Role of Fe(II), phosphate, silicate, sulfate, and carbonate in arsenic uptake by coprecipitation in synthetic and natural groundwater

Mark C. Ciardelli\textsuperscript{a, *}, Huifang Xu\textsuperscript{a}, Nita Sahai\textsuperscript{a, b, *}

\textsuperscript{a}Department of Geology & Geophysics, 1215 W. Dayton Street, University of Wisconsin, Madison, WI 53706, USA
\textsuperscript{b}Environmental Chemistry and Technology Program, 1215 W. Dayton Street, University of Wisconsin, Madison, WI 53706, USA

ABSTRACT

Competitive effects of phosphate, silicate, sulfate, and carbonate on As(III) and As(V) removal at pH ~7.2 have been investigated to test the feasibility of Fe(II)\textsubscript{aq} and hydroxyapatite crystals as inexpensive and potentially efficient agents for remediation of contaminated well-water, using Bangladesh as a type study. Arsenic(III) removal ~50–55\% is achieved, when Fe(II)\textsubscript{aq} oxidizes to Fe(III) and precipitates as Fe(OH)\textsubscript{3} at 25 °C and 3 h reaction time, in the presence of all the oxyanion. Similar results were obtained for well-water samples from two sites in Bangladesh. Heating at 95 °C for 24 h results in 70\% As(III) uptake due to precipitation of magnesian calcite. A two-step process, Fe(II) oxidation and Fe(OH)\textsubscript{3} precipitation at 25 °C for 2 h, followed by magnesian calcite precipitation at 95 °C for 3 h, yields ~65\% arsenic removal while reducing the expensive heating period. In the absence of silicate, up to 70\% As(III) uptake occurs at 25 °C. In all cases, As(III) was oxidized to As(V) in solution by dissolved oxygen and the reaction rate was probably promoted by intermediates formed during Fe(II) oxidation. Iron-catalyzed oxidation of As(III) by oxygen and hydrogen peroxide is pH-dependent with formation of oxidants in the Fenton reaction. Buffering pH at near-neutral values by dissolved carbonate and hydroxyapatite seeds is important for faster Fe(II) oxidation kinetics ensuring rapid coprecipitation of As as As(V) in the ferric phases.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

Naturally occurring arsenic contamination in groundwater has become a major environmental concern on national and global levels, affecting large human populations in Nepal, Vietnam, Bangladesh, Taiwan, Eastern India, Chile, Argentina, Mexico, the western United States and even in mid western USA (e.g. Berg et al., 2001; Cheng et al., 2005; Dixit and Hering, 

*Corresponding authors. Department of Geology & Geophysics, 1215 W. Dayton St., University of Wisconsin, Madison, WI 53706, USA.
Tel.: +1 608 262 4972, fax: +1 608 262 0693.
E-mail addresses: mark.ciardelli@gmail.com (M.C. Ciardelli), sahai@geology.wisc.edu (N. Sahai).
0043-1354/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2007.08.011

Please cite this article as: Ciardelli, M.C., et al., Role of Fe(II), phosphate, silicate, sulfate, and carbonate in arsenic uptake by coprecipitation in synthetic and natural groundwater. Water Res. (2007), doi:10.1016/j.watres.2007.08.011
different strategy, synthetic amorphous and crystalline FePO4, H2PO4, including arsenic levels is shown in Table 1. Remediation strategies for arsenic have focused on sorption onto aluminum and iron (oxyhydr)oxides, and oxidation (primarily photocatalytic) of As(III) to As(V) followed by sorption (Beaulieu and Savage, 2005; Dutta et al., 2005; Gupta et al., 2005; Hug et al., 2001; Kanel et al., 2005; Meng et al., 2001; Su and Puls, 2003; Zhang and Itoh, 2005). A complicating factor in arsenic remediation strategies involving adsorption is competition by other oxyacids such as H4SiO4, HCO3−, H2PO4−, and HPO42− that commonly occur in groundwater (Jain and Loppert, 2000; Meng et al., 2000, 2002; Goldberg, 2002). These ions also inhibit precipitation of crystalline ferric oxyhydroxide phases (Rose et al., 1996; Wachunas et al., 1996; Masion et al., 1997, 2001; Doelsch et al., 2000). Using a different strategy, synthetic amorphous and crystalline FePO4 phases were studied for arsenic uptake by adsorption and coprecipitation (Lenoble et al., 2005). When iron is added to synthetic Bangladesh groundwater, ferric (oxyhydr)oxides precipitate, taking up arsenic simultaneously. Fe(II) is more effective than Fe(III), and repetitive additions of Fe(II) are more effective than a single, large dose (Roberts et al., 2004). It was proposed that Fe(II) promotes rapid oxidation of As(III) to As(V) by molecular oxygen via the involvement of reactive oxygen species in the Fenton reaction and of putative Fe(IV) and As(IV) reactive intermediates (Hug and Leupin, 2003). Repeated additions of Fe(II) and lemon juice have shown to be quite effective (up to 90% arsenic removal with an initial arsenic concentration of 500 μg L−1), because they promote faster oxidation of Fe(II) to Fe(III) and, apparently, of As(III) to As(V) (Hug et al., 2001; Roberts et al., 2004).

Preliminary aqueous speciation calculations indicated that the average Bangladesh groundwater composition is supersaturated with respect to hydroxylapatite (Ca5(PO4)3OH, HAP) (Giardelli, 2006), although we recognize that variations in Ca and P concentrations greatly impact the degree of supersaturation. The motivation for the present research is to investigate the efficacy of a strategy involving rapid coprecipitation of arsenic along with HAP such that competition from other oxyacids would be minimal.

Because of their ability for multiple ionic substitutions (Pan and Fleet, 2002), apatites have received attention for their potential to be used as a soil amendment, and as an additive to water for decreasing toxic and radioactive metal concentrations including lead, zinc, and uranium (Gomez de Rio et al., 2004; Lee et al., 2005; Mavropoulos et al., 2002; Ohnuki et al., 2004). The effectiveness of uptake depends on specific metal and on the conditions of the system. The anticipated ability to coprecipitate arsenic with HAP was based on the existence of the mineral, johnbaumite (Ca5(AsO4)2(OH)).

Our study is unique in several ways. First, we characterized not only the solution phase but, importantly, also the solid phases formed from nano- to micron-sized by high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy-dispersive spectra (EDS), and X-ray diffraction (XRD). Equally significant, instead of the highly simplified 1:1 electrolyte solutions and very high As concentrations typically employed in experimental studies, we used complex synthetic groundwater solutions of compositions similar to average Bangladesh groundwater solutions. We used Bangladesh as a type-case because the As contamination problem has been extensively characterized, represents a typical groundwater composition, and affects a huge human population. Further, we compared our results to actual Bangladesh well-waters from two locations.

### Table 1 - Chemical composition of average Bangladesh groundwater* compared with the concentrations of natural Bangladesh groundwater** and synthetic Bangladesh groundwater (SBGN)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Average BGW, Mean ± Std. dev</th>
<th>BGW, Mean ± Std. dev</th>
<th>SBGW</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ca2+]</td>
<td>1.90 ± 1.4 mM (76 mg L−1)</td>
<td>1.99 ± 0.5 mM (80 mg L−1)</td>
<td>2.5 mM (100 mg L−1)</td>
</tr>
<tr>
<td>[Mg2+]</td>
<td>1.30 ± 0.8 mM (30.9 mg L−1)</td>
<td>0.99 ± 0.25 mM (24 mg L−1)</td>
<td>1.6 mM (38 mg L−1)</td>
</tr>
<tr>
<td>[HCO3−]</td>
<td>7.8 ± 2.7 mM (488 mg L−1)</td>
<td>Not measured</td>
<td>8.2 mM (500 mg L−1)</td>
</tr>
<tr>
<td>[As]</td>
<td>2.65 ± 2.2 μM (199 μg L−1)</td>
<td>6.21 ± 0.87 μM (465 μg L−1)</td>
<td>6.67 μM (500 μg L−1)</td>
</tr>
<tr>
<td>[Fe]</td>
<td>0.095 ± 0.085 μM (5.3 mg L−1)</td>
<td>0.180 ± 0.054 μM (10 mg L−1)</td>
<td>0.180 μM (10 mg L−1)</td>
</tr>
<tr>
<td>[Si]</td>
<td>0.70 ± 0.17 μM (19.2 mg L−1)</td>
<td>0.8 ± 0.18 μM (22.5 mg L−1)</td>
<td>1.1 μM (30 mg L−1)</td>
</tr>
<tr>
<td>[S]</td>
<td>0.078 ± 0.031 μM (2.5 mg L−1)</td>
<td>0.037 ± 0.031 μM (1.2 mg L−1)</td>
<td>0.160 μM (5 mg L−1)</td>
</tr>
<tr>
<td>[P]</td>
<td>0.047 ± 0.048 mM (1.47 mg L−1)</td>
<td>0.052 ± 0.019 mM (1.6 mg L−1)</td>
<td>0.065 mM (2 mg L−1)</td>
</tr>
<tr>
<td>pH</td>
<td>7.2 ± 0.2</td>
<td>Initial: 7.2 ± 0.2 Final: 7.5 ± 0.2</td>
<td>Initial: 7.1 ± 0.1 Final: 7.6 ± 0.2</td>
</tr>
</tbody>
</table>

---

* Average BGW, surveyed from 3534 tubewells (Kinniburgh and Smedley, 2001; Roberts et al., 2004).

** BGW, Srinagar village, Munshiganj district.

*** SBGW.

Please cite this article as: Giardelli, M.C., et al., Role of Fe(II), phosphate, silicate, sulfate, and carbonate in arsenic uptake by coprecipitation in synthetic and natural groundwater. Water Res. (2007), doi:10.1016/j.watres.2007.08.011
2. Methods

2.1. Simplified synthetic Bangladesh groundwater (SSBGW)

SSBGW, containing only 2.5 mM Ca\(^{2+}\), 1.6 mM Mg\(^{2+}\), and 8.2 mM HCO\(_3^-\) was prepared fresh for each set of experiments by dissolving CaCO\(_3\) (Fisher) and MgCO\(_3\) (Fisher) in deionized water (18.2 MΩ-cm). To aid in the dissolution of the carbonate species, CO\(_2\)\(_{138}\) (99% pure, Linde Gas) was bubbled through the suspension with vigorous stirring for approximately 8 h or until all of the CaCO\(_3\) and MgCO\(_3\) was dissolved (Roberts et al., 2004). The resulting solution had a pH of 5.6–6.0. Complete synthetic Bangladesh groundwater (SBGW) is listed in Table 1.

2.2. Batch experiments: 1–24 h experiments with and without HAP at 25 and 95 °C

Experiments at 25 °C were conducted in triplicate with increasing complexity, as summarized in Supporting Information Table 1. For each experiment, 200 mL of SSBGW was dispensed into acid (HNO\(_3\))-washed low-density polyethylene (LDPE) bottles. Compressed air was bubbled through each solution to displace the excess CO\(_2\) and raise the pH to 7.1 ± 0.05. Depending on the experiment, Si, As, S, and P (concentrations given in Table 1) were added, in this order, from stock solutions of 0.1 M Na\(_2\)SiO\(_4\) (Aldrich), 0.01 M NaAsO\(_2\) or Na\(_2\)HAsO\(_4\)·7H\(_2\)O (Aldrich), 0.1 M Na\(_2\)SO\(_4\) (Fisher), and 0.01 M Na\(_2\)HPO\(_4\) (Fisher). Experiments were initiated by adding synthetic 0.5 g HAP L\(^{-1}\) (J.T. Baker) seeds with an average particle size of 100 nm and a BET surface area of 57 m\(^2\) g\(^{-1}\), followed by the addition of 180 µM of Fe(II) from a stock solution of 0.1 M FeCl\(_3\)·4H\(_2\)O (Fisher). A fresh Fe(II) stock solution was prepared for each experiment and used within 5 min of preparation.

All solutions were reacted open to atmosphere for 1, 3, 6, and 24 h. Over 24 h, the pH increased to 7.6 ± 0.3 due to degassing of CO\(_2\) from the solutions. This is also observed when natural Bangladesh groundwater is reacted open to atmosphere (Roberts et al., 2004). At the end of each reaction time, the suspensions were centrifuged for 30 min at 15,000 rpm and filtered through a 0.1 µm nylon filter. These solutions were then acidified (2% HNO\(_3\), ultra-high purity (Fisher)), and stored at 4 °C until ICP-OES analysis.

Heated batch experiments performed at 95 °C were prepared as described above in the presence of all oxyacids including As(III). Following Fe(II) addition, the solutions were placed in a water bath and heated to 95 °C. The time it took for the solutions to reach 95 °C was recorded (thermal equilibration time ~15 min). Once the solutions reached 95 °C, they were reacted open to the atmosphere for 1, 3, 6, and 24 h, and sampled as previously described.

2.3. Batch experiments: two-step process

The two-step process combined the methods used for the batch experiments at 25 and 95 °C. The SBGW solution was prepared as previously described. Following Fe(II) addition, the solutions were reacted open to atmosphere at 25 °C for 2 h, and filtered with a 0.1 µm nylon filter to remove the precipitates. Each filtered solution was sampled, stored, and analyzed as described above. HAP seed crystals (0.5 g HAP L\(^{-1}\)) were added to the filtered solutions, heated to 95 °C for 3 h, filtered, sampled, and analyzed as described above.

2.4. Batch experiments: natural Bangladesh groundwater

Two sets of experiments were preformed using natural Bangladesh groundwater taken from two different rural wells. Both wells were located in the Munshiganj district, close to the village of Srinagar, which is 30 km south of Dhaka. At each well, two 250 mL LDPE bottles were filled with 200 mL of well water. About 100 mg of HAP seed crystals were added to one of the solutions (200 mL). Both solutions were equilibrated open to atmosphere for 24 h, filtered, sampled, and stored at 25 °C without centrifugation. A week after the samples were taken, they were mailed back to the University of Wisconsin—Madison. During the week-long mailing period, the samples were not kept cold.

2.5. Solution analysis

Solutions were analyzed for aqueous concentrations of [As]\(_{\text{total}}\), [Ca]\(_{\text{total}}\), [Fe]\(_{\text{total}}\), [K]\(_{\text{total}}\), [Mg]\(_{\text{total}}\), [Na]\(_{\text{total}}\), [P]\(_{\text{total}}\), [Si]\(_{\text{total}}\), and [Si]\(_{\text{total}}\) by using ICP-OES on a Perkin–Elmer Optima 4300 DV instrument. All solutions were analyzed within 2 weeks of being sampled. In order to determine the concentration of As(V) in solutions produced by oxidation of As(III), [As]\(_{\text{total}}\) measured from solutions, passed through As speciation cartridges (MetalSoft, Inc.) was subtracted from [As]\(_{\text{total}}\) measured before the solution was passed through the cartridge. Thus,

\[
\text{[As]_{total}}\text{–cartridge} – \text{[As]_{total}}\text{–post–cartridge} = \text{[As(V)]}
\]

These cartridges are reported to have an As(V) retention efficiency of 91–95% (Meng and Wang, 1998; Dr. Linda Roberts, EAWAG, Switzerland, pers. comm.).

2.6. Analysis of precipitates

Precipitates were filtered out of solution with a 0.1 µm nylon filter and characterized by powder XRD using a Scintag PAD V Diffractometer with a Cu Kα X-ray tube rated at 2000 W. All samples were analyzed with the X-ray diffractometer set at 40 mV and 35 keV, and with a step size of 0.02 2θ and 4 s dwelling time.

HRTEM and SEM were also used to analyze precipitated solids in the nanometer size range. TEM/SEM samples were prepared by dropping precipitate-bearing suspensions onto holey-carbon-coated copper grids. All the TEM and EDS analyses were obtained by using a JEOL 2010F FASTEM equipped with Oxford Instruments EDS system and Gatan GIF system at the University of New Mexico, and a Tecnai F30 equipped with a EM Vision 4.0 EDS system at the University of Chicago.

SEM was preformed on precipitated solids in the micro-meter size range using a Hitachi S-3400N SEM and EDS system at the University of Wisconsin—Madison.

Please cite this article as: Ciardelli, M.C., et al., Role of Fe(II), phosphate, silicate, sulfate, and carbonate in arsenic uptake by coprecipitation in synthetic and natural groundwater. Water Res. (2007), doi:10.1016/j.watres.2007.08.011
2.7. Thermodynamic modeling

Arsenic speciation, mineral stability, and saturation indices were calculated using the Act 2 and React modules of Geochemist’s Workbench® 3.1 (Bethke, 1996), for solutions having SSBGW composition. The program uses the DTA0 thermodynamic database that is also used in the SUPCRT and EQ3NR/EQ6NR programs (Johnson et al., 1992; Wolery, 1992a, b).

3. Results and discussion

3.1. Arsenic removal at 25°C

Fig. (1a–c) shows data for As removal at 25°C and uptake at 95°C is shown in Fig. (1d) discussed later. In control experiments with SSBGW containing As(III) or As(V), no arsenic uptake was detected, and concentrations of Ca²⁺ and Mg²⁺ also stayed constant. Visually, the solutions appeared clear. In contrast, all systems with Fe(II) turned reddish-brown in color within the first 15–30 min of reaction time, and significant arsenic uptake was measured. The equilibration period (1, 3, 6, and 24 h) had little effect on the amount of arsenic uptake after the first hour. As(III) removal achieved was ~73% for the 24 h time period (Fig. 1a), and greater than 90% removal of As(V) was observed (not shown). Maximum arsenic removal occurred in the presence of Fe(II), and where no other oxyacids were present.

Oxyacids greatly affected the amount of arsenic uptake in the As(III) systems. Fig. (1a) shows that silicate has the worst effect. Arsenic(III) removal in the presence of silicate or phosphate was 67% and 63%, respectively, which are less by 5% and 9% than the systems without competing oxyacids. The uptake at 24 h was further reduced to 52% when all oxyacids were present (Fig. 1b). For all systems with As(V), the oxyacids had no significant effect (> 90% As removed; not shown). In all systems with As(III) and As(V), HAP seed crystals only minimally affected arsenic uptake (Fig. 1). Greater than 99% removal of iron was observed in all experiments.

Samples of natural Bangladesh groundwater turned reddish-brown in color within 15–30 min of being exposed to the atmosphere. The initial Fe(II) concentration in wells number 1

---

Fig. 1 – Amount of arsenic removed at 24 hours from systems with SSBGW, As(III) and Fe(II) with (a) individual oxyacids, and (b) multiple oxyacids. (c) Amount of arsenic removed from natural Bangladesh groundwater. (d) Amount of arsenic removed at 95°C from SSBGW. Arsenic was added as As(III) in all experiments.
and 2 was ~7 and ~12 mg L\(^{-1}\), respectively. Almost 100% iron was removed during aeration, along with 37–44% and 44–53% arsenic removal, respectively, in the absence and presence of HAP seed crystals (Fig. 1c).

In studies where very similar synthetic groundwater solutions were used, precipitation of ferric oxyhydroxides was observed with efficient As removal (Hug and Leupin, 2003; Roberts et al., 2004). The oxidation of Fe(II) to Fe(III) involves reactive oxygen intermediates via the Fenton Reaction. The rate of As(III) oxidation to As(V) by molecular oxygen is usually very slow. It was proposed that in the presence of Fe(II), reactive intermediate species such as Fe(IV) and As(IV) may be involved in accelerating the rate of As(III) oxidation to As(V), followed by uptake in the Fe(III) oxyhydroxides formed. A similar process is likely responsible for As uptake in our systems that initially contained As(III).

HRTEM analysis showed that particles formed in the absence of HAP in the SBGW system were sub-spherical, ~50 nm in size, and lacked any lattice fringes (Fig. 2a). The particles appeared remarkably similar to the precipitates obtained from natural Bangladesh groundwater at 25 \(^\circ\)C (Fig. 2b). Fe, O, As, Si, P, and Ca peaks were identified in the HRTEM-EDS spectra (Fig. 2c). The Fe and O peaks are consistent with Fe(II) oxidation to Fe(III) and precipitation of amorphous ferric (oxyhydr)oxide, nominally Fe(OH)\(_{3}\), observed visually as a reddish-brown color in our iron-bearing solutions and as expected from thermodynamic modeling (SI Fig. 1).

The presence of As peaks in the EDS spectra and the lower [As]\(_{tot}\) measured in Fe-bearing solutions indicate that As is associated with the Fe(OH)\(_{3}\) phase. In order to infer the mode of arsenic uptake, as adsorbate or coprecipitate, we considered the EDS spectra. In general, the low sensitivity of the EDS technique precludes positive identification of adsorption as a potential uptake mode, because the concentration of sorbed species would be too low for detection. Thus, the very presence of As in the EDS spectrum suggests uptake by coprecipitation. Given the nanometer size of the particles, however, it is difficult to distinguish clearly between surface and bulk atoms, so labeling the uptake mode as adsorbate versus coprecipitate is somewhat semantic.

Similar to As, the presence of Si and P peaks in the EDS spectra suggests that silicate and phosphate were taken up as coprecipitates with the Fe(OH)\(_{3}\). Numerous studies have shown that silicate and phosphate exhibit a high affinity for adsorption and coprecipitation in the presence of iron (oxyhydr)oxides (Holm, 2002; Jain and Loeppert, 2000; Meng et al., 2000, 2002; Roberts et al., 2004; Su and Puls, 2001; Swedlund and Webster, 1999), and can inhibit formation of crystalline iron oxyhydroxide phases (Masion et al., 1997, 2001). Furthermore HAP precipitation was not induced by addition of seed crystals at 25 \(^\circ\)C, but the EDS spectra and
solution analyses indicate the presence of Ca in the solid phase and a slight decrease (<1%) of Ca in solution.

3.2. Arsenic removal at elevated temperatures

Because HAP did not precipitate at 25 °C, solutions were heated to 95 °C. As(III) removal increased with longer heating time, up to 70% at 24 h with HAP (Fig. 1d). The system without HAP was insensitive to changes in heating time, remaining constant at ~46% arsenic uptake.

White to tan and reddish-brown precipitates of different particle sizes, were observed for all heating times in all solution compositions at 95 °C. The larger-sized fraction (>2 μm) of these precipitates showed irregularly shaped, “amorphous” particles, as well as well-crystallized, rhombohedral particles identified as magnesian calcite using SEM-EDS and XRD (Fig. 3). The EDS analysis showed Mg and Si but no P associated with the amorphous particles, and Si plus P in the magnesian calcite, but no As peaks in either. Yet, solution analyses indicate that heating increased arsenic uptake at 95 °C compared to 25 °C. This suggests that arsenic does not coprecipitate with the magnesian calcite phase, but is probably taken up as an adsorbate. The point of zero charge of calcite varies from 7 to 10.8 and is a function of experimental conditions associated with the formation of the calcite (Romero et al., 2004), so the surface would be positively charged at our experimental pH ~7, allowing for As adsorption.

The smaller-sized fraction (75–100 nm) showed particles with two morphologies, sub-spherical and foil-like (Fig. 4a and b). For the foil-like particles, a high-energy As peak at ~11.7 keV corresponding to \( K_{\beta} \) is seen in the HRTEM-EDS spectrum (Fig. 4c). D-spacings from XRD (Fig. 4d) and selected area electron diffraction (SAED) (Fig. 4b) combined with the EDS chemical analysis (Fig. 4c) show that these solids do not correspond to any mineral phase but are closest to the peaks for ferroan saponite \((\text{Ca}_0.5\text{Mg},\text{Fe})_3\text{Si}_4\text{O}_{10}(\text{OH})_2\cdot\text{H}_2\text{O})\) (SI Table 2). The XRD peaks for our precipitate were slightly shifted from the reference ferroan saponite (Fig. 4d), postulated to be the result of Fe\(^{3+}\) substituting for Al\(^{3+}\) in the ferroan saponite structure, because there is no Al in our system. The sub-spherical particles appear similar to the
amorphous Fe(OH)$_3$ precipitates obtained for SBGW and natural BGW.

The presence of amorphous Fe(OH)$_3$ is consistent with visual observations of a reddish-brown precipitate within the first 15 min, before the solution reaches thermal equilibrium. Once the system reaches 95°C, we infer that the remaining iron precipitates as the ferroan saponite-like phase; some of the amorphous Fe(OH)$_3$ may also be converted to ferroan saponite with retention of the As, as seen in the EDS spectrum. Thermodynamic modeling results suggest that neither phase should be present, and even ferroan saponite is predicted to be metastable only if several other phases are prevented from precipitating (SI Fig. 2). Thus, the presence of both phases indicates that the system is metastable even at 95°C.

3.3. Two-step process

As expected, 50% arsenic uptake is seen from SBGW in the As(III) system at 25°C and 2 h equilibration in air, and up to 62% uptake by subsequent heating to 95°C for 3 h in the presence of HAP seed crystals (Fig. 5). Thus, the two-step process is designed to maximize As(III) uptake by coprecipitation with nanoparticulate, am. Fe(OH)$_3$ in the first step, and adsorption onto coarse-grained magnesian calcite and coprecipitation with the fine-grained ferroan saponite-like phase in the presence of HAP seed crystals.
the second step. By breaking up the process into two steps, roughly 5% more arsenic is removed than during a “one-step” heating experiment for 3 h.

3.4. Implications for As remediation

When developing an arsenic remediation strategy for Bangladesh, Eastern India and other developing countries, one must consider the economic feasibility and simplicity of the system being developed. We have shown here that employing a “passive removal system” where naturally present Fe(II) is allowed to oxidize and precipitate as Fe(OH)₃ can be effective at removing arsenic contamination in the absence of silicate and phosphate and in the presence of carbonate. However, this effectiveness is decreased to ~55% As uptake when initial concentrations of Fe(II) are low, and when silicate and phosphate are present.

In a parallel study, we have studied As(III) and As(V) uptake from solutions of very similar composition to the present study except that phosphate was present but carbonate and silicate were absent (Sahai et al., 2007). The HRTEM-EDS and synchrotron X-ray Absorption Spectroscopy, both EXAFS and XANES, results showed the formation of a mixed ferric oxyhydroxide phosphate arsenate phase, Fe₃[AsO₄] · PO₄ · AsO₃ · nH₂O. In the absence of carbonate, pH buffering on addition of Fe(II) was provided by HAP seed crystals but less efficiently than the carbonate in the present study, so that solution pH dropped from ~7.2 to ~6.5, and Fe(II) oxidation rate was slowed down. As a result, incomplete Fe(III) removal was obtained with correspondingly reduced As uptake ~55% (Sahai et al., 2007). Thus, we have seen that the presence of phosphate and silicate and incomplete pH buffering reduces As(III) uptake by coprecipitation with ferric phases from groundwater that initially contained Fe(II). Silicate is shown in our study to have the greatest effect on As uptake. The inhibitory effect of Si on ferric oxyhydroxide precipitation is well-studied. Mixed ferric oxyhydroxide phosphate arsenate phases, in some cases with silicate and calcium, have been reported in the natural estuarine and lake sediments at slightly acidic to neutral pHs (Perret et al., 2000; Webb et al., 2000; Hyacinthe and Van Cappellen, 2004), and mixed ferric arsenate sulfate phases exist under acid mine drainage conditions (Craw and Chappell, 2000; Morin et al., 2003).

The results of this research suggest that simply adding HAP seed crystals to average synthetic and natural Bangladesh groundwater solutions at 25 and 95 °C is not sufficient to induce hydroxylapatite precipitation and adsorption and/or coprecipitation of arsenic. On the other hand, coprecipitation of As with ferric oxyhydroxide phases, and mixed ferric oxyhydroxide phosphate arsenate phases does present a promising strategy, although competitive effects of silicate and phosphate must be considered. By employing a two-step remediation strategy, where passive removal is allowed to occur for 2 h, followed by the addition of HAP seed crystals and heating at 95 °C, the competitive effects of silicate and phosphate on arsenic removal are partially mitigated, although still not to levels below the drinking water limit. The effectiveness of this proposed strategy is dependent on the heating time during the second step with greater efficiency at longer heating times. Although heating water is potentially expensive for people in developing countries, this method would also be a means of simultaneously sterilizing the drinking water against many bacteria. Future work will focus on developing practical methods for inducing coprecipitation in a more cost-effective manner.

4. Conclusions

In the presence of competing oxyanions in groundwater solutions, As(III) uptake efficiency can be increased from ~50% up to ~65–70% by coprecipitation with ferric oxyhydroxides and calcium carbonate, where Fe(II) is oxidized and hydrolyzed to ferric oxyhydroxides and As(III) is oxidized to As(V) by molecular oxygen, followed by heating to about 95 °C for 2–3 h.

Acknowledgments

We thank Dr. Stephan Hug, EAWAG, Switzerland for originally drawing us into the arsenic problem in Bangladesh, and for performing the field experiments; Drs. Xiao-Zhou Liao University of New Mexico-Albuquerque and Ying-Bing Jiang-University of Chicago for assistance with HRTEM analysis; Dr. John Fournelle for SEM analysis; and Dr. Martin Schafer and Brian Majestic for assistance with ICP-OES analysis. This project was funded by NSF EAR CAREER Grant 0346689 and faculty start-up funds from UW-Madison to N.S.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2007.08.011.

References


Please cite this article as: Ciardelli, M.C., et al., Role of Fe(II), phosphate, silicate, sulfate, and carbonate in arsenic uptake by coprecipitation in synthetic and natural groundwater. Water Res. (2007), doi:10.1016/j.watres.2007.08.011


