



Assessing Arsenic Removal Technologies

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Since the U.S. Environmental Protection Agency (EPA) revised the arsenic drinking water standard to 10 parts per billion (ppb), there has been great interest in technologies for removing arsenic compounds from potable water supplies. The good news is that there are many methods that will remove arsenic from drinking water to levels below 10 ppb. The bad news is that the most efficient method is case specific, and depends on the speciation of the arsenic, the pH, the ionic composition of the water, and the size scale of the treatment operation. Cost and convenience issues associated with disposal of the waste from the various technologies must also be considered when selecting a treatment method.

In anticipation of a revised standard, the EPA commissioned a comprehensive study to evaluate the costs and effectiveness of a wide range of arsenic removal technologies (EPA, 2000). The EPA report evaluates several commercially available technologies, including: co-precipitation methods, membranes, ion exchange, and adsorption, and also reports briefly on several emerging technologies. Since publication of the EPA report in December 2000, new laboratory and pilot test data suggest that several of the emerging technologies may become widely accepted due to their low costs and high specificity for arsenic removal.

The quintessence of the arsenic removal problem is the low concentration that must be achieved. Although many organic

compounds on the EPA priority pollutant list must be removed to levels below 10 ppb, most removal methods for organic compounds are not impaired by background electrolytes that are present in all sources of potable water. Because there are no removal technologies that specifically remove only arsenic, removing As(III) (arsenite) and As(V) (arsenate) species concomitantly removes a wide

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range of other compounds that are usually present at much higher concentrations than the targeted arsenic species. Complicating the arsenic removal problem is the fact that arsenic may be present as one of several As(V) species (e.g., H_2AsO_4^- and HAsO_4^{2-}), one of several As(III) species (e.g., H_2AsO_3^- and H_3AsO_3), as an organoarsenical compound (e.g., herbicides), or as an arsenic complex with another dissolved or colloidal species (e.g., FeHAsO_4). At neutral pH, the most common form of As(III) and As(V) are H_3AsO_3 and H_2AsO_4^- , respectively. Therefore, most removal methods focus on removing As(V) anions and uncharged As(III) species.

Common Removal Technologies

The most commonly used method for removing both As(V) and As(III) compounds in water treatment plants involves chemical precipitation using iron

and aluminum salts. Ferric salts are more widely used than aluminum salts since they are generally more effective for removing As(III). Removal of arsenic occurs through chemical adsorption and co-precipitation during the formation of ferric hydroxides. The chemical bond that forms between ferric hydroxides and both As(III) and As(V) species makes this method less susceptible to competition by background electrolytes.

Chemical co-precipitation using ferric chloride has been shown to be effective for removing As(V) to levels below 2 ppb in a number of different source waters. However, these levels are achieved only when there is

a filtration step to remove colloidal arsenic. Removal of As(III) by ferric chloride precipitation is less efficient and is more affected by water composition. Therefore, a pretreatment step that involves oxidation of As(III) to As(V) is often used in conjunction with the co-precipitation methods.

The National Drinking Water Advisory Council has concluded that most of the utilities to be affected by the new 10 ppb standard are small-scale treatment systems serving fewer than 10,000 customers. Small-scale treatment systems are prevalent in the Southwest and are not well suited for co-precipitation as an arsenic removal technique. Co-precipitation methods require a large contact and/or settling basin and a filtration step to remove the precipitates. This makes co-precipitation best suited for

Current Arsenic Studies in the Southwest

A small number of water suppliers have started pilot tests for mitigating arsenic with new technologies. Details about three of these test sites are listed below.

Water Supplier	Technology	Pre-test Arsenic Concentrations	Size of Study	Significant Dates	Companies Involved
Southern California Water Company Century Removal Facility	Testing four different adsorption media: aluminum sorbent, granular ferric hydroxide, surface modified granular activated alumina, activated alumina	14-18 ppb	550 gpm	Start date: October 2001 Finish date: September 2002	Englehard, GEH Wasserchemie GmbH, Alcan, Apyron, AwwaRF. A portion of funding was provided by a local basin management agency – WRD
Southern California Water Company Centralia Removal Facility	Testing ferric-chloride coprecipitation removal method through the existing dual media Fe/Mn filter	20 – 30 ppb	1150 gpm	Start date: April 2002 Finish date: October 2002	HDR Engineering, AwwaRF
California Water Services	Demonstrating Sulfur Modified Iron (SMI) unit	18 ppb	5-7 gpm	Start date: May 2002 Finish date: November 2002	Prima Environmental, SMI, Inc.

The four jars pictured contain adsorption media currently being tested at Southern California Water Company's Century Removal Facility. [Opposite Page] Four vessels at the Century Removal Facility. Photo Credit: Jason Wen

large-scale water treatment facilities that already employ coagulation/filtration unit operations in their process train.

Packed bed methods, such as ion exchange and adsorption, are better suited to small-scale treatment operations than co-precipitation. The main drawback to ion exchange is its low specificity for arsenic removal. Ion exchange methods for removing As(V) anions are inefficient due to competition for exchange sites by background electrolytes that are normally present at concentrations several orders of magnitude greater than As(V). Another drawback to ion exchange is its ineffectiveness for removing uncharged As(III) species or uncharged As(V) complexes.

Although membrane processes are also well suited for small-scale treatment operations, their applicability for arsenic removal appears to be limited. A major drawback to membrane methods is that many source waters require pretreatment to remove organics, particulates, iron, manganese, and scale-forming compounds in order to prevent membrane fouling. Reverse osmosis is capable of removing dissolved arsenic species to levels below 10 ppb. However, the process concomitantly

removes other ions to very low levels, and thus generates large volumes of brines that require disposal. In some cases, co-precipitation with iron salts is combined with microfiltration in order to decrease the operating pressures and the brine volumes generated.

Adsorption with activated alumina is more specific for arsenic removal than membranes or simple ion exchange. The greater specificity results from the formation of a chemical bond between the adsorbent and the arsenic species. The strength of the adsorption is pH dependent, and there is still some competition for adsorption sites by other ions such as

phosphate, silicate, sulfate, and fluoride.

Alumina will remove both As(V) and As(III) species, but competition for adsorption sites with background electrolytes affects As(III) adsorption much more than As(V). This essentially makes alumina useful for only As(V) removal. A drawback to alumina is the strong chemical bonds that are formed between a variety of adsorbates and the adsorbent. The strong bonding limits its regenerability to only 50 to 70 percent of its initial adsorption capacity. In many cases, disposal of the spent media is less expensive than regeneration. Although alumina has been widely used in the past for arsenic removal,

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it may prove less useful with the lower 10 ppb standard, since it appears to be less specific for arsenic binding than iron oxide based adsorbents.



The Centralia Project conducted by Southern California Water Company is testing a ferric-chloride co-precipitation removal method. Photo Credit: Jason Wen

Emerging Technologies

Although still in the developmental stages, two very promising arsenic removal media are granular ferric hydroxide (GFH) and zerovalent iron (ZVI) filings. The operational simplicity of GFH and ZVI filters make them suitable for point of use, individual well-head, or other small-scale treatment systems. Both of these methods involve chemical adsorption of As(III) and As(V) species to iron oxides. Neither media is intended to be regenerated, and the spent adsorbent generally passes the EPA leaching test.

GFH is composed of a poorly crystallized FeOOH and is similar to the mineral akaganeite. GFH tested under field conditions has outperformed activated alumina for both As(V) and As(III) removal

over a wide pH range. Although the GFH appears to be more specific than alumina for arsenic binding, it also suffers from competitive adsorption of phosphate and silicate. Competitive displacement of arsenic by sulfate is minor. Since complex formation of arsenic species with iron oxides is known to be extremely rapid, the removal process appears to be limited by diffusion of the arsenic species into the porous iron oxides.

ZVI filings have been used for about 10 years as a reactive medium for in situ treatment of groundwater containing both organic and inorganic contaminants. Additionally, ZVI filings are commonly being used in Bangladesh as a point of use water treatment method. Several laboratory investigations using columns packed with ZVI filings have reported that the filter media removes As(V) and As(III) compounds to levels below 1 ppb. Long-term column experiments lasting more than one year in duration have shown that the capacity for ZVI media to remove arsenic compounds is several orders of magnitude greater than conventional adsorbents. In packed bed systems, arsenic removal by ZVI appears to be limited by the rate of iron corrosion. However, for influent arsenic concentrations lower than 100 ppb, the iron corrosion rate appears to be sufficiently fast to maintain complete arsenic removal even in anaerobic waters.

Some investigators have reported that As(V) compounds may be reduced by ZVI to As(III), but others have reported no reduction of As(V), even after more than

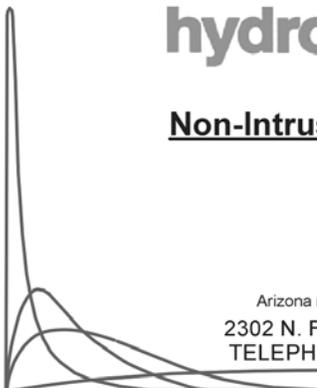


California Water Services is testing this Sulfur Modified Iron (SMI) unit on a 5-7 gpm side stream from an 800 gpm well. Photo Credit: Dick Wrath

one year of contact time. Reduction notwithstanding, the removal mechanism for both As(III) and As(V) compounds involves chemical adsorption to iron oxides produced from corrosion of the iron. Some investigators have reported more favorable adsorption of As(III) versus As(V), while others have reported more favorable adsorption of As(V). Differences in the relative ease of As(V) versus As(III) removal can likely be attributed to differences in iron oxide morphology, iron oxidation state, water chemistry, and pH.

Given the high affinity of iron oxides for complex formation with both As(V) and As(III) species, iron oxide based adsorbents appear to be the most promising for arsenic removal in small treatment systems. This may be especially true in the Southwest where much of the arsenic occurs in the +3 oxidation state, making treatment with activated alumina impractical. The optimal system design, whether it be packed or fluidized beds of GFH, ZVI, or some other engineered iron oxide media, will depend on the specific treatment scenario.

Source
U.S. Environmental Protection Agency (2000). Technologies and Costs for Removal of Arsenic from Drinking Water, EPA 815-R-00-028. www.epa.gov/safewater/ars/techcosts.pdf



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