



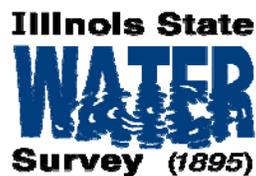
Development of Low Cost Treatment Options for Arsenic Removal in Water Treatment Facilities

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DEVELOPMENT OF LOW COST TREATMENT OPTIONS
FOR ARSENIC REMOVAL IN WATER TREATMENT
FACILITIES

by

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DEVELOPMENT OF LOW COST TREATMENT OPTIONS FOR ARSENIC REMOVAL IN WATER TREATMENT FACILITIES

ABSTRACT

Many water treatment plants that utilize groundwater will be burdened with additional expenses in order to meet the new Maximum Contaminant Level of 10 µg/L for arsenic. The objective of this project was to develop an inexpensive treatment option for arsenic removal, suitable particularly for small communities, by extending and optimizing the Fenton chemistry that already occurs during iron removal at many drinking water treatment plants. Improvement of the efficiency of arsenic (III) oxidation to arsenic (V) by hydrogen peroxide addition and addition of more iron to furnish more hydrous ferric oxides (HFO) for adsorption of the arsenic allow removal of arsenic from 40 to 5 µg/L (compared to 30 µg/L during normal iron removal) in high-DOC (13 mg C/L) groundwater, while increasing chemical costs only slightly, and requiring no large capital equipment costs.

INTRODUCTION

Arsenic Maximum Contaminant Level

Chronic exposure to arsenic (As) in drinking water at high concentrations has been linked to serious dermatological conditions, such as blackfoot disease (Lu, Hsieh et al. 1991), cancer of the skin, bladder, lung, liver, and kidney (Hindmarsh 2000) and other ailments (Karim 2000). The maximum contaminant level (MCL) for arsenic in drinking water for many years was 50 µg/L, which was assumed to provide a wide safety margin. However, recent research (Smith, Hopenhayn-Rich et al. 1992) has suggested that the cancer risk at 50 µg/L is unacceptably high. A review of the available arsenic- and health-related data prompted the USEPA to lower the MCL to 10 µg/L, which is the same as the World Health Organization standard. Public water supplies have until 2006 to comply with the new MCL.

All water utilities in Illinois meet the 50 mg/L MCL but 30-50 facilities would probably exceed the 10 µg/L MCL (Wilson et al., 2004). Most of these facilities serve communities with fewer than 10,000 residents. The per-capita cost of upgrading treatment systems to meet the new MCL can be particularly severe for these small communities (Frost, Tollestrup et al. 2002).

Many small drinking water systems rely on groundwater and dissolved arsenic concentrations greater than 1 µg/L are common in groundwater. In some aquifers and under certain conditions, much greater arsenic concentrations can be found, and concentrations above 10 µg/L are not uncommon. A review of 2,262 public groundwater supply sources revealed that over 8% had over 10 µg/L As and that the median concentration for all groundwater samples from Illinois was 1 µg/L (Focazio, Welch et al.

2000). A review of analyses of 30,000 groundwater samples from throughout the United States found that about 10% had over 10 µg/L As (Welch, Westjohn et al. 2000).

Arsenic Speciation

Arsenic in groundwater occurs almost entirely in two chemical forms (species). As(III) includes H_3AsO_3 (arsenious acid) and H_2AsO_3^- . As(V) consists mostly of H_2AsO_4^- and HAsO_4^{2-} . (See Appendix A) Although methylated forms of arsenic are sometimes found in surface waters, they have only rarely been found in groundwater (Irgolic 1982; Chatterjee, Das et al. 1995). Low concentrations (< 2 µg/L) of methylated species have been found in groundwater from West Bengal, although the inorganic arsenic concentration in those samples was extremely high (> 300 µg/L) (Shraim, Sekaran et al. 2002).

Both arsenic species are usually found in groundwater. In most published studies of arsenic speciation, both As(III) and As(V) were found and the less abundant species was at least 2% of the total arsenic (Matisoff, Khourey et al. 1982; Ficklin 1983; Welch, Lico et al. 1988; Chen, Yeh et al. 1995; Smedley 1996; Smedley, Edmunds et al. 1996; Boyle, Turner et al. 1998; Yan, Kerrich et al. 2000). In these studies, As(III) was generally predominant under reducing conditions while As(V) was predominant under oxidizing conditions. Korte and Fernando (Korte 1991) found only As(III) in shallow wells in an alluvial aquifer in Missouri.

Concurrent Arsenic and Iron Removal

Groundwater from glacial aquifers that has 10 µg/L As or more usually has at least 1 mg/L of iron (Fe) (Kelly, Holm et al. 2005). Many water utilities remove soluble Fe because of aesthetic issues such as taste and laundry staining. The most common Fe removal method involves oxidizing the soluble ferrous Fe to insoluble hydrous ferric oxides (HFO) and filtering the HFO out. Both As(III) and As(V) adsorb to HFO and as a result Fe removal also removes some As, although the efficiency varies widely (McNeill and Edwards 1995). Arsenic is also removed in treatment plants that add FeCl_3 as a coagulant (Cheng, Liang et al. 1994; Scott, Green et al. 1994).

Many factors may affect As adsorption and, therefore, removal at Fe-removal plants. In a study of Fe removal plants in Illinois, it was found that the Fe:As ratio was a critical parameter. Treatment facilities with high Fe:As ratios generally have better As removal efficiencies than those with low Fe:As ratios (Wilson et al., 2004). Other solutes commonly found in groundwater, including bicarbonate, silica, phosphate, and organic matter also adsorb to HFO and may decrease As adsorption through competition (Holm 2002; Redman, Macalady et al. 2002). FeCl_3 coagulation removes As(V) more efficiently than As(III) under a wide range of conditions (Hering, Chen et al. 1996; Hering, Chen et al. 1997). Therefore, speciation may also affect As removal in Fe removal plants. Appendix A summarizes research on As adsorption to HFO.

Prior Work in the Area of Oxidation/Coagulation/Filtration for Arsenic Removal.

A candidate process for use in small drinking water treatment plants should be simple, inexpensive, and effective. It has been known for some time that some removal of arsenic takes place during the iron removal treatment used by plants that utilize groundwater. Examination of that removal within the framework of known iron and arsenic chemistry indicated that it should be possible to improve removal efficiency by manipulating the treatment chemistry to promote more arsenic oxidation. It is widely recognized that preoxidation of arsenic aids removal by coagulation of the iron present (USEPA 2003; Ghuyre and Clifford 2004). Arsenic has been shown to be easily oxidized by all the common fairly strong oxidants, such as ozone, hydroxyl radical, chlorine, permanganate, etc. (Kim and Nriagu 2000; Ghuyre and Clifford 2004), but only slowly by oxygen or hydrogen peroxide (Pettine, Campanella et al. 1999; Kim and Nriagu 2000). Although the thermodynamics are favorable for oxidation in all these cases, the kinetics for oxygen and hydrogen peroxide reactions are too slow to be practical for water treatment. The stronger, less specific oxidants are, however, subject to interferences from reaction with other solutes, and are more costly to use.

Another oxidant which has seen some use in water treatment is the combination of hydrogen peroxide and Fe(II). This combination is known to produce a strongly oxidizing species, generally thought to be hydroxyl radical, and is referred to as Fenton's reaction (Walling 1975). It will be seen below that Fenton chemistry already takes place to some extent during air oxidation of iron during iron removal. There have been numerous investigations of the use of Fenton's reaction in water treatment, but most of those examples employed such large peroxide concentrations that they are not practical, particularly for drinking water treatment, where costs must be kept especially low. In one study of arsenic removal from drinking water (Krishna, Chandrasekaran et al. 2001), the optimum doses were found to be 6 mg/L of peroxide and 100 mg/L of ferrous ammonium sulfate for treatment of 100 to 2500 $\mu\text{g/L}$ of arsenic in tap water, but 40-50 $\mu\text{g/L}$ of arsenic still remained. The authors found that passage through a zero-valent iron column following the Fenton treatment further reduced the arsenic concentration to 10 $\mu\text{g/L}$. While these peroxide and iron doses are relatively high, the initial arsenic concentration was also high. In addition, the use of a two-stage process is not desirable. Probably the most important factor in assessing these results, however, was the fact that these experiments were performed in tap water, which typically contains very low concentrations of other solutes like dissolved organic carbon (DOC) to compete for active species. Groundwater, on the other hand typically contains enough DOC to consume a high enough fraction of the active species to lower the treatment efficiency by one to two orders of magnitude.

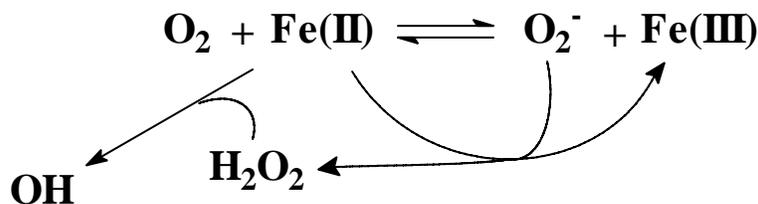
Fenton Process Chemistry

In 1894, H.J.H. Fenton reported (Fenton 1894) that Fe(II) strongly promoted the oxidation of malic acid by hydrogen peroxide. It was forty years later that Haber and Weiss (1934) proposed that hydroxyl radical was responsible for this reactivity, which was supported by the mechanistic and laboratory studies of Merz and Waters (Merz

1947) in the 1940's, and later by Walling (1975). Hydroxyl radical is one of the most strongly oxidizing species known, and can be thought of as what would be left if one pulled a hydrogen atom off of a water molecule. Since oxygen-hydrogen bonds are in general stronger than carbon-hydrogen bonds in organic (carbon-containing) compounds, the hydroxyl radical can pull a hydrogen atom off of an organic compound, and thus initiate its degradation.

Hydroxyl radical processes are one member of the larger family of water- and air-treatment processes referred to as Advanced Oxidation Processes (AOPs), which have stirred interest over the last two decades as treatment methods for destroying toxic organic compounds. There are many methods of producing hydroxyl radical, but most are fairly energy-intensive and therefore see use primarily in critical applications, where cost may be less important than is completeness and certainty of treatment. Fenton's reaction, however, is more of a "low-tech" AOP, since it does not require the use of ozone, ultraviolet light, electron beams, or plasma. For this reason, it has often been tried in water treatment, but usually at sufficiently high hydrogen peroxide doses that it was not cost-effective. As discussed above, the primary need for oxidation during arsenic treatment is to oxidize As(III) to As(V), which is both less toxic and more strongly adsorbed to the hydrous ferric oxides (HFO) that precipitate during iron removal. Hydroxyl radical reacts very quickly with As(III), with most of the reaction being complete within tenths of a millisecond. The groundwater used in this project contains only about 35-40 $\mu\text{g/L}$ of arsenic, approximately 2/3 of which is present as As(III). This corresponds to about 0.3 μM arsenic, so with an optimum yield of one hydroxyl radical produced per hydrogen peroxide molecule used, only 0.3 μM hydrogen peroxide (0.01 mg/L) would be required if the reaction was specific for As(III). However, hydroxyl radical also reacts very quickly with many other substances present in the water, including natural organic material (NOM), so that As(III) only scavenges a few percent of the hydroxyl radical that is generated (see Appendix B for a more detailed discussion). As a result, considerably more than the stoichiometric ratio of hydroxyl radical is required for near-complete As(III) oxidation.

As described above, the very reactive but transient species that is responsible for the oxidative power of the Fenton reaction is generally thought to be hydroxyl radical, although interpretations invoking other plausible alternatives, particularly Fe(IV) (Hug and Leupin 2003) have been proposed. For the purposes of discussion of the present work, the reaction system that assumes hydroxyl radical (OH) production will be used. The species represented by OH is not the same as the negatively-charged hydroxide ion, represented by OH^- , but instead is neutral and is a radical, i.e., has an unpaired electron. The unpaired electron is sometimes indicated by a dot, but in this report a dot will only be used when necessary in discussions of electron transfer. Within the OH framework, the core mechanism for OH generation by the oxidation of Fe(II) by oxygen (O_2) (Barb, Baxendale et al. 1951; Barb, Baxendale et al. 1951; Rush and Bielski 1985) is shown in Scheme I



Scheme I

In this scheme, oxygen (O_2) reacts with Fe(II) to produce the superoxide radical (O_2^-), which can react with another Fe(II) to make hydrogen peroxide (H_2O_2), which can then react with another Fe(II) to make OH . Thus, three Fe(II) species are required for the production of one OH radical, with the result that Fe(II) is typically the limiting reactant, and that the OH yield per Fe(II) available is $\leq 1/3$. OH could also react with Fe(II) (not shown) in systems when no other solutes are present to react with OH , leading to the often-heard ratio of four Fe(II) consumed per O_2 used; however, in most natural waters, enough natural organic material (NOM) is present that the reaction of OH with dissolved organic carbon (DOC) dominates the fate of the OH that is produced.

Consideration of the above mechanism shows that, on the basis of Fe(II) consumed, OH can be generated more efficiently by adding hydrogen peroxide so that only one Fe(II) is required per OH generated. Thus, use of the Fenton reaction can give OH radical yields a factor of three or more greater than those obtained during air oxidation of Fe(II) , which provides a considerable advantage when trying to utilize the substances already present to promote arsenic removal. Based on this analysis, one goal of the project was to enhance the Fenton component of the iron removal process, in order to encourage the production of more OH radicals with the amount of Fe(II) available in the water.

During the course of this project, a paper was published by Hug and Leupin (2003), in which the authors made arguments for Fe(IV) being the active species that was primarily responsible for arsenic oxidation in the Fenton system at near-neutral pH. Those authors constructed a kinetic model, primarily from known reactions and rate constants, but with a few rate constants used as fitting parameters. The model was successful in explaining their iron and arsenic oxidation data obtained from experiments performed using synthetic groundwater. Unfortunately, no similar studies were made in water containing organic materials, so the effects of high NOM concentrations on the reaction system are unknown.

Another helpful paper was published during the course of the project this year (Roberts, Hug et al. 2004) in which the adsorption of arsenic in the presence of competing silica and phosphorus was modeled as a function of added iron. As with the above paper, no results were included in which the participation of NOM was considered. However, it provided additional evidence of the importance of the need for sufficient HFO to adsorb arsenic in the presence of competing solutes such as silicate and phosphate. The authors found that addition of Fe(II) was more effective than Fe(III) in their system.

Project Approach

The premise of this project was that 1) the iron already present in the water could be used in conjunction with hydrogen peroxide (the Fenton reaction) to produce a strongly oxidizing species, and 2) that the process could be optimized by manipulating the chemistry of the two important process steps: Arsenic (III) oxidation to arsenic (V), and the sorption of both forms of arsenic to hydrous ferric oxides (HFO). This optimization can be carried out through the use of a reaction mechanism and kinetic and/or equilibrium models, to determine the sensitivity of the treatment efficiency to various treatment parameters. If successful, this method can be more efficient than trial and error or factorial design experiments. Therefore, the intended approach was to conduct the mechanistic and experimental investigations in parallel: A) construct a preliminary mechanism from the abundant information in the literature, check for information gaps resulting from omission of known reactions from previous models, then analyze the resulting kinetic model for the primary factors controlling process efficiency. In parallel with that investigation would be B) an experimental effort in which basic experimental techniques were developed and the range of a few important reaction rates established by simple batch experiments. The results of this two-pronged approach would provide an optimum range of conditions, the utility of which would then be verified in flow experiments in a laboratory system simulating the water treatment system at Danvers, Illinois, plus any additional unit processes that were found to be necessary. Finally, the most favorable configurations and conditions resulting from the laboratory flow studies would be used in on-site pilot-scale flow experiments at the Danvers drinking water treatment plant to confirm the effectiveness and conditions of the process.

Danvers is a community of about 1,100 people in central Illinois, near Bloomington. Danvers draws its raw water from wells in the Mahomet Aquifer. Although wells with high arsenic content in Illinois tend to contain higher dissolved organic carbon (DOC, mean value = 6.3 mg/L for 49 Illinois wells, Wilson et al., 2004) than in many other regions (mean value = 1.2 mg/L for 100 samples from 27 states, Leenheer et al., 1974), the Danvers water DOC is particularly high (13 mg/L). Since DOC acts as an active species scavenger in competition with arsenic, it was thought that this water would provide a stringent test of the process capability to oxidize As(III) to As(V).

MATERIALS AND METHODS

Chemicals

All chemicals used were reagent grade and were used as received. Ferric chloride solution (40% w/v), ferrous sulfate heptahydrate (101.5%), glacial acetic acid (99.5%), hydrogen peroxide (31.3%), concentrated hydrochloric acid (37%), concentrated sulfuric acid (95-98%), and concentrated nitric acid (69-71%) were obtained from Fisher Scientific. Ferrous ammonium sulfate hexahydrate (98.5-101.5%) and sodium hydroxide (97%) were obtained from EM Science. Ammonium acetate (98.4%) was obtained from Acros. Laboratory water was from a Milli-Q system with ion exchange and a carbon canister.

Analytical Methods

Arsenic

Arsenic was determined by graphite furnace atomic absorption spectrophotometry (GFAAS) using a Varian SpectrAA 220Z spectrophotometer with Zeeman background correction with a GRA 110Z graphite tube atomizer and a PSD 100 programmable sample dispenser. Palladium nitrate was used as a matrix modifier (Welz, Schlemmer et al. 1988). The GFAAS system was calibrated at the beginning of a run and recalibrated after the first 20 samples. The system performed a re-slope, a blank plus mid-range standard, after 10 and 30 samples. A commercial QA standard (VHG Laboratories) was run before the first sample to verify the calibration and after the last sample to verify analytical stability. Approximately 20% of samples were run in duplicate to check precision and 10% of samples were spiked with 10 µg/L As to check accuracy.

Arsenic speciation was determined by anion exchange (Ficklin 1983; Edwards, Patel et al. 1998; Fields, Chen et al. 2000). Briefly, the anion exchange resin (AG1-X8, Bio-Rad) in 20 cm³ mini-columns was converted to the chloride form by passing 2 bed volumes of 1M HCl to remove sulfate and any arsenate and phosphate from the previous run. Next, the resin was converted to the hydroxide form using 20 bed volumes of 1M NaOH, then to the acetate form using 2 bed volumes of 1M acetic acid, and finally rinsed with deionized water until the pH of the effluent was over 4. Resin conversion was done in the laboratory before field sampling. A water sample for As speciation was collected by filtering approximately 100 mL into a bottle containing sufficient ultra-pure H₂SO₄ (Optima®, Fisher) for a final concentration of 0.05% (v/v). Within one hour the acidified sample was poured through a column. The first 70 mL of effluent was discarded and the next 10 mL was collected in a bottle containing sufficient ultra-pure HNO₃ preservative (Optima®, Fisher) for a final concentration of 0.2% (v/v). Arsenic(V) was retained in the column while As(III) passed through. The effluent was analyzed by GFAAS. As(III) blanks were obtained by running deionized water through the entire procedure.

Iron

Ferrous iron was determined by the phenanthroline colorimetric method (Clesceri, Greenberg et al. 1998), after samples were diluted by a factor of 10. Ferrous ammonium

sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, was used to make the stock solution for the iron standards. Total iron was measured by reducing Fe(III) to Fe(II) using thioglycolic acid prior to derivatization. Absorbance was measured at 510 nm using a Hitachi U-2000 UV-visible spectrophotometer after the absorbance value stabilized.

Hydrogen Peroxide

Hydrogen peroxide was analyzed by using a modification of the titanium (IV) chloride method (Parker 1928). The absorbance was measured at 415 nm. The concentration was calculated using the equation:

$$\text{Concentration}(mM) = \frac{\text{absorbance}}{0.553} = (1.81)(\text{absorbance})$$

The response factor 0.553 was determined by analysis of hydrogen peroxide solutions by both the Ti(IV) method and by iodimetry in boric acid-buffered solution (Flamm 1977) with an ammonium molybdate catalyst, measuring I_3^- spectrophotometrically. The spectrophotometric method was calibrated using potassium iodate as a primary standard.

Other Instrumental Measurements

Dissolved oxygen measurements were made with an Orion Oxygen Meter model 820. The dissolved oxygen meter was calibrated against air saturated water by placing into a calibration sleeve (model 080014) which had a water-soaked sponge at the bottom. The pH was measured using an Orion pH Meter model 920A with an Orion pH probe model 910600. The pH meter was calibrated at two points using standard buffers of pH 4 and 7 or 7 and 10, depending on the pH range of the sample to be analyzed.

Experimental Procedures

Sample Collection.

From Well Head at Danvers Water Treatment Plant – Water for laboratory experiments was collected at the well head of Well #5, one of the wells that supplies groundwater to the drinking water treatment plant at Danvers, Illinois, and brought back to the laboratory. All samples were collected in acid-washed and deionized water-rinsed glass bottles. To prevent oxidation of Fe(II) in the anoxic groundwater, bottles were filled, overflowed to flush the contents, and then capped quickly while avoiding any trapping of headspace containing oxygen. On later sampling trips, septum caps were used so that atmospheric exposure could be minimized during sample manipulation in the laboratory when anoxic conditions were required for experiments.

Sample Collection during Experiments - Samples collected during some experiments could not be analyzed immediately. Therefore, acid was added to keep iron and arsenic from changing oxidation states and prevent HFO formation, which would adsorb some dissolved arsenic. Samples for Iron(II) and total iron analysis were preserved with dilute HCl. Arsenic samples were preserved with dilute nitric or sulfuric acid, depending on the analysis to be performed. All preservatives used were added to sample bottles before

sample collection. Measured concentrations were volume-corrected for the dilution by preservative.

Flow Experiments

Laboratory Flow Experiments - The treatment train in the Danvers water treatment plant is shown schematically in Figure 1.

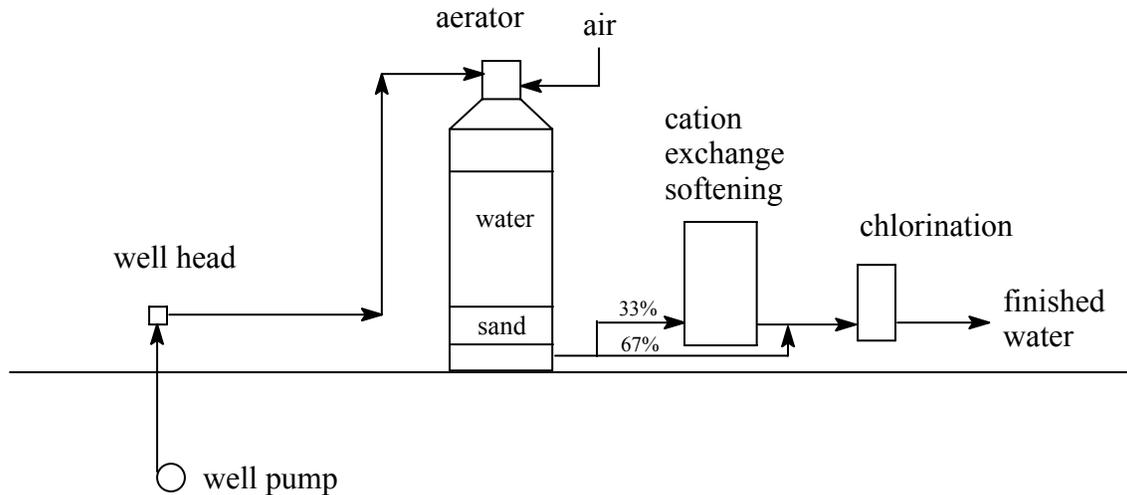


Figure 1. Danvers, IL municipal drinking water treatment plant.

Groundwater is pumped to the top of the aerator and percolates down through perforated plates with countercurrent air flow provided by a blower to oxidize Fe(II). The tank above the sand filter serves as the flocculation basin, with a residence time of about 30 minutes at 220 gpm flow. (Aeralator®, U. S. Filter)

The apparatus (Figure 2) for the flow experiments carried out in the laboratory was designed to simulate the Danvers plant, with regard to residence times in the various unit processes.

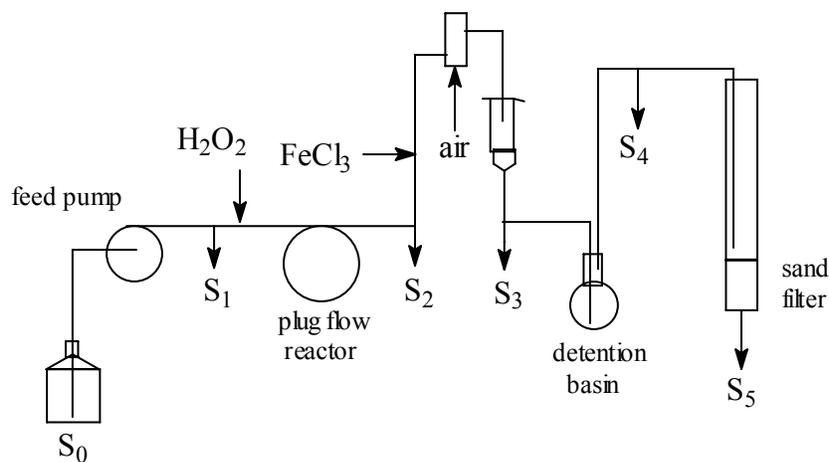


Figure 2. Apparatus for flow experiments in the laboratory.

Water was pumped from sample bottles through a peristaltic pump and hydrogen peroxide was added using a Sage Instrument model 355 syringe pump to deliver a fixed flow of dosing solution. The syringe pump flow rates were measured several times during each experiment by reading the volume of solution in the dosing syringes and noting the time. The values were averaged by a linear regression of the volume vs time values, and those values were used in calculations. Flow rates for the peristaltic pumps were measured similarly, using a fine calibration scale attached to the reservoir. A plug flow reactor made of $\frac{1}{4}$ " o.d. PTFE tubing was used to provide sufficient time for complete reaction with ferrous iron in the groundwater before FeCl_3 addition using another syringe pump. The water then moved into an aeration vessel through which was passed a steady flow of compressed air (zero grade) to completely aerate the water. The air was passed through a water bubbler to visually indicate flow and to pre-saturate the air with water to avoid any possible evaporation from the aerator. After aeration, an inverted, plunger-less 30-mL syringe was used as a gas-liquid separator and mixing vessel. The calibrations on the syringe provided a way of monitoring the constancy of the flow rate. The flow was then passed back through another channel of the multi-channel peristaltic pump to keep the sample flowing through the second half of the apparatus at the same rate as the first. The water was then passed through a 100-mL round flask to allow flocculation. The flask had an actual volume of 126 mL, which provided a residence time of approximately 21 minutes at the experimental flow rate. The water was then passed through a sand filter (0.0059" to 0.0132" sized particles, Global Drilling Suppliers, Inc.) with an empty bed volume of 40 mL in the bottom of an open-top column (2.7 cm diameter and 45 cm height). The sand was backwashed between experiments and kept wet when not in use.

Water for use in the flow experiments was brought back to the laboratory in

1-L bottles with septum caps, since sample manipulation within a glove bag swept with nitrogen did not adequately protect the samples from oxygen. Water was pulled from the sample bottle through sharpened PEEK tubing inserted through the septum. Very slight nitrogen gas (oxygen free) pressure was applied to the bottles through another sharpened PEEK tube to replace the volume of water consumed throughout the experiment and to keep the samples as anoxic as possible. A water bubbler was used to maintain the low pressure during the experiment, and ensure that the system did not overpressurize. Sample bottles could be chained by joining sharpened lengths of PEEK with short pieces of tygon tubing and then inserting into adjacent bottles. This was necessary since most experiments consumed more water than the individual sampling bottles held.

Several experiments were performed at different hydrogen peroxide and iron doses. The system was allowed an equilibration time equal to three times the sum of the individual unit residence times before sampling. To avoid disturbing steady-state operation, samples were taken from the effluent port first, progressing toward the influent end. The sampling order was: S_5 (after sand filtration), S_4 (after the retention basin), S_3 (after the aeration basin), S_2 (after peroxide addition and before iron addition), S_1 (influent before peroxide addition). Samples were also taken directly from the sample bottle (S_0). Triplicate samples were collected for all iron and arsenic measurements except for the total (unfiltered) arsenic samples. All iron and arsenic samples were analyzed in triplicate.

The system influent flow rate was maintained at approximately 6 mL/min for each experiment. The average relative standard deviation (RSD) for the influent flow in all the experiments was 2.3%, with a range from 0 to 7.3%. The peroxide and iron dosing solutions were fed at 0.3 mL/min. The average RSD for peroxide and iron flow rates were 9.8% (from 6.5 to 12.0%) and 4.8% (from 2.0 to 6.7%), respectively. The peroxide dose was varied from 9.3 to 27.2 μM (0.32 to 0.93 mg/L) while the iron dose was varied from 3 to 20.55 mg/L. All concentrations, including final concentrations reported for iron and arsenic remaining after treatment, were corrected for the dilutions caused by the peroxide and iron additions. Samples taken from S_0 and S_1 required no correction. The correction for samples taken from S_2 was approximately 5%, while samples from S_3 to S_5 were corrected by approximately 10%, all based on actual measured flows in the individual experiment.

On-Site Pilot-Scale Experiments - Information collected from the flow experiments carried out in the laboratory was used to design the pilot-scale equipment, shown in Figure 3 and schematically in Figure 4. The unit was assembled in the laboratory and relocated to the water treatment plant for the pilot-scale experiments. All basins and vessels were made by cutting the tops off of polyethylene bottles or carboys, except for the sand filtration column, which was a 3-foot piece of 6-inch diameter borosilicate pipe. All units were mounted on a Unistrut rack, which was fitted with casters.

For the experiments at the Danvers plant, the apparatus was connected directly to a sample tap at the well head. A check valve and gas-liquid separator physically separated the apparatus from the water in the supply pipe. The gas-liquid separator was placed outdoors and was designed so that the outgassing methane formed a constant blanket over

the source water to help protect it from air. Other open vessels in the apparatus were vented with fans and flexible pipe to the outdoors to ensure that no buildup of methane occurred in the room where the equipment was located. The gas-liquid separator provided a constant-head source water for the feed pump to the apparatus. The water flow from the well head faucet to the gas-liquid separator was maintained at a slightly higher rate than water flow through the apparatus, and the excess water overflowed the vessel at the top, providing additional protection of the water from oxygen.



Figure 3. Pilot scale flow apparatus

Water was pulled from the gas-liquid separator and metered to the apparatus by a Cole-Parmer Multichannel Peristaltic Cartridge Pump (model 7519-00). The iron and peroxide dosing solutions were added using smaller tubing and cartridges in the same pump, in order to maintain a constant ratio between influent and dosing solutions in the event of flow fluctuations due to line voltage changes or other causes. Hydrogen peroxide was added first, while the water was still anoxic. After peroxide addition, the water was

pushed through a static mixer and slightly uphill through a plug flow reactor constructed from 1-in. PVC pipe. The slight uphill gradient prevented trapped gas spaces from forming due to additional outgassing, which would have shortened the reaction time for iron and hydrogen peroxide. The plug flow reactor provided a 1.5-minute reaction time for the peroxide. Preliminary laboratory experiments had indicated that complete reaction between hydrogen peroxide and iron required less than 22 seconds.

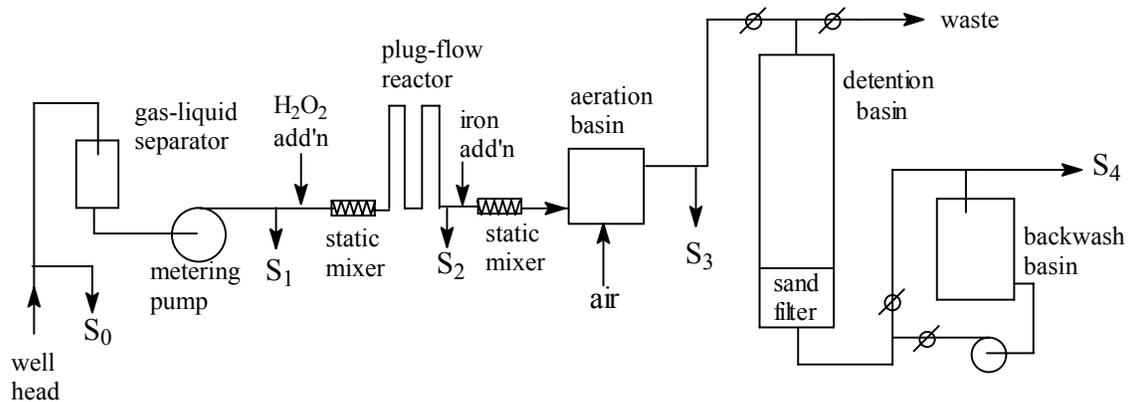


Figure 4. Schematic diagram of pilot scale flow apparatus

Following the plug flow reactor, $\text{Fe}(\text{Cl})_3$ was added before the water was introduced into the bottom of the aeration basin. An air pump provided the air flow to the aeration basin at a rate that provided good agitation of the water. Air was added through an X-shaped sparger constructed of $\frac{1}{2}$ -in. PVC pipe with $\frac{1}{16}$ -in. holes drilled evenly across the surface of the pipe. The sparger sat at the bottom of the aeration basin so that the water coming in at the bottom would be completely aerated as the water flowed up and out the exit point toward the top on the opposite side. Water flowed from the aeration basin into the top of the 16.7-L column (3 feet tall and 6 inches in diameter), made of borosilicate pipe containing approximately 2.5-L (bed volume) of the same sand as was used in the laboratory flow experiments. The space above the sand served as a flocculation basin, with a detention time of approximately 30 minutes. The superficial velocity (loading rate) through the sand filter was calculated to be 0.58 gpm/ft^2 (0.39 mm/s) in the pilot-scale apparatus and 0.26 gpm/ft^2 (0.18 mm/s) in the laboratory system, compared to 2.9 gpm/ft^2 (2.0 mm/s) for the Danvers plant. The effect of the filtration rate on effluent quality is not generally significant for rates up to 5 gpm/ft^2 , even for weak chemical floc (James M. Montgomery 1985). The finished water was collected in a large basin which was used for backwashing the sand filter between experiments.

Because the amount of sample taken at each sampling point was negligible compared to the system flow, the sampling order was slightly different than that of the laboratory flow

experiment. The sampling order was S₀, S₃, S₂, S₁, and S₄ (there was no S₅ in the pilot scale apparatus). All samples were collected in their respective bottles with pre-added acid as described in the experimental sample preparations section. Triplicate samples were collected for all iron and arsenic samples, and ion exchange for arsenic speciation was performed on-site.

The system influent flow rate was measured to be between 380 to 405 mL/min for all experiments. The iron and peroxide flows were measured to be between 14.40 and 19.57 mL/min. The influent flows were calibrated for each experiment by timing flow into a graduated cylinder. Although there was some variation from day to day, reproducibility of system flow measurement during any given day was found to be an average of 0.33% relative standard deviation (RSD) for all of the experiments, with a variability ranging from 0.12% to 0.71% RSD. The flows for the peroxide and iron addition were calculated by pumping from a volume-calibrated vessel and noting time and volume throughout the experiment. The hydrogen peroxide dose varied from 0 to 55.6 μ M (1.89 mg/L) during this series of experiments, while the iron dose was varied from 0 to 22.9 mg/L. Average RSDs for the peroxide and iron flow for all experiments were 5.0% and 6.1%, respectively, not counting three outlying values (46%, 48%, and 32%). The reason for these outliers is not known, but the high RSDs calculated for those values are the result of one very low value in each group of measurements. Flows were calculated between successive readings of time and volume, which is sensitive to reading errors. Even when those three values are included, the average of the successive individual flow calculations during an experiment agreed with the average flow calculated as (total volume of solution used)/(total time) within 2-5%. It seems likely that the isolated outlying calculated values were the result of reading errors, or a failure to note when the feed pump was turned off briefly for some reason. Considering the fact that all three flows (system, peroxide, and iron) were metered by the same pump, it is likely that a constant dose rate was maintained throughout the entire experiment. As described above, all concentrations were corrected for the dilutions caused by the peroxide and iron additions in these experiments, including the final reported values of iron and arsenic remaining, since the peroxide and iron dosing contributed a somewhat higher volume than they would in a treatment plant. This was a necessary trade-off to enable the use of the same peristaltic pump for both influent and dosing flow to ensure a constant flow ratio. S₀ and S₁ required no correction, S₂ was corrected by approximately 5% (when peroxide was added), while S₃ and S₄ needed an additional 5% correction when iron was added during an experiment.

Calculational Methods

Kinetic Calculations

The reaction mechanism was constructed from known reactions, and the set of differential rate equations obtained from the mechanism. These topics are discussed in more detail in Appendix B. The differential equations were solved analytically when possible, within the steady-state approximation. When that was not practical, the equations were solved numerically using the software SCIENTIST (MicroMath), which makes use of a stiff differential equation solver. The reaction equation set was expanded to include known reaction types that have not previously been included in published

models for Fenton reaction, and SCIENTIST was used to examine the range of effects of these “new” reactions.

Equilibrium Calculations

Adsorption of the arsenic species to HFOs was modeled to predict arsenic removal as a function of pH, extent of arsenic oxidation, etc., for comparison with actual removals. Chemical equilibrium computations were performed using Mineql+ (Schecher and McAvoy 1994). Additions to the equilibrium constant database are described in Appendix A.

RESULTS AND DISCUSSION

Preliminary Laboratory Experiments

Determination of Rates of Iron Oxidation by Oxygen

The Fe(II) represented in Scheme I is actually made up of a number of iron species, including Fe^{2+} , $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_2$, as well as numerous complexes with chloride, sulfate, phosphate, and bicarbonate, if those anions are present in the water. Each of these iron complexes reacts at a different rate with oxygen or hydrogen peroxide, which are the reactions that determine the rate of OH formation in Scheme I. Fortunately these reactions are well understood, and a number of the reaction rate constants have been determined (King 1998; King and Farlow 2000). More problematic is the fact that natural aquatic organics also form Fe(II) and Fe(III) complexes, which also have their own rate constants. Aquatic NOM does not consist of pure organic compounds, but is an inhomogeneous mixture of large molecules including breakdown products from plant material, as well as other substances that have been biosynthesized from those breakdown products. Our knowledge of these substances is limited and is characterized in terms of surrogate parameters for surface water organics. Similar knowledge is practically nonexistent for organic substances in anoxic groundwaters such as those which typically have arsenic problems. Therefore, it was felt that the first few experiments should be aimed at characterizing the rate of iron oxidation by oxygen for the Danvers water under study.

Figure 5 shows how quickly Fe(II) was oxidized in various waters. As a control experiment, Fe(II) was added to deionized water (DI) along with sufficient bicarbonate to mimic the alkalinity of Danvers raw water, and the concentration of Fe(II) was monitored while air was bubbled through the solution to simulate aeration in the plant. The half-life of Fe(II) was about 22 minutes in this experiment. Another experiment used Danvers raw water that had been previously exposed to air (preoxidized) so that the Fe(II) that was present had already been oxidized. This water was spiked with Fe(II) to replace that which had been oxidized, then the water was aerated, resulting in an initial Fe(II) disappearance that was more than ten times faster than in the control, with a half life of about 3 minutes. Since the alkalinity and the pH were compensated for in the control, the difference in rates is probably due to the difference in rate constants of iron complexes with the chloride, phosphate, silicate, and NOM that are present in the groundwater. Rose and Waite (Rose and Waite 2002) found that complexation of iron by fulvic acid increased the rate of air oxidation of iron in seawater, and Voelker and Sulzberger (1996) found that fulvic acid increases the rate of hydrogen peroxide reaction with iron in model systems.

When anoxic Danvers raw water still containing Fe(II) was aerated in a beaker, the initial Fe(II) disappearance rate was about twice that of the control (half-life about 17 minutes), but slower than that of the Fe(II)-spiked pre-oxidized water. When anoxic Danvers raw water was spiked three times with 1 μM peroxide over a period of 70 minutes inside of a nitrogen-filled glove bag and periodically sampled, the Fe(II) disappearance rate was the slowest of all, but still had a half-life of about 32 minutes, implying that our system was

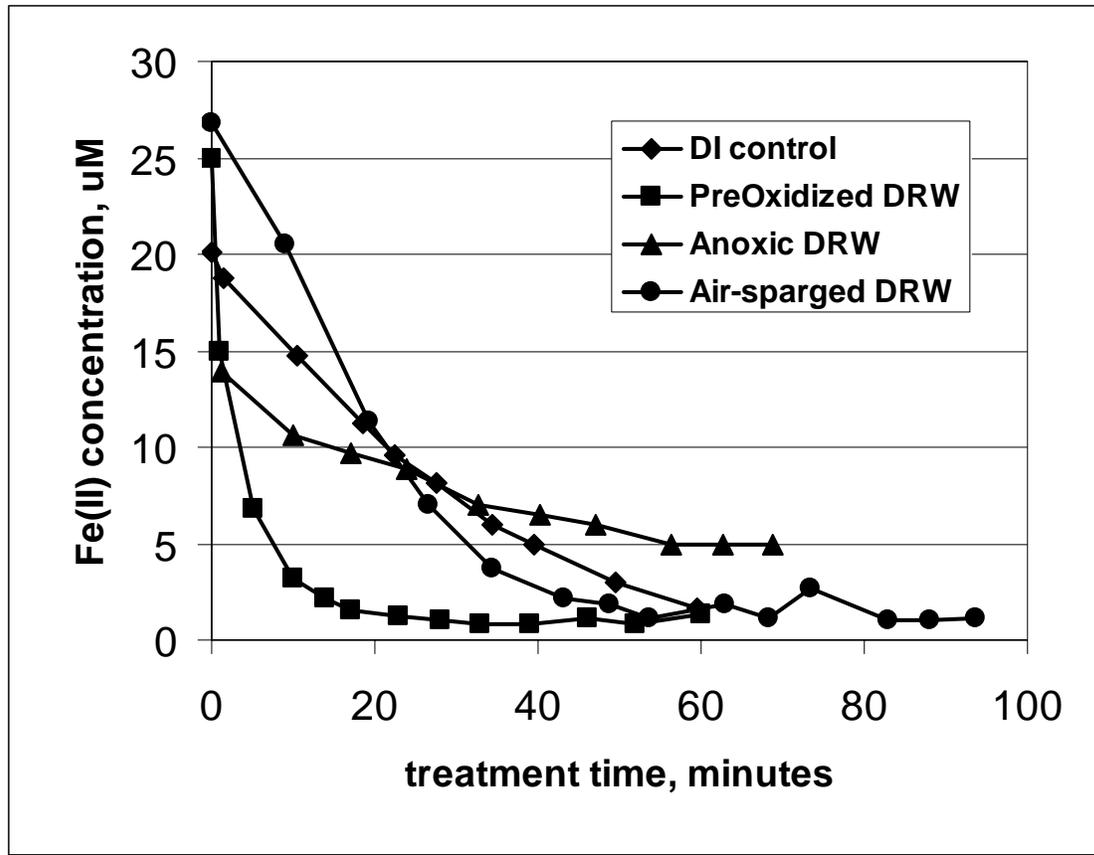


Figure 5. Effect of water composition on Fe(II) oxidation rate. DRW is Danvers raw water.

not oxygen free. The amount of oxygen carried in by the water in the three unsparged spikes was negligible – approximately 3 nM total – and any formation of hydroxyl radical by the peroxide should have actually reduced the oxygen concentration through the formation of carbon-centered radicals (see Appendix B - Treatment System Chemistry). Therefore, the glove bag method did not appear to be adequate to avoid slight oxygenation of the water, and more suitable techniques were subsequently developed to allow more selective rate measurements. Slight decreases in Fe(II) concentration due to the peroxide addition can be seen in the iron concentration between points 1 and 2, 4 and 5, and 7 and 8.

Thus, the results of the above experiments and others demonstrate that 1) iron oxidation is faster in Danvers groundwater than in DI water with similar bicarbonate alkalinity added, 2) Fe(II) oxidation is faster in the presence of more oxygen and it is difficult to keep a water anoxic during experiments, 3) previous exposure to air changes more about the water than just the Fe(II) concentration, so that raising the Fe(II) concentration back to its initial value does not produce a water that is chemically similar to the original water, and 4) oxidation of iron by hydrogen peroxide occurred at an observable rate, even with peroxide additions of only 1 μM . However, little effect was observed on the arsenic concentration in this experiment (data not shown).

Effect of Hydrogen Peroxide on Iron Oxidation Rate

A series of experiments was performed to investigate the effect of larger peroxide additions. Figure 6 shows the changes in iron and arsenic as a result of three 8 μM additions of hydrogen peroxide. The change in Fe(II) concentration between the first and second point is due to air oxidation of the iron. The first peroxide addition was made after the third point (overlapping the second point), and is indicated by the left-most arrow in both panels. This addition resulted in a large and rapid drop in iron concentration (to about 1/10 of its original concentration), as well as a significant drop in total dissolved arsenic (TDAs) and As(III). The second addition removed about half the remaining Fe(II) but caused no visible change in the TDAs or As(III), presumably because the Fe(II) was almost entirely consumed by the first peroxide addition. Hydrogen peroxide reacts only slowly with As(III), with a half life of 2.1 days at pH 7.5 (Pettine, Campanella et al. 1999). These results confirm that Fe(II) must be present for the rapid oxidation of As(III), and that Fe(II) must be used efficiently, reacting with hydrogen peroxide rather than with oxygen, to achieve good arsenic removal.

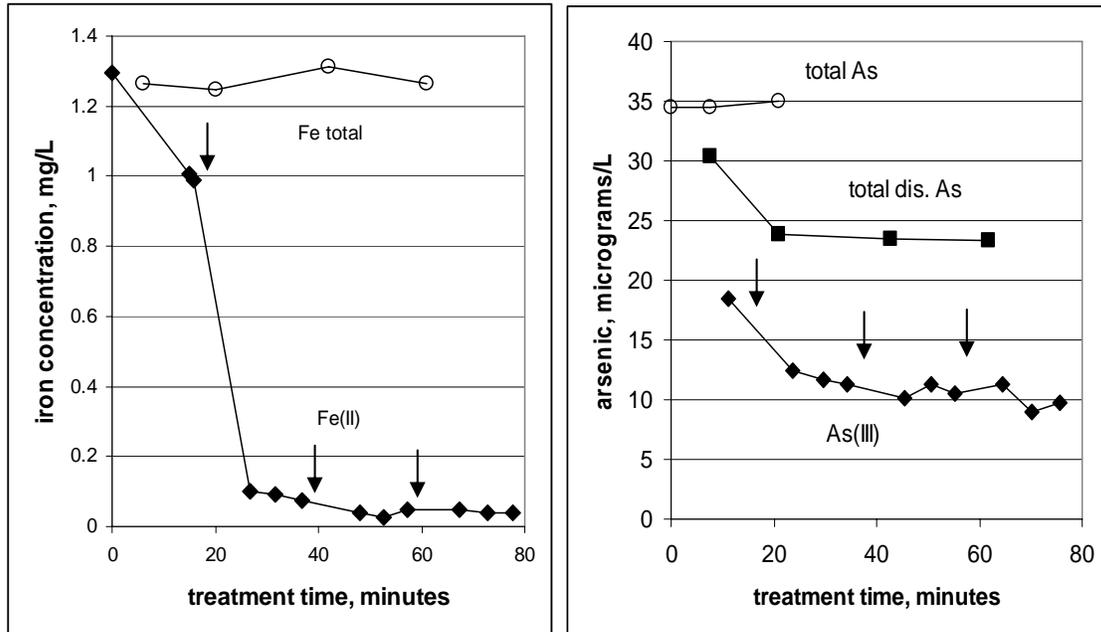


Figure 6. Effect of 8 μM additions of hydrogen peroxide on iron and arsenic concentrations. Arrows indicate time of peroxide additions.

Another series of experiments was conducted to investigate the effectiveness of various peroxide concentrations in promoting the oxidation of As(III). Figure 7 shows As speciation upon addition of various amounts of hydrogen peroxide, both to anoxic samples (designated “an” in the figure) that were sealed in septum vials, and to samples that were poured into beakers, spiked with peroxide, and left open to the atmosphere for 1 hour (designated “ox”). Arsenic (III) concentrations decreased with increasing peroxide concentration, and were reduced to 2-3 $\mu\text{g/L}$ with 20 or 30 μM hydrogen peroxide

addition. However, almost no decrease in dissolved arsenic was observed. That is, the As concentrations in unfiltered and filtered samples were the same within experimental error, implying that almost no arsenic was being removed by the mechanism of adsorption to the HFO, which was removed by filtration.

Two similar experiments were performed, in which the oxic samples were actively aerated for 30 seconds before spiking with peroxide, instead of simply being poured into a beaker. Results are shown in Figure 8, normalized for easier comparison. In the earlier experiment (I, oxic samples not aerated) the oxic samples showed more As(III) oxidation than the anoxic samples for 5 and 10 μM hydrogen peroxide addition, but similar oxidation for 20 and 30 μM hydrogen peroxide. In the second experiment (II, oxic samples actively aerated), oxidation of As(III) was more complete in the anoxic samples (anox II) than in oxic II for peroxide additions of 5, 10 and 20 μM , and showed greater than 90% oxidation in the 30 μM vial. Unfortunately, the sample for the oxic II 30 μM hydrogen peroxide addition was lost in a laboratory accident.

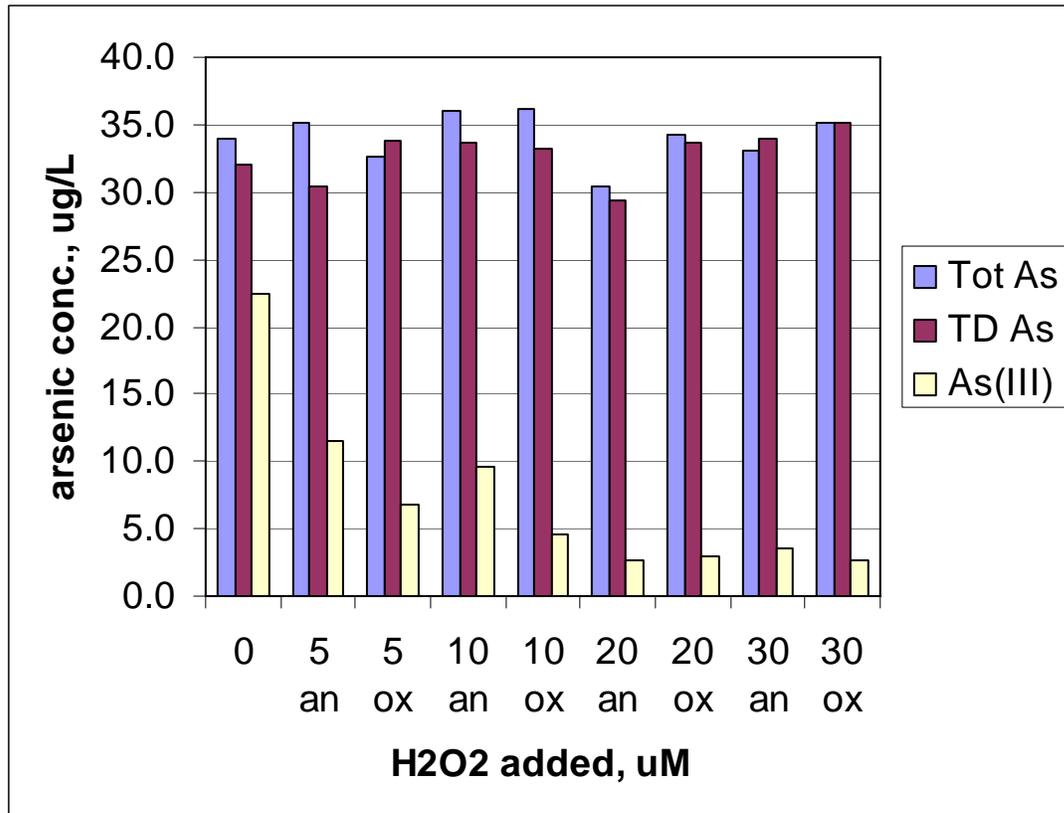


Figure 7. Effect of added hydrogen peroxide concentration on As(III) oxidation.

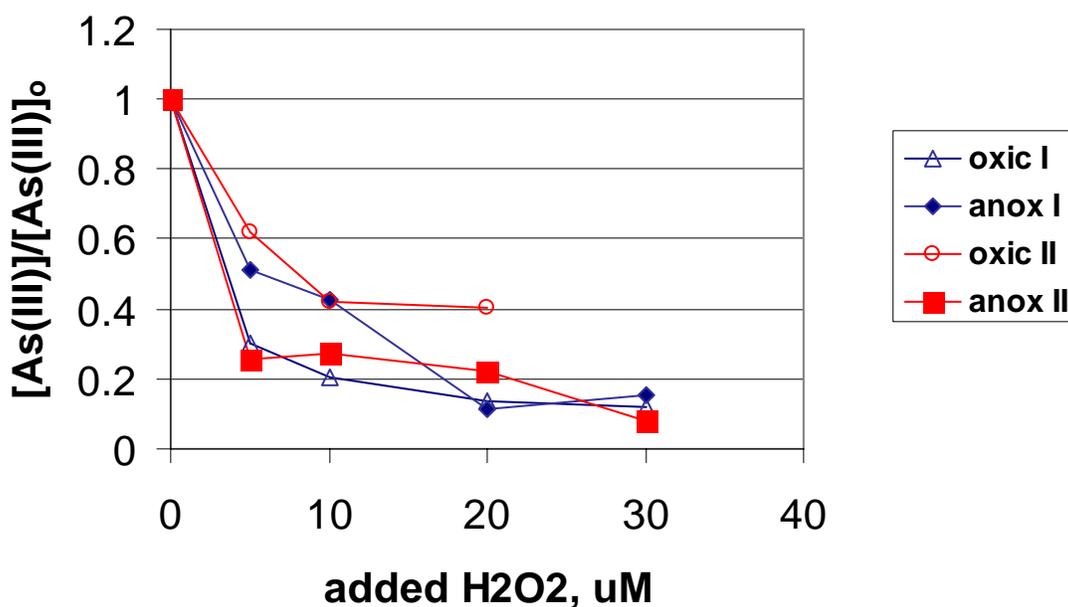


Figure 8. Effect of hydrogen peroxide addition to oxic vs anoxic Danvers groundwater. Hydrogen peroxide was added to oxic water before (I) and after (II) active presparging with air.

The difference between the two experiments shown in Figure 8 is that the oxic samples in experiment I were not immediately aerated, so the very fast reaction between peroxide and iron still had time to occur to some extent, as it did in the anoxic sample. However, the oxygen in the sample continued to react with remaining Fe(II) after the peroxide was gone, and had an hour reaction time before the samples were analyzed. Therefore, the oxic sample had the benefit of both peroxide and oxygen reaction with iron, while the anoxic sample contained very little oxygen to react with iron, and thus only got the benefit of Fe(II) reaction with peroxide, but no oxic step. Considerable unreacted Fe(II) (about 60%) was found in the anoxic samples corresponding to low doses (5 and 10 μM) of peroxide when they were analyzed, implying that if an air-oxidation step had followed the anoxic reaction period, considerably more removal would have occurred in that oxic step as well, and removals for anox I would have approached those of oxic I. On the other hand, the oxic samples in experiment II were aerated immediately before peroxide addition, so oxidation of iron by oxygen had already begun before peroxide was added. This means that a smaller percentage of the iron reacted with peroxide, which is the more efficient reaction with respect to OH yield per Fe(II). These results, while not conclusive, seem to indicate that peroxide should be added while the sample is still anoxic and allowed to react before the sample is oxygenated to use the rest of the Fe(II), if any is still left. This is consistent with the results of Woods, et al. (1963; 1963; 1964), who showed that in the oxidation of arsenic during iron oxidation, a chain reaction could be maintained under low oxygen conditions.

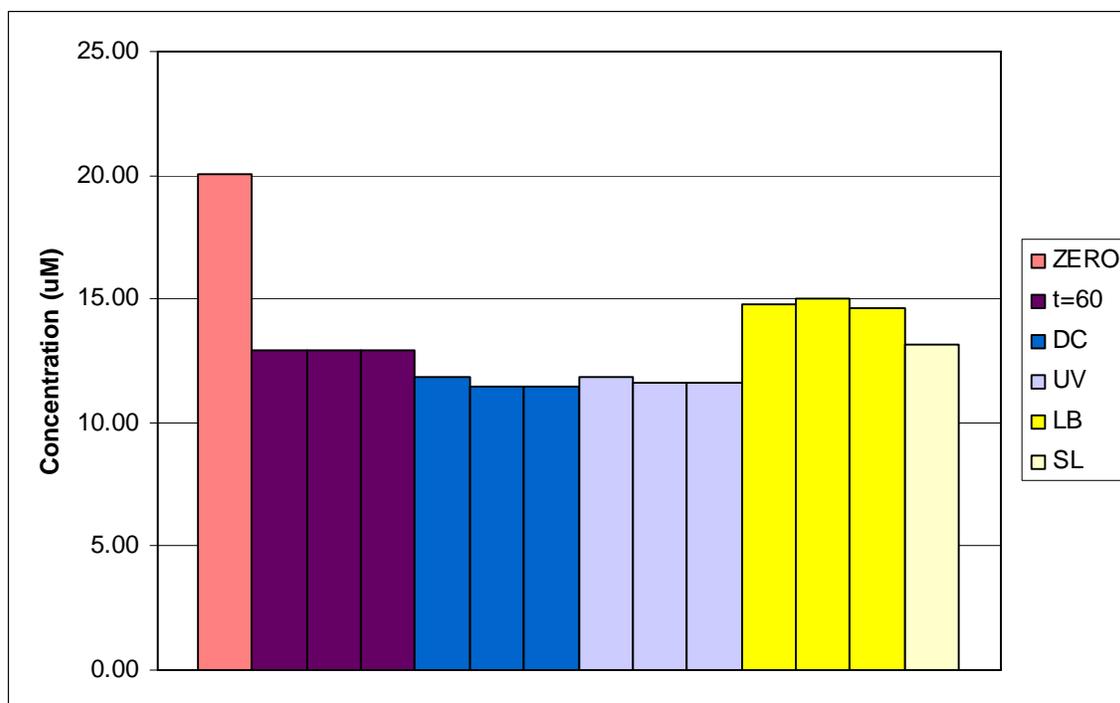


Figure 9. Photochemical Regeneration of Fe(II) from Fe(III). T=60 is after 20 µM peroxide addition and 1 hour reaction time. DC is the dark control experiment. UV, LB, and SL indicate ultraviolet lamp, incandescent light bulb, and sunlight, respectively.

In the early stages of this project, it was difficult to predict the efficiency of As(III) oxidation that could be achieved with the amount of Fe(II) available in the groundwater. Therefore, experiments were also carried out to investigate the possibility of utilizing the well known (Faust and Hoigne 1990) photochemical regeneration of Fe(II) from Fe(III), which could perhaps even be carried out using sunlight. Light has been used with the Fenton reaction to regenerate Fe(II), a process known as the Photo-Fenton reaction (Pignatello 1992, Zepp et al. 1992). To investigate this regeneration process, a bottle of anoxic Danvers groundwater was spiked with 20 µM hydrogen peroxide and allowed to react for 60 minutes before being poured into four 30-mL polyethylene syringes. Polyethylene is essentially transparent to ultraviolet and visible light. Iron (II) analyses were performed on the water before peroxide addition and after the 60 minute reaction period. One syringe was wrapped in aluminum foil and placed in the dark as a control, while each of the 3 remaining syringes was exposed to a different kind of light, including a UV pen lamp, sunlight and an incandescent light bulb. After 10 minutes of exposure, the contents were analyzed for Fe(II). The results are shown in Figure 9. The initial Fe(II) concentration of 20.1 µM (1.12 mg/L) was reduced to 12.9 µM (0.72mg/L) by reaction with peroxide over a period of 1 hour. This concentration dropped further to 11.6 µM (0.65 mg/L) in the dark control and in the solution irradiated by UV light, and stayed the same at 13.1 µM (0.73 mg/L) in the sunlight-irradiated sample, but increased to 14.0 µM (0.83 mg/L) in the sample irradiated by incandescent light. This surprising result indicates that low-tech photoregeneration of Fe(II) may hold some promise. Although this Fe(II) regeneration was found to be unnecessary in the present project, the results of these experiments are of interest, perhaps for future needs.

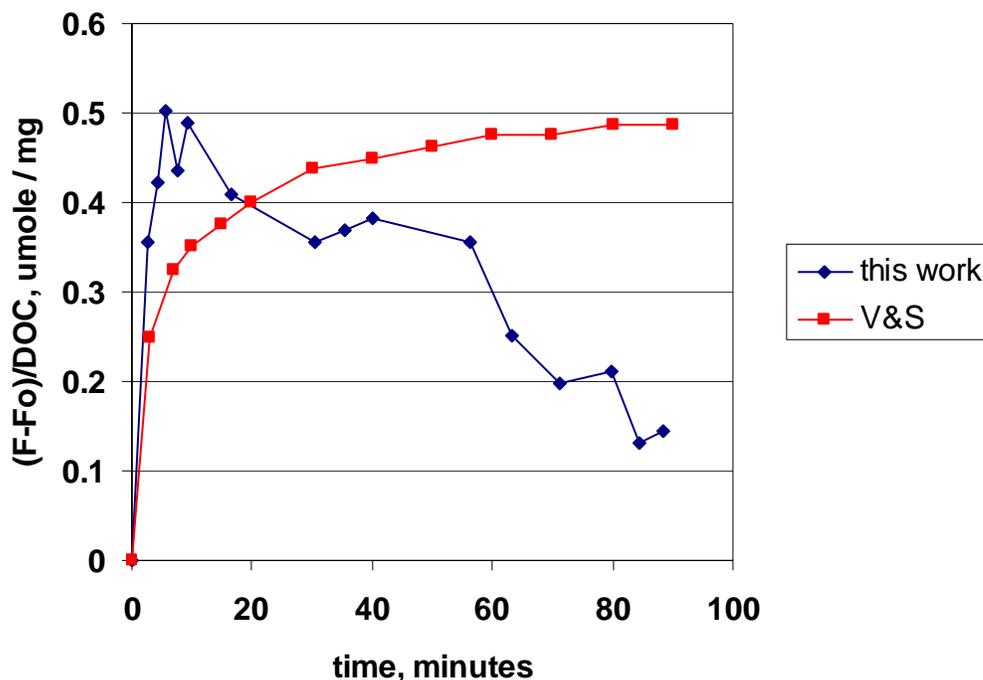


Figure 10. Reduction of Fe(III) to Fe(II) by Danvers groundwater. V&S data is from Voelker and Sulzberger (1996)

For some samples, the Fe(II) appeared to increase upon standing. Voelker and Sulzberger (1996) previously reported the reduction of Fe(III) by surface water NOM under oxic conditions. It is reasonable to assume that NOM from an anoxic water might also be a strong reductant. To test this hypothesis, a 250-mL septum bottle of anoxic Danvers groundwater was spiked with a nitrogen-sparged (45 minutes) solution of ferric nitrate to add an Fe(III) concentration of 39 μM , and the Fe(II) concentration measured periodically over a period of 1 hour. The data, along with those of Voelker and Sulzberger (1996), are plotted in Figure 10 as the change in Fe(II) divided by the DOC of the water. Approximately 30 % of the Fe(III) was converted to Fe(II) before the concentration leveled off and began to drop, due to some reaction that consumed Fe(II) in competition with its production. The slow oxidation responsible for the Fe(II) decrease could be due to trace quantities of oxygen entering the system or slow reaction of Fe(II) with some oxidative component of, or formed from, the NOM. The timescale and yield of the Fe(III) reduction (Fe(II) production) are similar to those observed by Voelker and Sulzberger (1996). Maximum formation of Fe(II) was at 5.7 minutes in this experiment. The implication is that some regeneration of Fe(II) may take place on the timescale of the treatment reactions if the water is kept anoxic. Despite the agreement of these results with the findings of Voelker and Sulzberger, other explanations for Fe(III) reduction are also possible.

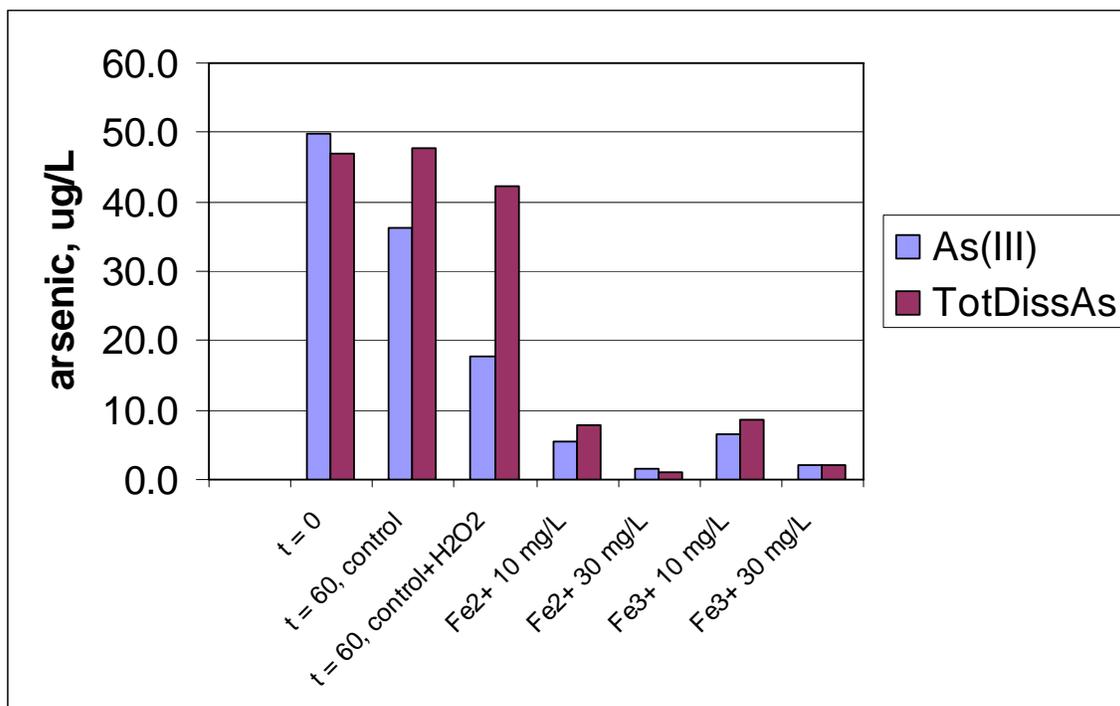


Figure 11. Effect of additional iron on arsenic removal. H₂O₂ dose 20 μ M. Control had no Fe or H₂O₂. TotDissAs is total dissolved arsenic.

Up to this point in the project, good oxidation of As(III) to As(V) had been demonstrated, but removal of dissolved arsenic was disappointing. Current water treatment practice, as well as a recent paper by Roberts, et al. (2004), suggested that there was not enough iron present in the groundwater to provide sufficient sorption sites for the arsenic in competition with other substances such as bicarbonate, silicate, and phosphate in the groundwater. Therefore, a series of experiments was performed to determine the effect of added iron on arsenic removal. Septum bottles of anoxic Danvers groundwater were spiked with 20 μ M hydrogen peroxide and allowed to react for 15 minutes, then poured into beakers and aerated for 5 minutes, spiked with Fe(II) or Fe(III), and allowed to stir for 1 hour before being filtered prior to As(III) and total dissolved arsenic determinations.

The results are shown in Figure 11 which shows from left to right, arsenic present in the samples: initially; after stirring in air for 60 minutes with no added peroxide or iron; after stirring in air with added peroxide but no iron; and with addition of peroxide with 10 or 30 mg/L of Fe(II) or Fe(III), respectively. Some arsenic (III) is oxidized simply by stirring in air, as in the treatment plant, and more than half of the arsenic (III) is removed by the addition of 20 μ M of peroxide before stirring. However, addition of 10 or 30 mg/L of iron promotes removal of 83 and 97% of the total dissolved arsenic, respectively, regardless (\pm 1%) of whether Fe(II) or Fe(III) is used.

The following conclusions were drawn from the preliminary experiments. Near-complete oxidation of As(III) to As(V) is possible with reasonable peroxide doses. The peroxide should be added while the sample is still anoxic. Additional iron is required for total As

removal. There does not appear to be much difference between results obtained with Fe(II) and Fe(III) addition. NOM can reduce Fe(III) to Fe(II) in Danvers anoxic groundwater. Photoregeneration of Fe(II) from Fe(III) appears to be feasible and may be useful in some situations. Iron oxidation by air is faster in Danvers groundwater than in DI water with similar bicarbonate alkalinity added and at the same pH. The first four conclusions were used, along with parameters (residence times, etc.) from the Danvers plant to design the configuration for the laboratory flow system.

Laboratory Flow Experiments

Based on the results from the preliminary experiments, the laboratory flow system (Figure 2) was assembled and used to verify conclusions from the preliminary experiments, and to determine appropriate conditions for the pilot-scale experiments. The experimental results for arsenic removal under various conditions are summarized in Figure 12, which shows the total (unfiltered) As concentrations in samples from sampling point S5, the effluent from the sand filter, as a function of added iron. It was felt that this would simulate the operation of a water treatment plant better than 0.2 μm -filtered samples. Points shown as open circles correspond to a 26 μM hydrogen peroxide dose with various Fe(III) doses. Within the range tested, which spans the MCL for arsenic, increasing iron

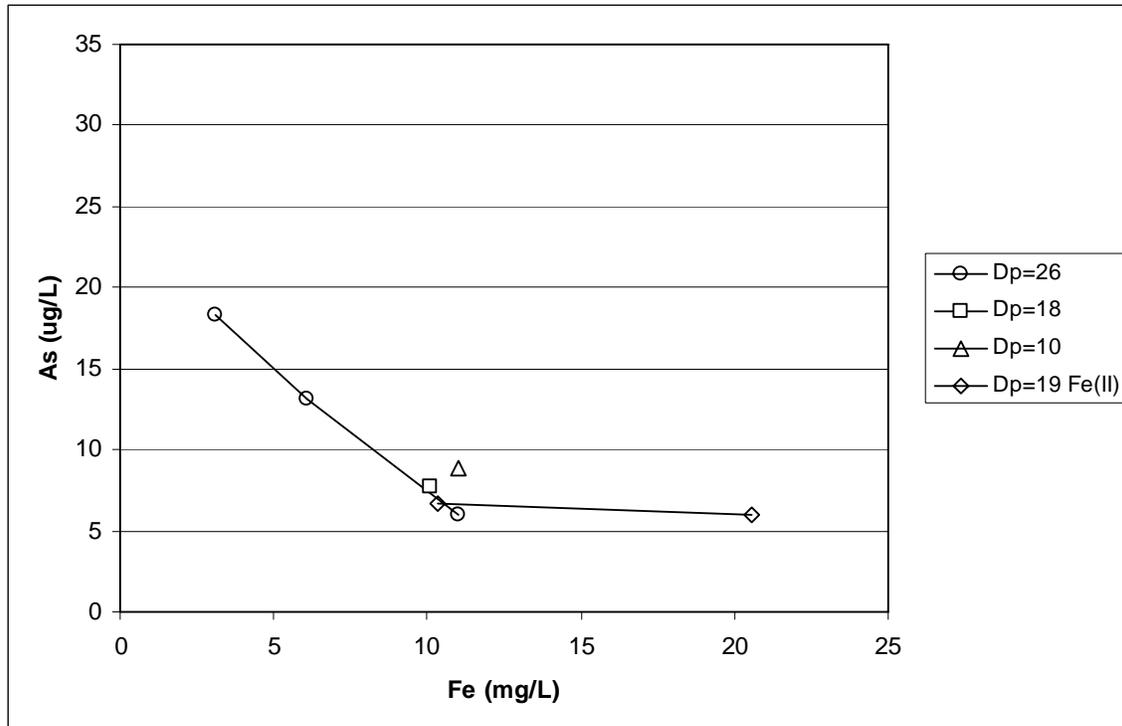


Figure 12. Total arsenic remaining after various treatments in laboratory flow experiments. Numbers in legend show H_2O_2 doses. The iron dose added (beyond the natural content) is plotted on the x-axis.

addition strongly promotes additional arsenic removal. At about 10 mg/L of added iron, lowering the peroxide dose to 18 and 10 μM results in slightly less arsenic removal. Use of 10 mg/L of Fe(II) (diamond symbols) instead of Fe(III) does not make much difference, and at about 20 mg/L Fe(II), arsenic removal looks to be the same or slightly less than it would have been with Fe(III).

From the general shape of the curves, it appears that a small iron addition has a strong effect on arsenic removal, as a result of providing additional sites for arsenic sorption. Beyond about 10 mg/L, however, little is gained by addition of greater amounts of iron. It is not known whether 30 mg/L of Fe(III) would have improved removal, since that experiment was not run, in favor of obtaining more points around the break point in the curve, as well as moving on to the pilot studies.

Thus the laboratory flow data appears to confirm most of the trends seen in the batch data described above, and indicate addition of 4 to 12 mg/L Fe as the range of interest.

On-Site Pilot-Scale Flow Experiments

Based on the flow results from the lab-scale apparatus, several pilot-scale experiments were performed, using various peroxide and iron dosages. The longest single series of experiments was performed at a peroxide dose of about 27 μM and various Fe(III)

concentrations. The filled diamonds in Figure 13, show total (unfiltered) arsenic in samples from sampling point S4, the effluent from the sand filter, versus the added concentration of iron. As for the laboratory flow experiments, it was felt that unfiltered samples simulated the operation of a water treatment plant better than filtered samples. Increasing the added iron dose causes a dramatic drop in the total arsenic concentration of the treated water up until about 5 mg/L iron added. Beyond that point, additional iron causes minimal improvement of arsenic removal, presumably because the needed additional sorption sites on HFO have been supplied. Indeed, the raw groundwater contains about 2 mg/L of iron and removes about one-fourth of the total arsenic, so an additional 4-5 mg/L should provide sufficient adsorption sites, assuming a constant ratio of HFO to adsorbed As. Extrapolation of the initial slope of the curve for $D_p=27 \mu\text{M}$ gives an x-intercept of 4-5 mg/L. (D_p is the peroxide dose.)

The second series of experiments were run with no peroxide added, to show the extent of removal that could be achieved using iron alone. This curve, shown with filled square symbols, approaches or crosses the $D_p=27 \mu\text{M}$ curve at low iron doses, and probably also at iron doses greater than about 15 mg/L. However, in the critical region between $D_i=3-13 \text{ mg/L}$ (D_i is the added iron dose), the curve demonstrates that considerable iron (3-4 mg/L) can be saved by the addition of $27 \mu\text{M}$ (0.9 mg/L) of peroxide. This represents a significant cost savings for chemicals, as described in a later section on treatment costs, and would lower the required number of backwashes by about 1/3.

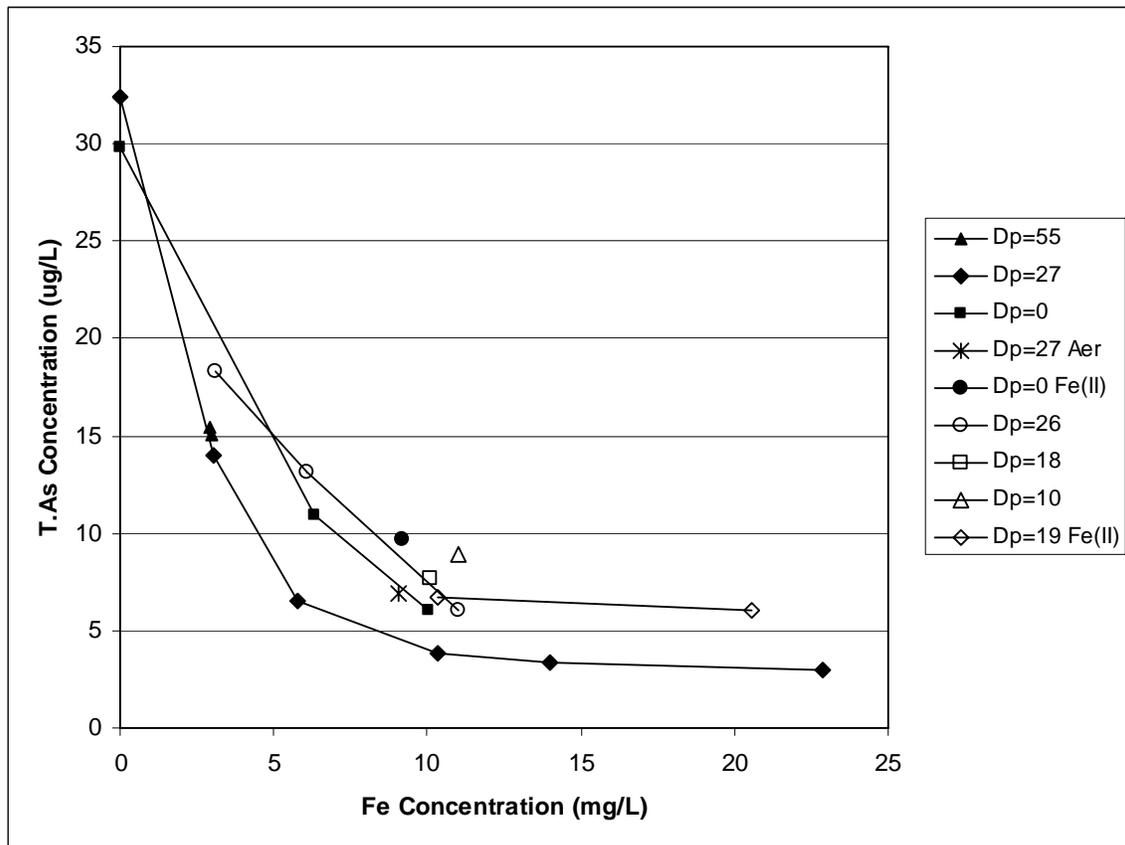


Figure 13. Arsenic remaining as a function of added iron concentration. Numbers in legend show peroxide doses.

One experiment was run using ferrous sulfate rather than ferric chloride to supply the iron, with no peroxide addition. Intuitively, it would seem that Fe(II) should perform better than Fe(III), since it has been stated to be the limiting reactant and would add oxidative power to the system. In addition, Hug and Leupin (2003) and Roberts et al. (Roberts, Hug et al. 2004) saw better performance when using Fe(II) to produce HFO, instead of Fe(III). However, as in the laboratory experiments, the single point for the Fe(II) experiment lies above the corresponding line for Fe(III) use. The reason for this is not currently known, but it may be related to the fact that Danvers water has a high DOC content (13 mg/L) while no DOC was present in the synthetic groundwater used by the previous investigators.

One experiment was performed with the addition of peroxide ($D_p=27 \mu\text{M}$) to the aerator, (Aer) rather than to the head of the process. This simulates adding the peroxide to the aerator in the Danvers plant through the existing chemical feed line located just after the perforated plate aerator and before the flocculation basin for the sand filter. When plotted, the arsenic removal point for this experiment fell on the line made by the points for experiments in which no peroxide was added. This is consistent with the assumption that peroxide was ineffective because there was insufficient Fe(II) left in the aerator to react with the peroxide, and confirms the need to add the peroxide before aeration.

An experiment was performed to determine whether additional arsenic removal could be obtained by using a higher peroxide dose ($D_p = 55 \mu\text{M}$). The point for this experiment fell on the line for $D_p=27 \mu\text{M}$. To be sure that this result was correct, the experiment was rerun one week later. The point for the second experiment plots over the first, confirming that higher peroxide dose does not gain additional arsenic removal, and also indicating the reproducibility of the experiment.

Information about treatment can also be gained from other data that were collected. The primary purpose of adding hydrogen peroxide is to initiate the chemical reactions that oxidize As(III) to As(V). A plot of As(III) measured at sampling point S2 (after peroxide addition and 1.5 minutes detention time in the plug flow reactor) versus the amount of peroxide added (D_p) is shown in Figure 14, where it can be seen that there is a linear correlation between arsenic oxidation and peroxide added. The notable exception is the one experiment in which the peroxide was added to the aeration basin, which is downstream of the S2 sampling point. This plot verifies that peroxide is doing what was intended with good consistency.

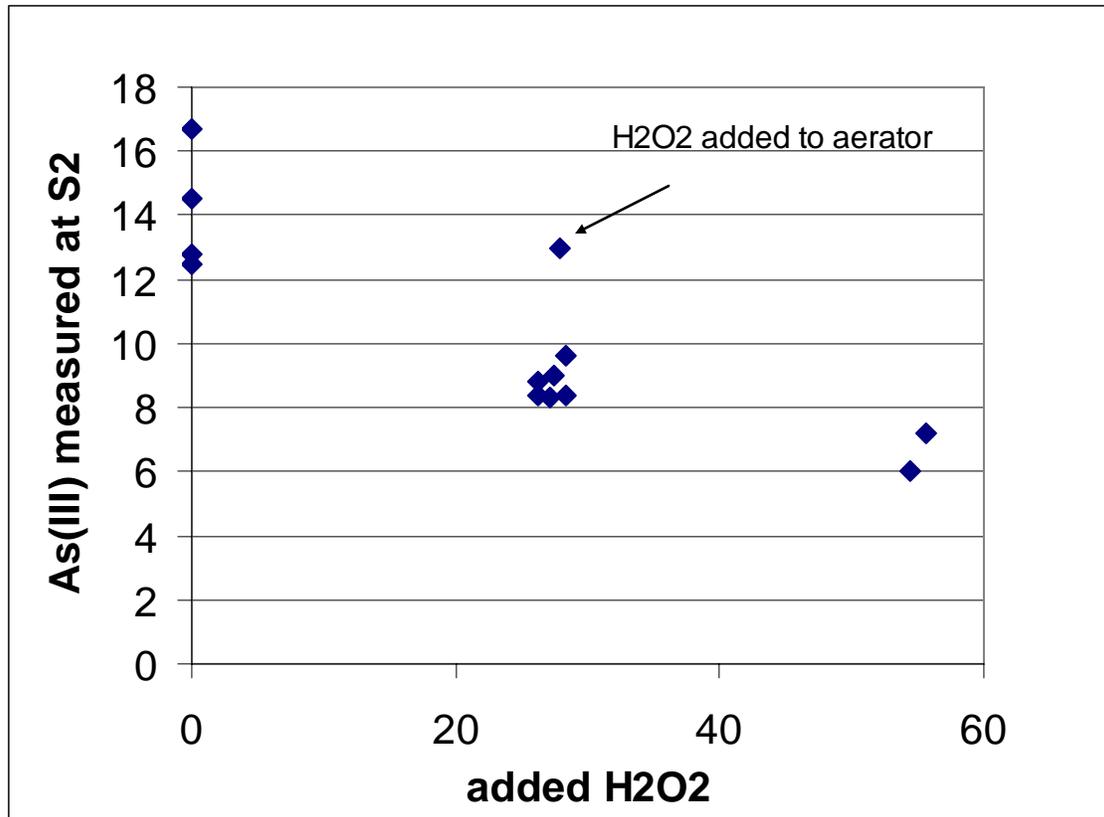


Figure 14. Effect of added hydrogen peroxide on As(III) measured at sampling point S₂.

Figure 15 shows the same plot for As(III) concentrations in final effluent samples taken from S₄. There may be a weak correlation, but it is clear that other factors are also important. In this plot, the experiment in which peroxide was added to the aerator does not stand out as unique. The upper edge of the concentration range of the S₄ samples starts at about the lower edge of the S₂ samples, so significant As(III) oxidation was still occurring between S₂ and S₄. Calculated reaction rates of hydrogen peroxide with Fe(II) species imply that reaction should be over very quickly, with a four half-life period (94% consumption of H₂O₂) on the order of eleven seconds (see Appendix B), indicating that the 90-second residence time in the plug flow reactor should be adequate. This observation could therefore imply that some longer-lived active species may be present, such as more-stable radicals resulting from radical oxidation of NOM. However, it is also likely that removal of arsenic between S₂ and S₄ includes some adsorption of As(III) to

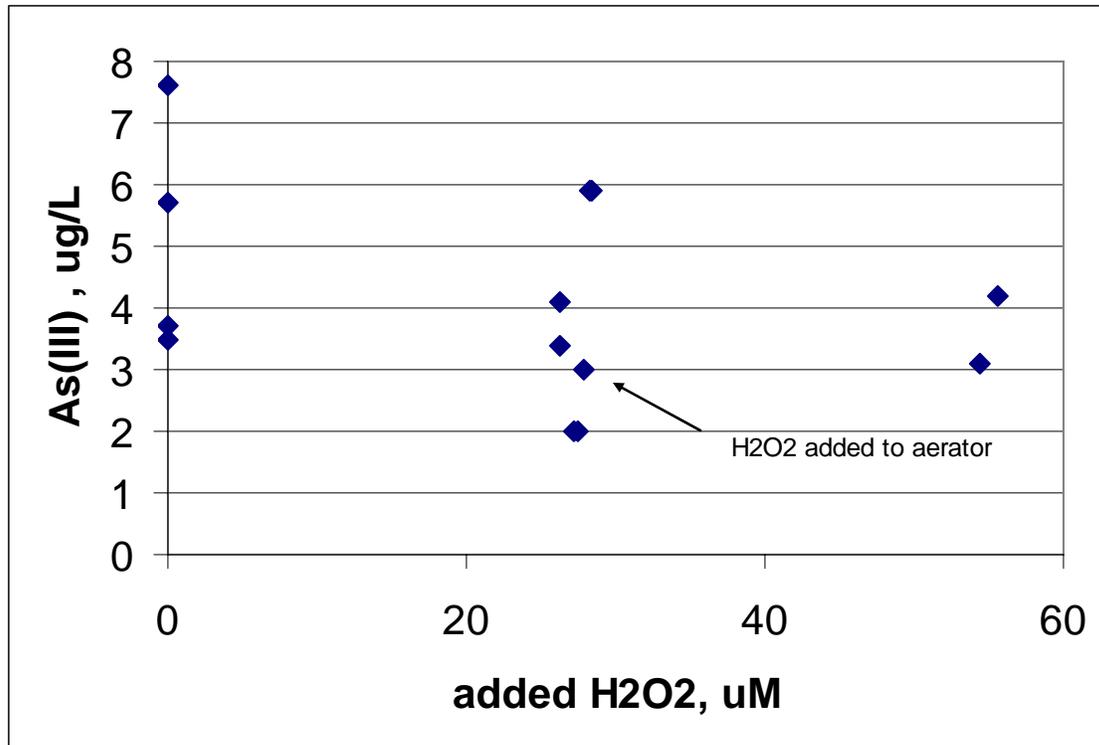


Figure 15. Effect of added hydrogen peroxide on As(III) measured at sampling point S₄.

the HFO, and perhaps even some further oxidation as the As(III) in the exiting water comes in intimate contact with HFO and sorbed species in the sand filter, where diffusion is less of an issue for reaction or sorption rate than in bulk solution.

The As(III) concentrations in S₄ samples generally decreased as the added Fe dose increased (Figure 16). The dependence of As(III) on added iron seems to imply that much of this As(III) is lost by sorption to HFO, or at least by some sort of chemistry that relies on Fe(III).

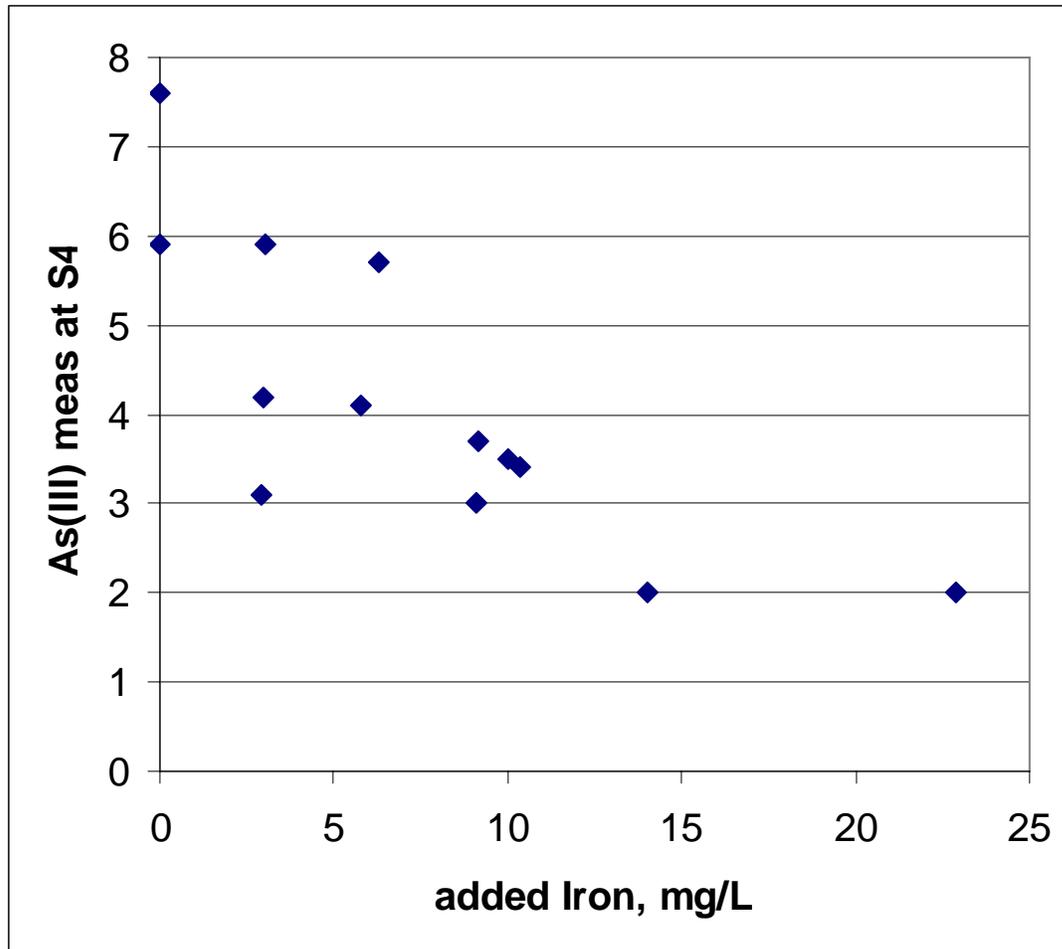


Figure 16. Effect of added iron on As(III) measured at S₄ (μg/L)

The total arsenic concentrations in S₄ samples were independent of the peroxide dose (Figure 17). However, for each peroxide dose, the remaining arsenic decreases with iron dose. The numbers beside the symbols are the added iron doses. This is a general correlation over all sets, rather than for just one set at a time, as was seen in Figure 13. This dependence on Fe dose is consistent with As removal by adsorption to HFO.

Adsorption modeling was carried out for comparison with actual arsenic removal data. The adsorption model included aqueous speciation and competition between As(V), As(III), PO₄³⁻, CO₃²⁻, and SiO₂, for HFO adsorption sites (Appendix C). The results are shown in Figure 18, organized into various test groups, as indicated by the legend. Dp indicates the hydrogen peroxide dose in μM, Aer indicates the peroxide was added to the aerator instead of at the head of the treatment train, Fe(II) means that the iron dose was added as Fe(II) rather than Fe(III), and Ads 70% and Ads 100% indicate that in the sorption calculation 70% and 100% of the arsenic was assumed to be As(V). The experimental range of this value for all of the experiments was 82 to 52% As(V), but was significantly different for the various test groups, with 80±3, 74±5, 68, 61±5, and 52% of the arsenic in the As(V) form for Dp=55, 27, 27 Aer, 0, and 0 Fe(II), respectively.

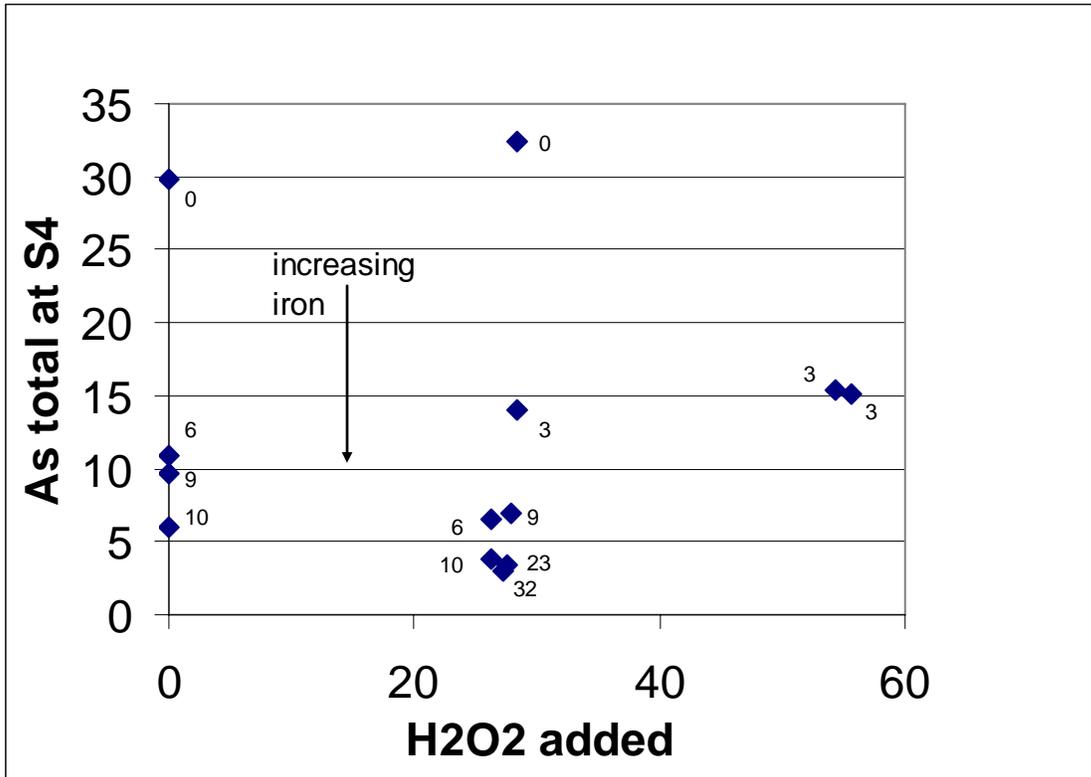


Figure 17. Dependence of total arsenic concentration on hydrogen peroxide dose. The numbers beside the symbols are the added Fe doses (mg/L).

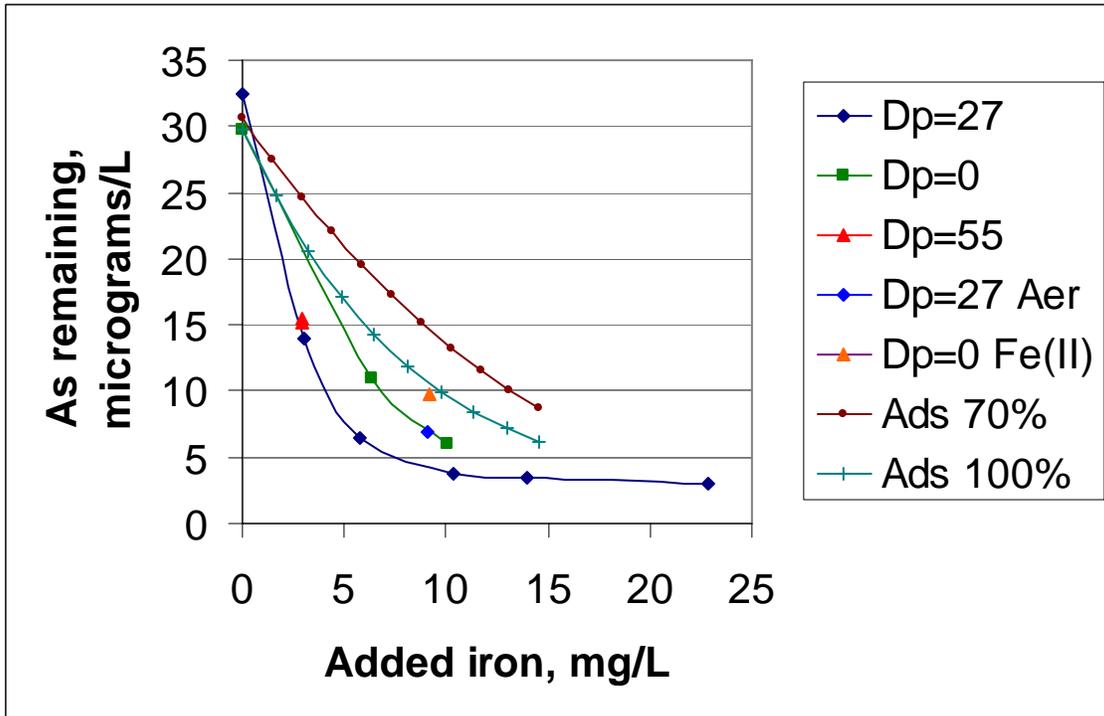


Figure 18. Comparison of adsorption modeling results with pilot-scale data. D_p is the peroxide dose (μM), Ads 70% and 100% are calculated adsorption results (see text).

The adsorption model and the experimental data agree quite well for no added Fe (~ 2 mg/L in the groundwater). The degree of arsenic adsorption was greater for 100% As(V) than for 70% As(V)/30% As(III). This is consistent with greater arsenic removal for $\text{H}_2\text{O}_2 + \text{FeCl}_3$ than for FeCl_3 alone. The model predicted increasing arsenic adsorption with increasing FeCl_3 dose which is also consistent with the data. However, the model under-predicted the rate of decrease in As with added Fe. This may have been due to the NOM. Although NOM sorbs to HFO (Gu, Schmitt et al. 1994), this reaction has not been incorporated in adsorption models. Nevertheless, it is significant that the trend is the same between the calculated and experimental values. Roberts et al. (Roberts, Hug et al. 2004) developed a model of As(III) and As(V) adsorption to HFP and fit their model to their data with close agreement. However, neither their experiments nor their model included NOM.

Treatment Cost Estimates

Treatment cost estimates were made for the chemical cost portion of the operating cost. Comments on the other costs are made on the basis of this treatment being an upgrade to an existing treatment plant that is already removing iron, which would be true for most of the plants in Illinois that have an arsenic problem in their groundwater. The chemical cost calculation is based on an iron dose of 6 mg/L and a hydrogen peroxide dose of 27 μM (0.9 mg/L), using current chemical costs from a local chemical supplier, of \$108/barrel for 32-45% ferric chloride solution (assuming 38.5% leads to approximately 254 lb of FeCl_3 or \$0.43/lb) and \$167/500 lb of 35% hydrogen peroxide (approximately \$1/lb of H_2O_2)

For the iron dose:

$$\frac{6 \text{ mg Fe}}{\text{L}} \times \frac{1 \text{ lb Fe}}{454 \times 10^3 \text{ mg Fe}} \times \frac{161.8 \text{ lb FeCl}_3}{55.9 \text{ lb Fe}} \times \frac{\$108}{254 \text{ lb FeCl}_3} \times \frac{3.8 \times 10^3 \text{ L}}{\text{kgal}} = \frac{\$0.062}{\text{kgal}}$$

For the peroxide dose:

$$\frac{25 \times 10^{-6} \text{ mole H}_2\text{O}_2}{\text{L}} \times \frac{34 \text{ g H}_2\text{O}_2}{1 \text{ mole H}_2\text{O}_2} \times \frac{1 \text{ lb H}_2\text{O}_2}{454 \text{ g H}_2\text{O}_2} \times \frac{\$1}{\text{lb H}_2\text{O}_2} \times \frac{3.8 \times 10^3 \text{ L}}{\text{kgal}} = \frac{\$0.007}{\text{kgal}}$$

or less than \$0.07/kgal for both. Implementing this process in addition to iron removal may require additional backwashing of the sand filter, because of the additional iron that is added to the water. However, the use of 0.9 mg/L of peroxide reduced the iron dose required by 3-4 mg/L over that required when no peroxide was used, which represents a chemical cost savings of about 30% (about \$0.029/kgal) compared to not using peroxide, and could reduce the backwash frequency by about the same percentage. In addition, no

large capital equipment costs are required to implement this process. Only two chemical metering pumps and two tanks would be required.

CONCLUSIONS

- The combination of low hydrogen peroxide doses followed by ferric chloride addition was capable of oxidizing most of the arsenic (III) to arsenic (V) in Danvers, Illinois groundwater, and reducing total arsenic from about 40 $\mu\text{g/L}$ to less than 5 $\mu\text{g/L}$ in batch, laboratory flow, and pilot-scale flow experiments.
- The estimated chemical costs for treatment totaled about \$0.07/thousand gallons. Equipment required to update the existing plant would be two pumps and two tanks.
- In pilot-scale experiments, the residual As concentration was well below the MCL (10 $\mu\text{g/L}$) with an added Fe dose of 6 mg/L and a hydrogen peroxide dose of 0.9mg/L.
- Arsenic removal is more efficient when peroxide is added to the anoxic groundwater rather than aerating first.
- Aeration oxidizes less than 25% of the As(III) in groundwater to As(V) for a reaction time of 30 minutes. This is typical of the residence time in an aeration/sand filtration unit and is representative of present performance of the Danvers plant.
- Hydrogen peroxide added to anoxic groundwater oxidizes over 50% of the As(III) in less than one minute. On the other hand, H_2O_2 added to aerated (oxic) groundwater oxidizes less than 9% in the same time. The likely explanation is that in anoxic groundwater the Fenton reaction produces hydroxyl radical and/or other reactive species which rapidly oxidize the As(III), whereas there is very little Fenton reaction in oxic water after most of the Fe(II) has been consumed.
- The degree of As(III) oxidation is roughly proportional to the H_2O_2 dose, which is much higher than the As(III) concentration. The likely reason is that most of the hydroxyl radical reacts with dissolved organic matter and only a small fraction reacts with As(III).
- After oxidation and filtration of the groundwater with no iron addition, over 70% of the original As is still dissolved. Adding increasing amounts of FeCl_3 results in progressively lower dissolved As concentrations, with 11% (6.5 $\mu\text{g/L}$) remaining after an iron dose of 5.8 mg/L, and 7% (3 $\mu\text{g/L}$) remaining after an iron dose of 23 mg/L. The likely explanation is that the As has to compete with other dissolved substances for the HFO adsorbent. Increasing the amount of HFO increases the adsorption capacity.
- The dependence of As adsorption/removal in the pilot-scale experiments was consistent with a chemical equilibrium model of As adsorption.

FUTURE WORK

There are two areas that need considerable further work. The first is an empirical study of the effectiveness of this process in groundwaters of various composition, to evaluate the general utility of the process for inexpensive arsenic removal, and to provide treatment guidelines. A follow-on project has been funded to investigate this question, by performing pilot-scale experiments at various water treatment plants in Illinois. The second need is to better determine the chemical pathways that most contribute to arsenic oxidation, in order to better optimize the process. Preliminary investigations indicate that there is a mechanistically-rich reaction system, including chain reactions and oxygen-dependent branching points, that may be amenable to considerable manipulation. The fact that the system is chemically complicated does not mean that such optimization can only be achieved using high-tech treatment to yield an efficiency improvement, as demonstrated in the present project.

ACKNOWLEDGEMENTS

The authors thank Mr.Scott Seniff, Director of Public Works, Village of Danvers, for allowing access to the well head and treatment facilities, and Dr. Timothy Strathmann for many helpful discussions. This research was supported by the Midwest Technology Assistance Center for Small Public Water Systems.

APPENDIX A ARSENIC CHEMISTRY

Speciation

Arsenic in groundwater occurs almost entirely in the +3 and +5 oxidation states as oxoacids and their conjugate bases. The methylated species monomethylarsonic acid and dimethylarsinic acid are usually either undetectable or comprise a small fraction of dissolved arsenic (<1%) (Irgolic 1982; Chatterjee, Das et al. 1995; Shraim, Sekaran et al. 2002).

Arsenic in the +3 oxidation state occurs as arsenious acid (H_3AsO_3) and its conjugate base H_2AsO_3^- . The sum of concentrations of H_3AsO_3 and H_2AsO_3^- is denoted As(III). The first pK_a of H_3AsO_3 is 9.29 (Martell and Smith 1974) so in the pH range of most groundwater H_3AsO_3 predominates (Figure A1).

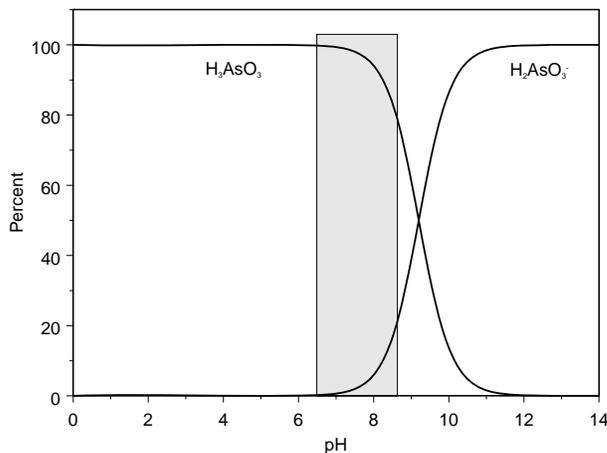


Figure A1. Concentrations of As(III) species as functions of pH. The shaded area is the pH range of most groundwaters.

Arsenic in the +5 oxidation state occurs as the conjugate bases of arsenic acid (H_3AsO_4), which has three pK_a values that are similar to those of phosphoric acid (2.24, 6.96, 11.50) (Martell and Smith 1974). The sum of concentrations of H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} is denoted As(V). In the pH range of most groundwater the predominant As(V) species are H_2AsO_4^- and HAsO_4^{2-} (Figure A2).

In water treatment operations the system is undersaturated with known As-containing minerals, such as $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$. Therefore, the most likely control on As solubility is adsorption to the HFO produced by oxidizing Fe^{2+} .

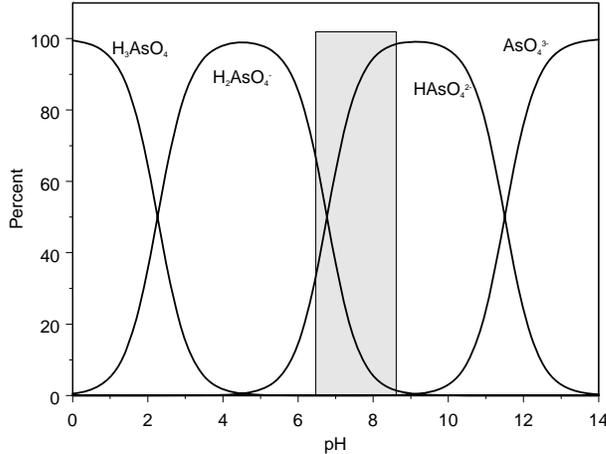


Figure A2. Concentrations of As(V) species as functions of pH. The shaded area is the pH range of most groundwaters.

Arsenic Adsorption

Arsenic removal at an iron-removal plant is the result of adsorption of As(III) and As(V) to the freshly precipitated hydrous ferric oxide (HFO). Adsorption is the specific binding of a solute to a solid surface. It is unlike organic partitioning, which is non-specific and depends on a compound's hydrophilic/hydrophobic character. HFO particles have charged surfaces with the sign and magnitude of the charge dependent on the pH (Stumm and Morgan 1996). If the ion and surface charge both have the same sign, the electrostatic attraction will favor adsorption but if the ion and surface have opposite charges the electrostatic repulsion will oppose adsorption. However, an ion can adsorb to a surface with the same charge. Therefore, adsorption is also unlike ion exchange, which is mostly electrostatic. Besides electrostatic interactions, adsorption involves the formation of a chemical bond. An ion can adsorb to a surface even though the system is undersaturated with known salts of the ion. As a result, the concentration of the ion can be reduced to a very low level.

Arsenic(V) adsorption to HFO proceeds through two phases. The rapid initial phase is complete within minutes, while the second phase takes up to three days (Fuller, Davis et al. 1993). However, the dissolved As(V) concentration in As(V)/HFO coprecipitation experiments was found to be essentially the same after 10 minutes and 24 hours (Holm 2002). Therefore, since the hydraulic residence time in an iron-removal water treatment plant is on the order of minutes and is much shorter than 24 hours, it is safe to assume that the reaction reaches "pseudoequilibrium" and use the tools of thermodynamics (mass action and mass balance equations) to solve for the dissolved concentrations of As(III) and As(V).

Two types of experiments have been performed to characterize arsenic adsorption. In one type the amount of adsorbent (HFO) and the pH are held constant and the total (dissolved plus adsorbed) concentration of As(III) or As(V) is varied. A plot of the adsorbed

concentration as a function of the dissolved concentration is commonly called an adsorption isotherm. In the other type of experiment the total amounts of HFO and arsenic are held constant and the pH is varied. A plot of the degree of adsorption (usually the percent) vs pH is commonly called an adsorption edge.

Arsenic(V) is strongly adsorbed to HFO as shown by the adsorption isotherm for an Fe concentration and pH value that are typical of the Mahomet Aquifer in central Illinois (Figure A3). The concentration of adsorbed As(V) increases rapidly for low dissolved As(V) concentrations. For total As(V) concentrations up to $\sim 100 \mu\text{g/L}$ essentially all of the As(V) is adsorbed. A Langmuir isotherm fits the data, which is consistent with surface complex formation (Stumm and Morgan 1996).

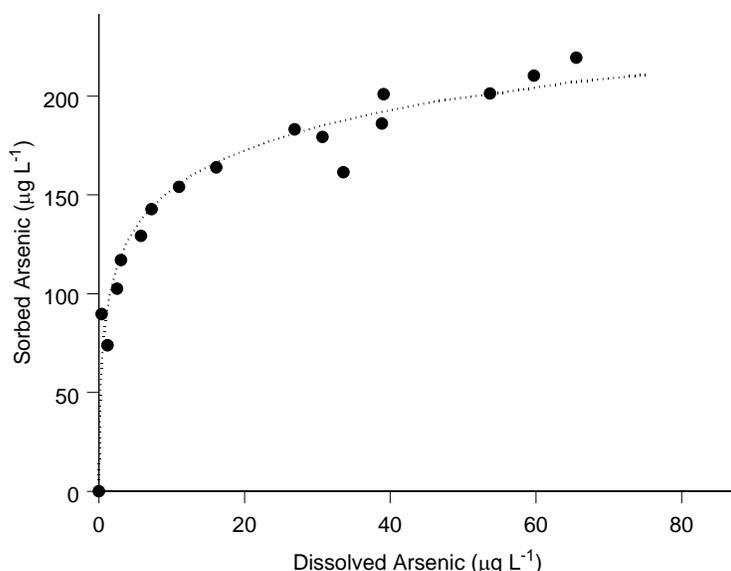


Figure A3. Adsorption isotherm for As(V), 1.4 mg/L Fe, pH 7. The dotted line is a Langmuir isotherm (Holm 2002).

The variation of As(V) adsorption with pH (adsorption edge) is typical of that of oxyanions (Figure A4). At low pH values adsorption is near 100%. Above pH ~ 8 the adsorbed fraction decreases as the pH increases. The HFO surface has no net charge at pH ~ 8 and becomes increasingly negatively charged at higher pH values (Dzombak and Morel 1990). Arsenic(V) adsorption decreases at high pH values because of the repulsion between the H_2AsO_4^- and HAsO_4^{2-} anions and the negatively charged HFO surface. The pH at which adsorption starts to decrease is higher for the higher HFO concentration. In this system, which contains only As(V) and Fe at concentrations typical of the untreated water at the Danvers plant (Holm 2004), As removal is over 90% in the pH range of the untreated water. In a system with a lower Fe:As ratio, As removal may be less than 100% at all pH values.

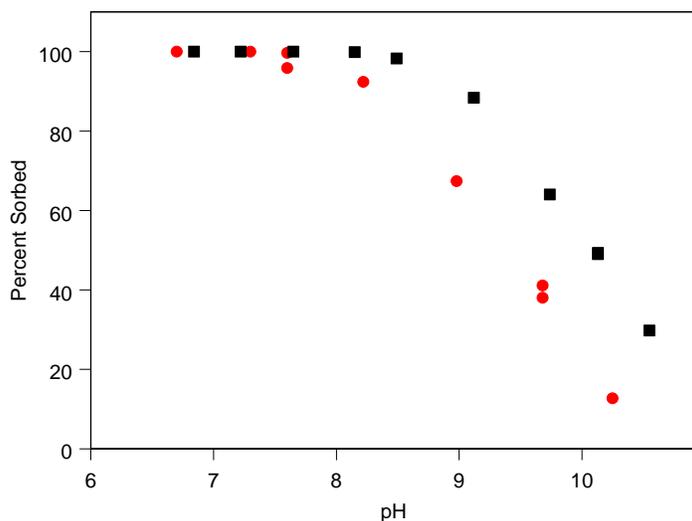


Figure A4. Adsorption of As(V) to hydrous ferric oxide. The Fe(III) concentrations are 1.4 mg/L (circles) and 5.2 mg/L (squares). The As(V) concentration is 38 µg/L for all points (Holm 2002).

In contrast to As(V), As(III) adsorption to HFO has a broad maximum for near-neutral pH values and decreases somewhat at both high and low pH values (Figure A5). Unlike As(V), which is anionic, As(III) is largely in the neutral H_3AsO_3 form for $pH < 9$, so there is no repulsion from the negatively charged surface at high pH values. For relatively low As(III) concentrations the adsorption maxima are near 100% but for the high As(III) concentrations the maxima are less than 100%.

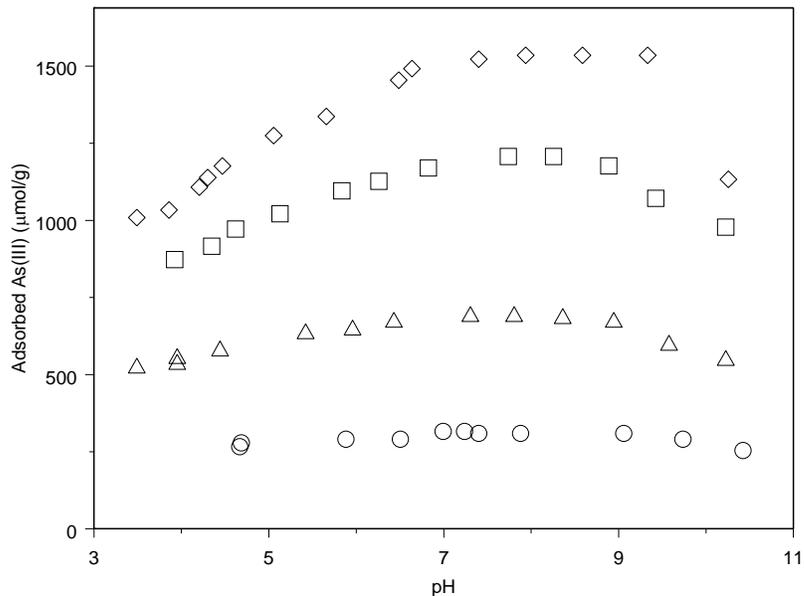


Figure A5. Adsorption of As(III) to ferrihydrite. Arsenic(III) concentrations are 100 (diamonds), 50 (squares), 25 (triangles), and 10 µM (circles). The Fe concentration for all points is 30 mg/L (After Dixit and Hering 2003).

Figure A6 compares As(V) and As(III) adsorption to HFO. For low pH values As(V) is more completely adsorbed than As(III) whereas for high pH values As(III) is more completely adsorbed. The crossover point is ~pH 6.4 for 100 µM As (7,500 µg/L) and shifts to ~6.5 for 50 µM. The crossover point may be different for the lower Fe (1-5 mg/L) and As (10-100 µg/L) concentrations in Illinois water treatment plants. Although the As oxidation state clearly affects As adsorption, other factors must also be considered. Nevertheless, As(V) is not always more strongly adsorbed than As(III) as is commonly believed.

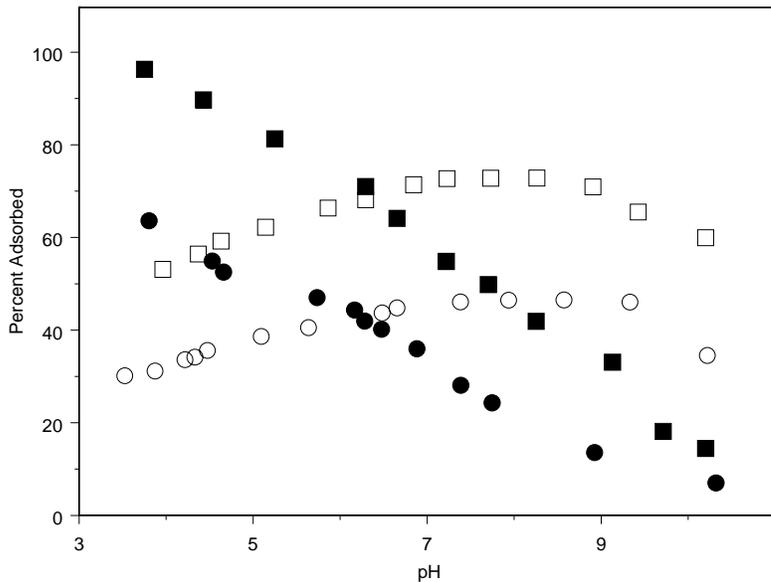


Figure A6. Comparison of As(V) and As(III) adsorption to ferrihydrite. Squares 50 μM total As, circles 100 μM , open symbols As(III), closed symbols As(V). Fe(III) concentration for all points is 30 mg L^{-1} (After Dixit and Hering 2003).

Adsorption of Other Common Solutes and Its Effect on Arsenic Adsorption

Several substances that are commonly found in groundwater adsorb to HFO and may compete with As(V) or As(III) for adsorption sites. As a result, arsenic removal may be reduced. Phosphate, like As(V), strongly adsorbs to HFO (Dzombak and Morel 1990). The degree of As(V) adsorption from a solution containing 133 μM As(V) ($\sim 10,000 \mu\text{g/L}$ As) and phosphate ($\sim 4.1 \text{ mg/L P}$, 133 μM) was significantly less than from a solution containing only As(V) (Manning and Goldberg 1996). For As(V), P, and Fe concentrations typical of the Mahomet Aquifer, P also reduced As(V) adsorption (Figure A7). Phosphate competition may affect As(III) and As(V) differently, especially for $6.5 < \text{pH} < 8.5$, the pH range of most groundwater (Figure A8). Phosphate competition drastically reduces As(III) adsorption for low pH values and the crossover pH changes from ~ 9 for no phosphate to ~ 8 for 0.1 mM P.

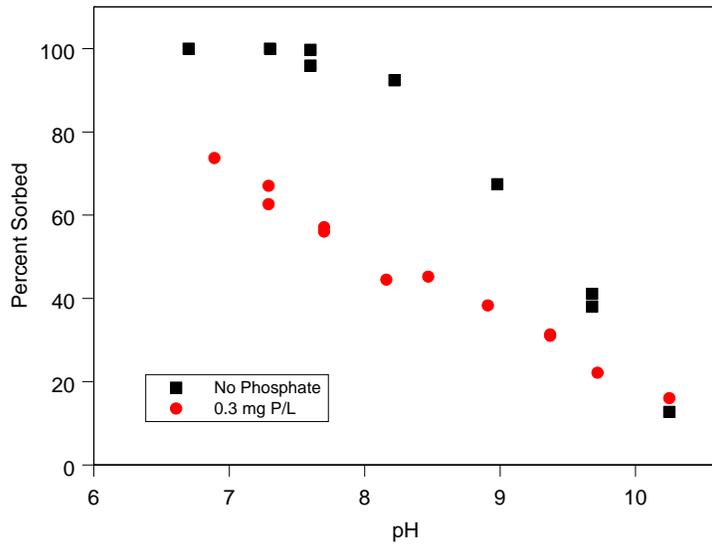


Figure B1. Effect of phosphate on As(V) adsorption to hydrous ferric oxide, As(V) 38 $\mu\text{g/L}$, Fe 1.4 mg/L (Holm 2002).

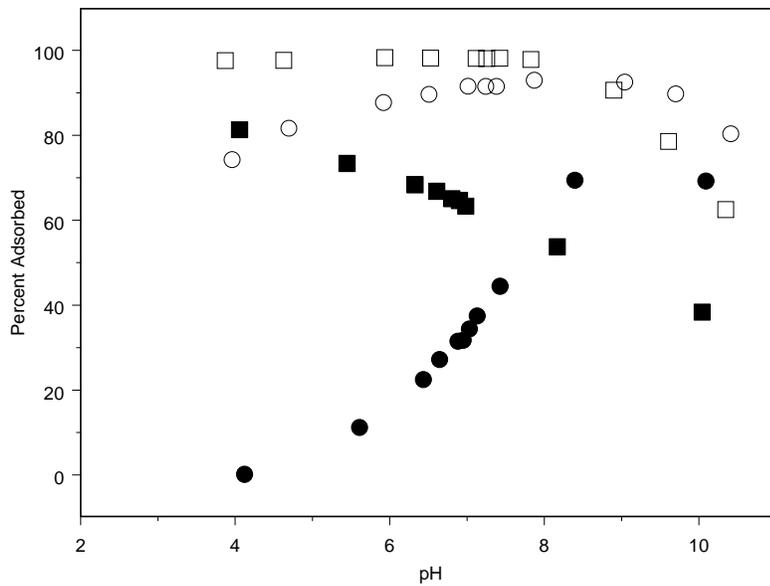


Figure A8. Adsorption of As(III) and As(V) to ferrihydrite in the presence and absence of phosphate. Filled symbols 100 μM phosphate (3.1 mg/L), open symbols no phosphate, squares 10 μM As(V) (750 $\mu\text{g/L}$), circles 10 μM As(III) (After Dixit and Hering 2003).

Silica sorbs to HFO and, although it is not as strongly adsorbed as As(V), it is present in groundwater at ~100 times the As concentration. Therefore it may affect As(V) adsorption to HFO (Swedlund and Webster 1999; Meng, Bang et al. 2000; Holm 2002). For As, Fe, and Si concentrations typical of Illinois Groundwater As(V) adsorption is significantly lower in the presence of silica than in its absence (Figure A9).

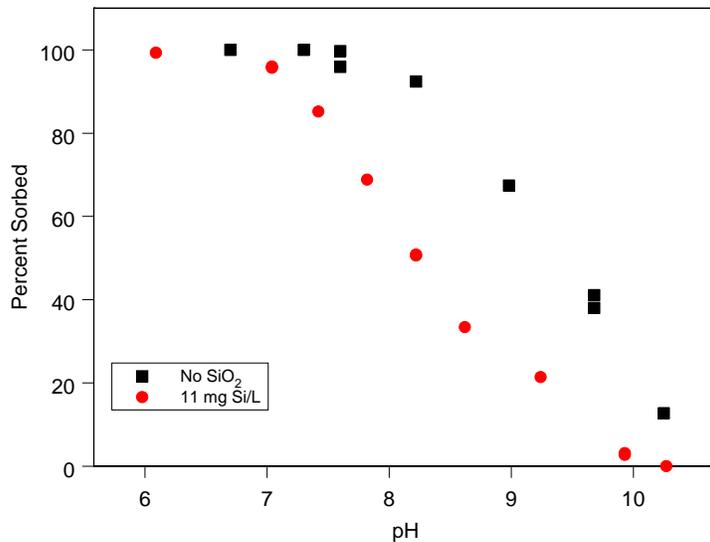


Figure A9. Effect of dissolved silica on As(V) sorption to HFO, As(V) 38 $\mu\text{g/L}$, Fe 1.4 mg/L (Holm 2002).

Carbonate sorbs to HFO (Zachara, Girvin et al. 1987; van Geen, Robertson et al. 1994). Although carbonate adsorption is much weaker than that of As(V), total carbonate concentrations in groundwater are typically ~10,000 times those of As. At low carbonate concentrations (<1 mM or 50 mg/L CaCO₃) and pH < 8, carbonate has a minimal effect on As(V) adsorption to hematite (Arai, Sparks et al. 2004). However, adsorption modeling indicates that for higher carbonate concentrations (~10 mM) carbonate competition may reduce As(V) adsorption (Appelo, Van der Weiden et al. 2002; Arai, Sparks et al. 2004). For a carbonate concentration similar to that of the Mahomet Aquifer, carbonate does significantly reduce As(V) sorption to HFO (Figure A10).

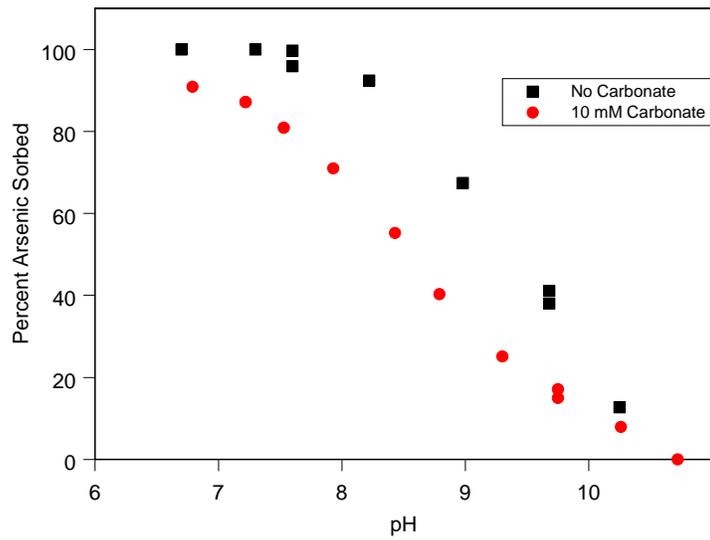


Figure A10. Effect of carbonate on As(V) adsorption to HFO. As(V) 38 $\mu\text{g/L}$, Fe 1.4 mg/L (Holm 2002).

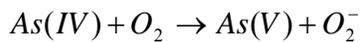
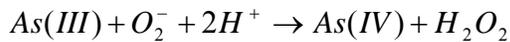
Natural organic matter may also affect As adsorption to HFO (Redman, Macalady et al. 2002), but little data is available for the prediction of the magnitude of the effect, and almost nothing is known about the properties of NOM in anoxic groundwater.

APPENDIX B TREATMENT SYSTEM CHEMISTRY AND KINETICS

Competition Kinetics

The core process in the air oxidation of iron was discussed in the Introduction section in the body of the report, where it was seen that the reaction of oxygen with Fe(II) led to Fenton's reaction between Fe(II) and hydrogen peroxide. This reaction produces a very reactive oxidative species which is generally thought to be hydroxyl radical (Walling 1975), but there is also some evidence (Hug and Leupin 2003) for participation of Fe(IV) under some conditions. The following discussion assumes for the sake of illustration that hydroxyl radical is the primary active species responsible for arsenic oxidation.

Superoxide (O_2^-) has been suggested (Lee and Choi 2002) as a possible oxidant for As(III), but that seems unlikely, since it is known (Klaning, Bielski et al. 1989) that the intermediate product, As(IV), reacts with oxygen to produce superoxide. This would create a chain reaction



which, once initiated by the reaction of Fe(II) with oxygen, should result in the rapid removal of As(III) requiring no additional oxidant, in addition to the formation of peroxide to drive the Fenton reaction. Clearly, this is not the case because once initiated by the iron-oxygen chemistry, As(III) would spontaneously oxidize to As(V) via the chain reaction.

Hydroxyl radical (OH) is a very nonspecific oxidant, reacting at nearly diffusion controlled rates with most organic substances (i.e., second-order rate constants of $k_{oi} > 10^9 \text{ M}^{-1}\text{s}^{-1}$). As an illustration of how rapid a reaction this is, for reaction with an organic compound *i* at a concentration of $C_i = 10^{-5} \text{ M}$ (about 1 mg/L) with a rate constant of $k_{oi} = 2 \times 10^9$, the pseudo-first order rate constant (indicated by a "prime" symbol) is

$$k'_{oi} = k_{oi} C_i = 2 \times 10^9 * 10^{-5} = 2 \times 10^4 \text{ s}^{-1}$$

The half life of OH radical due to that reaction is then

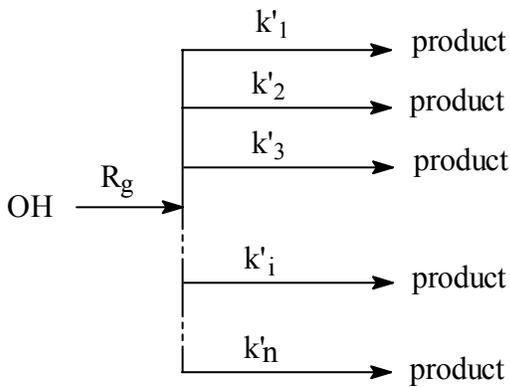
$$t_{1/2} = \frac{\ln 2}{k'_{oi}} = 70 \mu\text{s}$$

Thus, if OH is generated at rate R_g and consumed in a number of such fast reactions (Scheme B1), it is essentially consumed as fast as it is made, with the result that the concentration of OH is

$$[OH] = \frac{R_g}{\sum_j k_{oj}} \quad \text{Equation B1}$$

and the fraction of OH that reacts with species i is given (Peyton 1996) by

$$f_{oi} = \frac{k_{oi}C_i}{\sum_j k_{oj}C_j} \quad \text{Equation B2}$$



Scheme B1

This very useful expression can be used to calculate the rate and/or extent of removal of a contaminant by OH radical processes. The nominal composition of Danvers groundwater is given in Table B1. By calculation and summing of the pseudo first order rate constants, it can be determined that the dissolved organic carbon in the groundwater is the most important scavenger in this system, and that DOC and bicarbonate together consume 96% of any OH radical produced at the beginning of treatment. Furthermore bicarbonate is not consumed by reaction with hydroxyl radical, because it produces carbonate radical, which regenerates bicarbonate when it functions as a one-electron oxidant of organic material. Overall, the DOC is changed very little by OH and carbonate radical reaction, since the amount of OH formed (on the order of the Fe(II) or peroxide concentration, about 25-35 μM) is small compared to the amount of carbon atoms in the NOM (about $1.1 \times 10^{-3} \text{ M}$). It is notable and fortunate that Fe(II) captures only a small fraction of OH, since Fe(II) is needed to generate more OH. The rate of oxidation of As(III) is given by the product of the rate of OH radical generation and the fraction of those radicals that is captured by As(III).

Table B1. Competition-Kinetic Calculations for Danvers Groundwater

solute	concentration		OH radical rate const., $k_{OH,i}$ L/mole-s	Pseudo first order rate const., k_{O_i} , 1/s	Fraction of OH that reacts with species i
	mg/L	mole/L			
As(III)	0.04	5.3e-7	8.5e9 (a)	4.5e3	0.012
Fe(II)	2	3.6e-5	3.0e8 (b)	1.1e4	0.031
HCO ₃ ⁻	500 (c)	1.0e-2	8.5e6 (b)	8.5e4	0.236
DOC (d)	13	n/a (e)	2.0e4 (f)	2.6e5 (g)	0.721
Sum = 3.61e5					
Notes: a) Klänning et al., (1989) b) rate constant value from Buxton et al.,(1988) c) bicarbonate alkalinity, as CaCO ₃ d) Dissolved Organic Carbon e) no well-defined molecular weight f) units of L/mg-s. Value measured by Peyton et al., (1998) g) concentration (mg/L) x rate constant (L/mg-s) = k' (1/s)					

Therefore, as the amount of As(III) decreases during treatment, its fraction of OH captured decreases proportionally, resulting in first order disappearance:

$$\frac{dA}{dt} = -R_g f_{OA} = -R_g k_{OA} \frac{A}{\sum_o} \quad \text{Equation B3}$$

where $A=[As(III)]$, f_{OA} is the fraction of OH that reacts with A (Eq. B2), and \sum_o is the sum of the pseudo first order rate constants for hydroxyl radical reaction with solution components (Eq. B1), and is nearly constant for reasons discussed above. Separation of variables in preparation to integrate the above differential equation yields

$$\frac{dA}{A} = -\alpha R_g dt \quad \text{Equation B4}$$

where $\alpha = k_{OA}/\sum_o$, which is assumed constant, as discussed above. However, the integral of the radical generation rate with respect to time is simply the total dose, D_o , of hydroxyl radical generated up to that point, so that

$$-\ln \frac{A}{A_o} = \alpha D_o \quad \text{Equation B5}$$

Using this method of calculation, if a 27 μ M peroxide dose is converted quantitatively to OH and $\alpha=k_{OA}/\sum_o = 2.4e4$ using values from Table B1, then $A/A_o = 0.52$. The fraction of As(III) remaining after arsenic oxidation (sample point S₂) averaged 0.58 ± 0.12 for the six experiments with a peroxide dose of 27 μ M, in good agreement considering the simplicity of the calculation, and showing that the OH radical model gives reasonable results.

An upper bound for the reaction time required for consumption of the peroxide and generation of hydroxyl radical can be estimated from the second-order expression for the reaction of peroxide (P) with Fe(II), represented by F in equation B6:

$$\frac{dP}{dt} = -k_{FP}FP \quad \text{Equation B6}$$

The symbol k_{FP} is the rate constant for reaction of F and P, approximated as the product of the rate constant (2.2e4 L/mole-s) of the most reactive form of iron (FeCO₃) (King and Farlow 2000) and the fraction of iron in that form (0.70, calculated for Danvers raw water, using Mineql+ (Schecher and McAvoy, 1994)). Integration of the rate expression in equation B6 (Moore and Pearson 1981) gives

$$t = \frac{1}{k_{FP}(F_o - P_o)} \ln \left[\frac{P_o(F_o - x)}{F_o(P_o - x)} \right] \quad \text{Equation B7}$$

where F_o and P_o are the initial molar concentrations of Fe(II) and hydrogen peroxide, respectively, and x is concentration of P that has reacted by time t . Substitution of $15P_o/16$ for x gives the result that 11.2 seconds is required for the peroxide concentration to decrease by four half-lives (94%). The concept of half-life is still convenient even though the reaction is not first-order. Since not all forms of iron have been included in the calculation, the resulting time is an upper bound, and would be shorter if all forms of iron were included. This time is much longer than the time that it takes hydroxyl radical to react, calculated earlier, so that essentially OH radical reacts as quickly as it is made.

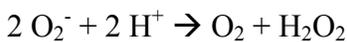
While the simple concepts above are useful, the chemistry of the system is not that simple. When OH radical (or other one-electron oxidants such as Fe(IV)) reacts with organic compounds, the reaction consumes the OH radical but creates a carbon centered radical HR· (where R is an organic chain or ring):



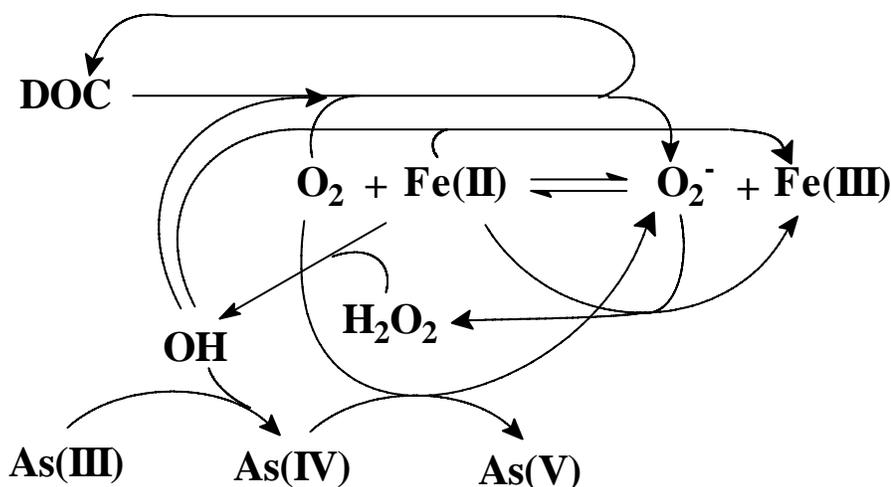
These carbon-centered radicals (CCR) can be either oxidizing radicals or reducing radicals. Oxidizing radicals will react similarly to OH radical, but are less reactive. The reducing radicals formed can be among the strongest reductants present. It is well-established (von Sonntag 1987) that CCRs react with oxygen to form peroxy radicals (HRO₂·) which can further react in a number of ways. If the CCR was a reducing radical, then its peroxy radical will rapidly decompose to produce superoxide:



From the previous discussion of the core mechanism for Fenton's reaction, it can be seen that production of additional superoxide increases the opportunity for not only regeneration of Fe(II) from Fe(III), but also the production of additional hydrogen peroxide through the disproportionation reaction



If only the effects of the reductive radicals producing superoxide are considered, then the simplest mechanism that describes arsenic oxidation is shown in Scheme B2, which includes the rapid oxidation of the intermediate As(IV) to As(V) by oxygen, producing superoxide. However, it is very unlikely that the organic oxidizing radicals can be ignored. NOM contains aromatic rings some of which are phenolic groups that can be oxidized to *o*- or *p*-dihydroxybenzenes. These groups are easily further oxidized to quinones that can serve as electron shuttles in either the oxidative or reductive direction. Furthermore, the possibility must also be considered, that these radicals can also react with the various forms of arsenic and iron. When these reactions are considered as well, the reaction system becomes extremely complicated.

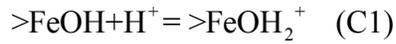


Scheme B2

In summary, the mechanistic investigation identified a number of reactions that have not previously been considered in the published models of arsenic oxidation. The calculations of Hug (2003) were performed for experiments carried out on synthetic groundwater which contained no organic carbon, which, while perhaps mechanistically illuminating for the synthetic groundwater, have little bearing on the mechanism in real-world groundwater. The preliminary competition-kinetic calculations indicate that the reaction of OH and carbonate radical with organic material simply cannot be ignored in our water, which contains a very significant amount of NOM, since those pathways consume 96% of the OH radical that is formed. All of those reactions result in the production of additional radicals that may well react with arsenic. Thus, the fact that our experimental data could be successfully fit with a simpler model is irrelevant, and therefore, no kinetic simulations are reported for the entire reaction system at this time, since we feel that to do so would be misleading. Further work is ongoing to narrow the possibilities through carefully designed probe compound, surrogate, and scavenger experiments.

APPENDIX C
MODELING ARSENIC ADSORPTION TO HYDROUS FERRIC OXIDE

A model of As adsorption to HFO can help in understanding and optimizing As removal at water treatment plants. It is assumed that adsorption is sufficiently rapid to reach equilibrium in the Fe oxidation phase. HFO particles in water have surface hydroxyl groups ($>FeOH$) that can gain or lose a H^+ ion to become positively or negatively charged (Schindler and Stumm 1987).



The net surface charge depends on the relative amounts of $>FeO^-$ and $>FeOH_2^+$, which in turn depend on the pH. For a system containing only HFO particles and an inert (non-adsorbing) salt, HFO particles have no net charge at pH~8. At higher pH values the HFO surface charge is negative and at lower values it is positive. Ions of opposite charge (counter-ions) accumulate near the HFO surface (within a few nm) at concentrations above those of the bulk solution. This region of unsymmetrical charge distribution is called the electrical double layer (Stumm and Morgan 1996).

The protonation and deprotonation of $>FeOH$ groups can be quantitatively described by mass-action equations that are analogous to equations describing the dissociation of dissolved acids and bases.

$$K_1 = \frac{[>FeOH_2^+]e^{-F\psi/RT}}{[>FeOH][H^+]} \quad (C3)$$

$$K_2 = \frac{[>FeO^-][H^+]e^{F\psi/RT}}{[>FeOH]} \quad (C4)$$

In equations C3 and C4, K_1 and K_2 are equilibrium constants, ψ is the surface potential, which is a function of the surface charge, and the other terms have their usual meanings. These equations are similar to those for dissolved species except for the coulombic term ($e^{-\Delta z F \psi / RT}$), where Δz is the change in charge of the $>FeOH$ group upon gaining or losing an H^+ ion. The coulombic term accounts for the attractive or repulsive interactions between the H^+ ion, the charged HFO surface, and the electrical double layer. It is analogous to an activity coefficient.

Adsorption of As(V) and As(III) to HFO is a surface complexation ligand exchange reaction. Clearly, adsorption of an anion changes the charge of the surface complex.



These reactions are analogous to complexation reactions in homogeneous solution except the metal ion is at the surface of an HFO particle. The mass-action equations that relate the dissolved and adsorbed concentrations of As(V) and As(III) are similar to those for homogeneous complexation except for the coulombic term.

$$K_3 = \frac{[>FeOAsO_4^{2-}]e^{2F\psi/RT}}{[>FeOH][HAsO_4^{2-}]} \quad (C7)$$

$$K_4 = \frac{[>FeOAs(OH)_2]}{[>FeOH][H_3AsO_3]} \quad (C8)$$

Equation C8 has no coulombic term because the surface complex has the same charge as the >FeOH group.

Conceptual models of the electrical double layer differ in the structure of the double layer and in the resulting relation between the surface charge and surface potential. Dzombak and Morel (Dzombak and Morel 1990) developed a model assuming a Boltzmann distribution of counter ions in the double layer. That is the model used in the present work.

Adsorption Calculations

Dzombak and Morel (Dzombak and Morel 1990) critically reviewed publications on the adsorption of metals and anions to HFO and fit their model to the data sets that satisfied their criteria. The anions they modeled include As(V), As(III), and PO_4^{3-} , which may affect As(V) and As(III) adsorption through competition. The Dzombak-Morel (1990) model and its database of HFO properties and adsorption equilibrium constants is incorporated in the chemical equilibrium computer program MINEQL+ (Schecher and McAvoy 1994), which was used for adsorption modeling in the present work. The adsorption database compiled by Dzombak and Morel (1990) was supplemented by equilibrium constants for silica (Swedlund and Webster 1999) and carbonate (van Geen, Robertson et al. 1994).

Carbonate and silica may affect As(III) and As(V) adsorption to HFO by competing for adsorption sites, but they may also affect As(V) adsorption by changing the HFO surface charge.



As the HFO surface charge becomes more negative the repulsion of $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ increases.

The input for MINEQL+ is the pH and total (measured) concentrations of As(V), As(III), Fe, SiO_2 , CO_3^{2-} , and PO_4^{3-} . The program solves the system of mass-action and mass-balance equations. The adsorbed As is assumed to be removed in the treatment process.

The published adsorption equilibrium constants were derived from experiments that used aged HFO to improve reproducibility. However, adsorption calculations based on the properties of aged HFO under-predict As(V) adsorption to freshly precipitated HFO (Fuller, Davis et al. 1993; Edwards 1994; Holm 2002). Therefore, such a model would be inappropriate for modeling an iron removal plant. The “effective HFO concentration” for a system containing freshly precipitated HFO is calculated by multiplying the actual Fe concentration by 3.75 (Holm 2002). The adsorption equilibrium constants are the same as for HFO. This modified adsorption model fit the data from adsorption experiments with just HFO, As(V), carbonate, silica, and phosphate (Holm 2002) and is the model used in the present work.

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