Tech Brief

PUBLISHED BY THE NATIONAL ENVIRONMENTAL SERVICES CENTER

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

Summary

Illinois State Water Survey and University of Illinois researchers experimented with different combinations of chemical additives and steps along the treatment process. They found that the addition of hydrogen peroxide combined with iron that was already present in the groundwater (approximately 2 milligrams per liter [mg/L]) to the Danvers water system produced a significant reduction in arsenic (III) levels to below 3 micrograms per liter (ug/L). To accomplish this reduction, they added as much as 30 micro molar (uM) hydrogen peroxide to the water treatment system before the water was aerated. This procedure reduced arsenic (III) levels but did not decrease the dissolved arsenic indicating that no arsenic was being absorbed to the iron or other oxidants. To correct this problem, they implemented an additional experiment to determine if hydrogen peroxide combined with additional iron would provide active sites for the dissolved arsenic to combine with and, therefore, be removed in the iron removal step. They found that the addition of iron (II) or iron (III) at a concentration of 5 to 6 mg/L along with the addition of hydrogen peroxide at a concentration of 20uM, would indeed remove 83 to 97 percent of the dissolved arsenic.

Arsenic Found in Groundwater

The arsenic rule is one of the most controversial regulations in the history of the Safe Drinking Water Act. Intended to protect public health, focus has been on the rule's cost to implement rather than the beneficial health effects the public would receive from reduced exposure.

Arsenic is typically found in groundwater, the source that many small communities rely upon for their drinking water supplies. Until recently, water systems had to comply with a maximum contaminant level (MCL) of 50 parts per billion (ppb). But the U.S. Environmental Protection Agency did not believe that level was low enough to protect people from long-term, chronic exposure to arsenic in drinking water, which can cause serious dermatological conditions such as blackfoot disease* and cancer of the skin, bladder, lung, liver, and kidney, and other ailments.

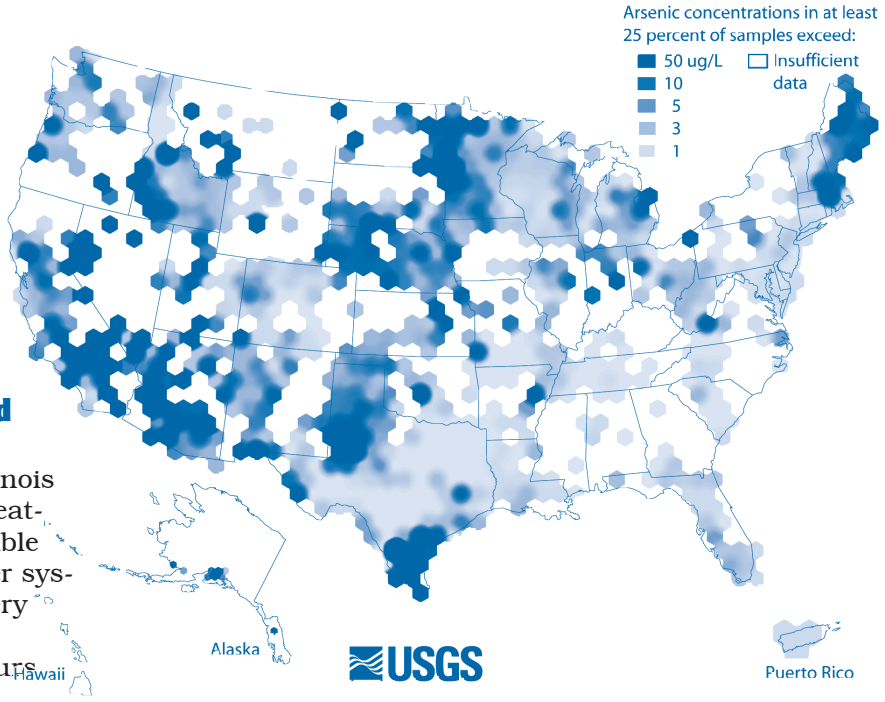
**Blackfoot disease is a severe form of peripheral vasculardisease in which the blood vessels in the lower limbs are severely damaged, eventually resulting in progressive gangrene.*

Although arsenic composes only two parts per million (ppm) of the Earth's crust, there are regions where higher concentrations occur in the mineral strata. Groundwater in the deep levels of such strata has been exposed to and has absorbed arsenic over a greater period of time and contains high levels. Shallow levels of mineral strata contain groundwater that has not had as long of a residence time and as such has not absorbed as much and consequently contains less arsenic. Arsenic that occurs in high levels in the U.S. is in the Southwest and Northwest and other areas that may be in close proximity to geothermal activity. Other areas that may have higher than average concentrations include parts of Michigan, Illinois, and Minnesota.

What is the new level?

Because of public health concerns, EPA researched what it believed to be a safer arsenic consumption level. The agency set the new MCL at 10 ppb.

Unfortunately, drinking water from many small water systems continues to exceed this MCL. Problems arise because many of these systems do not have the funds to pay for additional treatment costs. Because of this situation, the Midwest Technology Assistance Center (MTAC) for Small Public Water Systems funded research to help small communities meet the new standard.



Team Researches Removal Method

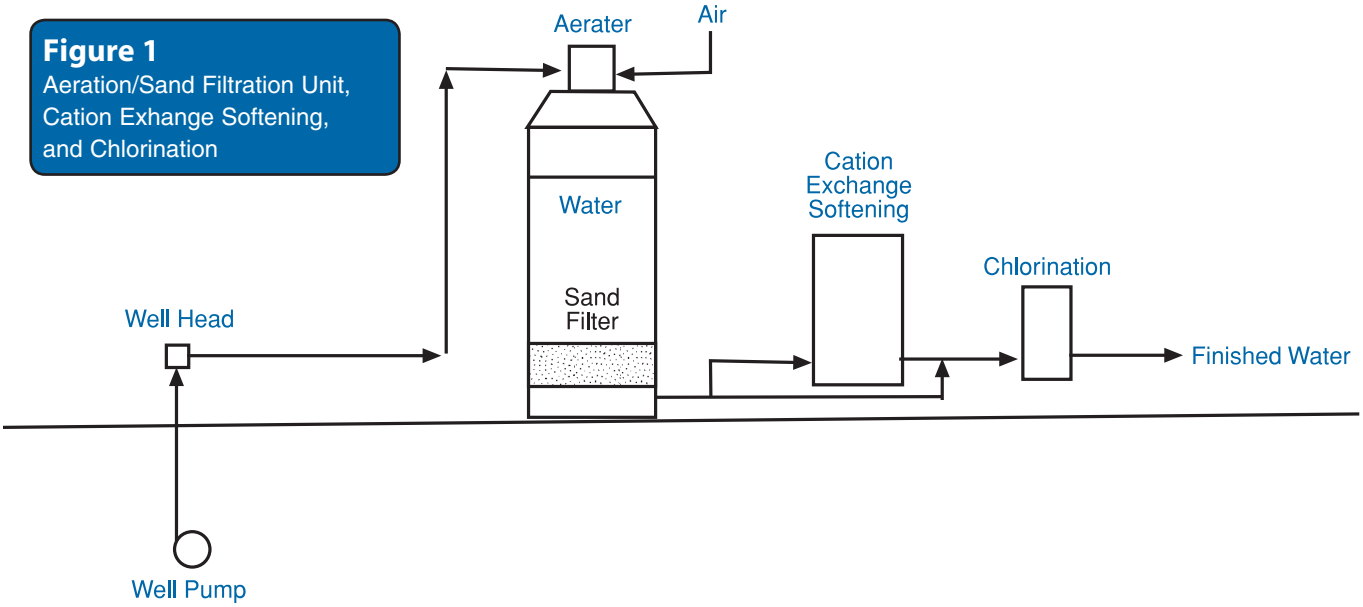
A research team at the Illinois State Water Survey and the University of Illinois proposed to develop an inexpensive treatment option for arsenic removal, suitable particularly for small community water systems. The team came up with some very interesting results. By extending and optimizing a reaction that already occurs during iron removal at many drinking water treatment plants, they remarkably improved arsenic removal, while increasing chemical costs only slightly and requiring no large capital equipment costs.

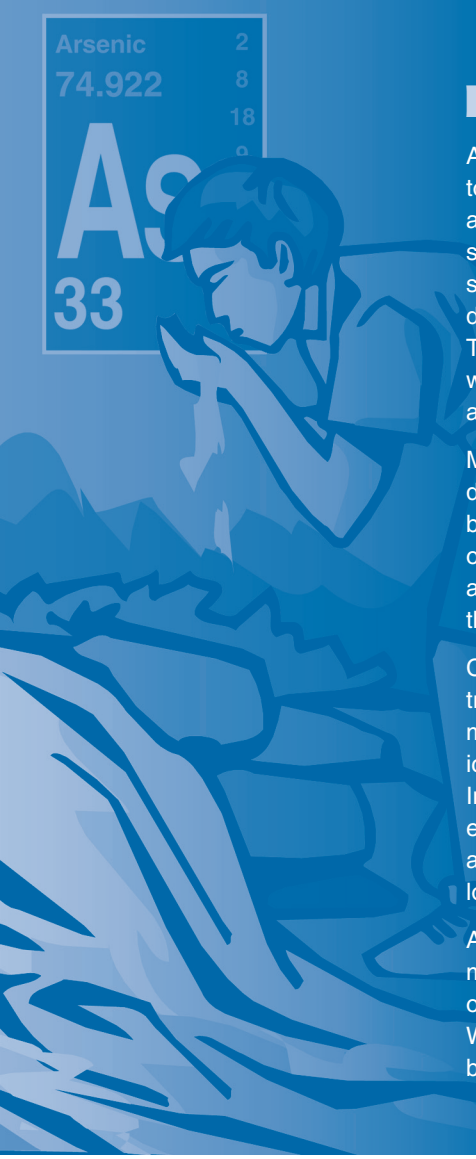
The premise of this project was that 1) the iron already present in the water could be used in conjunction with hydrogen peroxide to produce a strong agent to oxidize arsenic to a form that is easier to remove, and 2) that by manipulating the chemistry, the process could be optimized for arsenic removal.

The Fenton reaction, in which hydrogen peroxide and iron combine to form a strong oxidizing agent called hydroxyl radical, was discovered by H.J.H. Fenton in 1894. This reaction occurs naturally during aeration treatment of groundwater containing iron, and forms hydrogen peroxide as an intermediate. Hydroxyl radical reacts quickly with arsenic (III) changing it to arsenic (V), which is much less toxic and adsorbs more completely to iron as it precipitates during iron removal. When the iron precipitate is removed by filtration, the arsenic is removed with it.

Many water systems already have such treatment procedures in place for iron removal because of aesthetic issues such as taste and laundry staining. Typically, systems that have high concentrations of iron can remove up to 25 percent of total arsenic during stan-

Figure 1
Aeration/Sand Filtration Unit, Cation Exhange Softening, and Chlorination





How does arsenic affect humans?

Arsenic exists in groundwater in two forms, arsenic (III) and arsenic (V). Studies have shown that the toxicity of arsenic (III) is several times greater than arsenic (V). The body's gastrointestinal tract will absorb arsenic in either form. The arsenic enters the bloodstream and initially accumulates in the liver, spleen, kidney, and gastrointestinal tract. Clearance or detoxification from these tissues is rapid via a series of oxidative-reduction reactions that terminates in the arsenic being methylated or changed into dimethylarsenoic acid. This methylation process is the body's principal mechanism for detoxification. The methylated arsenic form is less toxic and easily excreted via the kidneys as urine. Two to four weeks following exposure any remaining arsenic found in the body is found in kinetin-rich tissues such as the skin, hair, and nails.

Methylation efficiencies in humans appear to decrease at high doses of arsenic or if exposed to chronic doses. The body has a limited capacity to detoxify a quantity of arsenic that enters the body. When the body reaches that point arsenic is retained and is stored in soft tissues and in the cellular components of those tissues. One of the most striking effects of this accumulation is the significant interference that arsenic causes with enzyme reaction systems, especially with the cell's energy production mechanisms that occur in the mitochondria.

Cell respiration or the breakdown of cellular glucose to form carbon dioxide, water and adenosine tri-phosphate (ATP is a high energy producing compound) occurs in a cell component called the mitochondria. The process of respiration is performed by many enzymatic reactions and arsenic toxicity interferes with this process. Arsenic (III) has the propensity to bind to sulfur containing enzymes. In doing so, the arsenic-sulfur binding site results in a structural deformation that incapacitates the enzyme. This binding can occur with any number of enzymes along the pathway, which contain sulfur and once incapacitated, the pathway process will not go forward and high-energy compounds are no longer formed.

Arsenic (V) will substitute for phosphorus (P) ion in many biochemical reactions, especially in the formation of high- energy ATP. This results in a breakdown of high-energy compounds and an overall loss of cellular energy. This disruption of the high-energy pathways limits the availability of cellular energy. Without the energy to allow the cell to perform its functions, the tissue composed of these cells slowly becomes nonfunctional over time, resulting in the neurological and physiological impairments and disabili-

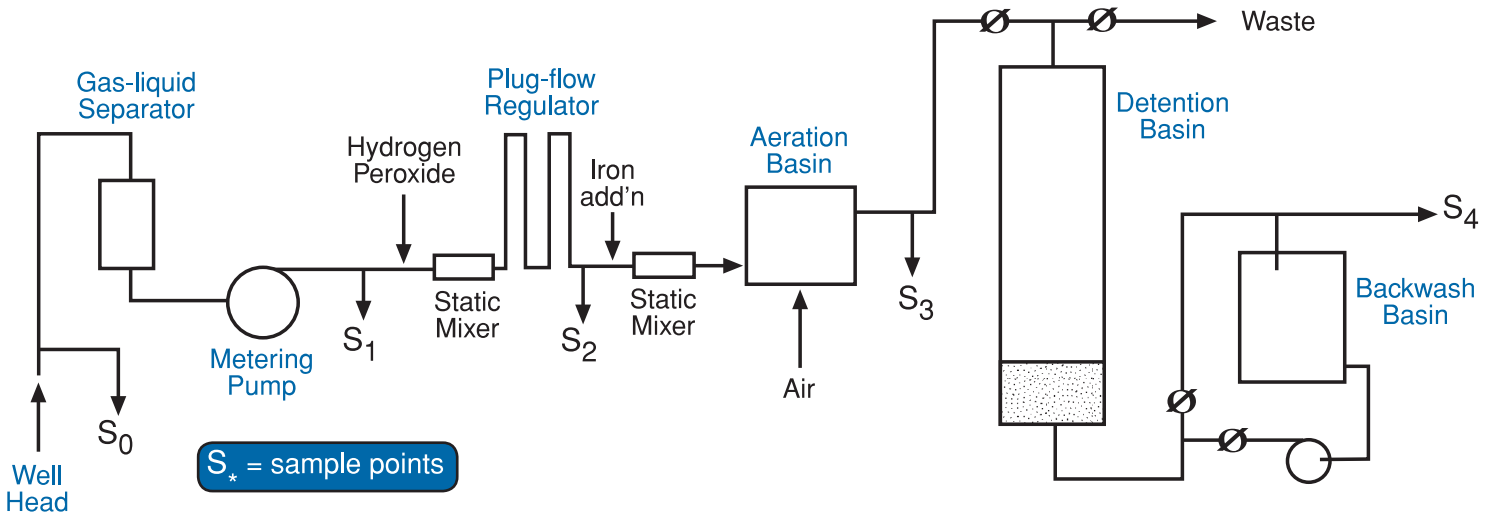
dard aeration processes. However, previous research had shown that more of the hydroxyl radical is produced using hydrogen peroxide than with aeration alone, which would be helpful to arsenic removal.

Hydrogen peroxide had been tried as a treatment chemical prior to this study, but usually at levels that were too high to be cost-effective for a small system. This experiment showed, however, that the combination of low doses of hydrogen peroxide and iron added to groundwater before it was aerated was capable of oxidizing most of the arsenic (III) in Danvers, Illinois, groundwater and reducing total arsenic from approximately 40 ppb to less than 5 ppb in batch, laboratory flow, and pilot-scale flow experiments (compared to 30 ppb remaining after normal iron removal) in groundwater with a high level of dissolved organic carbon. The estimated chemical costs for this treatment totaled about 7 cents per one thousand gallons of treated water.

What they found in this study was that not only was the iron/arsenic ratio critical to arsenic removal, but the hydrogen peroxide concentration was as well. In addition, the researchers found that supplementing the iron already in the water increased the adsorption of arsenic to iron. They also found that arsenic removal is more efficient when hydrogen peroxide is added to the anoxic groundwater. The researchers wanted to be careful not to expose the water to oxygen, because oxygen could use up the dissolved iron before it could react with hydrogen peroxide.

The researchers set up a pilot plant that simulated the treatment plant at Danvers, Illinois, to use as an example, because this municipal system was already set up to remove iron, and used water that was expected to be difficult to treat, providing a more difficult challenge for the treatment process. Danvers is a small community of about 1,100 people in central Illinois, near Bloomington, that draws its raw water from the Mahomet Aquifer.

Figure 2 - Danvers Pilot Plant Diagram



Danvers Plant Experiment

The Danvers plant treatment train consists of an aeration/sand filtration unit, cation exchange softening, and chlorination. (See Figure 1, page two.) During pilot experiments the researchers connected their pilot plant directly to a sample tap at the wellhead, allowing them to add various doses of hydrogen peroxide and iron to this sidestream of raw water in parallel with the actual water treatment system. The connection consisted of a check valve and a gas-liquid separator that physically divided it from the water in the supply pipe.

In their pilot plant, the researchers added iron and hydrogen peroxide dosing solutions while the water was still anoxic. (See Figure 2.) Next, the water was pushed through a static mixer and through a plug-flow reactor to give the iron and peroxide time to react. The plug-flow reactor provided a 1.5-minute reaction time for the peroxide. Preliminary laboratory experiments had indicated that the complete reaction between hydrogen peroxide and iron required less than 22 seconds.

Following the plug-flow reactor, iron was added before the water was introduced into the bottom of the aeration basin, where it would be completely aerated before flowing to a bed of sand for filtration. The space above the sand served as a flocculation basin with a detention time of approximately 30 minutes. The finished water was collected in a large basin, which was used for backwashing the sand filter between experiments.

For More Information

Development of Low-Cost Treatment Options for Arsenic Removal in Water Treatment Facilities by Gary R. Peyton, Thomas R. Holm, and John Shim, June 2005, was funded by the Midwest Technology Assistance Center. The University of Illinois at Urbana-Champaign and the Illinois State Water Survey sponsored the report. Copies of the final report are available by calling (217) 333-9321.

MTAC provides technical assistance to small public water systems as well as water systems serving Native American communities. Their mission is to provide small system administrators and operators with the information necessary to make informed decisions about planning, financing, and selecting and implementing technological solutions to address needs.

Midwest Technology Assistance Center
2204 Griffith Dr.
Champaign, Il 61820-7495
Phone: (217) 333-9321
Fax: (217) 244-3054
mtac.sws.uiuc.edu

National Environmental Services Center
NESC Assistance. Solutions. Knowledge.

West Virginia University
An Equal Opportunity/Affirmative Action Institution

Published by The National Environmental Services Center at West Virginia University, P.O. Box 6064, Morgantown, WV 26506-6064