

## Research Paper

# The influence of silica and calcium on arsenate sorption to oxide surfaces

Sheryl D. Smith and Marc Edwards

### ABSTRACT

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 pH, and to closely monitor the progress of sorption in these systems. At pH 8.5, calcium dramatically increased arsenic sorption to amorphous iron hydroxide in the presence of silica over relatively short reaction times, but the effects gradually disappeared over longer reaction times. Additionally, batch tests indicated that activated alumina granular media was more sensitive to silica interference than granular ferric hydroxide. However, relatively low levels of calcium could reduce silica interference to arsenic sorption onto activated alumina. While future confirmation research is needed, severe silica interference can occur in practice due to exclusion of arsenate from interstitial granular media pores.

**Key words** | adsorption, arsenic, kinetics, silica

**Sheryl D. Smith**  
CDM 5400 Glenwood Avenue, Suite 300,  
Raleigh, NC, 27612,  
USA

**Marc Edwards** (corresponding author)  
Department of Civil Engineering,  
Virginia Tech,  
Blacksburg, VA, 24061-0246,  
USA

### INTRODUCTION

Arsenic can be effectively removed from water by sorption onto amorphous or granular iron or aluminum oxides, but in some circumstances significant interferences have been noted in the presence of competing anions such as silica (Tong 1997; Ghurye *et al.* 1998; Swedlund & Webster 1999; Davis *et al.* 2001; Meng *et al.* 2000; Holm 2002). Meng *et al.* (2000) also noted that the extent of silica interference was reduced in the presence of calcium and magnesium, consistent with other evidence suggesting that calcium may help eliminate competitive effects of anionic NOM on arsenic sorption (Hering & Elimelech 1996). Enhancement of arsenic sorption in the presence of calcium has also been noted for systems without silica (Misra & Tiwari 1963; Emmett & Khoe 1994; Wilkie & Hering 1996). The national arsenic occurrence database (Frey & Edwards 1997; Chen *et al.* 1999) indicates that waters with higher arsenic content also have a wide range of silica (0.8–62 ppm as  $\text{SiO}_2$ ) and calcium (1.5–211 ppm  $\text{Ca}^{2+}$ ) as co-occurring ions.

With respect to the kinetics of arsenate sorption onto oxide surfaces, “equilibrium” has reportedly been reached after reaction times ranging from 50 s (Tong 1997) to 200 h (Swedlund & Webster 1999) for amorphous iron hydroxides. Highly porous sorbents such as activated alumina have required 2–7 d (Rosenblum & Clifford 1984) since diffusion limitations are likely significant (Table 1). However, recent studies have indicated that, when silica was present, arsenate sorption to goethite increased slowly over reaction times longer than 1 week (Waltham & Eick 2002). Most studies examining sorption kinetics have evaluated only one or two representative water conditions in the preliminary stages of research to pick a representative time to achieve “equilibrium” (Table 1), and impacts of water quality constituents such as silica and calcium were not systematically examined.

Considering that conventional processes used for arsenate removal in drinking water may include various

**Table 1** | Summary of studies that examined kinetics of arsenate sorption to oxides

Result	Reaction time	pH	Sorbent	[As (V)]	[SiO <sub>2</sub> ]	[Ca]	[Mg]	Reference
90% of max adsorption @ 1 h; 99% of max adsorption @ 4 h	1–24 h	4.0, 8.0, 9.9	4.45 ppm am-Fe(OH) <sub>3</sub>	50–1000 µg/L				Pierce & Moore (1982)
No change in residual arsenic after 50 s rapid mixing	0–10 min	6–7	2.5 ppm Fe coagulant	24 µg/L	52.0 ppm	13.9 ppm	3 ppm	Tong (1997)
Dissolved As concentration constant from 1–60 min	1 min–1 h	7–10	1.4 ppm hydrous ferric oxide (HFO)	37.5 µg/L	11 ppm			Holm (2002)
Slow adsorption of As continued for at least 192 hr	5 min–192 hrs	8.0, 9.0	5e-4 M preformed Fe	7.5 ppm				Fuller <i>et al.</i> (1993)
Batch equilibrium reached by 7 d	24–336 h		0.5–2.5 g/L AA	5.0 ppm				Rosenblum & Clifford (1984)
Batch equilibrium reached in 2 d	24–168 h	7.7	1.25 g/L AA	500 µg/L				Wang <i>et al.</i> (2000)
50% arsenic removal within 10 min of reaction	10 min–50 h	6.5	2 g/L AA	4 ppm				Gupta & Chen (1978)
SiO <sub>2</sub> interference to As removal	20 s	6.5–8.5	1.5 ppm Fe	20 µg/L	52.0 ppm	13.9 ppm	3 ppm	Tong (1997)
SiO <sub>2</sub> interference to As removal	10 min	7–10	1.4 ppm HFO	37.5 µg/L	11 ppm			Holm (2002)
SiO <sub>2</sub> interference to As(V) removal	200 h	7–12	1.0 mM preformed Fe	4 ppm	1.8 mM			Swedlund & Webster (1999)
Pre-exposure of SiO <sub>2</sub> to preformed ferrihydrite decreases As sorption	24 h	4–9	0.01 M Fe	75 ppm	0.01 M			Emett & Khoe (1994)
Ca increases As sorption	2 h	9.0	50 µM HFO	35 µg/L				Wilkie & Hering (1996)
Adverse effect of SiO <sub>2</sub> on As sorption reduced with Ca and Mg	1 h	7–10	1 ppm Fe	100 µg/L	4.5 ppm	18 ppm	7 ppm	Meng <i>et al.</i> (2000)

Table 1 | (continued)

Result	Reaction time	pH	Sorbent	[As (V)]	[SiO <sub>2</sub> ]	[Ca]	[Mg]	Reference
Ca increases As removal for adsorption/coagulation	2 h/46 min	9.0	4.9 ppm FeCl <sub>3</sub>	35 µg/L/20 µg/L		120 ppm		Hering & Elimelech (1996)
Ca and Fe together produced lower residual As than when either was used separately at equivalent concentrations	?	7 – 9.5	720 ppm ferricydrite	200 ppm		Ca:Fe = 0.05, 0.1, 0.2		Emett & Khoe (1994)

combinations of sorption, co-precipitation and/or coagulation reactions, it is instructive to consider the range of kinetic phenomena that might be anticipated to impact removal efficiency. In cases where arsenate is removed by coagulation and filtration, rates of metal precipitation and particle agglomeration are relevant, since very small colloids with sorbed arsenate might pass through solid-liquid separation steps (Edwards 1994). The rate of arsenic sorption to oxide surfaces could affect removals achieved in processes with relatively short contact times, such as coagulation-microfiltration or granular oxide columns operated at high loading rates. Aging of amorphous solids to more crystalline structures can reduce the surface area available for sorption and therefore decrease arsenic removal, but this is not likely to be a factor in the case of granular media which are presumably already aged (Anderson & Benjamin 1985). Analogies to activated carbon sorption suggest that diffusion from bulk solution to internal surfaces can pose a significant kinetic limitation when using micro-porous media such as activated alumina or granular ferric hydroxide to remove arsenic (Snoeyink 1990).

The issue of silica interference is deserving of special consideration, since the molar ratio of silica:arsenate approaches 15,000:1 in some waters, and arsenate sorption is known to be highly dependent on the time surfaces are exposed to silica (Davis & Edwards 2001). In situations where oxyhydroxide surfaces are formed *in situ*, silica and arsenic initially have equal access to the oxyhydroxide surface (Figure 1). After a period of minutes, silica monomers and dimers likely coat the accessible surface, creating an anionic surface charge and competing with

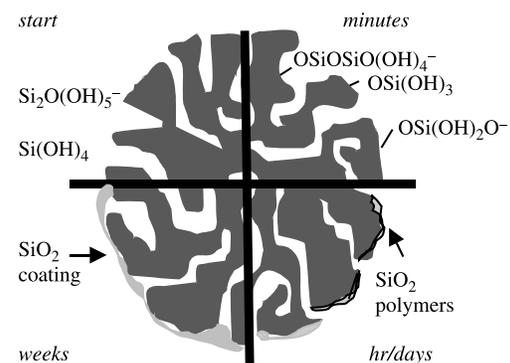


Figure 1 | Conceptualisation of possible phases in silica sorption to porous media oxyhydroxide surfaces. Similar reactions are occurring within pores but they cannot be clearly drawn at this scale.

arsenate for sorption sites. The size of monomers and dimers is of the order of 0.1 nm, which is much smaller than typical activated alumina pore sizes (of the order of 10 nm) and physical blockage of internal pores is unlikely to be an issue at this stage.

On the other hand, the characteristic double layer thickness is 9 nm in 0.001 M of a 1:1 electrolyte. Diffusion of anionic arsenate into internal pores would therefore be hindered by a negative surface charge due to charge exclusion. Considering a double layer compression mechanism alone, 0.01 M of  $\text{Ca}^{+2}$  would reduce the characteristic double layer thickness for an anionic surface to about 1.5 nm, which would help to reduce charge exclusion and make internal pores more accessible. Eventually, over a period of days and weeks, silica polymers and amorphous solid phases gradually form on the oxyhydroxide surface that can almost completely prevent arsenate removal (Davis & Edwards 2001). Silica polymers and gels can easily range to 100 nm (Iler 1979) and sorption of polymers or formation of surface precipitates could block access to internal pores of the activated alumina physically or by charge exclusion. While similar reactions undoubtedly occur within the pores, since >99% of granular media surface area is typically internal, reactions occurring on the outer surface that prevent access to internal surfaces may be disproportionately important.

This work was aimed at exploring the impact of silica and calcium on aspects of arsenate removal to oxide surfaces under conditions relevant in engineered systems.

## MATERIALS AND METHODS

Three experiments were designed to investigate the effects of silica and calcium concentration on arsenic sorption and ultimate sorption density for pre-formed amorphous iron hydroxides or granular media. The sequence of silica and arsenic addition, as well as solution composition, were manipulated to examine characteristic situations depicted in Figure 1.

### Sorption to 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 ppm as Fe acidified with  $1 \times 10^{-2}$

M  $\text{HNO}_3$ ) to 6.0 as described in Davis *et al.* (2001). The solids were aged for approximately 12 h on an orbital shaker.

Six solutions were prepared with distilled deionized water in 250 mL plastic bottles. The preformed  $\text{Fe}(\text{OH})_3$  solution was dosed into the containers to obtain a concentration of 20 ppm Fe, and pH was adjusted to 7.0, 8.0, 9.0, 10.0, 11.0 or 12.0. The solutions then equilibrated on an orbital shaker at this target pH ( $\pm 0.2$  units) for 2 h. Arsenate was then dosed from a stock solution of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (500 ppm as As) to provide a concentration of 100 ppb As. Samples were collected after 2 h, 1 d, 4 d, 8 d, 1 month and 2 months. Zeta potential measurements were also taken at 1 d, 4 d and 8 d. pH was re-adjusted to the target value throughout the experiment.

An 8,000 ppm as  $\text{SiO}_2$  solution was made with  $\text{Na}_2\text{SiO}_3$  salt, resulting in a pH of approximately 12.8. According to Davis *et al.* (2001) this solution contains a low percentage of polymerised silica as measured by molybdate reactivity.

In some experiments, the stock solution of  $\text{Na}_2\text{SiO}_3$  (8,000 ppm as  $\text{SiO}_2$ ) was added to the pre-formed iron hydroxide to a final concentration of 40 ppm  $\text{SiO}_2$ . The solution was equilibrated for 2 h. Thereafter, arsenate was added to initiate the experiment. In another case, 20 ppm Ca (from a stock solution of 0.1 M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) was added 5 min before the arsenate.

### Amorphous iron hydroxide – kinetics of sorption

All stock solutions and doses were the same as those used in the first set of experiments with 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. The preformed aged  $\text{Fe}(\text{OH})_3$  stock was dosed into all arsenic solutions to a final concentration of 20 ppm Fe. Samples were collected at various intervals from 10 min to 6 weeks. The pH was maintained throughout the experiment by the addition of small amounts of  $\text{HNO}_3$  or  $\text{NaOH}$ , with typical control of  $\pm 0.2$  units of the target value.

### Granular media

Activated alumina and granular ferric hydroxide were tested in batch using protocols similar to those for amorphous

solids at pH 8.5. Arsenic removal was compared for the following six combinations of silica and calcium in the water: 1) 0 ppm SiO<sub>2</sub> and 0 ppm Ca; 2) 40 ppm SiO<sub>2</sub> and 0 ppm Ca; 3) 40 ppm SiO<sub>2</sub> and 10 ppm Ca; 4) 40 ppm SiO<sub>2</sub> and 100 ppm Ca; 5) 0 ppm SiO<sub>2</sub> and 10 ppm Ca; 6) 40 ppm “polymeric” SiO<sub>2</sub> and 0 ppm Ca.

Doses of dry Alcan CPN activated alumina or GEH Wasserchemie GmbH granular ferric hydroxide were dosed at 2 g dry media/L. It is understood that water may be still associated with each of these media when shipped and no further attempt was made to remove this water. Each batch of media was washed twice with 200 mL aliquots of distilled deionised water. Media was added to solutions containing 1 mM sodium bicarbonate (for buffering) and 10 mM NaCl prepared using distilled deionised water in 500 mL plastic bottles. The bottles were placed on an orbital shaker for the duration of the experiment. Silica and/or calcium was added to each bottle, the pH was adjusted to 8.5 and the solutions were equilibrated for a period of 0 min or 1 week. Thereafter, kinetics of arsenate sorption were tracked after dosing arsenate at an initial concentration of 500 ppb. Samples were collected at various intervals from 5 min to 11 d. The solution volume decreased up to 16% due to collected samples and no attempt was made to replace the solution. The pH was maintained at the target value ( $\pm 0.25$  pH units) throughout the experiment.

Experimental variations were made to more closely examine silica behavior in tests with granular media. By diluting the original stock solution to 800 ppm as SiO<sub>2</sub>, then adjusting the pH to 8.5 and aging it for approximately 24 h, a sample of “polymeric” silica was produced in which 76–87% of the total silica was non-molybdate reactive. Less than 15% of this total polymeric silica reverted to monosilicic acid after dilution to 40 ppm and one week holding time at pH 7.0. No attempts were made to track changes in polymeric silica during the experiments. Silica concentrations for this solution are reported in terms of total silica present. Since it was determined that silica was adsorbing rapidly to the iron in batch tests with granular media, experiments were conducted in which silica was analysed every one or two days, and then restored to the initial concentration by small additions from the stock solution. This procedure maintained silica to within  $\pm 10\%$  of the 40 ppm initial concentration.

## Analysis

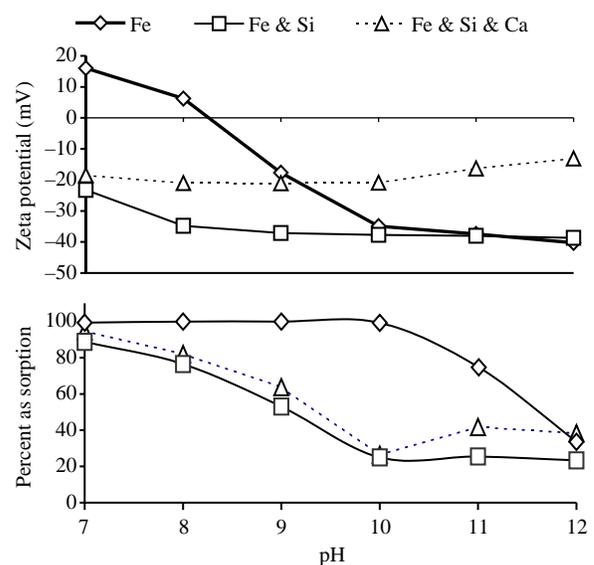
Samples from all experiments were first filtered through a 0.45  $\mu\text{m}$  pore size nylon disposable filter. They were then analysed for soluble arsenic, silicon, calcium, iron or aluminum on a JY Ultima Inductive Coupled Plasma – Emission Spectrometer (ICP-ES) according to Standard Method 3120B using continuous hydride generation (*Standard Methods 1998*). A Malvern ZetaSizer 3000HS was used to measure zeta potential.

## RESULTS AND DISCUSSION

Experimental results are organised into two sections based on the sorbent utilised.

### Amorphous iron hydroxide

The initial zeta potential of Fe(OH)<sub>3</sub> suspensions decreased from 15 mV to –39 mV as the pH increased from 7 to 12, with a PZC at about pH 8.2 (*Figure 2*). In contrast, suspensions exposed to 40 ppm silica for 2 h had a zeta potential less than –24 mV, regardless of pH, indicating that sorption of negatively charged silica species dramatically altered surface charge. When 10 ppm calcium was

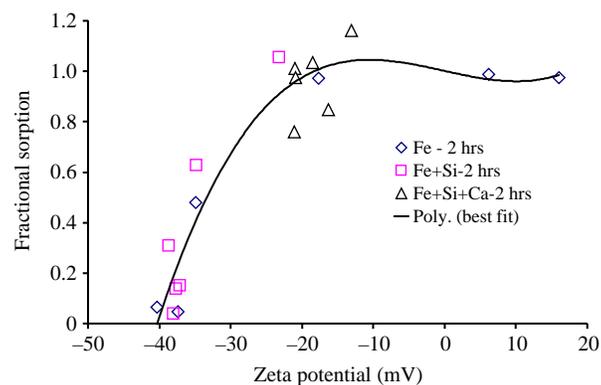


**Figure 2** | Zeta potential over pH 7–12 (upper part). Equilibrium sorption after 1368 h (lower part). Initial As = 100 ppb; Fe = 20 mg/L; SiO<sub>2</sub> = 40 mg/L; Ca = 10 mg/L.

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. Since measurements of sorbed silica were approximately constant in the solutions with and without calcium, it is clear that the positively charged calcium reduced much of the negative silica surface charge due to double layer compression, sorption to the iron surface or by complexation with sorbed silica (Iler 1979). Zeta potential did not change significantly in this system from 25 h to 8 d.

After 100 ppb arsenate was spiked into the suspensions described in Figure 2, arsenate removal after 1,368 h was found to decrease as zeta potential became less positive, consistent with overly simplistic electrostatic considerations for sorption of anionic species to solid surfaces. The final concentration of adsorbed arsenic was much lower in the presence of silica. For example, at pH 10, essentially 100% arsenate was removed in the absence of silica, whereas only 26% of the arsenate was removed in the presence of 40 mg/L silica. In general, calcium had only slight beneficial impacts on arsenate removal.

The approach to equilibrium was controlled by the zeta potential (Figure 3). Specifically, if the zeta potential was  $-20$  mV or higher, 80% or more of the arsenic ultimately sorbed at 1368 h had already sorbed after 2 h. In contrast, if the zeta potential was less than  $-35$  mV, less than 50% of the arsenic sorbed at 1368 h was sorbed at 2 h. From this perspective, calcium had a major benefit on arsenate sorption, since it maintained a more positive or less negative zeta potential (upper part, Figure 2).

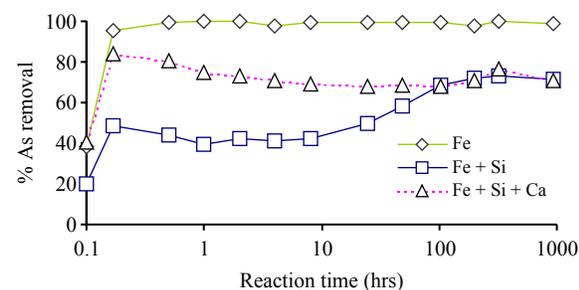


**Figure 3** | Fractional sorption (As sorbed at 2 h/As sorbed at 1368 h) versus zeta potential. Initial As = 100 ppb; Fe = 20 mg/L; SiO<sub>2</sub> = 40 mg/L; Ca = 10 mg/L.

The most interesting effects of silica and calcium on arsenic sorption were observed in the pH range of 8.0–9.0. Therefore, a second experiment was conducted at pH 8.5 with more frequent sampling at the start of the reaction. The same preformed Fe(OH)<sub>3</sub> was used. However, in this experiment the arsenic, silica and calcium were added to the solution first, after which time preformed iron was dosed. This approach exposed the arsenic and silica to the iron at the same time, as opposed to allowing the iron to contact silica for 2 h before the addition of arsenic, as in the previous experiment, consistent with the conceptualisation at  $t = 0$  in Figure 1. This approach is more representative of arsenic removal in engineered systems.

At pH 8.5, nearly 100% of the arsenate was sorbed to the iron after 1 h in solutions without silica (Figure 4). When 40 ppm silica was present with iron, arsenic removal reached 48% after 10 min of reaction, decreased to 40% after one hour and then slowly increased over time (about 1 week) to a constant value of around 71% arsenic removal (Figure 4). In contrast, when calcium was present with the silica, arsenate sorption initially tracked that of the system without silica. The peak removal was 84% after just 10 min, followed by a slow, steady decrease in removal to the same value as in the solution without calcium. Note that the peak reflects the highest percent removal sampled, and perhaps not the highest actual percent arsenic sorbed in the test. Clearly, calcium enhances arsenate removal at very short reaction times, but at longer reaction times it has little effect.

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. But in each case, more than 95% of the initial silica remained soluble throughout the test, or less



**Figure 4** | Percent arsenic removal over time with amorphous Fe(OH)<sub>3</sub>. pH = 8.5; initial As = 100 ppb; Fe = 20 mg/L; SiO<sub>2</sub> = 40 mg/L; Ca = 10 mg/L.

than 5% of the silica present had sorbed to the surface. These short term impacts of silica and calcium on removal of arsenate were repeated several times, and the result in Figure 4 was consistently observed.

### Granular media

Granular media are commonly packed into columns and used 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.

Batch experiments with granular ferric hydroxide (GFH) and activated alumina (AA) were conducted to develop preliminary insights into arsenic removal in the presence of silica and calcium at pH 8.5. In solutions without any silica or calcium, the two media performed similarly in removing arsenic as a function of time (upper part, Figure 5 and upper part, Figure 6). In the control, 50% of the arsenic was removed after 50 h in the case of AA whereas about 60 h were required for GFH. Nearly 100% arsenate removal was achieved in 11 d in both cases. Control experiments with bicarbonate indicated only a slight interference to arsenic removal (data not shown).

Several variations on these granular media experiments were then conducted. First, the granular media was added to a solution containing silica and/or calcium, and arsenic was dosed immediately thereafter (upper parts, Figures 5 and 6). In another test, the granular media was pre-exposed to the silica and/or calcium solution for 1 week prior to addition of arsenic (middle parts, Figures 5 and 6).

Arsenic removal trends were similar for granular activated alumina with and without pre-exposure to silica (upper part, Figure 5 versus middle part, Figure 5). Counter-intuitively, interference from silica was most significant in the case without silica pre-exposure. This is most likely due to extensive removal of silica from solution during the test (lower part, Figure 5). After 11 d, in some cases, silica levels in the water dropped from 40 to 5 mg/L. Because the

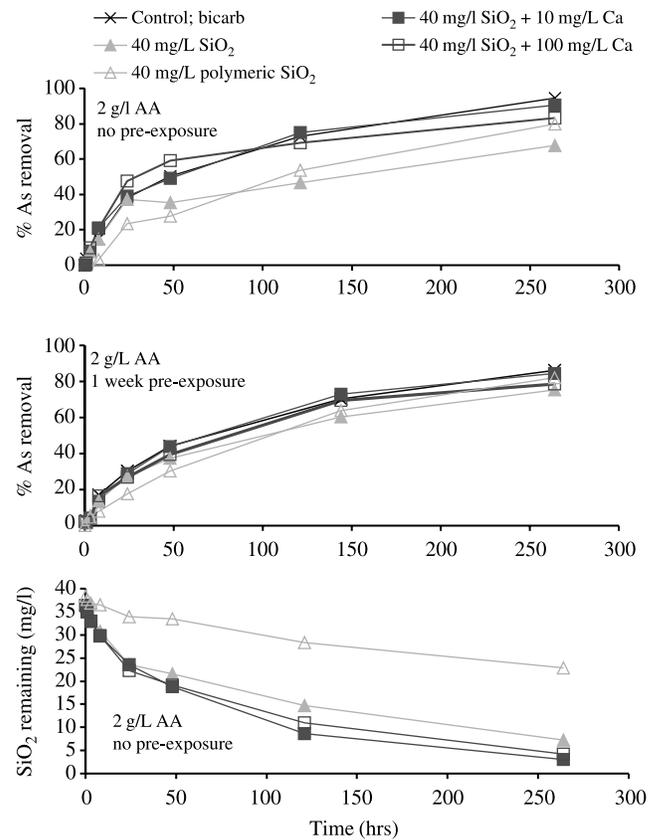
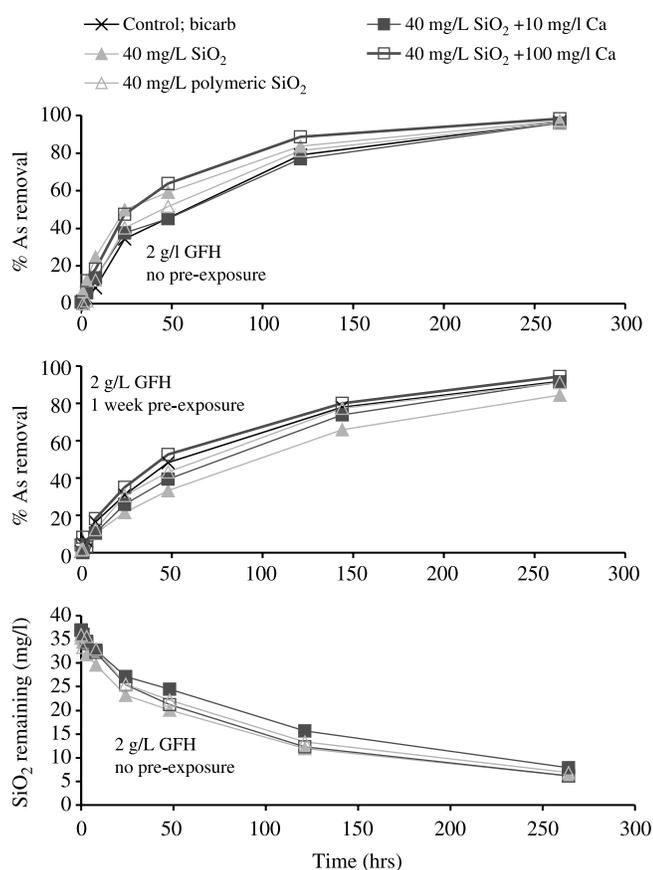


Figure 5 | Arsenic removal and silica remaining in solution over time with activated alumina. pH = 8.5; initial As = 500 ppb; 1 mM NaHCO<sub>3</sub>.

concentration of dimeric silica roughly increases with the square of the silica concentration (i.e. formation of dimeric silica:  $2\text{Si}(\text{OH})_4 \leftrightarrow \text{Si}_2\text{O}(\text{OH})_3^- + \text{H} + \text{H}_2\text{O}$ ) at constant pH, there would be as much as 64 times less dimeric silica in the bulk water in water at the end of the test (after 11 d) relative to the start of the test. If the outer surfaces of the granular media were in equilibrium with this water, interferences arising from sorbed polymers and dimers could actually decrease markedly during the test. The lower concentration of silica in bulk solution and on the outermost surfaces is compensated by the gradual transport of the silica to internal surfaces, which have lower silica sorption densities relative to the bulk solution. Similar transport of silica and arsenate (from external to internal granular media surfaces) can play a role in the “recovery” of arsenate removal capabilities during periods when columns are allowed to sit inactive.



**Figure 6** | Arsenic removal and silica remaining in solution over time with granular ferric hydroxide. pH = 8.5; initial As = 500 ppb; 1 mM NaHCO<sub>3</sub>.

After the one week pre-exposure (middle part, Figure 5), the silica concentration had already dropped to 5 mg/L before the arsenate was added ( $t = 0$  in middle part, Figure 5), and after the arsenate was added it dropped even further. The net result is that reduced interference with pre-exposure is not surprising given extensive removal of the competitive species during the batch test.

Interferences to arsenate removal in activated alumina systems were most severe in the presence of polymeric silica (upper part, Figure 5), consistent with the conceptual development in Figure 1. For instance, after 1 d, only 21% of the arsenate sorbed to AA in the presence of polymeric silica, compared to at least 35% sorption in all other solutions tested. But from 3 d onward, the solution that started with 40 ppm non-polymeric silica had a greater interference to arsenate removal. As was the case in earlier tests with amorphous Fe(OH)<sub>3</sub>, the addition of calcium

eliminated most silica interference to arsenate removal (Figure 5).

One interesting complication is that the soluble aluminum in the AA system with polymeric silica was 1.3 ppm versus 0.2–0.3 ppm soluble aluminum in all other AA solutions. Clearly, polymeric silica played a role in dissolving aluminum from the granular media. It is possible that this dissolution of aluminum, and subsequent reaction of the Al<sup>3+</sup> with silica polymers on the granular media surface, reduces the extent of electrostatic interference between anionic arsenate and the surface. This seems likely since the relatively strong interference to arsenate sorption at the start of the test with polymeric silica had largely disappeared by the end of the test (upper part, Figure 5). Likewise, formation of soluble aluminum–polymeric silica complexes may have also hindered sorption of the polymeric silica to the AA: by the end of the experiment less than 50% of the total silica had been removed versus >85% silica removal in other solutions. The potential use of trace soluble aluminum (and iron) to reduce silica interferences should be explored in future research. In the case when AA was pre-exposed to polymeric silica, the silica concentration in solution decreased to 24 ppm during the first week, and then from 24 down to 17 ppm after 11 d additional reaction in the presence of arsenate (data not shown).

While GFH had many similarities to AA, there were also noteworthy differences. For instance, after 11 d, silica did not significantly reduce arsenate removal relative to the control (upper part, Figure 6). Also, one week's pre-exposure to 40 ppm SiO<sub>2</sub> did significantly interfere with arsenate sorption to iron, whereas pre-exposure actually reduced silica interference in the case of AA, as mentioned earlier. Future research should examine this disparity in greater detail. Obviously, differences in pore size and internal surface area may have a significant effect on the relative performance of media and the kinetics of arsenate uptake. Polymeric silica uptake by GFH was virtually identical to that of monomeric silica (lower part, Figure 6) and no dissolution of iron media was observed. It is quite possible that such reactions may occur for GFH under different circumstances. This lends support to speculation that complexes between dissolved aluminum and polymeric silica interfered with sorption of silica polymers to AA (lower part, Figure 5).

In a granular media column after a few days of operation, the influent silica concentration would be relatively constant in the bulk water, since silica would be continually loaded from the influent. To better simulate this in batch tests, additional experiments were conducted in which the silica concentrations were held relatively constant with time. In solutions containing 40 ppm silica or 40 ppm polymeric silica, the percent arsenic removal by AA over time with silica replacement was similar to the arsenic removal without silica replacement (Figure 7). However, when AA was pre-exposed to the silica solution for 9 d and the concentration of dissolved silica was held constant at 40 ppm, arsenic removal was dramatically lower. In fact, less than 40% of the arsenic was removed after 11.6 d reaction (Figure 7), compared to greater than 60–75% removal in the other systems.

The initial uptake rate of arsenate in the solutions was also strongly impacted by silica and calcium. If the surface was pre-exposed to silica at a constant level of 40 ppm for one week, the uptake rate of arsenate was 4 times lower when compared to the same level of silica without pre-exposure. Thus, not only is the “equilibrium” value of arsenate sorption less with pre-exposure, but the rate of uptake is also reduced. This confirms the idea that, within granular columns, over a long period of exposure silica will have a dramatic impact on the ability of the media to sorb arsenate (Figure 1). Note that this severe interference from 40 mg/L silica would not be detected after 11 d in the

conventional batch test (e.g. Figure 7, no pre-exposure, no replacement of sorbed silica).

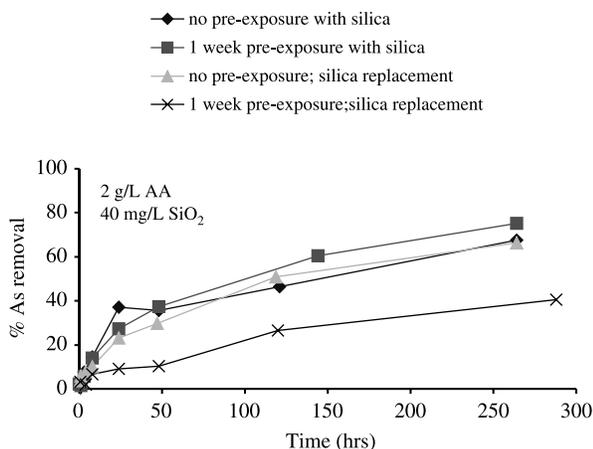
A cumulative total of 86 ppm silica was added during the one week pre-exposure period to maintain a constant silica concentration of 40 ppm. Therefore, 46 ppm silica (i.e. 23 mg sorbed Si/g AA) had sorbed to the granular AA before the addition of arsenic. By the end of the experiment, a total of 126 ppm silica (corresponding to 63 mg sorbed Si/g AA) had been added to maintain a constant silica concentration in the test with silica replacement and 1 week of pre-exposure. In contrast, for solutions with no pre-exposure, approximately 80 ppm silica was added and approximately 60 ppm polymeric silica was added over the reaction period to maintain a constant concentration of 40 ppm in solution. This agrees with the finding that less “polymeric” silica sorbed to granular AA relative to non-polymeric silica (Figure 5).

As with activated alumina, if GFH was pre-exposed to a constant 40 ppm silica in solution, or silica was replaced, silica interference was relatively severe. As before, conventional batch testing in which silica was not replaced, did not reveal the extent of the interference.

### Synthesis and practical relevance of the findings

These results demonstrate limitations in using batch scale testing to estimate run length capacity for granular media. Specifically, in column operation, the silica is continually loaded to the media over a period of several months. In tests for this research, the rate at which the media could sorb arsenic, and the “equilibrium” value of arsenate removal, was changed markedly after just one week of exposure to high silica levels. Without continual replacement of silica removed from solution in the batch test, or pre-exposing the media to the silica for a period of at least several days, the dramatic impact of silica on media capacity is not readily discerned. Consequently, results of conventional batch testing to determine media susceptibility to silica interferences (or other constituents) must be interpreted with caution.

Likewise, rapid small scale column testing (RSSCT) of arsenic sorption capacity has proven to be both highly desirable and reasonably accurate in predicting column run lengths to breakthrough in some circumstances



**Figure 7** | Arsenic removal over time with activated alumina in different solutions containing 40 mg/L silica. pH = 8.5; initial As = 500 ppb; 1 mM NaHCO<sub>3</sub>.

(Thomson *et al.* 2003; Westerhoff *et al.* 2003; Badruzzaman *et al.* 2004). The approach would overcome some grossly overoptimistic projections of column capacity that would be obtained based on batch testing. For instance, silica is continually loaded onto the granular media, and the testing directly accounts for certain diffusion limitations and reduced kinetics of adsorption. However, to the extent that interference may be attributable to surface polymerisation or precipitation of the silica, the kinetics of these processes cannot be “scaled” by the selection of media size and loading (Davis *et al.* 2001, 2002). It is therefore anticipated that RSCCT would give optimistic predictions of run length at influent pHs above about 7.8 in some waters with relatively high silica (Davis *et al.* 2001, 2002). Additional research would be necessary to confirm this hypothesis, to determine the magnitude of the error involved and to develop strategies that can overcome this limitation.

## CONCLUSIONS

- At pH 8.5, calcium improved arsenic sorption to amorphous iron hydroxide in the presence of silica over short reaction times (<4h), but had no effect at longer times. Calcium reduced the zeta potential of the surfaces and increased the rate at which stable arsenate values were obtained. Calcium did not dramatically alter the extent of arsenate removal by iron oxyhydroxide at very long reaction times.
- The rate of arsenate sorption has important implications for optimising arsenic removal in coagulation-based drinking water treatment processes. It implies that, under some circumstances, removal of the sorbent more quickly would enhance overall arsenic removal. At longer reaction times, arsenic removed by oxyhydroxide surfaces can leach back into the water.
- Silica reduced the extent and rate of arsenic sorption to activated alumina. The extent of the silica interference was not detected in traditional batch testing of arsenic sorption capacity, since the silica can be significantly removed from solution by the media. This is an underappreciated shortcoming of batch testing that could

apply to any interfering species. Consequently, previous interpretations of interference based on batch test results should be viewed with skepticism.

- It is logical to expect that RSSC testing of granular media for arsenic removal will not always accurately reproduce silica surface precipitation and polymerisation as it occurs in practice. Therefore, while RSSC is a dramatic improvement relative to batch testing, in practical situations where silica or similar interferences are significant, RSSC can overestimate run length to breakthrough. It is not yet possible to predict the magnitude of this possible discrepancy and further research is needed.
- Less polymeric silica sorbed to activated alumina than non-polymeric silica. The presence of polymeric silica increased dissolution of the activated alumina.

## ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (NSF) under grant BES-0201849. The opinions, findings, conclusions or recommendations are those of the authors and do not necessarily reflect the views of NSF.

## REFERENCES

- Anderson, P. R. & Benjamin, M. M. 1985 Effects of silicon on the crystallization and adsorption properties of ferric oxides. *Environ. Sci. Technol.* **19**, 1048–1053.
- Badruzzaman, M., Westerhoff, P. & Knappe, D. R. U. 2004 Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH). *Wat. Res.* **38**, 4002–4012.
- Chen, H., Frey, M. M., Clifford, D. A., McNeill, L. S. & Edwards, M. 1999 Arsenic treatment considerations. *J. AWWA* **91**(3), 74–85.
- Davis, C. C., Edwards, M. & Knocke, W. R. 2001 Implications of silica sorption to iron hydroxide: mobilization of iron colloids and interference with sorption of arsenate and humic substances. *Environ. Sci. Technol.* **35**(15), 3158–3162.
- Davis, C. C., Chen, H-w. & Edwards, M. 2002 Modeling silica sorption to iron hydroxide. *Environ. Sci. Technol.* **36**(4), 582–587.
- Edwards, M. 1994 Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. *J. AWWA* **86**(9), 64–78.
- Emett, M. T. & Khoe, G. H. 1994 Environmental stability of arsenic bearing hydrous iron oxide compounds. Warren, G. (ed.), *EPD Congress*, TMS, PA. pp. 153–166.
- Frey, M. M. & Edwards, M. 1997 Surveying arsenic occurrence. *J. AWWA* **89**(3), 105–117.

- Fuller, C. F., Davis, J. A. & Waychunus, G. A. 1993 Surface chemistry of ferrihydrite: Part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim. Cosmochim. Acta* **57**, 2271–2282.
- Ghurye, G., Clifford, D. A. & Tong, J. 1998 Iron coagulation/microfiltration for arsenic removal. *Inorganics Contaminants Workshop, San Antonio, TX, 22–24 February*.
- Gupta, S. K. & Chen, K. Y. 1978 Arsenic removal by adsorption. *J. Wat. Pollut. Control Fed.* **50**(3), 493–506.
- Hering, J. G. & Elimelech, M. 1996 *Arsenic Removal by Enhanced Coagulation and Membrane Processes*. AWWA Research Foundation, Denver, CO.
- Holm, T. R. 2002 Effects of  $\text{CO}_3^{2-}$ /bicarbonate, Si and  $\text{PO}_4$  on arsenic sorption to HFO. *J. AWWA* **94**(4), 174–181.
- Iler, R. K. 1979 *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*. John Wiley and Sons, New York.
- Meng, X. G., Bang, S. B. & Korfiatis, G. P. 2000 Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. *Wat. Res.* **34**(4), 1255–1261.
- Misra, S. G. & Tiwari, R. C. 1963 Studies on arsenite-arsenate system adsorption of arsenate. *Soil Sci. Plant Nutrition* **9**, 10–13.
- Pierce, M. L. & Moore, C. B. 1982 Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Wat. Res.* **16**, 1247–1253.
- Rosenblum, E. & Clifford, D. 1984 *The Equilibrium Arsenic Capacity of Activated Alumina*. EPA-600/S2-83-107.
- Snoeyink, V. L. 1990 Adsorption of organic compounds. In Pontius, F. W. (ed.) *Water Quality and Treatment*. McGraw-Hill, New York, pp. 13.1–13.76.
- Standard Methods for the Examination of Water and Wastewater* 1998 20th edn. APHA, AWWA and WEF, Washington, DC.
- Swedlund, P. J. & Webster, J. G. 1999 Adsorption and polymerisation of silicic acid on ferrihydrite, and its effect on arsenic adsorption. *Wat. Res.* **3**(16), 3413–3422.
- Thomson, B., Aragon, A., Anderson, J., Chwirka, J. & Carlson, M. 2003 Development of a rapid method of evaluating adsorbents for arsenic removal from drinking water. *Proceedings of the 2003 American Water Works Association Annual Conference*.
- Tong, J. 1997 *Development of an Iron(III)-Coagulation-Microfiltration Process for Arsenic Removal from Groundwater*. MS Thesis, University of Houston.
- Waltham, C. A. & Eick, M. J. 2002 Kinetics of arsenate adsorption on goethite in the presence of silicic acid. *Soil Sci. Soc. Am. J.* **66**(3), 818.
- Wang, L. *et al.* 2000 *Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants*. EPA/600/R-00/088.
- Westerhoff, P., Highfield, D., Badruzzaman, M., Yoon, Y. & Raghavan, S. 2003 Rapid small scale column tests for arsenate removal in iron oxide packed bed columns. *Proceedings of the 2003 American Water Works Association Annual Conference*.
- Wilkie, J. A. & Hering, J. G. 1996 Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids Surfaces* **107**, 97–110.

First received 25 October 2004; accepted in revised form 17 January 2005