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**REVIEW OF ARSENIC REMOVAL TECHNOLOGIES FOR
CONTAMINATED GROUNDWATERS**

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ABSTRACT

This review was compiled to summarize the technologies currently being investigated to remove arsenic from drinking waters, with a special focus on developing and third-world countries where the problem is exacerbated by flooding and depressed economic conditions. The reason for compiling this report is to provide background material and a description of competing technologies currently described in the literature for arsenic removal. Based on the sophistication and applicability of current technologies, Argonne National Laboratory may develop an improved method based on magnetic particle technology. Magnetic particle sorbents may afford improved reaction rates, facilitate particle-water separation, and offer reusability.

Developing countries like Vietnam and Bangladesh cannot afford expensive, large-scale treatments to remove arsenic from drinking waters to acceptable limits (from 50 ppb to 10 ppb, depending on the country). Low-cost, effective technologies that can be readily available at the household or community level are needed to solve the present crisis. Appropriate technologies should meet certain criteria, including the following:

- The treatment must be applicable over a wide range of arsenic concentrations.
- It should be easy to use without running water or electricity.
- The materials for the treatment should be cheap and readily available, and/or suitable for reuse.

Our review of arsenic removal technologies and procedures indicates that iron filings, ferric salts, granular ferric hydroxide, alumina manganese oxide, Aqua-bind™, and Kimberlite tailings are potentially low-cost sorbents that can remove arsenic after simple mixing in a relatively short time. However, all these technologies suffer from significant shortcomings. Ferric salts are cheap and very effective at removing arsenic but the reaction rates are slow. Fixed-bed columns make use of activated alumina and iron-coated sands but do not work well with groundwater having high concentrations of iron because iron precipitates in the presence of air, which could clog and foul the column. Synthetic sorbents are highly selective and effective and do not pose a significant waste disposal concern because they are generally non-hazardous. Aqua-bind™ is perhaps the most effective synthetic sorbent available for removing arsenic, but it must be mass-produced to realize low cost. Naturally occurring solids are cheap and remove arsenic well; however, the removal rate is often very slow and the solids can harbor bacteria. This report reviews competing technologies for removal of water-borne arsenic to establish a baseline for technology improvements. Specifically, the information in this report will serve as a basis for developing a low-cost separation technology using functionalized magnetic particles to adsorb arsenic and permanent magnets to separate the arsenic-loaded magnetic particles from the cleaned water.

1. INTRODUCTION

Arsenic is a well-known toxic metal and is present mainly as oxyanion compounds in groundwater (1). The World Health Organization's (WHO's) current provisional guideline for arsenic in drinking water is 10 $\mu\text{g/L}$, but all developing countries affected with contaminated groundwater are still struggling to keep up with the previous WHO guideline value of 50 $\mu\text{g/L}$ (2). Chronic exposure to arsenic $>50 \mu\text{g/L}$ in drinking water can result in serious health problems. Symptoms of chronic exposure to groundwater contaminated with arsenic at concentrations significantly $>50 \mu\text{g/L}$ include skin, cardiovascular, renal, hematological and respiratory disorders (1). An estimated 300,000 people in West Bengal alone suffer from arsenic-induced skin lesions. Serious illnesses related to arsenic such as melanosis, keratosis, cancer, and gangrene have been reported in West Bengal and Bangladesh (3).

Arsenic contamination of drinking water is presently a worldwide epidemic. Contaminated drinking water has been found in Argentina, Chile, Mexico, China, Hungary, West Bengal, Bangladesh and Vietnam. Of these regions, West Bengal and Bangladesh are most seriously affected in terms of the size of the population at risk and the magnitude of the health problems. A recent survey of shallow groundwater aquifers in Bangladesh showed that 27% of the aquifers have arsenic concentrations $>50 \mu\text{g/L}$ (2). Although the percentage does not seem remarkably high, it is alarming considering that more than 90% of the rural population in Bangladesh gets drinking from 4-5 million tubewells (4).

Most of arsenic problems in third-world countries today are caused by natural erosion. One important mechanism through which the groundwater is polluted with arsenic is the reduction of iron oxyhydroxide (FeOOH) by bacteria and subsequent desorption of arsenic from the iron surfaces. In the Bengal Basin (part of Bangladesh and West Bengal), it is the main mechanism by which groundwaters become contaminated with arsenic (5). That does not mean humans are exempted from blame for the present arsenic crisis; significant arsenic pollution has occurred through the use of pesticides, herbicides, crop desiccants and additives to animal feed (6). The impact of producing arsenic-containing chemicals on the environment was felt by Calcutta, India, where more than 7,000 people consumed arsenic-contaminated water caused by the release of arsenic through the manufacturing of insecticides by a chemical factory in the region (7).

The focus of this report is on current technologies for arsenic removal through adsorption, precipitation, and coprecipitation processes. These processes make use of inorganic sorbents and adsorption medias, such as ferric chloride and iron-oxide-coated sand. Precipitation involves the formation of insoluble compounds, adsorption involves the electrostatic binding of arsenic to metal hydroxide surfaces, and coprecipitation involves the incorporation of soluble arsenic species into a growing metal hydroxide phase (8). Most technologies utilizing those processes require an oxidation pretreatment to convert As(III) to As(V) because As(V) adsorbs and reacts more strongly onto the solid phase than does As(III) .

2. ARSENIC CHEMISTRY

2.1 ARSENIC FORMS AND MOBILITY

Arsenic rarely occurs in a free state and is found largely in combination with sulfur, oxygen, and iron. In groundwater, arsenic combines with oxygen to form inorganic pentavalent arsenate and trivalent arsenite. Unlike other heavy metalloids and oxyanion-forming elements, arsenic can be mobilized under a wide range of oxidizing and reducing conditions at the pH values typically found in groundwaters (pH 6.5-8.5). Whereas all other oxyanion-forming elements are found within the $\mu\text{g/L}$ range, arsenic can be found within the mg/L range (9).

Arsenic has four main chemical forms having oxidation states, -3, 0, +3, and +5, but in natural water its predominant forms are inorganic oxyanions of trivalent arsenite (As^{3+}) or pentavalent arsenate (As^{5+}) (9). The toxicity of different arsenic species varies in the order arsenite > arsenate > monomethylarsonate > dimethylarsinate. Trivalent arsenic is about 60 times more toxic than arsenic in the oxidized pentavalent state, and inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds (10). The organic forms of arsenic are quantitatively insignificant and are found mostly in surface waters or in areas severely affected by industrial pollution (9). The relative concentrations of As(III) to As(V) vary widely, depending on the redox conditions in the geological environment (10).

2.2 EFFECTS OF pH AND REDOX POTENTIAL

The two most important factors controlling the speciation of arsenic (and, to some extent, solubility) are pH and redox potential. Under oxidizing conditions at pH less than 6.9, H_2AsO_4^- is the dominant species, whereas HAsO_4^{2-} predominates at higher pH. Under reducing conditions at a pH value less than 9.2, the uncharged arsenite species H_3AsO_3 is dominant. In contrast to the pH dependency of As(V), As(III) was found virtually independent of pH in the absence of other specifically adsorbed anions (9). Most often, more trivalent arsenic than pentavalent arsenic is found in reducing groundwater conditions, whereas the converse is true in oxidizing groundwater conditions. The stabilities of arsenic species under different pH and redox conditions are shown in Table 1 (11).

Table 1. Stability of Arsenic Species

| Reducing Conditions | | Oxidizing Conditions | |
|---------------------|----------------------------|----------------------|----------------------------|
| pH | As(III) | pH | As(V) |
| 0-9 | H_3AsO_3 | 0-2 | H_3AsO_4 |
| 10-12 | H_2AsO_3^- | 3-6 | H_2AsO_4^- |
| 13 | HAsO_3^{2-} | 7-11 | HAsO_4^{2-} |
| 14 | AsO_3^{3-} | 12-14 | AsO_4^{3-} |

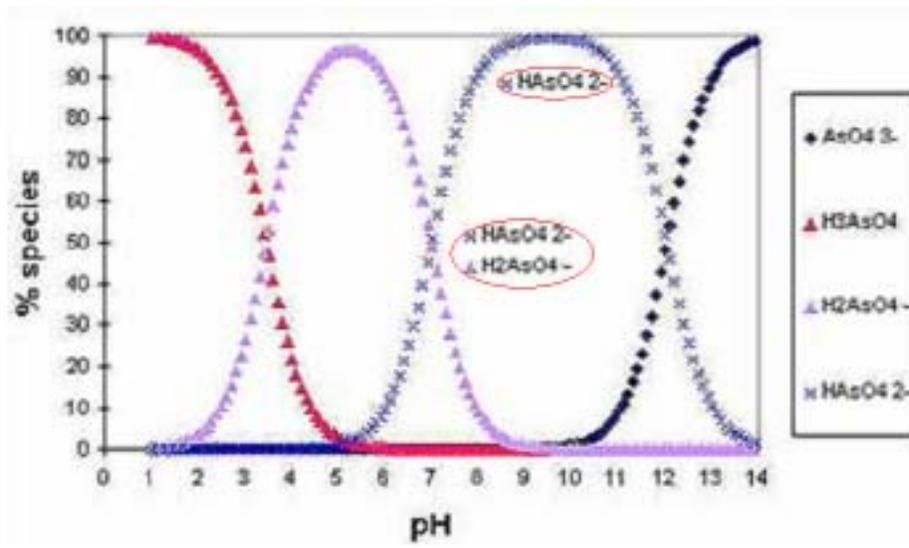


Fig. 1. pH diagram for As(V)

Unlike other toxic trace metals whose solubilities tend to decrease as pH increases, most oxyanions, including arsenate (As^{5+}), tend to become more soluble as pH increases (Fig. 1). When most other metals become insoluble within the neutral pH range, arsenic is soluble at even near-neutral pH in relatively high concentrations. That is why groundwaters are easily contaminated with arsenic and other oxyanions (9).

3. GROUNDWATER ENVIRONMENTS

3.1 FEATURES

High-arsenic groundwaters are usually present in two types of environment: inland or closed basins in arid or semi-arid areas (an oxidizing environment) and in strongly reducing aquifers. Both environments contain young sediments where water flow is slow enough to allow arsenic to accumulate. As(III) is usually the predominant species under reducing conditions, whereas As(V) usually predominates under oxidizing conditions. The extent of arsenic presence in groundwater is very small compared with the levels in associated minerals, particularly Fe oxides. In the presence of metal oxides, most arsenic becomes immobilized either through compound formation or adsorption. Desorption of arsenic from the minerals could pose serious problems because only a small percentage of As is needed to dissolve or desorb and render groundwaters unsafe for consumption (9).

3.2 TRIGGERS FOR DISSOLUTION OF ARSENIC FROM MINERALS

There are two main triggers that lead to the release of arsenic from its solid-iron oxide phase (9). The first is a pH change under oxidizing conditions, and the second is the development of strongly reducing conditions at near-neutral pH. Under oxidizing conditions at pH <8.5, most As adsorbs strongly to metal oxides as As(V). At pH >8.5, As(V) desorbs from the oxide surfaces, raising the total concentration of arsenic in groundwater. Some factors that may be responsible for the increase in pH in oxidizing environments are the effect of other anions, especially phosphate; the uptake of protons in solution due to weathering and ion-exchange reactions; and the effect of evaporation in arid and semi-arid regions. The most common factor that is responsible for creating reducing condition at near-neutral pH is the rapid accumulation of young sediments. Arsenic release under reducing conditions has many possible causes, such as dissolution of arsenic-containing minerals (9).

4. DISTRIBUTION OF ARSENIC IN GROUNDWATERS WORLDWIDE

4.1 REDUCING ENVIRONMENT: BANGLADESH, WEST BENGAL, VIETNAM, CHINA, AND TAIWAN

Approximately 30-35 million people in Bangladesh and 7 million people in West Bengal are exposed to elevated levels of arsenic in drinking water. Arsenic concentrations were found from $>0.5 \mu\text{g/L}$ to $3200 \mu\text{g/L}$, with As(III) present as the dominant species. The relative ratio of dissolved As(III) to As(V) is often greater than 1 because As(III) is more mobile under reducing conditions. The groundwaters in these regions usually have high iron content, as well. High concentrations of arsenic are more often found in shallow wells (100-150 m deep). About 27% of shallow wells less than 150 m deep have arsenic concentrations $>50 \mu\text{g/L}$, whereas wells greater than 150-200 m deep usually have arsenic concentration $<5 \mu\text{g/L}$ (9).

The Bengal Delta and North Vietnam have similar reducing geological features, with relatively young alluvial sediments and anoxic groundwaters (12). Many Vietnamese depend on aquifers of the large deltas of the Mekong and Red Rivers for drinking water. More than 10 million people are exposed to harmful arsenic concentrations from drinking well water (9). The groundwaters usually have high concentrations of Fe, Mn, and NH_4 . Shallow tube wells in Hanoi have been found to have significant concentrations of As, ranging from 1 to $3050 \mu\text{g/L}$ (mean = 159). Investigations of tube wells indicated that arsenic concentrations in 48% of them were $>50 \mu\text{g/L}$ (20% were $>150 \mu\text{g/L}$). In highly affected areas, the groundwaters had an average arsenic concentration of $430 \mu\text{g/L}$ (12). Arsenic contamination in Vietnam was not well understood until recently, and the work is ongoing to better understand the problem (9).

China faces similar contamination, with more than 5 million people exposed to arsenic from drinking contaminated groundwater. Inner Mongolia and the Xinjiang and Shanxi Provinces in Northern China were found to have high arsenic concentrations in groundwater. Concentrations of arsenic ranged from 40 to $750 \mu\text{g/L}$ in deep artesian groundwater from Dzungaria Basin on the north side of the Tianshan Mountains. High arsenic concentrations were found less frequently in non-artesian groundwater, however. In Inner Mongolia, aquifers were found to have arsenic concentrations $>50 \mu\text{g/L}$, with As(III) present as the dominant species (60-90% of the total). (9)

4.2 ARID OXIDIZING ENVIRONMENT: ARGENTINA, MEXICO, AND CHILE

Oxidizing groundwater environments favor mobilization of As(V) at above-neutral pH. Below pH 8.5, arsenate strongly adsorbs to the mineral oxides or becomes part of the mineral structure. Some large areas in Argentina, Mexico, and Chile were found to have arsenic-contaminated groundwater under oxidizing conditions (9). Of those regions, groundwaters from the Chaco-Pampean Plain of central Argentina were most seriously affected. The groundwaters there also had low dissolved Fe and Mn concentrations (in contrast to high Fe and Mn oxides under reducing conditions) and typically had high salinity and neutral-to-high pH. Several studies were carried out to determine the severity of the problem in some provinces of the Chaco-Pampean Plain. Arsenic concentrations ranged from <10 to $720 \mu\text{g/L}$ (mean $201 \mu\text{g/L}$) in Cordoba and Santa Fe, <4 to $5280 \mu\text{g/L}$ (median $145 \mu\text{g/L}$) in La Pampa, and 12 to $1660 \mu\text{g/L}$

(median 46 $\mu\text{g/L}$) in Tucuman (9). The primary factor in their mobilization was believed to be arsenic-bound metal oxides, especially Fe and Mn oxides under high pH conditions. In La Pampa province, As(III)/As(V) ratios typically were low at about 0.017, mostly as As(V) (1).

Problems due to arsenic contamination have also affected Central America. Significant chronic arsenic-related health problems have arisen in the Lagunera Region in Northern Mexico. Groundwater is an important source of drinking water there because the region is arid. The groundwater environment is predominantly oxidizing, with neutral-to-high pH (6.3-8.9). The main form of arsenic present in the region is As(V), and total arsenic concentrations are 8 to 624 $\mu\text{g/L}$ (mean = 100 $\mu\text{g/L}$) with 50% of the groundwater samples investigated having arsenic concentrations >50 $\mu\text{g/L}$. The exposed population was estimated at more than 400,000 in the Lagunera Region (9).

In South American, Chile's Administrative Region II was seriously affected by high concentrations of arsenic in both surface and groundwaters. Water resources in the region are limited because of arid conditions. Arsenic concentrations in both surface and groundwaters are usually >100 $\mu\text{g/L}$, with arsenate anion present as the main species. Although arsenic treatment plants were installed in the towns several decades ago, rural populations still rely largely on groundwater for drinking (9).

4.3 AREAS AFFECTED BY MINING

Mining activities can also cause release of arsenic into groundwater. About 1,000 people were diagnosed with arsenic-related skin disorders in the Ron Phibun District in Nakhon Si Thammarat Province of southern Thailand in the late 1990s. Arsenic concentrations up to 5000 $\mu\text{g/L}$ were found in shallow groundwater, induced or exacerbated by mine workings. Another important mining area is the Ashanti Region of central Ghana, but arsenic was found at surprisingly low concentrations in the region. Some mining areas in the USA also are seriously contaminated by arsenic, such as the Fairbanks, Alaska, gold-mining district, the Leviathan Mine in California, and Kelly Creek Valley, Nevada. (9).

4.4 SUMMARY

Table 2 summarizes the contamination problems in the countries discussed in the preceding sections of this report.

Table 2. Major Countries Facing Serious Arsenic Contamination in Drinking Water^a

| Country/Region | Population Exposed | Concentration Range, µg/L | Groundwater Properties | Other Dissolved Ions |
|---------------------------------|---------------------------|----------------------------------|---|--|
| Bangladesh | 30x10 ⁶ | <0.5-2500 | Strongly reducing conditions, neutral pH, high alkalinity | High Fe |
| West Bengal | 6x10 ⁶ | <10-3200 | As for Bangladesh (27% >50 µg/L) | High Fe |
| China | 5.7x10 ⁶ | 10-1820 | Strongly reducing artesian conditions | |
| Argentina (Chaco Pampean Plain) | 2x10 ⁶ | <1-5300 | Oxidizing conditions, neutral-to-high pH, high alkalinity; arsenic present mainly as As(V). | |
| Mexico (Lagunera) | 0.4x10 ⁶ | 8-620 | Oxidizing conditions, neutral-to-high pH; arsenic present mainly as As(V) | Low concentrations of dissolved Fe and Mn |
| Northern Chile (Antofagasta) | 0.5x10 ⁶ | 100-1000 | Oxidizing conditions, high pH; arsenic present mainly as As(V) | |
| Red River Delta, Vietnam | >10x10 ⁶ | 1-3050 | Reducing conditions, high alkalinity | High concentrations of Fe, Mn, NH ₄ |
| USA river water, baseline | -- | 2.1 | -- | -- |

^aFrom Reference 9.

5. OVERVIEW OF ARSENIC TREATMENTS

Most arsenic treatments fall into four process categories: ion exchange, membrane process, adsorption, or chemical precipitation. Ion-exchange treatments are very limited in their ability to remove arsenic because of exchange competition from other anions found in groundwater. Membrane processes are very effective at removing arsenic from groundwater, but the cost is high. Accordingly, adsorption and chemical precipitation processes are being explored for low-cost, effective treatments (4).

5.1 ADSORPTION AND CHEMICAL PRECIPITATION TREATMENTS

Most adsorption and chemical precipitation treatments require an oxidation pretreatment to convert As(III) into As(V) because As(V) usually adsorbs and reacts more strongly than As(III). Arsenic can be oxidized by ozone, free chlorine, hypochlorite, permanganate, birmessite, manganese oxide, hydrogen peroxide and Fulton's reagent (4). Although ozone has a very high oxidation potential, it can lead to side reactions with natural organic matter (13). Using chlorine poses the risk of introducing harmful trichloromethane into the drinking water. The most common oxidizing reagents used in developing countries are atmospheric oxygen, hypochlorite (HClO), and permanganate. Air oxidation is very slow compared with permanganate (KMnO₄) and chlorine, which can oxidize As(III) rapidly under a wide range of conditions (4). Permanganate is a very effective and stable oxidizing agent, but gives water an unattractive color, which can be removed by an adsorbing media such as sand (14).

Agents that can bind to arsenic through adsorption or through formation of insoluble compounds with arsenic by precipitation or co-precipitation are referred to as sorbents. Many kinds of sorbents have been tested in both laboratory and field studies. Those sorbents are too numerous to account for in this report, and thus only the most common ones that have undergone extensive laboratory and/or field tests are examined.

The present focus on arsenic remediation in third-world countries is on using iron-containing compounds because they are both cheap and effective (15, 16). Other synthetic sorbents such as lanthanum compounds (17), manganese oxides (18), Aqua-bindTM (19), and granular ferric hydroxide (20) have also proved effective for arsenic removal. Clays and mineral-containing rocks are very capable of absorbing arsenic but often at a much slower rate (11, 16). Laboratory tests might show high arsenic removal results for many adsorbents, but experience show that the adsorbents are not as effective in the field because of the presence of Mg²⁺ and Ca²⁺ and other naturally occurring ions, which compete with arsenic for adsorbent sites (21). The majority of the technologies discussed in this report have yet to be field-tested, and so the results from laboratory research indicate only their probable performance in the field.

5.1.1 Ferric Salts and Aluminum Alum

Coagulation-flocculation processes using alum, ferric chloride, or ferric sulfate are effective at removing arsenic. They are the most well known arsenic treatments and have been more extensively tested in both laboratory and field studies than other technologies. Since both alum and ferric salts are more efficient at removing arsenate, oxidation of As(III) is required to

achieve maximum removal efficiency. On a weight basis, ferric salts are more efficient at removing arsenic than alum. Ferric salts are also effective in removing arsenic over a wider range of pH than alum (4).

Methodology: KMnO_4 is added to water to oxidize As(III). Coagulants (ferric salts or alum) are then added, and the solution is stirred well for a few minutes. Microflocs begin forming rapidly as the solution is stirred gently to allow the formation of easily settable flocs. Finally, the arsenic adsorbed on coagulants is removed by sedimentation. A filtration step may be needed for complete removal of all flocs.

Laboratory Results: The Bucket Treatment Unit (BTU) developed by DPHE-Danita Project made use of the coagulation-flocculation process using ferric salts. The first bucket (both are 20 L) was used for mixing chemicals, and the second one contained treated water. Field studies showed that by using 100 mg/L of ferric chloride and 1.4 mg/L of KMnO_4 , the arsenic content in treated water was well below 50 $\mu\text{g/L}$ and never exceeded 37 $\mu\text{g/L}$. The arsenic range in untreated water was between 375 and 640 $\mu\text{g/L}$. Arsenic removal efficiency of ferric salts is often well over 90%.

5.1.2 Iron Filings

Zerovalent iron (Fe^0) has many important applications in environmental chemistry. It has been used to destroy chlorinated hydrocarbons and to remove inorganic contaminants, such as CrO_4^{2-} , via reductive precipitation. Fe^0 has also proved effective at removing As(III) and As(V), and the predominant mechanistic pathways seems to be surface precipitation or adsorption (16). Fe^0 is a strong reducer and thus is an effective agent for removing both inorganic and organic arsenic. Another advantage of using Fe^0 is that it is nontoxic and inexpensive. Literature data show that Fe^0 is effective at removing As at low pH and in high-sulfide-containing water. Although the reducing strength of Fe^0 decreases significantly at neutral pH, the hydroxide species forming on the surface of Fe^0 are effective adsorption sites for both As(V) and As(III) at neutral and basic pH (1).

5.1.2.1 Ramaswami et al. Study

Ramaswami et al. (10) investigated Fe^0 for arsenic removal using a batch-mixed iron treatment with zerovalent iron. High removal efficiency (93%) was achieved for a short contact time (0.5-3 hours). Only As(III) species were tested, however. The highest rate of removal was found in headspace-free systems when sulfates were present in solution, whereas slower rates were found when phosphate was present because it tends to retard sorption uptake by iron. Arsenic was found to adsorb strongly to the iron filings, and the treated water could be easily decanted. Residual dissolved iron was at low concentrations that were safe for drinking water. The treatment was most appropriate for in-home point-of-use techniques. The iron could be reused at least 100 times. A treatment of 10 L of water per day for a year would cost a family in India or Bangladesh \$0.60, a reasonable charge.

Methodology: Only As(III) solutions were used in the study (10). The pH value in all vessels was maintained at 5. Optimal conditions for arsenic removal were first determined by

running a batch-mixed experiment with high-arsenic-content water (2000 µg/L). The conditions were then evaluated with water containing 200 µg/L to test the performance of the technology over a wide concentration range. Three sets of systems were evaluated for effectiveness at removing arsenic:

- Vessel containing arsenic, sulfate, and some natural minerals with no air present
- Vessel containing arsenic and sulfate with some air present
- Vessel containing arsenic and phosphate with some air present

Solid iron filings were added to the vials at both high (2500 mg/L) and low loadings (1250 mg/L and 625 mg/L). The vials were mixed, and a sample from each vial was collected for analysis.

Laboratory Results: Arsenic removal was not efficient in the presence of air and/or phosphates. The results from headspace-free systems (filled with water) show that high removal efficiency can be achieved over a wide range of arsenic concentrations using iron filings, while maintaining a low level of dissolved iron in water. A headspace-free system containing a high-iron dose of 2,500 mg/L and an initial arsenic concentration of 2,000 µg/L can remove 95% of arsenic in 30 minutes. The final arsenic concentration was 120 µg/L, and the amount of dissolved iron was below the regulatory limit. Smaller iron doses (625 mg/L and 1250 mg/L) in the same headspace-free system containing initial arsenic concentration of 2,000 µg/L showed 95% removal in 3 hours of contact time (compared with 30 minutes contact time with an iron dose of 2500 mg/L). In contact with arsenic at low concentration (200 µg/L), solid iron (625-2500 mg/L) can achieve >90% arsenic removal efficiency while maintaining a safe level of dissolved iron in water. In another study where BaSO₄ was added to promote the formation of arsenopyrites (22), a simple tube filled with sand and iron filings, designed to fit in a well outlet, can achieve 97% arsenic removal for initial arsenic concentration of 45-8600 µg/L.

5.1.2.2 Su and Puls Study

Four types of zerovalent iron filings (Fisher, Peerless, Master Builders, and Aldrich) were investigated for removal of As(III) and As(V) from drinking water (16). The metals were allowed to react with arsenic, and relative removal efficiencies were achieved in the following order: Fisher > Peerless, Master > Aldrich. With the exception of Aldrich Fe⁰, arsenic concentrations decreased exponentially with time in other Fe⁰ solutions and were <10 µg/L in four days.

Methodology: A 50-mL polypropylene tube (headspace-free) was filled with arsenic water (2 mg/L) containing As(V), As(III) or equal parts of As(III) and As(V) in 0.01 M NaCl. To these tubes, 1.0 g of Fe⁰ was added and the solutions were mixed in a reciprocating shaker. The suspension was then centrifuged, and the resultant supernatant was filtered through a 0.1-µm membrane and analyzed for arsenic content.

Laboratory Results: Arsenic concentrations decreased exponentially with time in all systems. The relative rate constants for the removal of As(III) and As(V) by Fe⁰ were as follows: Fisher > Peerless, Master > Aldrich. With the exception of the Aldrich Fe⁰, arsenic concentrations in the other three systems decreased to less than 0.010 mg/L within 96 hours. At

pH above 7, As(III) was removed faster than As(V), whereas the rate constant for As(III) + As(V) was between the rates of As(III) and As(V). The sorption capacities were 730 mg/kg As(V) and 1770 mg/kg As(III) for Peerless iron. An iron oxide layer could form on the surface of Fe⁰ due to corrosion, and this layer was likely the predominant adsorption site for both As species.

5.1.3 Gravel Bed Containing Iron-Coated Sand

Methodology: Iron-coated sand was tested for As removal in glass burettes with sand bed depths of 20 and 40 cm (23). Groundwater spiked with both As(III) and As(V) was passed through the burettes, and the effluent was collected for analysis. Coating the sand with iron required washing it first with 20% commercial grade acid for 24 hours. After drying, the sand was mixed with 2M FeNO₃ and 10 N NaOH. To every 200 cm³ of sand, the addition of 80 mL of ferric nitrate solution and 4 mL of NaOH solution was required. The mixture was then heated in an oven for 14 hours at 110°C. Thereafter, the sand was thoroughly washed with distilled water.

Laboratory Results: For an arsenic concentration of 300 µg/L, 200 to 225 bed volumes of groundwater could be treated using a 20-cm sand bed before the arsenic content of the effluent reached breakthrough. With the 40-cm sand bed, 350 to 400 bed volumes of water could be treated before breakthrough occurred. Contact time between arsenic-bearing water and iron-coated sand was about 1 min in the 20-cm sand bed and 3 min in the 40-cm bed. For the 40-cm sand bed, the flow rate varied from 10 to 15 mL/min. Unlike the results found in coagulation experiments with ferric salts, both As(III) and As(V) species were removed indiscriminately. Hence, there was no need for preoxidation of As(III) using this treatment. Moreover, the sand could be regenerated after initial use with little reduction in its removal capacity.

5.1.4 Gravel Bed Containing Iron Sludge

Methodology: Iron sludge is a ferric hydroxide/water slurry containing ferric sulfate, ferrous sulfate and ferric chloride. It was prepared by changing the pH of the iron salt solution through the addition of sodium hydroxide. Iron sludge was then introduced onto gravel media (a straight plastic tube 1.5" long). Arsenic removal was evaluated by passing groundwater spiked with known amounts of arsenic through the media (23). Iron sludge was introduced onto the media in two ways: pouring down or passing through in an upflow mode.

Laboratory Results: Iron sludge did not adhere well to the gravel bed and was very sensitive to the flow rate of water passing through the gravel bed. Most of the iron sludge accumulated on top of the media. Arsenic removal efficiency was very low, with a maximum value of 50% at the initial arsenate concentration of 300 µg/L. The main reason for low removal efficiency probably was the formation of flow channels through the iron sludge accumulated on top of the gravel bed. These flow channels reduced the contact time between arsenic-bearing groundwater and iron sludge.

5.1.5 Lanthanum Compounds

Lanthanum is one of the cheapest rare-earth elements. Lanthanum hydroxide (LH), lanthanum carbonate (LC), and basic lanthanum carbonate (BLC) were investigated (17) for removing arsenate (V) ion from aqueous solutions. Two proposed mechanisms for arsenic removal by lanthanum compounds are adsorption by exchange of CO_3 and/or OH group with As^{5+} ions in the neutral-to-basic pH range when La does not dissolve, and precipitation of insoluble lanthanum arsenate, LaAsO_4 , in the acid pH range.

Methodology: A 100 mL solution of 0.25 mM As(V) was prepared at pH range 2-12. To this solution was added 0.10 g of La compound. The resultant solution was mixed at 20°C, and an aliquot from the sample was collected at intervals and filtered with a 0.45- μm membrane filter. The filtrate was then analyzed for La and As ions.

Laboratory Results: The dissolution of lanthanum compounds was appreciable at pH <3.3, <4.3 and <4.0 for LH, LC and BLC, respectively. The highest As removal rates for LH, LC and BLC were found at initial pH 2.98, 3.75, and 3.01 respectively. The optimal initial pH for As removal was found at ranges 3-8, 4-7 and 2-4 for LH, LC and BLC, respectively. All lanthanum compounds could lower As(V) concentrations in aqueous solutions to below regulatory limits (<0.001 mM).

LH removed As(V) ion fastest at a wider pH range (3-8) compared with other lanthanum compounds. In the initial pH range 2.98 to 6.99, it took less than 4 hours to lower initial As(V) concentration to <0.001 mM. LH could still remove most of As(V) at pH 8.75, but at a much slower rate.

5.1.6 Kimberlite Tailings

Kimberlite tailings were investigated in batch studies for adsorption kinetics, equilibrium isotherm, and factors controlling its effectiveness at removing arsenic (24). Column studies were also conducted to investigate the performance of fixed-bed Kimberlite. This sorbent could remove 90-94% of arsenic from both tap water spiked with arsenic and from groundwater collected from various provinces in West Bengal, India. The batch studies provide the basis for designing column filters for low-cost, effective removal of arsenic.

Methodology: Kimberlite tailings particle sizes of 150-300 μm (geometric mean size = 212 μm) and 300-500 μm (geometric mean size= 387 μm) were used in the study. The particles were prepared as follows. Kimberlite tailings were first thoroughly cleaned with tap and distilled water. They were then dried, powdered, and sieved through 150-, 300- and 500-micron sieves. The sieve material was then washed thoroughly with tap and distilled water and dried at 100°C for 10 hours. After the dried material was cooled in a desiccator for 10 hours, it was sieved once more to the required size. The material was then stored in an air-tight bottle. The selected particles were used in the absorption experiment. An adsorbent (geometric mean size, GMS = 0.212 mm) dose of 20 g/L was used to investigate isotherm equilibrium, adsorbent kinetics, and arsenic removal from groundwater collected from various parts of West Bengal. A column

study was also carried out. Average flow rates (10.13 cm/min) and arsenic concentrations in the influent (1 mg/L) were maintained throughout. The adsorbent was supported in the column by glass wool. Arsenic content in the effluent was periodically analyzed.

Laboratory Results: Batch tests showed that arsenic removal was dependent on pH, and the highest removal efficiency was observed in the neutral pH range. Arsenic-saturated Kimberlite tailings can be regenerated with 0.2 N NaOH. Kinetic studies showed that pore diffusion was not the rate-limiting step, and film adsorption appeared to be the mechanism. Removal efficiency was found to be higher for smaller adsorbent size (more surface area sites for adsorption). Groundwater from eight affected districts in West Bengal were collected and tested for arsenic removal using the tailings. The treatment showed 90-94% removal in 12 h of contact time. In column studies, the breakthrough point of Kimberlite tailings was found at 0.27 mg/g, about one-fourth that of activated alumina. While the capacity for arsenic removal of activated alumina is greater than that of Kimberlite tailing, activated alumina is much more expensive.

5.1.7 Alumina Manganese Oxide

Kepner et al. (21) tested alumina-metal oxide composite particles (Al-MOC) for arsenic removal and found that among the Al-MOCs, alumina-manganese oxide composite particles were most effective at removing arsenic.

Methodology: The enhanced hybrid aluminas (EHAs) were prepared by heating boehmite to 400°C and treating with acetic acid. Alumina-manganese oxide composite (Al-MOC) particles were prepared by binding the EHAs and metal oxides using a proprietary colloidal alumina binder system. About 1 g of Al-MOC was tumbled with 495 mL of 50 ppm arsenic solutions (very high levels) for 24 hours. The solutions were then filtered and analyzed for arsenic content. The effect of pH on arsenic removal was analyzed by changing the pH of arsenic solutions.

Laboratory Results: “Synthetic” well water, typical of groundwater found in West Bengal, was treated with alumina manganese oxide. It removed up to 94% of As with the groundwater at initial arsenic concentrations of 50 mg/L. Alumina manganese oxide was most effective (removal percentage) when its manganese composition was greater than 10% in pH 7 solution. Increasing manganese content greater than 10% had no effect on the removal capacity of alumina manganese oxide, however. Alumina manganese oxide was also effective at removing other toxic metals such as iron, cadmium, antimony, lead, and uranium from the well water.

5.1.8 Activated Alumina

Activated alumina can be used as a fixed adsorbent for arsenic removal. Since Fe^{2+} , which often occurs in high concentrations in groundwater, is oxidized to insoluble Fe^{3+} when exposed to air, it is necessary to remove iron prior to passing groundwater through an activated alumina column to prevent fouling. Oxidation of As(III) is also necessary because As(III) adsorbs poorly to activated alumina.

Methodology: Naturally occurring iron in groundwater is removed simply by aeration followed by flocculation and sedimentation. After macro-iron flocs settled out, KMnO_4 was added to the supernatant to make sure all arsenic species were in the pentavalent form. The supernatant was sand-filtered to remove any remaining macro-iron flocs. The water was then passed through the column filled with activated alumina particles.

Laboratory Results: Field studies (14) operated by the project team in Bangladesh showed that the unit reduced arsenic concentrations from an initial range of 176-240 $\mu\text{g/L}$ to 2.2-7.5 $\mu\text{g/L}$. One concern was that some sand filters became harbors for bacteria, but the cause was most likely unhygienic practices of the users. The cost for each unit is Tk. 1500 (~\$25.60), but a survey indicated that majority of people were willing to pay between Tk. 300 (~\$5.10) and Tk. 500 (~\$8.50).

5.1.9 Zeolites

Zeolites are an important group of minerals due to their catalytic, sieve, and exchange properties. They are naturally abundant and are potentially low-cost materials for arsenic removal. Six zeolites were tested for removal of arsenic from aqueous solutions (11). The primary focus in this research was the most common naturally occurring clinoptilolite-containing zeolite (ZMS, ZMT, and ZH types). Arsenic removal was also investigated with zeolite-modified with iron.

Methodology: ZMS, ZMT, and ZH clinoptilolite-bearing zeolites, ZS-M and ZME mordenite-containing zeolite, and erionite-containing ZMA were tested for arsenic removal. Their activation consisted of washing them with 2M HCl, followed by mixing, decantation, and drying. Sorption of arsenic by these solids was investigated in batch studies. The solutions were allowed to equilibrate and were initially shaken in an ultrasonic bath. Iron-modified zeolites were prepared by equilibrating the solids with Fe^{2+} solutions.

Laboratory Results: As(III) was simultaneously oxidized and removed. The resultant As(V) was subsequently sorbed by the zeolite. Both As(III) and As(V) were removed efficiently in the pH interval 4-11 after contact with zeolite ZH and ZMA for a few days. Residual arsenite and arsenate were 0-5 $\mu\text{g/L}$ and 30-40 $\mu\text{g/L}$, respectively. Erionite-bearing ZMA showed highest removal efficiency in the iron-modified group, and natural clinoptilolite ZMS showed highest removal efficiency in the unmodified group. Compared with conventional treatment using iron hydroxide, iron-modified mordenite ZM-M and ZMA removes As(III) up to 89% and 75%, respectively, of the amount removed by conventional iron treatments.

5.1.10 Fixed-Bed Upflow Bioreactors

This technology (25) utilizes biological oxidation of Fe and Mn ions to remove arsenic from groundwater. The oxidized forms of these metals can be removed by transforming them into insoluble oxides and subsequent separation by a filter medium. Removing these metals would simultaneously remove arsenic because the resultant metal oxides are effective adsorbents for arsenic. Under optimal conditions, 97% of the metal oxides and up to 80% of arsenic can be removed. Since most physiochemical treatments for arsenic, such as coagulation, require the

addition of oxidizing agents to oxidize As(III), this technology could be a low-cost alternative because it does not require such additives. The applied linear velocity afforded by this technology is often higher than in physicochemical treatments. Also, there is no need to monitor the breakthrough point because iron and manganese oxides are continuously produced in situ. Another advantage this technology has is that it removes all three contaminants—Fe, Mn, and As—in one treatment.

Methodology: Oxidizing bacteria (*Gallionella ferrunginea* and *Leptothrix ochracea*) were cultured as oxidizing sources for Fe and Mn, respectively. During biological oxidation, iron and manganese oxides were deposited in a filter media. As arsenic water was passed through the filtering media, arsenic was removed by adsorption or coprecipitation with the iron and manganese oxides. The system was based on a two-stage upflow fixed-bed filtration unit preceded by a separate controlled aeration unit to maintain the bacteria.

Microorganisms were cultivated inside the columns. The groundwater flow was continuous and was mixed with As-spiked water just prior to passing into the aeration column. Air was injected to provide oxygen for the bacteria. The effluent was collected and samples were analyzed for As(III), total arsenic, and iron and manganese concentrations. Periodic backwashing (every 3 days) of the column was carried out to prevent clogging from the formed iron and manganese oxides. The experiment was carried out at pH 7.2 and at linear velocity 8.25 m/h.

Laboratory Results: Iron was oxidized mainly by the bacteria under the following conditions: dissolved oxygen = 2.7 mg/l, redox potential = 280-290 mV, and pH = 7.2. Residual iron and manganese were always found below regulatory limits (0.2 mg/L for Fe and 10 mg/L for Mn). Arsenic (both trivalent and pentavalent form) was removed mainly in the first filtration unit by adsorption on iron oxides. The linear velocity was kept constant throughout at 8.25 m/hr. Highest arsenic removal efficiency (80-84%) was achieved at an initial arsenic concentration range of 35-80 µg/L and under a linear velocity range of 7-14 m/hr. The removal efficiency slightly decreased when the initial arsenic concentration was >80 µg/L.

5.1.11 Soyatal Formation

Soyatal Formation, an abundant clay-rich limestone in the Zimapan Mining District of Mexico, was used to extract arsenic from groundwater (26). Soyatal Formation contains kaolinite and illite in its calcareous shale, and these minerals are known to adsorb arsenic efficiently.

Methodology: Native water samples were collected from wells and groundwater sources in the region. Soyatal Formation was collected along the road between El Detzani and El Dedho in Cerro del Morro. The rocks of the Soyatal Formation were crushed to pea size and then powdered using a shatterbox. Arsenic removal potential and optimal conditions for removal were investigated through batch reactions. After frequent shaking of the solutions containing arsenic and rock, the particles were allowed to settle. Safe drinking water could be obtained by filtering the fluid through several layers of cloth.

Laboratory Results: The results demonstrated that an increase in reaction time, rock-water ratio, and shaking frequency would result in an increase in arsenic removal. Continuous shaking using a wrist-shaker for 12 hours decreased initial arsenic concentration from 768 µg/L to an average of 55 µg/L, a 93% removal efficiency. The highest removal efficiency for powdered rock at a 1:5 rock:water ratio was 87±5%, whereas the highest removal efficiency for crushed rock was 91%±5% at rock:water ratios of 1:2, 1:10, and 1:20. Water having a 1:5 rock:water ratio tasted salty, whereas water having 1:10 rock:water ratio tasted normal.

5.1.12 Manganese Greensand

Manganese greensand is a zeolite-type glauconite mineral, artificially coated with a layer of active hydrous manganese dioxide and other high oxides of Mn (7).

Methodology: Manganese greensand was prepared by treating the glauconite sand with KMnO_4 . The greensand produced was a granular material, coated with a layer of active hydrous manganese dioxide and other high oxides of Mn. Greensand (0.005 m³), KMnO_4 (10g), and water (972 mL) were added to a column to condition the material. Tap water spiked with As(III) (200 µg/L) was used for all tests. Arsenic water was pumped into the column filter and the effluent was collected for analysis. KMnO_4 was continuously added to generate the column and to oxidize the Fe(II), Mn(II) and As(III). Amberlite IR-120 cation exchange resins and iron-oxide-coated sand were also tested for arsenic removal and were compared with manganese greensand for effectiveness.

Laboratory Results: In the presence of iron (Fe:As ratio = 20:1), manganese greensand was more effective at removing arsenic than iron-oxide-coated sand and resin. Arsenic removal of 81.8% was achieved from an initial arsenic concentration of 100 µg/L. The initial solution pH was neutral and was not adjusted throughout the tests.

5.1.13 Goethite

Goethite is an α -iron(III) hydroxy-oxide mineral [$\text{FeO}(\text{OH})$] and is the most stable form of iron oxide in soil. Synthetic goethite particles were investigated (27) for removal of As(V) from dilute aqueous solutions. The small size of the particles necessitated an efficient solid/liquid separation technique.

Methodology: A solution of 1g/L goethite, 10 µg/L As(V), and 0.1 mg/L polyelectrolyte was magnetically stirred for 30 min at 300K. Following flocculation, the dispersion was settled for 15 minutes and a sample was analyzed for residual turbidity. The average size of the goethite particles was 2.5 µm in diameter.

Laboratory Results: Goethite particles are stable at pH 4-9. Outside that pH range, the particles become unstable and begin releasing soluble ferric ions into solution. Wet goethite form (a paste) was found to have higher adsorption capacity than the dry form and was used throughout. As(V) was removed almost completely from the solution up to pH 6. When ionic strength was raised, very high arsenic removal efficiency (>95%) was achieved up to pH 9. Although increasing ionic strength can facilitate arsenic removal, the quality of water was low at

pH >5 due to high residual turbidity. Ionic strength does not play a significant role in removing arsenic at lower pH. Goethite particles sizes were found smaller (thus more adsorption capacity) at low pH and larger at pH 5 and above. Larger and more stable flocs of goethite can be achieved by adding alum or ferric chloride to the solution. Dissolution of FeAsO₄ increased at pH value greater than 5, and FeAsO₄ can decompose at pH greater than 6.

5.1.14 Granular Ferric Hydroxide

Technical University of Berlin introduced a new adsorbent, granular ferric hydroxide (Adsorpas®), poorly crystallized α -FeOOH. In a review of selected arsenic technologies (20), Pal concluded that granular ferric hydroxide is a superior adsorbent because it meets four important criteria: high removal efficiency, safety, simple operation, and minimum residual mass. Pal quoted results from studies claiming removal efficiency of Adsorpas® being 5 to 10 times higher than that of activated alumina (20) and capacity of 45 mg/g of AsO₄⁻ (0.32 mmol As/g). Adsorpas® is effective at a wide pH range (5.5 to 9), although there is a slight decrease in adsorption capacity with pH.

Methodology: Arsenic is removed through a process using granular ferric hydroxide reactors, which are fixed-bed adsorbers that operate similarly to conventional filters with a downward water flow. The process consists of coagulation-filtration step with fixed-bed adsorption, and it can be used for both large-scale and small-scale applications.

The system is easy to make since it consists of only a gravel filter and an adsorption tower. Water first passes down a gravel filter (iron and suspended particles are removed), and second through an adsorption tower, where arsenic will be decreased to a safe level. The system is very self-sufficient since there is no need to adjust or maintain it around the clock as is the case with the precipitation and flocculation methods. Disposal of Adsorpas® is not problematic since it is non-toxic and non-hazardous and the authors claim that As does not leach from it.

Laboratory Results: The ferric hydroxide material handled 40,000-60,000 bed volumes of natural groundwater containing 21 μ g As/L before the 10 μ g/L regulatory limit (Germany) was exceeded. The residual mass of hydroxide was 5-25 g/m³ of treated water.

5.1.15 Manganese-Coated Sand

Manganese dioxide (δ -MnO₂) can both oxidize As(III) and adsorb As(V). A media of manganese dioxide was prepared (28) using manganese-dioxide-coated sand. Groundwater was passed through the coated-sand media, and the arsenic content in the effluent was measured. The data showed very good arsenic removal; however, this was a limited experiment because important variables such as pH and competing anions were not investigated.

Methodology: Manganese dioxide was prepared in the presence of sand from the oxidation of manganous ion by permanganate. Initially 250 g of river sand was added in a KMnO₄ solution. NaOH solution was then added to neutralize the acid and to keep the solution basic. A 0.3 M MnCl₂ solution was introduced into the sand mixture dropwise while stirring with a magnetic stirrer. The mixture was then dried in an oven at 105°C for 24 hours. The dried

sand was washed with distilled water until the after-wash water was clear. Finally, the sand was dried overnight at 10°C and stored in a capped bottle.

One of two chambers made of a galvanized iron sheet was placed on top of the other. The top chamber contained 4 L of manganese-dioxide-coated sand. A small orifice at the base of the top chamber controlled the flow rate at about 6 L/hr. The bottom chamber had a tap near its base. Seven liters of groundwater (spiked with 0.5 µg/L As³⁺ and 0.5 µg/L As⁵⁺) was placed in the top chamber and passed through the bottom one. The groundwater was allowed to pass until the arsenic content in the effluent exceeded 0.01 µg/L (a cycle). Between each cycle, the medium was regenerated in situ by washing it with 10 L of 0.2 N NaOH until the influent and effluent pH were comparable.

Laboratory Results: A total of 740 L of water was produced before the arsenic content in the effluent reached undesirable levels. The amount of water produced was 700 L in the second cycle, a little less than the first cycle. It was found that water spiked with As(III) or a mixture of As(III) and As(V) had a much greater removal efficiency than water spiked with As(V) alone. Material and fabrication costs for the whole unit are \$5; the medium is \$2, and regeneration costs \$0.13, which is considered reasonable.

5.1.16 Hydrotalcite (Mg-Al-CO₃²⁻)

Hydrotalcite-like materials are sorbants that can remove anions. Since the sorbants are in powder form, they pose problems in the solid/liquid separation process following the sorption stage. Sorption combined with separation by flotation was investigated (29), and the results showed effective solid/liquid separation and satisfactory removal of arsenic by hydrotalcite.

Methodology: Synthetic hydrotalcites (HT) were prepared by calcining Mg-Al-CO₃²⁻ at 500°C for 10 hours. The HT was then added to a spiked As(V) solution (20 mg/L). The experiments were conducted in a dispersed-air flotation environment and various non-thioionisable surfactants were used in the flotation process.

Laboratory Results: The efficiencies of both As(V) removal and downstream flotation recovery were well over 90% at natural pH (initial arsenic concentration 20,000 µg/L). Arsenic removal was most effective at high ionic strength.

5.1.17 Mesoporous Anion Trap (Cu-EDA-Si)

Selective binding of anions is a great challenge in chemistry, biology, and materials and environmental sciences. Cu-EDA-Si, a synthetic metal-chelated ligand immobilized on mesoporous silica, was used (30) as an anion binding material. The binding begins with electrosteric coordination, followed by displacement of one ligand and direct binding with the Cu(II) center.

Methodology: Mesoporous silica materials were first synthesized with cetyltrimethylammonium chloride/hydroxide (surfactant), tetramethylammonium silicate, HiSil silica powders, sodium aluminate, and mesitylene solutions, and then functionalized with ethylenediamine

(EDA)-terminated silane. Then, they were hydrated and coated with EDA-terminated silane coatings. The functionalized silica was then stirred in a copper (II) chloride solution for a few hours to produce Cu-EDA-Si.

Laboratory Results: With a solution (mL) to sorbent (g) ratio of 100, nearly complete arsenic and chromate removal was achieved. Initial arsenic (V) concentration was very high, ranging from 1000 to 500,000 $\mu\text{g/L}$, and the resin capacity was 1 mmol As/g. Anion competition was investigated using SO_4 ; no significant effects were found, but chromate was found to be more specifically bound than arsenate.

5.1.18 Clay Minerals (Kaolinite and Illite)

Methodology: Kaolinite and illite were obtained from Washing County, Georgia, and Silver Hill, Montana, respectively. Batch experiments were conducted by shaking clay suspensions in 40-mL polycarbonate centrifuge tubes containing 500 mg of clay in 20 mL of 0.4 μM As(III) or As(V) solution for 16 h (31). The pH and ionic strengths also were investigated for optimal arsenic removal capability. After 16 hours of contact time, the tubes were centrifuged followed by filtering with a 0.1- μm Whatman cellulose nitrate membrane. The supernatant was analyzed for residual arsenic concentrations.

Laboratory Results: Ionic strength had minor effects on the adsorption of arsenic to clay minerals. The adsorption of As(III) was low at low pH, and maximum As(III) adsorption capacity for both minerals was between pH 7.5 and 9.5. As(V) was removed most efficiently. Approximately 90-99% of As(V) was removed by both kaolinite and illite at pH 6-8.8.

5.1.19 Aqua-BindTM

Aqua-BindTM consists of highly activated hybrid aluminas and alumina composites (19). An arsenic treatment unit (ATU) based on this technology was developed and field-tested (19). Demonstration units have been operating in India for 3 years and others are operating in Bangladesh. The results show a reduction of As from as much as 3500 $\mu\text{g/L}$ to <10 $\mu\text{g/L}$ in a wide range of redox and arsenic concentrations. Best of all, this technology can remove arsenic within seconds and is highly selective because it is designed to remove only As(III) and As(V). The ATU is simple to use, easy to maintain, and relatively cheap, if mass-produced. Moreover, it is nontoxic and resistant to bacterial growth and poses no health or disposal concerns. The units are designed to be backwashed every couple of weeks and replaced after six months.

5.1.20 Calcium Oxide

Field experiments (32) on arsenic removal by calcium oxide were conducted at Goneshampur Village from November 2000 to March 2001. Calcium oxide was added to untreated water in different doses. The mixture was then allowed to settle for several hours in a container. Laboratory results showed that adding 0.1% (by weight) of lime to contaminated water reduced arsenic to safe levels after a settling time of 10 hours. After 16 hours, no arsenic was detected.

5.1.21 Wood Charcoal

Contaminated water was passed through a unit (32) made of three pitchers (11 L each) at a controlled rate. The top pitcher, having a small orifice at the bottom, contained contaminated groundwater, and the middle pitcher contained layers of wood charcoal and sand. There was a small orifice in the middle container to prevent sand from leaking out. The last pitcher was used to collect treated water. About 97-99% removal efficiency was observed when 4480 g of sand and 606, 754 or 757 g of charcoal were used, with the flow rate varying from 12 to 54 mL/min.

5.1.22 Laterite

Laterite is vesicular clay residuum that is abundant in tropical regions. It is composed mainly of hydrous oxides of iron and aluminum. Laboratory tests (22) showed that removal efficiency was in the range of 50-90% for 5 g of added laterite per 100 mL water after undergoing equilibrium for 20 minutes. Increased adsorption capacity of laterite was found when it was treated with 0.01 M HNO_3 .

5.1.23 Birnessite

Synthetic birnessite MnO is representative of many naturally occurring manganese oxide materials, which are noted for their oxidizing potential. The O/Mn ratio for most synthetic birnessite is 2. In this study (18), reactions of As(III) and As(V) with synthetic birnessite were evaluated for arsenic removal potential. The results indicated that MnO_2 oxidized As(III) and the resultant As(V) was removed through adsorption to the MnO_2 solid phase. Further analysis showed that oxidation of As(III) by MnO_2 created more reaction sites on MnO_2 surfaces for sorbing As(V). Synthetic birnessite proved to be an efficient oxidant for As(III), although birnessite removes only about 20-30% of As(V).

Methodology: As(III) and MnO_2 were mixed in a rotating, propeller-stirred reactor in a temperature-controlled bath (22°C) at pH 6.5.

Laboratory Results: The results showed that MnO_2 was a very efficient oxidizing agent. Dissolved As(III) in 250 mg/L MnO_2 was found below detection limits after 1 hour. Adsorption within the MnO_2 removed 20-30% of As(V).

5.1.24 Read-F

Read-F is a new adsorbent recently introduced by Shin Nihon Salt Co. Ltd, Japan (4). It can remove arsenic in a wide range of conditions and shows great selectivity for both arsenite and arsenate without the need of pretreatment. The chemical composition of Read-F is ethylene-vinyl alcohol copolymer (EVOH)-borne hydrous cerium oxide (4).

5.1.25 Anion Exchangers

Korngold et al. (33) used a transparent column loaded with strong-base anion-exchange resins (Purolite A-505 and Relite-A-490) to investigate adsorption of arsenic anions by the resin.

Laboratory results showed that strong-base anion-exchanger resin could remove >99% of arsenic from drinking water. The column could be regenerated with either HCl or NaCl. The treatment was very inefficient in the presence of phosphate, chloride, and other anions at high concentrations. Therefore, low salinity (<1000 TDS) is a prerequisite for effective arsenic removal. Relite-A-490 was more selective for H_2AsO_4 and HAsO_4^{2-} and more effective at removing arsenic than Purolite A-505 and had higher breakthrough limits.

5.2 ARSENIC WASTE DISPOSAL

Arsenic waste can be disposed of by converting it into volatile organic forms through the activities of the microbes in soil or sediments. One such disposal method was used in Bangladesh where arsenic waste was disposed in soil in the backyard with cow dung added. Das et al. claim that the microbes residing in the cow dung helped convert arsenic into volatile arsenic species (34) since analyses of the soil failed to produce concentrated As values. This result appears dubious and it is worth noting that disposal of arsenic-rich residues is rarely addressed in the literature.

Table 3 summarizes the technologies reviewed here.

Table 3. Summary of Technologies Reviewed

| Sorbent | Amount of Sorbant Used | Range of Arsenic Tested | Efficiency | Reaction Time | Arsenic Species Tested | pH | Advantage | Disadvantage | Work Cited |
|---------------------------------------|---|-------------------------|-------------------------------------|---------------|------------------------|--|---|--|------------|
| Aqua-Bind™ | | 152-3500 µg/L | Almost 100% | 15 sec | Both | Wide range | Cheap; no pretreatment; high selection for both As(III+V); rapid kinetics | None | (19) |
| Ferric chloride | 100 mg/L of ferric chloride and 1.4 mg/L of KMnO ₄ | 375-640 µg/L | >90%, often 95% or more | 15 L/ min | Both + oxidation | Wide range | Effective at a wide range of pH; arsenic occurrence correlates best with Fe; low cost, simple operation, common chemicals (4) | Preoxidation, filtration may be needed to remove all flocs; water should not have high silicate or phosphate concentrations (27) | (4) |
| Aluminum alum | 20 mg/L | 0.1 mg/L | 96% | 6 h | Both | pH 6.6 | Low cost, simple operation, common chemicals (4) | Toxic waste (sludges); pre-oxidation required for high removal efficiency (4); less soluble than FeCl ₃ (27) | (4) |
| Read-F | | | Very efficient | Brief | Both | | High selectivity | Adsorbent not as effective at high iron concentrations | (4) |
| Iron filings type (Su and Puls study) | 1g | 2 mg/L | 99% | 4 days | Both | 7 and above | Cheap Very simple to use Nontoxic | Not effective in presence of phosphate; effective in presence of sulfate | (16) |
| Iron filings (Ramaswami et al. study) | 2000 mg/L | 200-2000 µg/L | 95% | 30 min | As(III) | pH 7 | Very cheap | Not effective in presence of phosphate | (10) |
| Manganese coated sand | 4L of coated sand | 500 µg/L | Breakthrough = 740 L in first cycle | 6L/h, column | Both | Bangladesh water pH; wide distribution | Very cheap; no oxidation required | Complicated | (28) |
| Alumina manganese oxide | 1g | 50 ppm | 94% | 24 h | As(III) | Range 5.5-8, most effective at 7 | "Self protecting" from Mg and Ca; also effective at removing other toxic metals | Long contact time | (21) |
| Kimberlite Tailings | 20 g/L | 1 mg/L | 90-94% | 8-12 h | As(III) | Acidic to neutral pH (7) | Cheap; no oxidation required | Slightly less effective at pH >7 | (24) |

Table 3. Summary of Technologies Reviewed

| Sorbent | Amount of Sorbant Used | Range of Arsenic Tested | Efficiency | Reaction Time | Arsenic Species Tested | pH | Advantage | Disadvantage | Work Cited |
|-----------------------------|---|--------------------------------------|--|---|-----------------------------|--|--|---|------------|
| Lanthanum Hydroxide | 0.10 g | 0.25 mM | Lower arsenic to well below safe limit | Most rapid at pH 3-6.99, >1 day contact time for pH >8.75 | As(V) | 3-8 | Cheap, simple | Long contact time at high pH | (17) |
| Fixed-bed upflow bioreactor | Fixed bed | 30-60 µg/L | 80% | 7-14 m/h | Both | pH 7.2 | No need for pre-oxidation; Fe, Mn, As can be removed | Somewhat elaborate process; low arsenic capacity | (25) |
| Activated alumina | Fixed bed | 170-240 µg/L | ~98% | | As(V) | Bangladesh water tested | | | (14) |
| Granular ferric hydroxide | Fixed bed | Huge adsorbent capacity | >95% | | Both | 5.5-9 | Safe technology, toxic-free waste, simple operation and little maintenance | Iron pretreatment needed to avoid clogging of filter bed (4) | (20) |
| Anion-exchangers | 100 ml of resin | 600 µg/L | 99% removal | 20 bed vol/h | Only As(V) | Tap water Ph | Very high As(V) removal | Sulfate and nitrate exchange before arsenic (4); TDS, selenium, and fluoride can also decrease life of resin (21) | (33) |
| Illite clay minerals | 1:40 rock:water ratio | .4 µM As(III) and .4 µM As(V) | 80% for As(III), 90-100% for As(V) | 16 h | Both As(V) and As(III) | 6-8.5 for As(V) 7.5-9.5 for As(III) | Cheap | Long contact time; low As(III) removal | (31) |
| Kaolinite clay minerals | 1:40 rock:water ratio | | 50% for As(III), 90-100% for As(V) | 16 h | Both As(V) and As(III) | -8.5 for As(V) 7.5-9.5 for As(III) | Cheap | Long contact time; low As(III) removal | (31) |
| Soyatal formation | 1:2, 1:10, or 1:20 solid:water weight ratio | About half of samples have ~500 µg/L | 94% for crushed rock | 24 h frequent shaking | As(V) predominantly | pH average of 7.1 | Cheap, simple, abundant; high arsenic removal efficiency | Long contact time | (26) |
| Manganese greensand | .005 m ³ greensand + 10g KMnO ₄ in 972 ml | 100 µg/L | 81% | Filtration rate of 1.5 L/min/m ² | As(III) and oxidizing agent | Around neutral pH; pH not adjusted or tested | | Expensive | (7) |
| Goethite | 1g/L | 10 µg/L | Near-complete removal at 3<pH<6 | 1 h contact time | As(V) | pH 3-9, but high residual turbidity at pH >5 | Can remove both cations and anions | Best at pH range 3-5; high turbidity outside that range | (27) |
| Hydrotalcite | 1g/L | 20 µg/L | Well over 90% | 10-15 h | As(V) | Test | | High ionic strength | (29) |

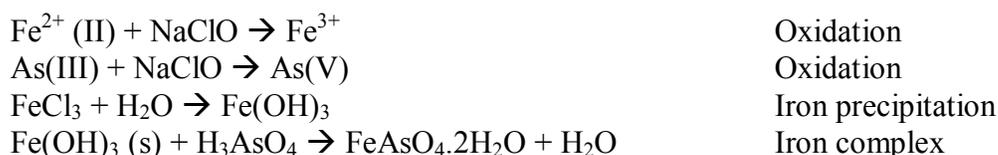
Table 3. Summary of Technologies Reviewed

| Sorbent | Amount of Sorbent Used | Range of Arsenic Tested | Efficiency | Reaction Time | Arsenic Species Tested | pH | Advantage | Disadvantage | Work Cited |
|--|---|---------------------------|---------------------|---------------------------|------------------------|---|--|--|------------|
| | | | | | | conducted at natural pH | | needed for best removal; complicated procedure | |
| Mesoporous anion trap (Cu-EDA-Si) | 10 g/L | 1.0 mg/L and higher | 98.5% | Shaken overnight for 12 h | As(V) | Solutions tested generally had pH 5 and 6 | Not affected by anion competition for adsorbent site; high arsenic removal | High-tech operation | (30) |
| Gravel bed containing iron-coated sand | 80 mL of 2 M FeNO ₃ per 200 cm ² sand | 300 µg/L | 200-225 bed volumes | Several minutes | Both | | Can remove both As(III) and As(V) indiscriminately. (4, 35); sand can be regenerated | Toxic waste sludge; complicated process to make sand | (23) |
| Gravel bed containing iron sludge | | 300 µg/L | 50% | | Both | | Low removal efficiency | Does not adhere well to gravels; sensitive to flow rate | (23) |
| Clinoptilolite-bearing zeolites, ZH | | 100 ml of untreated water | Efficient | At least 4 days | Both | | Cheap, can be found everywhere | Very long contact time; water needs to be further filtered after treatment | (11) |
| Calcium oxide | 0.1% lime/water ratio by weight | | 99.9% | 16 h | | | High arsenic removal | >10 h contact time | (32) |
| Wood charcoal | 600-757 | | 97-99% | 12-45 mL/min | | | High removal shown, but not all studies suggested so | Complicated | (32) |
| Laterite | 5g | | 50-90% | 10 min | Both | | Brief contact time | Low removal efficiency | (22) |

6. CHEMISTRY AND MECHANISMS OF SOME MAJOR SORBENTS

The following is a description of the reactions responsible for arsenic sequestration by the various technologies described in Section 5. Unbalanced reactions are written to highlight important species.

Ferric salts: As(III) and Fe²⁺ are oxidized to As(V) and Fe³⁺ respectively. Ferric chloride reacts with water and form Fe(OH)₃, which strongly adsorbs As(V) (4).



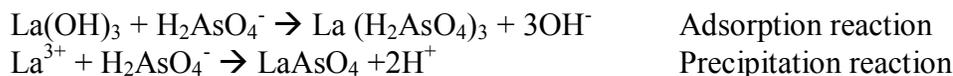
Aluminum co-precipitation: Alum dissociates in water and forms aluminum hydroxide, which co-precipitates with arsenic (4).



Iron filings: Under aerobic conditions Fe⁰ is oxidized to Fe²⁺, resulting in depletion of O₂ in water, and anoxic conditions eventually develop. Further reductions can produce a stable FeAsS precipitate. Therefore, the presence of sulfate is important for removing arsenic. An iron oxide layer could also form on the surface of Fe⁰ due to corrosion, and this layer was likely the predominant adsorption site for both As species (15).

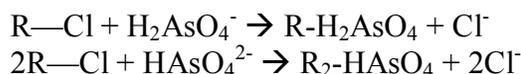


Lanthanum hydroxide (LH): Two proposed mechanisms for arsenic removal by lanthanum hydroxides are adsorption by exchange of OH⁻ group with As ions in the neutral to basic pH range when La does not dissolve [La(OH)₃], and precipitation of insoluble lanthanum arsenate, LaAsO₄, in the acid pH range when La is dissolved (La³⁺) (17); for example:



Adsorption of HAsO_4^{2-} can also occur in the alkaline range.

Strong base anion-exchanger: A strong base anion-exchanger can remove only the pentavalent form of arsenic, As(V) (4, 33).



where R stands for organic ligand of the anion exchange resin.

Birnessite: MnO_2 oxidizes As(III) and some As(V) gets adsorbed to the hydroxyl group on MnO_2 surface (18).



Mesoporous anion traps: Cu-EDA—Si (30). Initially, Cu(II) is bonded to ethylenediamine ligands to form octahedral complexes on the surface of the mesoporous silica. This gives rise to a shape with a positive charge that can match the geometry of tetrahedral arsenic anions. The binding begins with electrosteric coordination, followed by displacement of one ligand and direct binding with the Cu(II) center.

Hydrotalcite materials (29): Hydrotalcite-like compounds have the general formula $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2](\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$. M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively, A^{n-} is a n-valent exchangeable anion and x can have values between 0.2 and 0.33. Unlike anion-exchanger resins, which induce an ion exchange reaction with a hydrated anion, hydrotalcite compounds induce reactions with bare, nonhydrated anions.

Goethite (18): Goethite is an α -iron(III) hydroxy-oxide mineral $[\text{FeO}(\text{OH})]$. Arsenic is removed through surface complexation with goethite.

Soyatal Formation (26): A possible mechanism for arsenic removal by Soyatal Formation rocks is adsorption of arsenic to clay minerals in the calcareous shale.

7. TECHNOLOGY EVALUATION

Developing countries like Vietnam and Bangladesh cannot afford expensive and/or large-scale treatments. Low-cost, effective technologies that are readily available at the household or community level are needed to solve the present crisis. Large-scale treatments are not appropriate because many people in third-world countries obtain water from wells rather than from large municipal water plants. Appropriate in-home technologies to be implemented in third-world countries should meet certain criteria to be effective. The treatment must be applicable over a wide range of arsenic concentrations and easy to use without running water or electricity, and the materials for the treatment must be cheap, readily available, and/or reusable to reduce costs. Finally, such technology should not introduce any harmful chemicals into drinking water (15).

Quite often it is a very complex task to select a method because of the many difficulties that arise when a particular technology is applied in the field. These difficulties include a wide range of arsenic concentrations, effects of other elements and their variable concentrations in water, the need to adjust pH for optimal removal, optimized dose, proper operation and maintenance, and safe disposal of arsenic waste (35). Another major issue concerning a technology is that it should not pose risk of bacteriological contamination and should be broadly acceptable to users. Field studies in Bangladesh showed that the main reasons for rejection of some technologies are the amount of operational effort, the level of maintenance, the amount of time until clean water is available, and the volume of water that the technologies can provide on a daily basis (36).

Our review of arsenic removal technologies indicates that iron filings, ferric salts, granular ferric hydroxide, alumina manganese oxide, lanthanum hydroxide, Aqua-bind^m, and Kimberlite tailings are potentially low-cost sorbents that can remove arsenic after simple mixing in a relatively short time. The most well known treatment makes use of a ferric salt (such as ferric chloride and ferric sulfate). Ferric salts are cheap and very effective at removing arsenic. Ion exchange resins can remove As(V) very well, but competing anions such as nitrate and sulfate strongly reduce arsenic removal potential. Therefore, this sorbent is not practical to use in groundwaters where anions such as nitrate and sulfate are present in high concentrations. The next-most-effective very common arsenic technology consists of a fixed column of sorbents that can remove arsenic simply by passing groundwater through the column. The most well known fixed-bed columns make use of activated alumina and iron-coated sands. These fixed bed columns often do not work well with groundwater having high concentrations of iron because iron precipitates in the presence of air, which could clog and foul the column.

Many synthetic sorbents have also recently been developed that have many advantages over other sorbents. These synthetic sorbents are highly selective and effective and do not often pose much waste disposal concern since they are usually non-hazardous. Aqua-bindTM is perhaps the most effective synthetic sorbent available for removing arsenic, but it must be mass-produced to realize low cost. Aqua-bind can be used as a fixed-bed column that can be attached directly to wells.

Naturally occurring solids also remove arsenic well, but the removal rate is often very slow. The advantages of using naturally occurring solids over other sorbents are that they are cheap and often can be obtained free of charge. One difficulty that has surfaced from using these natural solids is that the treated water often harbors bacteria.

Another highly innovative treatment makes use of biological oxidation. Certain bacteria are cultured to oxidize iron and manganese, which are often present in high concentrations in groundwater. Arsenic was removed through adsorption to the iron and manganese solids. One advantage of this technology is that all three contaminants, Fe, Mn, and As, are removed simultaneously.

8. FUTURE OPPORTUNITY: REMOVAL OF ARSENIC USING MAGNETIC PARTICLES

This report serves as a basis for comparing existing candidate technologies with magnetic particle technology. Most of the technologies discussed have slow reaction rates and are not very simple to use. The quest for a simple, low-cost, effective technology that can remove arsenic in a short time is still ongoing.

Magnetic particle technology may provide a viable, low-cost option. This procedure would consist of adding functionalized magnetic particles directly to a drinking water storage vessel or small pitcher. After stirring the contents with a spoon for a short period, the magnetic particles would be removed with a simple bar magnet. A plastic sheath around the magnet can be removed to free the bar magnet for additional use. The particles may be regenerated similarly to the technologies described above, depending on the functional material sorbed to the surface of the magnetic particles.

The advantage of magnetic particle technology stems from high surface areas and simplified water clarification. Magnetic particles for arsenic removal would have to be composed of magnetic material (magnetite) of very small size ($<10\ \mu\text{m}$). To take advantage of the properties of iron, manganese, and alumina, they may be co-precipitated with the magnetite to increase its versatility in treating arsenic under various pH. The reaction rates may be greater because the reactions occur at the high specific surface areas. Fouling would be avoided since these particles are not kept in a static column but are removed after each cleaning and can be dried and stored. The cost of this technology has not been evaluated but the magnetite or co-precipitated magnetite is expected to be more expensive than naturally occurring material like Kimberlite tailings.

More thorough evaluation is needed to determine the efficacy of magnetic particles in removing arsenic.

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