

ARSENIC REMOVAL FROM DRINKING WATER: A HANDBOOK FOR COMMUNITIES

NADIM R. KHANDAKER,
PATRICK V. BRADY,
AND
JAMES L. KRUMHANSL

*Contact Information: Nadim Khandaker -
nadimkhandaker@hotmail.com; Pat Brady and
Jim Krumhansl - Sandia National Laboratories,
Albuquerque, New Mexico, 87185- 0750,
pvbrady@sandia.gov and jlkrumh@sandia.gov*



SANDIA NATIONAL LABORATORIES
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UNITED STATES OF AMERICA

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PREFACE

“Sometimes the road to hell is paved with good intentions”. This certainly was the case during the green revolution of the 1960’s when prominent world organizations promoted the tapping of groundwater in Bangladesh for pathogen-free drinking water. Unlike untreated surface water, groundwater was assumed to be clean and free of the organisms that led to widespread waterborne diseases such as cholera, diarrhea, and typhoid fever. Now over 97% of the population in Bangladesh consumes groundwater from borehole wells - locally known as tubewells (British Geological Survey, 2000; UNICEF, 2000) that are typically pumped to the surface using hand-operated pumps. Meanwhile groundwater utilization soared elsewhere in the developing world as well. Decades later, this well-intentioned public health measure is showing an ugly side as millions are being slowly poisoned by drinking and cooking with groundwater once thought safe, but now known to be contaminated with arsenic.



Arsenic contamination of drinking water is a global problem that will likely become more apparent in future years as scientists and engineers measure the true extent of the problem. In the meantime, arsenic contamination in the developing world has somewhat by accident focused attention on the often substantial arsenic contamination of rural, agricultural, and urban groundwater in the developed world.

Arsenic poisoning is preventable though as there are several methods for easily removing even trace amounts of arsenic from drinking water. These can be applied from the scale of large cities to single households. Doing it cheaply and in the most effective fashion though requires a clear understanding of treatment options, as well as arsenic chemistry and sampling procedures. Some traditional treatment methods designed to lower hardness or remove iron (e.g. lime softening or iron removal by coagulation) occasionally remove arsenic as well. Even more arsenic-specific treatment approaches have been developed in the last decade though and many are making their way into practice. All tend to rely on a small number of common chemical processes. We believe that the principles underlying arsenic removal are sufficiently well understood that arsenic-affected communities should be able to choose the right arsenic removal approach for their situation the first try. To that end, here we critically review the important features of arsenic removal technologies; where

technologies work, and where they won't. In addition, we outline arsenic chemistry and the sampling procedures that are critical to successful arsenic removal strategies.

Glossary

AA	Activated alumina
AAFS50	Ferric-coated activated alumina
As	Arsenic
ASR	Aquifer storage and recovery
BCSIR	The Bangladesh Council of Scientific and Industrial Research
CCA	Chromated copper arsenate
CMF	Coagulation/Microfiltration
EBCT	Empty bed contact time
EDR	Electrodialysis reversal
EPA	U.S. Environmental Protection Agency
GFH	Granular ferric hydroxide
GIM	Granular iron media
IX	Ion exchange
MCL	Maximum contaminant level (in drinking water)
MG	Million gallons
MGD	Million gallons per day
M&O	Maintenance and operation
MIT	Massachusetts Institute of Technology
NF	Nanofiltration
O&M	Operations and maintenance
OCETA	Ontario Center for Environmental Technology Advancement
PRB	Permeable reactive barrier
RO	Reverse osmosis

CHAPTER 1 INTRODUCTION

Although arsenic contamination is a worldwide problem, some of the most affected regions lie in the flood plains of the great rivers of Bangladesh, Nepal, and West Bengal, India (Ahmed, 2003; Bagla and Kaise, 1996; Murphy and Guo, 2003; Neku and Tandukar, 2003). In Bangladesh alone, seventy million people are impacted (British Geological Survey, 2000; UNICEF, 2000). Problems associated with drinking groundwater were first noticed in Bangladesh by healthcare workers in the early 1990s (Personal Communication to NRK, Dhaka Community Hospital). At the time, Dhaka Community Hospital was conducting health camps in Western Bangladesh, which borders arsenic-affected regions of West Bengal province, India. Healthcare workers observed skin lesions in the local population and linked it to the presence of arsenic in the drinking water. Since then, numerous organizations have documented the plight of the affected communities: farmers unable to work their fields because of keratosis in the palm to the extent that they cannot handle tools; early deaths of family earners from cancer due to chronic arsenic poisoning, and increases in the numbers of stillborne babies. The fallout from chronic arsenic poisoning is not just physical - there are also severe negative social consequences. Severe skin lesions from chronic arsenic poisoning are mistakenly stigmatized as leprosy. As a result entire families are ostracized and isolated. There are reports of marriages breaking up as a consequence of chronic arsenic poisoning.



Skin lesions on feet and palm from chronic arsenic poisoning (with permission: Dr. Mickey Sampson: Resource Development International, Cambodia).

Arsenic contamination of groundwater is a well-known problem in the Eastern districts of Bihar and West Bengal in India, where about 6.7 million people are living in arsenic-affected areas (Bagla and Kaise, 1996). In Nepal, it has been estimated that approximately 3 million people are drinking arsenic-contaminated water in the Southern plainland districts (Neku and Tandukar, 2003). Between 5 to 14 million people are thought to be drinking arsenic-contaminated water in the arid regions of China (Ahmed, 2003).

Although not as widely reported, arsenic contamination of drinking water is also a problem in the Red river delta regions of Vietnam, and the Mekong river delta of Cambodia (Ahmed, 2003; Murphy and Guo, 2003). There is



Bangladeshi village women cooking rice.

the potential that closer monitoring of arsenic levels and health impacts in the future will point back to the present situation as being but the tip of the iceberg.

Although the largest number of people affected worldwide by the contamination of drinking water with arsenic are in Bangladesh, the problem is not unique to Bangladesh. As early as 1960, scientists reported the link between various forms of cancer and arsenic in drinking water in Taiwan (Guo, 2003). Communities in North and South America, Europe, Asia and Australia also face the problem of arsenic-contaminated drinking water. In Latin America, communities in Mexico, Chile, Bolivia, Brazil, Peru, and Argentina are affected (de Esparza 2003). In Mexico and Argentina, the problem of arsenic in drinking water is severe enough that it has achieved formal state recognition as a public health concern. Although the problem is not as severe as elsewhere, arsenic-contaminated groundwater is found in communities throughout Canada (Boyle et al., 1998). Many communities in the western US that use groundwater as their source of drinking water are affected – several dozen in New Mexico alone (e.g. Bitner et al., 2001).

Key Points:

- Drinking water arsenic contamination affects millions,
- Impacts are global,
- Affected populations are likely to increase.

CHAPTER 2 HISTORY

Arsenic oxide, termed “white lace”, was once a poisoner’s tool of choice because it was effective, ubiquitous, and had no taste. Napoleon was once thought to have been poisoned with arsenic while in exile at Elba in 1821. In turn, Rasputin routinely took arsenic to protect himself from poisoning. After 1836, when an English chemist named James Marsh developed a reliable technique for detecting arsenic in the bodily fluids of the deceased, arsenic poisoning began to wane. Not long after, agricultural applications of arsenic in pesticides and herbicides, as well as its use in pigment, became widespread. Arsenic was combined with lead to make lead arsenate, an early insecticide. Arsenic was an important component of Salvarsan, an early treatment for syphilis, and in embalming. CCA – a compound of copper, chromate, and arsenate is widely used as a wood preservative. As_2O_3 was used as an insecticide, in rat poison, and as a weed killer. The introduction of organic pesticide alternatives (for example, DDT), coupled with environmental and human health concerns, led to the gradual discontinuation of many arsenic-based pesticides by the 1960s, but many areas contaminated by the practice remain.

On the other hand, arsenic has been used in the past to boost sexual power and physical performance. The most notable case of the latter is the “arsenic eaters”, mid-19th century mountaineers of Styria (in Central Austria) who ingested roughly 200 micrograms of arsenic every 3 to 4 days to enhance their ability to carry heavy loads at the high altitudes of the Alpine passes.

Health Impacts

Chronic arsenic exposure is linked to irritation of the digestive tract, nausea, vomiting, and diarrhea. Characteristic skin abnormalities attributed to chronic arsenic consumption is the appearance of dark or light spots on the skin and small corns on the palm, sole, and trunk. Some of the corns may ultimately progress to skin cancer. Furthermore, chronic arsenic consumption has been linked to increased risk of cancers of the lung, kidneys, and liver (ATSDR, 2000; Gosselin et al., 1984). More recent studies also link prolonged consumption of low concentrations of arsenic to heart attacks, stroke, hypertension and diabetes mellitus (OEHHA, 2004). Inhalation of arsenic can cause irritation of the throat and lungs, and chronic inhalation exposure can result in skin conditions and an increased risk for lung cancer. Skin exposed to arsenic may become irritated but such exposure does not usually result in any internal damage.

The amount of arsenic required to cause adverse health effects depends on the chemical and physical form of the ingested arsenic. In general, soluble inorganic forms of arsenic are more toxic than organic and insoluble forms of arsenic. The oxidation state of the arsenic also affects its toxicity. The reduced form of the inorganic arsenic (III) is more toxic than the oxidized form of arsenic (V). Trivalent methylated metabolites of inorganic arsenic can be more toxic than arsenite in both *in vitro* and *in vivo* studies (Styblo et al., 2002).

Infants and children are particularly vulnerable. There are indications of differential toxic effects in children due to arsenic exposure in human studies on birth weight (Borzsonyi et al.,

1992; Yang et al., 2003), congenital malformations, and neurological developments (Beckmann and Nordstrom, 1982; Nordstrom et al., 1978; Nordstrom et al., 1979a; Nordstrom et al., 1979b; Siripitayakunkite et al., 1999). Higher risks of fetal, neonatal, and post-neonatal mortality have been attributed to low levels of arsenic in drinking water studies conducted in Chile (Hopenhayn-Rich et al., 2000). In Bangladesh, higher incidences of spontaneous abortions, stillbirths, or pre-term births have been associated with arsenic in drinking water (Ahmad et al., 2001).

The U.S. Environmental Protection Agency (US EPA) has established a national primary drinking water regulation, or maximum contaminant level (MCL), for arsenic of 10 µg/L (U. S. Environmental Protection Agency, 2001b). The regulation came into effect in 2006. U.S. EPA's upper boundary (90th percentile) estimates of lifetime cancer risk at 10 µg/L arsenic ranged up to 6.1 in 10,000. The National Research Council's (NRC) Subcommittee on Arsenic in Drinking Water also reports risk estimates up to 23 in 10,000 for bladder cancer and up to 18 in 10,000 for lung cancer in males at 10 µg/L arsenic (National Research Council, 1999; National Research Council, 2001). The state of California Public Health Goal (PHG) is 0.004 µg/L (4 parts per trillion) for arsenic in drinking water is based on the mortality of arsenic-induced lung and urinary bladder cancer observed in epidemiological studies of populations in Taiwan, Chile, and Argentina. The functional equivalent of the California PHG is the U.S. EPA maximum contaminant level goal (MCLG), which is set at zero (U. S. Environmental Protection Agency, 2000).

Contamination

Arsenic is common in soils; background concentrations are 2.2 to 25 ppm (Kabatas-Pendias and Pendias, 1984). Low concentrations of arsenic are found in most fossil fuels (oil, coal, gasoline) and wood as well. Industrial arsenic is obtained primarily as a by-product of the smelting of copper, lead, cobalt and gold ores. Arsenic volatilizes in the smelting process and sublimates in the flue gasses as impure As₂O₃, which is subsequently purified through resublimation or hydrometallurgical leaching to produce commercial grade As₂O₃. Arsenic also goes into production of CCA, the most widely used wood preservative in the world. Other applications include the use of metallic arsenic in the production of alloys for use in lead-acid batteries, and of high-purity arsenic in the manufacture of semiconductor material. Metallic arsenic may also be added to alloys involved in the production of type metal, ammunition and automotive solder. Arsenic was also fed to livestock for weight gain.

Industrial Arsenic Contamination

As₂O₃ was used widely as an herbicide, in the US notably at electric power substations. Arsenic also exist in many soils underlying cattle dipping vats that used arsenic-containing solutions to kill cattle ticks. Although industrial arsenic contamination is locally a problem, much of the arsenic that contaminates drinking water is naturally occurring. Sometimes, agricultural or industrial activity can mobilize it though. Since arsenic is present in typical soils at roughly 2-20 ppm, most soils contain at least one hundred times the MCL (10 ppb). Transfer of only a small fraction from the soil solids to solution would cause the latter to exceed the MCL.

Arsenic sulfide minerals tend to predominate in reduced soils and rocks. Arsenic is also enriched in the rocks around hot springs. Some arsenic impurities exist in calcium carbonate minerals and in calcium phosphates where it substitutes for, respectively, carbonate and phosphate groups. Arsenic can also exchange onto clay minerals. In most oxidizing or mildly reducing soils arsenate is bound to ferric hydroxide minerals such as goethite, ferrihydrite, and hematite. A shift to strongly reducing conditions converts ferric iron to soluble ferrous iron, in effect dissolving the As host and causing dissolved levels to increase. This is thought to be a primary pathway that has caused As mobilization in Bangladesh and in Vietnam. The same mobilization sequence is increasingly seen down-gradient of landfills in the US where reducing landfill effluent prompts the release of naturally occurring arsenic from soils. Petroleum spills in soils might have the same effect.

Arsenic Contamination in Bangladesh

Naturally occurring arsenic levels in Bangladesh approach 1 mg/L and are highest in relatively shallow (0 - 100 meters), high recharge aquifers where degradation of organic matter has caused fluids to become anoxic. Deeper wells are substantially less contaminated - except where mixing with shallower waters has occurred in the well. Aquifer materials are sand-silt sediments that consist of clays, feldspars, calcite (and dolomite), several accessory oxides, as well as authigenic pyrite and the As-bearing sulfides arsenopyrite (FeAsS), realgar (AsS), and orpiment (As_2S_3). Arsenic is also associated with Fe(III)-hydroxides that coat some mineral grains, and possibly calcite.



Snout of hand pump painted green to show that arsenic levels are safe.

Originally arsenic contamination was thought to come primarily from dissolution of As-bearing sulfide minerals. More recent work emphasizes the importance of reductive dissolution of the arsenic-containing Fe(III)-hydroxide coatings. Arsenic contaminated water is being drawn from sediments that were originally deposited under at least mildly reducing conditions. The sequence was subsequently exposed and oxidized during the Pleistocene. Ongoing degradation of aquifer organic material has caused the present-day reducing conditions in the aquifer. In general, oxidation of organic matter leads to the breakdown of ferrihydrite and release of trace amounts of arsenic that are bound up in/on the ferrihydrite. Arsenic liberation as a trace constituent from iron hydroxide hosts to contaminate drinking water is routinely observed elsewhere as well.

Key Points:

- Most arsenic is naturally-occurring,
- Sometimes human activities mobilize it.

CHAPTER 3 ARSENIC CHEMISTRY AND SAMPLING

Arsenic in soils and groundwaters is usually either arsenite with +3 charge, or arsenate with a +5 charge. But because both arsenate and arsenite tend to combine with multiple oxygens, each having a -2 charge, dissolved arsenite and arsenate compounds tend to have an overall negative charge. Arsenite typically forms aqueous $\text{As}(\text{OH})_3$, $\text{As}(\text{OH})_4^-$, and AsO_2OH^- , depending on pH (Fig. 3-1). Arsenite exists under anaerobic conditions, for example in water-logged soils. Under more oxidizing conditions arsenic converts to arsenate. Dissolved arsenate forms AsO_4^{3-} , HAsO_4^{2-} , or H_2AsO_4^- and is chemically somewhat similar to phosphate. At $6.9 < \text{pH} < 11.5$, HAsO_4^{2-} is the primary species. At $2.2 < \text{pH} < 6.9$, H_2AsO_4^- is the primary arsenate species (Fig. 3-1).

Arsenate sorbs to soil minerals, particularly iron oxides and hydroxides. Arsenate sorption to iron oxides peaks around pH 5 - 7 and is less pronounced in more basic solutions. Arsenite tends to sorb less strongly than arsenate. Arsenic can form insoluble sulfide minerals.

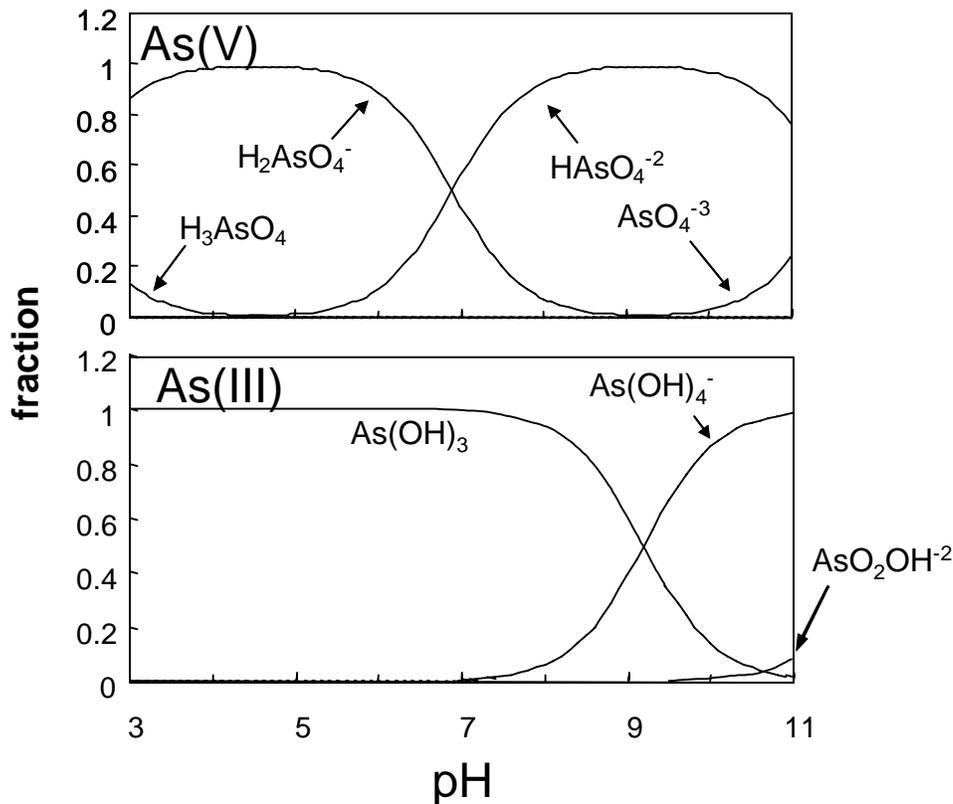


Figure 3-1. pH-dependent speciation of As(V) and As (III) at 25°C.

Figure 3-2 compares arsenate and arsenite speciation against redox and pH-dependent soil iron mineralogy. The stability of iron minerals is particularly important because of their tendency to sorb arsenic. At pH 7 surface waters and near-surface waters range from 0.7 down to 0.3 V. Bogs, organic rich waters, water-logged soils and deep groundwaters range from 0.3 down to ~ -0.2 V.

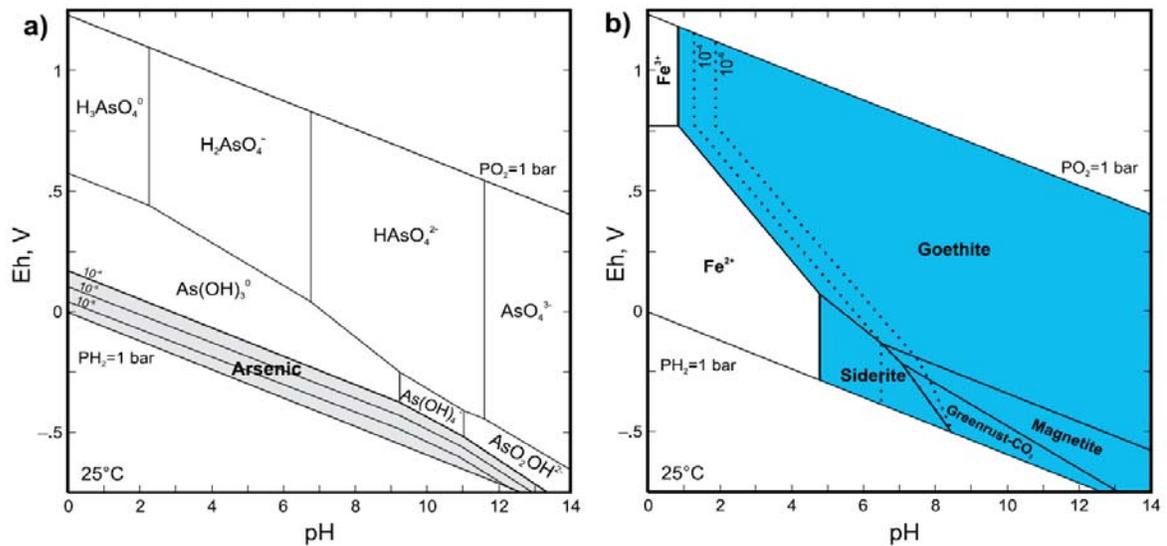


Figure 3-2. Eh-pH diagrams for arsenic and iron at 25°C for iron-reducing systems (from U.S. Environmental Protection Agency, 2007). These paired diagrams show the relative distribution of potentially adsorbing arsenic species (left) relative to representative types of Fe-bearing sorbents (right) that are predicted to occur as a function of Eh and pH. (a) System As-H₂O, with Σ As contoured from 10⁻⁸ to 10⁻⁴; region for elemental arsenic is shaded gray. (b) System Fe-C-H₂O (no sulfur) with Σ Fe contoured from 10⁻² to 10⁻⁶ and Σ C=10⁻³; Hematite and Wüstite are suppressed.

A rise in pH in high iron soil, a drop in pH in lime soil, or a change in redox potential may lead to resolubilization of otherwise immobile sorbed arsenic. Arsenate, initially sorbed to iron (hydr)oxides under aerobic conditions, might be released and transported in groundwaters if a shift to anaerobic conditions were to cause the dissolution of the host iron oxide. However, over time and under anaerobic conditions, the arsenate might convert to less soluble arsenite. Under strongly reducing conditions, microorganisms tend to methylate arsenic to a mobile form.

Arsenic in water and soil may be reduced and methylated by fungi, yeasts, algae, and bacteria. Bioconcentration of arsenic occurs in aquatic organisms, primarily in algae and lower invertebrates. Biomagnification in aquatic food chains does not generally appear to be significant, although some fish and invertebrates contain high concentrations of relatively inert arsenic compounds. Plants may accumulate arsenic via root uptake from soil solution and certain species may accumulate substantial concentrations.

Key Points:

- Arsenate, As(V), is most common in surface waters.,
- Arsenite, As(III), is more common in groundwaters, particularly reducing ones,
- Arsenate sorbs strongly to iron oxides, particularly at pH 5 – 7, arsenite less so,
- Reducing conditions can release arsenic to solution by destroying iron oxides.

Sampling

Central to any program of arsenic mitigation is the ability to properly detect arsenic in source water or treated water. To achieve this, the field and laboratory must have proper sampling, preservation, shipment and analysis procedures. Critical issues are:

1. How the speciation chemistry of arsenic relates to sampling, preservation and analysis,
2. The flushing procedure of bore hole well and pipeline prior to sampling,
3. Sample preservation and shipment of arsenic samples,
4. Use of field kits for arsenic testing,
5. Laboratory analysis for arsenic,

Proper sampling, sample preservation and sample analysis for arsenic from water should proceed from an initial idea of the chemical form of the arsenic. The Eh-pH diagram (Figure 3-2) is a helpful guide for using water pH and redox condition to anticipate this. The sampled water may also contain other non-arsenic anionic species that interfere with the measurement of arsenic. It is therefore prudent to discuss with the analytical laboratory or the manufacturer of the field test kit matrix corrections for analysis in the field or laboratory. Species such as dissolved iron or silicates, when exposed to oxygen, may rapidly change to insoluble species, and in the process, strip out arsenic species from water, thus contributing to errors in analysis. This calls for proper sampling and sample storage procedures to eliminate the possibility of induced errors from precipitating species. Although regulations require only the measurement of total inorganic arsenic in water, for research purposes one may need to measure the amounts of different arsenic species (e.g. arsenate vs. arsenite). This is beyond the scope of this book, but would require special sampling, storage, and measurement techniques best discussed with advanced research laboratories prior to setting up an analytical protocol.



Young man holding water pitcher.

Good Field Practices for Sampling and Sample Storage

Well Flushing

The first step in collecting water samples is flushing of pipelines prior to sampling. Ground waters normally contain dissolved species such as iron, which when exposed to air, will form insoluble precipitates, such as $\text{Fe}(\text{OH})_3$. Dissolved arsenic species will co-precipitate or sorb into the formed insoluble species and settle, thereby lowering the soluble arsenic concentration of the stagnant water in the pipe. For this reason, the stagnant water in the pipes needs to be flushed out before sampling so that a representative inorganic arsenic concentration of the aquifer can be determined. Pumps or hand pumps should be operated

sufficiently long to ensure that stagnant water in the pipes have been flushed out. Deeper wells require longer flushing (purging) than shallower wells. The purging time before sampling can be calculated as follows:

$$\text{Purging time (t)} = 1.5V/Q$$

Where: V = volume of static water in pipeline = $3.142 \times L \times D_i^2/4$

Q = pump discharge rate,

L = length of pipeline,

D_i = internal diameter of pipeline,

1.5 = safety factor to account for static water not associated with pipe length, for example, the pump cavity itself.

When conducting a large scale well screening program in a developing country, quite often it is not possible to calculate the flushing volume precisely. Instead application of local rules of thumb might be required. For example, in Bangladesh, roughly one stroke of the hand pump is required for every foot of piping in the well. This rule seems to work and different organizations in Bangladesh are using it to test well water for arsenic.

Example: Calculation of Well Flushing Duration

We are carrying out a well screening program for arsenic in rural Cambodia, arrive on a rural homestead, and ask the farmer the following question regarding his bore-hole well. (1) What is the diameter of the well pipe? (2) What is the total length of pipe below and above ground? (3) What is the length of the intake screen at the bottom of the pipe? The farmer replies: (1) The pipe diameter is 1.5 inches. (2) Total length of pipe used is 150 ft. (3) The screen at the bottom is 1 ft in length.

Scenario 1: Lets us assume that the pump used to draw the water is a hand cranked pump.

We know that the total length of piping (L) is $(150 + 1) \text{ ft} = 151 \text{ ft}$.

We know that the internal diameter of the pipe (D_i) is 1.5 inches

We know that there are 12 inches to a ft.

So the internal diameter is $(1.5/12) = 0.125 \text{ feet}$.

According to the equation for volume calculation the volume of static water in the pipeline (V) is equal to:

$$V = [3.142 \times 151 \times (0.125)^2] / 4 = 1.8 \text{ ft}^3$$

As a safety factor we multiply the 1.8 ft^3 by 1.5 to account for static water in bends and pipe casing.

Thus, the volume we need to flush is $1.8 \times 1.5 = 2.7 \text{ ft}^3$

Which is equal to $(2.7 \times 7.48 \text{ US gallons/ ft}^3) = 20 \text{ US gallons}$

The next step is to calculate how much water one crank of the hand pump. To do this fill a water pitcher to the brim and note how many cranks that required. Let us assume that it takes five strokes of the hand pump to fill a 20 liter (5.28 US gallons) water pitcher. This implies to purge the pipe work with a static water volume of 20 US gallons we would require:

$$(20/5.28) \times 5 = 19 \text{ strokes}$$

Scenario 2: Let us assume that the pump used to draw the water is a motorized centrifugal pump with a capacity (Q) of 5 gallons per minute. This implies to purge the pipe work with a static water volume of 20 US gallons would take:

$$\text{Purging time (t)} = (20/5) = 4 \text{ minutes}$$

Sample collection and preservation

Samples should be collected in bottles made of inert materials such as borosilicate glass or plastic. Sample bottles must be carefully cleaned before every use. For sample bottles to be used for storage of samples they should be washed in an acid bath with 10% nitric acid solution, followed by rinsing with de-ionized water, to minimize adsorption to bottle side walls. If de-ionized water is not available, the bottles should be rinsed with clear iron and arsenic-free water. Sample preservation for total inorganic arsenic analysis is achieved by acidifying to $\text{pH} < 2.0$ with nitric acid (HNO_3). The recommended minimum sample size is 1000 mL of water. Samples may be stored for up to six months prior to analysis after acid preservation (American Public Health Association, 1998). It is important to confirm that any acids used in preservation of samples for arsenic analysis do not themselves contain arsenic.

Acids specified for use in metal analysis generally have arsenic concentrations < 0.004 ppm and should therefore not introduce measurable contamination of the sample.

Pre-acidified bottles may have to be used because, due to logistical constraints, accurate pH adjustments cannot be done in the field. When collecting water samples in pre-acidified bottles, the bottles should not be flushed or filled to the point where water overflows and changes the amount of acid placed in the bottle. A little head space should also be kept in the bottle to allow for liquid volume expansion during transportation. Preserving samples with nitric acid may interfere with some laboratory analytical procedure for arsenic analysis. Hence, one should check that the acid used for sample preservation and the volume of sample collected is acceptable with the laboratory where the samples will be sent for arsenic analysis. Also arsenic field tests kits that require non acid-preserved samples calls for testing of samples with field test kits soon after collection.

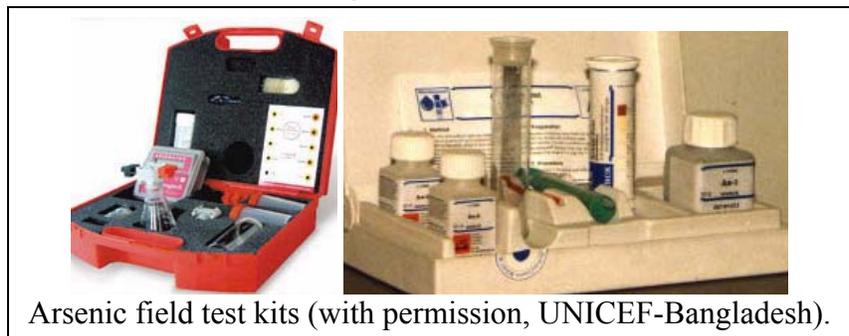
Samples should in theory be transported only under temperature conditions between 4 to 8°C (American Public Health Association, 1998). This is impossible to ensure in rural resource-strapped environments in, for example, Bangladesh, Nepal, and Cambodia due to logistical constraints. At such locations, one should try as best as possible to keep samples as cool during transportation and keep holding and transportation time to a minimum. It is important to ensure that laboratories test the samples soon upon receiving them. If laboratories are storing the samples before testing, the samples should be stored as per Standard Methods (American Public Health Association, 1998).

Field Kits for the Detection of Inorganic Arsenic in Water

Arsenic detection field kits are being used worldwide to screen wells for arsenic and also to monitor the performance of arsenic removal technologies. Various companies are marketing different arsenic field kits. Three of the more commonly used field test kits are: MERCK, HACH, and Peters

Engineering (PeCo75). Each is based on the Mercury Bromide Stain Method. To a measured amount of water, reducing agents are added to convert arsenate to arsenite, followed by adding zinc or sodium

borohydride to generate arsenic hydride (arsine gas) in a closed reaction vessel. The arsine gas bubbles out of solution to stain a detection strip or pad placed in the head space of the reaction vessel. The strips or pads are impregnated with mercury bromide which changes from yellow to brown when contacted by arsine gas. The more arsenic in the sample, the more arsine gas produced, the darker the stain on the strip or pad.



The detection strips or pads are placed in contact with the arsine gas for a fixed period of time. The color of the strip or pad is visually compared to a calibrated color chart (the darker the stain, the higher the concentration of arsenic in solution) to get an indication of the

arsenic concentration in the water. The PeCo75 kit is an exception to the rule; instead the color in the pad is quantified by a portable photometer with a liquid crystal display monitor, which gives a numerical readout of the arsenic concentration. The PeCo75 kit also provides a color chart which can be used if the photometer fails. Figure 3-3 below shows pictures of the HACH and MERCK field test kits in use in the field in Nepal and in Bangladesh. According to the manufacturers' calibrated color chart provided with the kits, all three kits are sensitive enough to detect arsenic at 50 and 10 ppb.

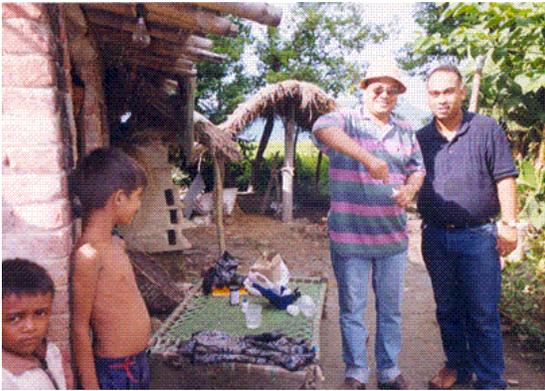


Figure 3-3. (a) Hach field kit in use in Nepal. (b) MERCK field test kit in use in Bangladesh.

Field evaluations suggest that arsenic test kits are not very accurate in measuring arsenic concentrations in natural ground water around the critical regulatory arsenic concentrations of 10 and 50 ppb (Erickson, 2003; Jalil and Feroze, 2003; Khandaker, 2004), but are accurate enough to identify high concentration areas that deserve greater attention. But since most rural communities are resource-strapped, and sending water samples out for analysis is not feasible, field test kits are the only available option. A reasonable solution is to periodically cross-check field test kit analyses against more laboratory-determined values, especially near the regulatory limits - be it 50 ppb or 10 ppb.

Important Points regarding Field Test Kits

1. It is imperative to follow the operational instructions and to maintain the timed sequence of steps specified by the instruction manual provided with the kit. Deviating from the precise time specified in the kit after addition of reaction chemicals will affect the sensitivity of arsenic detection.
2. The user of an arsenic field test kit should have the ability to distinguish the different shades of yellow provided in the color chart. If a person is color blind, he or she may have a problem in using the color-coded arsenic concentration charts.
3. The mercury bromide impregnated strips or pads are sensitive to light and their effectiveness may be compromised with repeated exposure. Care should be taken not to unduly overexpose the stored strips to light when removing strips from the opaque storage container.
4. When testing raw well water, the well should be flushed sufficiently to ensure that stagnant water in the pipes have been flushed out to get a more representative sample of the water from the aquifer. The water should be tested immediately after sampling. This is to ensure that the dissolved arsenic does not come out of solution as a co-precipitate with the iron present in the water, thereby giving a false lower estimate of arsenic in the sample.
5. Once the water sample is acidified for preservation, the field kit cannot be used to detect for arsenic. Also if nitric acid is used in sample preservation, it will interfere with arsenic detection by field arsenic kits.
6. The presence of sulfide in water (detected by the smell of rotten egg) interferes with arsenic detection using field arsenic kits. Hydrogen sulfide generated the same time as the arsine gas makes a black stain on mercury bromide-impregnated detection strip or pad, which interferes with the arsenic stain. If water is suspected of containing sulfide, then the lead acetate scrubber provided with most of the kits should be used to scrub out the generated hydrogen sulfide.
7. Periodically, the sensitivity of the field kit being used should be checked against a known standard. If this is not practical, the field kit should be checked against an already-tested well with a known arsenic concentration.
8. Tests should be carried out in a well-ventilated area to minimize exposure to the arsine gas and other fumes generated during the test. The part of the strip or pad which is impregnated with mercury bromide should not be touched. Mercury bromide is toxic and can penetrate the skin by exposure. Care should also be taken that the corrosive chemicals used in the kit do not come in contact with the skin or eye.
9. Once the test is complete, the content of the reaction vessel should be disposed in a safe manner. For example, in a rural setting, it might be placed in an enclosed pit latrine. The used mercury bromide strip or pad should be collected in a container or bag and then disposed of as hazardous waste at a later time.

Laboratory Detection of Inorganic Arsenic in Water

Ground water being screened from arsenic-contaminated wells, or treated water samples being monitored for the effectiveness of arsenic-removal systems, periodically need to be sent to a laboratory for analysis. The more common laboratory inorganic arsenic testing methods include: UV-Visible Spectrophotometry (Silver Diethyldithiocarbamate

procedure), Hydride Generation Atomic Adsorption (AA) Spectroscopy, Graphite Furnace Atomic Absorption Spectrometry, and Inductively Coupled Plasma Mass Spectrometry.

Silver Diethyldithiocarbamate Procedure

The silver diethyldithiocarbamate procedure for measuring total inorganic arsenic (American Public Health Association, 1998) is still being used extensively in field laboratories. The procedure is based on the formation of a red color when arsine gas (AsH_3) is passed through a solution of silver diethyldithiocarbamate morpholine in chloroform. For determination of total inorganic arsenic, arsine gas is generated through reduction by sodium borohydride at $\text{pH} = 1$ (the pH is lowered using HCl). High purity nitrogen gas is used to strip the arsine from solution. The gasses are then passed through a lead acetate scrubber to remove H_2S interference, then they are passed into a reaction vessel containing the silver diethyldithiocarbamate solution. The intensity of the red color is measured at 520-540 nm using a spectrophotometer. This method is appropriate for measuring total inorganic arsenic in water at the regulatory level of 50 ppb but is not appropriate for measurements at the level of 10 ppb.

Hydride Generation-Atomic Adsorption Method

In the hydride generation process (American Public Health Association, 1998), sodium borohydride (NaBH_4) is used to reduce arsenic to arsine gas, which is then passed to an atomic absorption spectrometer for arsenic measurement. Elemental arsenic has electronic transition spectral lines at 189.0, 193.7 and 197.2 nm, with 193.7 nm being the primary line used for atomic absorption spectroscopy. For total inorganic arsenic measurement, oxidation of all As to As(V) is followed by reduction with NaBH_4 in a strong acid solution. In traditional hydride generation methods, the production of the arsine gas occurred in a batch reactor, but present day AAs are equipped to continuously generate the hydride. In the continuous hydride generation mode, a quantitatively large number of samples can be analyzed in a day, and can measure inorganic arsenic down to 10 ppb.

Graphite Furnace Atomic Absorption Spectrometry

In the graphite furnace AA method of measuring arsenic (U. S. Environmental Protection Agency, 2001a), the sample and a matrix modifier is pipetted precisely onto a pyrolytic graphite tube, a device that allows delayed atomization. The sample is dried at approximately 120°C , with a continuous flow of premixed gas of 95 percent argon and 5 percent hydrogen. Once dry, the sample is ashed to minimize matrix interference effects. After the char step, the sample is cooled then atomized. Atomization occurs by rapid heating of the furnace to a temperature in which the analyte is atomized from the pyrolytic graphite tube into a stopped gas flow atmosphere of 95 percent argon and 5 percent hydrogen. The resulting atomic cloud absorbs the element-specific atomic emission produced by a hollow cathode lamp or an electrode-less discharge lamp. The amount of light energy absorbed is proportional to atomic concentrations. Multiple samples can rapidly be analyzed by this method down to 10 ppb As.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is a highly sensitive instrument for the simultaneous measurement of metals and non-metals in solution (U.S. Environmental Protection Agency, 1994). Ionization of the sample is achieved using an inductively coupled plasma; separation and detection of ions is

done with a mass spectrometer. After atomization and ionization metals and non-metals are separated on the basis of their mass to charge ratio by a mass spectrometer and detected by an electron multiplier or Faraday detector. As mentioned earlier, ICP-MS is highly sensitive, and can measure inorganic arsenic down to 10 ppb.

Normally, samples are sent to certified laboratories for analysis. In countries in which there are no certification processes by which laboratories are evaluated, and the standards of most water quality laboratories are poor, the list below may be useful as a guide to select laboratories for water sample analysis:

1. Visit the laboratory to develop a working relationship.
2. Check if the laboratory has past experience in analyzing the water quality parameters of concern. The laboratory should have sufficient instruments and trained personal to handle the analyses in a timely fashion.
3. The laboratory should have written standard operating procedures for the analytical methods of interest.
4. Check if the laboratory has undertaken any external proficiency tests for the analysis of concern. Have a look at the results and see if they are acceptable.
5. Check if the laboratory has a sample tracking (chain of custody) system in place.
6. Look at a sample data reporting sheet that will be provided to you after completion of the test. Typically, along with the data, quality assurance information should also be included.
7. Check if the laboratory has a quality assurance and quality control plan in place. The efficacy of the plan may be evaluated by referring to the quality assurance and quality control plan detailed in Standard Methods for Examination for Water and Wastewater (American Public Health Association, 1992).
8. Discuss with the laboratory the volume of samples needed for analysis, the required sample bottle and sample preservation method, and how to ship samples to the laboratory from the field.

If possible, it is good practice to check the process by requesting measurement of a limited number of samples having known concentrations of arsenic.

Key Points:

- Workers should always follow proper sampling procedure and proper sample preservation techniques,
- Arsenic field test kits may not be reliable at the regulatory limits and some laboratory cross checking to validate test results using field test kit is recommended,
- It is important to establish a good working relationship with testing laboratory and follow their recommendations for sample preservation and shipment and to,
- Ensure that the testing laboratory is following standard procedures for analysis and sample handling as outlined in this section.

CHAPTER 4 INTRODUCTION TO ARSENIC REMOVAL

The introduction that follows emphasizes arsenic removal in the developed world. The following chapter then applies the underlying principles to consider arsenic removal strategies in the developing world. The primary methods for removing arsenic from drinking waters in the developed world include:

- Ion exchange – using a resin to remove anionic As species,
- Coagulation/Micro-filtration – Adding Fe(III) or Al(III) salts to form arsenic-sorbing flocs which are subsequently removed from solution by granular media or membrane filtration,
- Fixed bed adsorption – Removal of arsenic with an adsorbent, typically a metal (hydr)oxide such as ferric hydroxide or AA (activated alumina),
- Lime-softening – Adding lime to soften water (remove Ca and Mg) often removing appreciable amounts of arsenic in the process through sorptive uptake by metal carbonates and hydroxides,
- Iron removal – Oxidizing reduced iron to remove arsenic through sorption/co-precipitation/coagulation,
- Physical filtration – To remove colloiddally-bound arsenic,
- Membrane processes – Membrane removal of arsenic by Reverse Osmosis (RO) or nanofiltration (NF)

Arsenic removal involves far more than removing arsenic from water. It also requires disposal of waste solids (e.g. spent filter material, coagulant sludges) and residual fluids likely to contain high levels of arsenic and possibly other hazardous or radioactive (e.g. uranium, radon) constituents. If the water requires pretreatment (e.g. lowering of pH for adsorption processes, or raising it for lime-softening) the waste situation becomes more complicated. At the same time, most treatments tend to affect effluent levels of dissolved components other than arsenic - sometimes in a deleterious fashion. For example, removal of arsenic through ion exchange also tends to lower bicarbonate levels increasing the corrosivity of the effluent. Coagulation using Al(III) or Fe(III) salts can result in increased concentrations of these metals in the treated water, as well as the anions (e.g. sulfate) from the salts used in the process. Lastly, most arsenic treatment technologies work better for arsenate than arsenite, so a preoxidation step is often used.

Table 4-1 outlines the types, volumes, and arsenic-content of residuals produced by various treatment approaches. Note that in general RO and NF produce the largest quantities of liquid waste in the form of reject waters; coagulation/microfiltration and lime softening produce the greatest amount of solid waste. Table 4-2 considers treatment residuals disposal options.

Table 4-1. Arsenic treatment residuals characteristics (after Narasimhan et al., 2005).

Technology	^aType of residual produced	Volume (gal/MG)	As in liquid wastes (mg/L)	Quantity of solid residuals (mg/kg dry)	As in solid residuals (mg/kg dry)	TCLP level in dewatered solids (mg/L)
Coagulation filtration	Sludge	4300	9.25, particulate, non-hazardous	180	1850	9.3 (alum), 1553 (iron)
Lime softening	Sludge	9600	4.2 (particulate)	2000	165	0.9 to 28.4
IX IX w/brine recycle	Liquid	10260 1030	1.95 (dissolved) 19.5	14.3	11700	Not available
AA with regeneration	Liquid	1080	18.47 (dissolved)	5.92	11350	< 5
Throwaway AA	Spent media	solids	Not applicable	300	500	0.2
Throwaway GFH	Spent media	solids	Not applicable	40	2000	0.2
NF/RO/EDR	Liquid	126300	0.13 (dissolved, non-hazardous)	Not applicable	Not applicable	Not applicable
CMF	Backwash	67368	0.24 (particulate, non-hazardous)	110	1930	Not available

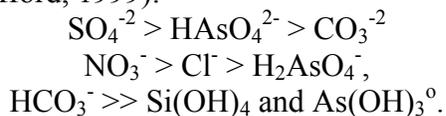
^aMore than one type of residual may be produced. Only most critical residual stream is considered here. GFH = granular ferric hydroxide; EDR = electro dialysis reversal; MG = million gallons.

Table 4-2. Summary of potential disposal alternatives for arsenic treatment wastes (from Narasimhan et al., 2005).

Treatment technology	Discharge to Receiving Stream	Discharge to Sanitary Sewer	Land Application	Municipal Solid Waste Landfill	Hazardous Waste Facility
Conventional Water Treatment	No	Not likely	Possible	Yes	Only if necessary
Softening	No	Not likely	Possible	Yes	Only if necessary
IX	No	Not likely	Possible	Yes	Only if necessary
AA	No	Not likely	Possible	Yes	Only if necessary
Nanofiltration/RO	Possible	Possible	No	No	No
CMF	No	Possible	Possible	Yes	Only if necessary
Throw-away Adsorption Media	No	No	Possible	Yes	No
Backwash from IX, AA and other media	Possible	Yes	No	No	No

Ion exchange

Ion exchange is a mature technology that is widely used for contaminant removal (see e.g. Clifford, 1999), though rarely for high volume drinking water applications (Wang et al., 2000). Its most familiar application involves use of cationic exchange of Na^+ for Ca^{2+} and Mg^{2+} in home water softeners. Polystyrene-based, strong base resins remove anionic arsenate species but not H_3AsO_4 . IX tends to be hampered by the presence of other anions, particularly sulfate (see e.g. Clifford and Lin, 1991). The selectivity sequence for strong base anion exchange resins is (Clifford, 1999):



Note that because anion resins preferentially remove SO_4^{2-} over As(V) species, the run length for an IX column is often controlled by the SO_4^{2-} level in the feedwater. In effect, anion exchange to remove arsenic in practice becomes a SO_4^{2-} removal process. Resin regeneration is done with a NaCl brine, which must ultimately be disposed of (note that it may carry an appreciable As load in addition to the salinity). Another concern with ion exchange is the potential for chromatographic peaking. Long runs using inputs of high sulfate waters can cause flushing of initially bound arsenic at levels exceeding input values.

Coagulation/ Filtration

Coagulation Filtration uses either Fe(III) or Al(III) salts to form flocs that sorb and sequester (co-precipitate) dissolved arsenic (Chang et al., 1994; Fields et al., 2000a) and that are subsequently filtered out. The ability of various iron oxides to scavenge dissolved As is a recurring theme in arsenic treatment. Ferric salts are the more effective on a weight basis (Sorg, 1993; Sorg and Logsdon, 1978) and is the more widely used of the two. The precipitated Fe(OH)_3 or Al(OH)_3 can be removed either by granular media filtration or membrane microfiltration. If granular media filtration is used (sometimes referred to as direct filtration) a flocculation step must be included to facilitate growth of floc particles. In contrast, use of a membrane microfilter can eliminate the need for this step. Arsenic removal processes which are based on adsorption and/or coprecipitation onto an Al or Fe hydroxide floc work best at $\text{pH} < 7.5$ (Edwards, 1994). Because coagulation/microfiltration removes F^- as well as arsenic, subsequent fluoridation may be required. Alternatively, fluoride uptake might be seen as a benefit at the occasional site where F^- levels exceed health-based limits. Sludge disposal is an important part of operator costs, but generally Al and Fe residuals from arsenic removal treatment are not classified as hazardous wastes.

Arsenic Adsorption

Adsorption of arsenic onto metal oxide or metal hydroxide surfaces has been well known for many years. Early studies focused on the use of activated alumina ($\gamma\text{-Al}_2\text{O}_3$) primarily as a selective adsorbent for As and F (Sorg and Logsdon, 1978) (Clifford and Lin, 1991; Xu et al., 1988), but in recent years a wide variety of other adsorbents have been used. Al and Fe(III)-based sorbents tend to work best at pHs at or below 7 whereas many groundwaters have pHs greater than 7. pH adjustment is therefore likely to be an important factor in technology selection. The outlays associated with initially lowering, and subsequently raising, water pHs (to avoid corroding plumbing) increase costs, complexity, and perhaps most importantly, and may require handling of hazardous acid and caustic solutions.

Activated Alumina

Activated Alumina (AA) has received a great deal of attention as a sorber of arsenic (Wang et al., 2000) and is prepared by partially dehydrating $\text{Al}(\text{OH})_3$ at high temperatures. AA sorbs arsenate more completely than arsenite. The selectivity sequence for AA is (Clifford, 1999):



AA sorption of arsenic works best at pHs below 6.5. If the raw water has a pH significantly greater than 7 pH adjustment may be required. AA is regenerated using 1 – 4% NaOH followed by a sulfuric acid wash which causes some destruction of the media, and limits the number of times the media can be cycled.

Ferric Media

Iron based surfaces are widely recognized for their affinity for arsenic, however, not all Fe minerals have high capacity. Amorphous $\text{Fe}(\text{OH})_3$ is especially effective and is commercially available as GFH. GFH is roughly 50% FeOOH and 50% water. Because of its high water content, special care is required in the shipping and handling of GFH. Occasionally, “clumping” of GFH media causes a decrease in permeability and headloss, requiring back-washing to remove fines.

Similar to AA the performance of Fe(III)-based media decreases above pH 7 - an important region of arsenic treatment. Phosphate and silicate also interfere with arsenic uptake by iron oxides. A number of proprietary Fe(III)-based materials exist – for example Bayer Incorporated’s E33 (which is sold by Severn Trent as a dry solid) that differ primarily in their mode of preparation and surface area. Fe(III)-coated alumina – AASF50 has also been used for arsenic removal. To the extent that exposed Fe(III) sites are the reactive component of each, similar effects of pH, phosphate, silicate, and fluoride on performance might be expected. Unlike AA, Fe(III)-based media are not typically regenerated; spent media is simply replaced by fresh media. Experience to date has shown that AASF50, GFH and E33 are not hazardous and can be disposed of in landfills.

Greensand

Greensand is a naturally-occurring material which contains both Mn and iron-rich glauconite. Greensand filtration removes arsenic by oxidative sorption where manganese in the greensand oxidizes any arsenite to arsenate which subsequently sorbs to iron phases in the greensand. Potassium permanganate is used to regenerate the greensand once its oxidative capacity is exhausted. Greensand is not an especially effective adsorbent compared to Fe-based media (Subramanian et al., 1997). Other media which have been proposed for arsenic adsorption include TiO_2 , $\text{La}(\text{OH})_3$, and zircon $\text{Zr}(\text{OH})_4$.

Lime Softening and Iron Removal

Lime softening is effective for arsenic removal, but involves considerable effort. Generally, arsenic uptake increases at higher pH during lime softening (Sorg and Logsdon, 1978), particularly when $\text{Mg}(\text{OH})_2$ forms at $\text{pH} > 10.8$. Uptake is thought to be a combination of sorption, coprecipitation, and occlusion on the calcium and magnesium solids (McNeill and Edwards, 1997b). A small number of utilities might therefore be able to approach regulatory targets by softening their water (Chen et al., 1999).

Soluble, reduced iron must occasionally be removed from drinking water sources. Iron oxidation through aeration or chlorination tends to result in arsenic removal as well. Therefore some utilities might approach compliance with arsenic targets indirectly through Fe removal (see Fields et al., 2000b). McNeill and Edwards (1997a; 1997b) showed that Al and Fe precipitation processes in conventional water treatment plants can be optimized for removal of arsenic at low cost. The same authors did similar work for lime softening treatment plants (McNeill and Edwards, 1997a).

Reverse Osmosis/Nanofiltration

Reverse osmosis and nanofiltration (NF) primarily remove arsenic by size exclusion. Subjected to a pressure gradient, a semi-permeable membrane allows water to pass through while retaining certain ions. RO membranes are more selective than NF membranes but require higher driving pressures (hence higher energy costs). Arsenic rejection in RO and NF is relatively insensitive to pH except that arsenite is rejected more completely at pHs > 8 (e.g. Narasimhan et al., 2005) because it is anionic at high pH, but uncharged at lower pH. Both NF and RO are relatively expensive, generate a waste brine, and consume large amounts of water (See Table 4-3).

Table 4-3. Water waste (Narasimhan et al., 2005)

Technology	Water waste (%)
IX	1 – 2
GFH	0.1 – 0.3
CMF	0.1
NF or RO	15 - 30

The presence of suspended solids, scale, microbes, hydrogen sulfide, iron and manganese, and organics can also limit membrane life and are therefore typically the primary target of pretreatment efforts.

Others

Newer technologies that are being tested include sand ballasted coagulation sedimentation, fluidized-bed *in situ* oxidation adsorption, coagulation–assisted ceramic media filtration, and immersed media with carrier particles (Narasimhan et al., 2005). Sand ballasted coagulation sedimentation uses sand and polymer additions to coagulation to boost arsenic removal. Fluidized-bed *in situ* oxidation adsorption involves adsorbing ferrous iron onto a continuously generated sand surface. Oxidation of the iron leads to uptake and removal of arsenic. Coagulation–assisted ceramic media filtration is similar to CMF except that ceramic filters are used in the floc removal step. Immersed media with carrier particles is an *in situ* filtration process.

Table 4-4 summarizes the effectiveness and industry acceptance of various treatment approaches.

Table 4-4. Summary of arsenic removal technologies - from Johnston et al. (2001) – with permission.

Technology	Removal Efficiency		Institutional experience and issues
	As (III)	As (V)	
Coagulation with iron salts	++	+++	Well proven at centralized plants, piloted at community and household levels. Phosphate and silicate may reduce arsenic removal rates. Generates arsenic-rich sludge. Relatively inexpensive.
Coagulation with alum	-	+++	Proven at central level, piloted at household levels. Phosphate and silicate may reduce arsenic removal rates. Optimal over a relatively narrow pH range. Generates arsenic-rich sludge. Relatively inexpensive
Lime softening	+	+++	Proven effective in laboratories and at pilot scale. Efficiency of this chemical process should be largely independent of scale. Chiefly seen in central systems in conjunction with water softening. Disadvantages include extreme pH and large volume of waste generated. Relatively inexpensive, but more expensive than coagulation with iron salts or alum because of larger doses required, and waste handling.
Ion exchange resins	-	+++	Pilot scale in central and household systems, mostly in industrialized countries. Interference from sulfate and TDS. High adsorption capacity, but long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. Moderately expensive. Regeneration produces arsenic-rich brine.
Activated alumina	+/ ++	+++	Pilot scale in community and household systems, in industrialized and developing countries. Arsenite removal is poorly understood, but capacity is much less than for arsenate. Regeneration requires strong acid and base, and produces arsenic-rich waste. Long-term performance of regenerated media needs documentation. Waters rich in iron and manganese may require pre-treatment to prevent media clogging. Moderately expensive.
Membrane methods	-/ +++	+++	Shown effective in laboratory studies in industrialized countries. Research needed on removal of arsenite, and efficiency at high recovery rates, especially with low-pressure membranes. Pretreatment usually required. Relatively expensive, especially if operated at high pressures.
Fe-Mn oxidation	?	+/ +/ +++	Small-scale application in central systems, limited studies in community and household levels. More research needed on which hydrochemical conditions are conducive for good arsenic removal. Inexpensive.
Porous media sorbents (iron oxide coated sand, greensand, etc.)	+/ ++	+/ +/ +++	Shown effective in laboratory studies in industrialized and developing countries. Need to be evaluated under different environmental conditions, and in field settings. Simple media are inexpensive, advanced media can be relatively expensive.
In situ immobilization	++	+++	Very limited experience. Long-term sustainability and other effects of chemical injection not well documented. Major advantage is no arsenic-rich wastes are generated at the surface, major disadvantage is the possibility of aquifer clogging. Should be relatively inexpensive.

Key: +++ Consistently > 90% removal
 ++ Generally 60 – 90% removal
 + Generally 30 – 60% removal
 - < 30% removal
 ? Insufficient information

Clearly there are a number of technologies which have a demonstrated ability to remove arsenic to safe levels. Selection of an appropriate arsenic removal approach at a given site

should: 1. Consider all life-cycle costs including residuals disposal, and 2. Take advantage where possible of existing treatments that also remove arsenic (e.g. filtration, iron removal, lime softening). Particular attention needs to be paid to the chance that M&O (maintenance and operation) costs will over time outweigh the initial savings gained from installing a less expensive physical plant. Often government assistance is more easily secured for plant construction than M&O expenses.

For those sites that do no treatment other than chlorination the choice of treatment approach is most uncertain. Often these are sites that use groundwater; many are small systems serving fewer than 10,000 people. Figure 4-1 is a decision tree analysis that gives an idea how the effectiveness of the various treatment approaches might be considered at such a site. Often batch sorption and column tests are done to better anticipate performance of sorbing media. Similarly, pilot testing provides useful indications of technology performance (Figure 4-2), as will be discussed in the following section. The larger problem of how small systems might remove arsenic is examined in greater detail in Chapter 6.

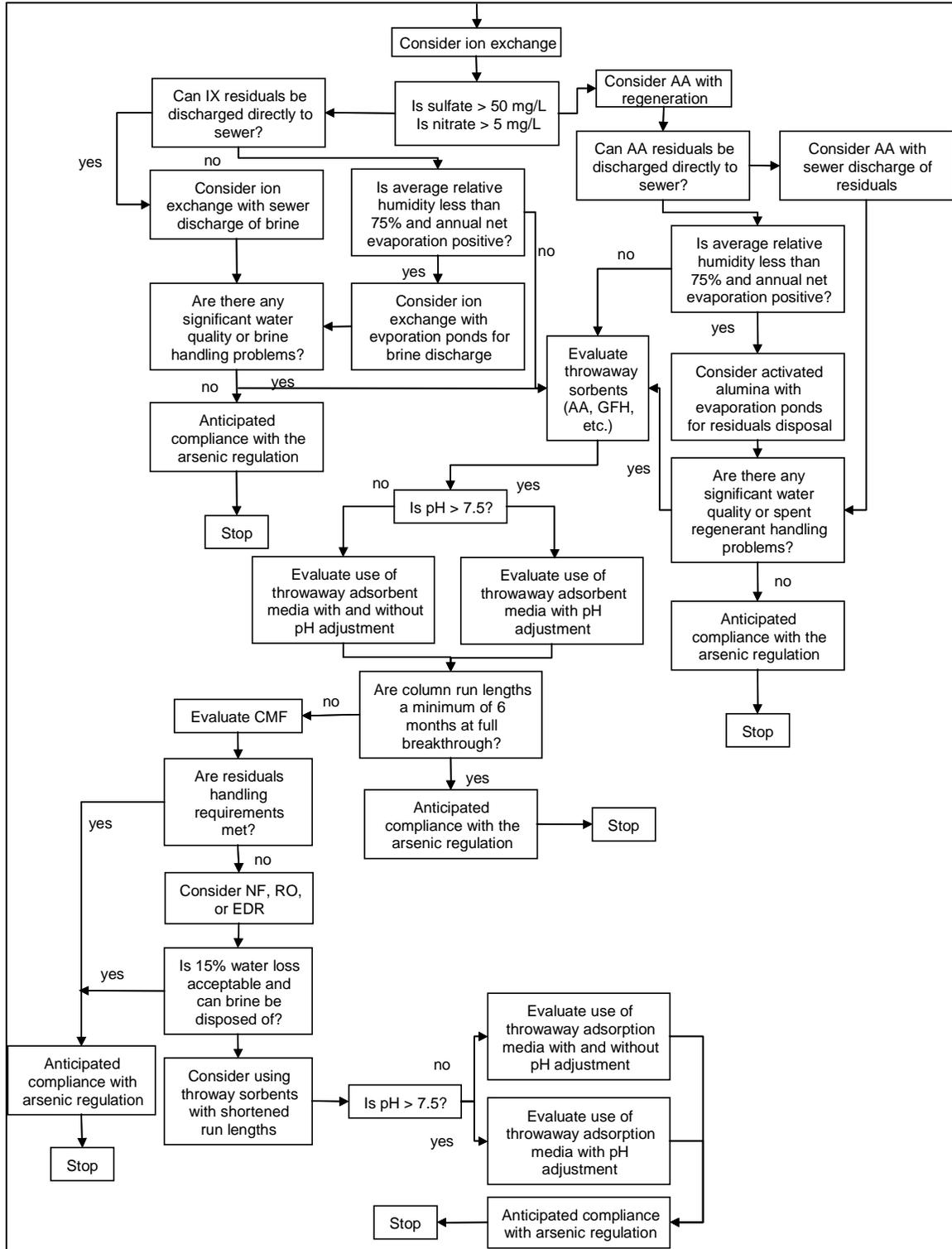


Figure 4-1. Decision tree leading to process selection for arsenic treatment of disinfected ground water (after Narasimhan et al., 2005).



Figure 4-2. Batch sorption, column, and pilot testing (from left to right).

Case Study – Treatment for Arsenic and Fluoride

Fluoride is often a co-contaminant present with arsenic in drinking water. Excessive fluoride causes dental fluorosis and, ultimately, bone disease. The US EPA has set the fluoride maximum contaminant levels to 4 ppm and a secondary standard of 2 ppm to protect against fluorosis. Like dissolved arsenic, dissolved fluoride is anionic and therefore less likely to sorb to soil minerals. Groundwater from Yuma, Arizona (Table 4-5) contains 30 ppb As and 6.7 ppm F. Yuma groundwater has high pH (8 – 8.85) and total dissolved solids which would rule out ion exchange for arsenic and fluoride removal (American Water Works Association, 1999). Further, the high silicate in the water could possibly limit the performance of metal oxyhydroxides for adsorption of both arsenic and fluoride. There is also the concern that the high fluoride levels might displace arsenic from the sorbents. To evaluate treatment approaches the kinetics of arsenic and fluoride adsorption from Yuma groundwater onto activated alumina (AA), granular ferrihydrite (GFH), and ferric-coated activated alumina (AAFS50) were studied and the arsenic and fluoride adsorption capacities of the media at different pHs modeled. Rapid scale column studies were conducted to compare breakthrough profiles of fluoride and arsenic (Rapid scale column tests are conducted with small columns that are thought to roughly mimic the relative behavior of larger, treatment columns).

In batch kinetic tests, a fixed liquid to sorbent ratio was maintained and samples were collected at pre-set time intervals for 48 hrs. Data obtained were fitted to a first order kinetic model (American Water Works Association, 1999). In the batch equilibrium studies each sorbent was equilibrated with the feed water for 48 hrs at varying sorbent to liquid ratios. Data obtained from the batch studies were used to develop Freundlich isotherms; $Q = K_f C_i^n$; where Q is the mass of arsenic or fluoride sorbed (mg/g); C_i is the concentration of arsenic or fluoride in solution (mg/L) and K_f and n are constants.

Table 4-5. Groundwater from Yuma, Arizona, USA.

Parameter	Value
pH	8-8.85
TDS (mg/L)	810
Sulfate (mg/L)	130
Phosphate as P (mg/L)	< 0.05
Total Alkalinity (mg/L)	89
Vanadium (mg/L)	0.018
Iron (mg/L)	< 0.1
Silica (mg/L)	44
Total Hardness (mg/L)	64
Fluoride (mg/L)	6.7
Arsenic Total ($\mu\text{g/L}$)	30

Figure 4-3 shows rapid sorption of both arsenic and fluoride, fluoride uptake being noticeably faster than arsenic. Figure 4-4 shows Freundlich isotherm fits to GFH arsenic and fluoride sorption data and emphasizes the strong role that pH plays in uptake of both. Each of the media sorbs both arsenic and fluoride. Media performance at a given pH for fluoride is AAFS50 > AA > GFH; for arsenic AAFS50 \geq GFH > AA. Alumina-based media work better for fluoride. Iron-based media work better for arsenic.

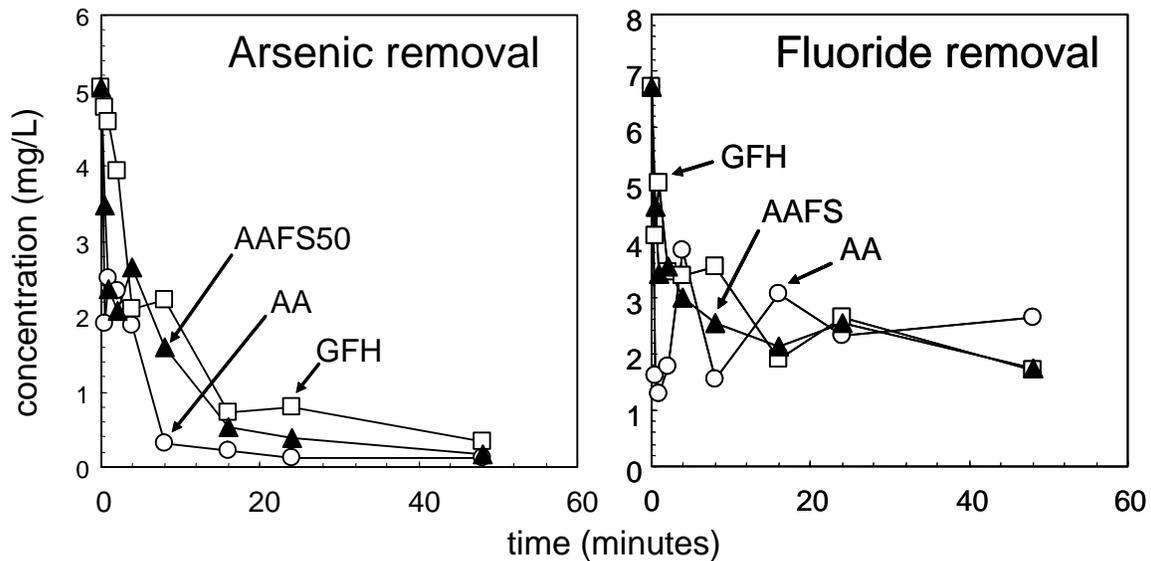


Figure 4-3. Kinetics of arsenic and fluoride adsorption on sorbents measured in batch tests using As-doped Yuma groundwater.

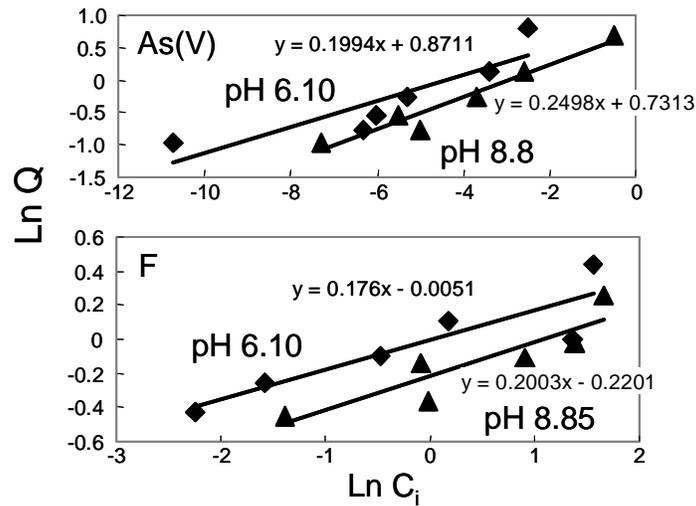


Figure 4-4. Arsenic and fluoride sorption onto GFH and Freundlich isotherm fits.

Figure 4-5 shows profiles of arsenic and fluoride for AAFS50 and GFH for the rapid scale column test using the ground water at the optimum adsorption pH of 6.1 at the arsenic and fluoride concentrations seen at the well head, 30 ppb and 6.7 ppm respectively. Obviously both arsenic and fluoride are removed simultaneously by GFH and AASF50 (and AA too, not shown). Due to the 1000 fold higher fluoride concentration, fluoride breakthrough occurs rapidly, while arsenic breakthrough does not occur.

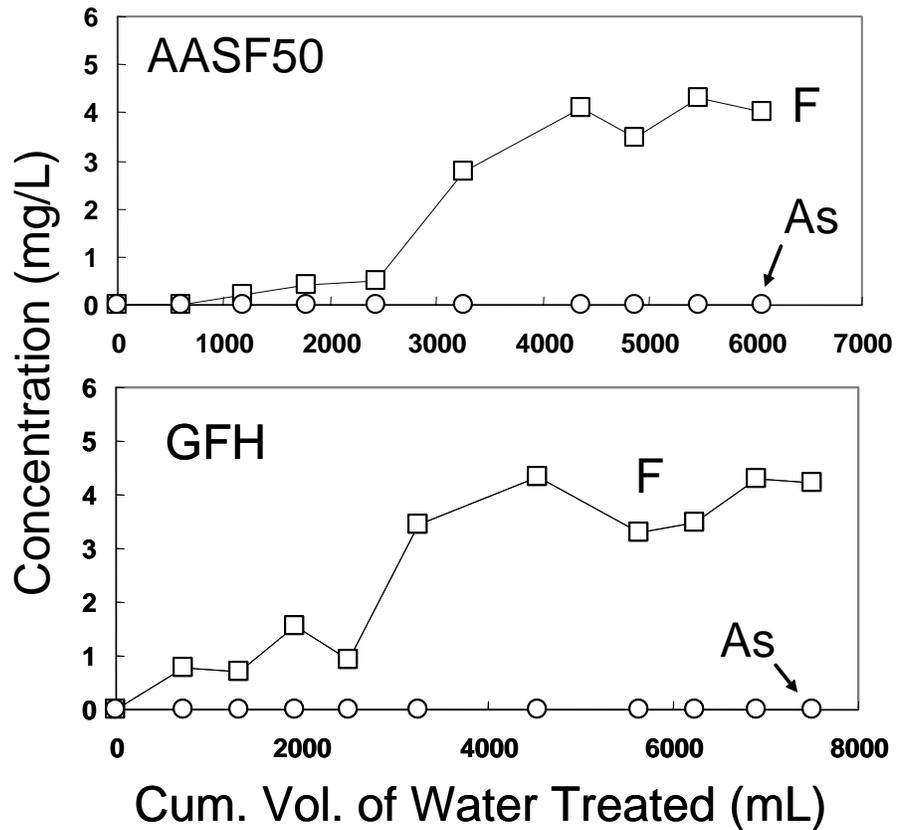


Figure 4-5. Column breakthrough profiles for Yuma groundwater for fluoride and arsenic with GFH and AASF50.

Key Points:

- Arsenic sticks to iron making iron the critical component in most treatment methods,
- Increasing iron surface area tends to increase arsenic removal,
- As sticks most strongly to iron based-media, fluoride to alumina-based media,
- Sorption of both arsenic and fluoride is strongest below neutral pH,
- Arsenic removal is only part of the problem; waste streams must also be considered.

CHAPTER 5 ARSENIC REMOVAL IN DISPERSE SETTINGS: DEVELOPING WORLD

Applying the sorts of developed world arsenic removal strategies outlined above to rural settings is hindered by the decentralized nature of the population. We highlight the obstacles and approaches to arsenic removal in disperse settings - small communities and rural areas - using examples from rural Bangladesh and Nepal in this chapter.

Water treatment systems serving small communities or single households must be stand-alone, easy to operate, and cost effective and require minimal technical supervision and minimal handling of process chemicals.

To begin with, the average water demand for the community or household of concern must be known. For small communities, it may be necessary to also consider the future water demand of a particular community for the next ten years. Population growth, based on statistical projections relevant to a demographic region, may be necessary; the national average growth rate may not be an appropriate estimate for rural communities. It is also important to estimate peak water demand for the community or household of concern. Average and peak water needs will serve as the basis for selecting the arsenic removal technology for a small community or a household.



Volunteers training in the use of arsenic removal filter in Nepal.

1. For technology selection, it is important to know the concentration range of total arsenic detected in the source water and, quite possibly, the speciation of the arsenic in the source water. The relevant local authority should have a public access database from which the required information can be obtained. If the data is not available, one may have to send samples to the laboratory to ascertain the concentration range and speciation of the arsenic in the source water. Multiple samples spaced over a year may have to be analyzed to obtain a true idea on the range of concentration of arsenic in the source water. This will account for any seasonal variation in arsenic concentration.
2. A thorough characterization of the source water quality is helpful to determine the best treatment option or required treatment system. For example: high iron levels in water can foul adsorption media and it would be prudent to place an iron removal filter prior to an arsenic removal adsorption system. The source water quality parameters that are known to affect the performance of arsenic removal systems are:
 - pH,
 - Total dissolved solids (TDS),
 - Turbidity,
 - Total arsenic concentration,
 - Arsenic speciation,
 - Competitive anions such as phosphates, silicates, bicarbonates, and fluoride,

- Total iron.
3. If there is a requirement for storage or piping of water disinfection may be required.
 4. The process and logistic issues listed below should be discussed at length with vendors:
 - Technology capabilities,
 1. Can it produce water with arsenic concentrations below regulatory standards?
 2. Can it produce the required quantity of water?
 3. Based on the source water quality data, what is the expected life of the system, along with any required effluent arsenic monitoring regime?
 - Operation and maintenance requirements,
 - Operator skill level,
 - Capital cost,
 - Operation and maintenance (O&M) cost,
 - Can the system be run with off-grid power such as diesel engine, manual cranking etc?
 - Logistical support,
 - Waste disposal.
 7. The sustainability of the treatment system must be discussed at length with the community. Can the community sustain the technology given to them in the future? Local water authorities must be involved in the decision-making process. Local water treatment and distribution regulations must be followed and the proper authorization to install water treatment systems applied for. Especially for a community system, it is important know what water quality parameters have to be measured and the measuring frequency needed to be in compliance with the regulatory agencies.
 8. Safe handling and proper disposal of exhausted media or generated process waste from the arsenic removal system is normally regulated and must be adhered to by law. Safe handling and proper disposal of all solid and liquid waste generated should be clearly discussed with the vendor of the technology in consultation with the local water authority. Prior to committing to a technology, all technical and regulatory responsibilities to process and dispose of generated waste should be worked out with the technology vendor and the local water authority.



Zero valent iron based filter introduced by MIT in Nepal.

Rural Bangladesh

The quality of groundwater varies in Bangladesh based on the geology associated with the aquifer. Table 5-1 summarizes water quality parameters several regional aquifers of Bangladesh. The data in Table 5-1 is the average of five tubewells in each of the five test regions which themselves are shown in Figure 5-1.

Table 5-1. Groundwater quality of five regional aquifers in Bangladesh.

Region	pH	TDS (mg/L)	Iron (mg/L)	Total P (mg/L)	Silicate (mg/L)	As (III)/As(Total) (mg/L/mg/L)
Bera	7.2	261.4	12.0	3.6	32.8	0.8
Habiganj	7.7	255.8	2.4	8.8	16.1	0.6
Manikganj	7.3	497.5	11.4	0.0	21.5	0.7
Nawabganj	7.2	266.3	5.0	1.8	26.0	0.8
Faridpur	7.2	409.9	8.4	1.4	19.2	0.8



Figure 5-1 Locations of aquifers in Bangladesh.

Obviously groundwater quality in Bangladesh varies regionally. pH is the only parameter that is similar across regions. The majority of the arsenic present in the groundwater is in the form of As(III), which exists as the uncharged species As(OH)_3 in water at pH values less than 9.2. Typically most arsenic removal technologies are less effective at removing As(III) compared to As(V). Ion exchange technologies are particularly vulnerable because anion exchange resins can only remove charged ionic species and dissolved As(III) is mostly uncharged at relevant pH values. Note also the generally high levels of groundwater phosphorous and silicate in the groundwater in most regions. Phosphates, silicates and even uncharged phosphorous and silica in colloidal form are known to reduce the arsenic capacity of most arsenic removal technologies (Chwirka et al., 2000; Clifford, 1999; McNeill and Edwards, 1997a).

Case Study: Source Water Quality and Arsenic Removal Technology Performance

The Bangladesh Council of Scientific and Industrial Research (BCSIR), with technical assistance from the Ontario Center for Environmental Technology Advancement (OCETA), evaluated and certified for use in Bangladesh different arsenic removal technologies. The arsenic removal systems were based on ion-exchange, and sorbents of metal oxy-hydroxide and zero valent iron. Household units were evaluated that serve both the cooking and drinking requirements of a single family (Figure 5-2a) (35 to 40 Liters/day) and small community units (Figure 5-2b) that serve the cooking and drinking needs of ten or more families.

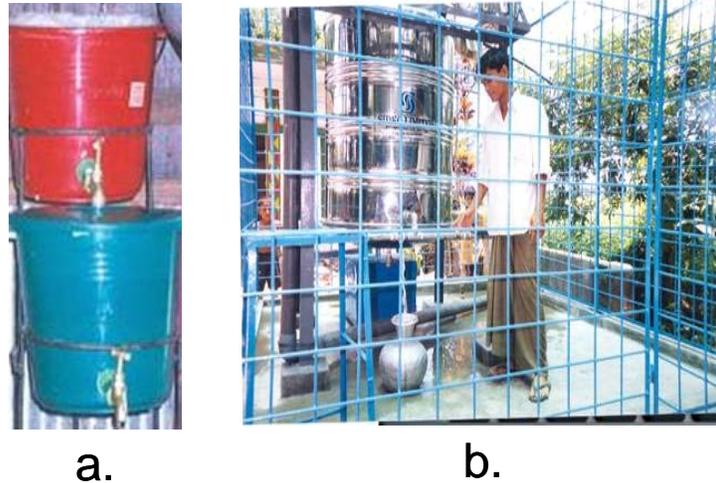


Figure 5-2. Metal oxy-hydroxide based (a) household and (b) community level arsenic removal systems.

The arsenic removal systems were evaluated in different regions with different groundwater matrix. A particular effort was made to understand the effects of phosphate and iron on the performance.

Metal oxy-hydroxides and zero valent iron sorbents worked considerably better than the ion exchange exchange. The high total dissolved solids (TDS) in all the well waters (255-497) limited the volume of arsenic safe water the ion exchange system could produce before system breakthrough occurred. All technologies were sensitive to the groundwater chemistry. Figure 5-3 shows the sensitivity of ferric-coated activated alumina media performance to groundwater phosphate levels. Performance was most adversely affected when phosphate was between 7.3-11.5 mg/L, and the well water pH ranged between 7.6-7.7.

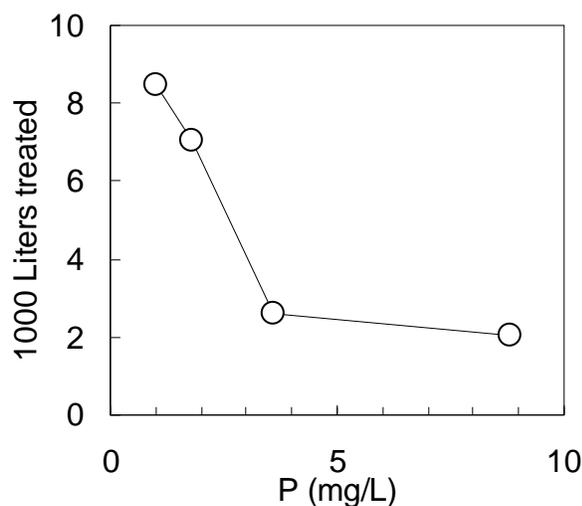


Figure 5-3. Volume of water treated before breakthrough for ferric-coated activated alumina-based filters as a function of groundwater phosphate concentration.

Another interesting observation was that for high iron groundwaters, arsenic removal systems with an iron removal pre-filter prevented surface fouling of the sorbent, but also enhanced overall arsenic removal by scavenging arsenic onto the iron caught by the pre-filter.

Case Study – Low Cost Arsenic Solution from a Fish Hatchery

Shibaloy, a village in the Manikgonj district of Bangladesh, found its own solution to arsenic contamination in its fish hatchery. Like much of Bangladesh, Shibaloy relies on groundwater for its drinking water. Unfortunately, and again like much of Bangladesh, the groundwater beneath Shibaloy contains high levels of arsenic as well as iron. Shibaloy has a fish hatchery, operated by a non-government organization called PRISM, which uses groundwater and provides the fish farmers in the Manikgonj district with fish hatchlings. Dissolved iron must be removed ahead of time otherwise it will oxidize upon contact with air to insoluble precipitates, which coagulate fish spawns, preventing germination. A simple slow sand filtration system consisting of layers of local ‘Sylhet’ sand, gravel and stones was used to remove the iron from around 9.0 mg/L to less than 0.01 mg/L. When the filter becomes clogged the sand in the filter bed is changed. When people in the adjacent villages started to build small household sand filters – earthen Kolschi pitchers - to remove the iron from their own well water, they chose to use the discarded iron-coated sand from the fish hatchery. These home-made filters (See Figure 5-4) have the capacity to process roughly two liters of water per hour and cost about two dollars in materials to build. In mid January 2004, a test of selective households in Shibaloy showed that the homemade filters removed both iron and arsenic. The groundwaters where the filters were successful at removing arsenic to below 50 ppb, had relatively high concentration of iron (>5.0 mg/L), near neutral pH (6.8-7.2), and total arsenic concentration less than or equal to 100 ppb. The arsenic is removed from solution by co-precipitation with the rapidly forming insoluble iron hydroxides which are then caught by the sand filter. The iron oxyhydroxide coatings on the sand particles also

themselves sorb arsenic. The experience at Shibaloy is important because a large percentage of the shallow groundwater wells in Bangladesh contain dissolved iron pointing to the Kolschi filters as a potentially safe, cheap, and socially acceptable means for cleaning the drinking water of Bangladesh.

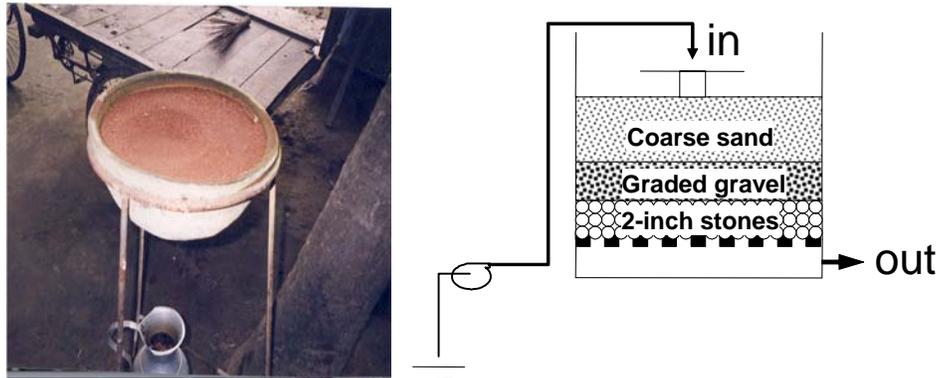


Figure 5-4. Home-made arsenic/iron filter from Shibaloy.

Table 5-3. Arsenic treatment results from Shibaloy.

Well	Filter	Well Water Iron (mg/L)	Well Water pH	Well Water Arsenic (ppb)	Treated Water Iron (mg/L)	Treated Water Arsenic (ppb)
PDB-Teptra	Large Iron Removal Unit	6.0	Not measured	10-25	0.2	Not Detected
Hatchery	Large Iron Removal Unit	9.6	6.8-7.2	50-75	Not Detected	Not Detected
House Minudin	Home Made Kolshi Filter	8.0	6.8-7.2	100	0.5	Not Detected
House Rahim	Home Made Kolshi Filter	10.0	6.8-7.2	100	1.0	Not Detected
House Saiful	Home Made Kolshi Filter	9.0	6.8-7.2	50-75	Not Detected	Not Detected
House Haq	Home Made Kolshi Filter	8.5	6.8-7.2	50-75	Not Detected	Not Detected
House with Filter	Commercial House hold Iron Water filter	10.0	6.8-7.2	50-75	Not Detected	10

Case Study - Zero-Valent Iron Arsenic Filters in Nepal: Importance of Field-Level Follow-Up and Design Modification

The active ingredient in an arsenic removal filter developed by MIT and being tested in the Tari region of Nepal is iron from nails. The iron is released as the nails corrode to form dissolved iron, then iron oxy-hydroxide phases. Dissolved arsenic is removed by precipitation, co-precipitation and adsorption onto the iron oxy-hydroxides. The arsenic-rich iron oxy-hydroxides are then removed by sand filtration. The nails lie on a perforated basket on top of the sand filter and are exposed to air. Water poured on top of the nails then moves through the nails and a perforated plate, and then flows through the sand bed. Over time channeling of flow can bypass the nails and their alteration products (Figure 5-5a). Short-circuiting compromises arsenic removal and can result in effluent total arsenic concentration above the MCL of 50 ppb set by the government of Nepal.

Figure 5-5b shows how iron nails underneath a layer of sand in a three pitcher application over time can become fused into a single layer, decreasing the flow of water through the filter due to the decrease in porosity of the iron layer. The two observations emphasize the need for continual follow-up of arsenic removal approaches and possible design modifications based on field performance. Here a key is to periodically distribute the nails evenly and break up any oxyhydroxide hard pan.



Zero-valent iron-based arsenic removal filter in a rural house in Nepal.



Figure 5-5. (a) Short circuiting of nail-based filter and (b) hardening of a nail layer in a three pitcher filter.

Key Points:

- High pH and groundwater phosphate and silicate can adversely affect arsenic removal by iron-based sorbents,
- Iron removal filters, used in high iron waters, should enhance arsenic removal in two ways: in the pre-filter, and by extending the life of the media,
- Arsenic removal systems should be routinely monitored to maintain and improve performance.

CHAPTER 6 ARSENIC REMOVAL IN DISPERSE SETTINGS: DEVELOPED WORLD

Disperse settings pose severe difficulties for cheaply removing arsenic in developing countries too. Widely separated rural communities whose groundwater is arsenic-contaminated are at a disadvantage because they cannot achieve the economies of scale in arsenic removal that a large community might. Specifically, the capital outlays and operations and maintenance costs of arsenic treatment in disperse settings is inordinately high using existing approaches. The basis for this is outlined immediately below using rural New Mexico as an example. The high costs of disperse treatment have prompted the search for new approaches that are substantially cheaper in rural areas. Two experimental approaches— in-tank filtration and in situ treatment - are described below to emphasize the ongoing need for new solutions to arsenic removal in rural settings.

Arsenic Treatment in rural New Mexico

When the US MCL for arsenic was lowered to 10 ppb the financial burdens fell heavily on small and rural water systems. Roughly 4,000 small water systems across the US (serving less than 3,300 people) are required to lower arsenic in drinking water. In rural New Mexico, where there are roughly 100 arsenic-affected small water systems, costs to comply with an MCL of 10 ppb work out to an estimated consumer monthly cost of roughly \$100 (Bitner et al., 2001). In the past, the only water treatment these small water systems needed was disinfection, usually involving the addition of sodium hypochlorite or chlorine gas to the water prior to storage/distribution. Systems with water containing more than the new 10 µg/L arsenic level must now install and operate a treatment system for the first time.

How might the high outlays be lowered? The arsenic-sorbing iron media used in a fixed bed filtration setup generally accounts for less than 10% of the capital cost and a third of the annual O&M cost. The bulk of both capital and O&M outlays to pay for fixed infrastructure (buildings, filter galleries) and for an operator. Media costs might come down with time; capital and operator costs probably won't.

Low-cost arsenic removal, particularly in developed rural settings, means coming up with an operator/infrastructure-free way of removing small amounts of arsenic (roughly half of the small water systems in New Mexico have arsenic levels in the 10 – 25 ppb range) from small systems that use groundwater. Conceptually this might be done by taking advantage of the existing water infrastructure: a submerged pump at the bottom of a well in a shallow aquifer, a chlorination setup, and a large water tank from which water is subsequently distributed.

Working up from the aquifer:

1. In situ removal of arsenic from aquifers is in its infancy and will be discussed in a later chapter.
2. Submerged pumps are removed from wells only infrequently, which hampers the implementation of down-hole filtration schemes.
3. On the other hand, storage tanks are readily accessible and have already been budgeted for.

In theory, if a community could treat the water in the tank (“In-tank Filtration”) for example, with a submerged pump+filter operating 24/7 the added expense of filter galleries and new building might be avoided.

In-tank Filtration

Removing arsenic while the water is inside the community water storage tank would work (Dwyer et al., 2008) by recirculating the water in the tank at a significantly greater velocity than conventional adsorption, through a column filled with arsenic adsorbing media. This concept might be implemented by either a remotely powered treatment device weighing at most 120 lbs. attached external to the side of the water tank (Figure 6-1) or manually lowered into the tank. A pump (either an exposed air centrifugal or a submersible type) would continually recirculate the storage tank water through a column containing arsenic-sorbing media removing arsenic from the water in the tank 24 hours a day, 7 days a week. The only construction requirements would be fabrication of the pumping recirculation column unit and attachment to the tank. Upon startup of the recirculation column, the arsenic concentration in the well water would be at normal ambient levels; however, once the desired steady state concentration in the tank were attained the relatively large storage tank volume would act to buffer fluctuations in the arsenic levels in the distribution water. Output arsenic levels would be maintained by optimizing the flow rate through the media column. The ability to control the output concentration would provide a significant advantage by only removing enough arsenic to meet the 10 ppb MCL requirement thereby enhancing the media utilization, which would extend media life.

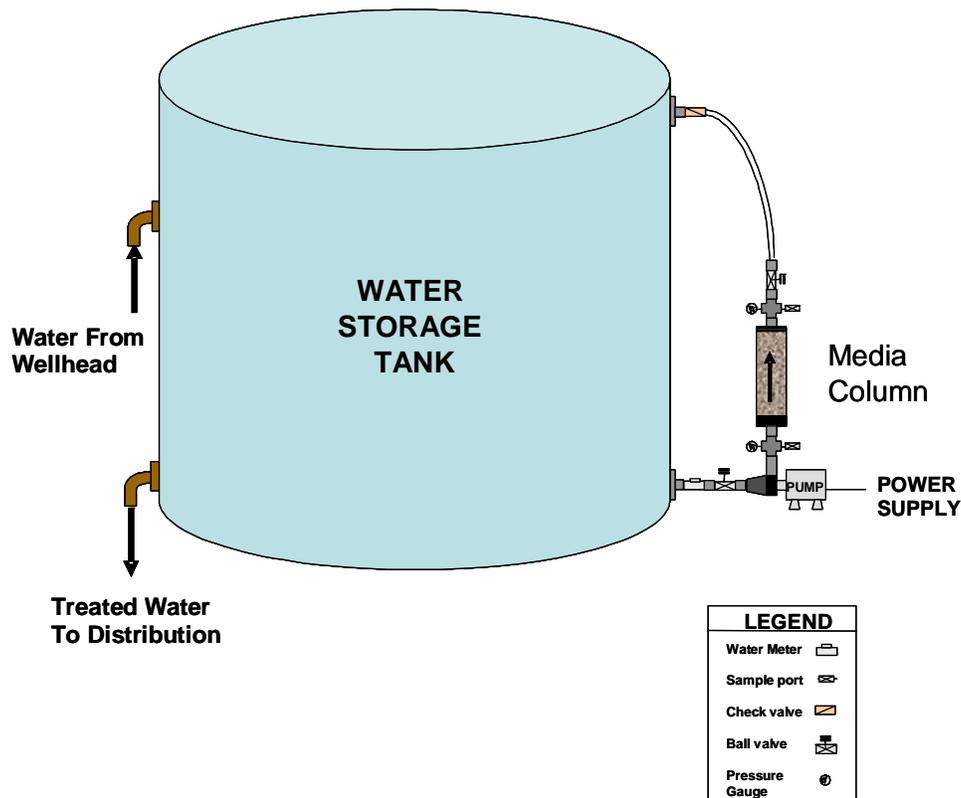


Figure 6-1. Schematic of in-tank arsenic removal system with external recirculation column (Dwyer et al., 2008).

Spent media change out at pre-determined intervals would involve removing the treatment vessel, emptying out the spent media and disposing of it in a landfill, re-filling the filter bed column with fresh media, and reinstalling the vessel. Alternatively, fresh pre-manufactured columns could be exchanged for exhausted columns which could be recharged by the manufacturer or disposed of. The change out frequency is one critical determinant of the economic feasibility of In-tank Filtration, which would likely require more frequent media change outs than a conventional system because much less media is in use. However, the change outs would be much easier due to the ease of handling the relatively small treatment column and media contents. The change out frequency will ultimately depend on the arsenic uptake capacity of the media (As_{max} ; mg As/g media) which is a function of the media type, empty bed contact time (EBCT: minutes), and the chemistry of the water.

The change out frequency can be estimated as a function of system capacity and influent arsenic levels, assuming a filter media mass of 50 kg:

$$\text{Change out time (days)} = \frac{50000 \text{ g} * As_{max} \text{ (mg / g)}}{\text{Capacity}(\text{people}) * (757 \text{ L / day} * \text{person})(C_{in} - C_t) \text{ (mg / L)}}$$

Estimated filter bed change out times is shown in Figure 6-2 as a function of system capacity (number of people) and the filter media capacity.

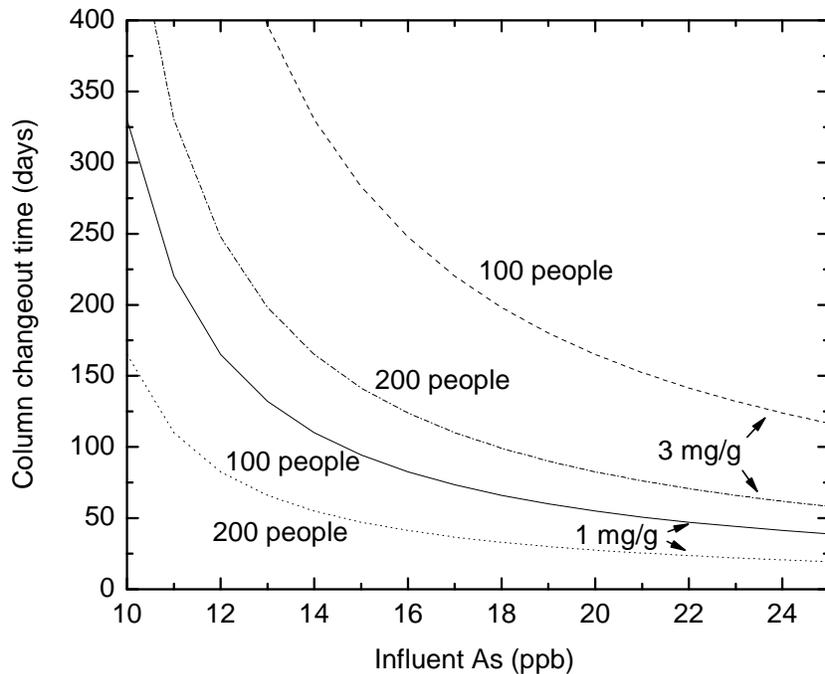


Figure 6-2. Change out time calculated as a function of system capacity, influent arsenic levels and adsorptive media capacity (from Dwyer et al., 2008).

Operation of the column at short EBCT and high hydraulic loading rates allows an installation that uses a much reduced volume of adsorbent medium yet provides a reasonable treatment interval between media changeouts. The absence of large capital and operator costs lowers the overall costs to roughly 1/3rd that of the conventional approach (fixed bed filtration using iron-based media) for small communities (Dwyer et al., 2008). There is also more than a factor of two improvement in efficiency in the amount of water delivered per unit weight of adsorbent medium. Because the system is sized to meet the continuous flow rate and short EBCT of the in-tank absorber rather than the peak flow demand and large EBCT of the once-through system the final arsenic concentration (in this case 8 ppb) can be selected, rather than removing essentially all the arsenic in the once-through system. Capital cost savings come by not requiring a building, strainer equipment and the associated installation costs, using a smaller pump, less piping, instrumentation, etc. O&M costs are lower because there is less equipment to operate and maintain.

In situ Treatment

In situ treatment of arsenic might be attractive in some cases if it can cheaply and effectively lower dissolved arsenic levels in the aquifer and at the wellhead – thereby minimizing infrastructure investments and the generation of wastes. The term *in situ* is here meant to encompass those approaches that immobilize arsenic in the subsurface environment – such as chemical treatment of the aquifer and selective pumping to avoid arsenic-rich zones (Aquifer storage and recovery (ASR) will be considered below).

The simplest path is to not draw arsenic-rich waters from an aquifer in the first place. In many situations high arsenic waters are heterogeneously distributed, both in an aquifer and between individual wells. In theory, surface treatment might be avoided if: 1. high arsenic areas could be identified beforehand, and/or 2. arsenic-producing zones in individual wells could be identified and sealed off. While arsenic availability in each case will be site-specific and depend on such parameters as system redox, hydrologic residence time and so on, sufficient field data is accumulating from arsenic-contaminated sites worldwide to indicate a limited number of arsenic mobilization modes (e.g. reductive degradation of ferric hydroxide hosts, oxidative dissolution of arsenic-bearing sulfides). There is therefore the potential that the often subtle differences in aquifer chemistry that control arsenic mobilization might be understood sufficiently to anticipate the location of high arsenic waters, and to avoid mobilizing arsenic into wells that draw drinking water. Accurate methods for making such assessments are needed. Nevertheless, because the primary consideration of most well owners is to maximize withdrawal rates, not minimize arsenic content, the expense associated with the first might completely overshadow the second.

Chemical treatments designed to enhance the existing arsenic uptake capacity might avoid the complexities of *ex situ* surface treatment and provide an inexpensive means for producing relatively arsenic-free water. One conceptually simple approach is to inject water that has been oxygenated by contact with the atmosphere at the surface. For aquifers that contain relatively high proportions of arsenite and/or ferrous iron, oxygenation might result in oxidation of the arsenite to arsenate and formation of ferric (hydro)xides in the aquifer matrix. Both processes would favor aquifer uptake of arsenic and, in theory, a reduction of dissolved arsenic at the wellhead. Complicating factors for this particular *in situ* treatment

might include well clogging by ferric hydroxides and/or carbonate minerals. Alternative *in situ* approaches might conceptually seek to enhance the existing high sorptive capacity of aquifers or precipitate arsenic *in situ* as a component of newly formed minerals. In particular, doping of aquifer solids with low levels of Cu^{++} or Zn^{++} has been shown to remove dissolved arsenic (Brady et al., 2004) by amplifying the sorptive capacity of the aquifer. In theory, one might inject either metal cation into a well to create an *in situ* filter bed able to sorb arsenic from the water that is subsequently pumped. Note that for all *in situ* approaches the small amount of practical experience hinders accurate estimates of their potential effectiveness.

Permeable reactive barriers (PRBs) are occasionally used to limit the transport of subsurface arsenic at hazardous waste sites through sorption, through reduction to insoluble phases, or both. The vast majority of PRBs are constructed of zero valent iron which acts as a reductant but is converted to highly sorptive ferric hydroxide in the process. Sorptive barriers of, for example, clinoptilolite and hydroxyapatite, which don't participate in redox reactions have also been used to limit the transport of contaminant ions. Rarely has arsenic been the primary PRB target though. In theory, arsenic-specific PRB material might be identified and applied in drinking water (non-hazardous waste) situations.

ASR and Mobilization Potential

Aquifer storage and recovery (ASR) is a form of inadvertent aquifer engineering that is included here because: ASR has the potential to contaminate otherwise non-contaminated waters with arsenic; and the underlying principles of arsenic mobilization by ASR might be used to “reverse engineer” arsenic-free groundwaters.

ASR efforts have been implemented worldwide and their use can be expected to increase in the future. Water injected into an aquifer as part of an ASR effort might lose arsenic to mineral surfaces. Alternatively, injection might increase dissolved arsenic levels if, for example, the input fluids contain phosphate (or silicate) at levels sufficient to desorb arsenic from ambient solids, or if redox changes prompt destruction of arsenic hosts. For example, Figure 6-3 shows arsenic increases observed at an ASR facility in Florida (Arthur et al., 2002).

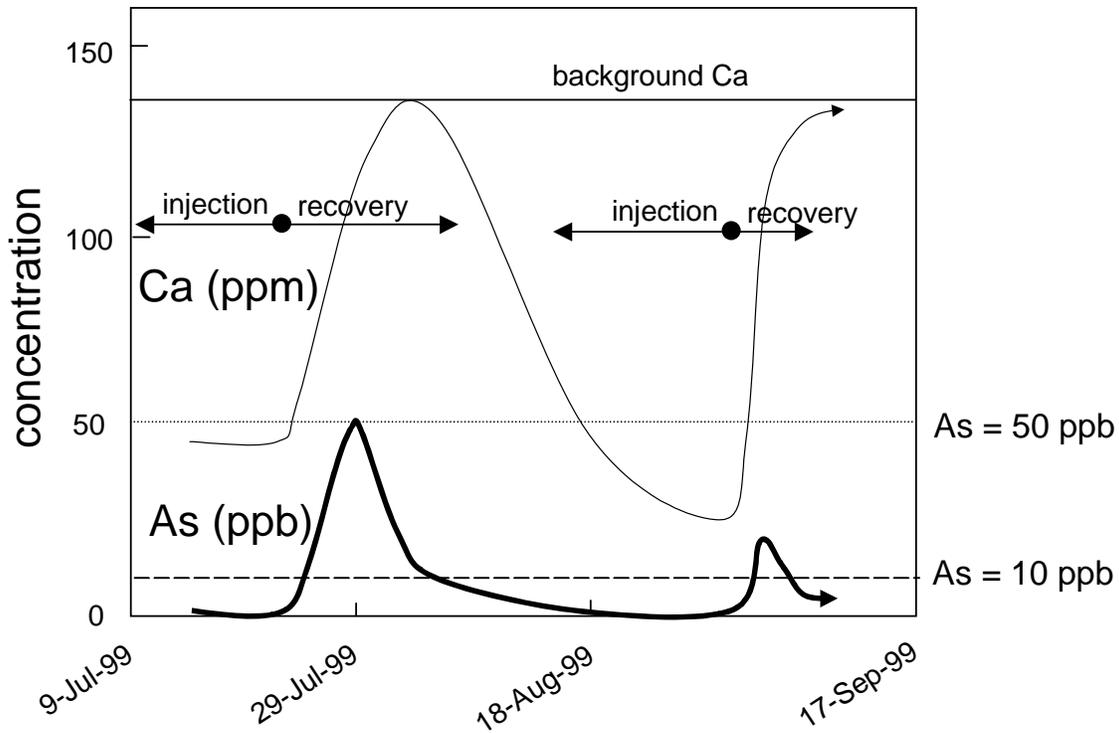


Figure 6-3. Schematic of As and Ca levels from ASR well in Florida (Arthur et al., 2002).

Unfortunately, the underlying controls over arsenic mobilization for a particular aquifer are often only hazily considered beforehand.

Because of the ubiquity of arsenic in the subsurface and its tendency to be in a desorbable fraction, every aquifer must be presumed to contain arsenic that can potentially be mobilized. Dissolved levels of arsenic appear to depend on the chemistry of the ambient groundwaters and less on solid phase arsenic levels. Relatively minor shifts in water chemistry often result in supra-MCL arsenic levels. The simplest way for this to occur is with the introduction of phosphate – for example as might occur agricultural runoff is injected into the subsurface. Phosphate is more strongly bound to ferric hydroxides and is routinely observed to displace previously sorbed arsenic into solution. Silicate sorbs less strongly relative to arsenic but tends to be present in much higher quantities (Silicate levels in waters are routinely found to exceed 10-20 ppm). Boron, another common component of surface waters, can displace arsenic from surface sites as well. Lastly, simple increases in pH can result in arsenic mobilization.

Arsenic can be remobilized when geochemical reactions cause reduction of sorbed arsenate to mobile arsenite and/or when a ferric hydroxide host is itself reductively dissolved. Either step requires a reduction in aquifer redox capacity such as is observed downgradient of municipal landfills or, more generally, whenever large quantities of organic matter are injected into the subsurface. Oxidation of reduced arsenic associated with sulfide minerals or organic matter can itself be mobilized through oxidation of the respective host. Table 6-1 categorizes arsenic mobilization pathways.

Table 6-1. Arsenic mobilization pathways (U.S. Environmental Protection Agency, 2007)

Location and Setting	Original Conditions (Arsenic Immobile)	Altered Conditions (Arsenic Mobilized)
Unconsolidated aquifer consisting of glacial outwash, glaciomarine clay, and till overlying bedrock; New Hampshire ^a	Arsenic bound to poorly crystalline iron hydroxides in glaciomarine clay under oxidizing conditions (Eh ~ 400 mV)	Reductive dissolution of iron hydroxides due to microbially driven Fe-reducing conditions stimulated by organic carbon in landfill leachate
Suwannee Limestone, Upper Floridan consolidated aquifer; Florida ^b	Arsenic hosted in pyrite that is most abundant in high porosity zones; anoxic aquifer	Oxidative dissolution of pyrite due to injection of oxygenated water
Unconsolidated, glacial outwash aquifer consisting of coarse (quartz) sand and gravel with Fe and Al oxide and/or silicate mineral coatings; New Hampshire ^c	Arsenic adsorbed to mineral coatings under oxidizing conditions	Adsorbed arsenic mobilized due to desorption in the presence of elevated phosphate derived from sewage disposal via land application coupled with reductive dissolution of Fe-bearing mineral coatings

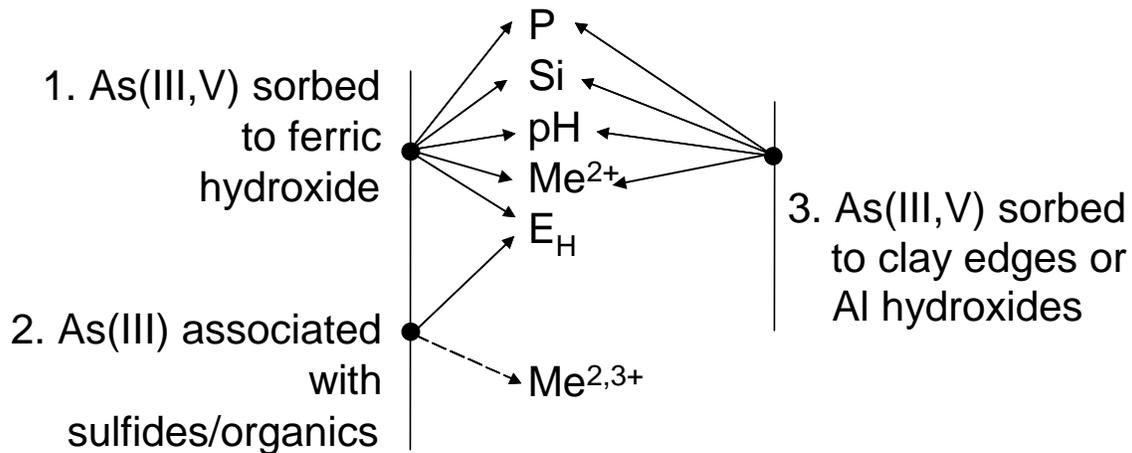


Figure 6-4. Absolute impacts of solution variables on 3 primary solids-associated aquifer arsenic sinks (labeled 1-3). Me^{2+,3+} = metal cation, e.g. Ca²⁺, or Fe³⁺. Upward pointing arrows indicate a variable whose increase will potentially result in a release of arsenic from a particular sink into solution. Downward pointing arrows indicate a variable whose increase will result in uptake of arsenic and a decrease in dissolved arsenic. E_H might be considered a proxy for total organic carbon.

Figure 6-4 schematically collects the fluid composition variables that should bear the greatest scrutiny during ASR and identifies their likely effect on dissolved arsenic levels depending

on the original state of arsenic in the aquifer – associated with ferric hydroxide or associated with sulfides and/or organic matter. The 3 most common sinks are labeled in Figure 6-4. There is an E_H -dependent saddle in arsenic mobilization potential. At very low redox potentials arsenic is immobile due to incorporation in sulfides. At high redox potentials arsenic is relatively immobile due to its incorporation in/onto ferric hydroxides (Again, pH, P and Si levels play a role as well). Higher levels of divalent cations promote arsenate uptake onto ferric hydroxide surfaces. In between, sulfide minerals are oxidized and ferric hydroxides reduced, leaving arsenic without a host and in the aqueous phase instead.

The right hand side of Figure 6-4 notes the general similarity between arsenic sorption to clay edge sites and other metal oxides (e.g. Al oxides and ferric hydroxides) minus the E_H -dependent stability of the latter. A dashed line connecting metal levels points to the unclear, but potentially important role of metal-arsenate/metal-arsenite-sulfide interactions. Figure 6-4 neglects the role of other anions potentially able to displace arsenate. It also neglects temperature which appears to mobilize arsenic, at least in some cases. The relationships in Figure 6-4 are qualitative guides.

Key Points:

- A variety of natural and man-made processes can trigger arsenic contamination of an aquifer,
- Arsenic contamination of an aquifer often doesn't require an external, non-natural source,
- Almost all existing remediation techniques center on engineering aquifer chemistry to cause iron oxides to sorb arsenic.

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