Evaluation of Concurrent Removal Of Arsenic and Iron for Wisconsin Public Water Supplies

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Project Summary

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PROJECT No. R/UW-REM-007

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Background & Need

New regulations and a greater understanding of the health effects of arsenic exposure will lead many water suppliers to consider reducing arsenic concentrations in their drinking water. Concurrent iron and arsenic removal may provide an opportunity for many small water systems to simultaneously address a significant aesthetic water quality problem and provide risk reduction from arsenic exposure. Unfortunately, current information on arsenic removal does not provide a clear discussion of the limitations and advantages of concurrent arsenic and iron removal particularly for small groundwater systems using conventional, low-residence time, oxidation/filtration systems.

Objectives

The research described in this report examined combined iron and arsenic removal, and in particular, arsenic removal during the oxidation and precipitation of iron followed by pressure filtration in short residence time systems. This project had two primary objectives. The first was to evaluate the likely utility of iron removal as a means to reduce arsenic concentrations in Wisconsin public water supplies. The second was to provide a detailed laboratory and field demonstration of iron and arsenic removal that was directed towards identification of kinetic and speciation concerns for oxidation/direct filtration processes.

Methods

This project combined a field and laboratory investigation of arsenic removal. Existing information on water quality at Wisconsin public water suppliers was used to evaluate the likely feasibility of iron removal as an arsenic treatment technique. Then the removal of arsenic was measured at two water treatment systems in Wisconsin that currently have arsenic in their raw water and also use iron oxidation followed by filtration to treat their water. The laboratory investigation examined the kinetics of simultaneous iron oxidation and filtration with arsenic removal. A laboratory evaluation of iron and arsenic removal focused on the rate of simultaneous iron and arsenic removal in reactors that mimicked conditions typically encountered at small water systems. Removal of both arsenite (As(III)) and arsenate (As(V)) were evaluated. Although the work used data collected at Wisconsin water systems, the results were developed to be applicable to many regions of the Midwestern U.S.

Results and Discussion

The field investigation showed iron is usually present in public water supply wells that contain arsenic. It also showed arsenic removal occurring at the two field sites currently removing iron. Removal of approximately 70% of the arsenic was observed at facilities that were treating water with an iron concentration of more than 2 mg/l and arsenic concentrations less than 15 μg/l.

The laboratory investigation found that in a water typical of many Wisconsin public water supplies, neutral pH, and a hard, high alkalinity (~2.5 mM), the removal of arsenate can be estimated assuming a pseudo-equilibrium partition between arsenate and forming iron solid with a rate of removal dictated by the removal of iron. At a solution arsenic concentration of 5 μg/l, the apparent arsenic density on ferric iron solids was 30-40 μg As/mg Fe. That is considerably higher than reported for preformed iron solids and more than double that reported during ferric coagulant addition and suggests that the reactivity or surface area of the iron solids is increased during coincident iron oxidation. In contrast, arsenite removal was much lower in these rapid reaction systems. Little adsorption of arsenite was observed during the first 15-20 minutes of iron oxidation/ferric hydroxide formation. This suggests both low reactivity and slow in-situ oxidation of arsenite is expected in Wisconsin treatment systems.

Conclusions and Recommendations

The results of this research confirm the utility of coincident iron and arsenic removal for the treatment of groundwater containing arsenic. In groundwater systems treating water through relatively short residence times, the oxidation/precipitation/filtration treatment process can effectively remove As(V). The solids generated can have a relatively high arsenic density compared to preformed solids, suggesting that the high surface area accessible to arsenate during iron precipitation can enhance the removal or arsenic. The rate of arsenic association with precipitating iron did not appear to be a significant limitation with respect to As(V), but may be a consideration with respect to As(III), particularly for those systems with very short hydraulic residence times. Although the reduced form of arsenic was not removed significantly over the short time in these experiments, it can be oxidized with chlorine and subsequently should then be sorbed by the iron solids.

Related Publications

Technical Presentation: Iron and Arsenic: What's the Connection. Presented at the Wisconsin Water Association Annual Meeting, September, 2002, Wisconsin Dells, Wisconsin.

Poster Presentation: Wisconsin State Environmental Health Meeting: Arsenic Removal with Iron (w/ undergraduate student Jesse Baumann), September, 2003

Poster Presentation: Arsenic Removal During Iron Treatment (w/ undergraduate student Jesse Baumann) at the American Water Resources Association Wisconsin Section Meeting, Lac du Flambeau, February, 2003.

Key Words: Arsenic removal, water treatment, iron oxidation

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INTRODUCTION

New regulations and a greater understanding of the health effects of arsenic exposure will lead many water suppliers to consider reducing arsenic concentrations in their drinking water. For some, that will be mandated because they currently exceed the new maximum contaminant level of 0.01 mg/l, for others, arsenic removal may be a consideration when evaluating the overall impact of future modifications to water quality. Concurrent iron and arsenic removal may provide an opportunity for many small water systems to simultaneously address a significant aesthetic water quality problem and provide risk reduction from arsenic exposure.

Iron is a relatively ubiquitous groundwater constituent and its presence can preclude the effective use of some treatment technologies without pre-treatment. However, previous research and field experience has shown that the formation of iron oxyhydroxides through precipitative iron removal generates an adsorptive media that can accumulate arsenic. Subsequent removal of the precipitated iron can then also remove the arsenic. Currently, many small water suppliers add chemicals to sequester or slow the oxidation/precipitation of iron during distribution. Removing this iron, although more expensive than chemical sequestration, could also remove arsenic that even at low concentrations might pose some long-term health risks. One of the most common iron removal systems uses oxidation and subsequent filtration of iron solids. This system generates iron oxyhydroxides within the reactor vessel. As these iron solids have been shown to be relatively reactive to arsenic ions, it is not surprising that such treatment systems have been shown to remove arsenic (Hering et al., 1996; Edwards, 1994).

Surveys of public water suppliers have shown that arsenic is more likely to be a water quality problem at small water suppliers using groundwater. Many such water systems treat their water minimally, perhaps chemical addition for disinfection and corrosion reduction. Those systems that do treat are likely to be either removing iron or hardness in relatively short residence time treatment units. These treatment systems can have reduced capital costs because they have low water residence time, but an understanding of the rates of coincident iron and arsenic removal will be an important component of estimating the likely efficiency of this treatment process.

Groundwater suppliers are also likely to find arsenic in two different oxidation states, and often some combination of the two. Although the most common forms of arsenic are both oxyanions, their charge and reactivity varies with pH and oxidation state. Pentavalent arsenic (As(V) or arsenate) is the more oxidized form. It exists as a charged anion at neutral pH and is typically reported as more strongly sorbed. The more reduced form is trivalent arsenic (As(III) or arsenite). Arsenite exists predominantly as a neutral ion at neutral pH.

The removal of arsenic during the oxidation of ferrous iron and subsequent filtration of ferric iron solids has been studied at higher concentrations of arsenic and relatively long residence times (4-20 hours) (Cheng et al., 1994; Fields et al., 2000). Several studies have suggested kinetic affects on the rate of arsenic removal could be important and iron precipitation can also be influenced by the reaction time (Hering et al., 1996). To date, little information is available on the rate of arsenic removal during the short time period of interest with respect to direct oxidation/filtration.

The research described here was designed to increase our understanding of the possibilities and limitations of conventional technologies for addressing arsenic in small water systems with an emphasis on Wisconsin water systems. Early reviews of the arsenic removal technologies developed nationally suggested a variety of treatment techniques, but many of these would offer little to Wisconsin water suppliers other than arsenic removal. In addition, some technologies will be limited by high hardness, dissolved solids and/or iron content of many Wisconsin waters. This research examined combined iron and arsenic removal during the oxidation and precipitation of iron in short residence time systems. This project had two primary objectives. The first was to evaluate the likely utility of iron removal as a means to reduce arsenic concentrations in Wisconsin public water supplies. The second was to provide a detailed laboratory and field demonstration of iron and arsenic removal that was directed towards identification of kinetic and speciation concerns for oxidation/direct filtration processes

PROCEDURES AND METHODS

Field Testing

A database of arsenic and iron concentrations was developed using previous DNR well testing programs that measured arsenic concentrations at municipal water supply wells. Iron concentrations could not be obtained from the database or other information available, so individual contacts were made with the water systems to obtain concentrations of iron associated with the different wells. A list of municipal wells that had raw arsenic concentrations greater than three parts per billion was created. This resulted in a list of 154 wells in Wisconsin. Raw iron concentrations for the corresponding wells were determined by contacting the water departments for the communities. We were able to obtain data for 95 of the 154 wells. Additional chemical concentrations and well construction data were obtained from the Wisconsin DNR Public Water Supply System web page.

Two field locations were identified for further testing. Both Whitewater and Greenville had wells with both iron and arsenic, and were currently treating to remove iron through oxidation and filtration. A sampling procedure similar to the one used by Fields et al. (2000) was used for the collection of samples. A piping manifold was attached to spigots connected to water pipes leading to the filter (raw samples) and to the community (entry point/post filtration). The first sample was collected through the piping valve into a 125 ml Nalgene bottle preserved with nitric acid. A second sample was collected in a 125 ml bottle from water that was directed through a 0.45 um filter attached to the piping manifold. This sample was then acidified to a pH of 2 with sulfuric acid. Approximately half of this sample was run through a 15 ml column filled approximately to a depth of 10 cm with a prepared ion exchange resin (Dowex 1x8-100 ion exchange resin) in order to separate the arsenic (III) and arsenic (V). Both of these samples were put on ice and delivered to a lab to be analyzed using both graphite furnace atomic absorption spectrometry (GFAAS) and inductively couple plasma (ICP-OES).

In Greenville, incoming water was sampled on 30 minute intervals, beginning after the filter had been backwashed. Samples were collected after treatment at a similar frequency starting 15 miuntes after the raw samples were collected.

In Whitewater five raw samples were collected on 20 minute intervals, beginning after the filter had been backwashed. Five entry point samples were collected, staggered 15 minutes after the raw sample was collected.

Analytical Methods

Iron and arsenic analysis was by both graphite furnace atomic absorption spectrometry (GFAAS) and inductively couple plasma (ICP-OES). Arsenic speciation was determined using the modified Ficklin method described by Edwards et al. (1998). The sample was acidified and then passed through an ion exchange resin to isolate As(III). The anion exchange resin was converted from the chloride form to the acetate form with a method used by Fields et al. (2000). 500 grams of the resin were placed in a beaker. 500 ml of 1 molar sodium hydroxide were added to the resin and stirred using a stir plate and stir bar for approximately an hour. This step was repeated three times. The resin was then rinsed with two 500ml batches of reagent grade water. This was followed by adding 500 ml of 1 molar reagent grade acetic acid, stirring for 5 minutes, and then draining the excess acid. The application of acetic acid was repeated three times, and rinsed with 1,500 ml of reagent grade water. The resin was stored and kept moist until use. The columns used were 12 x 1.5 cm Econo-pac columns from Bio-Rad Laboratories. The columns were filled to a depth of 10 cm with the drained resin. The columns were sealed with a cap to preserve moisture until used in the field.

Kinetic Experiments

Iron oxidation and arsenic removal experiments were performed in the laboratory using four liter glass borosilicate glass reactors. Continuous gas flow into the reactor and stirring was used to maintain mixing conditions. The reactor was shielded from light to reduce the possibility of iron photo-reduction. Gas mixtures of air and carbon dioxide were used to maintain pH conditions. During an experiment, the pH varied by less than 0.2 pH units.

The laboratory evaluation of iron and arsenic removal focused on the rate of simultaneous iron and arsenic removal in reactors that mimicked conditions typically encountered at small water systems. Experiments were performed in a groundwater collected from a surficial sand and gravel aquifer in Portage County, Wisconsin. The water was collected prior to the experiments and only stored for a brief time in the laboratory. Chemical characteristics of this water are summarized in Table 1. The water was spiked with arsenic and iron concentrations for the kinetic experiments. Ferrous iron stock solutions were prepared from ferrous sulfate (Fisher) diluted after acid addition. Arsenate and arsenite stock solutions were prepared from sodium salts (Baker) without acid addition. Experiments using anion exchange resin columns were used to verify the speciation of arsenite solutions. We found that solution preparation, such as acidification, could accelerate the oxidization of arsenite solutions. Arsenic speciation techniques and analysis standards were used to verify solution concentrations and speciation.

Table 1. Groundwater Analysis

Constituent	Concentration
Calcium	1.33 mM
Magnesium	1.24 mM
Potassium	0.04 mM
Sodium	0.16 mM
Iron	0.4 μM
Manganese	0.02 μM
Phosphorus	0.4 μM
Sulfate	4.5 μM
ANC	2.4 meq
pH	8.1

RESULTS AND DISCUSSION

Iron and Arsenic in Wisconsin Public Water Supplies

The potential importance of simultaneous iron and arsenic removal for meeting the new arsenic standard and improving public health in Wisconsin is evident by the relationship between iron and arsenic found in public water systems. Figure 1 shows the locations of public water systems in Wisconsin that had arsenic concentrations greater than 3 μg/l in the different testing programs. Although the majority of the water systems are found in the eastern half of the state, arsenic was found in all parts of the state. Combining the arsenic measurements with iron concentrations reported by different water systems allowed an iron:arsenic ratio to be determined for all water systems. Figure 2 shows how that ratio varies at different water systems and by location. It is clear from Figure 2 that iron is usually present when arsenic is found in public water supplies and the ratio of iron to arsenic usually exceeds 20. There are a group of public water systems in northeastern Wisconsin that may have relatively low iron/high arsenic water.

Previous research has used both an iron:arsenic ratio and iron concentrations to establish the likely utility of iron removal as an arsenic reduction strategy. It appears that in general, the concurrent presence of both iron and arsenic suggest that iron removal offers a possible treatment approach for public water suppliers.

Arsenic Removal at Whitewater and Greenville

The simultaneous removal of arsenic and iron was measured at both Whitewater and Greenville. These were both treatment systems designed for iron removal using pressure filtration. Incoming water was pumped directly into a pressure filter for solid formation and filtration. Greenville adds chlorine to their system to hasten the oxidation of ferrous iron to ferric iron. Whitewater uses an air injection system to facilitate oxidation. Table 2 summarizes the results of the treatment system testing. At both facilities, arsenic is removed with the iron, although the reduction percentage is greater for iron than for arsenic.

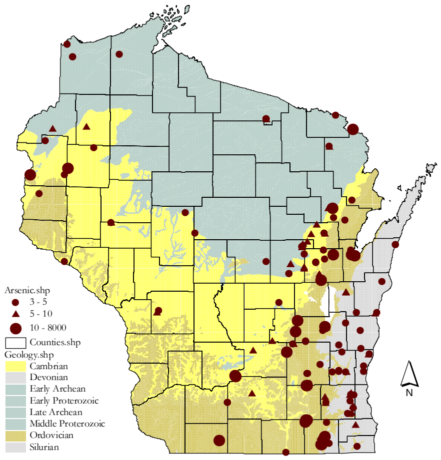

Figure 1. Location of public water systems with arsenic concentrations exceeding 3 µg/l. Different arsenic concentrations shown with symbols.

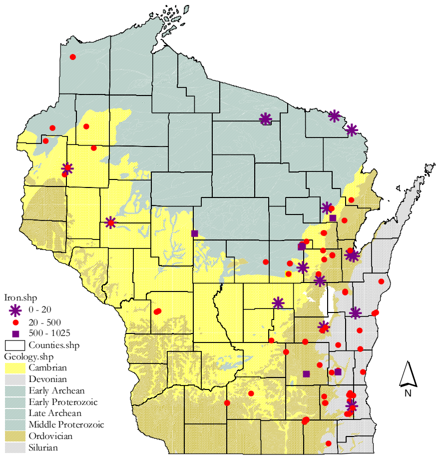

Figure 2. Ratio of iron to arsenic (mass ratio) for those wells with arsenic concentrations exceeding 3 mg/l. Different iron:arsenic ratios shown with symbols.

Table 2. Summary of Iron and Arsenic Removal in Iron Pressure Filter Systems

Facility	Iron (mg/l)	Iron Removal (%)	Arsenic (µg/l)	Iron/Arsenic Mass Ratio	Arsenic Removal (%)
Greenville	1.39	98	6	231	69
Whitewater	1.18	91	12	98	70

Kinetics of Simultaneous Iron and Arsenic Removal

Ferrous iron is oxidized to form ferric iron during the treatment in oxidation/filtration processes. The rate of ferrous iron oxidation has been studied extensively and shown in bicarbonate solutions to adhere to a rate expression (Stumm and Lee, 1961):

$$\frac{d[Fe^{2+}]}{dt} = -k[Fe^{2+}]p_{o_2}[OH^-]^2 \qquad (3)$$

where k can vary depending on solution conditions, but is usually in the range of 1x 10^{13} to 20 x 10^{13} atm^{-1} $mole^{-2}$ $liter^{2}$ min^{-1} at 20 to 25 degree C (Brezonik, 1994). The overall oxidation rate is strongly impacted by pH. Increasing the pH from 6.5 to 7.5, for example, increases the rate of ferrous iron disappearance one hundred-fold. The rate of oxidation can also be accelerated or slowed in the presence of other solution constituents. To hasten the oxidation rate, and reduce the impact of low pH or solution composition, oxidants such as chlorine are often used.

Once ferrous iron is oxidized, the ferric iron that is generated is subject to relatively rapid solid formation. The transition from dissolved to particulate iron is critical with respect to removal as it is the physical filtration of solids during direct treatment that removes iron. Solid formation is a complex process of hydrolysis, subsequent formation of polynuclear complexes, development of amorphous iron oxyhydroxides and eventually transformation to more crystalline ferric oxyhydroxides (Grundl and Delwiche, 1993). These reactions are typically strongly thermodynamically favored in water treatment systems at relatively neutral pH once the iron is oxidized, consequently, the removal of iron is likely controlled by the rates of these processes.

The rate of iron solid formation is poorly understood (Sung and Forbes, 1984). After iron oxidation, the initial hydrolysis reactions are considered to be fairly rapid (first-order half lives less than 1 second, Grundl and Delwiche, 1993) followed by a slower formation of amorphous solids. In general, this particle growth is likely to be initiated through a heterogeneous process in which sites for initial solid growth are very small particles or surfaces already present and solids need not form homogeneously solely from iron in solution. In laboratory experiments, Grundl and Delwiche (1993) show a two step process in lower pH ferric iron solutions (pH 2.5 – 3) and suggest an initial formation of spherical particles followed by particle growth. Under conditions typical of Wisconsin groundwater treatment, pH above 6, bicarbonate greater than 1 mM and iron concentrations several mg/l, the initial products are likely to be polynuclear complexes (Schneider, 1984). In natural systems, interaction with natural complexing agents could stabilize these particles and lead to substantial quantity of submicron particles even after several days (Pizarro et al., 1995).

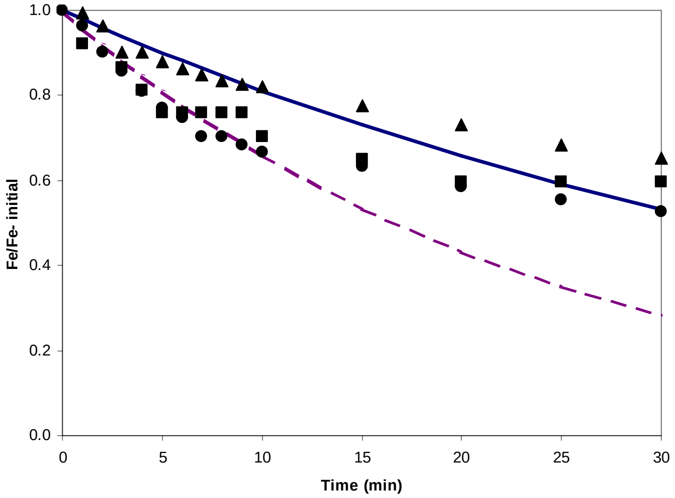

Figure 3. Results from three experiments with 2 mg/l ferrous iron added to pH 7 groundwater, showing ferrous iron (squares), filtered iron (diamonds), and filtered iron with 25 ug/l arsenate (triangles) compared to predicted iron oxidation with rate constants (atm^{-1} $mole^{-2}$ $liter^{2}$ min^{-1}) of 1 x 10^{13} (solid line) and 2 x 10^{13} (dashed line).

Results of laboratory experiments to measure iron solid formation in ferrous iron solutions show little difference between ferrous iron oxidation and solid retention on a 0.45 μm filter at pH 7. In Figure 3, the amount of iron that passes a 0.45 μm filter is shown over time and compared to the measured ferrous iron concentration. We found that the iron passing the filter was similar to the ferrous iron concentration measured. The removal rate coincides with a rate constant of 1×10^{13} to 2×10^{13} atm^{-1} $mole^{-2}$ $liter^{2}$ min^{-1} similar to the best estimate for iron oxidation reported in a recent summary (Brezonik, 1994). Although our solution conditions were similar between experiments, we did have slight variations in pH. Once the ferrous iron is oxidized, these systems are strongly supersaturated with respect to iron solids and the rate of solid formation should be rapid. Our observations that iron filtration and ferrous iron disappearance coincide would support the oxidation of ferrous iron as the rate-limiting step.

Arsenic (V) Removal

Iron oxyhydroxides formed during water treatment can adsorb arsenic that is then removed during solid/liquid separation (Fields et al., 2000; Cheng et al., 1994). The reactivity of the iron solid for arsenic has been studied but aspects of the process remain incompletely understood. The reactivity of the solid may be controlled by both specific surface area and the affinity of the surface. Variations in iron solid reactivity have been attributed to solution composition and solid formation conditions. Edwards (1994) found preformed oxyhydroxides to sorb less arsenic than those formed in-situ during coagulation. In contrast, Dixit and Hering (2003) found the transformation of hydrous ferric oxide to the more crystalline goethite did not alter the affinity for arsenate. Much of the previous work has been performed at higher solution concentrations of arsenic (i.e., > 1 mg/l) to determine a sorption maximum. In those systems, Edwards (1994) found approximately five times higher adsorbed arsenic concentration for the iron solids formed in-situ compared to solids that were preformed.

Few experimental studies have used oxidation of ferrous iron to generate ferric iron solids. Most experimental work examining arsenate reaction with iron oxyhydroxides has used either preformed solids or the addition of ferric iron to generate iron solids. Typically, in the direct treatment of groundwater, iron is oxidized and the ferric iron leads to oxyhydroxide formation. The usefulness of iron oxidation for arsenic removal has certainly been demonstrated. For example, Clifford and Lin (1991) found oxidation of ferrous iron and subsequent precipitation of 2 mg/l ferrous iron removed 60% of the arsenic at an initial concentration of 188 μg/l, and Fields et al. (2000) show the removal of arsenic by several iron removal plants. The absence of detailed kinetic information does limit our understanding of how reaction rates and iron solid properties influence removal in these systems.

Figure 4 shows the results of laboratory experiments using 2 mg/l ferrous iron added to 25 μg/l arsenate solutions. Filtered solution concentrations over time show a progressive decrease in arsenic concentration suggesting adsorption onto ferric oxides formed. In these experiments, oxidation and subsequent precipitation removed more than 90% of the arsenic after fifteen minutes.

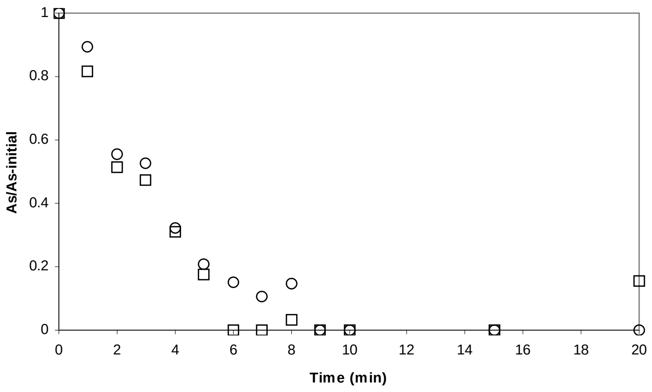

Figure 4. Change in arsenic concentration over time (shown as fraction of the initial arsenic concentration) after addition of 2 mg/l ferrous iron to 25-30 μg/l arsenate solutions (pH 7). Duplicate experimental results shown with different symbols.

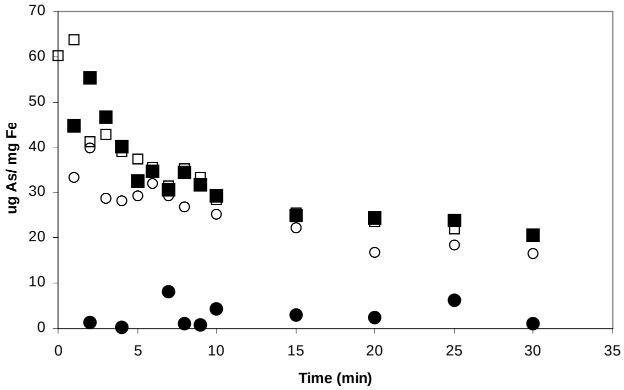

Figure 5. Apparent arsenic concentration of filtered iron solids after addition of 25 μg/l arsenic (III) (solid circles) and 25/25 μg/l As(III)/As(V) (solid squares) compared to the 25 μg/l As(V) only at pH 7.0.

The changes in iron concentration over time were used to compute the quantity of iron solid formed and an apparent concentration of arsenic in the solid. In Figure 5, the quantity of arsenic removed normalized for the amount of iron also removed is shown. Because the arsenic removal as a percentage is more rapid than the iron removal in these systems and there is adequate iron to remove all the arsenic (< 1 μg/l), the apparent arsenic concentration of the solids attains a minimum based on initial conditions. The addition of more iron to these systems would result in a lower apparent arsenic concentration of the solid.

To understand the density of arsenic in the solids removed, Figure 6 examines only those samples where measurable arsenic remains and compares the arsenic density to the solution concentration of arsenic. Although there is a rate component of these experiments and they do not necessarily represent equilibrium with respect to long term changes in the association of arsenic or the nature of the iron solids, it is clear that the apparent arsenic concentration of the solids typically exceeds 30 μg/mg at solution concentrations below the current MCL.

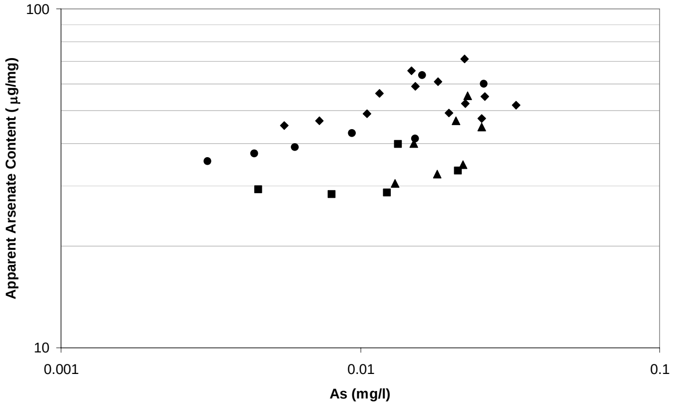

Figure 6. Apparent arsenate content of solids formed during iron oxidation in experiments using 25-50 μg/l initial arsenate and 2 mg/l ferrous iron, pH 7.

The arsenic concentrations on the iron solids found in these experiments is two to three times higher than was shown for ferric iron coagulation experiments by Edwards (1994) at concentrations near the current MCL. Higher reactivity towards arsenic in iron oxidation systems might be anticipated based on the 1) high specific surface area solids that predominate during the early stages of iron oxidation/precipitation may have a higher unit reactivity; and/or, 2) the kinetics of simultaneous arsenic association with the precipitating solid may be more favorable at the relatively low concentrations of ferric iron that are available in iron oxidation systems. Although these experiments may not represent an equilibrium distribution between arsenic and iron, the higher arsenic association with iron shows they have attained a degree of reaction that exceeds that often found at equilibrium in other iron solid systems.

The results indicate that in practice, the competitive effect of bicarbonate ion on the adsorption of arsenate may not be as important in oxidizing iron systems as might be assumed using the simulated results presented by Appelo et al. (2002). One reason that the bicarbonate may have a reduced affect is that our experiments show precipitating iron after oxidation has a relatively high affinity for arsenic. This high affinity may reduce the overall impact of other solutions components even in systems with relatively high bicarbonate ion concentrations (~2.5 mM).

The results were examined in terms of a partition of arsenic between iron solid and solution. Arsenic and iron removed by filtration were measured and the concentration of arsenic on the solid phase calculated. Previous research (Hering et al., 1994; McNeill and Edwards, 1997) presents a simplified approach to arsenic partition between solution and solid based on a low coverage region with the uniform adsorption sites of a Langmuir isotherm model leading to a linear distribution between solution and solid:

$$S_{As\,Fe} = S_{As\,Fe-T}\, bC_{As} = KC_{As} \tag{4}$$

where S_{AsFe} is the concentration of arsenic on the iron solid (mg-As/mg-Fe), $S_{As\ Fe\text{-}T}$ is the maximum arsenic adsorption (mg-As/mg-Fe), b is a constant reflecting the intensity of adsorption (L/mg) and C_{As} the solution concentration of arsenic (mg/L). The Langmuir model interpretation of the distribution coefficient, K, would incorporate both a site density and adsorption intensity. Such a K could be estimated from a surface complexation model and knowledge of solid and solution interactions (Hering et al., 1994), but can be estimated empirically from a linear relationship between solution and solid concentration. In Figure 4, the relationship between the concentration of arsenic on the iron solid and the concentration in solution was shown to be nonlinear across the concentration range examined. That would suggest a reaction that does not adhere to the simple assumptions of the Langmuir model. For example, the solid characteristics may change over time, and exhibit a variable intensity of adsorption. As previous investigators have suggested, there are multiple mechanisms possible for arsenic-iron association in precipitating iron systems (Edwards, 1994).

Including a linear partition between solid and solution in a mass balance around a treatment system leads to a relationship between the fraction of arsenic removed and the iron solid concentration:

$$\frac{Fe_T\, S_{AsFe}}{As_T} = \frac{KFe_T}{1 + KFe_T} \tag{5}$$

We applied this approach to the data collected during the rate experiments. Figure 7 shows the fraction of arsenic adsorbed at concentrations of removed iron solid. Comparison of the arsenate removed versus that predicted using the model of McNeill and Edwards (1997) shows that arsenate removal in these systems exceeds that anticipated. Although the results are not necessarily at equilibrium with the solid formed, it does appear that the partition between the solid and solution is at least as great as would be predicted using the full-scale best fit results of McNeill and Edwards (1997). This observation is consistent with the relatively high affinity of the iron solids for arsenic

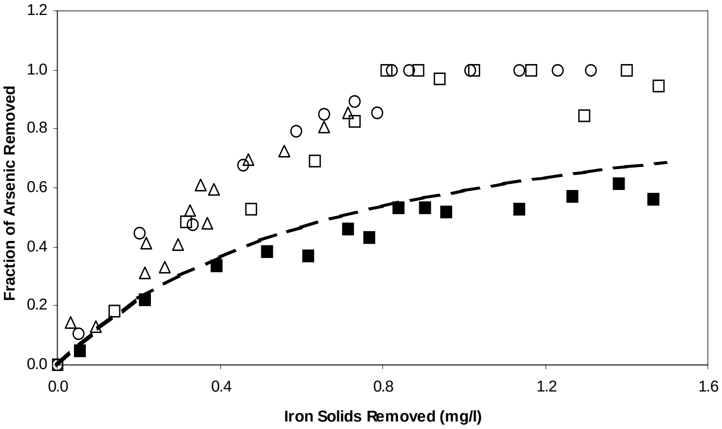

Figure 7 Fraction of arsenate removed shown versus the concentration of iron solids removed. Experiments using 25 μg/l arsenate (square and circle), 40 μg/l arsenate (triangle), and mixture containing 25/25 μg/l arsenate/arsenite (solid square) compared to predicted removal using full-scale treatment system model of McNeill and Edwards (1997).

As (III) Removal

The removal of arsenite by precipitating ferric oxyhydroxides is still more poorly understood than the removal of arsenate. In the relatively short-term experiments that were part of this work, little arsenite was removed in solutions of oxidizing 2 mg/l ferrous iron during the first thirty minutes. Figure 5 shows the results of several experiments where arsenite was present. When the oxidizing ferrous iron was present with arsenite alone little removal was observed.

When the reaction between arsenic was explored in mixtures, the combined arsenate/arsenite mixtures responded similarly to those of arsenate alone. Figure 7 compares the fraction of arsenic removed in arsenic mixtures with that for the arsenate. The overall arsenic reduction is substantially lower in the mixture consistent with a weak reaction with arsenite. Interestingly, the predicted removal is much closer to that observed in a mixture of arsenate/arsenite, and would be consistent with the mixed redox speciation of arsenic observed in actual groundwater.

CONCLUSIONS AND RECOMMENDATIONS

The research described here confirms the likely utility of simultaneous iron and arsenic removal for water systems in Wisconsin. Most of the water systems with elevated arsenic concentrations also have iron in the water at a concentration that is sufficient to remove much of the arsenic. The field investigation showed effective arsenic removal at two locations in Wisconsin at iron/arsenic ratios typical of many locations in Wisconsin. The laboratory work showed that oxidizing ferrous iron and precipitating ferric iron have a relatively high capacity for the oxidized form of arsenic (arsenate). The removal of the reduce form of arsenic (arsenite) is much slower and likely to be much less effective unless oxidants such as chlorine are part of the treatment process.

The laboratory and field investigations confirmed the utility of iron removal for the treatment of arsenic. At iron concentrations commonly encountered in groundwater systems (1-2 mg/l), removals of relatively low concentrations of arsenic (< 0.05 mg/l) ranged from approximately 60-80%. The laboratory investigation of coincident iron and arsenic removal rates confirmed this removal could largely be achieved within 10-15 minutes for As(V) at these conditions, and followed closely the rate of iron removal. The rate of As(III) removal during iron oxidation/precipitation at pH 7 and 7.5 was considerably slower.

REFERENCES

Appelo, C.A.J., M.J.J. Van der Weiden, C. Tournassat, L. Charlet. 2002. Surface complexes of ferrous iron and carbonate on ferryihydrite and the mobilization of arsenic. Environ. Sci. Technol. 36:3096-3103.

Brezonik, P.L. 1994. Chemical Kinetics and Process Dynamics in Aquatic Systems. Lewis Publishers, Boca Raton. 754 pp.

Cheng, R.C., S. Liang, H.-C. Wang, and M.D. Beuhler. 1994. Enhanced coagulation for arsenic removal. Journal AWWA September 1994:79-90.

Clifford, D.A. and Lin C.C. 1991. Arsenic (III) and arsenic (V) removal form drinking water in San Ysidro, New Mexico, Project Summary for USEPA, EPA 600/S2-91/011.

Dixit, S. and J.G. Hering. 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Tech. 37:4182-4189.

Edwards, M. 1994. Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. J. AWWA September, 1994:64-78.

Edwards, M., S. Patel, L. McNeill, H. Chen, M. Frey, A. Eaton, R. Antweiler, H. Taylor. 1998. Considerations in As analysis and speciation. J. AWWA March, 1998, 90:103-113.

Fields, K., A. Chen, L. Wang. 2000. Arsenic removal from drinking water by iron removal plants. EPA/600/R-00/086.

Grundl, T. and J. Delwiche. 1993. Kinetics of ferric oxyhydroxide precipitation. J. Contam. Hydrol. 14:71-97.

Hering, J.G., P.-Y. Chen, J.A. Wilkie, M. Elimelech, and S. Liang. 1996. Arsenic removal by ferric chloride. Journal AWWA April 1996:155-167.

McNeill, L.S. and M. Edwards. 1997. Predicting As removal during metal hydroxide precipitation. Journ. AWWA 89:75-86.

Pizarro, J., N. Belzile, M. Filella, G.G. Leppard, J.-C. Negre, D. Perret and J. Buffle. 1995. Coagulation/sedimentation of submicron iron particles in a eutrophic lake. Wat. Res. 29:617-632.

Schneider, W. 1984. Hydrolysis of Iron(III)- chaotic olation versus nucleation. Comments Inorg. Chem. 3:205-223.

Stumm, W. and G.F. Lee. 1961. “Oxygenation of ferrous iron” Industrial and Engineering Chemistry 53:143-146.

Sung, W. and E.J. Forbes. 1984. Some considerations on iron removal. Journal of Environmental Engineering 110:1048-1061.