

**AQUEOUS SILICA IN THE ENVIRONMENT:  
EFFECTS ON IRON HYDROXIDE SURFACE CHEMISTRY AND  
IMPLICATIONS FOR NATURAL AND ENGINEERED SYSTEMS**

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# **Aqueous Silica in the Environment: Effects on Iron Hydroxide Surface Chemistry and Implications for Natural and Engineered Systems**

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## **ABSTRACT**

Aqueous silica is present in all natural waters and exhibits a high affinity for the surfaces of iron oxides. Therefore, it is expected to play an important role in environmental systems. Experiments were conducted to investigate the fundamentals of silica sorption onto pre-formed ferric hydroxide at pH 5.0-9.5 and silica concentrations of 0-200 mg/L as SiO<sub>2</sub>. Over the entire pH range studied, sorption densities exceeding monolayer sorption were observed at silica levels typical of natural waters. Under some circumstances, sorption exceeded a monolayer while the particle zeta potential remained positive, a phenomenon which is inconsistent with available models. To address this deficiency, an extended surface complexation model was formulated in which soluble dimeric silica (i.e., Si<sub>2</sub>O<sub>2</sub>(OH)<sub>5</sub><sup>-</sup>) sorbs directly to iron surface sites. This model fits sorption density data up to 0.40 mol SiO<sub>2</sub>/mol Fe, and it accurately predicts trends in zeta potential and the observed H<sup>+</sup> release during silica sorption to ferric hydroxide at pH 5.0 and 6.0.

A second phase of research was aimed at identifying the practical implications of silica sorption to iron hydroxide in natural and engineered systems. Two types of surfaces were prepared by exposing pre-formed Fe(OH)<sub>3</sub> to aqueous silica (0-200 mg/L as SiO<sub>2</sub>) for periods of 1.5 hours or 50 days. The concentration of pre-formed iron passing through a 0.45 μm pore size filter at pH 6.0-9.5 increased as the solids aged in the presence of silica. Consistent with formation of small, stable colloids, “soluble” iron concentrations exceeded 0.2 mg/L only at zeta potentials ≤ -15 mV. When arsenate was added to iron hydroxide particles equilibrated with silica for 1.5 hours, percentage arsenate removals were high. In contrast, arsenate removals decreased markedly as pH and silica concentrations increased if silica was pre-equilibrated with the iron for 50 days. Trends in percentage removal of humic substances were similar. Competition for sorption sites was the main cause of hindered anionic contaminant removal. However, interference with hydrolysis and precipitation are expected to be important under some circumstances, particularly during water treatment.

## **DEDICATION**

To Jesus, who showers me with love and grace

Not to us, O Lord, not to us  
but to your name be the glory,  
because of your love and faithfulness.

Psalm 115:1

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## AUTHOR'S PREFACE

This work combines elements of a traditional thesis with the Virginia Tech manuscript format. The traditional elements include the literature review (Chapter I) and conclusions (Chapter IV). Chapters II and III are complete manuscripts written for submission to *Environmental Science & Technology*. A revised form of Chapter I will also be submitted to *Environmental Science & Technology*.

Chapter I includes an examination of the literature as it pertains to silica chemistry in natural and engineered processes. Findings from this review raised new questions about silica speciation in natural waters and implications for environmental systems. Thereafter, two phases of research were planned to address these issues. Chapter II, "The Role of Silica Sorption in Iron Hydroxide Surface Chemistry," is aimed at elucidating fundamental aspects of silica sorption to amorphous ferric hydroxide surfaces. Chapter III, "Implications of Silica Sorption to Iron Hydroxide: Mobilization of Iron Colloids and Interference with Sorption of Arsenate and Humic Substances," focuses on practical implications of silica sorption to iron hydroxide in environmental systems.

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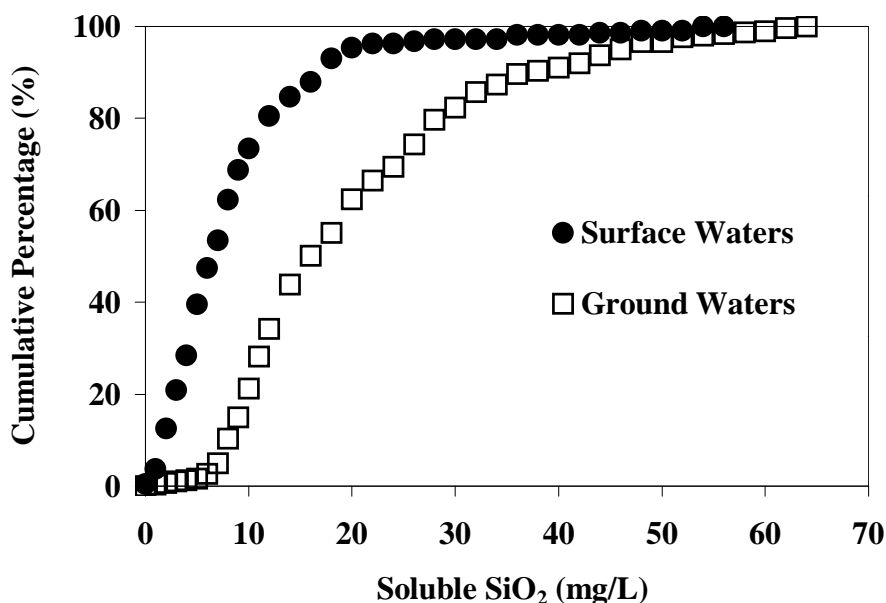
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# CHAPTER I

## Literature Review

Silicate minerals, which are distinguished by an  $\text{SiO}_4$  tetrahedral structure, comprise more than 90% of the earth's crust (1). Aqueous silica in natural waters is derived from weathering and dissolution of these abundant minerals. According to the National Arsenic Occurrence Survey (2) of US drinking water supplies, soluble silica concentrations range from 0.5-54 mg/L as  $\text{SiO}_2$  for surface waters and 0.8-63 mg/L as  $\text{SiO}_2$  for ground waters (Figure 1-1).



**Figure 1-1. Distribution of aqueous silica in US drinking water supplies.**

Most of our understanding regarding dissolved silica is based on the classic work of Lagerstrom (3), who determined equilibrium constants for monomeric and tetrameric silica species at 25°C and 0.5 m ionic strength (Table 1-1). Stumm et al. (4) applied these constants to delineate the region of amorphous silica ( $\text{SiO}_2$ ) insolubility over the range of pH 4-14 (Figure 1-2). These researchers also defined a “mononuclear wall,” which is a line demarcating combinations of pH and total Si at which 1% of the total Si exists as soluble polymeric species (Figure 1-3). Above this line, stable polymeric species become increasingly significant. Below the mononuclear wall, the authors hypothesized that monomeric silica species, specifically

Si(OH)<sub>4</sub> and its conjugate bases, are thermodynamically dominant. This diagram has been used to provide mechanistic interpretations for silica impacts in environmental systems (5-10). Moreover, since the silica concentrations and pH conditions typical of natural waters fall below the mononuclear wall, a key conclusion of this analysis was that polymeric silica species do not occur in natural waters.

**Table 1-1. Important Silica Equilibrium Reactions**

Eqn	Reaction	log K <sup>a</sup>	log K <sup>b</sup>
1-1	SiO <sub>2(s)</sub> + H <sub>2</sub> O ↔ Si(OH) <sub>4</sub>	-2.7	n/a
1-2	Si(OH) <sub>4</sub> ↔ SiO(OH) <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	-9.46	n/a
1-3	2Si(OH) <sub>4</sub> ↔ Si <sub>2</sub> O(OH) <sub>5</sub> <sup>-</sup> + H <sup>+</sup> + H <sub>2</sub> O	n/a	-5.0
1-4	4Si(OH) <sub>4</sub> ↔ Si <sub>4</sub> O <sub>6</sub> (OH) <sub>6</sub> <sup>-2</sup> + 2H <sup>+</sup> + 4H <sub>2</sub> O	-12.57	-8.9

<sup>a</sup> Constants used in analysis by Stumm et al. (4). Equilibrium constants for Equations 1-2 and 1-4 were determined by Lagerstrom (3).

<sup>b</sup> Constants determined by Svensson et al. (13).

Recent work using NMR spectroscopy (11-13) has unambiguously demonstrated that polymeric silica species are more important than previously suspected (4). Consideration of the stability constants proposed by Svensson et al. (13) for the new polymers (Table 1-1) substantially alters the location of the calculated insolubility line (Figure 1-2) and mononuclear wall (Figure 1-3). In this analysis, dimeric silica, formulated as Si<sub>2</sub>O<sub>2</sub>(OH)<sub>5</sub><sup>-</sup>, emerges as a significant and even dominant aqueous species under some circumstances (Figure 1-2). Contrary to conventional wisdom, silica levels and pH conditions typical of some natural waters are above the revised mononuclear wall, indicating that polymeric species likely occur at significant concentrations (Figure 1-3). For example, as pH increases beyond 6.0 or 6.5, polymeric species, particularly Si<sub>2</sub>O(OH)<sub>5</sub><sup>-</sup>, start to become quite important (Figure 1-4). At 11.6 and 42.8 mg/L, polymeric Si is dominant in solution at approximately pH 8.8 and 8.2, respectively. Furthermore, polymers are present at significant levels even at very low silica concentrations. At 1.90 mg/L as SiO<sub>2</sub>, 2% of the total Si is predicted to be in polymeric form at pH 7.5; at pH 9.5, 37% of the total Si is expected to be polymeric.

- |                     |                                  |                     |
|---------------------|----------------------------------|---------------------|
| 1 Dimer (p = -1)    | 4 Oligomer/32 Si atoms (p = -16) | 7 Dimer (p = -2)    |
| 2 Tetramer (p = -2) | 5 Octamer (p = -6)               | 8 Trimer (p = -3)   |
| 3 Monomer (p = -1)  | 6 Hexamer (p = -4)               | 9 Tetramer (p = -4) |

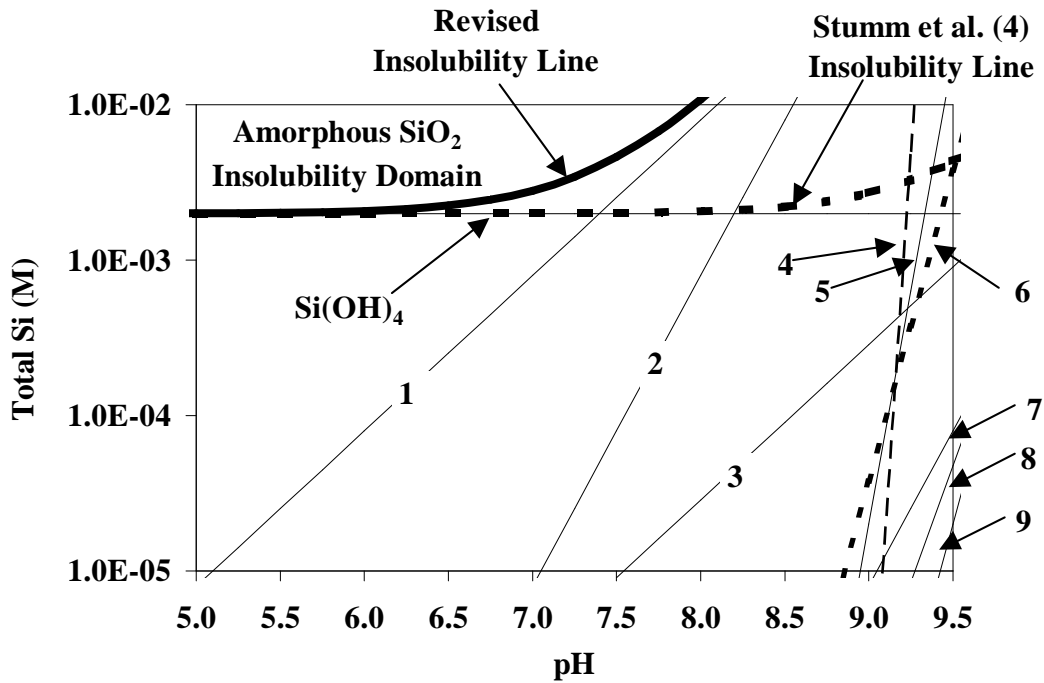


Figure 1-2. Amorphous silica solubility calculated with the equilibrium constants of Svensson et al. (13). The solubility calculated by Stumm et al. (4) is shown for comparison.

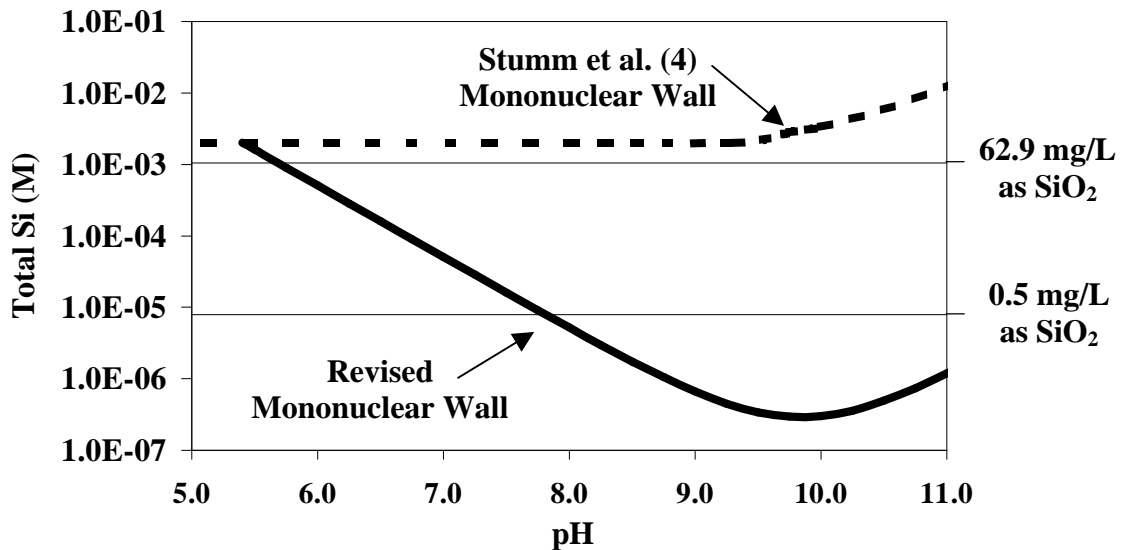
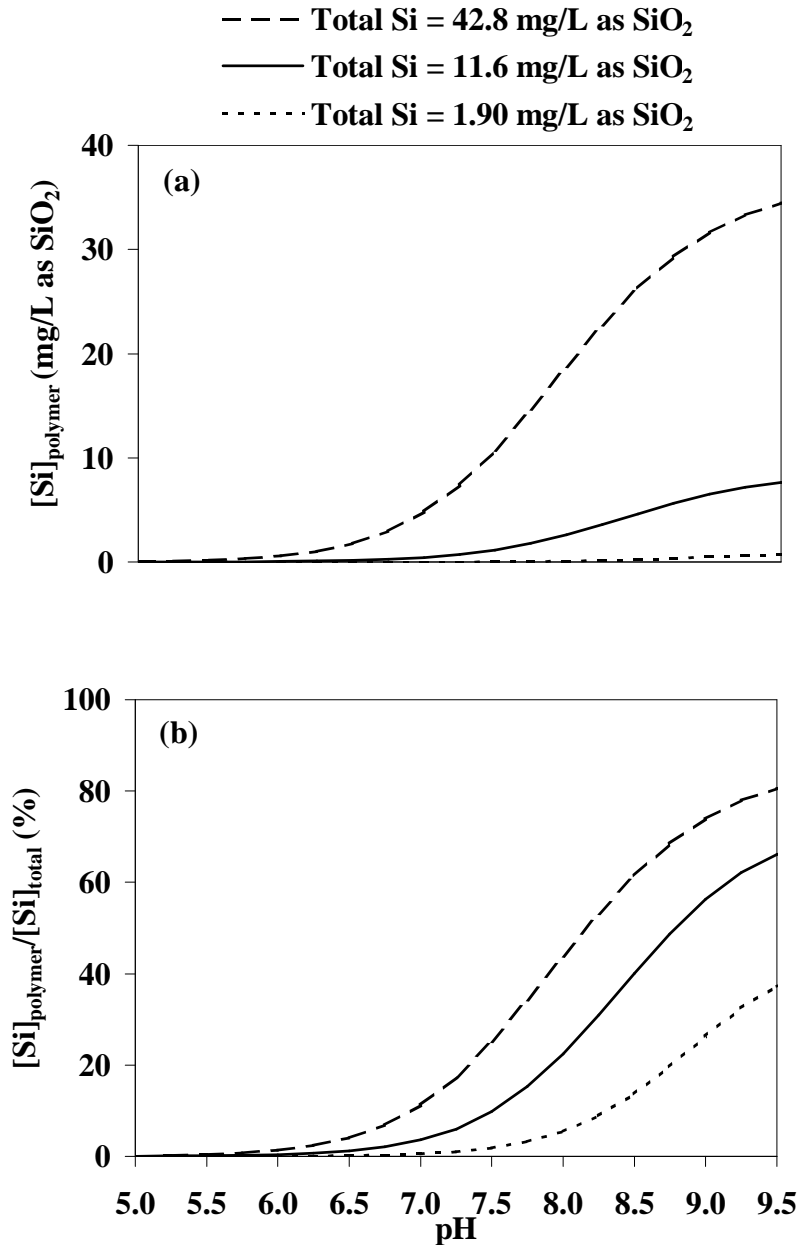


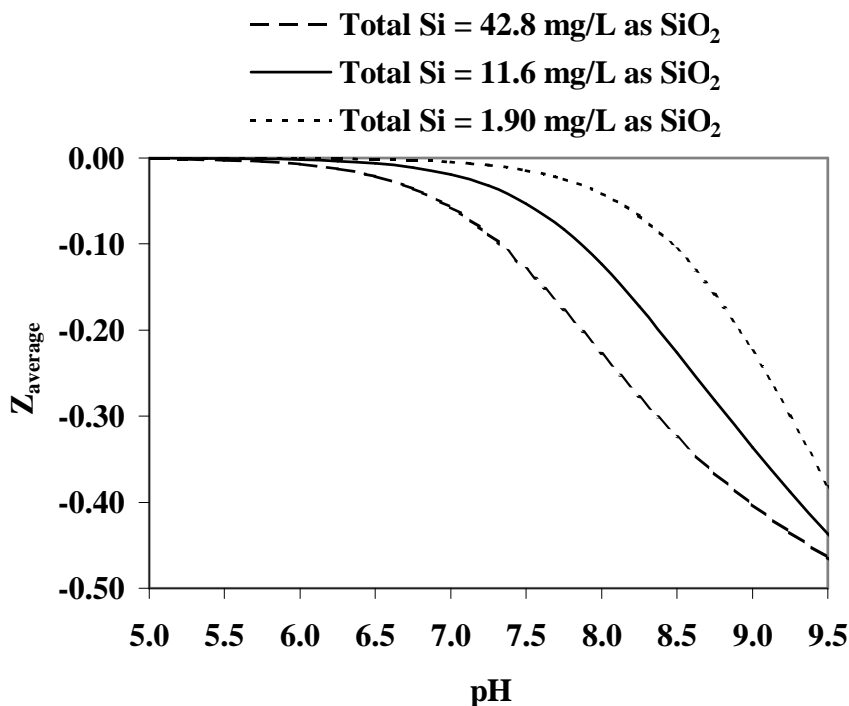
Figure 1-3. Consideration of equilibrium constants published by Svensson et al. (13) substantially alters the location of the mononuclear wall. Silica concentrations of 0.5 and 62.9 mg/L as SiO<sub>2</sub> represent the low and high levels encountered in natural waters (2).



**Figure 1-4. Calculated (a) concentration and (b) percentage of polymeric silica as a function of pH. Total silica concentrations represent the 5<sup>th</sup>, 50<sup>th</sup>, and 95<sup>th</sup> percentiles measured in US drinking water supplies (2).**

The charge on soluble and sorbed silica species is important from the perspective of particle stability in natural systems, complexation of metals, and behavior in engineered processes. When polymeric silica species are considered, the calculated average charge per soluble silica ( $Z_{\text{average}}$ ) changes markedly from prior conceptualizations (Figure 1-5). At  $\text{pH} \leq$

6.0, where most or all of the silica is in the  $\text{Si}(\text{OH})_4$  form,  $Z_{\text{average}} = 0$ , but as the pH and silica concentration increase, the dimer eventually becomes dominant. For the conditions examined,  $Z_{\text{average}}$  approaches an upper limit near  $-0.50/\text{Si}$ , which corresponds to the charge per Si on the dimer,  $\text{Si}_2\text{O}_2(\text{OH})_5^-$ .



**Figure 1-5. Average charge per Si as a function of pH. At low pH, where  $\text{Si}(\text{OH})_4$  is the dominant species, the  $Z_{\text{average}}=0$ . As  $\text{Si}_2\text{O}_2(\text{OH})_5^-$  becomes more significant,  $Z_{\text{average}}$  approaches  $-0.50$  per Si.**

## Implications for Environmental Systems

These model results require reconsideration of silicate behavior under a wide range of scenarios. Since silica is a constituent of all natural waters, the potential importance of dimeric silica as a complexing ligand and sorbing species must now be considered directly. Quite possibly, doing so might lead to theories and models which are more consistent with experimental data. Silica has an affinity for various forms of aluminum and iron, and it influences the chemistry of natural waters and engineered processes, such as coagulation, iron sequestration, and activated alumina sorption. Current understanding of silica reactions in environmental systems is reviewed below.

**Interactions with Aluminum.** Reactions between soluble silica and aluminum species result in the formation of hydroxy-aluminosilicate (HAS) solids. Exley and Birchall (14) examined HAS formation at very low aluminum concentrations (0.1 mg/L as Al); the silica concentrations (0-30.0 mg/L as SiO<sub>2</sub>) and pH (4.5-7.5) were in the range of natural waters. Using membrane filtration, they found that silica limited the growth of aluminum species to less than 0.04 μm, and the stability of HAS species increased at higher silicic acid concentrations. These authors hypothesized that “poisoning” of Al(OH)<sub>3</sub> polymerization by silica was mechanistically responsible for HAS formation. Brace and Matijevic (15) studied the properties of aluminosilicate colloids precipitated over a wide range of solution conditions. Like Exley and Birchall (14), they also found that higher silica concentrations increased aluminosilicate stability, thereby preventing particle precipitation and aggregation.

Hingston and Raupach (6) investigated the reaction between aqueous silica and the crystalline Al(OH)<sub>3</sub> surface. Multiple layers of silica eventually sorbed onto the surface, with maximum sorption at pH 9.2. Furthermore, their results revealed that silica sorption increased at higher initial silica concentrations, ionic strength, and temperature. Huang (7) found similar trends in experiments with aqueous silica and γ-Al<sub>2</sub>O<sub>3</sub>. Multiple layers of silica formed on the aluminum oxide surface, and the highest levels of sorption were achieved at pH 9 ± 0.2. Like Hingston and Raupach (6), Huang (7) observed that the first silica layer formed rapidly, and subsequent layers sorbed at a slower rate. However, while Hingston and Raupach (6) proposed that Si(OH)<sub>4</sub> was the reacting silica species, Huang’s (7) energetic model predicted that SiO(OH)<sub>3</sub><sup>-</sup> was the sorbing species. In either case, only sorption of monomeric species was considered.

Given the tendency of aluminum and silica to form aluminosilicates, the presence of silica in natural waters is expected to affect alum coagulation in water treatment. Lartiges et al. (16) investigated the mechanisms by which Al<sub>13</sub> polymers destabilized and flocculated a colloidal (particle size of 14 nm) silica suspension. Their proposed destabilization mechanism is initiated by the formation of negative aluminosilicate sites on the silica surface. Next, Al<sub>13</sub> polymers flocculate the silica colloids by either charge neutralization or bridging. Interestingly, the researchers found that the underlying destabilization mechanism was the same at pH 5.5 and 8.5.



Duan and Gregory (9, 10) examined coagulation and flocculation in a system of alum, aqueous silica, and kaolin clay (an aluminosilicate formulated as  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_5$ ). Their results revealed an optimum aqueous silica concentration which increased the rate of particle precipitation and aggregation. This optimum silica concentration, which was highly pH-dependent, decreased as the pH increased. Furthermore, coagulation was inhibited or altogether prevented at silica concentrations above the optimum. At pH 8, the optimum was only 4.8 mg/L as  $\text{SiO}_2$ . These results indicate that the presence of aqueous silica may be responsible for the poor coagulation generally observed at high pH. The exception is softening plants, where silica might react completely with calcium and magnesium hydroxides (17), thereby eliminating further interference with coagulation at high pH.

**Interactions with Iron.** Iron-silica interactions have not received as much attention in the literature as those between silica and aluminum. However, aqueous silica influences iron chemistry in several ways. Below pH 3.5, Weber and Stumm (18) demonstrated the formation of a soluble  $\text{FeSiO}(\text{OH})_3^{2+}$  complex. When dissolved iron (III) was exposed to aqueous silica (0-60.0 mg/L as  $\text{SiO}_2$ ), Schenk and Weber (5) found that the presence of silica resulted in higher solution absorbance and a higher percentage of iron passing a 0.45  $\mu\text{m}$  pore size filter. They concluded that aqueous silica inhibits the hydrolysis of iron (III), an effect which is expected to negatively impact ferric coagulation. In the same study, Schenk and Weber also observed that aqueous silica catalyzed the oxidation of iron (II) to iron (III). These findings have obvious implications for silica impacts in ferrous oxidation and removal in drinking water treatment, as well as dosing of silica for iron corrosion control in water distribution systems.

The iron hydroxide surface has a strong affinity for silica. Sigg and Stumm (8) examined sorption of aqueous silica (0-48.1 mg/L as  $\text{SiO}_2$ ) to the  $\alpha$ - $\text{FeOOH}$  surface. Consistent with the results of others (6, 7), they found that sorption increased as the silica concentration and pH increased, with maximum adsorption at approximately pH 9. They modeled sorption of silica over a wide pH range by the formation of two monomeric surface species,  $=\text{FeSiO}(\text{OH})_3$  and  $=\text{FeSiO}_2(\text{OH})_2^-$ . Using these findings, along with data generated from studies with the  $\alpha$ - $\text{FeOOH}$  surface and other anions, Sigg and Stumm produced a model to predict the surface speciation of the iron oxide in a natural water. Their results indicated that silicate, along with phosphate, was likely to dominate the iron hydroxide surface charge under some circumstances.

**Implications for Sorptive Removal of Anionic Contaminants.** Although silica is an important constituent in natural waters, only a few studies have examined how silica affects sorption, mobilization, and removal of anionic contaminants in environmental systems. Researchers (19-21) have observed that silica interferes with arsenate removal in coprecipitation (coagulation) experiments with iron (III) chloride. Tong (19) studied this interference for iron coagulation between pH 6.5 and 8.5 in the concentration range of 1-50 mg/L as SiO<sub>2</sub>, and determined that percentage arsenate removal decreased as the pH and silica concentration increased. Meng et al. (21) suggested that silica interfered with arsenic removal by increasing electrostatic repulsion and competing for sorption sites on the ferric hydroxide surface. Furthermore, Meng et al. found that the presence of 10.7 mg/L as SiO<sub>2</sub> hindered Fe(OH)<sub>3</sub> precipitation above pH 8.5. Interestingly, the only work on the role of silica in humic substance sorption to iron hydroxides is that of Tipping (22), who determined that 6 mg/L as SiO<sub>2</sub> reduced humic substance removal by 20%.

**Additional Insights Based on Studies of Polysilicates.** Although soluble silica is assumed to be exclusively monomeric in natural systems, polysilicates are produced commercially and are commonly added to drinking water. Polysilicates are formed by neutralizing basic solutions of concentrated sodium silicate (4). It is quite possible that our understanding of these polymeric species could be applied to reactions of dimeric silica. For example, Taylor et al. (23) found that a small silica polymer had an affinity for soluble aluminum that was “at least 1,000,000 times greater than monomeric” silica. Thus, even if dimeric silica was present at relatively low concentrations, it could play a disproportionate role in complexing soluble aluminum and sorbing to aluminum hydroxide surface sites due to a higher affinity. The presence of aluminum was also found to stabilize the silica polymer (prevent depolymerization), which suggests that polymers might be more stable when complexed by aluminum or ferric species.

It is well known that commercial polysilicates can sequester iron, and the effectiveness of these chemicals increases as the complexity and molecular weight of the polymers increase (24). The results of Browman et al. (24), typical of most research on this subject, suggest that polymeric silica species accomplish sequestration by stabilizing iron colloids. Interestingly, polysilicates, often referred to as “activated silica,” can also function as coagulant aids under

some circumstances. For instance, Baylis (25) found that polysilicates increased the rate of alum coagulation and resulted in the formation of stronger floc particles. Additionally, he observed that addition of polymeric silica enabled coagulation to proceed at any pH above 5.5. Baylis speculated that silica in the form that aided coagulation, likely polymeric silica, is lacking in waters that are difficult to coagulate, but this interpretation was later forgotten given assumptions regarding the exclusivity of monomeric silica in natural waters (4).

## **Summary and Statement of Research Objectives**

The literature review highlighted several practically important impacts of silica in environmental systems. In some cases, silica is beneficial; in others, it is detrimental. Given our poor understanding, it is currently not possible to predict the behavior of silica in these systems. Calculations presented here indicate that dimeric silica may be significant in natural waters, raising questions about aqueous silica speciation and providing a new basis for interpreting seemingly contradictory behavior. Clearly, polymeric and monomeric silica species behave differently, as evidenced by the fact that polymers can form much stronger complexes with metals.

Numerous studies have focused on interactions between aluminum and silica, a topic of interest in the context of both natural environments and engineered processes. However, there is little fundamental research on the subject of silica sorption to iron hydroxide surfaces. The literature also contains limited data suggesting that silica interferes with the sorption of other anions. However, the conditions and extent of silica interference are not well-defined, nor are the mechanisms by which silica interferes. Although previous results were generally interpreted in the context of sorption, solids in most of these studies were formed during coagulation. Therefore, hydrolysis, precipitation, and particle agglomeration were also involved, making it difficult to determine how silica interfered with sorption of other anions. Thus, it would be useful to study this problem in the absence of these other mechanisms.

Given these issues, a two-phase experimental plan was devised to further fundamental and practical understanding. The first phase of research is aimed at determining how silica mechanistically interacts with pre-formed ferric hydroxide surfaces. By varying pH, silica concentrations, and reaction times, the role of silica in amorphous ferric hydroxide surface

chemistry will be examined under the range of conditions encountered in natural waters. Data collected from this phase of research will be used to determine whether existing sorption models are consistent with observed trends, or whether consideration of polymeric silica species (i.e., dimeric silica) is necessary to provide a reasonable explanation of surface charge and silica sorption. Because pre-formed iron hydroxide particles will be used, confounding effects of hydrolysis, complexation, and particle stabilization will be minimized.

The second phase of research will examine the role of silica in preventing sorption of arsenate and humic substances, important anionic contaminants in drinking water treatment. Removal of humic substances is required by the Enhanced Coagulation Rule, whereas a new maximum contaminant level (MCL) is forthcoming for arsenic. An improved understanding of the possible interference from dissolved silica will assist engineers, researchers, and utilities attempting to comply with these regulations. As in the first experimental phase, use of pre-formed ferric hydroxide will minimize silica impacts on mechanisms other than competition for surface sites.

Interactions between aqueous silica and amorphous ferric hydroxide have important practical implications. This study is intended to provide insights into the mechanisms by which silica influences amorphous ferric hydroxide surface chemistry and the corresponding role of silica speciation. It is anticipated that this information, coupled with results from the anion interference studies, will advance fundamental understanding of the role of aqueous silica in natural and engineered systems.

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## CHAPTER II

### The Role of Silica Sorption in Iron Hydroxide Surface Chemistry

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Experiments were conducted to investigate the fundamentals of silica sorption onto pre-formed ferric hydroxide at pH 5.0-9.5 and silica concentrations of 0-200 mg/L as SiO<sub>2</sub>. At all pHs studied, sorption densities exceeding monolayer sorption were observed at silica levels typical of natural waters. Under some circumstances, sorption exceeded a monolayer while the particle zeta potential remained positive, a phenomenon which is inconsistent with available models. To address this deficiency, an extended surface complexation model was formulated in which soluble dimeric silica (i.e., Si<sub>2</sub>O<sub>2</sub>(OH)<sub>5</sub><sup>-</sup>) sorbs directly to iron surface sites. This model fits sorption density data up to 0.40 mol SiO<sub>2</sub>/mol Fe, and it accurately predicts trends in zeta potential and the observed H<sup>+</sup> release during silica sorption to ferric hydroxide at pH 5.0 and 6.0.

#### Introduction

Silica is omnipresent in natural waters, typically at 1-20 mg/L as SiO<sub>2</sub> for surface water and 7-45 mg/L as SiO<sub>2</sub> for groundwater (1). Previous work by Stumm et al. (2) indicated that soluble silica in natural systems occurred exclusively in the form of monosilicic acid and its conjugate base. However, more recent research using NMR has established new equilibrium constants that suggest up to 50% of the total soluble silicon concentration in natural waters is present in dimeric silica species, particularly as Si<sub>2</sub>O<sub>2</sub>(OH)<sub>5</sub><sup>-</sup> (3).

Several studies have established that soluble silica exhibits high affinity for surfaces of aluminum and ferric oxides (4-6), and formation of multiple layers of sorbed silica has been observed in these systems (5, 6). The general hypothesis was that monomeric silica species, specifically Si(OH)<sub>4</sub> and SiO(OH)<sub>3</sub><sup>-</sup>, were sorbing to the surfaces and sequentially forming layers. Taylor et al. (7) reported that an oligomeric form of silica, containing fewer than 35 Si atoms, exhibited “an affinity for [soluble] aluminum at least 1,000,000 times greater” than monomeric silica. The presence of polymeric silica is known to hinder precipitation of iron and manganese (8, 9), and silica was recently shown to interfere with arsenic removal by coagulation (10-12). If dimeric silica species in solution have an extremely high affinity for iron and

aluminum oxide surfaces, they might contribute to significant adverse effects on coagulation associated with silica.

The goal of this work was to characterize iron hydroxide surfaces produced after contact with varying levels of silica in the pH range of 5.0-9.5. A second objective was to determine whether existing sorption models could explain key trends in the data and to propose a new model conceptualization if necessary.

## Materials and Methods

**Sorption of Silica to Iron.** Sorption experiments were designed to investigate interactions of pre-formed  $\text{Fe}(\text{OH})_3$  with silica at concentrations ranging from 0 to 200 mg/L as  $\text{SiO}_2$ . The experiments were carried out at 20°C. HDPE plastic bottles were used to eliminate concerns with silica leaching from glass labware.  $\text{Fe}(\text{OH})_3$  was formed by raising the pH of an  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  stock (250 mg/L as Fe acidified with  $1 \times 10^{-2}$  M  $\text{HNO}_3$ ) to 6.0 with a single dose (1000  $\mu\text{L}$ ) of 2.34 M NaOH. The  $\text{Fe}(\text{OH})_3$  was then aged for 12-16 hours on an orbital shaker. Silica samples were prepared from a stock of  $\text{Na}_2\text{SiO}_3$  (8000 mg/L as  $\text{SiO}_2$ ), and  $\text{NaNO}_3$  was added to a concentration of  $1 \times 10^{-3}$  M in all samples to keep final ionic strength variations less than a factor of 5.5. Each silica sample was adjusted to pH 6.0 with  $\text{HNO}_3$  and stored in the same manner as the  $\text{Fe}(\text{OH})_3$ . pH measurements were made with a Corning 313 pH/Temperature meter and a Corning combination electrode.

After the solids aged 12-16 hours, the pHs of the  $\text{Fe}(\text{OH})_3$  and silica samples were adjusted to target values of pH 5.0, 6.0, 7.25, 8.5, or 9.5. All solutions were mixed at 400 rpm with a 1 inch stirbar. At  $\text{pH} \geq 7.25$ , bottles were covered with HDPE lids or polyvinyl chloride plastic wrap to minimize  $\text{CO}_2$  dissolution, but these steps did not completely eliminate it. The sorption experiment was initiated when the silica samples were dosed with pre-formed  $\text{Fe}(\text{OH})_3$  to achieve final concentrations of 10 mg/L as Fe. The quantity of base or acid required to maintain the target pH was recorded. In each sample, the pH was maintained within  $\pm 0.15$  units during the ensuing reaction period of 1.5 hours.

After completion of the experimental steps described above, the samples were aged on an orbital shaker for 50 days (1200 hours). During this aging period, the pH of each sample was regularly checked and readjusted to the target as necessary.

**Determination of Sorption Density.** The sorption density of each sample was measured after 1.5 hours and 50 days of reaction time. Selection of these reaction times was based on observations in preliminary experiments and the literature. In preliminary experiments, when pre-formed  $\text{Fe}(\text{OH})_3$  (aged 2 weeks) was exposed to aqueous silica (0-63 mg/L as  $\text{SiO}_2$ ) at pH 6.0 and 8.5, there were no significant differences (95% confidence) in zeta potential measurements at 1 hour, 1 day (24 hours), and 1 week (168 hours). These results indicated that surface changes occurring between 1 hour and 1 week did not produce detectable changes in zeta potential. Consistent with this observation, several studies have noted that silica sorption is rapid during the first 1-3 hours of exposure to an aluminum oxide surface; this initial, rapid sorption is followed by progressively slower sorption (5, 6). In this study, the 1.5-hour reaction time was chosen to investigate rapid sorption, while the 50-day reaction time provides insights into the nature of the slower silica sorption which occurs at longer exposure times. The 1.5-hour reaction time is representative of conditions in an engineered system, such as coagulation. In contrast, the 50-day reaction period models the long residence times encountered in a natural water.

A Nalgene vacuum filtration assembly was used to pass 50 mL of each sample through a 0.45  $\mu\text{m}$  pore size Millipore nitrocellulose filter. The filtrate was collected, and the filter with the captured solids was then digested in a  $\text{HNO}_3$  solution. Visible observations indicated that a 2%  $\text{HNO}_3$  solution dissolved the solids collected after 1.5 hours of reaction time within 5 days (120 hours). However, the 2% solution did not completely dissolve the solids collected after 50 days, even when the samples were heated to 90°C and sonicated. Therefore, a stronger digestion was employed for these samples by increasing the acid concentration to 5%  $\text{HNO}_3$  and the digestion time to 28-48 days (672-1152 hours). At this point, it appeared that most solids on the filter had dissolved, but some suspended particles were still visible in the solution as is discussed later. Upon completion of the digestion period, the digestate was filtered through a 0.45  $\mu\text{m}$  pore size Life Science Products, Inc. nylon syringe filter. Soluble iron and silicon in the filtrate and filtered digestate samples were measured with a JY 2000 Inductive Coupled Plasma - Emission Spectroscopy (ICP-ES).



**Characterization of Undigested Solids.** As previously stated, acid digestions did not completely dissolve solids captured on the filters after 50 days of reaction time. At the end of the digestion period, the samples were visually examined for color, size, and shape of the remaining particles. Representative particles were collected, mounted on aluminum bar stock (1-inch diameter), and dried in a dessicator at room temperature. The samples were analyzed with a CamScan Series 2 Scanning Electron Microscope (SEM). The SEM was equipped with an American Nuclear Systems Quantum System 4000 Energy Dispersive Spectrometry (EDS) feature which allowed semi-quantitative point analysis of elements with an atomic number greater than sodium.

**Zeta Potential.** A Malvern ZetaSizer 3000HS was used to measure zeta potential after 1.5 hours and 50 days of reaction time. The instrument performance was regularly checked with the manufacturer's electrophoresis standard and an independent Min-u-sil test colloid standard.

## **Results and Discussion**

General observations were made by first comparing two different approaches to analyzing silica sorption to iron. Thereafter, silica sorption density and particle zeta potential are quantitatively discussed. This analysis allowed formulation of a new, simplistic surface complexation model that can predict many important aspects of silica sorption for conditions commonly encountered in natural and engineered systems.

**Observations in Quantifying Silica Sorption to Pre-formed Iron.** Two approaches were used to quantify silica sorption to iron, each of which has unique advantages and disadvantages. The first approach determined sorbed silica based on the difference between initial silicon and final soluble silicon, as determined by filtration. This approach has large experimental error when the initial and final silicon concentrations are only slightly different from one another. The second approach relied on direct measurement of the silicon and iron dissolved from the filter by the acid digestion, and this approach is often more accurate when the first approach is less accurate. Complete mass balances on iron and silica were conducted by combining data from both approaches.

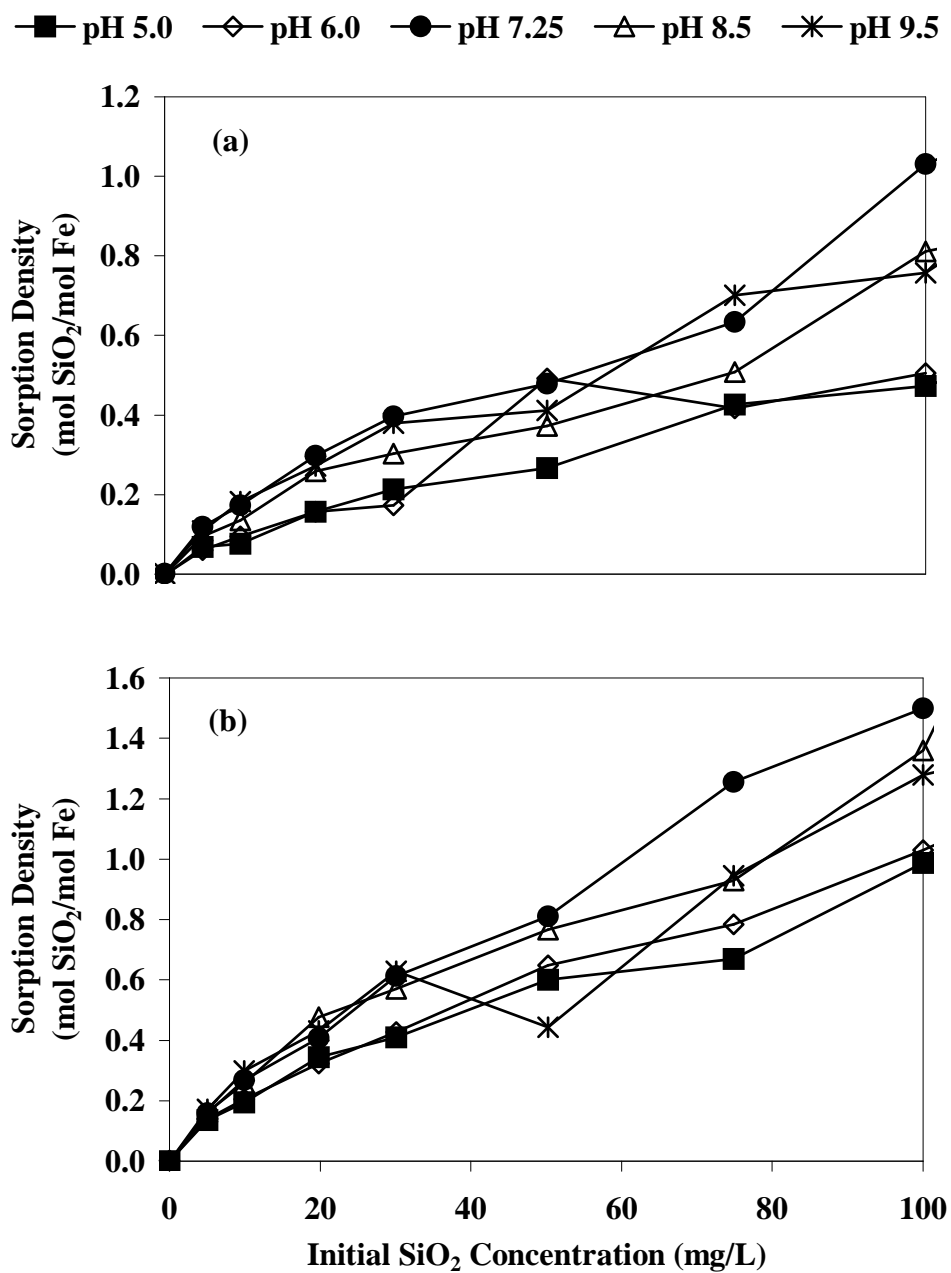
The overall recoveries of both iron and silicon were greater than 92% after 1.5 hours of reaction time, which is henceforth referred to as the “fresh iron” experiment. After an additional 50 days of reaction time, which is referred to as the “old iron” experiment, the overall iron recovery was  $79.9 \pm 15.9\%$ , and the silicon recovery was  $90.4 \pm 5.3\%$ . The percentage recovery of particulate silica can be estimated by comparing silicon released during digestion of the filter to the silicon removed by filtration (Appendix A). Viewed from this perspective, recovery of silica in a particulate form was only  $43.9 \pm 11.4\%$  in fresh iron experiments and  $49.1 \pm 15.6\%$  in old iron experiments. Recovery of particulate iron was much higher ( $92.8 \pm 5.3\%$  in fresh iron experiments and  $78.3 \pm 16.6\%$  in old iron experiments), clearly indicating that the acid digestion preferentially dissolved iron from the silica-iron particles trapped in the filters.

Given the low Si recoveries from the acid digestion, direct calculation of sorption density using this measurement leads to an underestimate of the ratio of sorbed  $\text{SiO}_2$  to Fe. This calculation was used to define the lower bound of silica sorption to iron. In contrast, the molar sorption density, SD, calculated according to the following:

$$SD = \frac{(Initial - Filtrate\text{SiO}_2) / Initial\text{SiO}_2}{(Initial - Filtrate\text{Fe}) / Initial\text{Fe}} \quad (2-1)$$

was not subject to this error. This approach, with appropriate consideration of experimental error, was used as the primary estimate of sorption density in the rest of this work (Figure 2-1).

Assuming an iron hydroxide site density of about 0.25 mol/mol Fe (13), sorption densities equivalent to a complete monolayer were observed in fresh iron samples with  $\text{pH} \geq 7.25$  at initial concentrations as low as 12-15 mg/L as  $\text{SiO}_2$  (Figures 2-1a and 2-2). At  $\text{pH}$  5.0 and 6.0, monolayer coverage appeared to require initial  $\text{SiO}_2$  levels near 40 mg/L. At much higher silica concentrations, sorption densities equivalent to bilayer coverage were observed after 1.5 hours for each  $\text{pH}$  studied. Sorption densities increased with higher initial silica concentrations. In systems with initial silica  $\leq 50$  mg/L, maximum sorption densities were observed at  $\text{pH}$  7.25 and 9.5, followed by  $\text{pH}$  8.5, 6.0, and 5.0. The measured sorption densities at  $\text{pH}$  7.25 and 9.5 were not significantly different from one another at 95% confidence; furthermore, sorption densities at  $\text{pH}$  7.25 were significantly higher than those at  $\text{pH}$  5.0 and 6.0 at greater than 95% confidence.



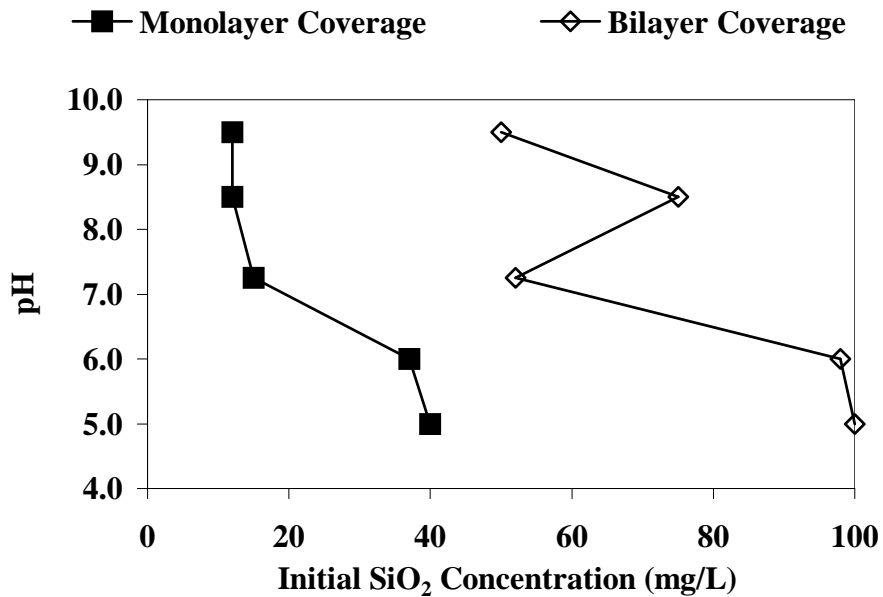
**Figure 2-1. Sorption densities in samples after (a) 1.5 hours of reaction time and (b) 50 days of reaction time.**

In the samples with old iron, sorption densities of 0.25 mol SiO<sub>2</sub>/mol Fe were achieved in samples with initial SiO<sub>2</sub> concentrations between 7 and 15 mg/L for the entire pH range studied (Figure 2-1b). Sorption densities equivalent to uniform bilayer coverage occurred at initial levels

of silica between 22-38 mg/L as SiO<sub>2</sub>. Comparing data for the fresh and old iron experiments, an average increase in silica sorption density of 81% occurred with age, as calculated by:

$$I = \frac{SD_{50days} - SD_{1.5hours}}{SD_{1.5hours}} * 100\% \quad (2-2)$$

and the range of increase varied from 8-153%. These differences were always significant at greater than 99% confidence. In the old iron samples, maximum sorption occurred in samples with pH  $\geq 7.25$ , followed by pH 6.0 and 5.0.



**Figure 2-2. Initial SiO<sub>2</sub> and pH conditions resulting in sorption densities equivalent to monolayer and bilayer levels of surface coverage after 1.5 hours of reaction time.**

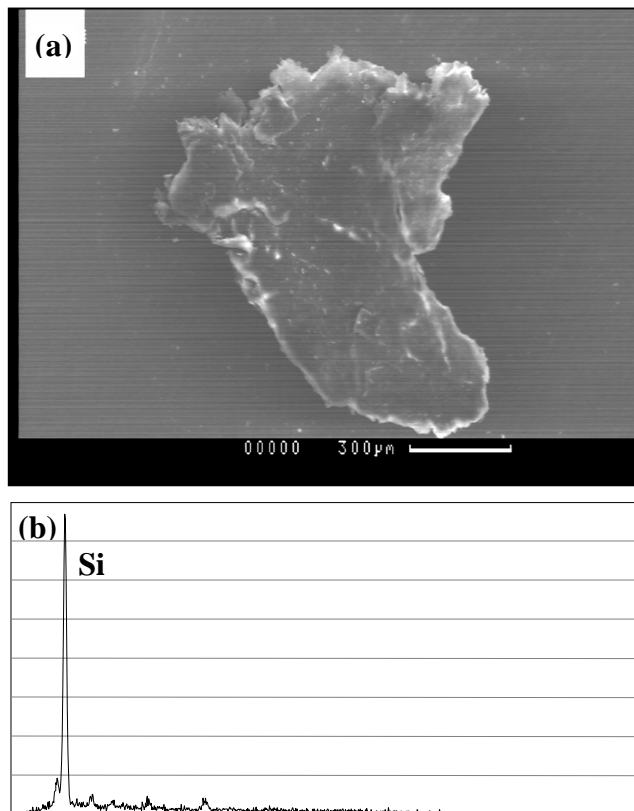
These results confirm the validity of the general experimental approach used to characterize silica sorption in previous research (4-6); they are also consistent with the increased sorption previously observed at higher concentrations of SiO<sub>2</sub> (4-6) and longer reaction times (5, 6). Huang (5) and Hingston and Raupach (6) reported that more than a monolayer of silica sorbed at concentrations below 100 mg/L as SiO<sub>2</sub> in the pH range of 4-11. One difference, however, is that previous work (4-6) reported a clear maximum sorption density at an

equilibrium pH of approximately 9.0, whereas very high sorption was observed in this work at constant pH 7.25-9.5.

**What was the nature of the iron and silica particles that could not be solubilized by the acid digestion?** Recovery of silica from acidified digested samples was very poor, and this question was worthy of follow-up study. Four representative types of these recalcitrant particles were collected and examined with an SEM to answer this question. Rust-colored, spherical particles were found in samples with  $\text{pH} \leq 6.0$  and silica concentrations  $\leq 10$  mg/L. The size of the representative particle, as determined by SEM, was 0.64  $\mu\text{m}$ . Elemental analysis revealed a high-intensity Fe peak with a trace of Si. Transparent, irregularly-shaped particles (representative particle size 3.0  $\mu\text{m}$ ) were found at silica concentrations  $\geq 75$  mg/L in pH 6.0 samples and at silica concentrations  $\geq 30$  mg/L in pH 7.25 samples. Only an Fe peak of medium intensity was visible in this case.

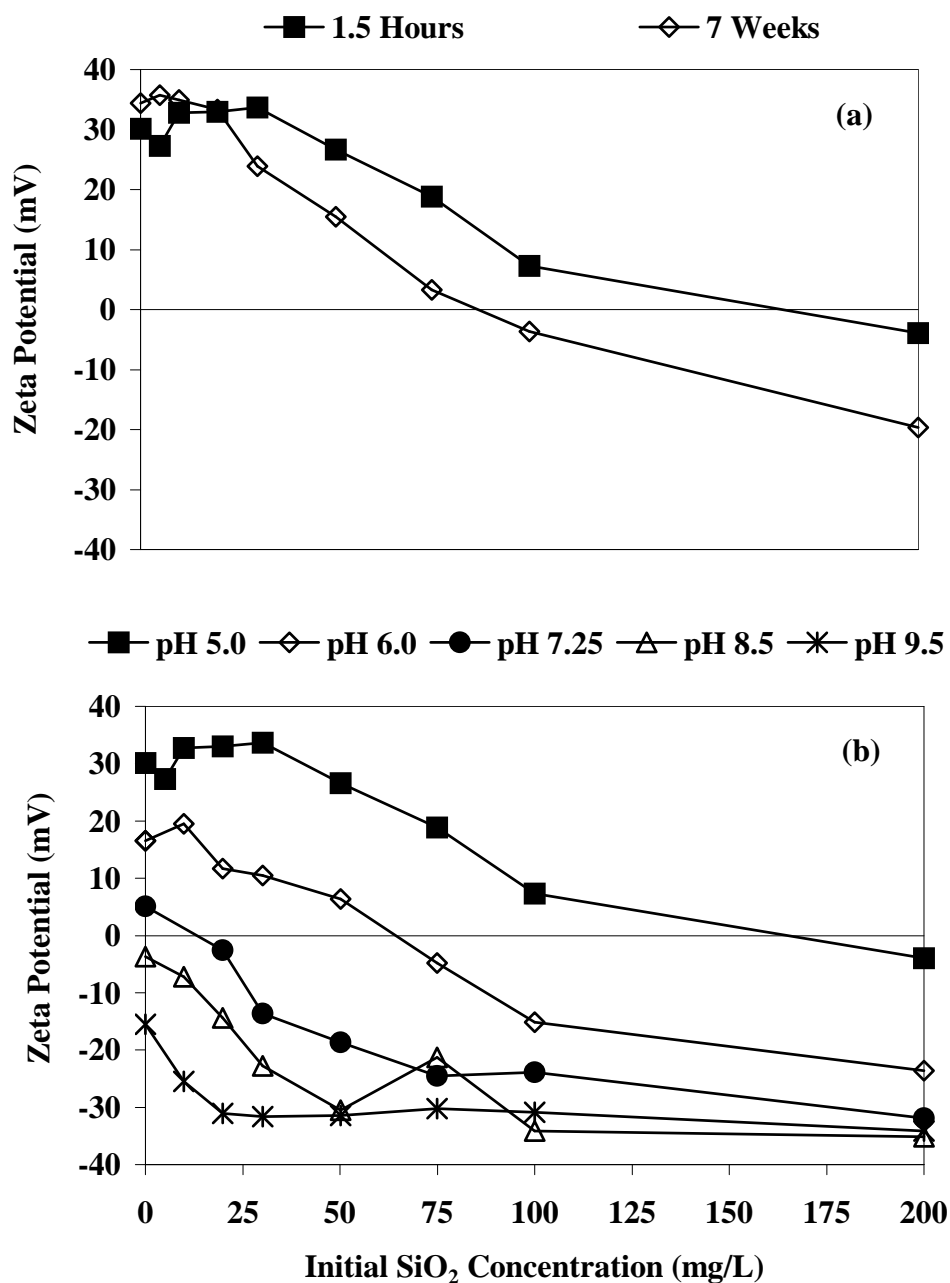
Interestingly, a black particle (representative particle size 1.2  $\mu\text{m}$ ) with a very significant Si peak and no detectable iron was found in eight samples (Figure 2-3). These particles were found at all test pHs, at silica concentrations ranging from 10 to 200 mg/L as  $\text{SiO}_2$ . Finally, white particles (representative particle size 1.3  $\mu\text{m}$ ) appeared in six of the nine pH 9.5 samples, at silica concentrations ranging from 5.0 to 200 mg/L. These particles also occurred at other pHs in samples with silica levels  $\geq 75$  mg/L. Although the elemental spectrum of the representative sample was fairly noisy, an Fe peak of medium intensity was observed. No further analysis was attempted to identify the mineralogy of these samples. However, these results support the idea that some solids removed by filtration could not be dissolved in strong acid and illustrate the necessity of measuring sorption density based on disappearance of Si from solution.

**Surface Charge.** Zeta potential was measured at the end of the 1.5 hour and 50 day reaction periods. For triplicate measurements with an average zeta potential between  $-10$  and  $+10$  mV, the average standard deviation was  $\pm 3.4$  mV in the experiment with fresh iron and  $\pm 1.5$  mV in the experiment with old iron. Although zeta potential appears to become more negative as the particles age and more silica sorbs, the general trend is similar at both iron ages (Figure 2-4a). Not surprisingly, the surface becomes more negative with increasing  $\text{SiO}_2$  levels and increasing pH (Figure 2-4b).



**Figure 2-3. (a) SEM photograph of a small, black particle remaining after 48 days of acid digestion. This particle formed at pH 8.5 with 200 mg/L initial SiO<sub>2</sub>. (b) Spectrum from elemental point analysis performed on this particle.**

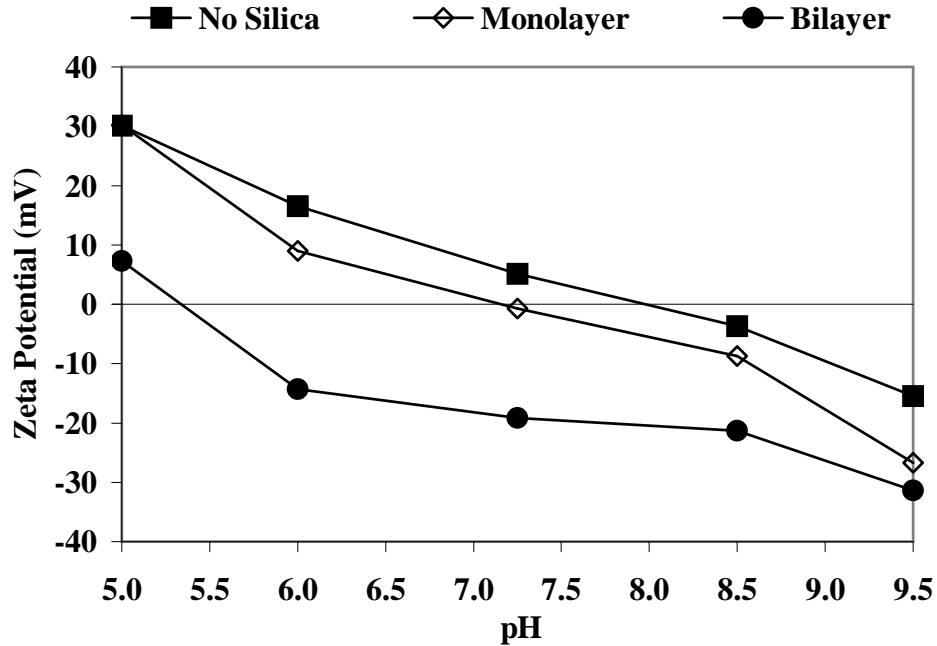
In earlier studies, where multiple layers of silica sorbed onto an aluminum oxide (5, 6), the data was not inconsistent with formation of discrete silica layers in a step-wise fashion. It was believed that the aluminum particles were coated with a monolayer, followed by a slower forming bilayer, etc. Hingston and Raupach (6) also reported that sorption of the bilayer energetically resembled silica polymerization. However, the data collected in this study at pH 5.0 are clearly inconsistent with this conceptualization. Iron surfaces at an initial SiO<sub>2</sub> concentration of approximately 40 mg/L had enough sorbed silica to form a monolayer (Figure 2-2); however, zeta potential measurements (Figures 2-4 and 2-5) demonstrate that the particles had a highly positive charge after 1.5 hours of reaction time. In fact, the net particle surface charge at pH 5.0 did not become neutral until enough SiO<sub>2</sub> had sorbed to form a bilayer.



**Figure 2-4. Measured zeta potential as a function of initial SiO<sub>2</sub> (a) in samples at pH 5.0 and (b) in all samples after 1.5 hours of reaction time.**

Accepting the basic validity of surface complexation model (i.e., Equations 2-3 and 2-4 in Table 2-1) proposed by Sigg and Stumm (4) for sorption of Si(OH)<sub>4</sub> to neutral  $\alpha$ -FeOOH sites, it is noted that silica sorption would always lead to formation of neutral or negative surface complexes. Thus, this model cannot describe sorption beyond a monolayer. Furthermore, it is

not possible to have monolayer coverage with a positively-charged surface—the capabilities of this model must be extended.



**Figure 2-5. Effect of pH on measured zeta potential at sorption densities equivalent to monolayer and bilayer levels of surface coverage. Zeta potential measurements were made after 1.5 hours of reaction time.**

**Table 2-1. Solution and Surface Complexation Reactions**

Eqn	Reaction	K <sup>a</sup>
2-3	$=\text{FeOH} + \text{Si}(\text{OH})_4 \leftrightarrow =\text{FeSiO}(\text{OH})_3 + \text{H}_2\text{O}$	$\leq 1.90\text{E}+01$
2-4	$=\text{FeOH} + \text{Si}(\text{OH})_4 \leftrightarrow =\text{FeSiO}_2(\text{OH})_2^- + \text{H}^+ + \text{H}_2\text{O}$	$\leq 1.97\text{E}-07$
2-5	$=\text{FeSiO}(\text{OH})_3 + \text{Si}(\text{OH})_4 \leftrightarrow =\text{FeSi}_2\text{O}_2\text{Si}(\text{OH})_5 + \text{H}_2\text{O}$	not modeled
2-6	$=\text{FeSiO}(\text{OH})_3 + \text{Si}(\text{OH})_4 \leftrightarrow =\text{FeSi}_2\text{O}_3(\text{OH})_4^- + \text{H}^+ + \text{H}_2\text{O}$	not modeled
2-7	$=\text{FeOH} + \text{Si}_2\text{O}_2(\text{OH})_5^- + \text{H}^+ \leftrightarrow =\text{FeSi}_2\text{O}_2(\text{OH})_5 + \text{H}_2\text{O}$	$9.50\text{E}+11$
2-8	$=\text{FeOH} + \text{Si}_2\text{O}_2(\text{OH})_5^- \leftrightarrow =\text{FeSi}_2\text{O}_3(\text{OH})_4^- + \text{H}_2\text{O}$	$3.90\text{E}+05$
2-9	$2\text{Si}(\text{OH})_4 \leftrightarrow \text{Si}_2\text{O}_2(\text{OH})_5^- + \text{H}^+ + \text{H}_2\text{O}$	$1.00\text{E}-05^b$
2-10	$=\text{FeOH}_2^+ \leftrightarrow =\text{FeOH} + \text{H}^+$	$5.13\text{E}-08^c$
2-11	$=\text{FeOH} \leftrightarrow =\text{FeO}^- + \text{H}^+$	$1.17\text{E}-09^c$

<sup>a</sup> Unless otherwise noted, K-values are optimized values determined during modeling.

<sup>b</sup> Svensson et al. (3)

<sup>c</sup> Dzombak and Morel (13)

Note: Optimized Site Density = 0.25 mol/mol Fe. Optimized Surface Area = 6.49E+03 m<sup>2</sup>/g.



Sorption and surface charge data at pH 5.0 suggest two possible simplistic approaches. The first possibility is that monomeric silica, specifically  $\text{Si}(\text{OH})_4$ , sorbs to surface sites on the ferric hydroxide surface (Equations 2-3 and 2-4), followed by formation of a dimeric silica species according to Equations 2-5 and 2-6. The second possible scenario involves direct sorption of dimers, such as  $\text{Si}_2\text{O}_2(\text{OH})_5^-$ , to iron surface sites, according to Equations 2-7 and 2-8. In either case, more than one silica can sorb per surface site while leaving the surface with a net positive charge.

Conceptually, although similar equilibrium equations describe either approach, we chose to consider direct surface complexation of dimeric silica, the existence of which in solution was unambiguously established recently by Cary et al. (14). According to the published formation constant (3) of Equation 2-9 (Table 2-1), the concentration of the dimer accounts for only about 0.2% of the total soluble Si at pH 5.0 and 50 mg/L of  $\text{SiO}_2$ . As previously discussed, however, Taylor et al. (7) found that oligomeric silica exhibited an affinity for aluminum that was  $1 \times 10^6$  higher than that of monomeric silica. Thus, these references support the idea that dimeric silica exists in solution, and that it could be important as a surface complex due to a much higher affinity for iron surface sites than monomeric silica.

**Modeling Sorption of Silica to Ferric Hydroxide.** A model using the basic Sigg and Stumm (4) model (i.e., Equations 2-3 and 2-4 of Table 2-1) provided a good fit of data points at low  $\text{SiO}_2$  concentrations and sorption densities less than 0.20 mol  $\text{SiO}_2$ /mol Fe. However, at higher sorption densities, this model could not possibly explain data at pH 5.0. Thus, the surface complexation model was extended to include dimeric soluble silica and two additional silica surface complexes, and an attempt was made to fit the sorption density data collected after 1.5 hours of reaction time with  $\text{SiO}_2$ .

This extended surface complexation model (see reactions in Table 2-1) was developed with inputs of pH, initial  $\text{SiO}_2$  concentration, particulate ferric concentration, and known ionic strength. For the model calibration, only experimental data with measured sorption densities  $\leq$  0.40 mol  $\text{SiO}_2$ /mol Fe were used, since higher sorption densities imply significant concentrations of sorbed silica beyond dimeric species. This limitation is not overly restrictive in the context of natural levels of silica, since the corresponding concentrations of soluble silica were 20-50 mg/L

as SiO<sub>2</sub>, depending on pH. Electrostatic corrections of intrinsic complexes were made using standard approaches based on surface charge and ionic strength (15). “Best fit” intrinsic constants, site density, and surface area (Table 2-1) were determined to minimize residuals between measured and predicted silica sorption densities.

The optimized value of the ferric hydroxide site density was very reasonable at 0.25 mol sites/mol Fe (13). The higher than anticipated surface area probably results from an overestimate of electrostatic interactions between sorbed anionic dimers and charged surface sites—that is, the “optimized surface area” is about 10 times higher than reported elsewhere for Fe(OH)<sub>3</sub> (13). The model fit based on sorption density is quite good ( $R^2 = 0.87$ ), especially when the estimated 95% confidence in the data based on analytical error alone is considered (Figure 2-6). It is noted that lower experimental errors can be obtained if much higher levels of iron are used, but this study was designed to use the highest level of iron commonly encountered in engineered systems such as coagulation. When the acidity constants for hydrous ferric oxide were varied from the values given by Dzombak and Morel (13), the correlation between measured and predicted sorption density increased to  $R^2=0.91$ . Although the model works well in the calibration region, attempts to extend the model to samples with measured sorption densities up to 0.50 mol SiO<sub>2</sub>/mol Fe were less successful, as would be anticipated since sorption did not proceed in progressive layering to a bilayer.

Perhaps even more importantly, the model, which was calibrated with sorption density measurements, exhibited good agreement between the predicted surface potential and the measured zeta potential (Figure 2-7). As anticipated, there is not a direct relationship between surface potential and zeta potential. However, the magnitude of the surface potential is greater than that of the zeta potential, and there is general agreement between the trends in magnitude and the sign of the two potentials. The model also predicted the net release of H<sup>+</sup> as SiO<sub>2</sub> sorbed onto the ferric hydroxide surface at pH 5.0 and 6.0. Over the range of SiO<sub>2</sub> considered (50 and 30 mg/L at pH 5.0 and 6.0, respectively), an average of 0.13-0.51 mol H<sup>+</sup> were released/mol SiO<sub>2</sub> sorbed. The model predicts 0.22-0.46 mol H<sup>+</sup> released/mol SiO<sub>2</sub> sorbed. Accurate data on H<sup>+</sup> release was not obtained at higher pHs in these experiments due to significant CO<sub>2</sub> dissolution at those values.

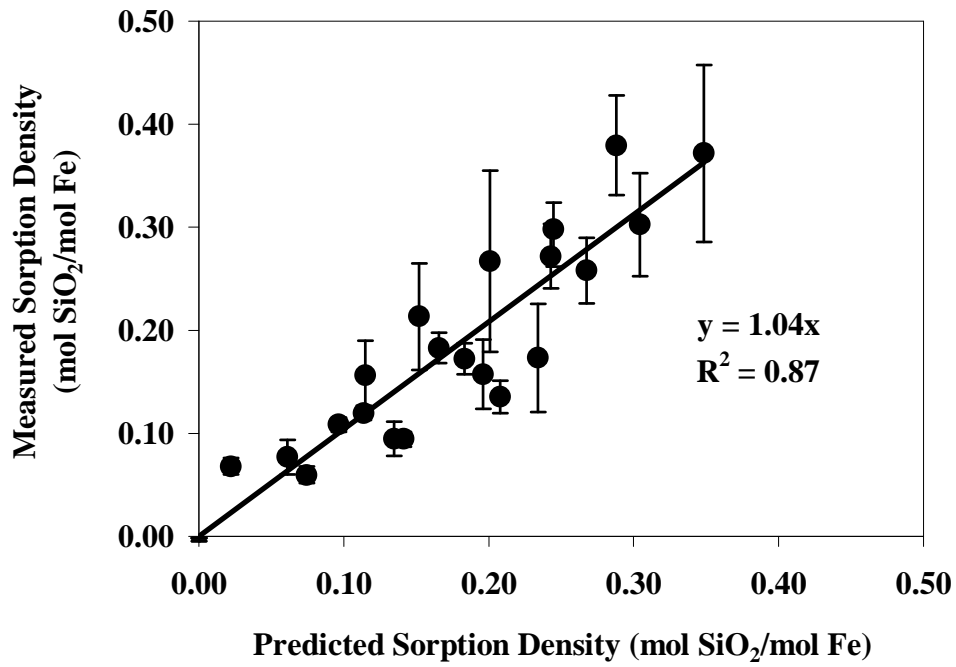


Figure 2-6. Results of model calibration using samples with measured sorption densities  $\leq 0.40$  mol SiO<sub>2</sub>/mol Fe. Error bars represent analytical error in measuring Si.

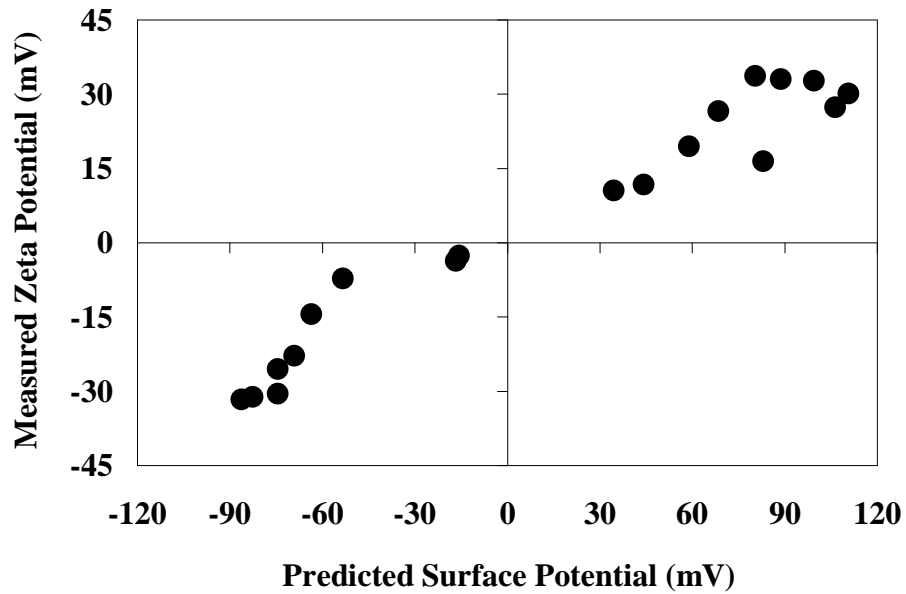
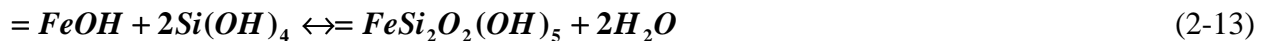


Figure 2-7. Correlation between measured zeta potential and model-predicted surface potential for all samples in the calibration region.

In sum, the model fit measured sorption densities well, and model predictions are consistent with measurements of zeta potential and proton release during sorption. It is interesting how this conceptualization changes our perception of silica sorption to the iron surface. At all pHs tested (pH 5.0-9.5) and typical levels of soluble silica, the dimeric surface species are predicted to be the dominant form of sorbed silica (Figure 2-8). Model predictions indicate that monomeric surface species are much less significant, occupying less than 0.5% of the surface.

Note that at pH 5.0, samples with at least 40 mg/L initial SiO<sub>2</sub> had sorption densities  $\geq$  0.25 mol SiO<sub>2</sub>/mol Fe, which would have previously been considered complete monolayer coverage. At this silica level, the model predicts that 57.0% of the ferric hydroxide surface consists of =FeOH<sub>2</sub><sup>+</sup> sites, 5.5% of the surface is =FeOH, and 37.4% surface consists of dimeric silica species (Figure 2-8a). The result is a net positive charge, which is consistent with zeta potential measurements. At an initial SiO<sub>2</sub> concentration of 75 mg/L, where the surface charge is still positive, the model predicts that approximately 50% of the surface is covered by dimeric silica species, which yields a sorption density equivalent to a monolayer. At 5.0 and 6.0, the net reactions, in terms of the dominant SiO<sub>2</sub> species in solution, may be written as:



According to Figure 2-8a, Equation 2-12 dominates at lower silica concentrations, leading to the measured stoichiometry of 0.5 H<sup>+</sup> released per Si(OH)<sub>4</sub> sorbed. As the initial silica level increases, Equation 2-13 becomes more important, and H<sup>+</sup> release declines. Although dimeric species are dominant on the surface at all pHs, they occupy a higher percentage of the surface as pH increases. At pH 8.5 and 50 mg/L initial SiO<sub>2</sub>, the model predicts that 70.5% of the surface sites exist as dimeric silica species compared with only 40.9% at pH 5.0 (Figure 2-8). The end result is higher sorption densities as pH increases, a trend which is evident in the data.

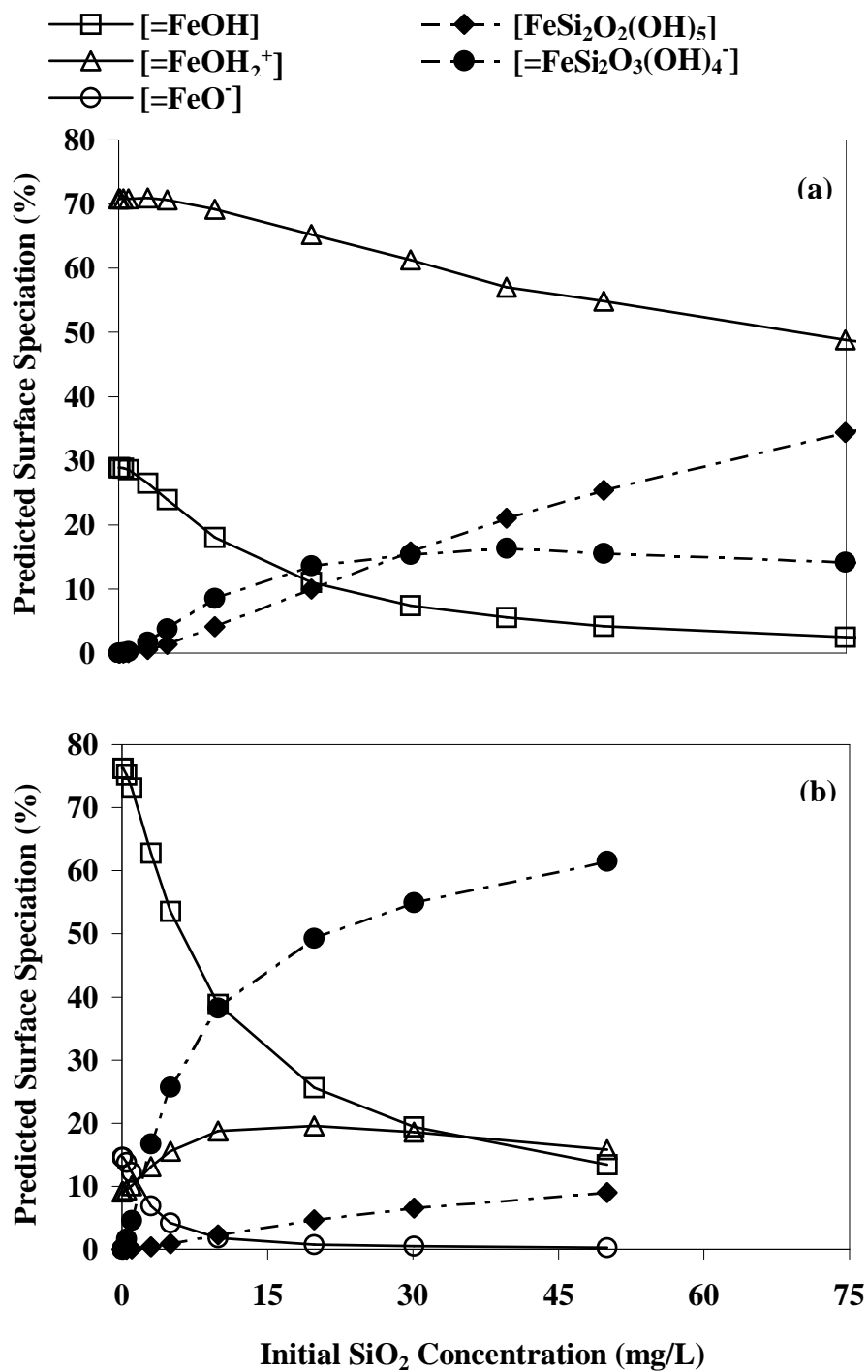


Figure 2-8. Model-predicted surface species as a function of initial SiO<sub>2</sub> concentration at (a) pH 5.0 and (b) pH 8.5.

Interactions between silica and iron oxides play an important role in numerous environmental systems, including natural waters, coagulation, membrane treatment, and water

distribution networks. Prior to this study, existing models did not consider direct sorption of dimeric silica species or provide the ability to predict sorption beyond a monolayer. However, an improved conceptualization of silica sorption to Fe(OH)<sub>3</sub> will result in an enhanced understanding of natural systems and improvements in the design and operation of engineered systems.

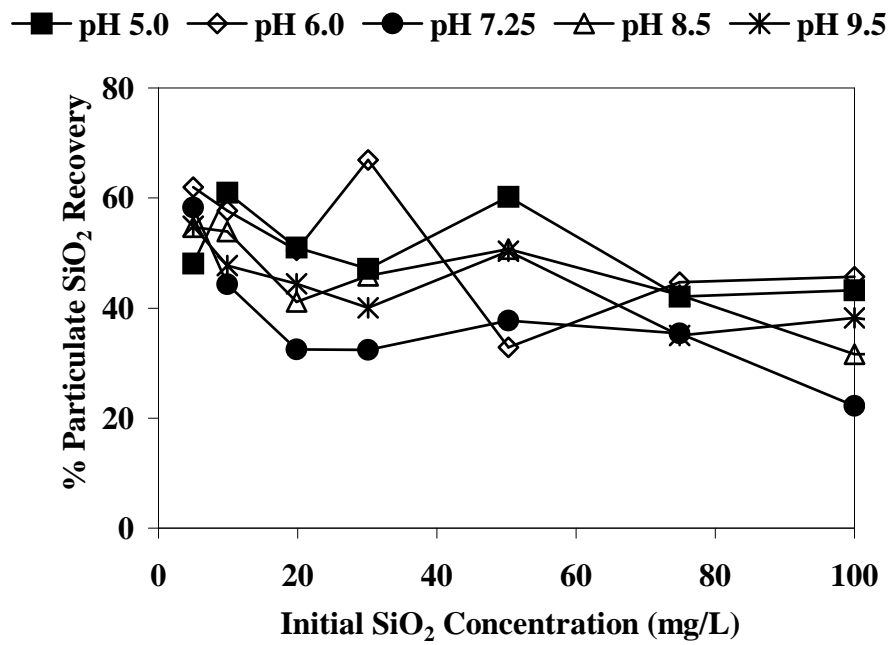
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**Appendix A. Recovery of particulate SiO<sub>2</sub> from solids collected after 1.5 hours of reaction time.**



## CHAPTER III

### **Implications of Silica Sorption to Iron Hydroxide: Mobilization of Iron Colloids and Interference with Sorption of Arsenate and Humic Substances**

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This work highlighted practical implications of silica sorption to iron hydroxide in natural and engineered systems. Two types of surfaces were prepared by exposing pre-formed  $\text{Fe}(\text{OH})_3$  to aqueous silica (0-200 mg/L as  $\text{SiO}_2$ ) for periods of 1.5 hours or 50 days. The concentration of pre-formed iron passing through a 0.45  $\mu\text{m}$  pore size filter at pH 6.0-9.5 increased as the solids aged in the presence of silica. Consistent with formation of small, stable colloids, “soluble” iron concentrations exceeded 0.2 mg/L only at zeta potentials  $\leq -15$  mV. When arsenate was added to iron hydroxide particles equilibrated with silica for 1.5 hours, percentage arsenate removals were high. In contrast, arsenate removals decreased markedly as pH and silica concentrations increased if silica was pre-equilibrated with the iron for 50 days. Trends in percentage removal of humic substances were similar. Competition for sorption sites was the main cause of hindered anionic contaminant removal. However, interference with hydrolysis and precipitation are expected to be important under some circumstances, particularly during water treatment.

#### **Introduction**

All natural waters contain silica, at typical concentrations of 1-20 mg/L as  $\text{SiO}_2$  for surface water and 7-45 mg/L as  $\text{SiO}_2$  for ground water (1). Aqueous silica can sorb to the surfaces of iron oxides (2, 3); therefore, it is expected to influence practical aspects of chemistry in environmental systems. The mechanisms by which silica can influence natural and engineered processes have not been completely defined, but may include competition for iron sorption sites and colloid stabilization.

Silica sorption to iron hydroxide can reduce contaminant removal during coagulation by competition, as has been hypothesized for the case of arsenic removal during ferric coagulation (4-6). Likewise, silica might also interfere with removal of other anionic contaminants of interest, such as humic substances. Furthermore, since silica influences arsenic removal in engineered processes, it likely affects arsenic sorption and mobilization in natural systems.

Commercially-produced silica polymers, which are often used to sequester iron in drinking water (7, 8), hinder ferric hydroxide precipitation by colloid stabilization (7). If aqueous silica in natural waters can also stabilize colloids, there are a number of significant implications. In the subsurface, detachment of colloids from stationary surfaces can cause mobilization of sorbed contaminants (9). Colloid stabilization during coagulation would also reduce the effectiveness of water treatment, because stable floc particles and associated contaminants are not readily removed during sedimentation and filtration.

Previous work provided insights into the role of aqueous silica in iron hydroxide surface chemistry under one set of well-controlled laboratory conditions (2). The goal of this research was to quantify the effects of sorbed silica on contaminant removal and particle stability in this well-defined system and to consider practical implications for natural and engineered systems.

## Materials and Methods

**Preparation of Iron-Silica Solids.**  $\text{Fe}(\text{OH})_3$  was formed by raising the pH of an  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  stock (250 mg/L as Fe acidified with  $1 \times 10^{-2}$  M  $\text{HNO}_3$ ) to 6.0 with a single dose (1000  $\mu\text{L}$ ) of 2.34 M NaOH. Silica samples, at concentrations ranging from 0-200 mg/L as  $\text{SiO}_2$ , were prepared from a stock of  $\text{Na}_2\text{SiO}_3$  (8000 mg/L as  $\text{SiO}_2$ , pH 12.8), and the pH of each sample was adjusted to 6.0 with  $\text{HNO}_3$ . All solutions were stirred at 400 rpm. The separate  $\text{Fe}(\text{OH})_3$  solution and silica samples were aged at pH 6.0 on an orbital shaker for 12-16 hours. pH measurements were made with a Corning 313 pH/Temperature meter and a Corning combination electrode.

After the aging period, the pHs of the  $\text{Fe}(\text{OH})_3$  solution and silica samples were adjusted to target values of pH 5.0, 6.0, 7.25, 8.5, or 9.5. Silica sorption was initiated when the silica sample was dosed with the pre-formed  $\text{Fe}(\text{OH})_3$  to achieve a final concentration of 10 mg/L as Fe. Additional details of the preparation procedure are given in Davis et al. (2). Two types of  $\text{Fe}(\text{OH})_3$  surfaces were prepared for experiments based on reaction times with silica of 1.5 hours and 50 days.

**Preparation of Silica Stock Solution.** Preparation procedures of silica stock solutions were carefully examined prior to experiments. When the  $\text{Na}_2\text{SiO}_3$  salt was dissolved to achieve a

final SiO<sub>2</sub> concentration of 8000 mg/L, the resulting pH was approximately 12.8. Based on conventional understanding, the silica solution is expected to consist primarily of monosilicate ions under these conditions (10). However, if the pH of silica stock solutions at high concentrations is decreased below 11.5, complex silica polymers and colloids begin to form (10-12). Since soluble, aqueous silica in natural systems is commonly thought to exist solely as monomers (10), formation of complex polymers and colloids in the stock solution is undesirable.

Molybdate-reactivity of two possible stock solutions was compared. The first solution was prepared by dosing 8000 mg/L as SiO<sub>2</sub> to deionized water (pH 12.8), whereas the second solution was prepared by dosing 1200 mg/L as SiO<sub>2</sub> and adjusting the pH to 6.0. Twenty-four hours after the stock solutions were prepared, each was used to make a sample with 50 mg/L as SiO<sub>2</sub> at pH 6.0. These samples were then aged for 16 hours on an orbital shaker. The molybdate-reactivity of these samples, along with two freshly-prepared replicate samples, was tested according to the silicomolybdate method with a Hach DR/2010 Spectrophotometer (Hach method 8185). Previous research has established that the degree of silica polymerization is related to the rate of reaction with molybdic acid (11).

In a high-purity silicon standard, 85.9% of the silica was molybdate-reactive. For the remaining 14.1% of the silica, it was impossible to distinguish between analytical error and non-molybdate-reactive silica in the standard. Compared to the standard, virtually all of the silica was molybdate-reactive in samples prepared with the high pH stock (Table 3-1). However, only 11% to 21% of the silica in samples prepared with the second solution was molybdate-reactive. These results verify that silica polymerization occurs in reality and must be considered when selecting a method for preparing solutions.

**Experiments with Arsenate and Fulvic Acid.** At the end of the 1.5-hour and 50-day reaction periods between silica and Fe(OH)<sub>3</sub>, aliquots were taken for sorption experiments with arsenic and organic carbon. Plastic bottles were used to conduct arsenic experiments with 25 mL samples. An Na<sub>2</sub>HAsO<sub>4</sub>•7H<sub>2</sub>O stock solution (2.55 mg/L as As(V)) at pH 7.0 was used to deliver a target arsenate dose of 50 µg/L. Low-level (target dose 5 µg/L) arsenate experiments were also conducted with the iron-silica particles after the 50-day reaction period. A fresh stock solution was prepared each week. Actual arsenate removals by sorption were calculated by

direct comparison between samples and spike and recovery to an appropriate blank. Following addition of the arsenate, the pH was maintained for 22-24 hours, at which point the samples were filtered with a 0.45 µm pore size Life Science Products, Inc. nylon syringe filter. Soluble arsenic, iron, and silicon in the filtrate were measured with a JY 2000 Inductive Coupled Plasma - Emission Spectroscopy (ICP-ES). The arsenic detection limit was 1 µg/L.

**Table 3-1. Variations in Silica Molybdate-Reactivity Resulting from Stock Solution Preparation Methods.**

Stock Solution	pH	Total SiO <sub>2</sub> (mg/L) in Diluted Sample	Molybdate-Reactive SiO <sub>2</sub>			
			Sample Age = 1 hour		Sample Age = 16 hours	
			mg/L	%	mg/L	%
Standard <sup>a</sup>	n/a	53.5	45.8	85.6	46.1	86.2
#1 <sup>b</sup>	12.80	50.2	41.8	83.2	42.8	85.3
#2	6.00	50.2	5.7	11.4	10.3	20.5
Meng et al. (4)	12.42	50.2	41.1	81.9	41.5	82.7
Tong (5)	12.64	50.2	42.3	84.3	42.5	84.7
Holm (6)	12.40	50.2	41.8	83.3	41.7	83.1

<sup>a</sup> Sample ages not applicable to measurements of the silica standard.

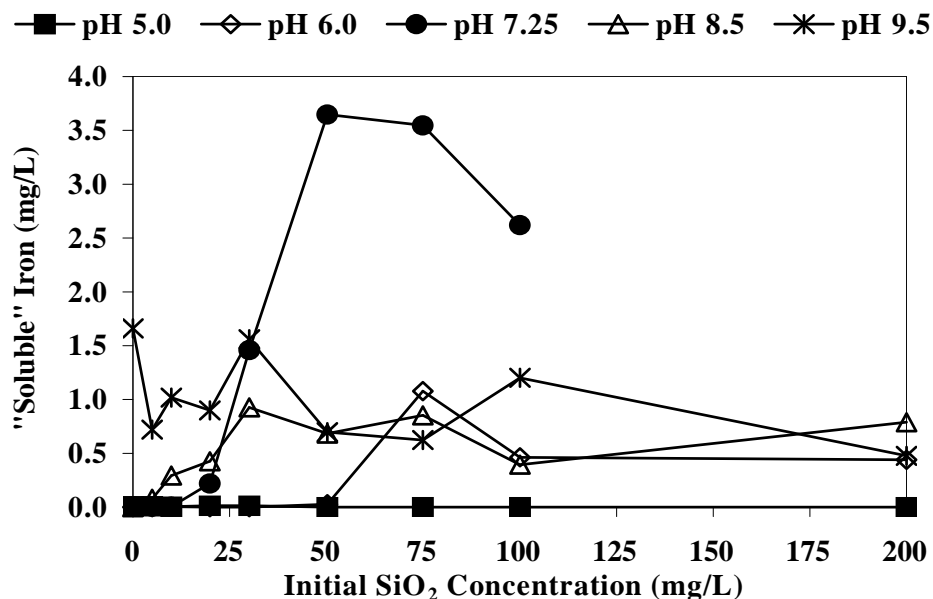
<sup>b</sup> Stock solution #1 was used for all experiments in this study.

Organic carbon experiments were conducted using 30 mL aliquots in glass bottles with teflon-lined lids. A purified fulvic acid isolate from Silver Lake was used to create a stock solution (approximately 600 mg/L as C), and the pH was adjusted to 7.0 with NaOH. The methods for concentrating (13, 14) and isolating (15) the fulvic acid are presented elsewhere. The detailed procedure, along with the specific chemical characteristics of the Silver Lake isolate, are given by Chen (16). The delivered dose of fulvic acid to suspensions of Fe(OH)<sub>3</sub> was 6.90 ± 0.4 mg/L as C. Organic carbon removals were calculated by direct comparison between samples and spike and recovery of an appropriate blank. Following addition of the fulvic acid, the reaction period and filtration steps were identical to the procedure used in the arsenic experiments. Soluble iron and silicon in the filtrate were measured with a JY 2000 ICP-ES. Two independent measures of organic carbon were employed. Total organic carbon was measured directly with a Sievers 800 Portable Total Organic Carbon (TOC) Analyzer equipped with an autosampler. UV<sub>254</sub> absorbance was measured with a Beckman DU 640 Spectrophotometer using a 1 cm path length.

## Results and Discussion

Experimental results illustrated that silica sorption to pre-formed iron hydroxide 1) increases the concentration of “soluble” iron, 2) interferes with arsenic removal, and 3) interferes with fulvic acid removal by sorption.

**Silica Mobilization of Iron Colloids.** After 1.5 hours of reaction time between silica and iron (“fresh iron” experiments), the measured “soluble” iron concentration was  $0.02 \pm 0.06$  mg/L, as defined by filtration through a  $0.45 \mu\text{m}$  pore size filter. However, after 50 days of reaction time (“old iron” experiments), significant increases in “soluble” iron were observed (Figure 3-1) at pH 6.0 (94% confidence), pH 7.25 (97% confidence), and pH 8.5 and 9.5 (99% confidence). Mobilization of iron depended on both the pH and initial silica concentration. As pH increased, the initial silica concentration required to produce “soluble” iron generally decreased, from 50 mg/L as  $\text{SiO}_2$  at pH 6.0 to 10 mg/L at pH 8.5. Although Figure 3-1 indicates there was substantial “soluble” iron at 0 mg/L  $\text{SiO}_2$  and pH 9.5, re-measurement of this sample during subsequent arsenic and organic carbon experiments confirmed that the “soluble” iron concentration was actually  $0.08 \pm 0.05$  mg/L.

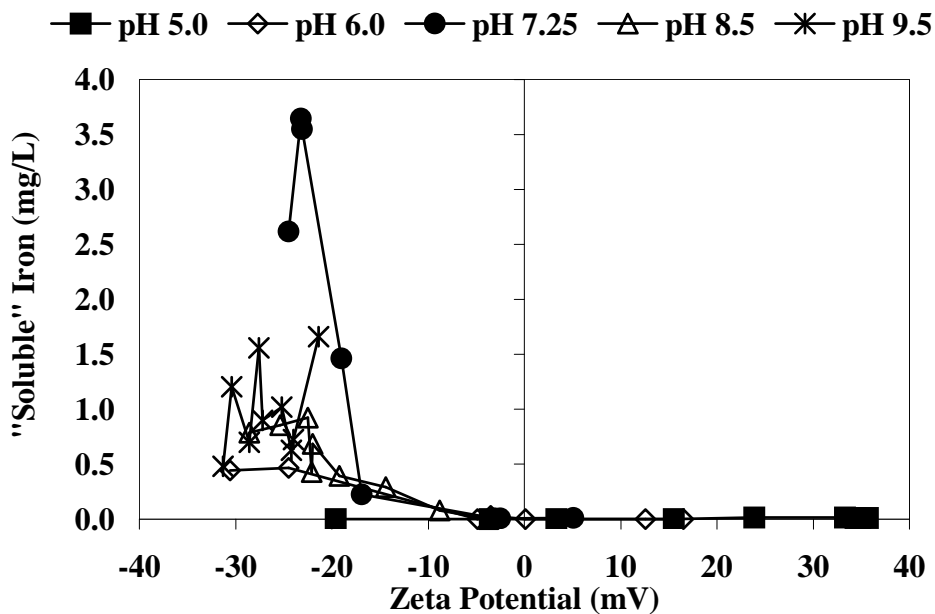


**Figure 3-1. Mobilization of colloidal iron after 50 days of reaction time with  $\text{SiO}_2$ .**

While mobilization of iron colloids was related to pH and silica concentration, these factors cannot entirely explain the observed trends. For instance, the highest levels of

“soluble” iron were observed at pH 7.25 for silica levels between 50 and 100 mg/L as SiO<sub>2</sub>. At 50 and 75 mg/L, approximately 35% of the total iron present was “solublized.” These points were re-sampled several times, and the results were repeatable. For example, four measurements at 50 mg/L SiO<sub>2</sub> and pH 7.25 indicated a “soluble” iron concentration of 3.14 ± 0.34 mg/L.

What is the nature of this “soluble” iron? Weber and Stumm (17) quantitatively demonstrated formation of a soluble FeSiO(OH)<sub>3</sub><sup>2+</sup> species. However, calculations using their complexation constant indicated that this species would not be a significant contributor to soluble iron in the system under consideration. Therefore, it seems most likely that small, stable colloids are formed in the presence of silica. Consistent with this hypothesis, concentrations of “soluble” Fe > 0.2 mg/L were only observed in samples at particle zeta potentials ≤ -15 mV (Figure 3-2). However, this effect is not dependent only on the magnitude of stabilizing surface charge, since similar stabilization was not observed at highly positive zeta potentials (i.e., ≥ +15 mV).



**Figure 3-2. Surface charge played a role in mobilizing colloidal iron in 50-day experiments.**

Since colloidal iron oxides and aqueous silica are common in the subsurface, these results have implications for colloid mobilization and contaminant transport. Mobilization of colloids in

groundwater is primarily attributable to changes in solution chemistry, including decreases in ionic strength, increases in pH, and adsorption of species that alter the surface charge (9). This data identifies silica as an important contributor to particle mobilization and dispersion.

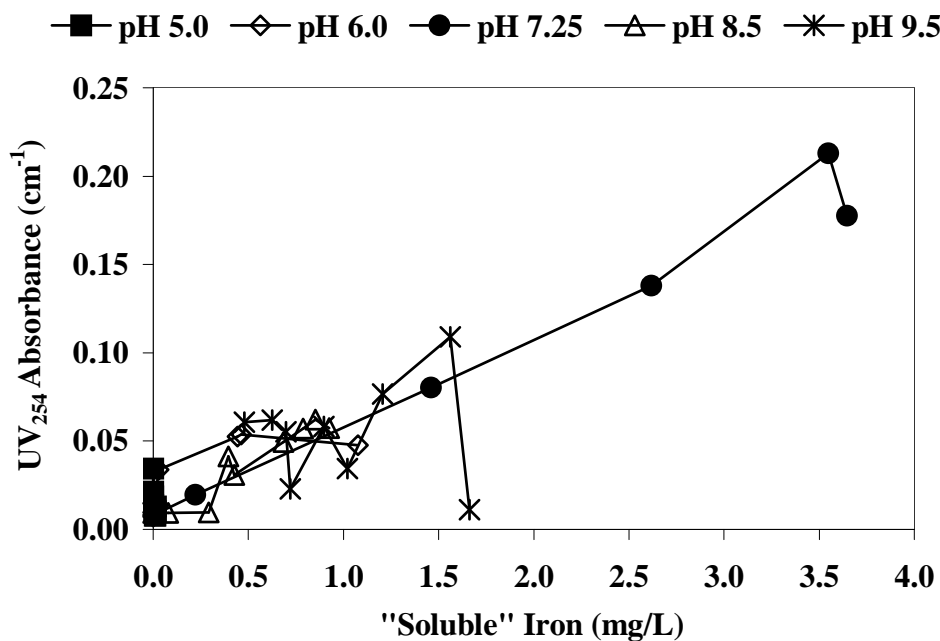
Prior to the experiments with fulvic acid, background levels of TOC and  $UV_{254}$  absorbance were measured. Not surprisingly, high levels of “soluble” iron after 50-day reaction periods led to high measurements of  $UV_{254}$  absorbance (Figure 3-3). Standard Methods lists colloidal particles and ferrous iron as interferents in  $UV_{254}$  analysis (18), but it does not mention the role of  $SiO_2$  in creating this iron. Since ferric oxides and silica are both present in natural waters, iron mobilization due to silica sorption may result in false high measurements of  $UV_{254}$  absorbance. Inaccuracies in  $UV_{254}$  absorbance measurements would result in an incorrect estimation of specific ultraviolet light absorbance (SUVA), a parameter used in determining compliance with the provisions of the US EPA’s Enhanced Coagulation Rule:

$$SUVA = \frac{UV_{254} \text{ Absorbance}}{DOC} \quad (3-1)$$

where  $UV_{254}$  absorbance is expressed in units of  $m^{-1}$  and DOC is the dissolved organic carbon concentration in (mg/L). Utilities and regulators should be made aware of this potential interference because the silica-stabilized iron is completely independent of the nature of organic matter present, which is the assumed interpretation of SUVA. This phenomenon was recently demonstrated for a source water in San Francisco, for which filtration through a 1.5  $\mu m$  pore size filter resulted in measured  $UV_{254}$  absorbances approximately twice as high as that resulting from filtration through a 0.45  $\mu m$  pore size filter (19).

**Removal of Arsenate from Solution.** Iron surfaces aged 1.5 hours in the presence of silica before arsenate addition sorbed high percentages of the contaminant from solution (Figure 3-4a). Greater than 85% removal was observed at all silica concentrations for samples at pH 6.0 and 7.25. At pH 8.5, arsenic removal was high at silica levels less than 5 mg/L as  $SiO_2$ , but declined to approximately 45% at 50 mg/L as  $SiO_2$ . In contrast, the effect of pH and silica was much more important for iron aged 50 days with silica before arsenate addition (Figures 3-4b and 3-4c). At both high and low doses of arsenate, removal generally decreased as the initial silica concentration and pH increased. This behavior is consistent with previous results which

indicated that more silica sorbs to the iron surface at higher pH, silica concentration, and reaction times (2, 20, 21). For a given silica concentration and pH, the discrepancy between the observed percentage arsenate removals at the high- and low-level dose was  $0.6 \pm 18.8\%$  removal. A paired t-test comparing the arsenic removals between the high- and low-level arsenic doses revealed no significant difference (95% confidence) between the two data sets. These results are consistent with the observations of McNeill and Edwards (22) and Hering et al. (23), who noted that percentage arsenic removal at full-scale water treatment plants is not dependent on the arsenic concentration.



**Figure 3-3. “Soluble” iron absorbs UV light at 254 nm and may interfere with accurate determination of SUVA.**

In the old iron experiments, it was hypothesized that the observed interference in arsenate removal was attributable to 1) formation of colloidal iron with sorbed As(V) that passed through filters and 2) competition with sorbed silica species for iron surface sites. The experimentally observed sorption density,  $SD_{observed}$ , represents the molar ratio of arsenic and iron removed from solution by filtration.

$$SD_{observed} = \frac{[As]_{spike} - [As]_{soluble}}{[Fe]_{initial} - [Fe]_{soluble}} \quad (3-2)$$



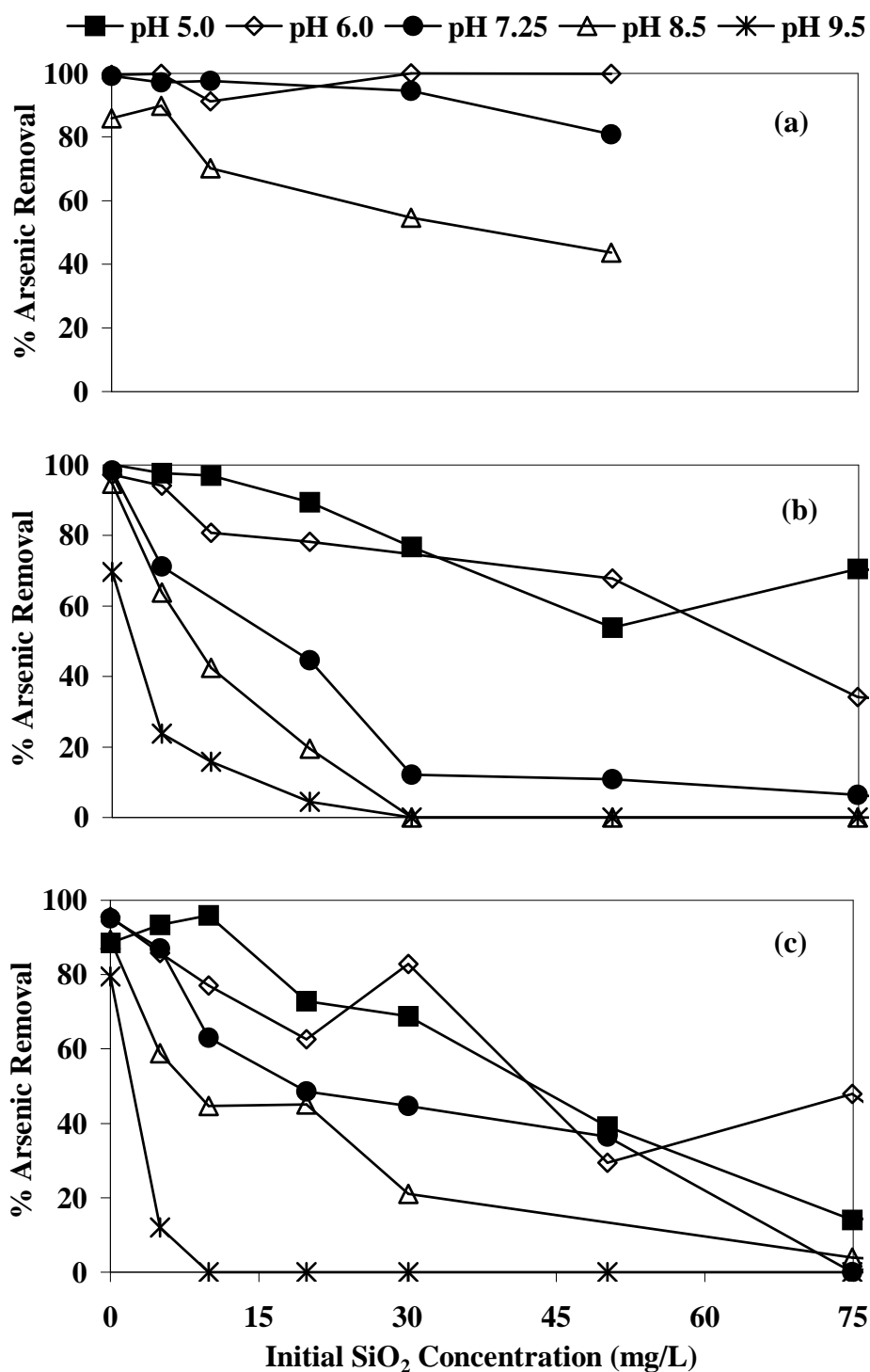
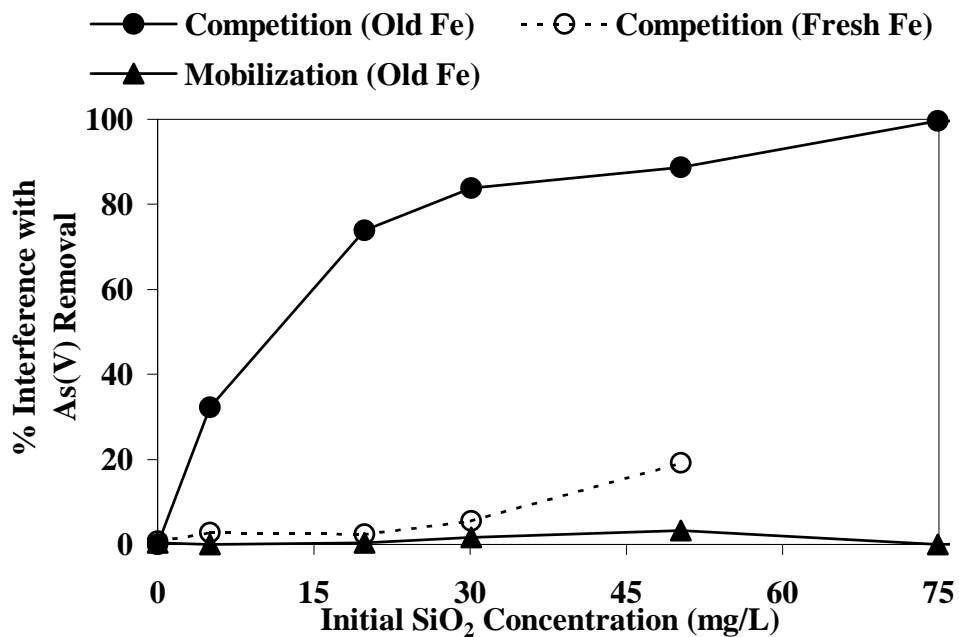


Figure 3-4. Arsenate removal as a function of pH and initial SiO<sub>2</sub> concentration in (a) fresh iron samples dosed with high-level arsenate, (b) old iron samples dosed with high-level arsenate, and (c) old iron samples dosed with low-level arsenate.

Assuming “soluble” iron had the same sorption density for arsenic allows estimation of the actual arsenic sorbed in the system. At each silica concentration, the interference due to silica competition for iron sites was then calculated as follows:

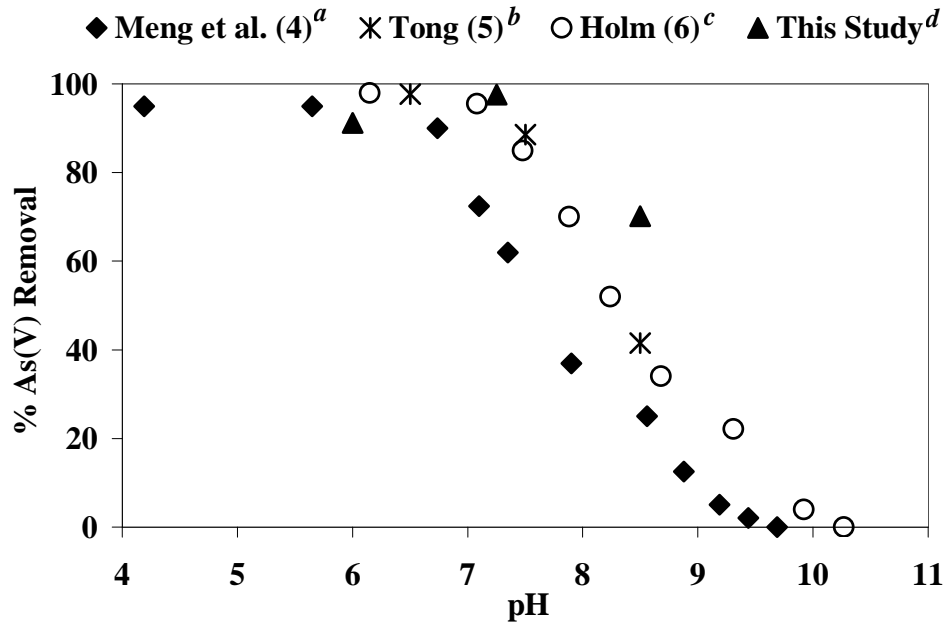
$$\% \text{Interference}_{\text{SiO}_2=x} = \text{AsSorbed}_{\text{SiO}_2=0\text{mg/L}} - \text{AsSorbed}_{\text{SiO}_2=x} \quad (3-3)$$

At pH 7.25 and the 50  $\mu\text{g/L}$  arsenic dosage, there was a negligible interference due to iron mobilization (Figure 3-5). In the samples where significant concentrations of iron were mobilized, as was the case at pH 7.25 and 50 mg/L as  $\text{SiO}_2$ , arsenic sorption was very low. Thus, interference with arsenate removal due to colloid mobilization was minimal compared to the competition effect. At the 5  $\mu\text{g/L}$  dose, competition interference was also higher than colloid mobilization interference. At the 1.5-hour equilibration time, there were no interferences attributable to stabilized colloid formation, because detectable levels of colloids had not yet formed. Silica competition did have detrimental effect on arsenic removal, but the interference was lower than was observed in the old iron experiments.



**Figure 3-5. Impacts of iron mobilization and competition for available sorption sites on arsenic removal at pH 7.25.**

Several other studies have investigated silica interference with arsenate removal by ferric hydroxide (4-6). Each of these authors used coprecipitation experiments, where the  $\text{Fe}(\text{OH})_3$  precipitate was formed in-situ in the presence of both silica and arsenate. Fe (III) concentrations varied between 1.0 and 1.5 mg/L, and As(V) concentrations ranged from 20 to 100  $\mu\text{g}/\text{L}$ . Silica concentrations varied between 9.6 and 11.0 mg/L as  $\text{SiO}_2$ . Typical results, along with further experimental details, are given in Figure 3-6. There was excellent agreement between the percent removals observed by Tong (5) and Holm (6), but the data collected by Meng et al. (4) consistently showed lower arsenic removals.



<sup>a</sup> 1.0 mg/L as Fe(III), 100  $\mu\text{g}/\text{L}$  as As(V), 9.6 mg/L as  $\text{SiO}_2$ , reaction time = 1 hour

<sup>b</sup> 1.5 mg/L as Fe(III), 20  $\mu\text{g}/\text{L}$  as As(V), 9.7 mg/L as  $\text{SiO}_2$ , reaction time = 20 seconds

<sup>c</sup> 1.4 mg/L as Fe(III), 37.5  $\mu\text{g}/\text{L}$  as As(V), 11.0 mg/L as  $\text{SiO}_2$ , reaction time = 10 min

<sup>d</sup> Pre-formed  $[\text{Fe}(\text{OH})_3]$  = 10.0 mg/L as Fe, exposed to 9.9 mg/L as  $\text{SiO}_2$  for 1.5 hours prior to addition of 50  $\mu\text{g}/\text{L}$  as As(V), reaction time = 22-24 hours

**Figure 3-6. Comparison with percentage arsenate removals observed in other investigations.**

The percentage arsenic removal during this study was expected to be lower than in the previous cited work for several reasons—the iron was pre-formed and exposed to silica for 1.5 hours prior to arsenate addition, maximizing silica sorption and reducing surface area compared to the in-situ studies. However, observed removals at pH 6.0 and 7.25 were comparable to the other investigations, and contrary to expectations, the percentage As(V) removal at pH 8.5 was

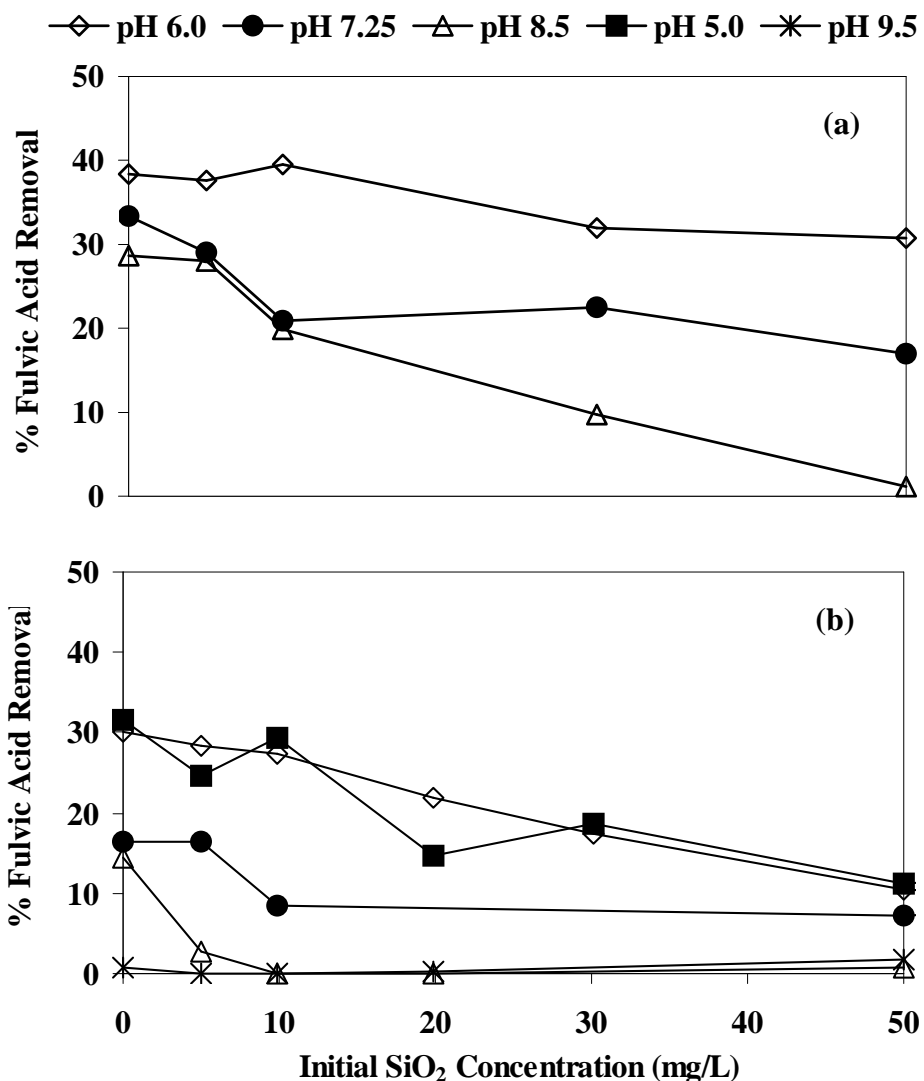
much higher in this study. Interestingly, arsenic removals in Figure 3-4a at pH 7.25 and 8.5 were also consistently higher than those observed by Tong (5) for pH 7.5 and 8.5 in the silica range of 0-50 mg/L as SiO<sub>2</sub>.

There are several possible explanations for these trends, including the higher iron (III) concentration in this study (10 mg/L as Fe) and the longer reaction time (22-24 hours vs. 1 hour or less for each of the other studies). Another difference between the investigations is the method of preparing the silica stock solution. Holm (6) used Na<sub>2</sub>SiO<sub>3</sub> and NaOH to create a stock solution that was 1983 mg/L as SiO<sub>2</sub> and 0.3 mM NaOH. Meng et al. (4) used a Na<sub>2</sub>SiO<sub>3</sub>•5H<sub>2</sub>O solution at 2139 mg/L as SiO<sub>2</sub>, and Tong (5) used a Na<sub>2</sub>SiO<sub>3</sub>•9H<sub>2</sub>O solution at 4390 mg/L as SiO<sub>2</sub>. However, when stock solutions at these concentrations were used to prepare samples at 50.2 mg/L as SiO<sub>2</sub>, most of the silica was molybdate-reactive (Table 3-1). In fact, the molybdate-reactivity in these samples was only 1-4% lower than the high-purity standard. Thus, it does not appear that the lower As(V) percentage removals observed in these studies was related to the method of preparing the silica stock solution. Instead, it seems most likely that the presence of silica in coprecipitation experiments negatively impacts Fe(OH)<sub>3</sub> precipitation and contaminant removal. This theory is consistent with earlier findings that aqueous silica inhibits with Fe<sup>3+</sup> hydrolysis and Fe(OH)<sub>3</sub> precipitation (24).

**Removal of Humic Substances from Solution.** As previously mentioned, UV<sub>254</sub> absorbance and TOC were used as independent measures of fulvic acid concentration. At high pH, leaching of organic carbon from the HDPE plastic sample bottles necessitated the use of UV<sub>254</sub> loss from solution as the primary measure of organic carbon removal. At lower pHs, TOC data is reported. The discrepancy between the two methods in calculating fulvic acid removal was 5.1 ± 2.5% removal in fresh iron experiments and 8.0 ± 7.0% removal in old iron experiments, so either approach was acceptable.

The trends in fulvic acid removal were similar to those observed in the arsenic experiments. Removal of TOC and UV<sub>254</sub> absorbance both decreased as the pH and initial silica concentration increased (Figure 3-7). Removals in the fresh iron experiments were higher than those observed in the old iron experiments, where silica competition appeared to play a more

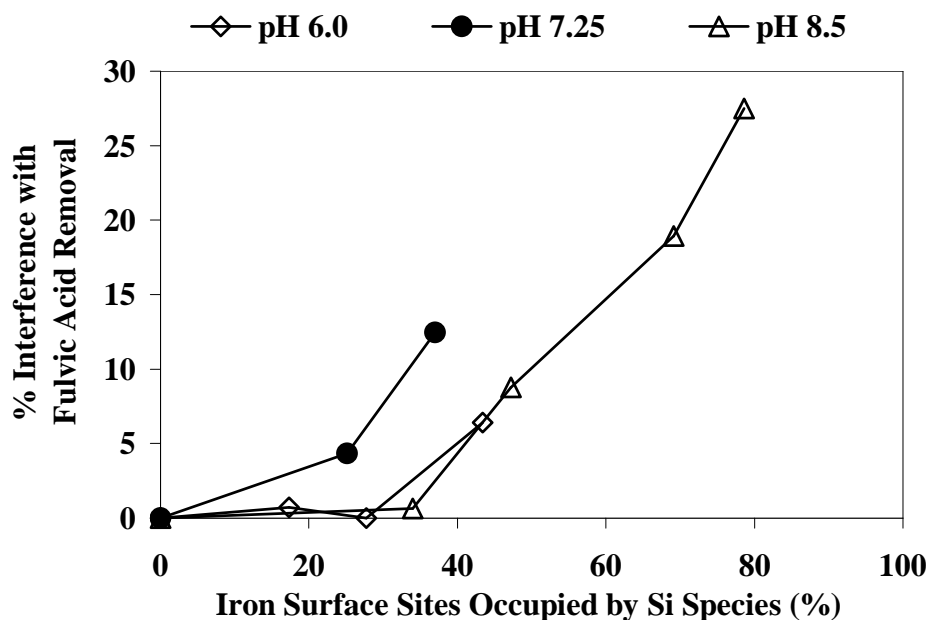
significant role in hindering TOC removal. These results confirm the work of Tipping (25) who found that silica levels of 6 mg/L as SiO<sub>2</sub> interfered with removal of humic substances at pH 7.0.



**Figure 3-7. Fulvic acid removal as a function of pH and initial SiO<sub>2</sub> concentration in (a) fresh iron samples and (b) old iron samples. TOC data is presented for pH 5.0-7.25, and UV<sub>254</sub> absorbance data is presented for pH 8.5-9.5.**

Figure 3-8 quantifies the effect of silica competition on TOC removal in the fresh iron experiments. A surface complexation model for silica sorption to ferric hydroxide (2) was used to predict the percentage of iron surface sites occupied by Si species at each sample point. Below a threshold level of surface coverage, where the model predicts 20-30% of the iron sites

are occupied by Si species, very little interference is observed regardless of pH. However, further increases in the Si sorption density produced linear decreases in fulvic acid removal.



**Figure 3-8. Silica interference with fulvic acid removal in fresh iron samples is related to the percentage of surface sites occupied by Si species.**

Aqueous silica impacts a number of important reactions in natural and engineered systems. This study suggests that silica may play a significant role in subsurface colloid mobilization, thereby contributing to contaminant transport. Mobilization of iron colloids also results in false high measurements of  $UV_{254}$  absorbance and erroneous determination of SUVA. Additionally, observations from this work indicate that silica interferes with sorption of arsenate and humic substances to ferric hydroxide, and the degree of interference increases as the pH and silica concentration increase.

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## CHAPTER IV

### Conclusions

- (1) Sorption of silica to amorphous ferric hydroxide increased as pH, silica concentration, and reaction time increased. Maximum sorption occurred between pH 7.25 and 9.5.
- (2) Sorption densities exceeding the mathematical equivalent of monolayer sorption (1 Si/surface site) were observed at pH and silica levels typical of natural waters. At pH 5.0, sorption densities greater than monolayer sorption were observed in samples with positive zeta potentials.
- (3) A surface complexation model was formulated to include sorption of soluble dimeric silica to the iron surface. This model, which was calibrated with sorption densities up to 0.40 mol SiO<sub>2</sub>/mol Fe, accurately predicts trends in zeta potential and the observed H<sup>+</sup> release during silica sorption to ferric hydroxide at pH 5.0 and 6.0. Modeling results predict that dimeric silica surface species are predominant on the ferric hydroxide surface.
- (4) In ferric hydroxide samples exposed to aqueous silica for 50 days, silica led to mobilization of iron colloids. Mobilization depended upon the pH and silica concentration. The mobilized iron resulted in a substantial false signal in the measurement of specific ultraviolet light absorbance (SUVA).
- (5) Sorptive removal of arsenate and humic substances decreased as the pH, silica concentration, and reaction time increased. Interference with contaminant removal in this study was attributed to competition for sorption sites.

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