



Arsenic Water Technology Partnership

Ferrous Carbonate beds as an Inexhaustible Source of $\text{Fe}(\text{OH})_3$ for Arsenic Removal



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Ferrous Carbonate Beds as an Inexhaustible Source of $\text{Fe}(\text{OH})_3$ for Arsenic Removal

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FOREWORD

The Water Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the drinking water community.

The Arsenic Water Technology Partnership (AWTP) program is a partnership between Water Research Foundation, Sandia National Laboratories (SNL) and WERC, a Consortium for Environmental Education and Technology Development at New Mexico State University that is funded by DOE and the Water Research Foundation. The goal of the program is to provide drinking water utilities, particularly those serving small and rural communities, with cost-effective solutions for complying with the new 10 ppb arsenic MCL. This goal is being met by accomplishing three tasks: 1) bench-scale research to minimize operating, energy and waste disposal costs; 2) demonstration of technologies in a range of water chemistries, geographic locales, and system sizes; and 3) cost effectiveness evaluations of these technologies and education, training, and technology transfer.

The AWTP program is designed to bring new and innovative technologies developed at the laboratory and bench-scale to full-scale implementation and to provide performance and economic information under actual operating conditions. Technology transfer of research and demonstration results will provide stakeholders with the information necessary to make sound decisions on cost-effective arsenic treatment.

The Foundation participates in the overall management of the program, helps to facilitate the program's oversight committees, and administer the laboratory/bench-scale studies. SNL conducts the pilot-scale demonstrations and WERC oversees the education, training, economic analysis, and outreach activities associated with this program.

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EXECUTIVE SUMMARY

CONCEPT

In-situ generated $\text{Fe}(\text{OH})_3(\text{s})$ is expected to possess greater arsenic sorption capacity (mg As adsorbed/g Fe) than granular iron media, e.g., granular ferric hydroxide (GFH) and granular ferric oxide (GFO), because literature reports and our previous Water Research Foundation research have shown that in-situ generated iron coagulants have a much greater and more accessible hydroxylated iron surface compared with granular GFH/GFO and similar media. Furthermore, the cost of frequent replacement of the granular iron media will be drastically reduced when using long-lasting beds of $\text{FeCO}_3(\text{s})$. For example, a 40% porous bed of siderite would treat more than one million bed volumes of feed assuming an in-situ dosage of 1.0 mg Fe /L, a dose that would be sufficient for most small systems to reduce the arsenic below the the maximum contaminant level (MCL).

Possible filter media for in-situ-generated iron coagulant include zero-valent iron (Fe^0 , density = 7.9 g/cm³), iron(II) oxide ($\text{FeO}(\text{s})$, i.e., wustite, density = 5.7 g/cm³), and ferrous carbonate ($\text{FeCO}_3(\text{s})$, i.e. siderite, density = 3.8 g/cm³). All three will initially produce Fe(II), which must be oxidized to Fe(III) using dissolved oxygen, chlorine or alternative oxidant to obtain the in-situ coagulant $\text{Fe}(\text{OH})_3(\text{s})$. Preliminary calculations and literature reports indicate that zero-valent iron and $\text{FeO}(\text{s})$ are very dense for filter media, and may be hard to control as they tend to generate more iron than is necessary for arsenic adsorption. We propose the use of $\text{FeCO}_3(\text{s})$ because of its low cost, natural abundance, lower density, and lower solubility (0.9 mg Fe(II)/L at pH 7.0 in water with 150 mg/L total alkalinity). Another reason to choose $\text{FeCO}_3(\text{s})$ is that any system that produces Fe(II) ions from iron or iron oxides will quickly precipitate $\text{FeCO}_3(\text{s})$ from the alkalinity present in a typical ground water, so we suggest starting with the siderite as the source of Fe(II).

OBJECTIVES

The objective of our proposed research was to determine the feasibility of using filter beds of ferrous carbonate (siderite) in combination with low levels (0–2 ppm) of chlorine to oxidize As(III) to As(V) and generate 0–3 ppm $\text{Fe}(\text{OH})_3(\text{s})$ as Fe for in-situ coagulation and removal of As(V). To attain the main objective, the following specific tasks were carried out:

1. Attempt to prepare ferrous carbonate in the laboratory.
2. Screen six different siderite samples collected from different parts of the world.
3. Study the arsenic removal efficiency of the best performing siderite using small scale column test.
4. Treat siderite bed using alkaline/acidic- Cl_2 to increase the arsenic adsorption capacity.
5. Conduct small-scale column tests (SSCTs) using pretreated siderite bed for arsenic removal.
6. Use $\text{Fe}(\text{II})\text{O}$ (wustite) and Fe(II) media manufactured by PEL technology as an alternative to siderite.
7. Construct a stainless steel column for electrolytic dissolution of siderite.
8. Run SSCTs to remove arsenic using siderite under electrolytic conditions.

APPROACH

Although siderite is a very common mineral, it is not readily available, commercially, presumably because of lack of current markets for it as a raw material. Thus, small samples of siderite from six different mineral deposits were obtained from two different vendors for screening tests to establish the best mineral for the arsenic removal tests. For the proof-of-concept, attempts were made to prepare ferrous carbonate in the laboratory. The SSCTs were conducted using the best performing siderite to remove arsenic in the presence 1–3 mg/L Cl_2 . Pretreatment of the siderite bed was done using alkaline or acidic Cl_2 solution to increase the solubility of siderite. SSCTs were conducted with other Fe(II) media (wustite and PEL Technology Fe(II) media. Finally, following up on to project advisory committee (PAC) members' suggestions, an electrolytic dissolution system was constructed, and SSCTs with siderite were performed using a stainless steel anode and a graphite-rod cathode.

CONCLUSIONS

The objective of our proposed research was to determine the feasibility of using filter beds of ferrous carbonate in combination with low levels (0–2 ppm) of chlorine to oxidize As(III) to As(V) and generate 0–3 ppm $\text{Fe}(\text{OH})_3(\text{s})$ as Fe for in-situ coagulation and removal of As(V). Based on the SSCT results, the first sample of siderite mineral (obtained from Ward's Natural Science) showed very poor arsenic-adsorption performance. The media was saturated at 1,000 bed volumes (BVs) and 10 ppb arsenic breakthrough occurred only at 40-BV throughput with a 3 cm^3 siderite bed in the presence of 1 mg/L Cl_2 at pH = 7.5. It appeared that Fe(II) was not dissolving as expected, thus little to no ferric hydroxide was produced to coat the siderite media. Due to the poor performance of the siderite material, the scope of work was revised, and proof-of-concept experiments were developed to more easily demonstrate the feasibility of using siderite for arsenic removal. The first step of the proof-of-concept was to synthesize ferrous carbonate in the laboratory. Unfortunately, we could not prepare ferrous carbonate in the laboratory due to its very rapid oxidation in the atmosphere.

Because the laboratory preparation $\text{FeCO}_3(\text{s})$ was not successful, screening tests were performed using six siderite samples obtained from around the world to select the most efficient siderite material to remove arsenic. The results showed that even at lower pH (pH 5.0) the performance of the siderite materials was not promising.

Based on the preliminary experimental results, it was concluded that under the experimental conditions, the solubility of siderite was much lower than the calculated theoretical value. A literature search revealed that the solubility of siderite depends on the redox potential of the environment, i.e., whether it's anoxic or oxic. Under oxic conditions at pH > 6.5, the dissolution rate of siderite is much slower than in the anoxic environment. The solubility of siderite increases dramatically under oxic conditions at pH 10 and higher or at highly acidic condition (pH 2 and lower), which suggested the possibility of modifying the adsorption by $\text{FeCO}_3(\text{s})$ concept to include a pretreatment of the bed with chlorinated dilute NaOH solution to dissolve ferrous iron and coat the media with $\text{Fe}(\text{OH})_3(\text{s})$ for arsenic adsorption. To improve the arsenic removal performance of the siderite, it was pretreated using acidic or alkaline Cl_2 solutions to better dissolve the siderite and produce more ferrous iron and subsequently more $\text{Fe}(\text{OH})_3(\text{s})$ on the siderite for arsenic adsorption. The “minicolumn” or SSCT results on

pretreated siderite showed that acid was preferred to alkaline pretreatment, but a short run length, 1,600 BVs, resulted, which was not considered long enough to further develop the arsenic-adsorption-on-siderite process.

Minicolumn tests with untreated wustite (FeO) demonstrated longer arsenic run length (3,200 BVs), but with the disadvantage of particulate iron in the column effluent. The particulate iron, which took up to 2,400 BVs to clear up, did not contain significant arsenic but would have to be filtered during a post treatment step in a drinking water treatment system. Reuse of wustite after washing was not possible due to its poor performance compared to fresh media. Attempts were made to remove arsenic using PEL Technology's synthetic Fe(II) media (reportedly a mixture of FeO and Fe₂O₃) under chlorinated and non chlorinated conditions. This media was not effective for arsenic removal.

Because the original concept failed, the PAC suggested developing an electrolytic-dissolution-of-siderite process using a stainless-steel column used as an electrode and a graphite rod as another electrode placed at the center of the SS column filled with siderite. We designed an electrolytic system and performed SSCTs after optimization of the potential difference between the anode and cathode. When the SS column was used as a cathode, there was no removal of arsenic. By changing the polarity of the electrodes, we obtained significant removal of arsenic in the siderite column with stainless steel as the anode. However, during a control experiment in which clean white sand was used in place of siderite it was apparent that the iron generated in the electrolytic system was not generated from the siderite. Rather, it was generated by dissolution of the stainless steel anode. Under these experimental conditions, the reduction of As(V) to As(III) was a possibility but was not verified.

RECOMMENDATIONS

Based on our experimental results it is recommended that siderite not be considered further as a source of iron hydroxide for arsenic removal from drinking water. Electrolysis of siderite also proved to be ineffective as a means of arsenic removal and should not be studied further unless different conditions, justified from theory, are utilized.

CHAPTER 1

INTRODUCTION

OVERVIEW

Inorganic arsenic is considered as a human carcinogen with multiple sites of attack. Epidemiological studies have demonstrated the higher risks of skin, bladder, lung, liver and kidney cancer along with other non-cancerous health effects that result from continued consumption of elevated levels of arsenic in drinking water (Guha Mazumder et al. 1998, Chen et al. 1988, Ferreccio et al. 2000). Due to the elevated health risk, based on the analysis of the United States Environmental Protection Agency (USEPA) and two independent reports by the National Research Council (NRC), USEPA has reduced the maximum contamination level (MCL) of arsenic in drinking water from 50 to 10 $\mu\text{g/L}$ (USEPA 2001).

Arsenic is a widely distributed element to which humans are exposed through ingestion of water and food, and by inhalation. Many countries around the world are exposed to elevated levels of arsenic in their drinking water. But, the most devastating incidence of arsenic poisoning has been reported in Bangladesh, and West Bengal, India (Chowdhury et al. 2000a, Chowdhury et al. 2000b, Das et al. 1995). Reportedly, more than 6 million people in West Bengal, India, and more than 70 million people in Bangladesh are drinking ground water containing elevated levels (50 $\mu\text{g/L}$ and above) of arsenic (Chakraborti et al. 2002). In Bangladesh out of an estimated 6–11 million shallow tube wells, approximately 27% are contaminated with arsenic above 50 $\mu\text{g/L}$ (Kinniburgh and Kosmus 2002). Here in the USA, according to the US Geological Survey (USGS) and the USEPA, high concentrations of arsenic are widespread in the Western, Midwestern, and Northwestern United States (<http://co.water.usgs.gov/trace/arsenic>). The EPA has reported that more than 5.5% of the total water supply systems in USA contain arsenic at a level greater than the new MCL (10 $\mu\text{g/L}$). Higher levels of arsenic tend to be found more often in groundwater than in surface water sources. About 4,100 of the nation's 54,000 Community Water Supplies and 1,100 of the 20,000 Non-Transient Non-Community water Supplies exceed the current 10 $\mu\text{g/L}$ limit. According to the Natural Resources Defense Council (NRDC 2000), over 34 million Americans drink water that increases their potential for arsenic-related cancer.

STATE-OF-THE ART ARSENIC REMOVAL TECHNOLOGIES

State-of-the-art technologies for arsenic removal from very small community water supplies can be classified into 5 categories: (1) precipitation-coagulation/filtration, (2) adsorption using activated alumina, (3) ion-exchange, (4) membrane filtration, and (5) alternative treatment process using granular iron media (GIM) filtration. For these small and very small systems, several key features predominate in the technology selection process: simplicity; cost; management of arsenic (III) and (V); operation and maintenance; and residuals management.

Small-scale systems and point-of-entry (POE) systems often use adsorption or ion-exchange (IX) in packed-bed processes for arsenic removal. Numerous factors including arsenic oxidation state (III or V), pH, competing anions, media particle size, and empty bed contact time (EBCT) significantly affect arsenic removal by adsorption and IX. However, the major factors limiting the use of adsorption processes include the high cost of the media, the complexity of regeneration, backwash and spent-regenerant disposal, and spent media disposal. Due to elevated arsenic concentrations in the spent IX regenerant, direct discharge to a sanitary sewer is usually not acceptable. Therefore, the spent regenerants may need to be further treated by a

precipitation/coagulation process to produce a sludge that can be thickened and dried prior to disposal. Since complex formation of arsenic species with granular ferric hydroxide (GFH)/granular ferric oxide (GFO) is known to be extremely rapid, the removal process is usually limited by diffusion of arsenic species through the porous iron oxides to available adsorption sites. One drawback of GFH/GFO media is that with aging, these media convert to more stable oxides with lower surface areas and porosities.

The arsenic removal by adsorption, IX, and coagulation–microfiltration (C–MF) was evaluated in laboratory and field studies in Albuquerque, NM conducted by researchers at the University of Houston (Clifford et al. 1997, Clifford and Wu, 2001). They reported that C–MF with FeCl_3 was effective and economical compared with adsorption and ion exchange (Ghurye et al. 2004). It was observed that pH and ferric dose were the most important variables controlling arsenic removal. Recently, experiments at the University of Houston have generated arsenic adsorption isotherms at several pHs and silica levels in the standard NSF-International (NSFI) challenge water for finely ground (<100 mesh) GFH in comparison with in-situ formed $\text{Fe}(\text{OH})_3(\text{s})$ formed during coagulation of FeCl_3 . It is clear that the freshly coagulated FeCl_3 yields a significantly higher loading of As(V), expressed as mg As(V)/g Fe, compared with the loading onto GFH, particularly at As(V) concentrations below 20 $\mu\text{g/L}$. So, Fe coagulation shows better performance than granular GFH based on arsenic loading on the iron.

The reason for the higher arsenic capacity on the formed-in-place coagulant is that the arsenate anions are adsorbed by surface complexation onto the short-chain polymers (oligomers) of $\text{Fe}_x(\text{OH})_y^{z+}$ as they are forming into $\text{Fe}(\text{OH})_3$ floc particles that can be filtered. Preformed $\text{Fe}(\text{OH})_3$ and granular ferric oxide/hydroxide (GFO/GFH) media simply do not have the available surface area by comparison to the oligomers and polymers of $\text{Fe}(\text{OH})_3(\text{s})$ that are formed during Fe^{3+} hydrolysis in coagulation processes. This leads to much higher arsenic loading on the coagulant and a smaller volume of $\text{Fe}(\text{OH})_3(\text{s})$ solids to be wasted in coagulation compared with adsorption onto GFH/GFO.

Reactions of arsenic compounds with Fe(II) have received much less attention than those involving Fe(III). This is likely due to the instability of ferrous oxides in water, which convert to magnetite or one of many possible ferric oxide phases over time periods of hour to days (Cornell and Schwertmann, 1996). Recent literature (Roberts et al., 2004) shows that application of Fe(II) instead of the usually applied Fe(III) is more advantageous, as oxidation of Fe(II) by dissolved oxygen causes partial oxidation of As(III) and Fe(III)(hydr)oxides formed from Fe(II) have higher sorption capacities. Figure 1.1 shows the removal of arsenic using Fe(II) and Fe(III) (Roberts et al., 2004). Thus, the use of Fe(II) instead of Fe(III) has some reported advantages in the removal of arsenic, though our recent studies (Lakshmanan et al. 2009) contradict the Roberts et al.(2004) observations. At lower pH Fe(II) is not as good as Fe(III) to remove arsenic from synthetic ground water.

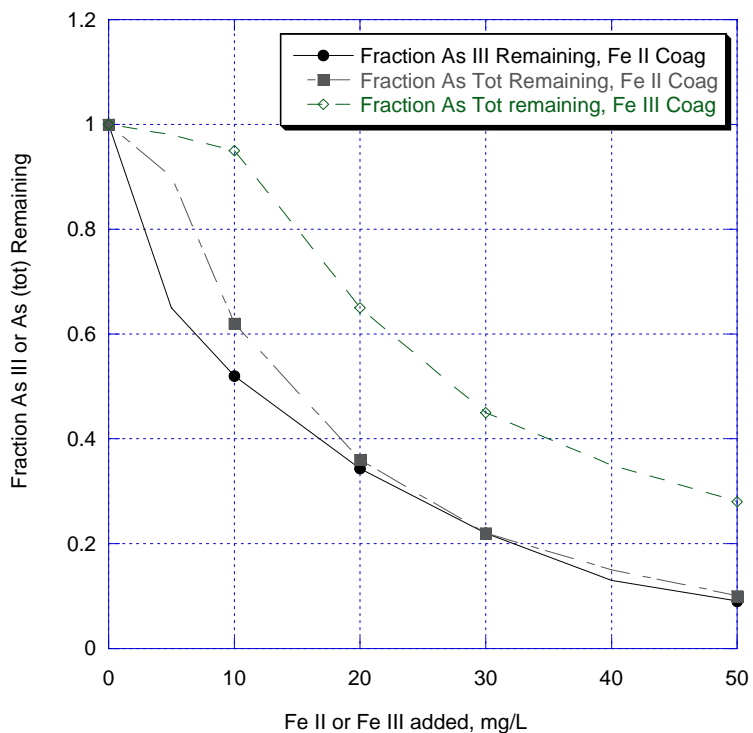


Figure 1.1 Removal of As(III) and As(Total) during ferrous and ferric coagulation, based on Roberts et al. (2004)

For Fe(II) source, zerovalent iron (Fe^0) has been used in several experiments for arsenic removal from drinking water (Su and Puls, 2001; Su and Puls, 2003, Lackovic et al., 2000; Melitas et al. 2002). Based on its iron content and significant solubility, FeO (wustite) is another possibility for the Fe(II) source. The operational simplicity of zerovalent iron makes it suitable for small-scale treatment systems. Corrosion of zerovalent iron results in the continuous generation of iron oxides at the surface of the iron filings. The oxides make complexes with arsenic species. Zerovalent iron overcomes some of the mass transfer limitation associated with GFO/GFH because of the continuous generation and hydrolysis of iron oxides. The major drawbacks with zerovalent iron for arsenic removal are (1) the rate of formation of oxides and adsorption sites is much greater than is required for arsenic complexation, and (2) there is the potential for possible release of sequestered arsenic due to subsequent mineralogical transformation of initially formed corrosion products (Su and Puls, 2004). Although Fe(II) oxide (wustite) may form less Fe(III) oxides than the zerovalent iron, still the amount of generated iron oxide may be more than that required for arsenic removal. (See Figure 1.2 and Table 1.1). The solubility of $\text{Fe(II)}_{\text{Tot}}$ in an $\text{Fe(OH)}_2(\text{s})$ system based on the chemical equilibrium modeling program Mineql+ is shown in Figure 1.2 (Schecher and McAvoy, 1998).

Figure 1.2. At pH 7.0, the solubility of Fe(II) is nearly 1 molar, i.e., much more than the required amount of iron to remove arsenic. (Our experimental data shows that only 2 mg/L Fe(III) can remove nearly 95% of As(V) in the NSF challenge water. See Figure 1.3). The excess $\text{Fe}(\text{OH})_3(\text{s})$ produced would tend to clog the system and force early breakthrough of iron and adsorbed arsenic. Moreover, in the presence of carbonate in the water, Fe(II) precipitates as FeCO_3 , which will complicate the formation of $\text{Fe}(\text{OH})_3$.

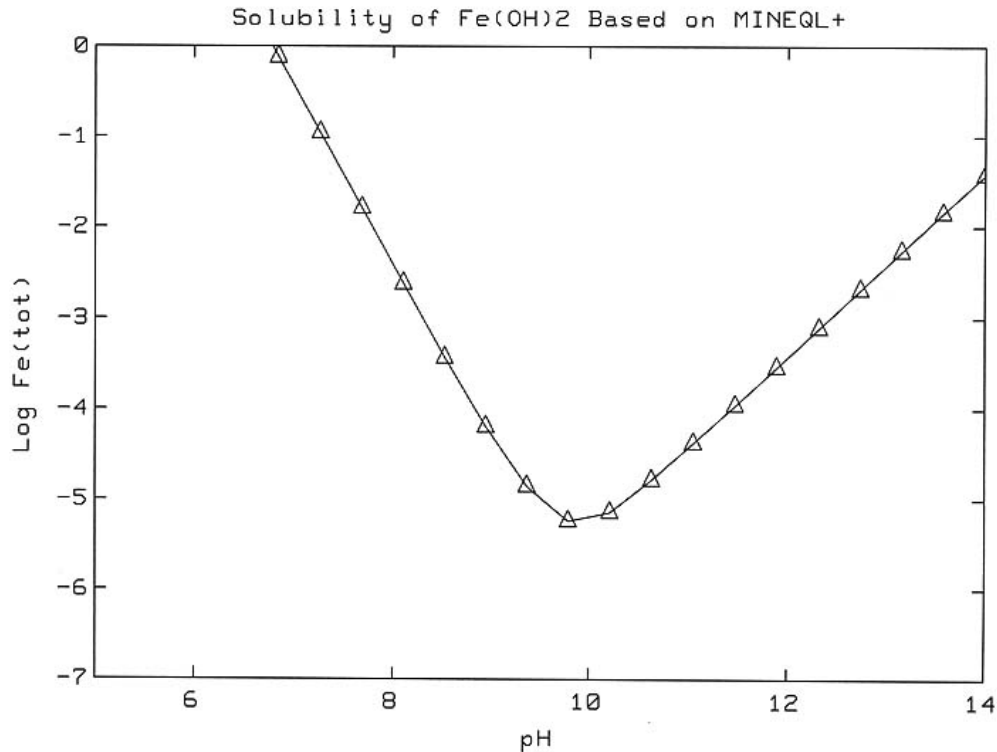


Figure 1.2 The pC–pH diagram for soluble $\text{Fe}(\text{II})_{\text{Tot}}$ in equilibrium with $\text{Fe}(\text{OH})_2(\text{s})$, at 25°C modeled by Mineql+, based on Schecher and McAvoy (1998)

Table 1.1
Solubility of Fe(II) in equilibrium with $\text{Fe}(\text{OH})_2(\text{s})$ and $\text{FeCO}_3(\text{s})$ in the 6.0–8.5 pH range at 25 °C, based on Mineql+ (Schecher and McAvoy, 1998)

pH	Solubility of $\text{Fe}(\text{OH})_2(\text{s})$ (mg/L)	Solubility of $\text{FeCO}_3(\text{s})$ (mg/L)
6.0	very high	88.5
7.0	28,000	8.85
8.0	280	0.885
8.5	17.7	0.35

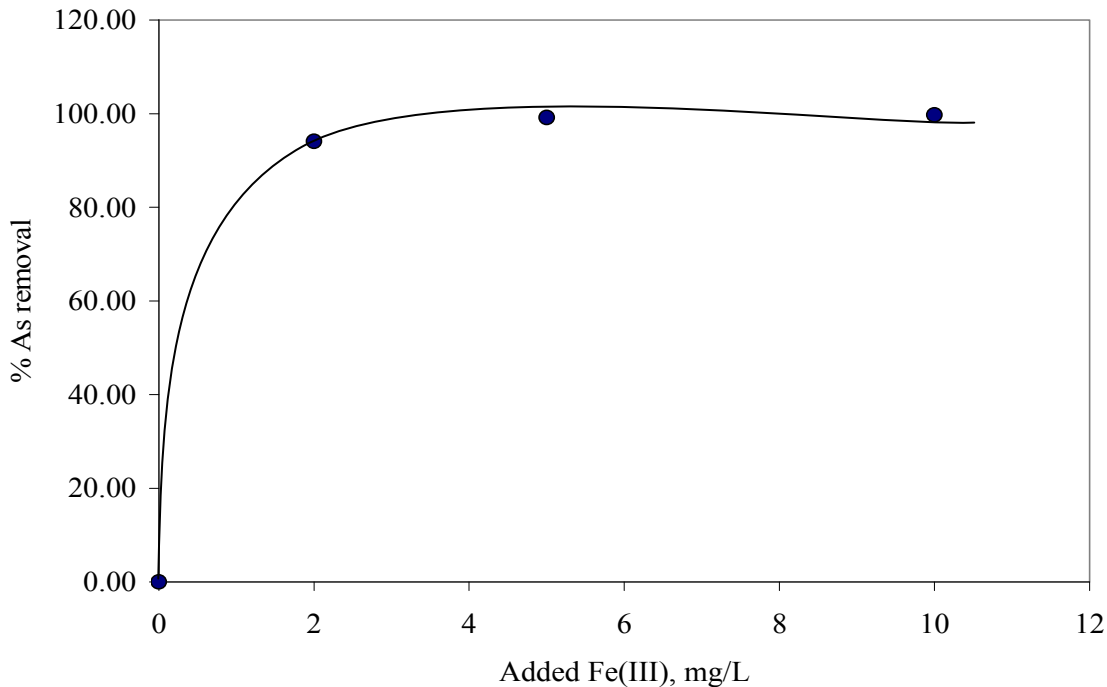


Figure 1.3 Removal efficiency of As(V) using ferric chloride measured as Fe with different dosages at pH 7.5 using NSF1 challenge water containing representative background levels of SiO₂, F⁻, and PO₄³⁻ (Lakshmanan et al. 2008)

FeCO₃ Bed for Arsenic Removal

Instead of Fe(II)-containing oxides (wustite), the concept of this research was to use FeCO₃(s) (siderite), a naturally occurring mineral, for arsenic removal in very small systems. Because FeCO₃(s) is not porous, it does not operate like the common granular iron media for arsenic removal — GFH and GFO — which are porous FeOOH adsorbents. With the non-porous FeCO₃, a portion of the FeCO₃(s), is slightly soluble (See Table 1.1) in ground water under typical E_h and pH conditions (the pc–pH diagram for soluble Fe(II) in equilibrium with FeCO₃(s) is shown in Figure 1.4), and will produce Fe²⁺ ions that can be oxidized to Fe³⁺ using chlorine, H₂O₂ or KMnO₄ etc. These ferric ions will hydrolyze and precipitate Fe(OH)₃(s) or ferric oxyhydroxide (FeOOH), which will, in turn, strongly adsorb As(V). Thus, the FeCO₃(s) is envisioned to act as a virtually infinite sink of ferric coagulant for arsenic removal. Application of FeCO₃(s) instead of the usually applied zerovalent iron and Fe(II) oxides (wustite) is expected to have advantages for three reasons: (1) no clogging due to slow release of Fe(II) and immediate oxidation of Fe(II) to Fe(III), (2) higher sorption capacity of the in-situ formed iron oxides, and (3) lower density of siderite (the specific gravity of wustite is 5.7 compared with 3.8 for siderite). So backwash of wustite is more problematic than siderite.

Wang and Reardon (2001) reported that a two-column reactor (first siderite column and second limestone column) could efficiently remove arsenic and other toxic elements from

contaminated water. The dissolution of siderite was increased by reducing the pH of the targeted water by sparging CO₂. They reported that most of the arsenic was removed in the first column.

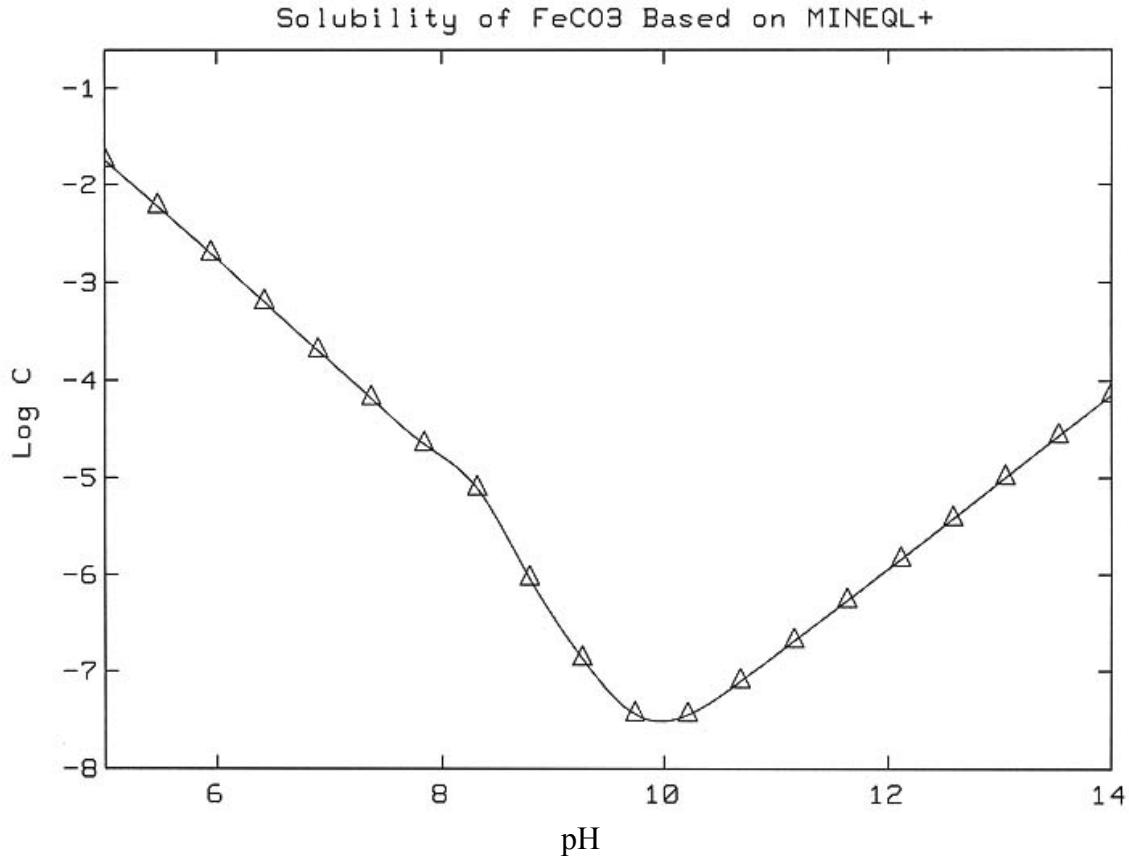


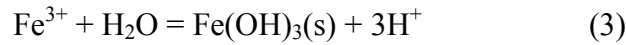
Figure 1.4 The pC–pH diagram for soluble Fe(II)_{Tot} in equilibrium with FeCO₃(s), modeled by Mineql+ with C_{T,CO3} = 10⁻³ M and T = 25°C, based on Schecher and McAvoy (1998)

Solubility of FeCO₃

The solubility of FeCO₃(s) as a function of pH of the solution is shown in Figure 1.4 and summarized in Table 1.1 for pH in the region of interest. Note that in Table 1.1 the solubilities are different. According to pC–pH diagram, in the region of pH 6.5 to 8.5, Fe²⁺ in equilibrium with CO₃²⁻ is the controlling soluble species and its concentrations in Table 1.1 have been calculated based on the K_{sp} of FeCO₃(s) and pH variable carbonate concentrations assuming a water with C_{T,CO3} = 0.003 M (approximately 150 ppm T. Alk).



The amount of Fe(II) produced by the solubility of FeCO₃ can be calculated by the Equation, $\text{Log}[\text{Fe}^{2+}] = -0.3 - \text{pH} - \text{log}[\text{HCO}_3^-]$. At pH 7.0, approximately 0.9 mg/L of Fe(II) will be generated, which will be oxidized by chlorine by the following reaction.



In the pH region of 6.5 to 7.5 the soluble Fe²⁺ will be 2.9 to 0.9 mg/L, which is in the ideal range for arsenic coagulation. At higher pH, the conversion of Fe²⁺ to Fe³⁺ will dissolve more Fe²⁺ as Fe(OH)₃(s) precipitates. Based on eq. (2), 1.0 mg/L chlorine will produce approx. 1.6 mg/L Fe³⁺, which will be removed from the system as Fe(OH)₃(s). So, the dissolution of FeCO₃(s) (eq. (1)) will be always in the forward direction and continuously generate Fe²⁺ in the system as long as free chlorine exists. In this way, the chlorine concentration was envisioned to control the solubility of the Fe²⁺ and eventually the production of the coagulant, Fe(OH)₃(s). Our recent work (Lakshmanan et al. 2008) showed that only 2 mg/L Fe(III) was required to remove nearly 95% of As(V) at pH 7.5 (Figure 1.3). Thus, the generated iron would be sufficient to remove arsenic from the contaminated water. At higher pH, slightly more chlorine would be required to dissolve the required amount of Fe²⁺.

OBJECTIVES

The objective of our proposed research was to determine the feasibility of using filter beds of ferrous carbonate (siderite) in combination with low levels (0–2 ppm) of chlorine to oxidize As(III) to As(V) and generate 0–3 ppm Fe(OH)₃(s) as Fe for in-situ coagulation and removal of As(V). Proof-of-concept batch tests, and small-scale column tests (SSCTs) were conducted to determine the efficiency for arsenic removal.

SIGNIFICANCE OF THE PROJECT

The water supply community would benefit from the results of this innovative research by having access to lower-cost and more effective arsenic removal for very small systems. Although FeCO₃(s) is not well known in water treatment, it is a potentially low cost, and-non-toxic coagulant-adsorbent for arsenic. It was expected that FeCO₃(s) would have the following advantages over zerovalent iron coagulation-filtration and granular FeO/Fe₂O₃ adsorption:

1. FeCO₃(s) would produce the amount of Fe(II) in the system that is required to remove arsenic from the drinking water, whereas, zerovalent iron or FeO based media would likely produce more Fe(II) than required. The excess amount of Fe(II), which oxidizes to Fe(III) and forms Fe(OH)₃ would clog the bed and force early termination of the filter run.
2. FeCO₃(s) filters are expected to outperform GFH and GFO filters for effective low cost arsenic removal in small systems.
3. The use of chlorine as an oxidant would solve the problem of oxidation of Fe(II) to Fe(III) and would also oxidize As(III) to As(V). Oxidation of Fe(II) to Fe(III) by

aeration is not a good approach due to very slow oxidation of Fe(II) by oxygen at near-neutral pH.

4. The envisioned chlorine–siderite process would be a simple coagulation–filtration process for arsenic removal that would not require metering the highly corrosive and hard-to-handle FeCl_3 into the water treatment system to produce $\text{Fe}(\text{OH})_3(\text{s})$.
5. The siderite could be used nearly infinitely by backwashing the system. Longer adsorption run lengths were expected due to the formation of a controlled amount of coagulant.

CHAPTER 2 MATERIALS AND METHODS

REAGENTS

All reagents used were of analytical reagent grade. Milli Q water (18 M Ω) was used to prepare all solutions. Primary standards of 100 mg As/L of each species were prepared from sodium m-arsenite (NaAsO₂) for As(III) and Sodium arsenate (Na₂HAsO₄) for As(V) both from Sigma Chemical Co, MO. Working standard solutions were prepared daily with proper dilution. Citric/citrate buffer solution was prepared using 2 M citric acid and pH was adjusted to 5.0 using NaOH. A 4-mg/mL solution of L-cysteine (Sigma Chemical Co, MO) in HCl solution was used to reduce As(V) to As(III). Sodium tetrahydroborate (EM Science, Germany) solutions were prepared fresh daily, and were supplemented with sodium hydroxide.

To prepare the NSF1-53 challenge water, the following salts were used NaNO₃, NaHCO₃, Na₂HPO₄·H₂O, NaF, Na₂SiO₃·9H₂O, MgSO₄·7H₂O, and CaCl₂·2H₂O. All the chemicals were purchased from Sigma Chemical Co or EM Science. Concentrated stocks were prepared from these salts and used for the preparation of challenge water on the day of experiment.

Although siderite is a very common mineral, it is not readily available commercially, presumably because of lack of current markets for it as a raw material. Thus, small samples of siderite from six different mineral deposits were obtained from two different vendors for screening tests to establish the best mineral for the arsenic removal tests. Identification and sources of the siderite materials are given in Table 2.1.

Table 2.1
Sources of Siderite materials

Siderite samples	Name of the vendor
Sample 1 (Siegen, Westphalia, Germany (DM 10822))	Excalibur Mineral Corporation, Peekskill, New York
Sample 2 (Dobschau, Hungary (No. 5244))	
Sample 3 (Roxbury, Connecticut, USA (DM 19490))	
Sample 4 (Lobenstein, Thuringia, Germany (No. 5240))	
Sample 5 (Ivigtul, Greenland)	
Sample 6 (Ward's Natural Sci., (Research gr # 49H5911))	Ward's Natural Science, Rochester, New York

PREPARATION OF NSFI-53 CHALLENGE WATER

For all coagulation studies, NSFI-53 Challenge Water (hereafter referred to as challenge water) whose composition is given in Table 2.2 was prepared and used as the background water for the isotherm tests. This water contains realistic concentrations of background contaminants such as silica, sulfate, phosphate, fluoride, and hardness, which are known to affect the arsenic capacity of adsorbents. Stability was not an issue with the NSFI water because it was made and used on the day of experiment. The pH of the synthetic groundwater was adjusted by using dilute HCl or NaOH solution. The required amount of As(III) or As(V) was spiked to the challenge water for the studies.

Table 2.2
Composition of NSFI-53 challenge water

Cation	MW	meq/L	mg/L	Anion	MW	Meq/L	mg/L
Ca ²⁺	40.1	2.00	40.1	HCO ₃ ⁻	61.0	3.0	183.0
Mg ²⁺	24.3	1.04	12.6	SO ₄ ²⁻	96.1	1.04	50
Na ⁺	23.0	3.864	88.87	Cl ⁻	35.5	2.0	71.0
				NO ₃ -N	14.0	0.143	2.0
				F ⁻	19.0	0.053	1.0
				PO ₄ -P	31.0	0.0013	0.040
				SiO ₃ -SiO ₂	60.1	0.666	20.0
				As(III)/(V)	74.9		0.050
Σ =		6.904	141.57	Σ =		6.904	327.09

LABORATORY PREPARATION OF FERROUS CARBONATE

For the proof-of-concept tests, attempts were made to prepare FeCO₃(s) in the laboratory by precipitating it from a mixture of FeSO₄ and NaHCO₃ according to the procedure described below.

The ferrous carbonate synthesis experiments were carried out in a 250-mL glass reaction vessel that contained multiple ports, which allowed introduction of N₂ gas, pH electrode, and other solutions. All solutions were 18 MΩ water made anoxic by sparging with N₂ for 1 h. For a typical experiment, the reaction vessel was filled with 15 mL of a bicarbonate solution (1 M), which was flushed with N₂ for 1½ h. After 1½ h, oxygen free ferrous sulfate (0.5 M) solution was added to the reaction vessel at a rate of 0.16 mL/min using a peristaltic pump. The pH of the solution was adjusted around 8.5. Precipitation started immediately. The white precipitate, presumably FeCO₃(s), was filtered through a 0.45µm filter, and the residue on the filter was collected.

PROOF-OF-CONCEPT TESTS

Short term batch equilibration tests were conducted to establish the feasibility of adding Cl_2 to As(III)-contaminated water in contact with fine particles of $\text{FeCO}_3(\text{s})$ for the purpose of generating $\text{Fe}(\text{OH})_3$ and adsorbing the oxidized As(V). The variables examined were pH, alkalinity, and chlorine dose. For these proof-of-concept tests, the laboratory-prepared $\text{FeCO}_3(\text{s})$ fine particles passing 100 mesh ($< 106 \mu\text{m}$) were used for the batch equilibrations. In the proof-of-concept batch tests, a standard jar-test apparatus was used; 100 mg freshly prepared $\text{FeCO}_3(\text{s})$ was added to square jars containing the pH-adjusted challenge water spiked with $50 \mu\text{g/L}$ As(III). Chlorine doses of 0–3 mg/L were used, and the total alkalinity was varied from 0–200 mg/L as CaCO_3 . The closed-system mixture was stirred rapidly for 5 min to (1) oxidize As(III) to As(V), (2) dissolve the requisite amount of Fe(II), and (3) oxidize Fe(II) to Fe(III) and hydrolyze it to $\text{Fe}(\text{OH})_3(\text{s})$ and adsorb the arsenic. After five minutes of reaction, the mixture was sampled and filtered through a $0.2 \mu\text{m}$ membrane filter and the filtrate was analyzed for As(III), total arsenic (As(Tot)), and total iron (Fe(Tot)).

SCREENING TESTS USING SIDERITE MINERALS

For screening tests, a standard jar-test apparatus was used; 100 mg of ground and sieved (150–250 μm particle size) siderite was added to square jars containing the pH-adjusted challenge water spiked with $50 \mu\text{g/L}$ As(III). A chlorine dose of 2 mg/L was used in the challenge water. The mixture was stirred rapidly (250 rpm) for 5 to 10 min to (1) oxidize As(III) to As(V), (2) dissolve the requisite amount of Fe(II), and (3) oxidize Fe(II) to Fe(III) and hydrolyze it to $\text{Fe}(\text{OH})_3(\text{s})$ and adsorb the arsenic. After five to ten minutes of reaction, the mixture was sampled and filtered through a $0.2 \mu\text{m}$ membrane filter and the filtrate was analyzed for As(Tot).

COLUMN TESTS TO VERIFY THE CONCEPT OF ARSENIC REMOVAL BY SIDERITE–CHLORINE FILTRATION

Each (SSCT) was conducted using a 1-cm diameter column operated at a rapid flow rate such that the empty bed contact time (EBCT) was 1 min. The column was packed with 3 cm^3 of $\text{FeCO}_3(\text{s})$ granules (250–500 μm particle size). Glass wool was packed into the bottom of the column to support the $\text{FeCO}_3(\text{s})$ granules. Figure 2.1 is a schematic presentation of the experimental set-up. The NSF challenge water (pH 7.5) spiked with $50 \mu\text{g/L}$ of As(V) and 1 mg/L Cl_2 was pumped into the column from top to bottom (down flow) at a constant flow rate by a peristaltic pump. After passing through the column, the effluent was collected for the measurement of As(Tot) at predetermined bed volumes (BVs).

PRETREATMENT OF SIDERITE BED

Pretreatment of Siderite with Alkaline Cl_2 Solution

To increase the solubility of siderite, the siderite bed was treated with 100 mL (about 33 BVs) of 0.01 M NaOH solution spiked with 10 mg/L Cl_2 at a flow rate of 1 mL/min. After

treatment with alkaline Cl_2 solution, the bed was washed thoroughly with deionized (DI) water until the pH of the effluent was nearly neutral.

Pretreatment of Siderite with Acidic Cl_2 Solution

In another attempt to increase the solubility of Fe(II), the siderite bed was treated with 100 mL of 0.10 M HCl solution spiked with 10 mg/L Cl_2 at the flow rate of 1 mL/min. After treatment with acidic Cl_2 solution, the bed was washed thoroughly with DI water until the pH of the effluent was nearly neutral.

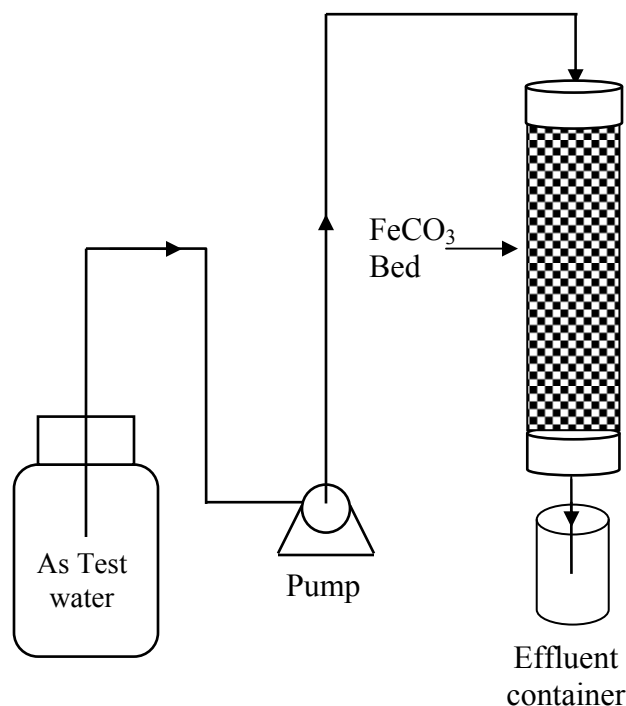


Figure 2.1 Small-scale column test (SSCT) apparatus

MINICOLUMN TESTS WITH IRON(II) OXIDE GRANULES

These minicolumn tests were conducted using 1-cm diameter columns operated at a rapid flow rate such that the empty bed contact time (EBCT) was 1 min. The column was packed with 4 cm³ of FeO(s) granules (250–500 μm particle size). Glass wool was packed into the bottom of the column to support the FeO material. The NSFI challenge water (pH 6.5) spiked with 50 μg/L of As(V) and 3 mg/L Cl_2 was pumped down flow through the column at a constant flow rate by a peristaltic pump. After passing through the column, the effluent was collected for the measurement of As(Tot) at predetermined effluent BVs.

ELECTROLYTIC DISSOLUTION OF SIDERITE (PROPOSED BY PAC MEMBERS)

After the research on this project had continued for nearly one year, a project advisory committee (PAC) meeting was held at the University of Houston (UH) on 6 July, 2006. The outcome of the meeting was as follows:

1. The PAC agreed that it would not be useful to continue working with siderite, wustite or PEL media for arsenic removal using the method described in the proposal — packed columns fed with chlorinated raw water. The experimental results obtained to date do not warrant further studies of this method.
2. Electrochemical activation of the siderite and PEL Technologies iron oxides should be attempted in an effort to produce a mineral with an activated surface and a high surface area for arsenic adsorption.
3. An electrochemical adsorption column should be constructed comprising a stainless steel (SS) cathode and graphite/carbon anode. The column should be filled with the fresh siderite or PEL iron oxide similar to that used in previous experiments without electrochemical activation. Potential (voltage to be determined from experiments) should be maintained on the column while challenge water containing As(V) is passed through the column with EBCT in the range of 0.5 to 5 min.
4. UH researchers should experiment with electrochemical potential and current to determine their effects on arsenic adsorption and on the ability to regenerate the surfaces by backwashing/cleaning the media after arsenic breakthrough.

Based on advice from the PAC, UH researchers designed and constructed an electrolytic minicolumn to dissolve iron-based media. This SS column was 6 cm long with as 1.3 cm i.d. The SS tubing acted as one electrode of the electrolytic cell while a graphite rod surrounded by siderite acted as the second electrode, which was located in the axial center of the minicolumn was insulated from the SS tube by means of a non-conducting plastic fitting. The schematic diagram is shown in Figure 2.2. An adjustable 12 V power supply system was used to provide voltage and current to the electrolytic cell. The current and potential differences across the electrodes were monitored throughout the experiments.

The SSCTs using the electrolytic column were conducted at a rapid flow rate such that the empty bed contact time (EBCT) was 1 min. The column was packed with 3–4 cm³ of FeCO₃(s) granules (40–60 mesh or 0.250–0.425 mm dia). Glass wool was packed into the bottom of the column to support the FeCO₃(s) granules. Figure 2.2 is a schematic presentation of the experimental set-up. The NSFJ challenge water (pH 7.5) spiked with 50 µg/L of As(V) was pumped into the column from top to bottom (down flow) at a constant flow rate by a peristaltic pump. A predetermined voltage was applied across the SS electrode and graphite electrode, and the cell polarity was changed in some experiments to determine the effect of current flow direction. The effluent was collected for the measurement of As(Tot), As(III), and iron at predetermined BVs.

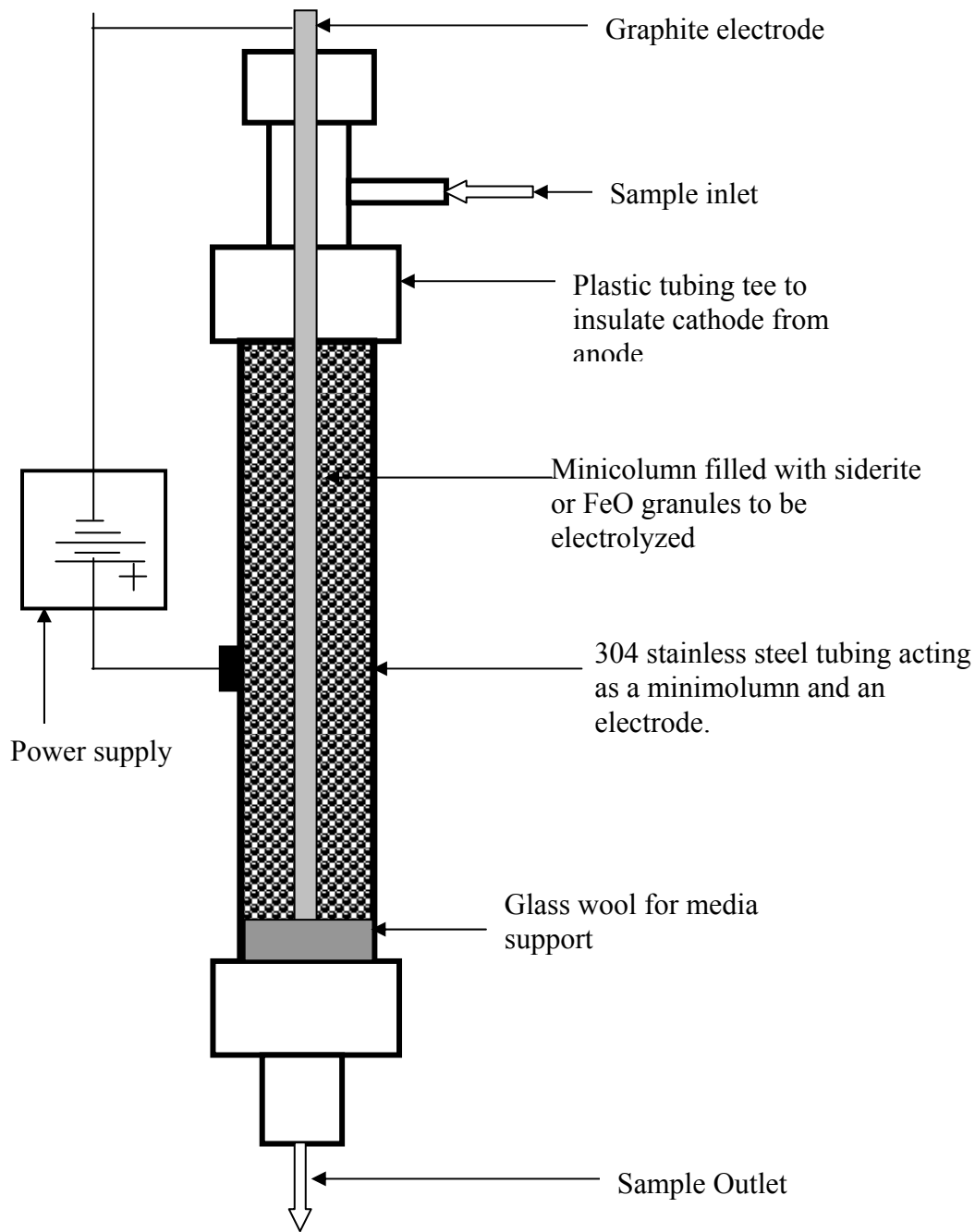


Figure 2.2 Schematic of electrolytic column designed for dissolution of siderite or FeO granules by imposed current and voltage from external power supply

INSTRUMENTATION

Most analyses were carried out using a flow injection hydride-generation atomic absorption spectroscopy (FI-HG-AAS) using a Perkin-Elmer (Model Zeeman 5000) atomic absorption spectrometer (AAS) equipped with an electrodeless discharge lamp (EDL) operated at 8W from an external power supply. The AAS was coupled with a Perkin-Elmer Flow Injection (FIAS-100) unit for hydride generation for the determinations of As(III) and As(Tot). Detail descriptions of the instrumental conditions are given in Table 2.3. Field samples for As(Tot) and speciated As(III) were analyzed by FI-HG-AAS. Fe was measured by flam AAS (Perkin-Elmer, model AA300). Details of the instrumental set up are given in Table 2.3.

Table 2.3
Experimental conditions for the determination of As(III) and As(Tot) by FI-HG-AAS

Parameters	Perkin-Elmer (Zeeman 5000)
Lamp	EDL, powered by 8 (W)
Wavelength	193.7 (nm)
Slit	0.7 nm(low)
Sample volume	500 (μ L)
HCl concentration	0.02 (M)
Citric/citrate buffer (pH 5.0)	2 (M)
HCl/citrate buffer flow rate	8 (ml/min)
NaBH ₄ concentration (for As(Tot))	0.4% in 0.2% NaOH
NaBH ₄ concentration [for As(III)]	0.2% in 0.05% NaOH
NaBH ₄ flow rate	5 (ml/min)
Carrier gas	Argon
Carrier gas flow rate	60-70 (ml/min)
Quartz cell temp	Electrically heated, ~900 ($^{\circ}$ C)

TOTAL ARSENIC AND ARSENIC(III) ANALYSIS

FI-HG-AAS

To determine As(Tot), samples were treated with L-cysteine in 2M HCl. The samples were kept for 15 minutes at room temperature for the reduction of As(V) to As(III) and then diluted to such a volume as to maintain the concentrations of L-cysteine and acid to 4 mg/mL and 0.02 M, respectively. The arsenic concentration was measured by FI-HG-AAS against As(III) standards prepared as samples. Reduced arsenic sample was injected into the stream of 0.02 M HCl (at 8mL/min) solution by means of a rotary valve fitted with a 500- μ L sample loop. The injected sample together with carrier solution, met subsequently with a continuous stream of sodium tetrahydroborate (0.4% in 0.2 % NaOH, at 5 mL/min). After mixing with sodium tetrahydroborate, the generated hydride (AsH₃) entered the gas-liquid separator. Inside this

apparatus a continuous flow of argon carrier gas (70–80 mL/min) carried the hydride to the quartz tube fitted on an electrically heated heater at 900 °C.

The peak height signals were measured at 193.7 nm. At least triplicate measurements were made for each sample and standard. For the determination of As(III) in the presence of As(V), the carrier HCl solution was replaced by 2 M citric/citrate buffer of pH 5.0. Arsine was generated using 0.2% sodium tetrahydroborate in 0.05 % NaOH. Under this condition As(V) does not generate AsH₃ and does not interfere in the determination of As(III). The detection limits (three times of standard deviation of the blank, n =10) for As(Tot) and As(III) were 0.04 µg/L and 0.096 µg/L, respectively. The relative standard deviations (RSD) of ten determinations of As(Tot) and As(III) were 1.86% and 3.34%.

CHAPTER 3 RESULTS AND DISCUSSION

PROOF OF CONCEPT TEST RESULTS USING PRECIPITATED $\text{FeCO}_3(\text{s})$

The proof-of-concept tests were designed to establish the feasibility of adding Cl_2 to As(III)-contaminated water in contact with fine particles of $\text{FeCO}_3(\text{s})$ for the purpose of generating $\text{Fe}(\text{OH})_3(\text{s})$ and adsorbing the oxidized As(V) under a variety of conditions. Because ferrous carbonate precipitated powder was not commercially available, we attempted without success to prepare it in our laboratory. Unfortunately these initial $\text{FeCO}_3(\text{s})$ precipitation experiments failed because, during filtration and drying, we could not prevent the oxidation of Fe(II) to Fe(III) of the white precipitates of ferrous carbonate. It appeared that, in the presence of air, white ferrous carbonate oxidized to brown ferric hydroxides. So, to prevent oxidation we would need an anoxic glove box purged with nitrogen or argon for further processing. We as well as the PAC do not recommend the continuation of these ferrous carbonate precipitation experiments as they are of questionable long-range value.

SIDERITE-MINERAL SCREENING-TEST RESULTS

Because we could not perform the scheduled proof-of-concept tests, and could not locate a commercially available supply of bulk siderite, we screened six small siderite mineral samples obtained from around the world. For the screening tests, samples of the siderite minerals were crushed and sieved, and 100 mg of the 60×100 mesh (0.150–0.250 mm dia) diameter particles were used for each batch test, which was carried out at pH 7.0 and 2.0 mg/L Cl_2 in the challenge water. The test results for the siderite screening tests are presented in Table 3.1, which shows that under the experimental conditions the performance of the siderite materials was not promising. The experiments were also repeated at pH 5.0 for two siderite materials (samples 5 and 6) (Table 3.2). Still, the performance was not improved at lower pH.

Table 3.1
Screening tests for siderite materials using challenge water (pH 7.0) containing 2.0-mg/L Cl₂ with rapid mixing for 5–10 min

Ground Siderite samples (60 × 100 mesh)	Equilibrium As conc. after 5 min, (µg/L)	Equilibrium As conc. after 10 min(µg/L)
Blank (challenge water without siderite)	48.5 ± 0.3	48.4 ± 0.1
Sample 1(Siegen, Westphalia, Germany (DM 10822))	48.5 ± 0.2	48.3 ± 0.3
Sample 2 (Dobschau, Hungary (No. 5244))	48.5 ± 0.2	48.1 ± 0.3
Sample 3 (Roxbury, Connecticut, USA (DM 19490))	48.3 ± 0.1	47.5 ± 0.7
Sample 4 (Lobenstein, Thuringia, Germany (No. 5240))	47.7 ± 0.8	46.3 ± 0.9
Sample 5 (Ivigtul, Greenland)	46.3 ± 0.9	43.2 ± 0.7
Sample 6 (Ward's Natural Sci., (Research gr # 49H5911))	44.9 ± 0.2	45.2 ± 0.5

Note: The initial As(III) concentration was 48.5 µg/L in the challenge water.

Table 3. 1
Screening tests for siderite materials using challenge water (pH 5.0) containing 2.0-mg/L Cl₂ with rapid mixing for 5–10 min

Ground Siderite samples (60 × 100 mesh)	Equilibrium As conc. after 5 min(µg/L)
Blank	49.6 ± 0.8
Sample 5 (Ivigtul, Greenland)	44.8 ± 0.1
Sample 6 (Ward's Natural Sci., (Research gr # 49H5911))	46.2 ± 0.3

Note: The initial As(III) concentration was 49.6 µg/L in the challenge water.

DISSOLUTION RATES FOR SIDERITE UNDER ANOXIC AND OXIC CONDITIONS

The screening tests for As(V) removal by siderite were not successful, presumably because sufficient ferrous iron did not dissolve and get oxidized by Cl₂ and eventually precipitate as Fe(OH)₃(s), which would adsorb the As(V).

Thus, the basic problem with the proposed concept of “ferrous carbonate beds as inexhaustible sources of $\text{Fe}(\text{OH})_3(\text{s})$ for arsenic removal” seems to be the less-than-theoretical solubility of siderite under the conditions of the experiments, i.e., NSF challenge water under aerobic (oxic) conditions. This tentative conclusion is supported by a recent publication by Duckworth and Martin (2004) entitled “Role of molecular oxygen in the dissolution of siderite and rhodochrosite”. Their research showed that the solubility of siderite under oxic conditions is much less than under anoxic conditions. See Figure 3.1 below, which is reproduced from their paper. It illustrates that, under oxic conditions, which we have in our atmospheric experiments with 1 mg/L Cl_2 present in the aerobic challenge water, siderite is virtually insoluble in the pH 6.5–10 range. Duckworth and Martin’s observed rates of siderite dissolution were far less than the mechanistic (theoretical) model predictions.

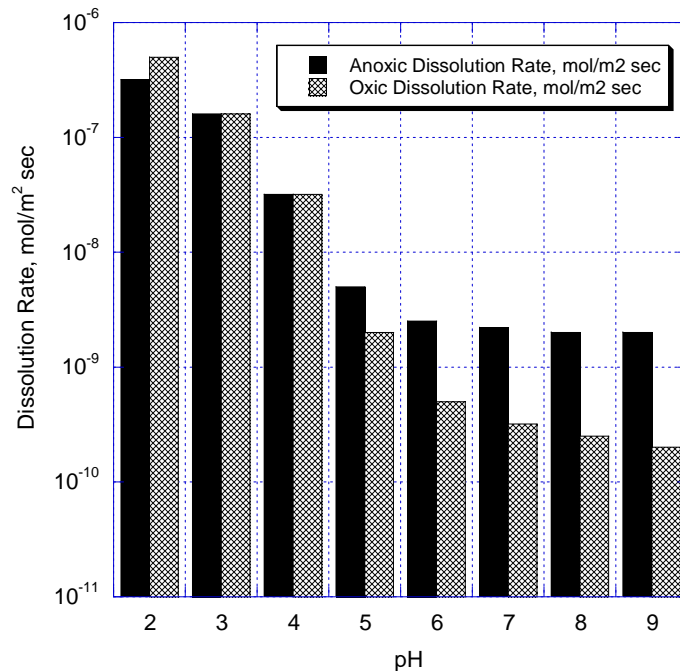


Figure 3.1 Dissolution rates of $\text{FeCO}_3(\text{s})$ as a function of pH under oxic and anoxic conditions, based on Duckworth and Martin (2004)

Our lack of $\text{As}(\text{V})$ adsorption on siderite and Duckworth and Martin’s experimentally demonstrated insolubility of siderite under oxic conditions suggest that the concept of feeding chlorinated water to a bed of ferrous carbonate as a source of $\text{Fe}(\text{II})$ and eventually $\text{Fe}(\text{III})$ and $\text{Fe}(\text{OH})_3(\text{s})$ is not a valid one.

A careful examination of Figure 3.1 shows that, under oxic conditions at pH above 10, and pH below 4.0, siderite has greater solubility. We considered that this greater solubility under

basic and acidic conditions might be used to our advantage. We could pretreat the siderite bed with chlorinated NaOH (e.g., 0.001 M or pH 11, 10 mg/L Cl₂) or HCl (0.1 M HCl and 10 mg/L Cl₂) to dissolve Fe(II) ions. In the presence of Cl₂, these ferrous ions would be immediately oxidized to Fe(III) with the subsequent precipitation of Fe(OH)₃(s), which would coat the siderite media and adsorb As(V) from the feed water. When the ferric hydroxide coated media was exhausted, it would be regenerated by backwashing to cause enough attrition to clean the siderite particles and allow another cycle of NaOH/HCl washing to dissolve more Fe(II), which would be oxidized to Fe(III) and eventually Fe(OH)₃(s) to again coat the media and adsorb As(V).

Our experimental results before and after pretreatment with acidic or alkaline Cl₂ solution are shown in Figure 3.2, which indicates that when the siderite bed was pretreated with acid or alkaline Cl₂ solution, the performance was better than the untreated siderite. The pretreatment of the siderite media significantly enhanced the performance. The effect was more prominent when the media was treated with HCl–Cl₂ solution. Without pretreatment in the presence of Cl₂ in the challenge water, very early arsenic breakthrough occurred. When pretreated with NaOH–Cl₂, 10 µg/L breakthrough of As(V) occurred at just 500 BV, whereas with HCl–Cl₂ pretreatment, the breakthrough occurred at nearly 1,600 BVs. However, a problem occurred with acid treatment, which resulted in a significant loss of iron during as evidenced by a brownish solution released from the column during acid pretreatment. Even with 1,600 BVs throughput to the arsenic MCL, the run length of siderite after acid treatment was considered too short for economical arsenic treatment of ground water in any size system.

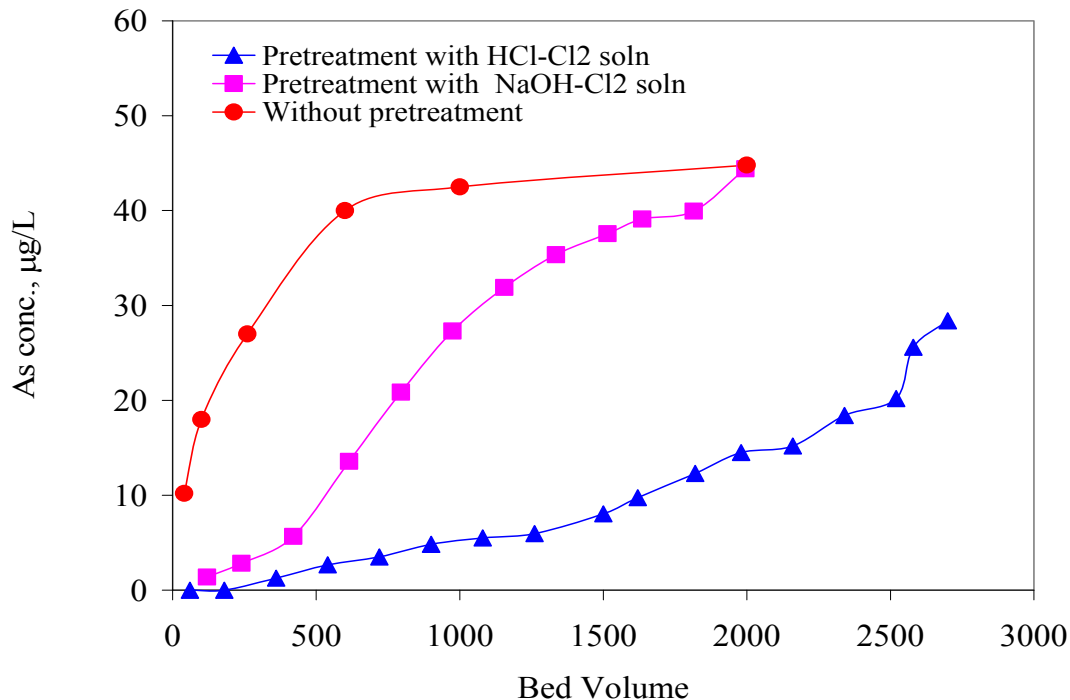


Figure 3.2 As(Tot) breakthrough from an SSCT column containing 9 cm³ siderite. Feed to minicolumn contains 50-mg/L As(III) at pH 6.5 with EBCT 1.0 min.

MINICOLUMN TESTS WITH WUSTITE, FEO

Based on the disappointing minicolumn test results with siderite, a decision was made to run experiments with another Fe(II)-based material mentioned in the original proposal: FeO, ferrous oxide or wustite. The solubility of FeO(s) is considerably greater than FeCO₃(s), which would yield more Fe(II) in solution, and finally more Fe(OH)₃(s) precipitate to coat the media and remove arsenic. A FeO minicolumn test was performed using NSFJ challenge water containing 3 mg/L Cl₂ at pH 6.5. The results are given in Figure 3.3 for filtered and unfiltered effluent samples. Membrane microfiltration (0.2 μm) was employed because the effluent, brownish in color, obviously contained insoluble iron, presumably Fe(OH)₃(s), which was visible during the first 2,400 BVs of the run.

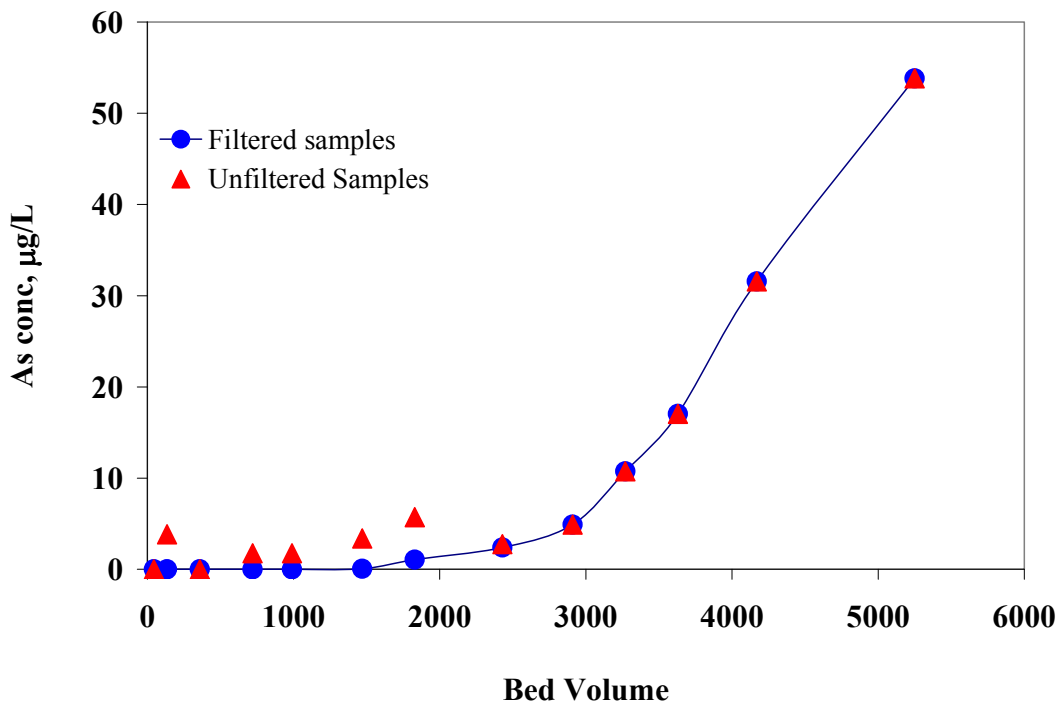


Figure 3.3 As(Tot) breakthrough from a minicolumn containing 4 cm³ wustite (FeO). Feed arsenic concentration: 54 µg/L As(V) plus 3 mg/L Cl₂, pH: 6.5, and EBCT: 1.0 min

After some hours, the iron settled and the minicolumn effluent solutions (contained in the 20-mL test tubes of the fraction collector) became clear on top with iron settled on the bottom. As is evident in Figure 3.3, up to about 2,500 BVs, neither the unfiltered nor the filtered effluent contained much arsenic, which indicates that the arsenic was removed on the iron deposited in the upper section of the column and did not pass into the effluent attached to the particulate iron released from the lower section of the column. This is a positive result in terms of applying the process for arsenic removal for drinking water treatment. However, in spite of the low level of

arsenic on the particulate iron released from the wustite during the run, particulate iron in the effluent presents a problem that would require post filtration before water distribution.

The arsenic removal performance (3,200 BVs) of the wustite column fed with NSF1 challenge water containing 3 mg/L of Cl_2 was twice as good as the HCl-pretreated siderite (1,600 BVs), thus on the basis of run length alone, the wustite would be preferred.

After exhaustion of the wustite, FeO, bed, the media was taken out of the column and washed several times with DI water under stirring condition until brown color in the washing liquid was disappeared. Finally, the washed media was used for another column test under the same experimental conditions. Under this experimental condition the initial effluent was not brown, which was noticed for with the fresh media. The experimental results are shown in Figure 3.4, which indicates that the properly washed and reused Fe(II)O media was not performing as original media. From the experimental results it was concluded that FeO could not be used in this way for the removal of arsenic for small water treatment systems.

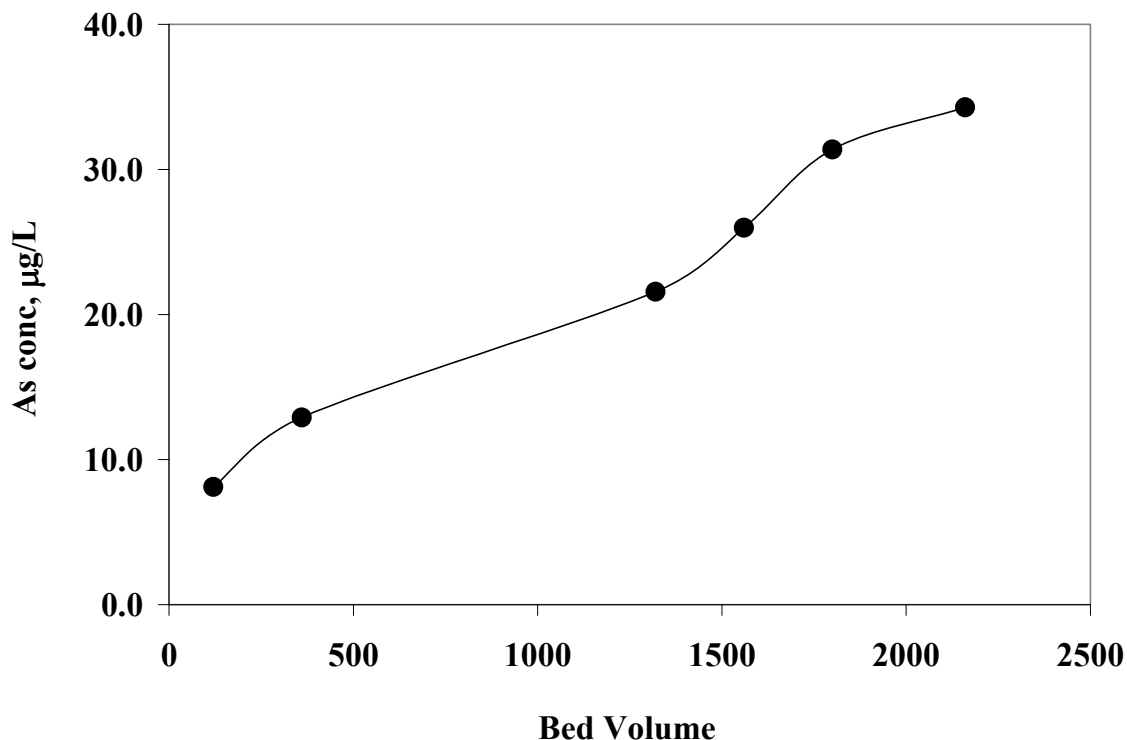


Figure 3.4 As(Tot) breakthrough from a minicolumn containing 4 cm³ reused and washed wustite (FeO). Feed arsenic concentration: 54 µg/L As(V) plus 3 mg/L Cl_2 , pH: 6.5, and EBCT: 1.0 min

MINICOLUMN TESTS WITH PEL TECHNOLOGIES MIXED IRON OXIDES MEDIA

Due to the failure of siderite and FeO, we tested a mixed iron oxides media available from PEL Technologies. The approximate composition of the media was <20% FeO, < 5% Fe₂O₃ and balance being Fe₃O₄ (which is FeO·Fe₂O₃). The SSCTs were conducted using 1-cm diameter column operated at a rapid flow rate such that the empty bed contact time (EBCT) was 1 min. The column was packed with 5 cm³ of mixed-oxide material (40–60 mesh). The NSFII challenge water (pH 7.5) spiked with approx. 56 µg/L of As(V) and 3 mg/L Cl₂ was pumped into the column from top to bottom (down flow) at a constant flow rate by a peristaltic pump. After passing through the column, the effluent was collected for the measurement of As(Tot) at predetermined BVs. Same experiment was conducted without Cl₂ in the challenge water. The experimental results are shown in Figure 3.5, which indicates that with or without Cl₂, the media was not removing arsenic.

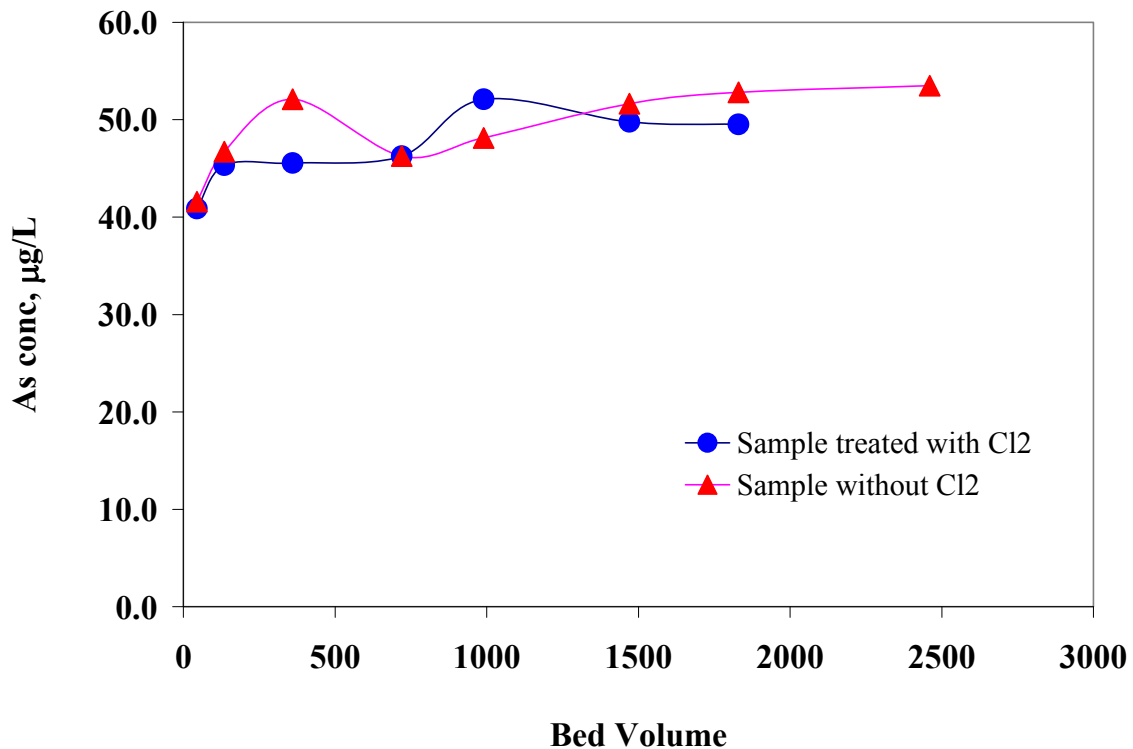


Figure 3.5 As(Tot) breakthrough from a minicolumn containing 5 cm³ PEL Technologies mixed iron oxides media. Feed arsenic concentration: 56 µg/L As(V) plus 3.0 mg/L Cl₂, pH: 7.5, and EBCT: 1.0 min

ELECTROLYTIC DISSOLUTION OF SIDERITE AND REMOVAL OF ARSENIC

Optimization of Potential Differences for Dissolution of Siderite

Following on the advice of the Project Advisory Committee, an electrochemical adsorption column was designed and constructed comprising a SS cathode and graphite anode. (Note: In some experiments the polarity was switched.) The minicolumn column was filled with siderite (4 cm^3 , 40–60 mesh) and challenge water was pumped through the column at the rate of 4 mL/min by a peristaltic pump. The electrodes were connected with a 12 V power supply. To optimize the operational condition the potential difference was varied and current was monitored. The results were shown in Figure 3.6, which indicates that with the increase of potential differences the current increased and after 3 V potential difference sharp change in current was observed. Based on the experimental results we selected a potential difference of 2.5 V for our experiments so as to produce measurable current without having the voltage so high as to generate undesirable cell reactions such as oxygen or chlorine generation.

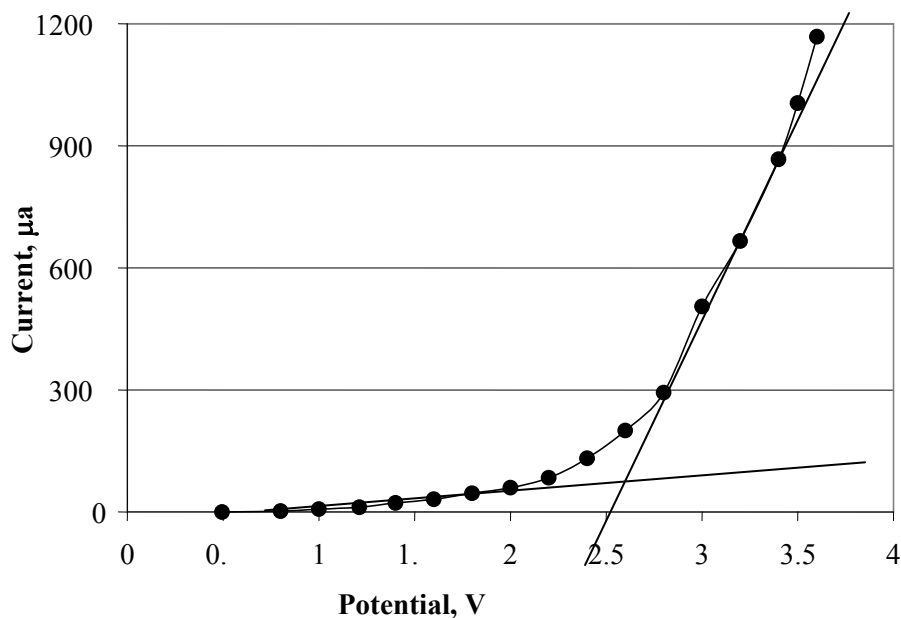


Figure 3.6 Plot for current vs. potential difference in the electrolytic minicolumn containing siderite

At the selected potential difference (2.5 V) arsenic removal experiments were conducted using 4.0 cm^3 siderite minicolumns with EBCT 1 min at pH 7.5. Experiments were conducted at two different conditions: (1) anodic graphite rod with cathodic SS tubing, and (2) cathodic graphite with anodic SS tubing. We also did few experiments at reduced potential difference (1.0 V). The experimental results are shown in Figure 3.7, which indicates that at low potential

difference (1.0 V) under both conditions, little if any arsenic removal was observed. When the polarity was increased to 2.5 V and SS was used as a cathode, the removal efficiency was very poor. After 1440 bed volume the effluent arsenic concentration was the same as influent arsenic concentration. But when the polarity of the electrode was reversed, i.e. SS used as the anode, arsenic was removed significantly and after 1,440 BVs the effluent arsenic concentration was about 10 $\mu\text{g/L}$. So for future experiments we used SS as an anode and graphite as a cathode with potential difference of 2.5 V.

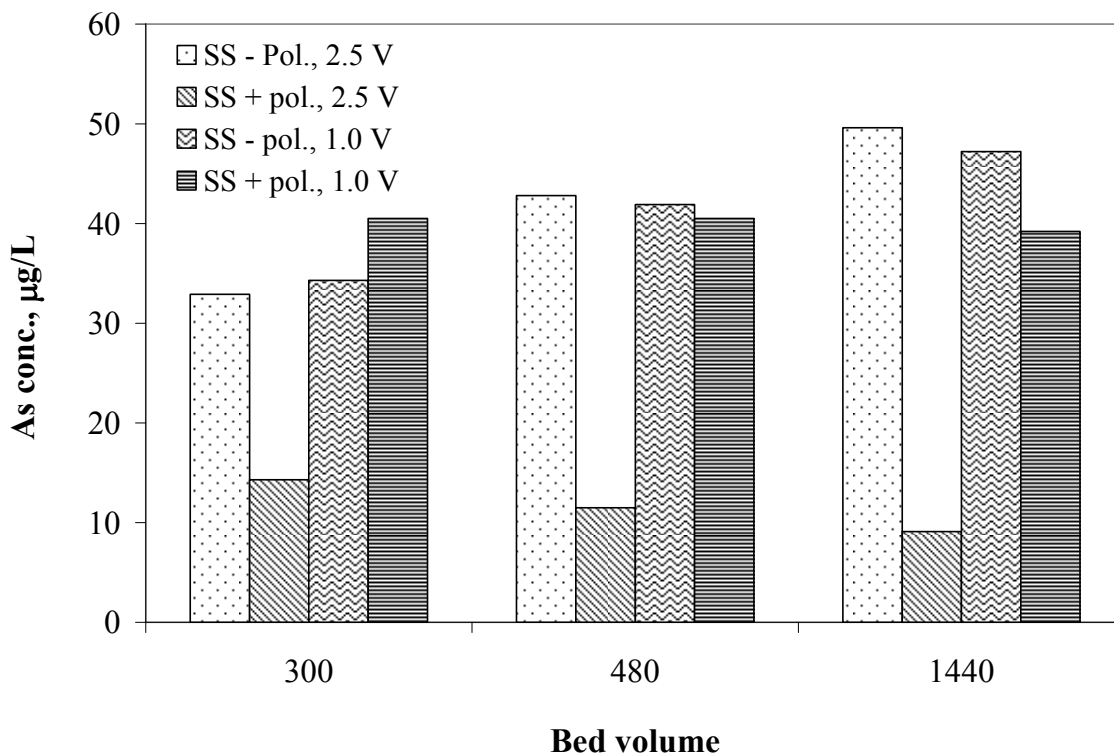


Figure 3.7 Removal of As(V) by electrolytic minicolumn containing siderite two difference cathode anode conditions. SS + polarity is using SS anode and graphite cathode. SS – polarity is SS cathode and graphite anode. Experimental conditions: siderite minicolumn containing 4 cm^3 media, EBCT 1 min, pH 7.5, initial As(V) concentration approximately 50 $\mu\text{g/L}$

SMALL-SCALE COLUMN TESTS FOR ARSENIC REMOVAL UNDER ELECTROLYTIC CONDITIONS

Performance of Electrolytic Siderite Column

A small-scale column test with siderite under electrolytic conditions was conducted to remove As(V) from the challenge water (pH 7.5). The SS column filled with 4 cm^3 siderite (40–

60 mesh) was used as an anode and the graphite rod was used as a cathode. The potential difference across the electrode was 2.5 V. The challenge water with about 50 µg/L As(V) was pumped through the column at the flow rate 4 mL/min. The effluent arsenic concentration was measured at predetermined bed volumes. The experimental results are shown in Figure 3.8, which indicates that under the experimental conditions the system could reduce the influent arsenic concentration significantly and the effluent arsenic concentration was in the range 10–15 µg/L. Though the effluent concentration was reduced, the concentration was not below the MCL of 10 µg/L, and was almost constant up to 3,500 BVs. We also noticed brown stain in the out let tube after 2,000 BVs, which was thought to be due to leakage of iron, which was generated in to the system. From these experimental results, the following questions were raised. (1) Was iron generated by the electrolytic dissolution of siderite? Or was this iron released from the SS anode as it dissolved? (2) Was the effluent arsenic in As(V) or As(III) state?

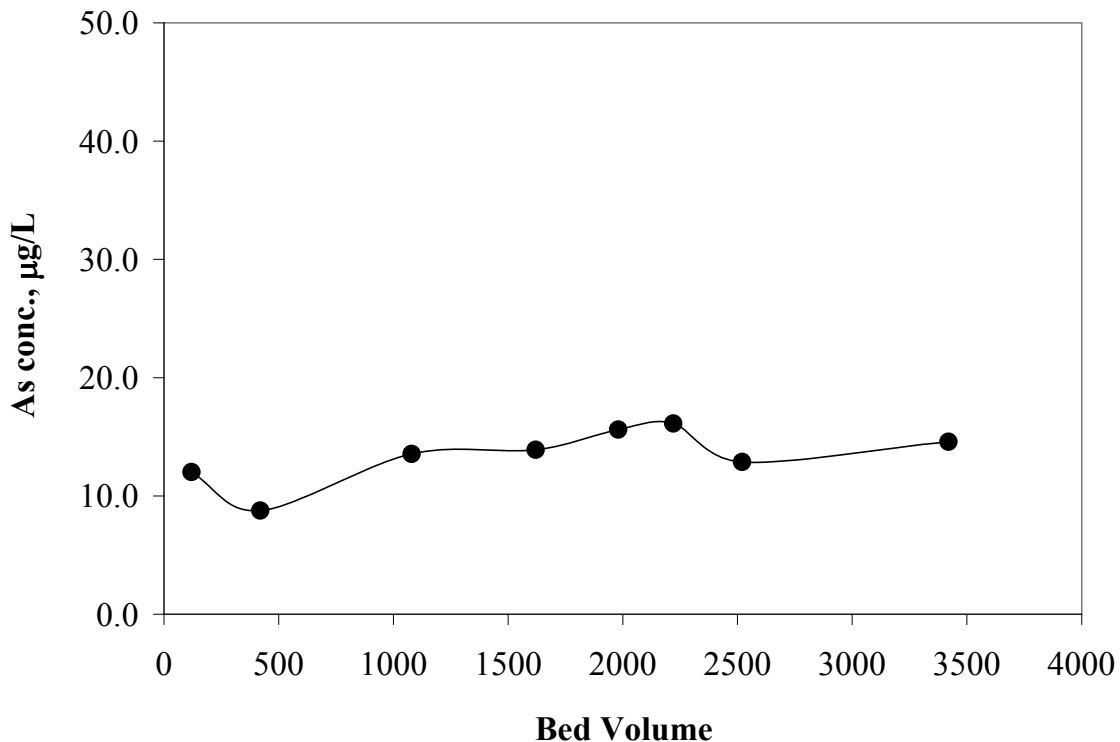


Figure 3.8 Electrolytic siderite minicolumn results. Breakthrough curve for As(V) using siderite at pH 7.5 and at EBCT 1.0 min (Initial As(V) concentration 50 µg/L) and at 2.5 V potential difference (SS anode and graphite cathode)

Performance of Electrolytic Sand Column

To answer the questions resulting from the initial electrolytic column tests we replaced the siderite with clean white silica sand. The objective was to determine what role, if any, the siderite played in arsenic removal in the electrolytic column. The sand was sieved through 40–60

mesh and washed with DI water thoroughly, and then poured in to the SS minicolumn. The NSFI challenge water with 50 µg/L As(V) was pumped through the column with EBCT 1.0 min. The effluent was preserved with 1% HNO₃ before and after filtration through 0.2 µm membrane micro filter for the determination of As(Tot) and Fe(Tot). To determine As(III) and As(V), the filtered samples were preserved with EDTA and acetic acid and speciated for As(III) and As(V) using the Clifford EDTA–HAc method (Karori et. al. 2006 and Clifford et. al. 2004). The As(Tot) concentrations in the filtered and unfiltered samples did not differ. Iron concentration in the effluent was in the ppb level. The experimental results are shown in Figure 3.9, which indicates that when the minicolumn was filled with sand, i.e., without any siderite in the column, the electrolytic system was removing arsenic to virtually the same extent as when the column was filled with siderite. Our conclusion was that iron was generated in the system with the SS anode by dissolution of the SS. This is based on (a) the absence of siderite, (b) the brown, apparently iron oxyhydroxide coating, on the sand, and (c) the obvious corrosion of the stainless steel.

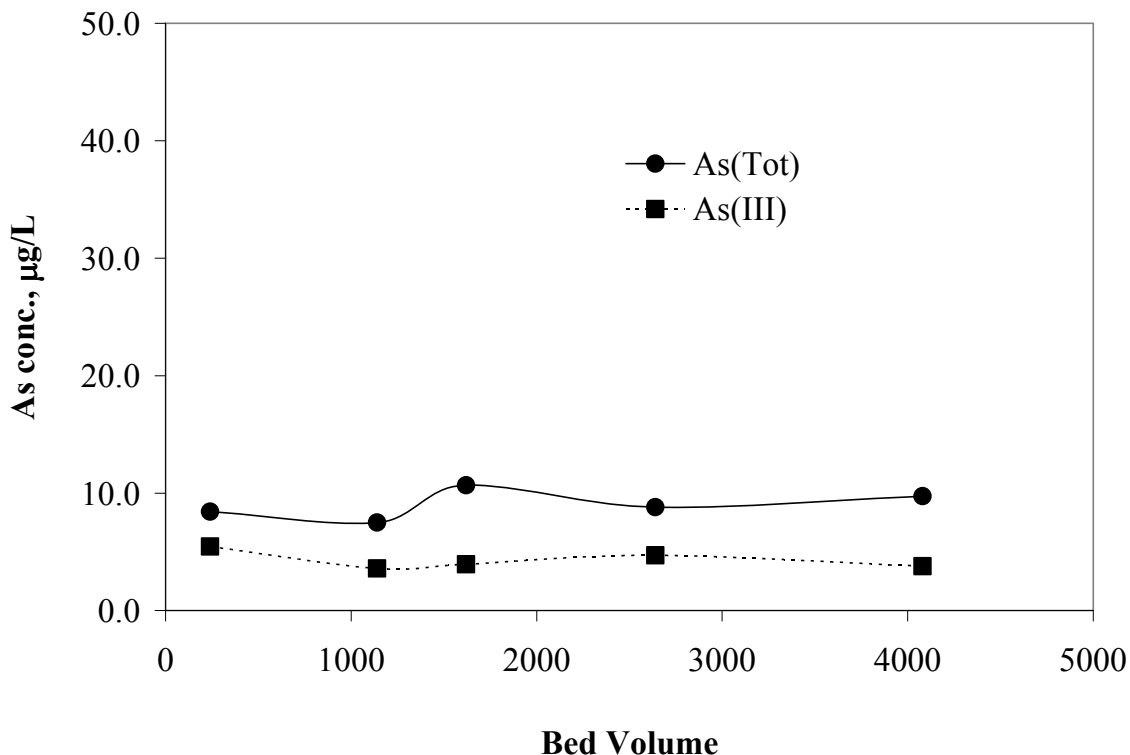


Figure 3.9 Electrolytic sand column results. Breakthrough curve for As(V) using clean white sand at pH 7.5 and at EBCT 1.0 min (Initial As(V) concentration 50 µg/L) and at 2.5 V potential difference (SS used as anode and graphite as cathode)

The speciation of arsenic indicated that about 50% of the total arsenic in the effluent was present in As(III) form. Reduction of As(V) to As(III) at the graphite cathode could not be

ignored. Due to poor adsorption capacity of As(III) on iron hydroxide, As(III) was eluted from the column and maintained a constant value through out the process. From this experiment it was concluded that electrolytic dissolution of siderite was not possible to remove arsenic from the drinking water. It was also concluded that, although it is possible to dissolve SS to produce ferric hydroxide and sorb arsenic, the process is not considered economical compared with iron(III) coagulation–microfiltration, electrocoagulation–microfiltration (Water Research Foundation project 3160 at UH), or granular iron media (GFH or GFO) adsorption.

CHAPTER 4 SUMMARY CONCLUSIONS AND RECOMMENDATIONS

SUMMARY AND CONCLUSIONS

The objective of our proposed research was to determine the feasibility of using filter beds of ferrous carbonate (siderite) in combination with low levels (0–2 ppm) of chlorine to oxidize As(III) to As(V) and generate 0–3 ppm $\text{Fe}(\text{OH})_3(\text{s})$ as Fe for in-situ coagulation and removal of As(V). Based on the minicolumn (small scale column tests) results, the first sample of siderite mineral (obtained from Ward's Natural Science) showed very poor arsenic-adsorption performance. The media was in equilibrium the influent arsenic at only 1,000 BVs, and 10 $\mu\text{g}/\text{L}$ arsenic breakthrough occurred only at 40 bed volumes throughput with a 3 cm^3 siderite bed in the presence of 1.0 mg/L Cl_2 at $\text{pH} = 7.5$. It appeared that Fe(II) was not dissolving as expected, thus little to no ferric hydroxide was produced to coat the siderite media. Due to the poor performance of the siderite material, the scope of work was revised, and proof-of-concept experiments were developed to more easily demonstrate the feasibility of using siderite for arsenic removal. The first step of the proof-of-concept was to synthesize ferrous carbonate in the laboratory. However, it was not possible to easily prepare ferrous carbonate in the laboratory because of its very rapid oxidation in the atmosphere.

Because the laboratory preparation $\text{FeCO}_3(\text{s})$ was not successful, screening tests were performed using six siderite samples obtained from around the world to select the most efficient siderite material to remove arsenic. The results showed that even at lower pH ($\text{pH} 5.0$) the performance of the siderite materials was not promising.

Based on the preliminary experimental results, it was concluded that under the experimental conditions, the solubility of siderite was much lower than the calculated theoretical value. A literature search uncovered a recent article indicating that the solubility of siderite depends on the redox potential of the environment, i.e., whether it's anoxic or oxic. Under oxic conditions at $\text{pH} > 6.5$, the dissolution rate of siderite is much slower than in the anoxic environment. The solubility of siderite increases dramatically under oxic conditions at $\text{pH} 10$ and higher or at high acidic condition, which suggested the possibility of modifying the adsorption-by- $\text{FeCO}_3(\text{s})$ concept to include a pretreatment of the bed with chlorinated dilute NaOH solution to dissolve ferrous iron and coat the media with $\text{Fe}(\text{OH})_3(\text{s})$ for arsenic adsorption. To improve the arsenic removal performance of the siderite, it was pretreated using acidic or alkaline Cl_2 solutions to better dissolve the siderite and produce more ferrous iron and subsequently more $\text{Fe}(\text{OH})_3(\text{s})$ on the siderite for arsenic adsorption. The minicolumn results on pretreated siderite showed that acid was preferred to alkaline pretreatment, but a short run length, 1,600 BVs, resulted, which was not considered long enough to further develop the arsenic-adsorption-on-siderite process.

Minicolumn tests with untreated wustite (FeO) demonstrated longer arsenic run length (3,200 BVs) but with the disadvantage of particulate iron in the column effluent. The particulate iron, up to 2,400 BVs when it cleared up, did not contain significant arsenic but would have to be filtered during a post treatment step in a drinking water treatment system. Reuse of wustite after washing was not possible due to its poor performance compared to fresh media. Attempts were made to remove arsenic using PEL Technology's synthetic mixed iron oxides media under chlorinated and non chlorinated conditions. Neither condition was successful.

Near the completion of the project, the Project Advisory Committee suggested developing an electrolytic-dissolution-of-siderite method by applying an electrical potential to the siderite column. An electrolytic minicolumn was designed and built using SS tubing filled with siderite and containing a central graphite rod as the other electrode. After optimizing the operating voltage at 2,5 V, electrolytic minicolumn tests were performed using the SS tubing as the cathode. No removal of arsenic was observed, however, when the polarity was switched, the cell with SS anode did remove about 80% of the feed arsenic. Arsenic removal was not due to iron from siderite, because, when sand replaced the siderite, similar (80%) arsenic removal was observed. It appeared that soluble iron was generated at the SS anode, hydrolyzed, and precipitated as $\text{Fe}(\text{OH})_3(\text{s})$ with $\text{As}(\text{V})$ adsorbed. The method was still not very effective for $\text{As}(\text{V})$ removal because some $\text{As}(\text{III})$ was produced in the process and leaked into the effluent, which hovered around a $\text{As}(\text{Tot})$ of about $10 \mu\text{g}/\text{L}$, sometimes exceeding the MCL.

RECOMMENDATIONS

Future research on the possible use of siderite as an arsenic removal media is not warranted based on the results of this research.

Although it is possible to dissolve SS to produce ferric hydroxide and adsorb arsenic, further work on the process is not recommended because is not considered economical compared with iron(III) coagulation–microfiltration, electrocoagulation–microfiltration (Water Research Foundation project 3160 at UH), or granular iron media (GFH, GFO) adsorption.

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ABBREVIATIONS

As(III)	arsenic in the +3 oxidation state
As(Tot)	total arsenic, $\mu\text{g/L}$
As(V)	arsenic in the +5 oxidation state
BV	bed volume, volume of effluent equal to the volume of media including voids
C_{T,CO_3}	total carbonate species concentration, molar
DI	deionized
EBCT	empty bed contact time, min
GFH	granular ferric hydroxide
GFO	granular ferric oxide
GIM	granular iron media, e.g., GFH or GFO
IX	ion exchange
M	molarity, moles/L
MCL	Maximum contaminant level
M Ω	megohm, millions of ohms electrical resistance, indication of water purity.
NRDC	Natural Resources Defense Council
NSFI	NSF-International
PAC	project advisory committee of Water Research Foundation
pC	negative log of species concentration, moles/L
pH	negative log of hydrogen activity in moles/L
POE	point of entry, when referring to a treatment system
SS	stainless steel
SSCT	small-scale column test, performed in a minicolumn with 3–10 cm^3 media in the particle size range of 40–100 mesh (0.42–0.15 mm particle dia.)
T	temperature, $^{\circ}\text{C}$
TDS	total dissolved solids, mg/L
UH	University of Houston
USEPA	United States Environmental Protection Agency
V	potential, volt