

**THE INFLUENCE OF WATER QUALITY ON ARSENIC SORPTION  
AND TREATMENT PROCESS PERFORMANCE**

Sheryl Dianna Smith

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Marc Edwards, Chair  
John Novak  
Andrea Dietrich

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## **ABSTRACT**

A new regulation has been proposed that would lower the acceptable level of arsenic in drinking water from the current standard of 50 ppb. Therefore, research into effective arsenic removal treatment is important, especially for hard to treat waters with high concentrations of silica.

The first phase of research was designed to determine if sand ballasted coagulation is a viable means of removing arsenic from drinking water, and if so, to identify the water qualities in which the technology performs best. A jar test protocol was developed and tested on a wide range of waters to compare microsand ballasted coagulation and other coagulation based treatment processes in terms of arsenic removal. Secondary impacts of the microsand process such as residual turbidity, iron, post-treatment membrane filter run length, and TOC removal were also considered as part of this evaluation. Microsand ballasted coagulation provided promising results for many of the simulated groundwater test conditions in which more than 80% of the arsenic regulation costs will be incurred. However, like conventional coagulation/sedimentation, microsand ballasted coagulation performed poorly in waters with high silica and high pH.

Thereafter, a second phase of research more closely examined the kinetic behavior of arsenic sorption to amorphous and granular oxides in the presence of silica and calcium. At pH 8.5, calcium dramatically improved arsenic sorption to amorphous iron hydroxide in the presence of silica over short reaction times, but had no long-term advantage. This result could have considerable applications for treatment in that it suggests water quality controls the required reaction times. Additionally, batch tests indicated that activated alumina granular media was more sensitive to water quality than granular ferric hydroxide; however, calcium eliminated silica interference to arsenic sorption onto activated alumina.

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## AUTHOR'S PREFACE

This work is presented in the Virginia Tech manuscript format. Each chapter is a separate manuscript formatted for journal submission. The first chapter, entitled “Bench Scale Evaluation of Innovative Arsenic Removal Processes,” was submitted to the *Journal American Water Works Association*. The second chapter, “Role of Silica and Calcium in Arsenic Uptake by Amorphous and Granular Media Oxides,” forms the basis for an article that will also be submitted to *Journal American Water Works Association*.

Both chapters deal with ways in which water quality can influence arsenic removal. Chapter I is an intensive bench scale comparison of arsenic removal by drinking water treatment processes, specifically microsand ballasted sedimentation, in various water qualities. This research was prepared for the AWWA Research Foundation. Chapter II more closely examines how water quality can affect arsenate sorption to both amorphous and granular media solids.

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# **CHAPTER I**

## **BENCH SCALE EVALUATION OF INNOVATIVE ARSENIC REMOVAL PROCESSES**

Sheryl D. Smith and Marc Edwards

Dept. of Civil and Environmental Engineering,  
Virginia Polytechnic Institute and State University,  
407 Durham Hall, Blacksburg, VA 24061-0246

This work was designed to determine if sand ballasted coagulation is a viable means of removing arsenic from drinking water in response to the forthcoming regulation, and if so, to also identify the water qualities in which the technology is most applicable. A jar test protocol was developed and tested on a wide range of waters to compare the relative effectiveness of microsand ballasted coagulation and other coagulation based treatment processes in arsenic removal. Secondary impacts of the microsand process such as residual turbidity, iron, membrane filter run length and TOC removal were also considered as part of this evaluation. In terms of arsenic removal, microsand ballasted coagulation provided promising results for many of the simulated groundwater test conditions, in which more than 80% of the arsenic regulation costs will be incurred. No synergistic benefits were typically observed when using microsand ballasted coagulation as a pretreatment to microfiltration. The addition of polymer was also examined and found to be critically important to the performance of the microsand ballasted coagulation process. Furthermore, it was discovered that rapid mixing of new microsand released fines that added to the turbidity of the water. However, after the initial release, very few additional fines were detached and this is not expected to be a problem in practice.

### **INTRODUCTION**

A proposed reduction in the arsenic MCL from 50 to 10 ppb is estimated to cost U.S. utilities 0.7 billion dollars per year (Frey et al, 1998). This figure considers costs including capital and operating expenses as well as residuals handling. Of course, a reduction in costs will be obtained if innovative treatment technologies are proven and implemented.

Sand ballasted flocculation sedimentation processes (i.e. microsand ballasted coagulation) have dramatically impacted the drinking water treatment field in recent

years – dozens of new installations in the US and abroad are currently providing highly effective, low cost removal of total organic carbon (TOC) and turbidity in surface water applications. The concept of sand or particle ballasted coagulation is not new: it has long been known that addition of bentonite, sand, or polysilicates to water can substantially improve sedimentation effectiveness even at conventional treatment plants. Process performance in removing anionic contaminants like natural organic matter and orthophosphate is often superior to conventional coagulation-sedimentation processes, with less susceptibility to process upsets and pH effects (Carlson & McEwen, 1997). This is due to the unique combination of microsand,  $\text{Fe}(\text{OH})_3$  and polymer which combine to form a dense, easy-to-settle floc that also allows sorptive removal of orthophosphate and NOM (Young & Edwards, 2000). Sand ballasted processes might also be successful in the removal of arsenate, which is chemically similar to phosphate (Figure 1-1).

Another innovative treatment technique, coagulation assisted microfiltration, was tentatively deemed the most desirable arsenic treatment process in Albuquerque, New Mexico when compared to ion exchange and activated alumina (Chwirka et al, 2000; Ghurye et al, 1998). Coagulation assisted microfiltration typically uses lower coagulant doses than conventional treatment to achieve a given level of anionic contaminant removal. The capital and operational costs of microsand ballasted coagulation, however, are very attractive when compared to coagulation assisted microfiltration. In fact, microsand ballasted sedimentation capital costs and operating costs are probably about 2 to 4 times lower than microfiltration (Table 1-1). It is also reasonable to expect that microsand ballasted coagulation might be used as an inexpensive pretreatment for microfiltration, since the dense sand flocs formed by sand ballasted coagulation may reduce filter loading (Figure 1-1).

As is the case for conventional coagulation and sedimentation processes, sand ballasted coagulation processes can be faithfully reproduced in a modified jar test apparatus (Topalian, 1999). Thus, a jar test protocol was developed to provide a relative performance comparison between conventional coagulation and sedimentation,

microsand ballasted coagulation, coagulation assisted microfiltration, and microsand ballasted coagulation/microfiltration (Table 1-1). The protocol was tested on a wide range of waters to compare the relative effectiveness of innovative coagulation based treatment processes in arsenic removal. The bench scale experiments also examined secondary factors to treatment process selection such as final turbidity, total iron, total organic carbon removal, and improvement to microfiltration by addition of microsand. This protocol might prove useful for utilities screening for least cost arsenic removal techniques in response to the new arsenic MCL.

## **MATERIALS AND METHODS**

**Water Types.** A drinking water containing 100 mg/L alkalinity as  $\text{CaCO}_3$  and 50 ppb As was synthesized from stock solutions of  $\text{NaHCO}_3$  and  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ . Thereafter, different amounts of TOC and turbidity were added to simulate a groundwater (no added TOC or turbidity), a low TOC and low turbidity surface water (approximately 3 mg/L TOC and 9 ntu turbidity), and a very high TOC and high turbidity surface water (approximately 8 mg/L TOC and 230 ntu turbidity). Bentonite was used as a source of turbidity and a Lake Pleasant fulvic acid isolate was used as a source of natural organic matter. For each water type, tests were conducted with both low (5 mg/L as  $\text{SiO}_2$ ) and high (40 mg/L as  $\text{SiO}_2$ ) levels of silica dosed from a stock solution of  $\text{Na}_2\text{SiO}_3$ .

Jar tests were conducted with the groundwater at constant pH 6.0, 7.5, and 8.5. Constant pH coagulation would not be employed in practice, however, since higher coagulant doses would also drop pH, it was deemed desirable in this scientific study to unambiguously decouple the effect of coagulant dose from coagulation pH. The remaining two waters were tested at constant pH 6.0 and 7.5 only, yielding 14 different combinations of turbidity, TOC, silica, and pH. Initially, pH was adjusted to the target value by bubbling air or  $\text{CO}_2$  into solution, but was maintained during testing by dosing small amounts of 0.5 M NaOH after coagulant dosing.

All 14 water conditions were tested with and without the addition of sand in 28 different jar tests according to the protocol below. Microsand<sup>1</sup> was washed and decanted three times then dried prior to use. A new batch of microsand was used for each test. In addition to a control jar with no added coagulant, five iron doses were used for each jar test ranging from 2.8 to 50 mg/L depending on the water type. For comparison, the same five doses were used for corresponding tests with and without sand.

**Jar Test Protocol.** Both conventional and microsand jar tests followed the same protocol using 1L jars and a Phipps & Bird PB-700 Jartester. While stirring at 300 rpm, 10 g/L sand was added (for microsand test only), followed immediately by the ferric chloride coagulant and an appropriate amount of NaOH to maintain target pH. After 2 minutes, 0.2 mg/L Allied Colloids LT 25 anionic polymer was dosed and rapid mixing (300 rpm) proceeded for 15 seconds. A mix at 200 rpm followed for 45 seconds. This step simulated the flocculation period for microsand. A slow mix at 30 rpm followed for 20 minutes. All the microsand immediately settled to the bottom of the jar test container at the beginning of this step (Figure 1-2).

Approximately 90 mL was extracted from each jar 2 minutes after the start of the slow mix. A portion of this sample was filtered through a 0.45 µm pore size nylon disposable filter; with the filtrate representing coagulation assisted microfiltration or microsand ballasted coagulation/microfiltration treatment depending on whether sand was present or not. During filtration, the volume of sample filtered in 5 minutes under a constant pressure (about 3.4 psi) was also recorded as a relative measure of microfiltration membrane performance. The remaining unfiltered portion of the water sample represented microsand ballasted coagulation treatment and was acidified prior to analysis. The pH of each jar was then checked and adjusted to the target value.

A period of 30 minute quiescent settling followed slow mixing, after which approximately 90 mL was extracted from each jar, part of which was filtered through a 0.45 µm filter to represent a sample collected after conventional sedimentation plus

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<sup>1</sup> Actiflo™ microsand, Kruger, Inc., Cary, NC.

microfiltration. The unfiltered portion represented water quality after conventional sedimentation. Turbidity of the unfiltered sample was also determined on a Hach 2100N turbidimeter.

**Analysis.** All samples were analyzed for arsenic, iron, and silicon on a JY Ultima Inductive Coupled Plasma – Emission Spectroscopy (ICP-ES) according to standard method 3120B using continuous hydride generation (*Standard Methods*, 1998). Samples for the low TOC and high TOC surface water tests were also analyzed for organic carbon on a Sievers Model 800 total organic carbon analyzer.

**Filter Simulation.** There is no way to perfectly simulate performance of a sand filter at the bench scale. During a typical sand filter run, it is reasonable to believe that the average removal of floc will be greater than that obtained by sedimentation alone, and less than that obtained by passage through a 0.45  $\mu\text{m}$  pore size microfilter, although it is also recognized that a properly ripened filter can achieve removals close to or even better than a microfilter. Nonetheless, for purposes of this work, the likely performance of conventional treatment (coagulation, sedimentation and filtration) was projected to be between results obtained by settling alone and those obtained after settling and microfiltration. In addition, since it is believed by some that sand filter performance is better represented by filtration through a Whatman 40 filter (8  $\mu\text{m}$  pore size), some limited comparative testing was conducted. As might be expected, results indicated that arsenic removal by the Whatman 40 filter was always greater than was achieved by sedimentation alone, but was always less than with 0.45  $\mu\text{m}$  pore size microfiltration post-treatment (Figure A1). In the case of the groundwater at the coagulant dose tested, the Whatman filter was closer in performance to the microfilter, whereas in low TOC surface water the opposite was true, and in the case of the high TOC surface water it seemed to depend on whether the microsand, coagulation assisted filtration or coagulation sedimentation processes were being simulated. The exact extent to which sand filtration improves arsenic removal by settling alone would need to be established on a case by case basis.

**Comparison of As Results.** Plots of As remaining versus Fe dose gave representative trends for the different treatment technologies tested, with a typical result represented in Figure 1-3. Arsenic remaining typically decreased with increasing Fe dose. The best arsenic treatment efficiencies were nearly always observed with coagulation assisted microfiltration and microsand ballasted coagulation/microfiltration.

The percentage of arsenic removed at a given iron dose for each treatment process simulated in jar testing was calculated as follows:

$$\% \text{ As removed} = \frac{([\text{As}]_{\text{initial}} - [\text{As}]_{\text{after treatment}}) * 100}{[\text{As}]_{\text{initial}}}$$

Data was synthesized for relative comparisons of process performance using two approaches. First, an average percent arsenic removal was calculated for the entire range of iron doses at each water condition (Table A1, Table A2). It should be noted that this average does not necessarily indicate the arsenic removal that could be expected at a given dose, but nonetheless provides a useful point for comparison. In addition, a paired t-test was used to compare arsenic removal at each iron dose between two processes, to determine if one process performed significantly better or worse than another at 95% confidence for water tested (i.e., Figure 1-5).

## **RESULTS AND DISCUSSION.**

**Arsenic Removal.** Treatment technology performance with respect to arsenic is discussed in separate subsections of water type including groundwater, low TOC surface water, and high TOC surface water. At the outset, it is noted that processes using a 0.45  $\mu\text{m}$  pore size filter as a final step (i.e. coagulation assisted microfiltration and microsand ballasted coagulation/ microfiltration) consistently had the highest percentage arsenic removal. Greater than 82% arsenic removal was achieved with these processes for at least one coagulant dose tested in all water types.

Using the paired t-test analysis, coagulation assisted microfiltration performed equal to or slightly better than the same process with microsand pretreatment in all but

two of the 14 water conditions. In those two cases, arsenic removal with coagulation assisted microfiltration was still very good (94% removal on average). Surprisingly, anticipated improvements to microfilter performance by pretreating the water with the microsand process were not always observed when compared to directly loading the floc to microfilters (Figure 1-5). While microsand pretreatment did provide benefits in some waters, no overall benefit from the use of microsand ballasted coagulation as a pretreatment to microfiltration performance could be generalized to all waters from this study. Therefore, the combined process performance of microsand ballasted coagulation/microfiltration is not discussed in detail below.

*Groundwater.* Microsand ballasted coagulation without filtration provided very promising treatment of groundwater. On average for pH 6.0 and 7.5 with low silica, the microsand ballasted coagulation process removed 14% more arsenic from water than conventional sedimentation (Figure 1-3, Figure 1-4), even though conventional sedimentation had a 30 minute settling period compared to no quiescent settling for the microsand. For these conditions, arsenic removal with the microsand process was very good, ranging from 80 to 98% for all iron doses. Average microsand removal of 97% arsenic also slightly surpassed conventional sedimentation at pH 6.0 in waters with high silica. As expected, coagulation assisted microfiltration was best overall, but given the higher costs for microfiltration, microsand ballasted coagulation could be a very attractive option for effective arsenic removal in many groundwaters.

In pH 7.5 groundwater with high silica, conventional sedimentation and microsand ballasted coagulation performed similarly with an average of 69% As removal (Figure 1-4). At iron doses of 7.5 mg/L and greater, however, microsand achieved removals of greater than 90%. By contrast, an average of 95% removal was achieved with coagulation assisted microfiltration for all iron doses (2.8 to 15 mg/L Fe). Therefore, microsand ballasted coagulation was competitive with coagulation assisted microfiltration for this water if higher iron doses were used, but microfiltration was better at lower Fe doses.

Finally, the paired t-test revealed no difference between the performance of microsand ballasted coagulation and conventional sedimentation for groundwater at pH 8.5 with both high and low levels of silica (Figure 1-4), again noting that sedimentation time was 30 minutes less for the microsand. The average removal with these two processes was poor at this high pH (39% with microsand; 43% with conventional sedimentation). Coagulation assisted microfiltration was much better in terms of arsenic removal for the low silica case. However, only 48% of the arsenic was removed using coagulation assisted microfiltration in waters with high silica at pH 8.5, a condition where none of the tested techniques could exceed an average of 52% for the iron doses tested. These results indicate that the presence of microsand does not eliminate interference to arsenic removal from soluble Si at high pH as previously reported (Meng et al, 2000; Ghurye & Clifford, 1998).

*Low TOC Surface Water.* Both conventional sedimentation and microsand ballasted coagulation performed similarly for the low TOC surface water (Figure 1-4). While removal up to 94% was seen at the highest iron dose, the average for both technologies was only about 18% As removed. Coagulation assisted microfiltration was a far better option for As removal. In all but one case, arsenic removal was greater than 70% with coagulation assisted microfiltration for all iron doses, pH, and silica levels, with an average of 87% As removed.

*High TOC Surface Water.* In many of the high TOC and high turbidity surface water test conditions, the iron floc did not stick to the added microsand, but instead remained in solution after the sand settled. Not surprisingly then, microsand ballasted coagulation provided poor arsenic removal for this water (Figure 1-4). Average percentage As removal for all iron dose, pH, and silica levels of high TOC surface water was only 4.5% with microsand. The extra settling time allowed by conventional sedimentation gave better results, with removals as high as 95% for an iron dose of 50 mg/L at pH 6.0. Nonetheless, on average only 43% As removal was achieved. In comparison, As removals of 80-100% were observed with coagulation assisted microfiltration at iron doses of 4.6 mg/L or greater. The average removal with

coagulation assisted microfiltration was 92% for all high TOC surface water conditions; thus, coagulation assisted microfiltration far outperformed other technologies for this water type. It is possible that addition of a sand filter to either the conventional sedimentation or microsand processes would enhance performance, but this could not be tested directly.

*Importance of Polymer.* An anionic polymer dose of 0.2 mg/L was used in every jar test described previously, and very large flocs were observed in some cases. Subsequent jar tests with groundwater at pH 7.5 were performed side by side with and without polymer to determine the extent to which the added polymer aids arsenic removal. The presence of polymer led to only about 9% improvement in arsenic removal by conventional sedimentation (Figure 1-6), even though the size and settling time of the flocs with polymer was much improved compared to when polymer was absent (Figure 1-7). Coagulation assisted microfiltration performance was similar with and without polymer addition.

In contrast, polymer was found to be essential to the microsand ballasted coagulation process. In the absence of polymer, the iron flocs did not stick to the sand, and only about 3% arsenic removal occurred compared to 100% with polymer (Figure 1-6). Recognizing the critical importance of polymer to the process, it is possible that a higher dose or different type of polymer could have significantly improved microsand arsenic removal in the difficult to treat surface waters, especially the high turbidity surface water in which flocs did not attach to the sand. Regardless, this dependency would be considered a drawback in such waters.

**Secondary Factors.** Since microsand ballasted coagulation provided promising arsenic removal for the groundwaters, where more than 80% of the arsenic regulations costs will be incurred, a number of secondary factors that could impact process selection were examined more closely. These included turbidity, total iron, total organic carbon, and filter performance.

*Turbidity.* Control tests conducted with microsand and without any other sources of added turbidity revealed that mixing at 300 rpm released sand fines that did not settle and initially added to the turbidity of the water. After 30 minutes of settling, microsand fines typically added 0.8 ntu to the settled water turbidity versus a final turbidity of 0.1 obtained in the jar without sand. Further testing again demonstrated that 0.8 ntu sand fines were released after the first two and a half minutes of rapid mix; thereafter, the release remained constant at a rate of about 0.02 ntu per minute of rapid mix (Figure 1-8). Consequently, if sand were recycled through the process many times, the release of fines is likely to be reduced as compared with the initial 0.8 ntu release observed in this work. This was confirmed in a jar test (Figure 1-8). Other researchers have noted increased residual turbidity after intense mixing conditions that they attributed to excess microsand that was not incorporated into flocs (Young & Edwards, 2000). The release of sand fines could also account for these observations.

Such a small increase in turbidity would most likely be insignificant for surface waters with a substantial amount of turbidity already present. In groundwater, however, sand fine turbidity could be important. In fact, in four of the six test conditions, groundwater turbidity measurements taken after 30 minutes of settling were greater at 95% confidence with sand than without (Figure A2). This represents a best case scenario for the microsand ballasted coagulation process, which would not have the 30 minute settling period. However, the average difference in turbidity between the two processes was less than the 0.8 ntu sand fines released, indicating that the iron coagulant removed some of the additional fines from solution.

Microsand ballasted coagulation and conventional sedimentation were similar in terms of final turbidity for low TOC surface water at pH 6.0. At pH 7.5, microsand ballasted coagulation resulted in a lower final turbidity than conventional sedimentation for lower iron doses (Figure 1-9). In the high TOC surface water, final turbidities for both processes were similar, and would have been unacceptable loading to filters at the doses tested.

In summary, these tests indicate that significant amounts of fine turbidity are released during the initial rapid mix, even though the sand was washed carefully prior to experiments. In practice, this source of turbidity is not likely to be significant, since the microsand is re-used and release of fines for used sand decreases markedly.

*Iron.* Total iron remaining in solution after treatment, which is attributable to iron flocs not removed during processes, was examined as another important secondary factor (Table A3, Table A4). In groundwater, total Fe was typically the same or less with microsand ballasted coagulation as compared to conventional sedimentation for lower pH (6.0 and 7.5). Total Fe was typically greater at pH 8.5 with the microsand process (Figure 1-10). These trends roughly correspond to those observed with arsenic removal and turbidity. However, at the higher coagulation pH, total Fe often exceeded the secondary MCL of 0.3 mg/L. As a general rule, if arsenic removal efficiency was above 80%, iron did not exceed the secondary MCL even without filtration.

The total iron resulting from microsand ballasted coagulation and conventional sedimentation was similar in all low TOC surface water tests. In the high TOC surface water, conventional sedimentation resulted in a lower total iron concentration after treatment. In every surface water test, total Fe was greater than 0.3 mg/L in processes tested without filtration. In fact total Fe was as high as 49 mg/L in high TOC surface water treated with the microsand process. Again, these trends are similar to those for arsenic removal and turbidity, and would undoubtedly be improved by filtration.

When coagulation assisted microfiltration treatment was used in groundwater, the soluble Fe remaining after treatment exceeded the SMCL of 0.3 mg/L only at the two lowest iron doses, pH 8.5, and high silica levels. Soluble Fe was greater than 0.3 mg/L in the low TOC surface water in nearly all cases except the highest iron doses, but the soluble Fe never exceeded 0.3 mg/L in the high TOC surface water. This is consistent with the conversion from stable iron colloidal suspensions which can pass through a 0.45 um filter, to unstable colloidal suspensions which cannot pass through the filter, with increasing iron dose (Edwards & Benjamin, 1992).

*Total Organic Carbon.* TOC removal by both microsand ballasted coagulation and conventional sedimentation was found to be about the same in the low TOC surface water (Figure A3). DOC was also measured after 30 minutes settling time with and without microsand in both low and high TOC surface waters. While filtration slightly improved organic carbon removal over just sedimentation, the removals were again similar with and without microsand (Figure A4).

*Volume of Water Processed by Filtration.* As noted earlier, it was hypothesized that microsand ballasted coagulation as a pretreatment to microfiltration would aid membrane performance as compared with simply coagulation assisted microfiltration. However, using a paired t-test at 95% confidence, filtration performance was actually worse with microsand pretreatment at pH 8.5 low silica and pH 7.5 high silica groundwater (Figure 1-5). Performance was improved with microsand pretreatment in pH 6.0 high silica groundwater and pH 7.5 high silica low TOC surface water. Microsand and coagulation assisted microfiltration performance was the same for all other groundwater and low TOC surface water conditions at 95% confidence. No trend could be discerned for tests with the high TOC and high turbidity surface water, since it was so difficult to filter the resulting water.

Clearly, no overall benefit from the use of microsand ballasted coagulation as a pretreatment to microfiltration performance could be generalized to all waters from this study, even though benefits were noteworthy in groundwater at lower pH. It is believed, however, that the discovery of fines released from new microsand were the cause for detriments from microsand pretreatment. Since the release of fines is greatly reduced for used sand, it is possible that microsand pretreatment would markedly enhance microfilter performance in practice, although this needs confirmation.

**Scottsdale, AZ Source Water.** Jar tests indicated that microsand ballasted coagulation could provide good arsenic removal in synthetic groundwater. However, behavior could be quite different in a natural water. Therefore, additional jar tests were

conducted on source water from Scottsdale, Arizona for comparison. Raw water characteristics are given in Table 1-2.

The jar test protocol was the same as that used for synthetic water; however, this time no attempt was made to maintain a constant pH after the ferric hydroxide coagulant was added. Thus, the pH decreased during jar testing as much as 1 unit (Table A5). In addition, 0.5 mg/L free chlorine was added to the raw water to ensure all arsenic was present as As(V). The first set of jar tests was performed at initial pH 8.7, the natural pH of the Scottsdale water. Fe(OH)<sub>3</sub> doses of 2.0, 4.0, and 8.0 mg/L as Fe were tested.

Arsenic removal with conventional sedimentation and microsand ballasted sedimentation was about the same, ranging from 0% removal with 2 mg/L Fe coagulant to 100% removal with 8 mg/L Fe coagulant (Figure 1-11). Arsenic removal with coagulation and microsand assisted microfiltration was also similar. Not surprisingly, microfiltration achieved better arsenic removal than sedimentation, especially at lower coagulant doses. Effluent Fe was always below the secondary MCL of 0.3 mg/L when microfiltration was used, however with conventional or microsand sedimentation, Fe was only below 0.3 mg/L at the highest coagulant dose.

In a second jar test, the pH of the Scottsdale source water was adjusted to 7.4. At this pH all of the treatment processes removed more than 60% of the arsenic from water, even at the lowest coagulant dose (Figure 1-11). The microfiltration processes performed slightly better at the lower Fe doses, but microsand ballasted sedimentation performed almost as good as microfiltration at the higher two Fe doses. Again, soluble Fe only exceeded 0.3 mg/L when sedimentation processes were used with low coagulant dose.

The results obtained with natural source water were in agreement with those obtained using the synthetic groundwater. Microfiltration processes performed best in terms of percentage removals, but the microsand ballasted process was competitive especially at the lower pH.

## CONCLUSIONS

- The coagulation assisted microfiltration process consistently achieved the best removal of arsenic at a given iron dose for the processes tested in this work.
- Microsand ballasted coagulation performed comparable to coagulation assisted microfiltration in the simulated groundwater at pH less than 7.5, even without a filtration step. However, the cost estimates for the microsand treatment are much less than microfiltration, making it an attractive option for arsenic removal in this type of water.
- For most groundwater and low TOC surface water conditions, microsand ballasted coagulation performed at least as good or better than conventional sedimentation in removing iron floc and arsenic.
- The addition of polymer is critically important to the microsand ballasted coagulation process.
- Rapid mixing of new sand released fines that added to the turbidity of the water and which hindered passage of water through microfilters. However, after the initial release, very few additional fines were detached.
- Typically, in terms of percentage arsenic removal or filtration, no synergistic benefits were observed when using microsand ballasted coagulation as a pretreatment to microfiltration.

## ACKNOWLEDGEMENT

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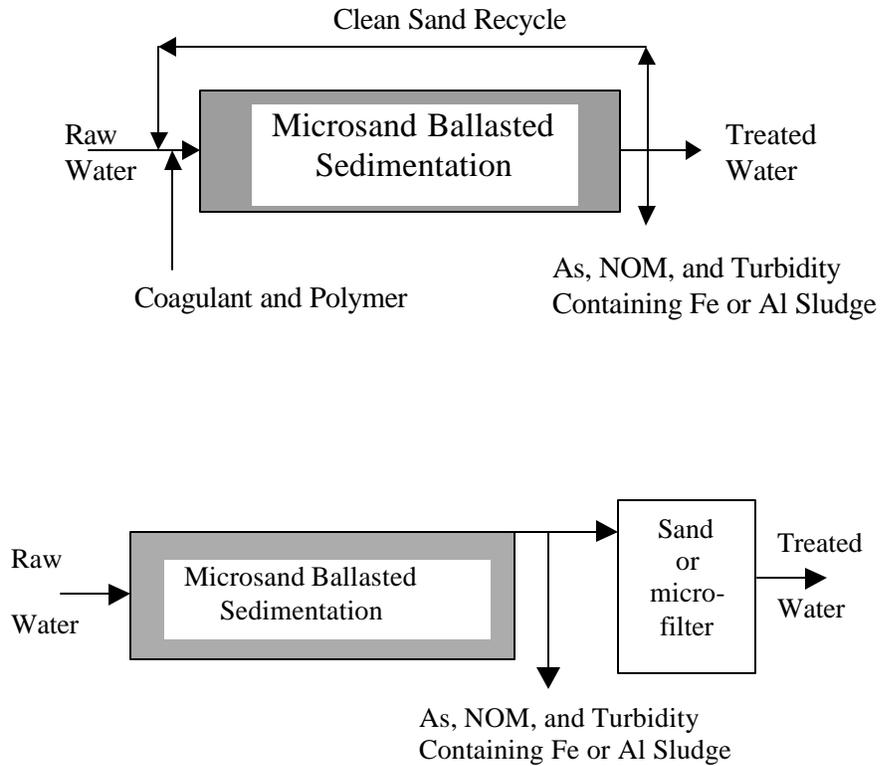
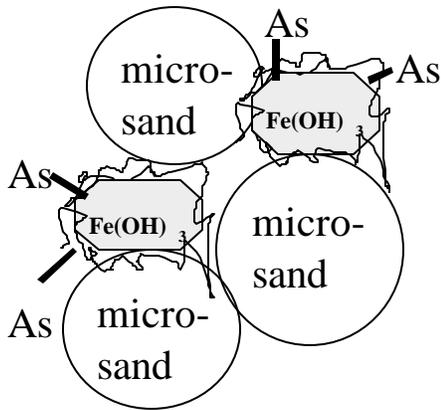
**Table 1-1. Summary of representative arsenic removal processes, and steps taken to simulate each process at bench scale.**

| <b>Process</b>                                    | <b>Simulated Treatment</b>   | <b>Possible Advantages/<br/>Disadvantages</b>  | <b>Approximate Capital &amp; Operating Cost*</b>  |
|---|--|--|---|
| Conventional Coagulation and Sedimentation        | Iron and polymer dosing; 15 sec. rapid mix @ 300 rpm; 45 sec. mix @ 200 rpm; 20 min. flocculation @ 30 rpm; 30 min. quiescent settling; sampling for As removal                              | Well proven treatment technology, not typically used for groundwater   | High capital costs will effectively limit use to existing installations                             |
| Microsand Ballasted Coagulation                   | Sand addition; iron and polymer dosing; 15 sec. rapid mix @ 300 rpm; 45 sec. mix @ 200 ; 2 min flocculation @ 30 rpm; sampling for As removal  | Low cost package plants available; lower coagulant dose possible; not proven for As removal or groundwater treatment | About \$0.3 million per MGD installed, operating cost of \$0.09/1000 gal. treated for surface water |
| Coagulation Assisted Microfiltration              | Iron and polymer dosing; 15 sec. rapid mix @ 300 rpm; 45 sec. mix @ 200 rpm; 2 min flocculation @ 30 rpm; filtration through 0.45 um filter under constant pressure; sampling for As removal | Lower coagulant dose possible; effective As removal; Si interference; high cost; frequent backwash                   | About \$1.3 million per MGD installed, operating cost of \$0.26/1000 gal. for groundwater           |
| Microsand Ballasted Coagulation / Microfiltration | Same as sand ballasted coagulation, but filtration through 0.45 um filter under constant pressure; sampling for As removal   | Less frequent backwash of filters possible; more expensive than sand ballasted filtration alone                      | Most expensive unless microsand dramatically improves filter performance                            |

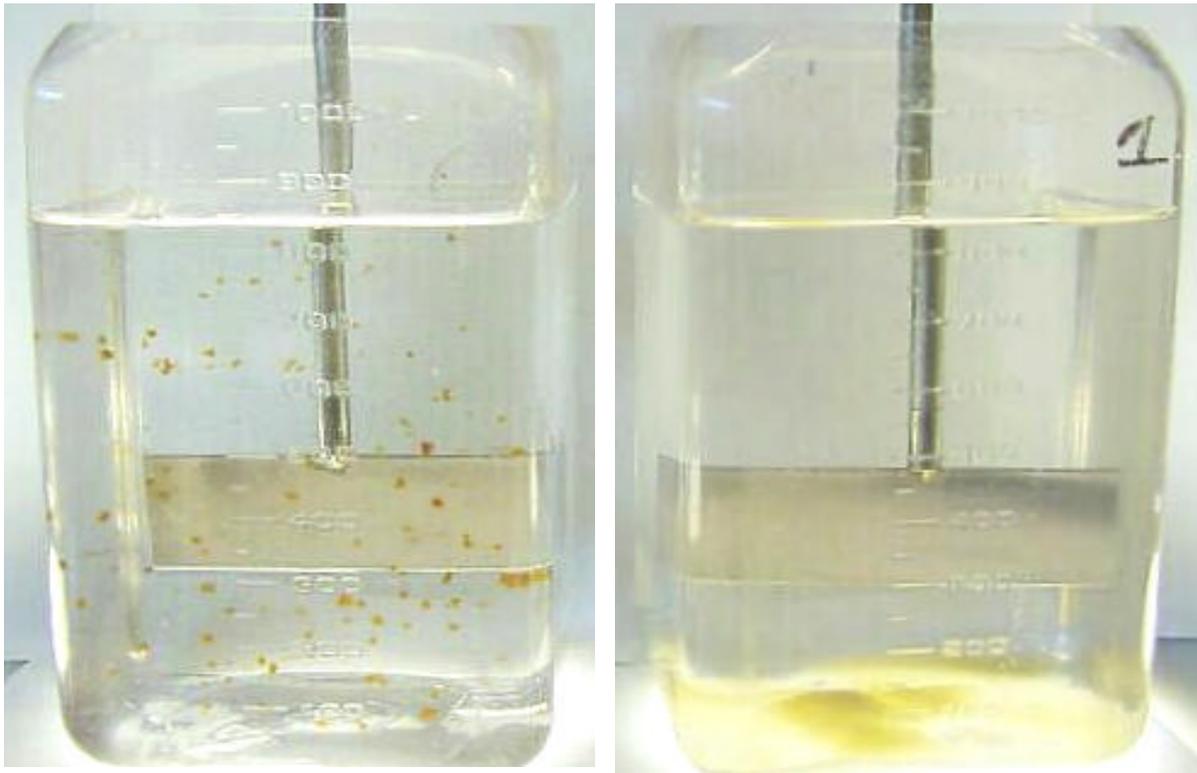
\*Capital and operating costs for microfiltration based on Chwirka (1999) at Albuquerque for 1 MGD flow. Approximate costs for microsand ballasted coagulation based on Carlson et al. (1997) and personal communication from Topalian (1999) for surface waters.

**Table 1-2. Characteristics of Scottsdale, AZ Water**

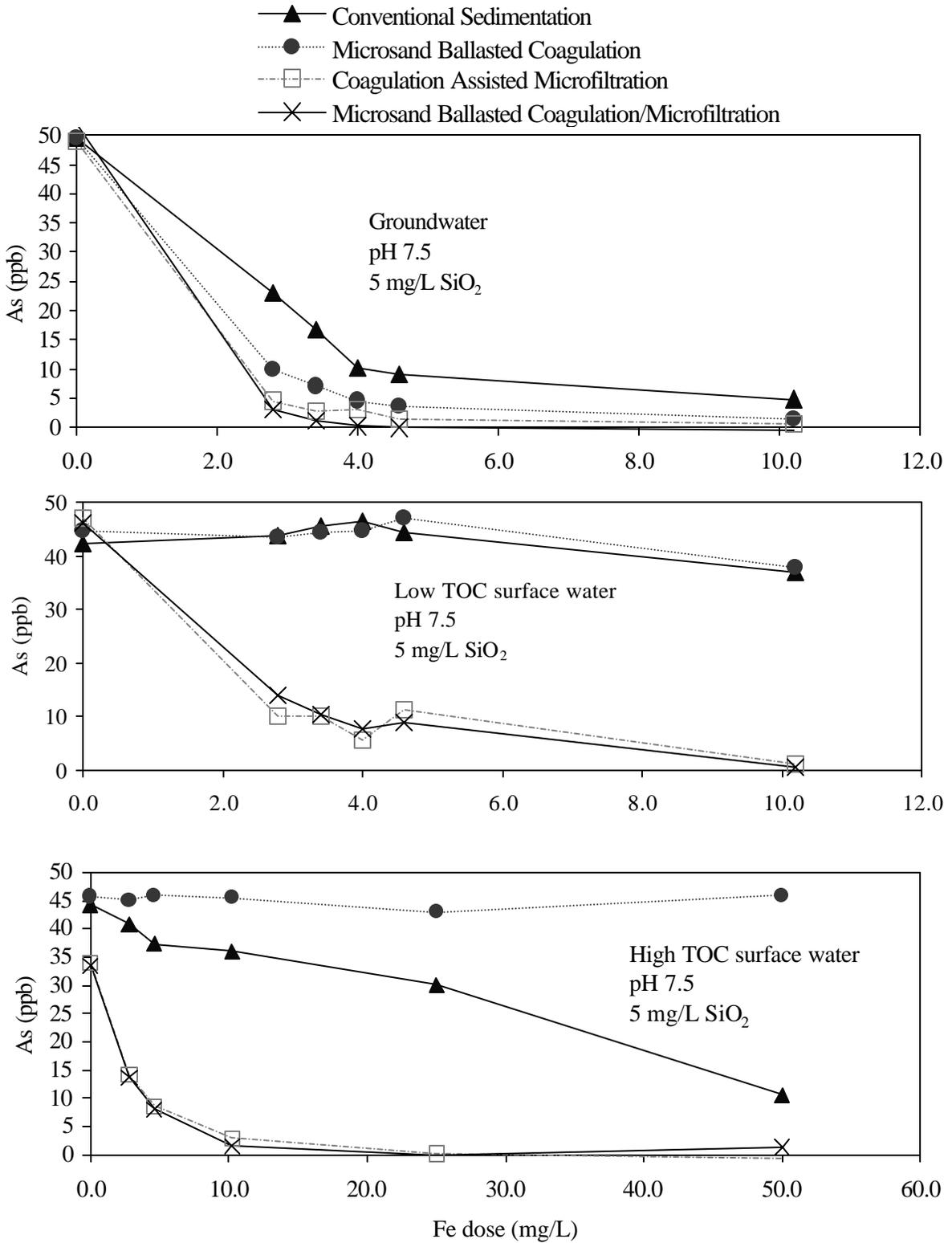
| <b>Parameter</b> | <b>Units</b>              | <b>Value</b> |
|------------------|---------------------------|--------------|
| Alkalinity       | mg/L as CaCO <sub>3</sub> | 116          |
| pH               |                           | 8.7          |
| Turbidity        | ntu                       | 0.5          |
| Total Arsenic    | ug/L                      | 48           |
| Soluble Arsenic  | ug/L                      | 45           |
| Total Iron       | mg/L                      | 0.1          |
| Silica           | mg/L as SiO <sub>2</sub>  | 18.4         |
| Calcium          | mg/L                      | 4.4          |
| Magnesium        | mg/L                      | 1.8          |
| Aluminum         | mg/L                      | 0.0          |



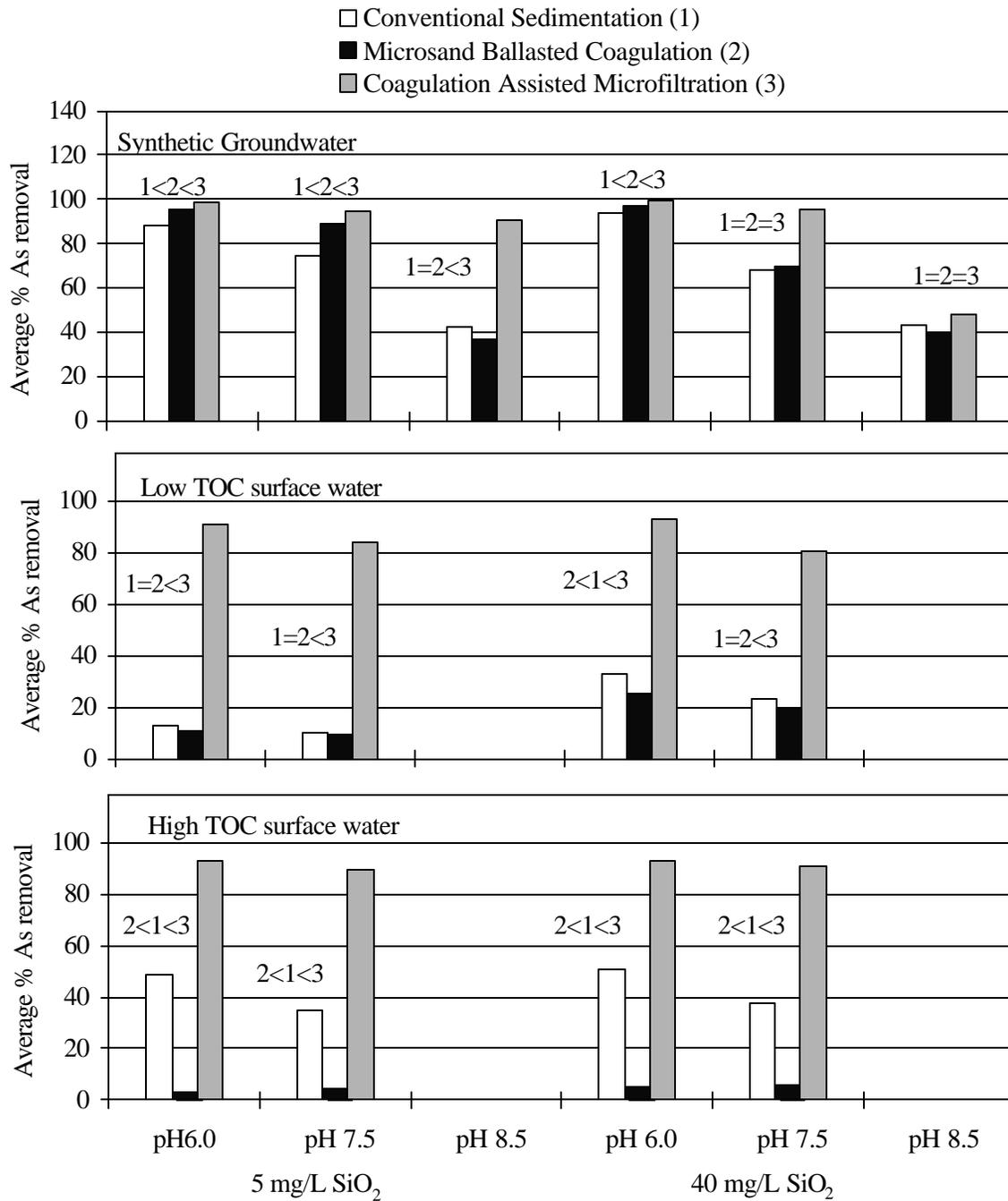
**Figure 1-1. Conceptualization of microsand ballasted floc formation in removal of arsenate in  $\text{Fe}(\text{OH})_3$  floc (left). Microsand ballasted treatment process might be used alone for treatment of groundwaters (upper right), or as a pretreatment to dramatically reduce solids loading to subsequent sand or membrane filters (lower right).**



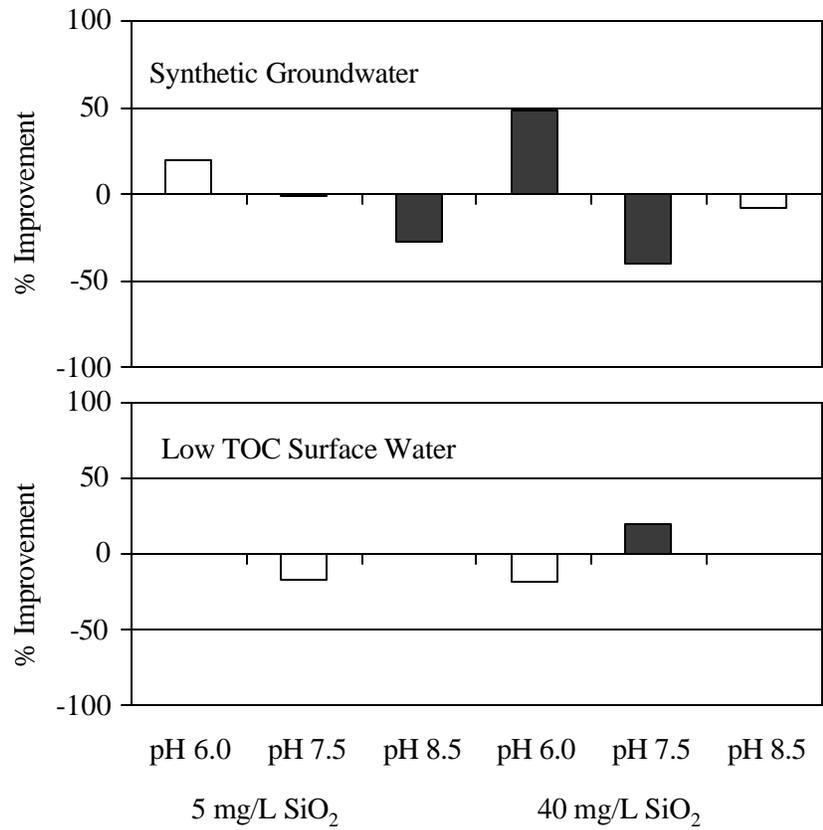
**Figure 1-2. Conventional sedimentation flocs (left) versus microsand sedimentation flocs (right) at beginning of slow mix step in jar test procedure.**



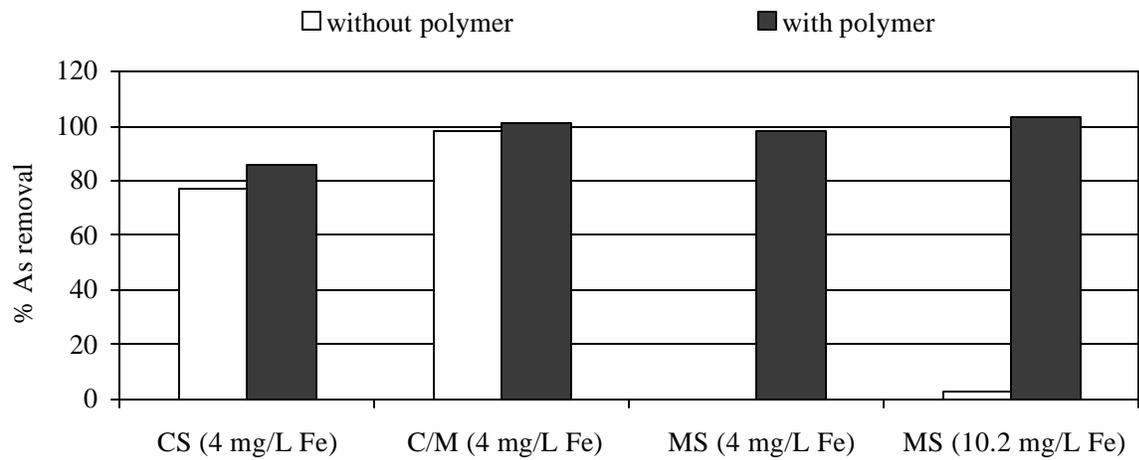
**Figure 1-3. Representative arsenic results.**



**Figure 1-4. Comparison of average arsenic removal for all 14 water conditions tested. Numbers above bars indicate comparison of As removal processes with 95% confidence using paired t-tests (i.e. conventional (1) vs. microsand (2), microsand (2) vs. microfiltration (3), and conventional (1) vs. microfiltration (3)).**



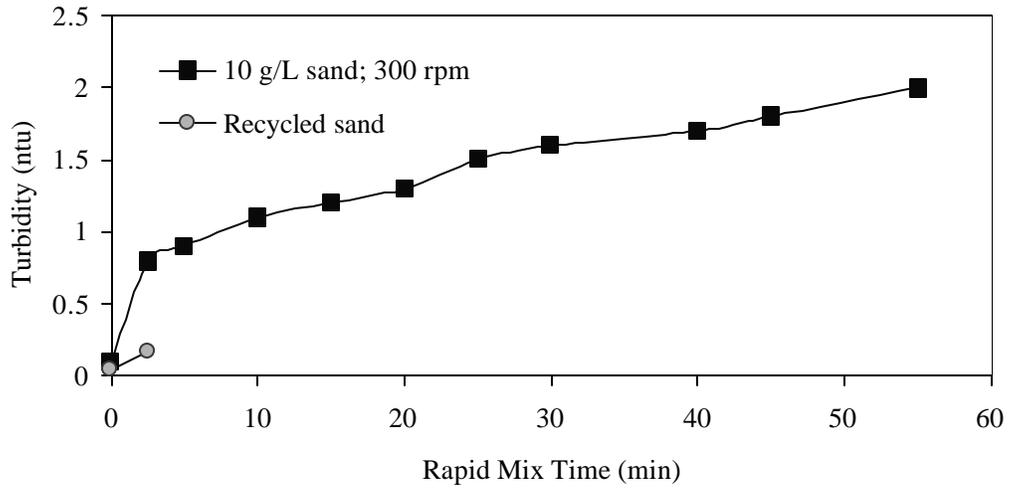
**Figure 1-5. Percent increase (improvement) in volume of water passed through a 0.45 mm pore size filter under constant pressure and filtration time after pretreatment with microsand ballasted coagulation. Shaded bars indicate a difference in volume filtered between with and without microsand at 95% confidence using a t-test on data paired at a given iron dose. Unshaded bars indicate differences that were not significant at 95% confidence.**



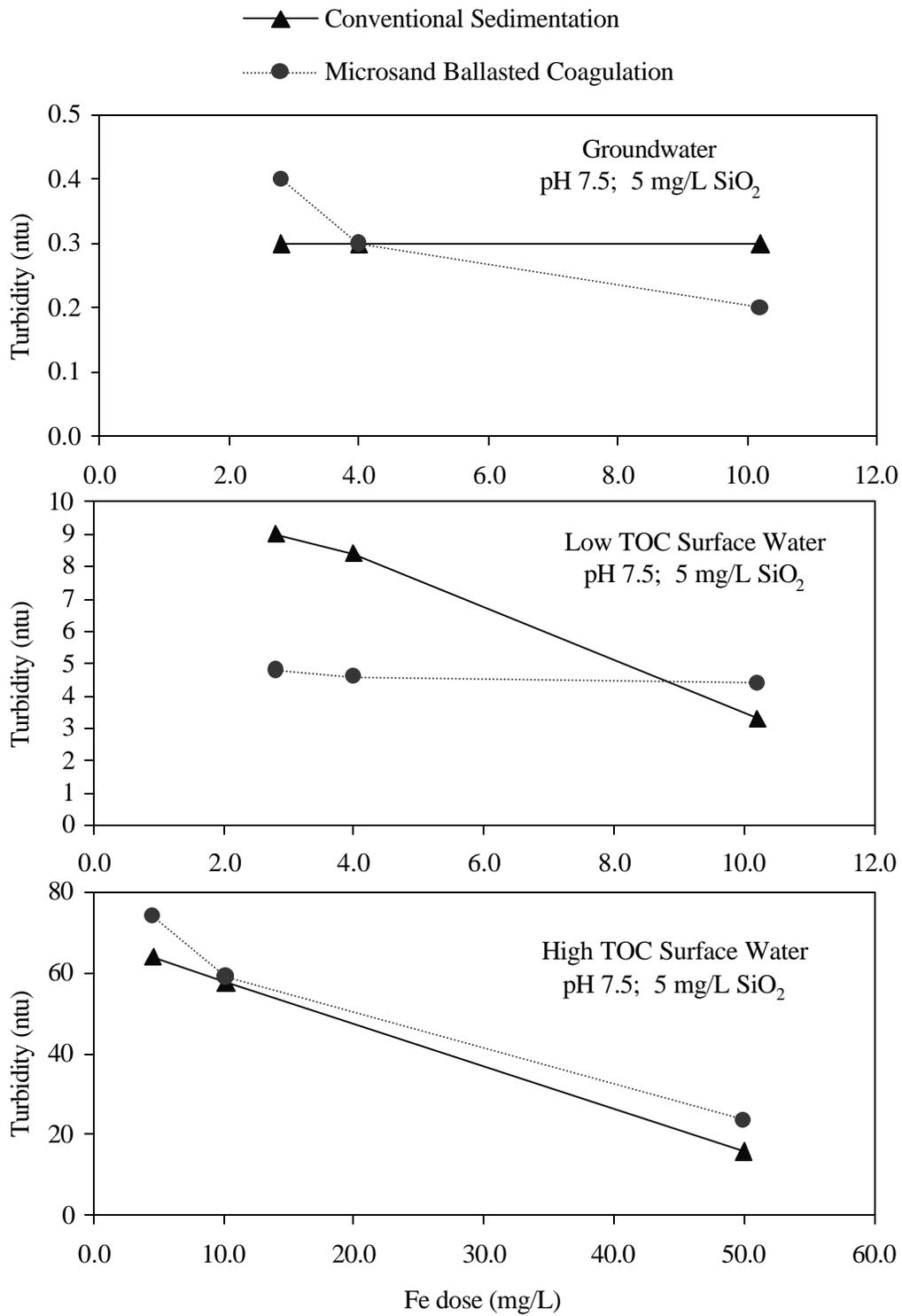
**Figure 1-6. As removal with and without polymer. CS = conventional sedimentation; C/M = coagulation assisted microfiltration; MS = microsand ballasted sedimentation.**



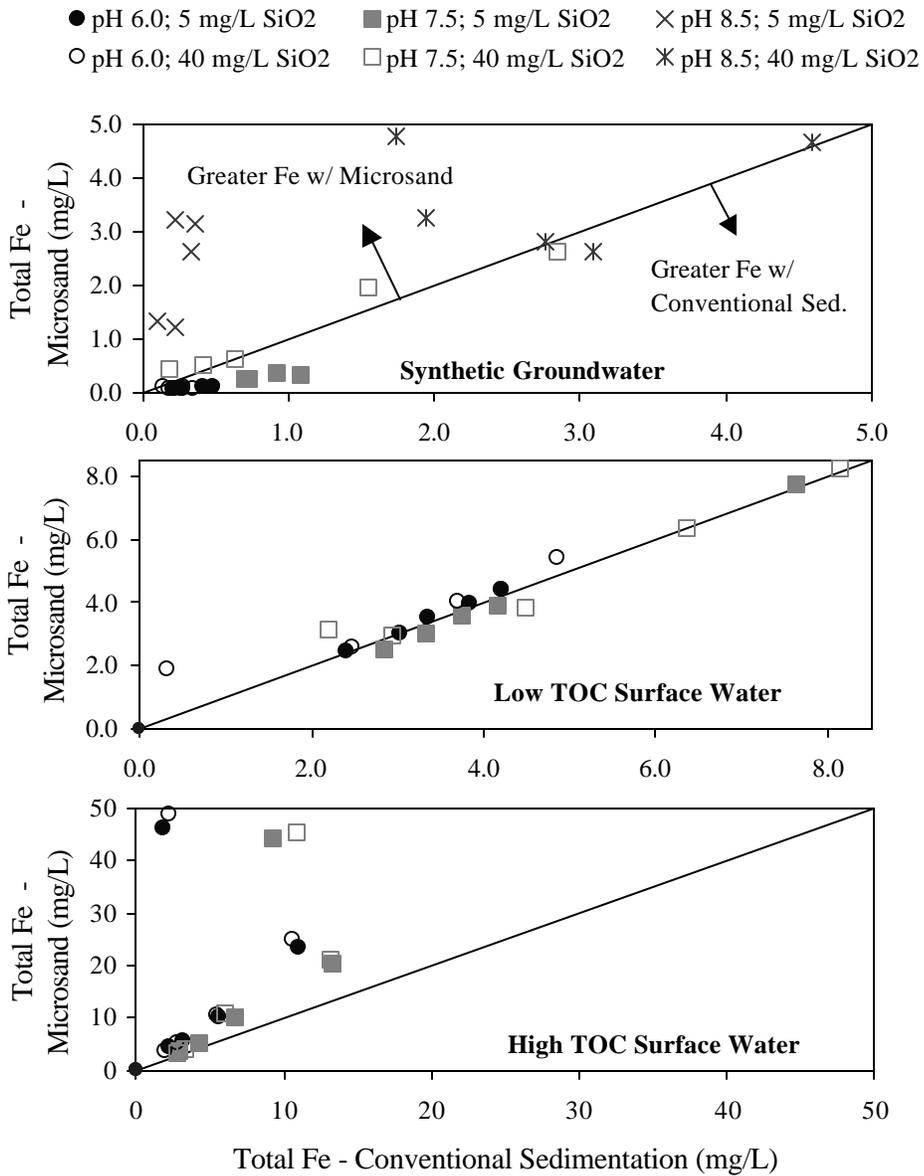
**Figure 1-7. Groundwater conventional sedimentation flocs with addition of 0.2 mg/L polymer (left) and no polymer (right).**



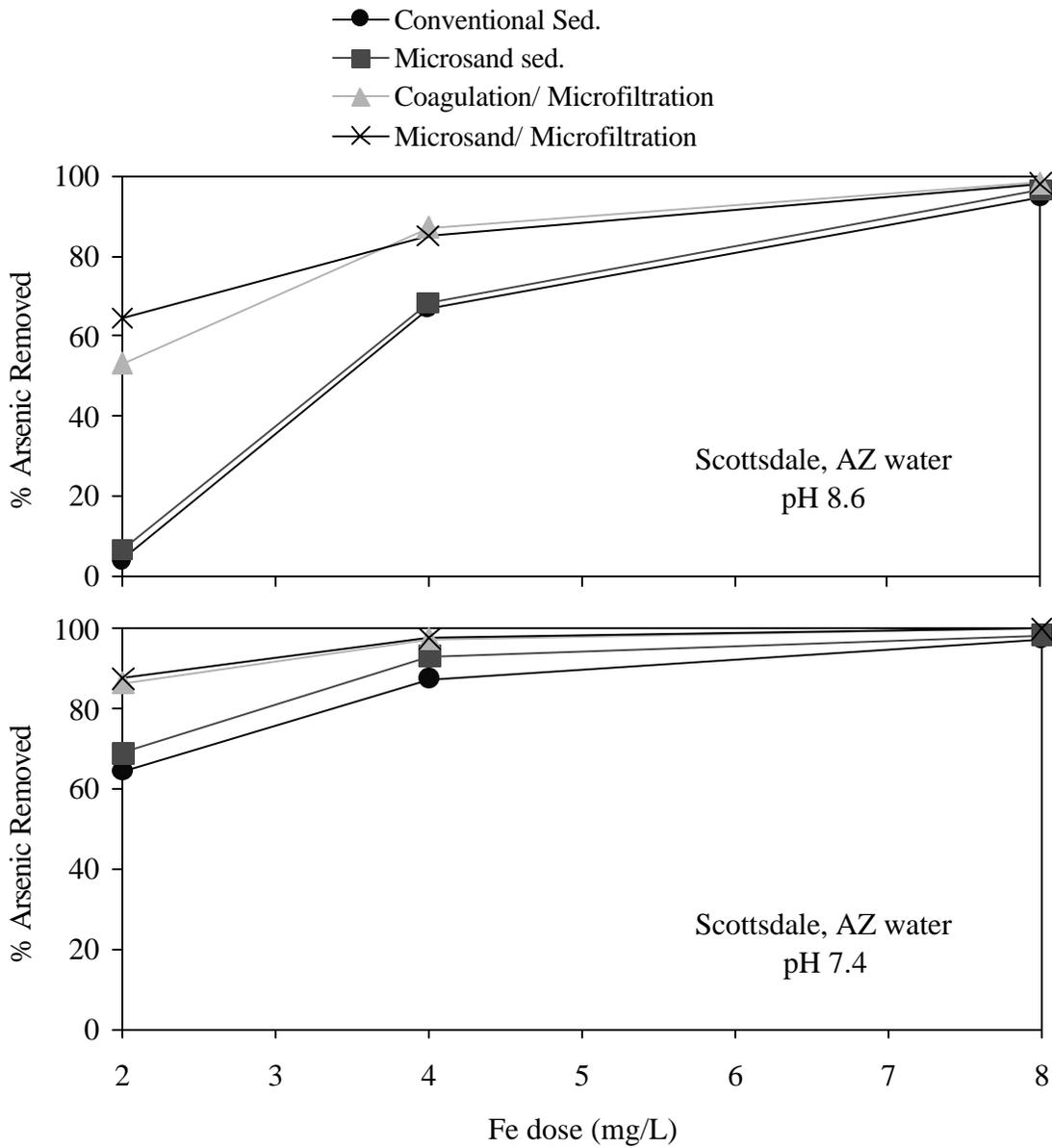
**Figure 1-8. Release of sand fines from new and recycled microsand to a single batch of water after the indicated rapid mix time.**



**Figure 1-9. Typical final turbidity results.**



**Figure 1-10. Total Fe remaining after microsand ballasted coagulation versus after conventional sedimentation. Data points above the line indicate more Fe with microsand; data points below indicate more Fe with conventional sedimentation.**



**Figure 1-11. Arsenic removal in Scottsdale, Arizona source water at pH 8.6 (above) and 7.4 (below). Initial arsenic = 45 ppb; SiO<sub>2</sub> = 18.4 mg/L**

## APPENDIX A

**Table A-1. Summary of arsenic results for simulated groundwater treatment by different approaches.**

| pH/SiO <sub>2</sub> | Fe dose (mg/L) | % As Removal |           |     |           |     |           |      |           |
|---------------------|----------------|--------------|-----------|-----|-----------|-----|-----------|------|-----------|
|                     |                | CS           |           | M/S |           | C/M |           | MS/M |           |
| pH 6.0<br>5 mg/L    | 2.8            | 82           |           | 89  |           | 97  |           | 94   |           |
|                     | 3.4            | 86           |           | 96  |           | 98  |           | 99   |           |
|                     | 4              | *            | <b>88</b> | 97  | <b>95</b> | 99  | <b>99</b> | 100  | <b>99</b> |
|                     | 4.6            | 91           |           | 97  |           | 100 |           | 100  |           |
|                     | 5.2            | 94           |           | 98  |           | 99  |           | 100  |           |
| pH 7.5<br>5 mg/L    | 2.8            | 54           |           | 80  |           | 91  |           | 94   |           |
|                     | 3.4            | 67           |           | 86  |           | 94  |           | 98   |           |
|                     | 4              | 79           | <b>74</b> | 91  | <b>89</b> | 94  | <b>95</b> | 99   | <b>99</b> |
|                     | 4.6            | 82           |           | 93  |           | 97  |           | 100  |           |
|                     | 10.2           | 90           |           | 97  |           | 99  |           | 101  |           |
| pH 8.5<br>5 mg/L    | 2.8            | 0            |           | 5   |           | 80  |           | 68   |           |
|                     | 3.4            | -4           |           | 3   |           | 88  |           | 80   |           |
|                     | 4.6            | 41           | <b>43</b> | 19  | <b>37</b> | 89  | <b>91</b> | 79   | <b>79</b> |
|                     | 10.2           | 85           |           | 76  |           | 97  |           | 86   |           |
|                     | 15             | 92           |           | 80  |           | 100 |           | 84   |           |
| pH 6.0<br>40 mg/L   | 2.8            | 87           |           | 93  |           | 97  |           | 97   |           |
|                     | 4.6            | 92           |           | 97  |           | 99  |           | 99   |           |
|                     | 5.2            | 96           | <b>94</b> | 98  | <b>97</b> | 100 | <b>99</b> | 99   | <b>99</b> |
|                     | 7.5            | 97           |           | 99  |           | 101 |           | 100  |           |
|                     | 10.2           | 99           |           | 99  |           | 100 |           | 100  |           |
| pH 7.5<br>40 mg/L   | 2.8            | 0            |           | 7   |           | 83  |           | 70   |           |
|                     | 4.6            | 62           |           | 56  |           | 97  |           | 93   |           |
|                     | 7.5            | 87           | <b>68</b> | 91  | <b>70</b> | 99  | <b>95</b> | 96   | <b>91</b> |
|                     | 10.2           | 94           |           | 96  |           | 99  |           | 98   |           |
|                     | 15             | 98           |           | 99  |           | 99  |           | 99   |           |
| pH 8.5<br>40 mg/L   | 2.8            | 5            |           | 2   |           | 5   |           | 10   |           |
|                     | 4.6            | 1            |           | 3   |           | 5   |           | 8    |           |
|                     | 10.2           | 55           | <b>43</b> | 56  | <b>40</b> | 68  | <b>48</b> | 77   | <b>52</b> |
|                     | 15.0           | 79           |           | 57  |           | 83  |           | 77   |           |
|                     | 25.0           | 76           |           | 85  |           | 78  |           | 91   |           |

**Numbers in bold are average percent arsenic removal for all iron doses tested at a given water condition. CS = conventional sedimentation; MS = microsand ballasted coagulation; C/M = coagulation assisted microfiltration; MS/M = microsand ballasted coagulation/ microfiltration.**

**Table A-2. Summary of arsenic results for simulated low TOC/ low turbidity and high TOC/ high turbidity surface water treatment by different approaches.**

| Water Type | pH/SiO <sub>2</sub> | Fe dose (mg/L) | % As Removal |           |     |           |    |           |    |           |
|------------|---------------------|----------------|--------------|-----------|-----|-----------|----|-----------|----|-----------|
|            |                     |                | CS           | MS        | C/M | MS/M      |    |           |    |           |
| Low TOC    | pH 6.0<br>5 mg/L    | 2.8            | 14           | 9         | 83  | 86        |    |           |    |           |
|            |                     | 3.4            | 8            | 9         | 91  | 90        |    |           |    |           |
|            |                     | 4.0            | 12           | <b>13</b> | 13  | <b>11</b> | 93 | <b>91</b> | 90 | <b>90</b> |
|            |                     | 4.6            | 13           | 13        | 90  | 92        |    |           |    |           |
|            |                     | 5.2            | 19           | 12        | 98  | 94        |    |           |    |           |
|            | pH 7.5<br>5 mg/L    | 2.8            | 9            | 10        | 79  | 71        |    |           |    |           |
|            |                     | 3.4            | 5            | 8         | 79  | 78        |    |           |    |           |
|            |                     | 4.0            | 4            | <b>10</b> | 7   | <b>10</b> | 88 | <b>84</b> | 84 | <b>83</b> |
|            |                     | 4.6            | 8            | 3         | 77  | 81        |    |           |    |           |
|            |                     | 10.2           | 23           | 21        | 98  | 99        |    |           |    |           |
|            | pH 6.0<br>40 mg/L   | 2.8            | 12           | 7         | 80  | 83        |    |           |    |           |
|            |                     | 4.6            | 15           | 9         | 94  | 91        |    |           |    |           |
|            |                     | 5.2            | 15           | <b>33</b> | 9   | <b>25</b> | 94 | <b>93</b> | 87 | <b>91</b> |
|            |                     | 7.5            | 31           | 21        | 98  | 96        |    |           |    |           |
|            |                     | 10.2           | 94           | 80        | 99  | 100       |    |           |    |           |
|            | pH 7.5<br>40 mg/L   | 2.8            | 3            | 3         | 57  | 56        |    |           |    |           |
|            |                     | 4.6            | 1            | 3         | 72  | 66        |    |           |    |           |
|            |                     | 7.5            | 10           | <b>23</b> | 6   | <b>20</b> | 87 | <b>81</b> | 79 | <b>78</b> |
|            |                     | 10.2           | 19           | 13        | 90  | 92        |    |           |    |           |
|            |                     | 15.0           | 82           | 75        | 98  | 96        |    |           |    |           |
| High TOC   | pH 6.0<br>5 mg/L    | 2.8            | 29           | 7         | 81  | 83        |    |           |    |           |
|            |                     | 4.6            | 32           | 7         | 92  | 93        |    |           |    |           |
|            |                     | 10.2           | 39           | <b>49</b> | 5   | <b>3</b>  | 96 | <b>93</b> | 97 | <b>95</b> |
|            |                     | 25.0           | 47           | 1         | 98  | 100       |    |           |    |           |
|            |                     | 50.0           | 95           | -4        | 99  | 100       |    |           |    |           |
|            | pH 7.5<br>5 mg/L    | 2.8            | 14           | 4         | 70  | 71        |    |           |    |           |
|            |                     | 4.6            | 21           | 3         | 82  | 83        |    |           |    |           |
|            |                     | 10.2           | 24           | <b>35</b> | 3   | <b>4</b>  | 94 | <b>89</b> | 97 | <b>90</b> |
|            |                     | 25.0           | 37           | 9         | 100 | 100       |    |           |    |           |
|            |                     | 50.0           | 78           | 2         | 101 | 97        |    |           |    |           |
|            | pH 6.0<br>40 mg/L   | 2.8            | 34           | 11        | 78  | 79        |    |           |    |           |
|            |                     | 4.6            | 39           | 8         | 92  | 91        |    |           |    |           |
|            |                     | 10.2           | 41           | <b>51</b> | 6   | <b>5</b>  | 97 | <b>93</b> | 98 | <b>94</b> |
|            |                     | 25.0           | 48           | 2         | 99  | 100       |    |           |    |           |
|            |                     | 50.0           | 93           | -2        | 100 | 101       |    |           |    |           |
|            | pH 7.5<br>40 mg/L   | 2.8            | 17           | 6         | 69  | 65        |    |           |    |           |
|            |                     | 4.6            | 28           | 18        | 87  | 84        |    |           |    |           |
|            |                     | 10.2           | 33           | <b>38</b> | 2   | <b>6</b>  | 96 | <b>91</b> | 95 | <b>88</b> |
|            |                     | 25.0           | 39           | 7         | 101 | 101       |    |           |    |           |
|            |                     | 50.0           | 72           | -4        | 102 | 97        |    |           |    |           |

Numbers in bold are average percent arsenic removal for all iron doses tested at a given water condition. CS = conventional sedimentation; MS = microsand ballasted coagulation; C/M = coagulation assisted microfiltration; MS/M = microsand ballasted coagulation/ microfiltration.

**Table A-3. Summary of iron remaining for simulated groundwater treatment by different approaches.**

| Treatment Conditions    |                     |                | Fe Remaining after treatment (mg/L) |      |      |      |
|-------------------------|---------------------|----------------|-------------------------------------|------|------|------|
| Water/ spiked turbidity | pH/SiO <sub>2</sub> | Fe dose (mg/L) | CS                                  | MS   | C/M  | MS/M |
| Groundwater (0 ntu)     | pH 6.0<br>5 mg/L    | 2.8            | 0.49                                | 0.11 | 0.00 | 0.00 |
|                         |                     | 3.4            | 0.42                                | 0.10 | 0.00 | 0.00 |
|                         |                     | 4              | 0.28                                | 0.09 | 0.00 | 0.00 |
|                         |                     | 4.6            | 0.26                                | 0.08 | 0.00 | 0.00 |
|                         |                     | 5.2            | 0.21                                | 0.08 | 0.00 | 0.00 |
|                         | pH 7.5<br>5 mg/L    | 2.8            | 1.08                                | 0.34 | 0.05 | 0.02 |
|                         |                     | 3.4            | 0.91                                | 0.35 | 0.01 | 0.02 |
|                         |                     | 4              | 0.73                                | 0.24 | 0.01 | 0.02 |
|                         |                     | 4.6            | 0.70                                | 0.25 | 0.00 | 0.01 |
|                         |                     | 10.2           | *                                   | 0.13 | 0.00 | 0.01 |
|                         | pH 8.5<br>5 mg/L    | 2.8            | 0.33                                | 2.62 | 0.04 | 0.19 |
|                         |                     | 3.4            | 0.36                                | 3.16 | 0.02 | 0.09 |
|                         |                     | 4.6            | 0.23                                | 3.22 | 0.03 | 0.04 |
|                         |                     | 10.2           | 0.22                                | 1.21 | 0.02 | 0.05 |
|                         |                     | 15             | 0.10                                | 1.33 | 0.01 | 0.03 |
|                         | pH 6.0<br>40 mg/L   | 2.8            | 0.28                                | 0.12 | 0.0  | 0.00 |
|                         |                     | 4.6            | 0.34                                | 0.08 | 0.0  | 0.00 |
|                         |                     | 5.2            | 0.19                                | 0.08 | 0.0  | 0.00 |
|                         |                     | 7.5            | 0.22                                | 0.08 | 0.0  | 0.00 |
|                         |                     | 10.2           | 0.15                                | 0.12 | 0.0  | 0.00 |
|                         | pH 7.5<br>40 mg/L   | 2.8            | 2.84                                | 2.62 | 0.16 | 0.5  |
|                         |                     | 4.6            | 1.55                                | 1.94 | 0.01 | 0.1  |
|                         |                     | 7.5            | 0.63                                | 0.63 | 0.01 | 0.1  |
|                         |                     | 10.2           | 0.41                                | 0.53 | 0.02 | 0.1  |
|                         |                     | 15             | 0.18                                | 0.44 | 0.01 | 0.0  |
|                         | pH 8.5<br>40 mg/L   | 2.8            | 2.76                                | 2.82 | 2.7  | 2.8  |
|                         |                     | 4.6            | 4.59                                | 4.67 | 4.4  | 4.3  |
|                         |                     | 10.2           | 1.95                                | 3.26 | 0.2  | 0.2  |
|                         |                     | 15.0           | 1.73                                | 4.79 | 0.1  | 0.4  |
|                         |                     | 25.0           | 3.09                                | 2.63 | 0.0  | 0.1  |

**CS = conventional sedimentation; MS = microsand ballasted coagulation; C/M = coagulation assisted microfiltration; MS/M = microsand ballasted coagulation/ microfiltration.**

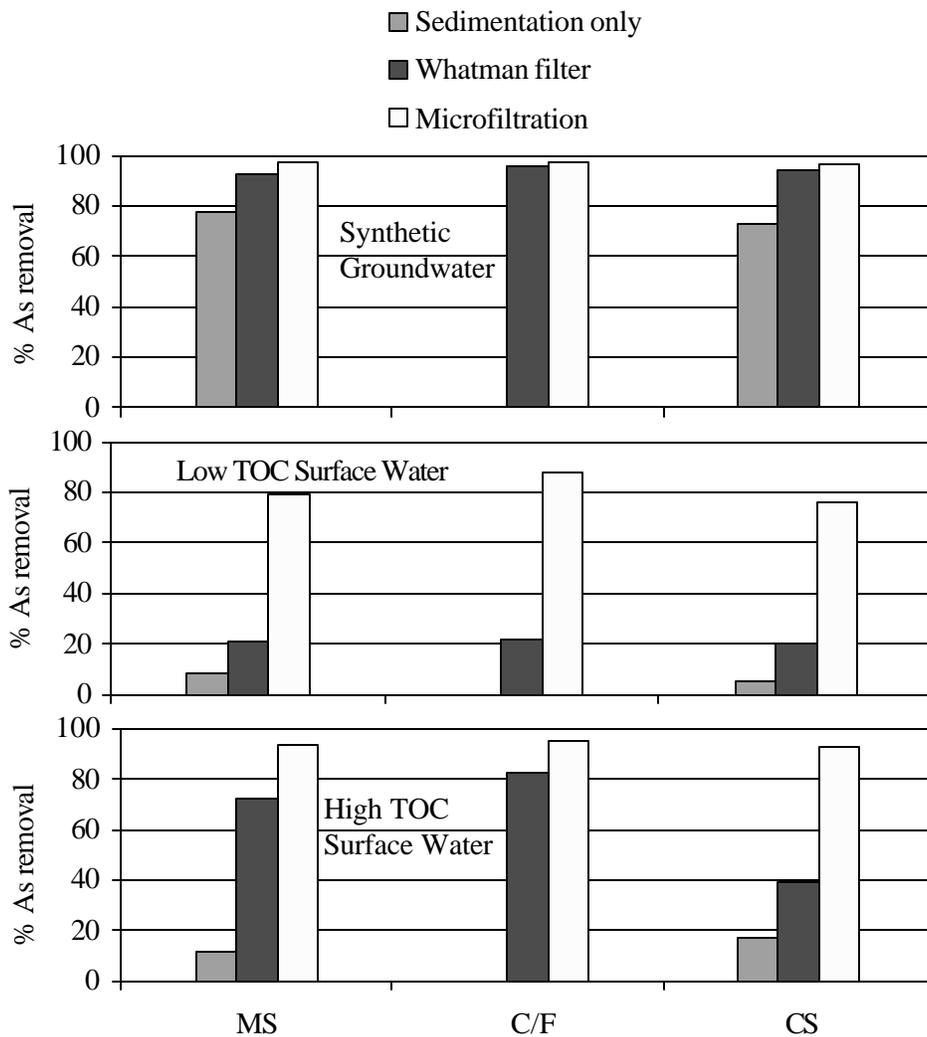
**Table A-4. Summary of iron remaining for simulated low TOC/ low turbidity and high TOC/ high turbidity surface water treatment by different approaches.**

| Treatment Conditions    |                     |                | Fe Remaining after treatment (mg/L) |       |      |      |
|-------------------------|---------------------|----------------|-------------------------------------|-------|------|------|
| Water/ spiked turbidity | pH/SiO <sub>2</sub> | Fe dose (mg/L) | CS                                  | MS    | C/M  | MS/M |
| Low TOC                 | pH 6.0<br>5 mg/L    | 2.8            | 2.40                                | 2.48  | 0.39 | 0.35 |
|                         |                     | 3.4            | 3.04                                | 3.04  | 0.30 | 0.31 |
|                         |                     | 4.0            | 3.36                                | 3.54  | 0.30 | 0.41 |
|                         |                     | 4.6            | 3.85                                | 3.96  | 0.48 | 0.39 |
|                         |                     | 5.2            | 4.20                                | 4.41  | 0.17 | 0.36 |
|                         | pH 7.5<br>5 mg/L    | 2.8            | 2.84                                | 2.54  | 0.33 | 0.54 |
|                         |                     | 3.4            | 3.32                                | 3.05  | 0.52 | 0.58 |
|                         |                     | 4.0            | 3.74                                | 3.61  | 0.32 | 0.49 |
|                         |                     | 4.6            | 4.15                                | 3.92  | 0.85 | 0.74 |
|                         |                     | 10.2           | 7.64                                | 7.73  | 0.10 | 0.22 |
|                         | pH 6.0<br>40 mg/L   | 2.8            | 2.46                                | 2.61  | 0.32 | 0.33 |
|                         |                     | 4.6            | 3.70                                | 4.05  | 0.19 | 0.33 |
|                         |                     | 5.2            | 4.21                                | 4.43  | 0.20 | 0.55 |
|                         |                     | 7.5            | 4.85                                | 5.42  | 0.10 | 0.24 |
|                         |                     | 10.2           | 0.33                                | 1.92  | 0.01 | 0.01 |
|                         | pH 7.5<br>40 mg/L   | 2.8            | 2.94                                | 2.98  | 0.65 | 0.70 |
|                         |                     | 4.6            | 4.48                                | 3.82  | 0.65 | 0.88 |
|                         |                     | 7.5            | 6.36                                | 6.37  | 0.53 | 0.94 |
|                         |                     | 10.2           | 8.14                                | 8.25  | 0.57 | 0.50 |
|                         |                     | 15.0           | 2.20                                | 3.15  | 0.14 | 0.17 |
| High TOC                | pH 6.0<br>5 mg/L    | 2.8            | 2.23                                | 4.23  | 0.00 | 0.00 |
|                         |                     | 4.6            | 3.23                                | 5.53  | 0.00 | 0.00 |
|                         |                     | 10.2           | 5.65                                | 10.25 | 0.01 | 0.00 |
|                         |                     | 25.0           | 11.02                               | 23.24 | 0.01 | 0.00 |
|                         |                     | 50.0           | 1.83                                | 46.28 | 0.30 | 0.09 |
|                         | pH 7.5<br>5 mg/L    | 2.8            | 2.92                                | 3.61  | 0.00 | 0.00 |
|                         |                     | 4.6            | 4.27                                | 5.04  | 0.00 | 0.00 |
|                         |                     | 10.2           | 6.73                                | 9.97  | 0.00 | 0.00 |
|                         |                     | 25.0           | 13.25                               | 20.53 | 0.00 | 0.00 |
|                         |                     | 50.0           | 9.17                                | 44.28 | 0.00 | 0.00 |
|                         | pH 6.0<br>40 mg/L   | 2.8            | 1.98                                | 3.57  | 0.01 | 0.00 |
|                         |                     | 4.6            | 2.84                                | 5.23  | 0.01 | 0.00 |
|                         |                     | 10.2           | 5.48                                | 10.51 | 0.01 | 0.00 |
|                         |                     | 25.0           | 10.63                               | 25.00 | 0.01 | 0.00 |
|                         |                     | 50.0           | 2.22                                | 48.66 | 0.17 | 0.11 |
|                         | pH 7.5<br>40 mg/L   | 2.8            | 2.76                                | 3.49  | 0.01 | 0.00 |
|                         |                     | 4.6            | 3.27                                | 3.89  | 0.00 | 0.10 |
|                         |                     | 10.2           | 5.98                                | 10.74 | 0.00 | 0.19 |
|                         |                     | 25.0           | 13.11                               | 20.99 | 0.00 | 0.00 |
|                         |                     | 50.0           | 10.84                               | 45.59 | 0.00 | 0.53 |

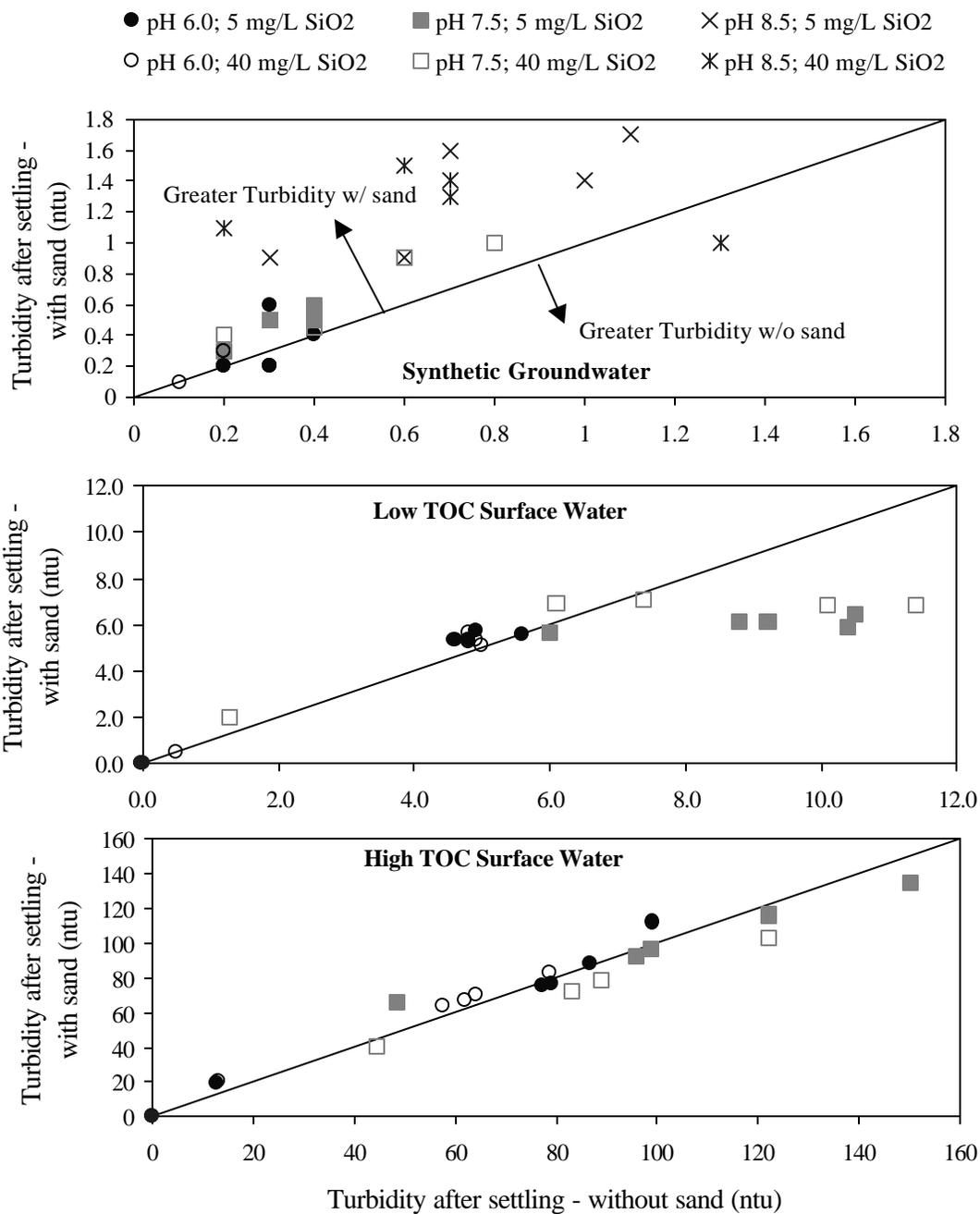
CS = conventional sedimentation; MS = microsand ballasted coagulation; C/M = coagulation assisted microfiltration; MS/M = microsand ballasted coagulation/ microfiltration.

**Table A5. Summary of initial and final pH in Scottsdale water jar tests.**

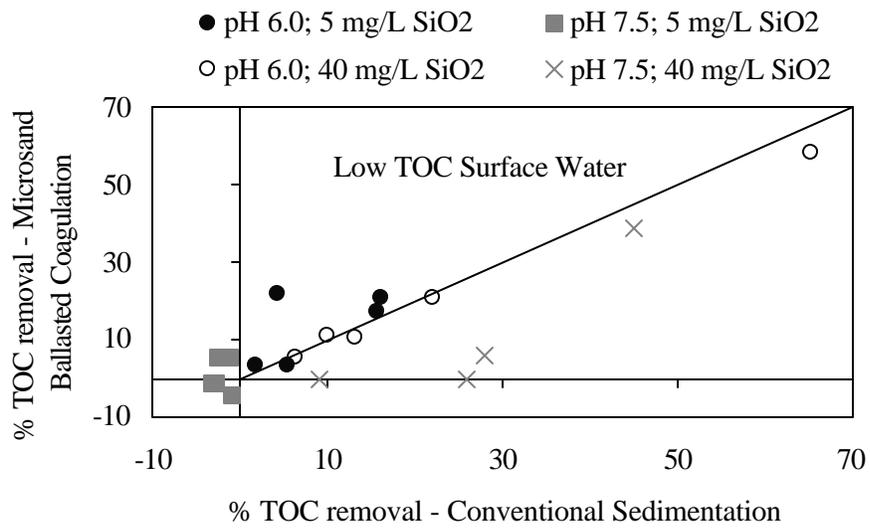
| <b>Initial pH</b> | <b>Conventional/Microsand jar test</b> | <b>Fe(OH)<sub>3</sub> dose (mg/L as Fe)</b> | <b>Final pH</b> |
|-------------------|--|---|-----------------|
| 8.7               | Conventional                           | 2.0   | 8.27            |
|                   |  | 4.0   | 7.96            |
|                   |  | 8.0   | 7.56            |
| 8.7               | Microsand                              | 2.0   | 8.26            |
|                   |  | 4.0   | 7.94            |
|                   |  | 8.0   | 7.55            |
| 7.4               | Conventional                           | 2.0   | 7.57            |
|                   |  | 4.0   | 7.52            |
|                   |  | 8.0   | 7.34            |
| 7.4               | Microsand                              | 2.0   | 7.51            |
|                   |  | 4.0   | 7.41            |
|                   |  | 8.0   | 7.24            |



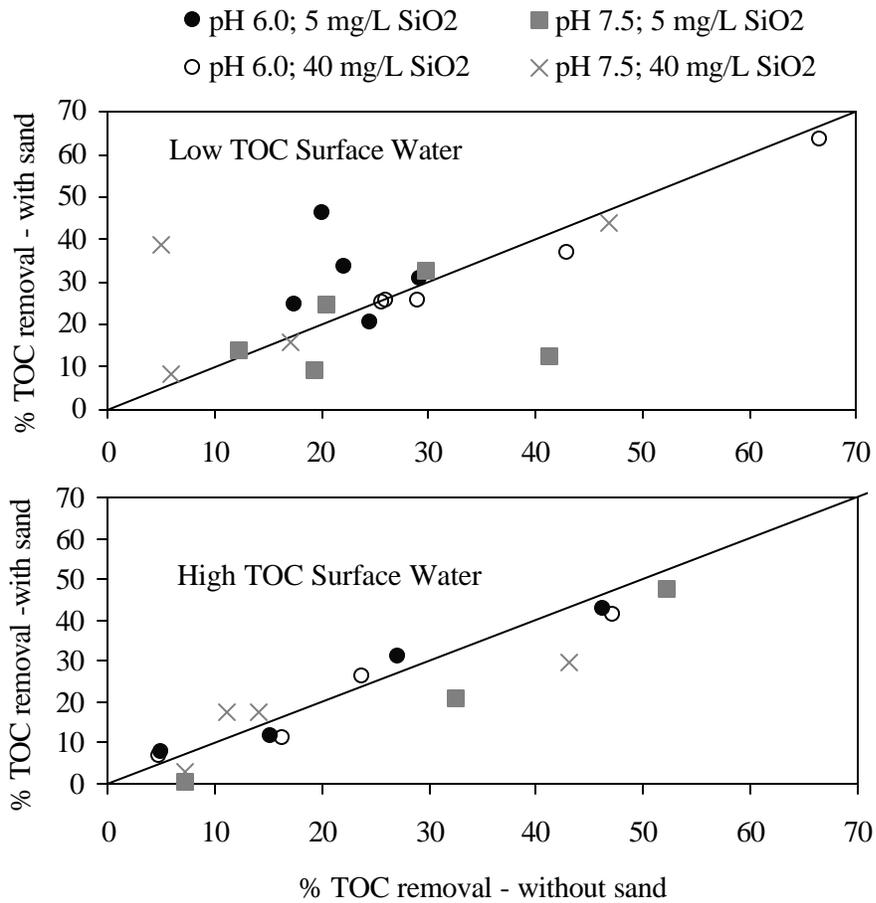
**Figure A-1. Percent arsenic removal without filtration, with a Whatman 40 filter, and with 0.45 um microfiltration. MS = microsand ballasted coagulation; C/F = coagulation assisted filtration; CS = conventional sedimentation. SiO<sub>2</sub> = 5 mg/L; pH = 7.5.**



**Figure A-2. Turbidity after 30 minutes settling with versus without microsand. Data points above the line indicate greater turbidity with microsand; points below indicate greater turbidity without microsand.**



**Figure A-3. Percent TOC removal comparison in synthetic low TOC/ low turbidity surface water. Data points above the line indicate greater removal with microsand; points below indicate greater removal with conventional sedimentation.**



**Figure A-4. Percent TOC removal after 30 minutes settling and filtration with 0.45  $\mu\text{m}$  pore size filter. Data points above the line indicate greater removal with microsand; points below indicate greater removal without microsand**

## **CHAPTER II.**

### **ROLE OF SILICA AND CALCIUM IN ARSENIC UPTAKE BY AMORPHOUS AND GRANULAR MEDIA OXIDES**

Sheryl D. Smith and Marc Edwards

Arsenic can be effectively removed from water by sorption to amorphous or granular iron or aluminum oxides, however, silica is known to interfere with arsenic sorption at  $\text{pH} > 7.5$ . The goal of this work was to examine arsenic sorption to amorphous and granular media oxides at various levels of silica, calcium, and  $\text{pH}$ , and to closely monitor the kinetics of key reactions that occur in these systems. At  $\text{pH} 8.5$ , calcium dramatically improved arsenic sorption to amorphous iron hydroxide in the presence of silica over short reaction times, but had no long-term advantage. This result could have considerable applications for coagulation processes. Additionally, batch tests indicated that activated alumina granular media was more sensitive to water quality than granular ferric hydroxide, however, calcium eliminated silica interference to arsenic sorption onto activated alumina.

#### **INTRODUCTION**

Arsenic can be effectively removed from water by sorption to amorphous or granular iron or aluminum oxides. However, competing anions can also adsorb to these surfaces and interfere with arsenic removal in engineered systems. Silica is present to a varying degree in all natural waters and has been shown to interfere with arsenic removal (1-6). The extent of silica interference increases with silica concentration and  $\text{pH} > 7.5$ . Consequently, it is very difficult to achieve effective arsenic removal in some waters. Few suggestions have been made to help overcome the problem of arsenic removal in waters with high  $\text{pH}$  and high silica, although Meng et al (2) found that the adverse affect of silica was reduced in the presence of calcium and magnesium. Other evidence suggests that calcium may help eliminate competitive effects of NOM on arsenic sorption (7). Enhancement of arsenic sorption in the presence of calcium has even been noted for systems without silica (8-10).

With respect to kinetics of sorption, 'equilibrium' has reportedly been reached between the oxide surface and soluble  $\text{As(V)}$  at reaction times ranging from 50 seconds

(1) to 200 hours (3) for amorphous iron hydroxide, and 2 to 7 days (11, 12) for highly porous sorbents such as activated alumina in which diffusion limitations are significant (Table 2-1). Some recent findings also show that kinetics are an important factor for arsenic sorption to goethite in the presence of silica, with arsenic sorption actually increasing over reaction times longer than 1 week (13). However, most studies that have examined kinetics have done so only for 1 or 2 representative water conditions, or at relatively high arsenic concentration (Table 2-1). While silica interference and calcium enhancement have been noted to impact equilibrium, their effect on kinetics has not been examined.

It is interesting to consider the role of kinetics of various reactions in arsenic removal (Table 2-2). First, kinetics can effect drinking water arsenic removal processes like coagulation through the rate of precipitation and agglomeration of flocs (14). If kinetics of arsenic sorption to the oxide surface were slow, it would have a strong impact on processes with a short reaction time like coagulation-microfiltration. Aging of amorphous solids to more crystalline structures can reduce surface area available for sorption and therefore impact arsenic removal in all processes except those with granular media, which are presumably already aged (21). Analogies to activated carbon sorption suggest that diffusion can also be a significant kinetic limitation when using highly porous media like activated alumina or granular ferric hydroxide to remove arsenic. Finally, silica ‘fouling’ can occur over weeks where layers of silica sorb to granular surfaces, effectively reducing the surface available for arsenic sorption (5).

The goal of this work was to examine arsenic sorption to amorphous and granular media oxides at various levels of silica, calcium, and pH, and to closely monitor the kinetics of key reactions that occur in these systems.

## **MATERIALS AND METHODS**

Three experiments were designed to investigate the effects of silica and calcium addition, pH, and kinetics on arsenic sorption to pre-formed amorphous iron hydroxides or granular media.

**Amorphous Iron Hydroxide - Effects of pH.**  $\text{Fe}(\text{OH})_3$  was pre-formed by raising the pH of an  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  stock solution (250 mg/L as Fe acidified with  $1 \times 10^{-2}$  M  $\text{HNO}_3$ ) to 6.0 as described in Davis et al (15). The solids were aged for approximately 12 hours on an orbital shaker.

Experiments proceeded as follows. Six solutions were prepared with distilled deionized water in 250 mL plastic bottles, magnetically stirred while sampling, or placed on an orbital shaker while aging. The preformed  $\text{Fe}(\text{OH})_3$  solution was dosed into the containers to obtain a final concentration of 20 mg/L Fe, and pH was adjusted to either 7.0, 8.0, 9.0, 10.0, 11.0, or 12.0. The bottles then equilibrated for 2 hours. Experiments were then initiated when arsenate from a stock solution of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (500 mg/L as As) was dosed into all bottles to a final concentration of 100 ug/L As. Samples were collected at 2 hours, 1 day, 4 days, 8 days, 1 month, and 2 months. Zeta potential measurements were also taken at 1 day, 4 days, and 8 days. pH was readjusted to the target value throughout the experiment.

In another set of experiments, the above protocol was repeated with slight variations. A stock solution of  $\text{Na}_2\text{SiO}_3$  (8000 mg/L as  $\text{SiO}_2$ ) was added to the pre-formed iron to a final concentration of 40 mg/L  $\text{SiO}_2$ . The solution was equilibrated for 2 hours. Thereafter, arsenate was added to initiate the experiment. In another case, 20 mg/L Ca (from a stock solution of 0.1 M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) was added 5 minutes before the arsenate to examine effects of hardness on sorption.

**Amorphous Iron Hydroxide - Kinetics of Sorption.** All stock solutions and doses were the same as those used in the first experiment. Likewise, all solutions contained 2 mM  $\text{NaNO}_3$  for background ionic strength. Solutions of As alone, As with Ca, As with  $\text{SiO}_2$ , and As with  $\text{SiO}_2$  and Ca were prepared and adjusted to pH 8.5. In contrast to the previous procedure, time zero was defined when iron from the preformed  $\text{Fe}(\text{OH})_3$  stock was dosed into all arsenic solutions to a final concentration of 20 mg/L Fe. Samples were collected at various intervals from 10 minutes to 6 weeks. The pH was

maintained throughout the experiment by addition of small amounts of HNO<sub>3</sub> or NaOH, but occasionally drifted as much as 0.8 units from the target value.

**Preparation of Silica Solutions.** An 8000 mg/L SiO<sub>2</sub> solution was made with Na<sub>2</sub>SiO<sub>3</sub> salt resulting in a pH of approximately 12.8. According to Davis et al (5) this solution contains an undetectable percentage of polymerized silica as measured by molybdate-reactivity. In one granular media experiment, a second solution was prepared by diluting the original stock solution to 800 mg/L as SiO<sub>2</sub>, adjusting the pH to 8.5, and aging it for approximately 24 hours. This solution was designated 'polymeric' silica since about 76 to 87% was non-molybdate reactive as reported by Davis et al (5).

**Granular Media.** Activated alumina and granular ferric hydroxide experiments were tested in batch similar to the previous experiments with amorphous solids at pH 8.5. Arsenic removal was compared for the following six combinations of silica and calcium in the water: 1) 0 mg/L SiO<sub>2</sub> & 0 mg/L Ca; 2) 40 mg/L SiO<sub>2</sub> & 0 mg/L Ca; 3) 40 mg/L SiO<sub>2</sub> & 10 mg/L Ca; 4) 40 mg/L SiO<sub>2</sub> & 100 mg/L Ca; 5) 0 mg/L SiO<sub>2</sub> & 10 mg/L Ca; 6) 40 mg/L 'polymeric' SiO<sub>2</sub> & 0 mg/L Ca.

Doses of dry Alcan CPN activated alumina or GEH Wasserchemie GmbH and Co. granular ferric hydroxide were weighed out so that the final concentration of media in solution would be 2 g/L. Each batch of media was washed twice with 200 mL aliquots of distilled deionized water. Media was added to solutions containing 1 mM sodium bicarbonate and 10 mM NaCl which were prepared with distilled deionized water in 500 mL plastic bottles. The bottles were placed on an orbital shaker for the duration of the experiment. A control experiment was prepared without bicarbonate to examine any effect of carbonate on arsenic removal. Silica and/or calcium was added to each bottle, the pH adjusted to 8.5, and the solutions were equilibrated for a period of 0 min or 1 week, after which time the experiment was started when arsenic was added to an initial concentration of 500 ppb. Samples were collected at various intervals from 5 minutes to 11 days. The pH was readjusted to the target value throughout the experiment.

**Analysis.** Samples from all experiments were first filtered through a 0.45  $\mu\text{m}$  pore size nylon disposable filter. They were then analyzed for soluble arsenic, silicon, calcium, iron, or aluminum on a JY Ultima Inductive Coupled Plasma – Emission Spectroscopy (ICP-ES) according to standard method 3120B using continuous hydride generation (22). A Malvern ZetaSizer 3000HS was used to measure zeta potential.

## RESULTS AND DISCUSSION

Results are organized into two sections including amorphous iron hydroxide and granular media.

**Amorphous Iron Hydroxide.** The zeta potential of  $\text{Fe}(\text{OH})_3$  suspensions spiked with 500 ppb arsenic decreased from 15 mV to  $-39$  mV as pH increased from 7 to 12, with a PZC at about pH 8.5 (Figure 2-1). In contrast, suspensions containing 40 mg/L silica, had a zeta potential less than  $-24$  mV regardless of pH, indicating the negatively charged silica species dominated surface charge. When 10 mg/L calcium was added to the solution with silica, the zeta potential was less negative, remaining relatively constant from  $-21$  mV to  $-13$  mV over the entire pH range, suggesting that the presence of positively charged calcium neutralized some of the negative charge from silica. Zeta potential did not change significantly from 25 hours to 8 days.

Arsenic removal, or percentage of arsenic in solution sorbed to the iron hydroxide solid surface, followed the trends in zeta potential. Kinetics of sorption were also found to be important to arsenic removal. At pH 7, arsenic removal was greater than 80% in all solutions (Figure 2-2). While solutions with 40 mg/L silica removed slightly less arsenic, no significant difference with and without calcium was observed. At pH 8, silica interference to arsenic removal was evident. However, kinetics of silica solutions with and without calcium were very important at shorter times ( $< 100$  hours). At the first sampling event (@ 2 hours) iron without silica removed 100% of the arsenic, iron with silica only removed 48% of the arsenic, and iron with silica and calcium removed 83%

arsenic (Figure 2-2). By 4 days, arsenic removal leveled off at about 70% in both solutions with silica.

As pH increased from 9 to 12,  $\text{Fe}(\text{OH})_3$  alone removed less arsenic from solution, and kinetics became more important (i.e. more arsenic was removed with increasing reaction time). In the pH range of 9-12, more arsenic was sorbed to  $\text{Fe}(\text{OH})_3$  in silica solutions with the addition of calcium, as opposed to without calcium. In fact, arsenic removal at pH 11 and 12 in solutions with iron, silica, and calcium was not a function of reaction time and could even exceed arsenic removal in the solution with iron alone (Figure 2-2). At pH 9-12, it is interesting to note that when silica was present, arsenic removal was slightly better in the first sample (2 hrs) as compared to the second sample (4 hrs). It is also important to consider that some of the change in arsenic removal over longer time periods may reflect a change in the iron solid from an amorphous iron hydroxide to a more crystalline form, as well as the kinetics of arsenic sorption (21).

The most interesting effects of silica and calcium on arsenic sorption were observed in the pH range of 8.0-8.5. Therefore, a second experiment was conducted in this range with more frequent sampling at the start of the reaction. The same preformed  $\text{Fe}(\text{OH})_3$  was used, however, this experiment was different from the previous one in that solutions of arsenic, silica, and calcium were prepared and preformed iron dosed into the solutions to initiate the experiment. In addition, arsenic and silica were both exposed to the iron at the same time, as opposed to allowing the iron to contact silica for 2 hours before the addition of arsenic, as in the previous experiment. This is more representative of arsenic removal by sorption to iron flocs in a drinking water treatment plant.

At pH 8.5, nearly 100% of the arsenic in solution was sorbed to the iron within 30 minutes for solutions without silica (Figure 2-3). When 40 mg/L silica was present with iron, arsenic removal sharply increased to 48% during the first ten minutes of reaction, decreased to around 40% within one hour, and then slowly increased over time (about 1 week) to a constant value around 71% arsenic removal (Figure 2-3). In contrast, when calcium was added, arsenic removal peaked at 84% after just 10 minutes, followed by a

slow, steady decrease in removal to the same value as the solution without calcium. Note that the peak reflects the highest percent removal sampled, and perhaps not the highest actual percent arsenic removal possible given the rapid changes that were occurring in the solution. This result suggests that the effect of calcium in reducing silica interference to arsenic sorption would be most pronounced at very short reaction times. The sorption density of silica in this experiment increased over time to 0.45 mol Si/ mol Fe, which is consistent with nearly complete saturation of the surface with dimeric silica consistent with the model of Davis et al (15).

**Granular Media.** Granular media are commonly used in columns to remove arsenic from drinking water. While arsenic is removed by a similar mechanism (sorption) onto granular media as with amorphous ferric hydroxide, the two solid surfaces are quite different. Granular media is larger, porous, and relatively well aged, while ferric hydroxide is formed in-situ and the solid can change to a more crystalline structure over time. Thus, arsenic sorption in the presence of silica and/or calcium may behave differently with granular media than with amorphous oxides.

A series of batch experiments with granular ferric hydroxide (GFH) and activated alumina (AA) were conducted to investigate effects of silica, calcium, and kinetics on arsenic sorption onto granular media oxides. Two types of silica solutions were prepared for granular media experiments. The first silica solution was prepared at high concentration and high pH. The second ‘polymeric’ silica solution was prepared at lower concentration and lower pH, and contained a higher percentage of polymeric silica.

AA and GFH were tested at a level of 2 g dry media /L. In solutions without any silica or calcium, both types of granular media were nearly identical in arsenic removal with time (Figure 2-4). After 11 days 100% arsenic removal, or arsenic sorption, was achieved in these control solutions. Since bicarbonate was added in this experiment, additional control solutions were prepared without bicarbonate for comparison. The carbonate was found to have a slightly detrimental effect on arsenic removal; more noticeably with AA (Figure 2-4).

Arsenic removal using granular activated alumina was reduced by the presence of 40 mg/L silica or 40 mg/L 'polymeric' silica (Figure 2-5). The addition of calcium with silica improved arsenic removal to a level comparable to solutions without silica. Arsenic removal with granular ferric hydroxide was relatively insensitive to the presence of silica and/or calcium (Figure 2-5). Thus, the performance of AA appears to be more susceptible to solution chemistry.

The silica remaining over time in the granular media solutions dramatically decreased as compared with the amorphous iron oxide experiments, since the 2 g porous granular media could adsorb much more silica from solution. After 11 days, the soluble silica decreased from the initial 40 mg/L SiO<sub>2</sub> to 6 mg/L SiO<sub>2</sub> in all GFH solutions (Figure 2-6). A similar decrease of silica in solution was observed with AA; however, silica dosed in the polymeric form only decreased to 23 mg/L after 11 days reaction (Figure 2-6). Additionally, the corresponding soluble aluminum in the AA polymeric silica solution was 1.3 mg/L as compared to 0.2-0.3 mg/L soluble aluminum in all other AA solutions. This suggests polymeric silica may play a role in dissolving aluminum, which in turn might somehow hinder soluble arsenic removal from solution. This result also demonstrates the importance of the method in which silica is prepared in results obtained.

Future work should examine the effects of granular media pre-exposure to silica and/or calcium for one week before the start of kinetic experiments. In addition, the differences between experiments discussed here, where the silica concentration in solution decreased significantly over time due to sorption to the granular solid, and experiments where a constant concentration of silica is maintained in solution should be examined. This approach would illustrate the extent to which silica concentration in solution controls arsenic sorption and also provide insight into some differences between sorption behavior in batch and in a column.

## CONCLUSIONS

- At pH 8.5, calcium dramatically improved arsenic sorption to amorphous iron hydroxide in the presence of silica over short reaction times (< 4 hours), but had no long-term advantage. This could have implications for coagulation-based drinking water treatment processes.
- Silica reduced arsenic sorption to activated alumina, however, addition of calcium with silica eliminated the interference.
- Activated alumina was more sensitive to solution chemistry as compared to granular ferric hydroxide.
- Less polymeric silica sorbed to activated alumina than non-polymeric silica. The polymeric silica also dissolved aluminum from the AA.

## ACKNOWLEDGEMENT

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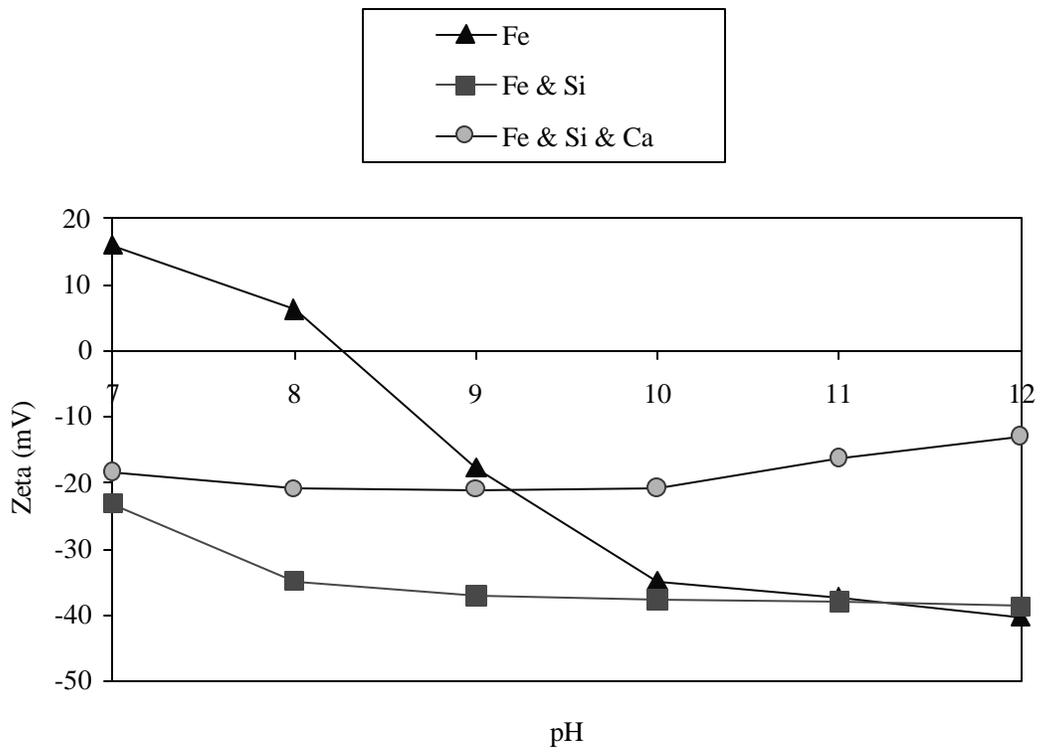
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**Table 2-1. Relevant kinetic findings for arsenic sorption with and without silica and/or calcium.**

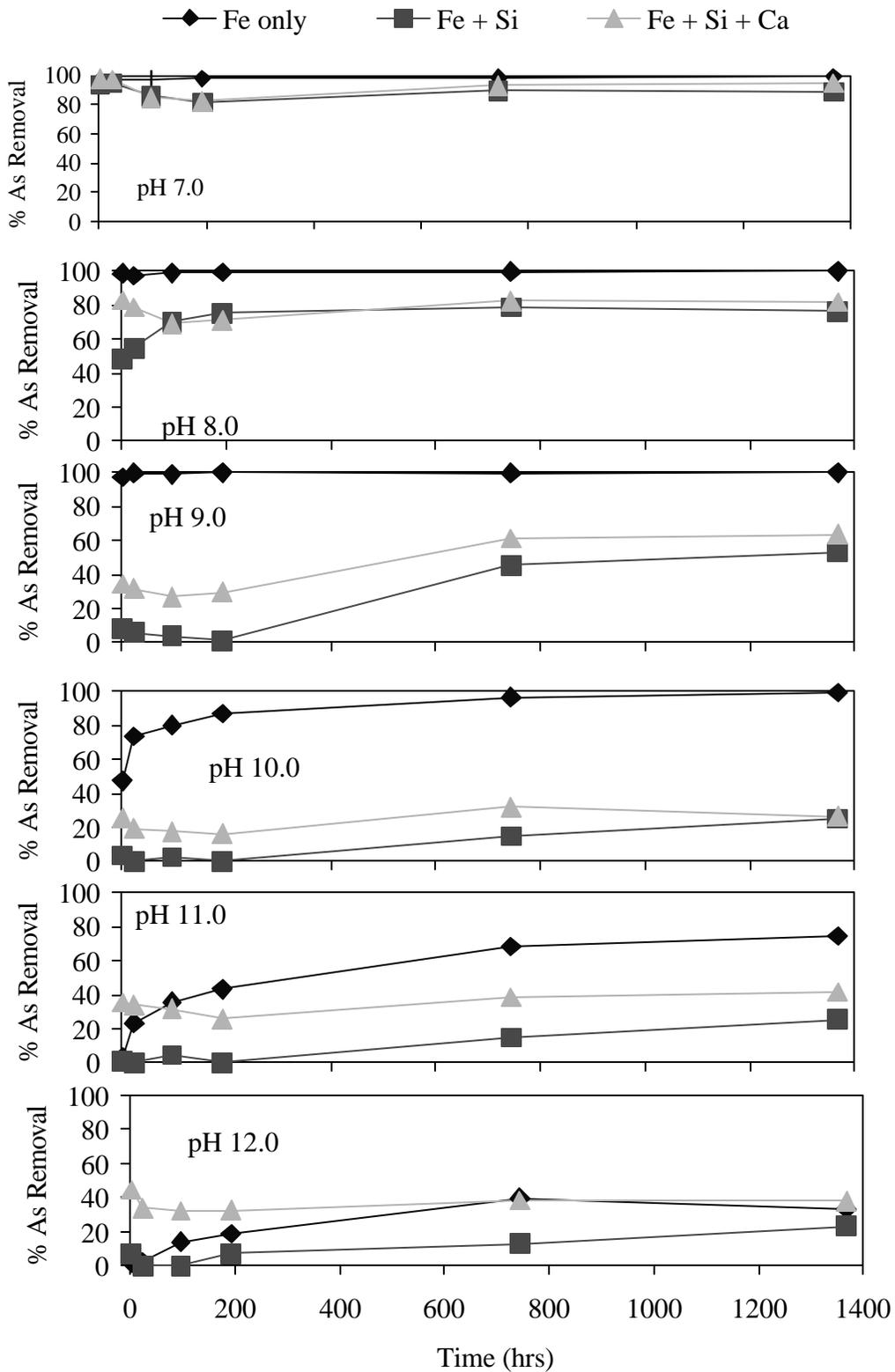
| Result  | Reaction Time      | pH               | Sorbent                                   | [As (V)]             | [SiO <sub>2</sub> ] | [Ca]                         | [Mg]   | Ref. |
|---|--------------------|------------------|---|----------------------|---------------------|------------------------------|--------|------|
| 90% of max adsorption @ 1hr;<br>99% of max adsorption @ 4hrs  | 1-24 hours         | 4.0, 8.0,<br>9.9 | 4.45 mg/L am-<br>Fe(OH) <sub>3</sub>      | 50-1000<br>ug/L      |                     |                              |        | 16   |
| No change in residual arsenic<br>after 50 seconds rapid mixing  | 0-10 min           | 6-7              | 2.5 mg/L Fe<br>coagulant                  | 24 ug/L              | 52.0<br>mg/L        | 13.9<br>mg/L                 | 3 mg/L | 1    |
| Dissolved As concentration<br>constant from 1-60 min.   | 1 min-1 hr         | 7-10             | 1.4 mg/L<br>hydrous ferric<br>oxide (HFO) | 37.5 ug/L            | 11 mg/L             |                              |        | 4    |
| Slow adsorption of As continued<br>for at least 192 hr  | 5 min-192<br>hrs   | 8.0, 9.0         | 5e-4 M<br>preformed Fe                    | 7.5 mg/L             |                     |                              |        | 17   |
| Batch equilibrium reached by 7<br>days  | 24-336 hrs         |                  | 0.5 - 2.5 g/L<br>AA                       | 5.0 mg/L             |                     |                              |        | 11   |
| Batch equilibrium reached in 2<br>days  | 24-168 hrs         | 7.7              | 1.25 g/L AA                               | 500 ug/L             |                     |                              |        | 12   |
| 50% arsenic removal within 10<br>minutes of reaction  | 10 min-50<br>hrs   | 6.5              | 2 g/L AA                                  | 4 mg/L               |                     |                              |        | 18   |
| SiO <sub>2</sub> interference to As removal   | 20 sec             | 6.5-8.5          | 1.5 mg/L Fe                               | 20 ug/L              | 52.0<br>mg/L        | 13.9<br>mg/L                 | 3 mg/L | 1    |
| SiO <sub>2</sub> interference to As removal   | 10 min             | 7-10             | 1.4 mg/L HFO                              | 37.5 ug/L            | 11 mg/L             |                              |        | 4    |
| SiO <sub>2</sub> interference to As(V)<br>removal   | 200 hr             | 7-12             | 1.0mM<br>preformed Fe                     | 4 mg/L               | 1.8 mM              |                              |        | 3    |
| Pre-exposure of SiO <sub>2</sub> to<br>preformed ferrihydrite decreases<br>As sorption                          | 24 hrs             | 4-9              | 0.01M Fe                                  | 75 mg/L              | 0.01 M              |                              |        | 10   |
| Ca increases As sorption  | 2 hrs              | 9.0              | 50 uM HFO                                 | 35 ug/L              |                     |                              |        | 9    |
| Adverse effect of SiO <sub>2</sub> on As<br>sorption reduced with Ca and<br>Mg                                  | 1 hr               | 7-10             | 1 mg/L Fe                                 | 100 ug/L             | 4.5<br>mg/L         | 18 mg/L                      | 7 mg/L | 2    |
| Ca increases As removal for<br>adsorption/ coagulation  | 2 hrs / 46<br>min. | 9.0              | 4.9 mg/L<br>FeCl <sub>3</sub>             | 35 ug/L /<br>20 ug/L |                     | 120<br>mg/L                  |        | 7    |
| Ca and Fe together produced<br>lower residual As than when<br>either was used separately at<br>equivalent conc. | ?                  | 7-9.5            | 720 mg/L<br>ferrihydrite                  | 200 mg/L             |                     | Ca:Fe =<br>0.05,<br>0.1, 0.2 |        | 10   |

**Table 2-2. Potential kinetic factors in arsenic removal from drinking water.**

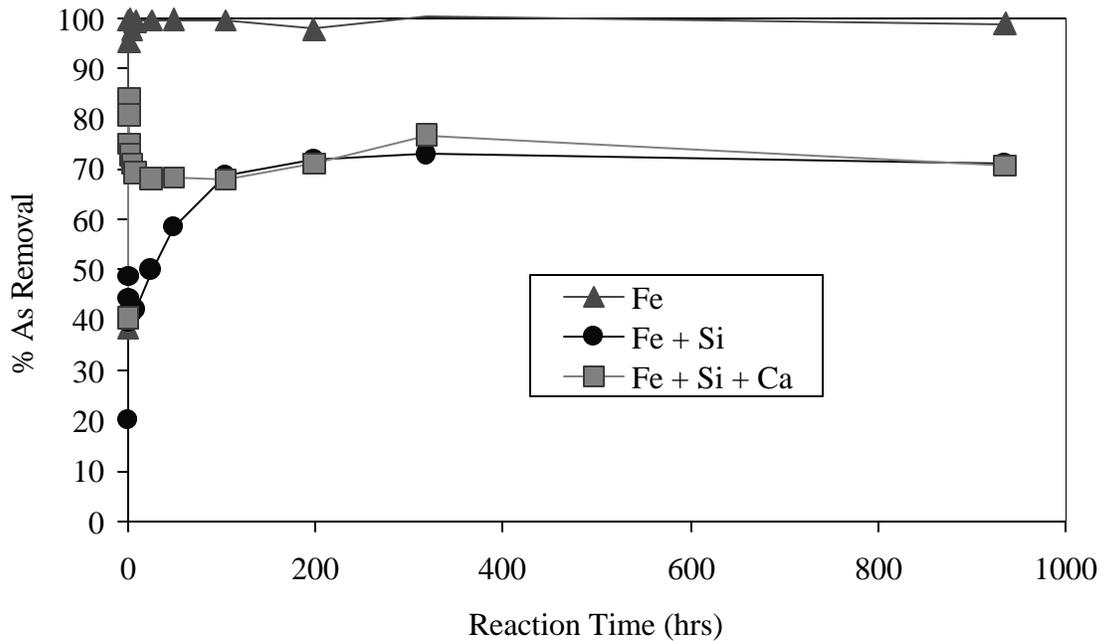
| <b>Factor</b>                   | <b>Relevant Timespan</b> | <b>Process Affected</b>       | <b>Reference</b> |
|---------------------------------|--------------------------|-------------------------------|------------------|
| Precipitation/<br>Agglomeration | Seconds – minutes        | Coagulation/<br>Sedimentation | 19               |
| Sorption                        | Seconds - days           | All                           | 1, 7, 11, 13, 17 |
| Aging of Solid                  | Hours - months           | All except granular<br>media  | 21               |
| Diffusion                       |                          | Porous and granular<br>media  | 20               |
| Silica Fouling                  | Weeks                    | Granular media                | 5                |



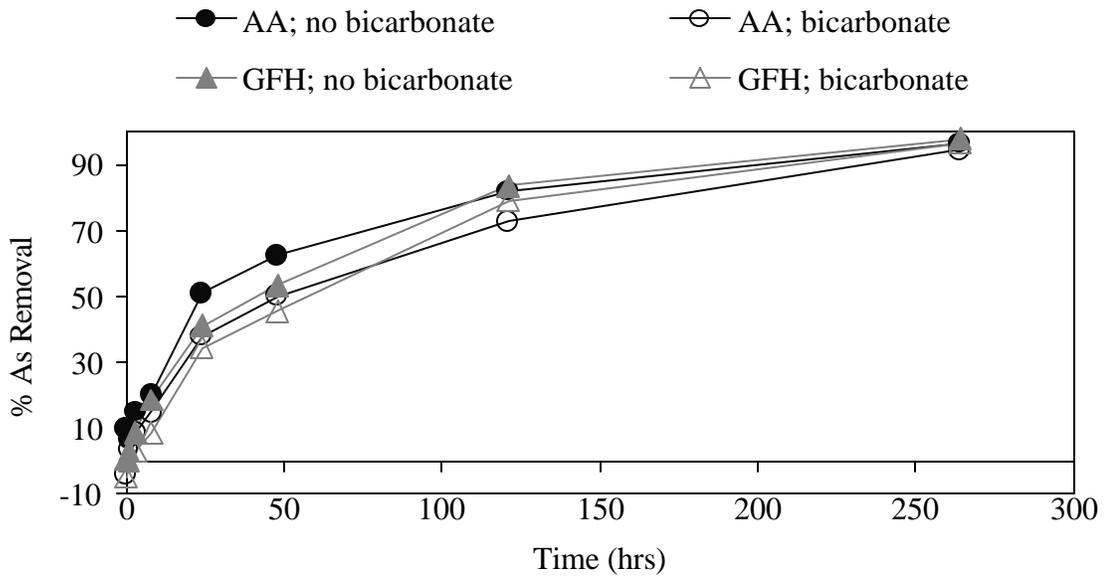
**Figure 2-1. Zeta potential over pH 7-12. Initial As = 100 ppb; Fe = 20 mg/L; SiO<sub>2</sub> = 40 mg/L; Ca = 10 mg/L**



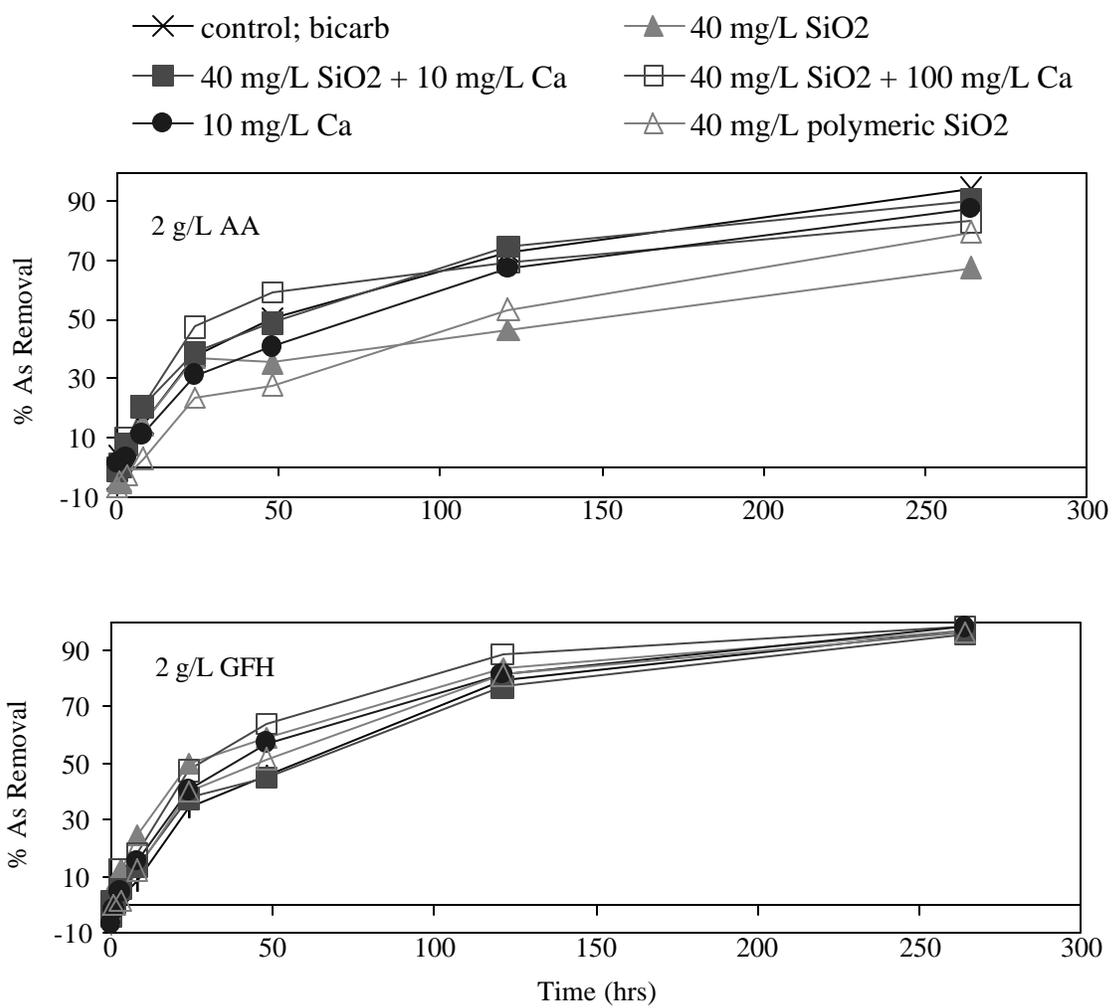
**Figure 2-2. Percent arsenic removal over time for pH 7-12 with amorphous Fe(OH)<sub>3</sub>. Initial arsenic = 100 ppb; Fe = 20 mg/L; SiO<sub>2</sub> = 40 mg/L; Ca = 10 mg/L**



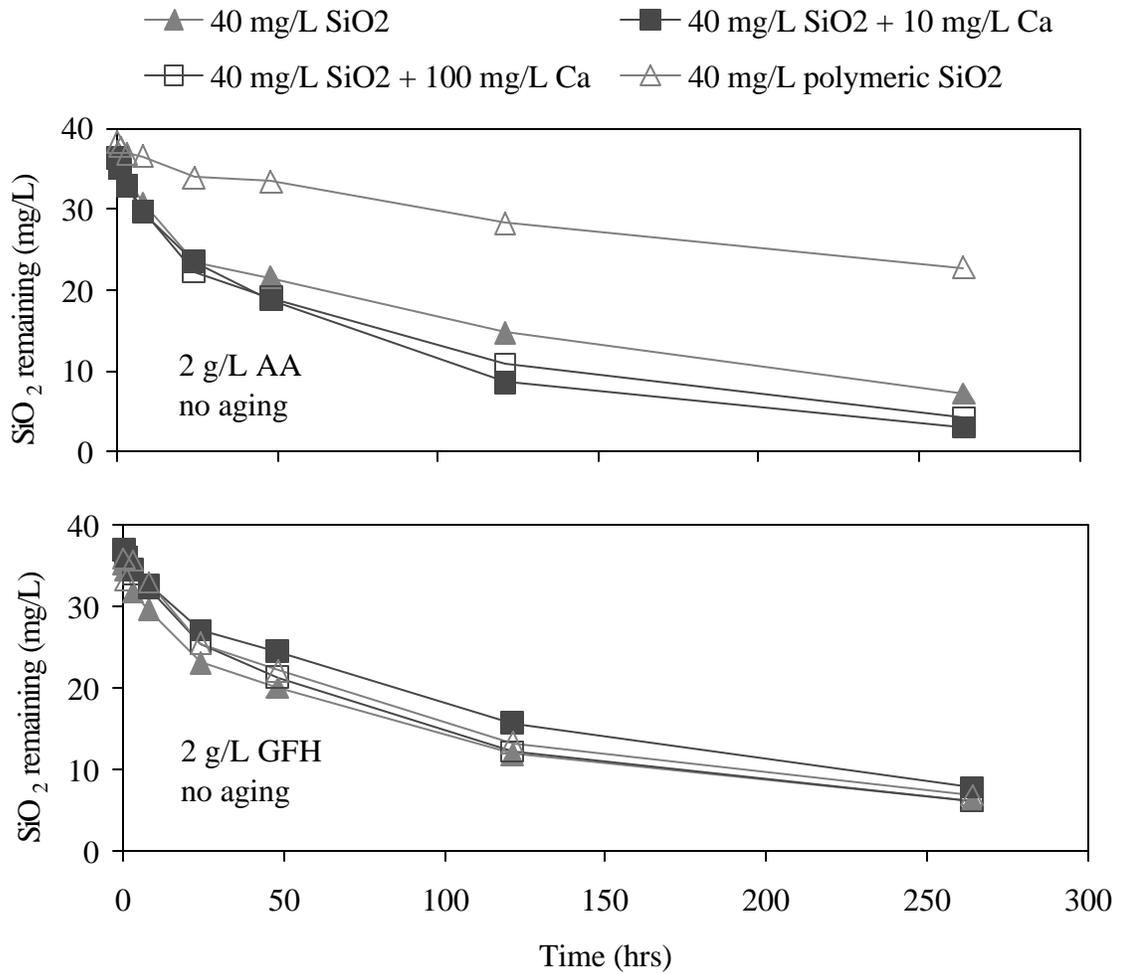
**Figure 2-3. Percent arsenic removal over time with amorphous  $\text{Fe}(\text{OH})_3$ . pH = 8.5; initial arsenic = 100 ppb; Fe = 20 mg/L;  $\text{SiO}_2$  = 40 mg/L; Ca = 10 mg/L**



**Figure 2-4. Percent arsenic removal over time for granular media control solutions. pH = 8.5; initial As = 500 ppb; CaCO<sub>3</sub> = 1mM**



**Figure 2-5. Arsenic removal over time for activated alumina (top) and granular ferric hydroxide (bottom). pH = 8.5; initial As = 500 ppb; CaCO<sub>3</sub> = 1 mM**



**Figure 2-6. Silica remaining in solution over time. pH = 8.5; initial arsenic = 500 ppb**

## VITA

Sheryl Dianna Smith was born on June 5, 1977 in Cumberland, Maryland. She attended Allegany High School and graduated in 1995. Upon graduation she enrolled at West Virginia University in Morgantown, WV. Sheri received a Bachelor's degree in Civil Engineering from WVU in 1999 and was named outstanding civil engineering senior. In August 1999 she began work on her Master's degree in environmental engineering at Virginia Tech. The first portion of her thesis work will be presented in June 2001 at the AWWA National Conference.