mg/L SiO_2, 0 TOC, 70mg/L SO_4^{2-}, and 53mg-$CaCO_3$/L hardness (*18*). The initial As[V] concentration was assumed to be 40 µg/L. Parameter values listed in Table 5-3 along with sulfate adsorption constants of $10^{13.83}$ and $10^{8.41}$ for $K_{sL1,SO4}^{int}$ and $K_{sL2,SO4}^{int}$, respectively (*13,14*), were used.

The SCM projected the iron dose as a function of pH required to reach the following criteria deemed necessary for effective treatment by coagulation: final As[V] lower than 10 µg/L (the MCL) and particle surface potential within ±30 mV for effective flocculation and particle removal (Figure 5-6). The actual surface potential required for effective particle removal is expected to vary from system to system, but the ±30 mV criterion seems to be representative of requirements in some systems.

As expected, the required dose of iron to achieve arsenic removal increased when the pH increased. While the data are not shown, sulfate and hardness did not significantly affect the range of iron doses giving acceptable treatment, although when the surface was positively charged, sulfate could interfere slightly. The effect of NOM was substantial. Because NOM increased the required iron dosage for effective particulate destabilization, the iron dose required to meet the same arsenic treatment goal was considerably higher. It is difficult to overdose (obtain a surface charge that is too positive) when both NOM and silica are high (Figure 5-6a). The most drastic impact was from silica, the adsorption of which greatly reduced the positive potential on the iron surfaces, and, therefore, was predicted to decrease the likelihood of overdosing. In the

54

absence of silica, only a narrow dosage of iron could meet treatment criteria below pH 7.5 (Figure 5-6b) because it was very easy to overdose coagulant. We believe that this might be the mechanistic explanation for dramatic improvements to flocculation that have been noted to occur in the presence of silica by Baylis (*22*).

CONCLUSIONS

The surface complexation model is a powerful tool to predict As[V], silica, and NOM removal and to estimate surface potential. Although it is based on adsorption theory, it may be applicable to forecasting outcomes of coagulation. Additional development and testing is necessary.

Consider both monomeric and dimeric silica species may be necessary under some conditions to accurately predict arsenic removal by iron coagulants. In the presence of NOM, a considerably higher dose of coagulant is required to accomplish the same As[V] treatment goal because a significant portion of the NOM must be removed before surface charge is acceptable for coagulation. For silica-deficient water, coagulation is expected to be very sensitive to iron dose below pH 7.5.

ACKNOWLEDGEMENTS
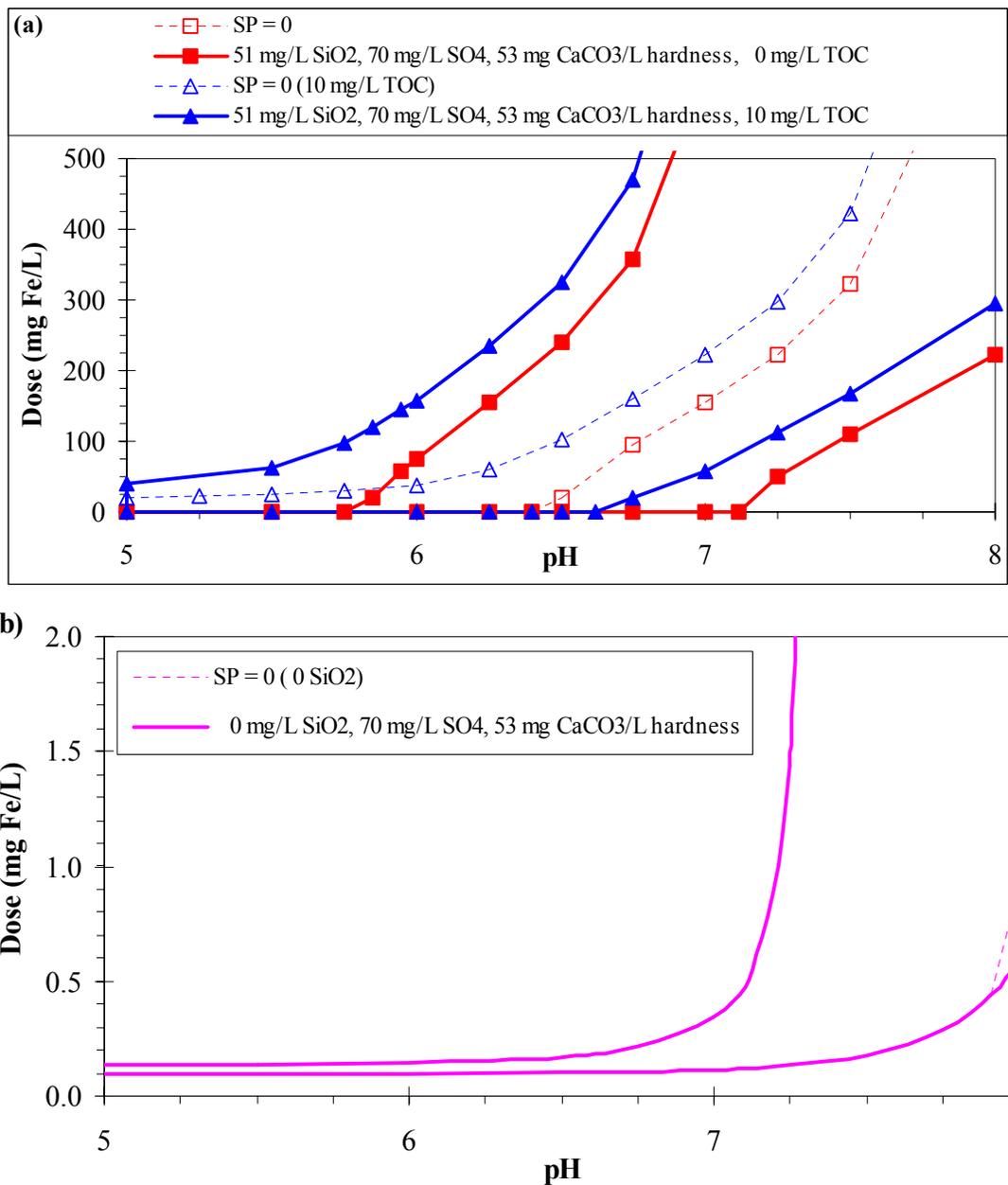
FIGURE 5-6 Isopleths demarcating conditions where treatment goals of 10μg/L final As[V] (the MCL) and ±30mV surface potential are achieved. Combinations of iron dose and pH encompassed by each solid line satisfy both criteria and represent feasible treatment conditions in terms of both arsenic sorption to iron and floc removal. The initial As[V] is 40 μg/L. The dashed lines indicate the dose-pH combinations that produce zero surface charge, which is ideal for particle removal by filtration and/or settling. Note the different dose scales in (a) and (b).

56

APPENDIX-DENOTATIONS

$\equiv$ surface species

{ }   activity

[ ]   molar concentration (mol/L)

< >   concentration in g/L

A_s specific surface area (m^2/g)

F   Faraday constant (96490 C/mol)

f_s surface site density, mol sites/mol Fe

H_2A^{n-} natural organic matter

K^{app} apparent equilibrium constant

K^{int} intrinsic equilibrium constant

n   valence of natural organic matter

R   molar gas constant ($8.314 \; J{\cdot}mol^{-1}{\cdot}K^{-1}$)

T   absolute temperature (K)

Ψ surface potential (V)

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VITA

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