Removing Arsenic from Water The Importance of pH, Background Contaminants and Oxidation
By Dennis Clifford, Ph.D., P.E.

Summary: *Last month, we discussed the problems of potential arsenic leaching from certain carbons used in filtration devices. In Part 2, we cover different species of arsenic and weigh various methods for effective removal from drinking water supplies.*

Since its isolation in 1250 A.D. by Albert the Great, arsenic has been known for its poisonous nature and acute toxicity. In the 1970s, arsenic was identified as a carcinogen associated with skin and lung cancer, and more recently it has been linked to bladder and prostate cancers, cardiovascular disease and diabetes. A re-evaluation of the health effects of arsenic—completed in March 2000 by the National Academy of Sciences (NAS)—concluded the current drinking water Maximum Contaminant Level (MCL) of 50 parts per billion (ppb) wasn't sufficiently protective of public health. It recommended the MCL be lowered as soon as possible. In May 2000, the U.S. Environmental Protection Agency (USEPA)—which is under legal mandate to provide a final MCL by Jan. 1, 2001—proposed an MCL of 5 ppb and announced it would take comments on levels for 3, 10, and 20 ppb. When the new MCL is set, it's unlikely it will be above the World Health Organization (WHO) guideline of 10 ppb, adopted as a standard in many parts of the world.

According to USEPA estimates, lowering the MCL to 5 ppb will impact 12 percent of the nation's 54,000 community water supplies (C WS) that provide water for an estimated 22.5 million people. A 10-ppb MCL would impact 6 percent of the CWSs and an estimated 10 million people. The USEPA's estimated cost of compliance per year for the 5- and 10-ppb MCLs are $445 million and $195 million, respectively.[1] Compliance cost estimates sponsored by the American Water Works Association (AWWA) Water Industry Technical Action Fund are much higher: $2.3 billion and $780 million per year, respectively[2]

Although arsenic occurs in surface waters, it's primarily a groundwater problem and a widespread one at that, as evidenced by the U.S. Geological Survey (USGS) arsenic-occurrence map just published on their website (http://co.water.usgs.gov/ trace). This map and other surveys have shown groundwater arsenic concentrations above 3 ppb are found in virtually every state. Those with the greatest number of supplies above 10 ppb include all western states plus Kansas, Nebraska, the Dakotas, Illinois, Wisconsin, Indiana, Ohio, Michigan, West Virginia and Pennsylvania.

Arsenic speciation in water

Arsenic is a metalloid (an element that exhibits properties of both a metal and non-metal), not a heavy metal as is often reported. It has two oxidation states, pentavalent arsenic (As-V) and trivalent arsenic (As-III). Dissolved arsenic is always an anion or neutral molecule—never a cation—in water. Although arsenic can exist in both organic and inorganic forms, only inorganic arsenic has been found to be significant in groundwater supplies.

Depending on the reducing or oxidizing condition in the groundwater, either arsenite (As-III) or arsenate (As-V) will dominate. The pH of the water is also very important in determining arsenic speciation. The primary arsenate species found in groundwater in the 6-to-9 pH range are monovalent H_2AsO_4 and divalent $HAsO_4^{2-}$. These anions result from the dissociation of arsenic acid, H_3AsO_4. Uncharged arsenious acid, H_3AsO_3 is the predominant species of trivalent arsenic found in natural waters. Only at pH values near and above pH 9.2 does the monovalent arsenite anion, $H_2AsO_4^-$ become significant.

Finally, the arsenic in contaminated groundwater will generally be soluble, but some particulate arsenic may be found associated with insoluble iron and manganese, clay and other particulate. To summarize, arsenic contamination of drinking water is predominantly a groundwater problem associated with soluble inorganic arsenic in the form of As-V anions or neutral As-III molecules.

Processes for arsenic removal

Arsenic can be removed from water using a variety of processes including iron and alum coagulation, lime softening (LS), activated alumina adsorption (AA1), granular ferric hydroxide adsorption (GFH), ion ex change (IX), coagulation assisted microfiltration (C-MF), reverse osmosis (RO) and nanofiltration (NF). Experience with all of these processes has demonstrated that As-V is better to far better removed than is As-III. Thus, oxidation of As-III to As-V will generally be required before any other treatment processes to meet the new effluent MCL requirement when using these processes to treat waters containing As-III.

This discussion will focus on A Al, GFH, IX, C-MF, RO and NF, because they're applicable to point-of-use/ point-of-entry (POU/POE) and small community systems. Keep in mind, amendments to the Safe Drinking Water Act (SDWA) during its 1996 reauthorization established for the first time that POU/POE technologies could be used as "best available technology[7]' (BAT) for small systems to come into compliance with federal drinking water regulations.

Activated alumina

AA1 adsorption is typically carried out using 28x48 mesh alumina in packed beds with 2-to-6 foot (ft) media depth and an empty bed contact time (EBCT) of 3-to-5 minutes. The major factors influencing run length are pH, competing ions, EBCT and arsenic oxidation state. The longest runs— 20,000 bed volumes (BV) and greater-are achieved in the 5-to-6 pH range with run length decreasing as pH increases (see *Figure 1).* Silica, phosphate and fluoride ions compete strongly with arsenates for adsorption sites. As-III is poorly adsorbed

Figure 1. Effect of pH on As-V removal by activated alumina
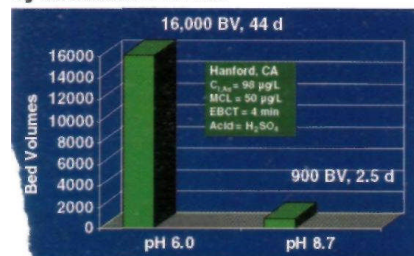
compared with As-V (see *Figure* 2). However, AA1 can be used to remove As-III for short run lengths (typically >1,000 BV) at neutral to slightly alkaline pHs. AA1 is regenerable using a fairly complicated base and acid regeneration process, which dissolves some of the media.

Granular ferric hydroxide

GFH adsorption is a relatively new process[3] developed in Germany and used in Europe to meet the new 10-ppb guideline. It employs packed beds of GFH, a poorly crystallized beta-FeOOH, which is available from only one source, GEH Wasserchemie. It generally gives longer runs than AA1 and is less sensitive to pH and EBCT. As with A Al, silica, phosphate and fluoride ions compete strongly with arsenates for adsorption sites, and As-V is much better removed than As-III. The exhausted GFH media isn't considered regenerable and

Figure 2. Effect of oxidation state on arsenic removal by activated alumina at pH 6.0
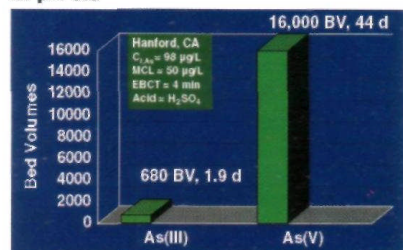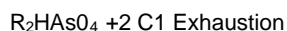
is simply thrown away. Spent GFH is considered a non-hazardous waste, because it reportedly passes the applicable leaching tests. For comparison, spent AA1 can usually be disposed of as a non-hazardous waste, too. Generally, EBCTs for GFH can be less than those required for AA1.
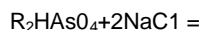
Ion exchange

The IX process removes only As-V. In it, the source water (oxidized if necessary) is passed through a 2-to-6 ft deep bed of chloride-form, strong-base anion exchange resin in which the chloride-arsenate ion-exchange reaction takes place in the 6.5-to-9 pH range. (See *Equation* 2, where "R" represents a positively charged resin exchange site.) Regeneration with excess NaCl according to Equation 2 is readily accomplished, and returns the resin to the chloride form, prepared for another exhaustion cycle.

Equation 1:

$$2 RCl + HAsO_4^2 =$$

$$R_2HAsO_4 +2 Cl \text{ Exhaustion}$$

Equation 2:

$$R_2HAsO_4+2NaCl =$$

$$2 RCl + Na_2HAsO_4 \text{ Regeneration}$$

This process is like IX softening except that strong-base anion (SBA) resin is used in place of strong-acid cation (SAC) resin. Generally, IX will give the

lowest effluent arsenic concentrations of any of the potential treatment processes including RO. Run lengths, which decrease as sulfate increases, are commonly in the 400-to-4,000 BV range. Recently, it was discovered the spent IX regenerant could be reused up to 25 times without removing the arsenic.[4] A significant disadvantage of ion exchange is the potential for arsenic peaking or dumping, i.e., effluent arsenic concentration exceeds influent concentration. Dumping occurs if sulfate is present in the feed water and if the run isn't stopped before arsenic breakthrough. For this reason, the USEPA isn't considering IX for POU and POE compliance to the MCL.[5] IX has an advantage over AA1 and GFH in that EBCTs of 1 minute and even less can be used.

Coagulation-microfiltration

In the C-MF process, I-to-10 ppm of ferric iron (Fe-III) is added to the raw water, which is mixed for 20-to-60 seconds before direct 0.2-micron microfiltration to remove the arsenic-contaminated $Fe(OH)_3$ precipitate that's formed. Arsenic removals (up to 98 percent for As-V) depend on Fe-III dosage, pH, competing ions (silicate, phosphate and fluoride). Typically, only 10-to-30 percent As-III removal is achieved. Complicated systems are required to recycle the backwash to increase water yield. Coagulation systems are prone to upsets if the feed water chemistry changes and aren't generally suitable for POU/POE devices.

Nanofiltration and reverse osmosis

Assuming one can afford to use them, NF and RO processes will effectively remove arsenic. NF membranes can do a good job (50-to-95 percent) of As-V removal but achieve much less removal of As-III. Typically, NF is not as good as RO, which removes >95 percent of As-V and >75 percent of As-III. Both processes are relatively expensive and produce a brine stream, which can be greater than 20 percent of the feed water flow rate and must be disposed of properly.

Oxidation of As-III to As-V

About 15 years ago, RO demonstrated that 1 ppm of chlorine was an effective oxidant for converting As-III to As-V in less than five seconds.[6] In that same research, oxygen was shown to be ineffective, and in-situ-formed monochloramine was shown to be 50 percent effective. Later, it was confirmed the partial effectiveness of in-situ-formed monochloramine, but demonstrated that pre-formed monochloramine was

completely ineffective as an oxidant for As-III.[7] This study also showed permanganate, ozone and manganese oxide media (Filox) were effective oxidants for As-III, while chlorine dioxide and UV light were ineffective. In the latter work it was shown as well that interfering reductants, particularly sulfide, slowed the oxidation rate.

Conclusion

A new 5-ppb arsenic MCL has been proposed, which will require thousands of water suppliers to treat for arsenic removal. Activated alumina adsorption, granular ferric hydroxide adsorption, ion exchange, Fe-III coagulation-microfiltration, nanofiltration, and reverse osmosis are proven arsenic removal processes. When choosing among the processes, one must consider arsenic oxidation state, pH, competing ions (especially silicate, phosphate, fluoride and sulfate) and the point of treatment (POU, POE or small community systems). In all these processes, As-V is more easily removed than is As-III, both of which are naturally present in many groundwaters. Chlorine, permanganate, ozone and solid oxidizing media (Filox) are effective oxidants, while oxygen, monochloramine, chlorine dioxide and UV light are ineffective.

References

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About the author

Dr. Dennis Clifford is a professor of environmental engineering and chairman of the Department of Civil and Environmental Engineering at the University of Houston. Also a professional engineer, he has more than 30 years experience in teaching, research and consulting related to water and soil treatment. During the last 20 years, he and his students—notably, Ganesh Ghurye, Jea Tong, C.C. Lin, A.R. Tripp, Eric Rosenblur Phyllis Frank and L.L. Horng—have extensively researched the subject of arsenic specification, oxidation and treatment.