

Arsenic Advances

By Paul Sylvester, Ph.D.

Solutions to an
age-old threat

Arsenic and its compounds have been known to be toxic for millennia. Arsenic trioxide (As_2O_3), often referred to as white arsenic, was a favored poison in the Middle Ages because it had little odor or taste, enabling it to be easily incorporated into the food or drink of a victim. As little as 300 mg can be fatal to an average person.

The symptoms of acute arsenic poisoning—nausea, diarrhea and stomach pains—are similar to those associated with food poisoning or cholera, so deliberate arsenic poisoning was frequently not diagnosed. The use of arsenic trioxide as a poison was so popular with European nobility that arsenic trioxide earned the nickname “inheritance powder” due to its use by young aristocrats unable to await the natural demise of their parents. The development of the sensitive Marsh Test for arsenic by the English chemist James Marsh in 1832 ended the reign of arsenic as an undetectable poison. The effects of chronic arsenic poisoning—continued exposure to low levels over long periods of time—are less dramatic and far slower but can be equally deadly given sufficient time.

Arsenic occurs in groundwater sources in many parts of the world at concentrations usually measured in micrograms per liter ($\mu\text{g/L}$) or parts per billion. The vast majority of arsenic contamination occurs naturally as a result of the weathering of arsenic-rich minerals. However, there are instances in which mining activities or the extensive use of arsenic-containing

pesticides and herbicides over many years has led to the contamination of groundwater supplies.

The best-documented area of arsenic contamination of groundwater is in the Bengal region of the Indian subcontinent. Millions of wells were drilled there in the 1970s to try to reduce mortality rates of the local population due to its reliance on surface water supplies contaminated by microbial pathogens.

At the time, the presence of arsenic in the groundwater was not suspected and the project was hailed as a huge success because the occurrence of waterborne diseases dropped dramatically. It was not until several decades later that the effects of chronic arsenic poisoning, including increased cancers, skin discoloration and ulcers, became apparent. This is now the scene of multinational efforts to combat the problem and remediate the contaminated water supplies.

Close to Home

Some regions of the U.S. also suffer from arsenic contamination of the groundwater, most notably the Southwest, New England and parts of the Midwest. In January 2006, the U.S. Environmental Protection Agency reduced the Maximum Contaminant Level for arsenic from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$, bringing the country in line with the level recommended by the World Health Organization. This tighter limit obliged a large number of public water companies to reduce the level of arsenic in the water they supplied to their customers, and also spurred a major research and development effort to come up with new and improved methods and materials to economically comply with this lower limit.

Currently, there are several technologies that have proven to be effective on a commercial scale. However, the choice of technique is influenced by a number of factors including water

chemistry, waste residuals generation and disposal and simplicity of use.

In groundwater, arsenic occurs in two main forms: arsenite (As(III)) and arsenate (As(V)). Arsenite, the reduced form, tends to occur in relatively anoxic waters under reducing conditions, while arsenate is more stable in oxidizing conditions that have a higher ORP. However, the rate of transformation from arsenate to arsenite (or vice versa) can often be slow, so it is not uncommon to find both arsenic species existing simultaneously in one groundwater source.

Organic arsenic compounds also exist in some waters but, in general, the concentrations are very low and, as a consequence, have little impact on the selection of a water treatment technology.

The Right Approach

One of the most common technologies for arsenic treatment is coagulation/filtration (CF), where an iron (or sometimes aluminum) salt is added to the groundwater to generate an iron hydroxide precipitate in situ. Arsenic is either precipitated as ferric arsenate or adsorbed onto the surface of the iron oxide, which is then removed using a media or membrane filter. A photograph of a CF plant is shown at bottom left. In most installations, an oxidant is added prior to the iron addition to ensure all the arsenic is present as As(V) and to oxidize any soluble ferrous iron (Fe(II)) present in the water. If sufficient iron occurs naturally in the water, additional iron may not be necessary. This approach to arsenic removal is effective and is often the method of choice for large systems where trained operators are readily available. Chemical costs and operating expenses are generally low, but one consideration that is often overlooked is the disposal cost of the waste ferric hydroxide sludges generated during the backwashing of the filter. In many localities, sewer access is not available and, as a consequence, waste disposal is the major O&M cost of the system.

The second major technique for arsenic removal is fixed beds of arsenic-selective adsorbent media. This approach is mechanically simple and involves passing the water through a bed of media where arsenic (and some other species) is selectively removed in



A CF arsenic removal system at Casa Grande, Ariz., designed to treat a flow rate of up to 1,350 gpm.

preference to the main anions found in water, such as chloride, sulfate and bicarbonate. Adsorption is most effective between pH 6.5 and 8.5. At higher pH values, the arsenic capacity drops dramatically and pH adjustment is usually recommended to minimize media change-out frequency and reduce overall treatment costs. Silica (especially at pH values greater than 8.0) and phosphate also interfere by competing with the arsenic for adsorption sites. High levels of ferrous iron also can be problematic because iron hydroxide may precipitate on the media beds, leading to unacceptable pressure drops across the system. Consequently, groundwaters with high iron concentrations are best treated by the CF technique.

Most, if not all, adsorption media will take out both arsenite and arsenate but the capacity for arsenate is many times higher, so oxidation before the adsorption system is generally performed if the water contains significant amounts of arsenite. A decade ago, activated alumina was deemed the best available technology for arsenic



A hybrid arsenic adsorbent media consisting of particles of hydrous iron oxide that have been precipitated within an anion exchange resin bead.

removal. This has been largely superseded by granular adsorbents based on oxides of iron, titanium and zirconium and hybrid media that consist of iron oxide immobilized in a durable polymer matrix. A photograph of a hybrid media is shown above.

The final technology occasionally seen in the field is ion exchange. This technique is a non-selective approach to arsenic removal and employs a standard strong base anion exchange resin to remove arsenic, along with bicarbonate and sulfate, from the groundwater. Unlike adsorption, the effective cycle time for an ion exchange bed is relatively short, so the resin has to be regenerated on a frequent basis, resulting in the generation of waste brine. A number of proprietary low-waste ion exchange systems are in use throughout the country but the disposal of waste brines can still be a major component of operating

expenses if direct sewer disposal is not an option. Unlike adsorption, ion exchange is not influenced to a great extent by pH or the silica concentration but is greatly affected by the concentration of the sulfate in the water because the resin has a greater affinity for sulfate than arsenate.

In high-sulfate waters, regeneration can be frequent, leading to the production of large volumes of waste brine. Arsenite is not removed by anion exchange under normal groundwater pH values because it exists predominantly as the uncharged species H_3AsO_3 . If arsenite is present, the water needs to be prechlorinated to oxidize the arsenite to arsenate, which occurs as the anions $H_2AsO_4^-$ and $HAsO_4^{2-}$ and is thus removed. Ion exchange has the advantage of being able to tackle multiple contaminants (e.g., nitrate, arsenic and uranium) in one process, allowing one system to be used as

opposed to a treatment train.

In summary, there are several commercially available technologies suitable for arsenic removal from drinking water. The technology selected will depend on the particular water chemistry, the skill level of the plant operators and the waste disposal options. Given the numerous factors affecting arsenic removal, it is therefore no surprise that arsenic removal costs are variable and can differ by an order of magnitude or more. *wqp*

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