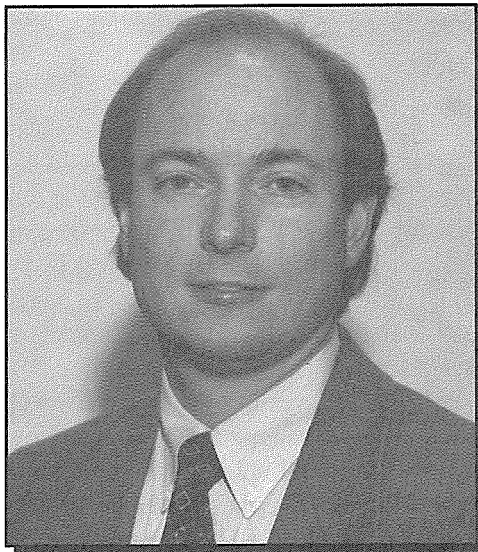


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ARSENIC REMOVAL TREATMENT TECHNOLOGIES FOR DRINKING WATER SUPPLIES

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Introduction

The U.S. Environmental Protection Agency (EPA) is in the process of re-evaluating the current arsenic maximum contaminant level (MCL) of 50 micrograms per liter ($\mu\text{g/L}$). It is anticipated that the EPA will publish proposed arsenic limitations by November 1995. Indications are that the revised MCL will likely be in the range of 2 to 20 $\mu\text{g/L}$. The revision of the arsenic MCL may require many public water systems to implement treatment for arsenic removal. In a recent study (Reid 1994), the EPA estimates that in the United States more than 27 million people are exposed to arsenic levels greater than 2 $\mu\text{g/L}$ and that 9 million people are exposed to arsenic levels exceeding 5 $\mu\text{g/L}$. Consequently, the revised MCL will have far-reaching effects.

Several treatment techniques for the removal of arsenic have been shown to be effective (Sorg and Logsdon 1978). These include coagulation, lime softening, ion exchange, and reverse osmosis. However, the implementation of arsenic removal technologies have been limited because most water supplies can meet the current MCL of 50 $\mu\text{g/L}$. Consequently, there is little or no operational data available to confirm arsenic removal technologies to the 20 $\mu\text{g/L}$ range.

This paper presents a survey of treatment alternatives that have the potential of removing arsenic from drinking water supplies. Treatment techniques to be presented include the following:

- chemical coagulation
- lime softening
- ion exchange resins

- activated alumina adsorption
- membrane separation
- coagulation and microfiltration
- in situ aquifer treatment

Chemical Coagulation

Conventional water treatment facilities routinely use chemical coagulants to aid in the removal of suspended solids. The coagulant is mixed rapidly with the raw water resulting in a metal hydroxide precipitate or floc. The floc will enmesh and destabilize suspended solids. The floc also has the ability to coprecipitate and adsorb arsenic in water.

The most commonly used coagulation chemicals are alum (aluminum sulfate) and ferric (ferric chloride). At an initial arsenic concentration of 50 $\mu\text{g/L}$, Gullledge and O'Connor (1973) found that as much as 99 percent of influent arsenic can be removed by ferric sulfate coagulation, and as much as 93 percent of arsenic can be removed by alum coagulation. The highest removal rates for ferric sulfate occurred at a pH between 5 and 7.5. Removal rates decreased by a few percentage points at a pH of 8. The highest removal rates for alum occurred at pHs between 5 and 7. Removal rates dropped off by 10 to 20 percent at a pH of 8.

A more recent study (Cheng et al. 1994) concluded that ferric was a more effective coagulant than alum for removal of arsenic. In this study, a 20- $\mu\text{g/L}$ arsenic concentration was reduced to 0.5 $\mu\text{g/L}$ using less than 10 mg/l ferric. No pH adjustment (acid) was required to achieve this level of removal. To achieve a high level of arsenic removal with alum, it will be necessary to adjust the pH to around 6.2 to 6.5 by acid addition to achieve optimum coagulation. This research indicates that when influent arsenic levels were greater than 13 $\mu\text{g/L}$, alum at 30 $\mu\text{g/L}$ dosage and pH adjusted to 6.3 could not produce an effluent arsenic concentration of 0.5 $\mu\text{g/L}$. It is interesting to note that there appeared to be no correlation between turbidity removal and arsenic removal. However, good turbidity removal is required for good arsenic removal.

Arsenic is found in water in several forms depending on the pH and redox potential of the water. In the oxidized form, arsenate has a +5 valence or oxidation state and has the form of H_2AsO_4^- at a pH of 7. In the reduced form, arsenite has a +3 valence or oxidation state and has the form of H_3AsO_3

between the pH range of 2 to 9. Surface waters will typically contain the oxidized arsenate form of arsenic while groundwaters may contain either the reduced form—arsenite, or the oxidized form—arsenate, or a combination. Arsenite, the reduced form of arsenic, may be more toxic to biological systems than the oxidized arsenate species.

Coagulation is much more effective at removing the oxidized arsenate form than the arsenite form. It has been shown (Sorg 1977) that alum and ferric coagulation are only capable of removing 20 percent and 60 percent of arsenite at an initial concentration of 300 $\mu\text{g/L}$, respectively. Consequently, it will be necessary to oxidize the arsenite prior to coagulation treatment. This can be accomplished by chlorine, ozone, or potassium permanganate. Depending on the natural organic material content of the raw water, it may not be desirable to use chlorine for arsenite oxidation due to the potential formation of chlorinated hydrocarbons.

The sludge produced by coagulation treatment may contain high levels of arsenic. The arsenic concentration will depend on the influent water arsenic concentration and the coagulant dosage. Current EPA regulations classify waste streams with arsenic concentrations greater than 5 mg/l as toxic waste. It is likely that the coagulant sludge will contain concentrations greater than 5 mg/l. For example, at a removal rate of 45 $\mu\text{g/L}$ and a ferric dosage of 30 mg/l, the sludge theoretically will contain around 114 mg/l arsenic at a sludge concentration of 3 percent solids (3,800 milligram per kilogram [mg/kg] on a dry weight basis.) This sludge can be landfilled if it is dewatered and passes the toxicity characteristics leaching procedure (TCLP). The TCLP test is conducted at a pH of 4.93 ± 0.05 , which is near the point of minimum solubility of aluminum and iron hydroxides. Limited tests have indicated that precipitated arsenic bearing sludges have passed the TCLP. However, each sludge must be tested to confirm its leaching characteristics. If the sludge fails the TCLP for arsenic, it will require disposal at a hazardous waste disposal site.

Lime Softening

Water treatment facilities often use lime softening for waters that require hardness removal. The addition of lime removes hardness by raising the pH of the water to a level at which most of the

hardness constituents are insoluble, and they precipitate out of solution. Lime softening is similar to coagulation in that lime mixed with the water produces a chemical floc, which is subsequently removed by sedimentation and filtration. Additional chemicals must be added after the hardness has been reduced to lower the pH to acceptable potable levels. It has been reported (Sorg 1977) that arsenic levels can be reduced 95 percent by lime softening at pH levels of 10.8 and higher. Removal efficiencies dropped off rapidly at lower pHs, and only about 30 percent of arsenic was removed at a pH of 8.5. Lime softening treatment is typically more expensive than coagulation and will probably not be recommended for arsenic removal unless the water requires softening.

The sludge generated by this treatment method will likely have arsenic concentrations similar to the coagulant sludges. Because lime sludge is composed mostly of calcium carbonate, it may dissolve at the low pH of the TCLP and release the precipitated arsenic. This should be confirmed by pilot testing prior to full-scale design.

Ion Exchange Resins

The principal of operation in ion exchange processes is the transfer of select ions in solution for an ion fixed to the surface of an ion exchange resin. The resins can be designed for the preferential removal of certain ions. The selectivity of the ions removed varies with the type of exchange resin, the ionic strength, the relative amounts of different ions, water temperature, and other factors. Arsenic found in natural waters is almost exclusively found in an oxyanion form such as arsenate (AsO_4^{-3}) or arsenite (AsO_2^{-1}). Therefore, an anionic ion exchange resin will be used for removing arsenic.

Pilot-scale testing of ion exchange was performed for the Fallon, Nevada, Naval Air Station (Hathaway and Rubel 1987). The groundwater contained arsenic levels ranging from 80 to 116 $\mu\text{g/L}$. Although these researchers anticipated the ion exchange medium (a strong-base anion resin) was potentially capable of removing high levels of arsenic, the pilot unit experienced breakthrough after only 300 bed volumes. It was concluded that this occurred because sulfate in the water had a higher affinity for the resin than the arsenic did. The effi-

ciency of the ion exchange process can therefore be impacted by other, more abundant competing ions such as sulfate. Therefore, the ion exchange process may have limited applicability for the removal of arsenic to the future MCL levels.

After treating a certain volume of water, the ion exchange resin becomes saturated with exchanged ions and must be regenerated. The regeneration process removes the ions exchanged to the resin and restores exchangeable ions to the resin. This produces a concentrated brine solution, which contains the contaminants that were removed from the water along with other substances that were attached to the resin. The regeneration of ion exchange resins will produce a reject brine solution, which contains a high level of arsenic. The brine solution will need to be treated before disposal to precipitate the arsenic. The resulting sludge can then be dewatered and should have characteristics similar to the activated alumina regenerated waste sludge.

Activated Alumina Adsorption

Adsorption is a process where contaminants in water are removed by attaching to the surface of some media. Activated aluminum has been shown to provide high removals of arsenic from water. Activated alumina is a granular compound composed of Al_2O_3 . The arsenic is removed from the water by adsorption onto the activated alumina.

Pilot-scale testing of activated alumina at Fallon, Nevada (Hathaway and Rubel 1987), indicated that arsenic was removed to below detection limit (5 $\mu\text{g/L}$) for approximately 8,000 bed volumes from an initial arsenic concentration of 90 $\mu\text{g/L}$. The arsenic removal was optimized by lowering the pH of the feed water to 5.5. The pilot system treated approximately 15,000 bed volumes before exceeding an effluent arsenic concentration of 50 $\mu\text{g/L}$. At a limit of 20 $\mu\text{g/L}$ arsenic, the pilot unit treated approximately 12,000 bed volumes of water.

Once the activated alumina is exhausted, it can be either disposed of or regenerated. The amount of arsenic contained in the activated alumina will depend on the concentration of arsenic in the feed water and other competing ions such as fluoride. Regeneration is accomplished by rinsing the activated aluminum with a 4 to 5 percent NaOH solution. In the Fallon study (Hathaway and Rubel

1987), the regenerated water solution contained approximately 23 to 40 mg/l arsenic at a pH of 12. This concentration exceeds the EPA limit of 5 mg/l and is considered a toxic and hazardous waste. However, the arsenic can be precipitated out of solution by lowering the pH to a range of 5 to 6.5. Preliminary testing indicates that the dewatered sludge can pass the TCLP test for arsenic. If regeneration is not practiced, the exhausted activated alumina will likely pass the TCLP test and can therefore be disposed of in a sanitary landfill.

Membrane Separation

Membrane separation refers to use of selective membranes such as reverse osmosis to remove arsenic. Reverse osmosis membranes are capable of removing a high percentage of almost all inorganic ions, turbidity, organic material, bacteria, and viruses. Water has a natural tendency to pass through a permeable membrane from an area of low ion concentration to an area of high ion concentration to equalize the ion concentrations on both sides of the membrane. This is referred to as osmosis. In the reverse osmosis process, pressure is applied (200 to 600 pounds per square inch [psi]) to one side of the membrane to force the water across the membrane from an area of high ion concentration to the area of low ion concentration in reverse of the water's natural tendency. Hence, the name reverse osmosis. Reverse osmosis has been used in industrial and laboratory applications where high-purity water is required. Although this process is expensive on a large scale, it has been used by a few water treatment facilities and water reuse plants where waters with high mineral content made it necessary to remove a broad spectrum of contaminants that cannot be removed by other treatment methods.

It has been reported that reverse osmosis was capable of removing arsenic from a concentration of 95 to 8 $\mu\text{g/L}$ in Sarasota County, Florida (Sorg et al. 1980). This removal rate is approximately 92 percent. Higher removal rates have been indicated by reverse osmosis manufacturers. Reverse osmosis also has the advantage of being capable of removing other undesirable contaminants such as lead, nitrates, and total dissolved solids (TDS) in addition to arsenic. However, it is an expensive treatment process and requires expensive pretreat-

ment to protect the membranes. The water produced by reverse osmosis is so pure that it has a poor buffering capacity and is corrosive. Another disadvantage of reverse osmosis is the amount of water that is rejected as brine, which can amount to 20 percent of the raw water. This has a large impact in locations where water is either scarce and/or is expensive. Reverse osmosis may be a good choice for arsenic removal especially if there is a concern with the presence of other substances, such as radionuclides, which cannot be cost-effectively removed with other treatment methods.

The reject water produced by reverse osmosis in the above-referenced study contained an arsenic concentration of 190 $\mu\text{g/L}$. This level is well below the EPA limit of 5 mg/l for toxic wastes. It is anticipated that the reject water can be discharged directly to a sanitary sewer. However, depending on the arsenic concentration and flow rate, the reject water can result in an increased level of arsenic in the wastewater treatment plant sludge.

Coagulation and Microfiltration

Microfiltration is a membrane process that is capable of filtering out particles down to a size of around 0.2 microns. Microfiltration systems operate at low pressures of around 20 to 30 psig. Coagulation will produce a floc that is capable of coprecipitating and adsorbing arsenic from water. Therefore, arsenic can be removed from water by first coagulating the water and then passing the water through a microfiltration unit. Current pilot testing at the Irvine Ranch Water District (Chang et al. 1994) has indicated that coagulation and microfiltration can reduce arsenic concentrations from 30 to 40 $\mu\text{g/L}$ to less than 0.5 $\mu\text{g/L}$ using around 10 mg/l ferric chloride coagulant dosage. The microfiltration unit can achieve higher arsenic removal than a conventional filter because of its ability to remove very small floc particles. This ability to remove small floc particles may be particularly important when treating groundwater of very low turbidity. Low turbidity groundwater may not have sufficient nucleation sites to generate large floc during coagulation.

The results of the Irvine Ranch Water District pilot testing can be summarized as follows:

- With microfiltration, ferric chloride was a more effective coagulant than alum for arsenic

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removal. To achieve the same level of arsenic removal, the ferric chloride dosage required was about half that required for alum.

- Microfiltration is more effective than conventional filtration in removing fine particles formed during enhanced coagulation, and thus, consistently achieved higher arsenic removal than a conventional filter.
- Microfiltration can also reduce the ferric chloride dosage required for the effective coagulation of arsenic. A ferric chloride dosage of 10 mg/l was required to achieve an effluent arsenic concentration of less than 0.5 µg/L.

This process has not been used in a full-scale arsenic removal application to date. However, this process appears to hold much promise of being able to achieve high arsenic removals especially with groundwater sources.

The coagulant sludge rejected by the microfiltration unit will contain high levels of arsenic. The sludge characteristics from this treatment process should be very similar to the coagulant sludge discussed previously. The pilot testing indicated that the sludge produced from the microfiltration unit will settle quickly. It appears that some compression of the sludge occurs in the microfiltration unit, which yields a sludge of higher density than conventional coagulation/sedimentation. The sludge will require dewatering and TCLP testing prior to disposal. The sludge quantities should be significantly less than the quantities generated by conventional coagulation because of the reduced coagulant dosage with microfiltration. This will be a significant benefit in terms of cost and environmental impact when sludge disposal is considered.

In Situ Aquifer Treatment

For groundwater sources with high arsenic concentrations, it may be possible to immobilize the soluble arsenic in the ground. This technique has been applied to the removal of iron and manganese in groundwater supplies. Under oxidizing conditions, iron and manganese will precipitate as insoluble iron and manganese oxyhydroxides. Arsenic will tend to adsorb to the iron and manganese precipitates in the soil matrix and will be removed as the water flows through the aquifer to the well. The iron and manganese oxyhydroxides must first be

precipitated and remain insoluble for the adsorption to be permanent and self-sustaining. Regulatory agencies usually consider aquifer treatment to be a feasible approach to the treatment of contaminants such as iron and manganese, which relate mainly to aesthetic concerns. The use of this indirect method for arsenic removal has not been documented to date. This method of arsenic removal will be site-specific depending on the geology, hydrogeology, and geochemistry of the aquifer.

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