

Report on Practical Methods for Removal of Arsenic from Subsurface Aquifers and Drinking Water Systems

By

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Introduction

In some areas of the world, arsenic presence in subsurface aquifers and drinking water systems is a potentially serious human health hazard. In certain areas of Bangladesh and also in parts of the West Bengal district of India, for example, a majority of shallow subsurface aquifers and tube wells are contaminated with arsenic at levels which are orders of magnitude above the recommended arsenic level of 50 micrograms/liter. Serious adverse health effects, including human mortality, from arsenic contamination of drinking water are well documented by numerous scientific studies (ref.1). Removal of arsenic from drinking water is therefore a worldwide priority.

This summary report is concerned with practical and proven methods for the removal of arsenic from groundwater aquifers and drinking water systems. A separate section of this report summarizes point-of-use arsenic removal methods for individual households and small groups of households. It should be noted that methods for arsenic removal in point-of-use systems are not always able to be scaled up for large municipal water system applications. Other references (refs. 2, 3, 4, 5) cover point-of-use systems well and should be consulted for any such arsenic removal systems not covered by this report.

Pre-oxidation of Arsenic (III) to Arsenic (V)

One significant problem encountered in the removal of arsenic from groundwater aquifers and municipal water systems is that arsenic exists as both arsenic (III) compounds and arsenic (V) compounds in water. Arsenic (III) compounds are primarily non-ionic whereas arsenic (V) compounds are primarily ionic at normal drinking water pH levels (ref. 6). Arsenic (III) compounds, or arsenites, are therefore not always readily removed from drinking water by methods that are very effective for removal of arsenic (V) compounds or arsenates. It is sometimes necessary to pre-oxidize any arsenites present to arsenates in order to effectively remove arsenic from drinking water to safe levels. An oxidant that itself or its' products of oxidation are not toxic must be introduced into the drinking water to accomplish this.

Oxidants that are most commonly used include oxygen (introduced as air), ozone, hydrogen peroxide, chlorine, sodium hypochlorite, potassium permanganate, solid iron (III) or manganese (IV) compounds and water soluble iron (II) compounds + hydrogen peroxide, also known as Fenton's reagent (refs. 7, 8). Table 1 summarizes the advantages of each oxidant and also the disadvantages of each oxidant for use in converting arsenites to arsenates prior to most technologies for arsenic removal from drinking water.

One disadvantage of the above mentioned oxidants is that they each add some degree of extra costs and complexity to the arsenic removal system. A concern where chemical reagents are required is that the correct dosage of the oxidizing agent in the raw water be maintained for optimum performance of the arsenic removal system. Well trained manpower, safe chemical storage facilities and accurate chemical metering devices are all required in those circumstances. This may not be possible under all circumstances.

In some parts of the world where there is arsenic contamination of drinking water, none of the oxidants mentioned in Table 1, except oxygen from ambient air, are readily available at low cost. These areas are either have minimal financial resources available for water purification or primarily have a barter instead of a money economy and thus limited resources to buy any of the other oxidation agents at either local or world market prices. Oxygen, however, has a slow rate of arsenite oxidation primarily because it is not very soluble in water. The rate of arsenites oxidation to form arsenates is therefore limited in the case of oxygen by the rate of oxygen dissolving in the drinking water to be treated. In order to increase the arsenite reaction rate, additional equipment such as aerators to more vigorously mix the air with the water may be needed which increase the system capital and operating costs. Oxygen in air, however, can be practical for point-of-use arsenic removal systems where small volumes of raw water can be exposed to air in intimate contact for long time periods prior to use for drinking or cooking purposes.

Table 1

**Comparison of Methods for Oxidation of Arsenites to Arsenates
Prior to Precipitation/Coagulation for Arsenic Removal from Water**

Oxidation Method	Advantages of Method	Disadvantages of Method
Oxygen (from air)	Oxidation agent is readily available everywhere in the world and is not hazardous	Oxidation is slow and additional equipment to speed it up increases system capital and operating costs
Ozone	Oxidation agent is generated at point of use which reduces exposure to ozone	Ozone is a known health hazard and the oxidation system has high operating and maintenance costs
Hydrogen Peroxide	The oxidation agent is a safe solution that can be manually or automatically metered in	The oxidation reaction may be too slow for practical use and oxidant solution can lose oxidation power
Liquid Chlorine	The oxidation reaction is very fast and completely removes any potential disease carriers	The oxidant is difficult to store or transport safely and system parts can be degraded by corrosion
Hypochlorite	The oxidation reaction is relatively fast and removes any potential disease carriers	The system parts can be degraded by corrosion and oxidant solution can lose oxidation power with time
Permanganate	The oxidation agent is a safe solution that can be manually or automatically metered in	The oxidation reaction results in a solid manganese compound that may interfere with system operation
Iron (III) or Mn (IV) Compounds	The system design allows oxidation and filtration steps to be combined in one unit	Iron (III) compounds can hydrolyze to form gelatinous solids which may plug up the oxidation/filtration bed
Fenton's Reagent	The oxidation rate is faster than hydrogen peroxide and oxidant solution more stable	Operator error in mixing the iron (II) compound with the hydrogen peroxide can degrade the results

Precipitation and Coagulation Methods

Precipitation and coagulation methods for arsenic removal from water depend upon the co-precipitation of both water insoluble arsenates and inorganic oxides of other metals. The water insoluble inorganic oxides are produced by the hydrolysis in the arsenic contaminated water of added coagulants such as alum (aluminum sulfate), ferric chloride or ferric sulfate. The coagulant must be uniformly mixed into the arsenic contaminated water in order to obtain maximum arsenic removal efficiency. The resulting gelatinous precipitate occludes water insoluble arsenic compounds such as arsenates into the structure. In addition, water soluble arsenic compounds such as arsenites can also be electrostatically bound to the external surface of the gelatinous precipitate. If alum is the coagulant, the pH of the contaminated water must be very close to neutral pH whereas ferric salts are useful coagulants over a wider pH range (ref. 9). The usual range of coagulant addition to the contaminated water is between 5 and 50 milligrams/liter. The amount of coagulant used can be significantly reduced by the addition of polymers or colloidal clays during the mixing of the coagulant with the arsenic contaminated water (ref. 10). This can substantially reduce the operating cost of the arsenic removal system.

Many aquifers where arsenic contamination is present also contain phosphates or silicates in the water. The presence of phosphates or silicates in the contaminated water reduces the efficiency of arsenic removal (ref. 11) and this also must be taken into consideration when precipitation and coagulation is the chosen arsenic removal method.

Another consideration when precipitation and coagulation methods are used for arsenic removal from water is the filtration step (ref. 12). Gravitational means are usually employed to initially separate the insoluble gelatinous precipitate from the treated water. Subsequent to that, filtration is used to separate any small particles of precipitate not removed by gravitational means in order to maximize arsenic removal efficiency. It is very important that the fluid velocity through the filter be low so that the smallest possible particles of precipitated arsenic are removed from the aqueous phase. The filter must also be frequently backwashed to prevent blockage of parts of the filter. If that occurs, the contaminated water flow through the filter will be channeled through the unblocked parts thus increasing the actual fluid velocity which in turn decreases the arsenic removal efficiency. In addition, it is very important for high arsenic removal that the gelatinous precipitate formed is not broken up into smaller particles by high velocities and turbulent flow areas that might be encountered in the system during the coagulant mixing, co-precipitation, gravitational separation or filtration steps.

Sand/anthracite filters have been found to be effective in removing traces of arsenic from groundwater when utilized as part of a precipitation based arsenic removal system that has an efficient gravity separator prior to the filter. Such a system has successfully removed arsenic from contaminated groundwater at an arsenic chemicals manufacturing facility to below 25 micrograms/liter when operated at low fluid velocity and with frequent filter backwash to prevent channeling (refs. 13, 14). The system utilizes iron (III) compounds as the coagulant and Fentons' Reagent to oxidize any arsenites present in the contaminated water into arsenates prior to the coagulation process.

Adsorption Methods

Adsorption methods have been successfully applied to the high efficiency removal of arsenic from groundwater and subsurface aquifers. Adsorptive media that have been most widely used are activated alumina, ion exchange resin, elemental iron or iron compounds, organic polymers, kaolin clay and silica sand. In some cases more than one of the media mentioned above are used together in order to maximize the adsorption of arsenic compounds. Adsorption media may also be used in combination with oxidants such as manganese compounds to pre-oxidize any arsenites present to arsenates which are more efficiently adsorbed from the contaminated water. Prefiltration of the contaminated water may also be required in order to remove particulate matter that can deactivate the adsorption media and/or physically plug the adsorption bed. Table 2 summarizes the advantages and disadvantages of each of the above mentioned adsorption media for the removal of arsenic from contaminated water.

Table 2

Comparison of Methods for Adsorption of Arsenic Compounds from Contaminated Groundwater or Subsurface Aquifers

Adsorption Medium	Advantages of Method	Disadvantages of Method
Activated Alumina	Very efficient removal and the adsorbent can be regenerated in situ to extend the useful life	Adsorption efficiency is highest only at low pH and arsenites must be pre-oxidized to arsenates before adsorption
Ion Exchange Resin	Removal efficiency independent of water pH and the adsorbent can be also be regenerated in situ to extend the useful life	Sulfates, nitrates or dissolved solids reduce adsorption efficiency and must monitor removal efficiency to prevent adsorbent saturation with arsenic
Iron or Iron Compounds	Higher removal efficiency at lower cost than some of the other adsorbents and also oxidizes arsenites to arsenates.	Adsorption efficiency is highest only at low pH and the adsorbent is not regenerable in order to extend life
Organic Polymer	Removal efficiency optimized by composition of adsorbent and is regenerable in situ	Adsorbent cost is higher than others and other water contaminants such as dissolved solids reduce efficiency
Kaolin Clay	Low cost adsorbent available worldwide and can be in situ regenerated to extend life	Adsorption efficiency lower than most other adsorbents and other water contaminants can deactivate it
Silica Sand	Low cost adsorbent available worldwide and can be in situ regenerated to extend life	Adsorption efficiency lower than most other adsorbents and other water contaminants can deactivate it

Membrane Methods

Membrane methods have been applied primarily to purify brackish water or seawater for use as drinking water. In the most prevalent technology, reverse osmosis, a high pressure is applied to the untreated water on one side of a permeable polymeric membrane. The water flows through the membrane whereas most of the water contaminants are retained. Not only are inorganic contaminants such as arsenic, lead and iron removed from the treated water, but pathogens and hazardous organic contaminants are removed (ref. 15).

The water thus produced is very pure, but any residual impure water that does not pass through the membrane contains a high concentration of contaminants and is totally useless. It becomes a waste product that must be disposed of. Since reverse osmosis has primarily been used for brackish water or sea water, the primary use is to produce drinking water in coastal locations. Successful application to the removal of heavy metals such as arsenic has not been widely reported although it could be used in these cases. Colloidal contaminants in the contaminated water can also foul the membranes so pretreatment to remove them may be required. The membranes can also be damaged by oxidizing agents, required to oxidize any arsenites present to arsenates, that may be present in the contaminated water.

Capital and operating costs of reverse osmosis systems can also be high relative to alternate methods especially for small scale applications. Membrane systems are therefore most suited for large scale applications where multiple contaminants must be removed from the contaminated water.

Point-of-Use Methods

As previously stated, point-of-use methods for removal of arsenic from groundwater or shallow aquifers are not the main thrust of this report. However, experience with these methods in Bangladesh, India and elsewhere indicate success with them in small communities, individual households or small groups of households seeking to remove arsenic from their drinking water source. Table 3 summarizes the technical approaches used in selected point-of-use methods for removal of arsenic. However, the advantages and disadvantages are not discussed in this report and some of these are presently unknown or even in dispute. Point-of-use methods summarized include:

1. Coagulation/precipitation/adsorption/filtration
2. Oxidation/coagulation/precipitation/filtration
3. Adsorption only
4. Oxidation/filtration/adsorption
5. Adsorption/filtration

There are therefore several methods that can be applied to a given contaminated water source, but it is not clear which is best technically or the most economically for a specific field application. Given the wide variation in arsenic concentrations in different locations as well as differences in water quality before treatment and that desired after treatment,

apples-to-apples comparison of the above mentioned arsenic removal methods may not be possible for many potential applications.

It should also be noted that some of these arsenic removal systems are undergoing field trials to determine the technical advantages/disadvantages of the method and also determine the actual installed and operating costs under field conditions. This report covers a period of time up to 2005 but does not purport to be a comprehensive study of arsenic removal systems for drinking water purification.

Table 3

Point-of-Use Methods That Have Been Applied for Arsenic Removal from Groundwater or Shallow Aquifers

Removal Method Name	Summary of Known Operating Principles
Double Bucket or BUET	Coagulation/co-precipitation/adsorption (Bucket 1) followed by sand filtration (Bucket 2)
DPHE or Danida	Oxidation/coagulation/co-precipitation (stirred tank) followed by sand filtration (second smaller tank)
AIPH in India	Mixing/oxidation (Tank 1) followed by flocculation (Tank 2) followed by sedimentation (Tank 3) followed by filtration (Tank 4)
Alcan	Activated alumina adsorption in a two bucket series
BUET Activated Alumina	Oxidation/coagulation/co-precipitation/adsorption/filtration followed by activated alumina adsorption
Sidko/Pal/Trockner	Aeration /filtration followed by ferric hydroxide adsorption
Sono-3-Kolshi	Sand/iron/brick filter (Bucket 1) followed by sand/charcoal/brick filter (Bucket 2) followed by clean water collection (Bucket 3)
Sono 45-25	Iron filings oxidation (Bucket 1) followed by sand filtration (Bucket 2)
Read-F	Copolymer/cerium oxide adsorption followed by sand filtration
SAFI	Kaolin adsorption simultaneous with ferric oxide oxidation
Tetrahedron	Chlorination/pre-filtration (Column 1) followed by ion exchange (Column 2)

Acknowledgement

The author of this summary report acknowledges the assistance of the excellent published and unpublished work done by others regarding point-of-use systems for arsenic removal from drinking water and shallow aquifers in making this report possible. Special thanks are given to the previous work of Professor Ahmed of Bangladesh University of Engineering and Technology (BUET), Professor SenGupta of Lehigh University and his colleagues in India, Mr. Johnston of UNICEF in Bangladesh, Drs. Minnatullah and Talbi of World Bank and Mr. Chand of Chand Associates.

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