POINT-OF-USE WATER TREATMENT FOR ARSENIC REMOVAL THROUGH IRON OXIDE COATED SAND: APPLICATION FOR THE TERAI REGION OF NEPAL

By

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ABSTRACT

Arsenic contaminated groundwater is prevalent in a number of countries around the world, most notably West Bengal, Bangladesh and now the Terai region of Nepal. Wide public awareness of the contamination was not until the 1990s, from years to several decades after tubewells were installed to extract groundwater for drinking water. Now, millions of people have arsenic poisoning which causes serious health effects such as arsenicosis, skin and liver cancer, circulatory disorder and hyperpigmentation. For the past three years, the MIT Nepal Water Project has been investigating arsenic contaminated tubewells in Nepal, and has begun to evaluate point-of-use arsenic removal technologies. These technologies must meet certain evaluation criteria: Effective removal of effective removal of total arsenic (As (III) + As (V)), minimally, below the Interim Nepali Standard of 50 μg/L; possibility of local manufacture with locally available materials; affordable to the Nepali citizens affected by arsenic contamination; socially acceptable in terms of maintenance, operation and water demand.

The 2001-2002 MIT Nepal Project investigated three new technologies which might meet these criteria. Iron oxide coated sand is one of these technologies. Iron oxides are known to adsorb arsenic. Previous studies of arsenic and metal adsorption onto iron oxide coated sand prompted this investigation. Based on the methods utilized in these prior studies, the author produced seven different iron oxide coated sands, varying concentration of ferric nitrate used, coating mixture, and drying temperature. The arsenic removal capability of these sands was tested in Parasi, Nepal, Pepperell, Massachusetts and Salem, New Hampshire. Percent total arsenic removal varied from 11-99%. Considering the evaluation criteria such as arsenic removal performance, cost, availability of materials, and local production, iron oxide coated sand technology successfully meets most or all of these requirements. However, in this study, social acceptability has not been determined. Detailed testing and evaluation of the iron oxide properties, as well as sufficient resources allocated to production of the media, is crucial before iron oxide coated sand technology could be implemented for point-of-use arsenic removal in Nepal or other developing countries.

The author also produced a digitized map representing the extent of arsenic contamination in the Terai using paper maps as a base.

ACKNOWLEDGEMENTS

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My family, for their never-ending support and love, which strengthen me and give guidance to my life.

To the "special people" who have encouraged me, comforted me, given me space, missed me, and welcomed me back once this writing process was over. You are my sisters for life.

Finally, to the life-long friends I have made in the Meng. program. This thesis would not have been possible without the laughter, stimulating conversations, reminders that there *is* life outside of MIT, and constant supply of Oreo® cookies. Sunrises have never been so enjoyable. We have survived, and my life has been truly enriched.

Veni vidi vici- Julius Caesar

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Chapter 1 INTRODUCTION

1.1 Background

The Kingdom of Nepal lies landlocked between the People's Republic of China to the north and the Republic of India to the south. Nepal, governed by a parliamentary democracy and a constitutional monarchy, is an official Hindu state slightly larger than the state of Arkansas, USA. The geography of Nepal consists of three regions: the Terai or flat river plain of the Ganges region in the south, the foothills in central Nepal and the rugged Himalayas to the north. The Terai and foothills regions are densely populated, and the capital of the Kingdom, Kathmandu is located in the central foothills (Figure 1.1). The population of Nepal is about 25.3 million with a growth rate of 2.32%. The life expectancy is on average 58 years with an infant mortality of 74.14 deaths/1000 live births (CIA, 2001). As of 2001, sixty-one percent of the population was literate (44% of females and 77% of males) (Encarta, 2001). The average GNI per capita is US$230, with about 42% of the population living below the national poverty line (World Bank, 2001). According to Shrestha (2001), only 43% of the rural population has access to safe water, and 90% of the urban population is served with piped water supply.

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Figure 1.1 Map of Nepal

1.2 Project Motivation

The MIT Nepal Water Project is an ongoing collaboration with The Environmental Public Health Organization, The International Buddhist Society (IBS), the Nepal Red Cross, the Rural Water Supply and Sanitation Support Program (RWSSSP) and other local organizations in Nepal. All organizations seek to improve the drinking water quality in the Kingdom of Nepal. The MIT Nepal Water Project began in 1999 after the founder, Susan Murcott, spoke at the 2nd International Women and Water Conference held in Kathmandu, Nepal in 1998, and was asked to join the effort to solve drinking water contamination problems that plague the country. The MIT Nepal Water Project was established within the Masters of Engineering Program in the Department of Civil and Environmental Engineering at the Massachusetts Institute of Technology. Students examine water quality parameters, explore existing technologies, design new technologies, and implement point of use household water treatment units for microbial contamination and arsenic removal during field tests in the Kingdom of Nepal.

Groundwater arsenic contamination has been found in Bangladesh and West Bengal. Due to Nepal's proximity to these areas (See Figure 1.1), in 2000, Patricia Hasley of the MIT Nepal Water Project tested tubewells in search of arsenic contamination in Nepal. Of the wells she tested, 18% of the samples taken from the Terai region were above the World Health Organization guideline of 10 µg/L and 9% were above the Interim Nepali Standard of 50 µg/L (Halsey, 2000). In 2001, Jessica Hurd of the MIT Nepal Project investigated three arsenic removal technologies at a field site in Parasi, Nepal in the Terai. Her preliminary evaluation of The Three-Gagri System, the Jerry Can System and the Arsenic Treatment Unit (ATU) in terms of effective removal and appropriateness for Nepal, revealed that neither met all criteria (Hurd, 2001). The 2002 MIT Nepal Project investigated three new technologies which might better suit the needs of the Nepali people and take us another step closer to a workable solution to the problem of arsenic contaminated tubewell water.

1.3 Arsenic Contamination in Bangladesh and West Bengal

Arsenic contaminated groundwater is prevalent in a number of countries around the world, most notably West Bengal, Bangladesh and now the Terai region of Nepal. To address microbial contamination in surface drinking water, tubewells were installed throughout the region to extract "safe" groundwater for consumption. Unbeknownst to the international aid agencies who originally promoted the construction of tubewells or to the residents of this region, naturally occurring arsenic leaches into the groundwater from chemical reactions occurring in geologic formations running throughout this area. Wide public awareness of the contamination was not until the 1990s. Now, millions of people have arsenic poisoning which causes serious health effects such as arsenicosis, skin and liver cancer, circulatory disorder and hyperpigmentation. Waters containing concentrations in the thousands of μg/L have been found in Bangladesh.

1.4 Arsenic in Nepal

Arsenic, in concentrations in the hundreds of micrograms per liter, has been discovered in Nepal. Only recently has the Government of Nepal acknowledged a problem exists. In 1999, the WHO funded a study of three Terai districts in the east of Nepal conducted by the Department of Water Supply and Sewerage (DWSS) and overseen by the National Arsenic Steering Committee (NASC). The role of this organization is to lead a united effort among active Non-Governmental Organizations (NGOs) in dealing with the arsenic problem. To date, testing has been limited to the Terai where tentative estimates suggest 390,000 people may be drinking water with arsenic concentrations greater than 50 μg/L (NASC, 2001). The Nepal Red Cross Society, the Environmental and Public Health Organization (ENPHO), the DWSS, and FINNIDA have tested wells in central and eastern Terai districts for presence of arsenic (Of almost 5,000 tubewells analyzed, about 4% of these samples were above 50 μg/L, the "Interim Nepali Standard" (NASC, 2001).

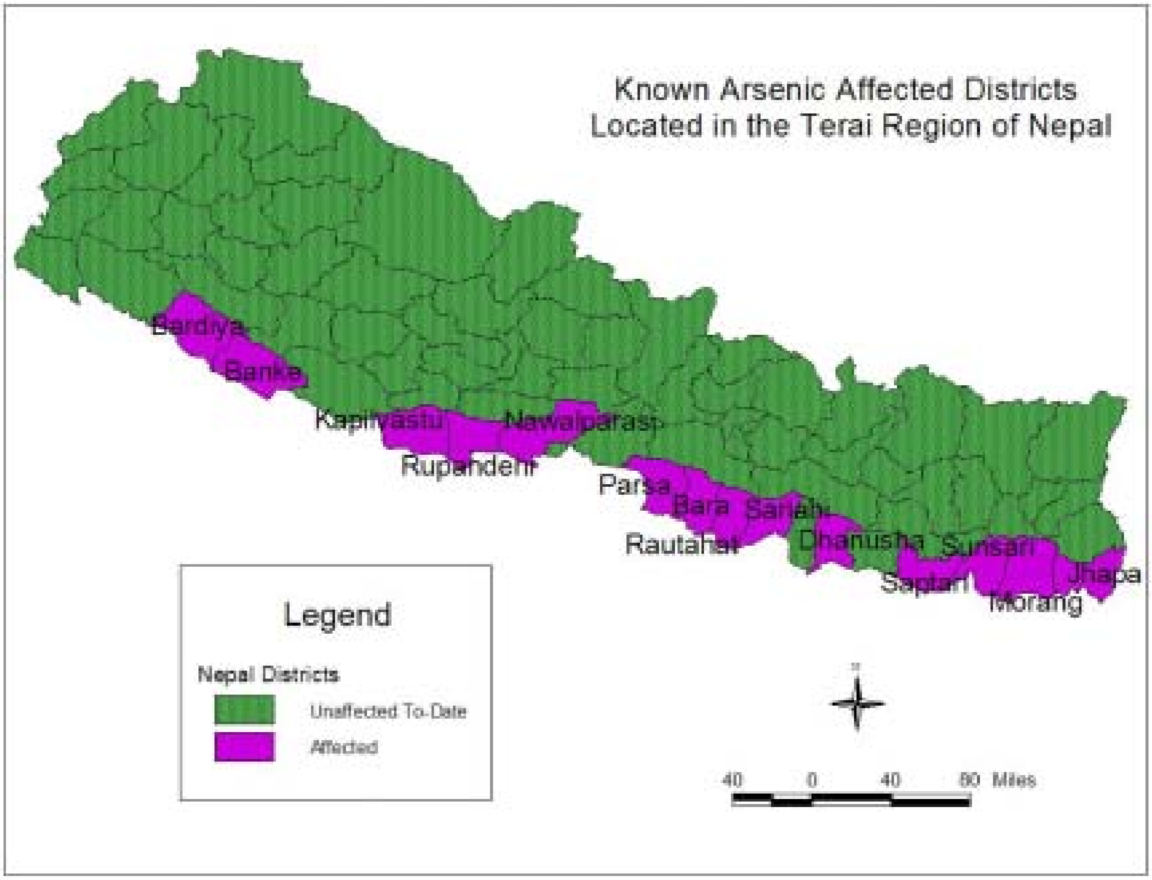


Figure 1.2 Arsenic affected districts in Nepal known to-date.

Figure 1.3 below represents data gathered by ENPHO and the Nepal Red Cross showing arsenic levels in 11 Terai districts. Almost 9000 samples were analyzed, and approximately 5% of these were above 50 µg/L. The percentages of arsenic presence in the samples analyzed within each district are shown in the graph. Of the samples collected in Nawalparasi, 55% were contaminated with arsenic concentrations above 10µg/L. In comparison, only 17.5% of the samples from Rupendehi contain arsenic levels above 10 µg/L. The data represented in Figure 1.3 is summarized in Appendix C.

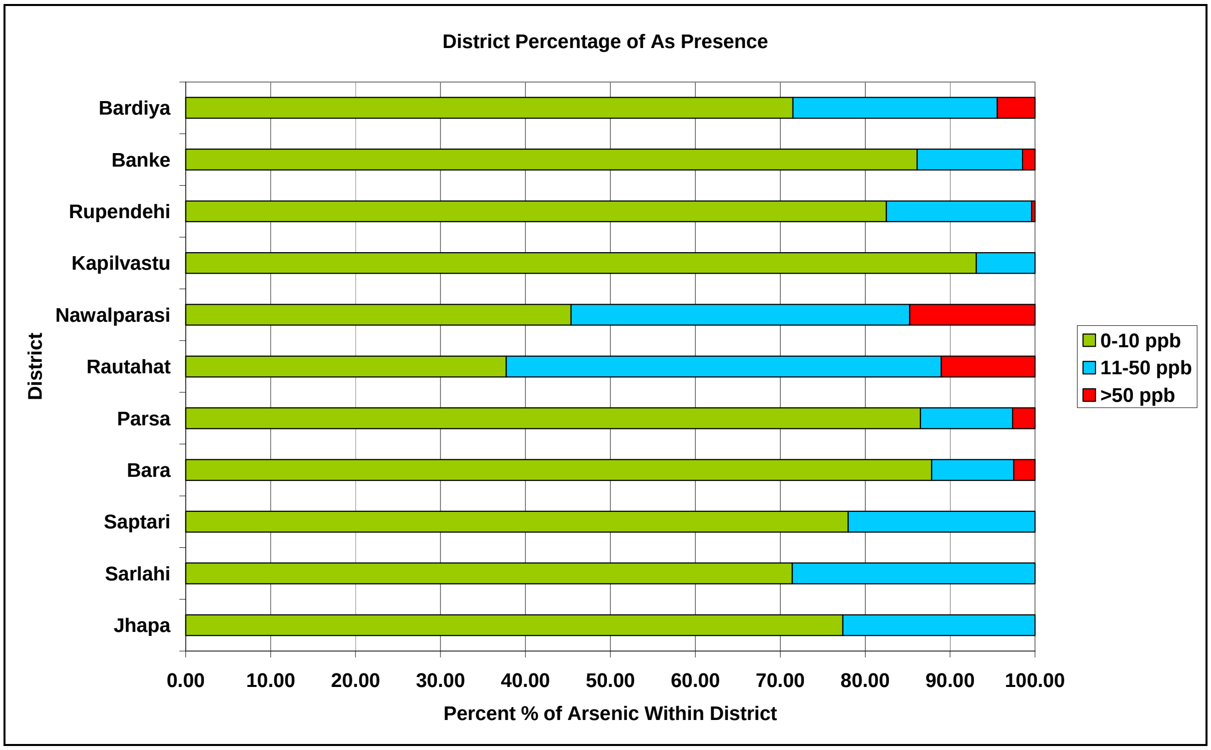


Figure 1.3 Percent arsenic presence within each District sampled.

Mitigation actions by the Drinking Water Quality Improvement Program (Nepal Red Cross Society/Environmental and Public Health Organization (ENPHO)) are underway for removing arsenic from tubewell water, educating the public of the problem, conducting health surveys, and extending testing and monitoring of wells.

1.5 Evaluation of Arsenic Removal Technologies

Arsenic removal technologies in Nepal should meet five assessment criteria:

1) Effective in the removal of arsenic (III) and arsenic (V);
2) Effective in removing total arsenic, minimally, below the Interim Nepali Standard of 50 µg/L, but ideally below the WHO standard of 10 µg/L;
3) Manufactured with locally available materials;
4) Affordable to the Nepali citizens affected by arsenic contamination;
5) Socially acceptable in terms of maintenance, operation and water demand.

Numerous studies involving arsenic adsorption on to iron salts, co-precipitation with iron and subsequent filtration, and adsorption to iron filings or chips have been previously investigated. These studies have identified iron as an effective medium for arsenic adsorption from natural waters. Jessica Hurd of the 2001 MIT Nepal Project, preformed zero valent iron adsorption experiments in Nepal, and achieved average arsenic concentrations in the treated water of 4 µg/L while the average influent arsenic concentration was 215 µg/L (Hurd, 2001). Researchers from Bangladesh University of Engineering and Technology (BUET) have implemented iron oxide coated sand filtration in Bangladesh and have found this method to be an improvement over the use of iron filings (Ali et al. 2001). While arsenic concentrations and the water quality in Nepal varies from that in Bangladesh, the hypothesis of this thesis is that iron coated sand media could meet all the assessment criteria stated above and therefore could be an effective technology for arsenic removal in Nepal. In terms of media preparation, this arsenic removal technology is quite involved. The sand must undergo a coating procedure and then be applied to a distribution system, but its effectiveness has now been shown in various laboratory and field tests, as is reputed in this thesis.

The author produced the iron oxide coated sand in a laboratory at MIT and assembled this technology in a rural field site in Nepal in order to test the system. The effectiveness was measured by quantifying the influent and effluent arsenic concentrations using Industrial Test System Arsenic Check kit in the field, and a Graphite Furnace Atomic Adsorption Spectrometer (GFAAS), Perkin and Elmer model 4100ZL upon returning to MIT. Effluent arsenic concentrations below the interim Nepali arsenic standard of 50 µg/L, would deem iron-oxide coated sand an effective removal technology for implementation in Nepal.

Chapter 2 ARSENIC BACKGROUND

2.1 Introduction

Arsenic is found throughout our environment as the twentieth most abundant element in the earth's crust. It is present in soil, water, air and all living matter. A member of periodic Group VA it has both metallic and nonmetallic properties. Arsenic can form alloys with many other metals and covalent bonds with carbon, hydrogen, oxygen, and sulfur (Tamaki et al.1992). Mobilization in our environment comes through many natural and anthropogenic processes, such as weathering, biological activity, volcanic emissions, mining activities, fossil fuel combustion, use of arsenical pesticides and herbicides and irrigation. Arsenic can occur in +5, +3, 0 and -3 states, but is found in inorganic form in natural waters as oxyanions of pentavalent arsenate (As(V)) or trivalent arsenite (As(III)), which is the more toxic of the two (Smedley and Kinniburgh 2002). Arsenic, in concentrations ranging from 0.5µg/L to more than 5,000µg/L has been found in natural waters. The toxic nature of arsenic causes serious health problems to organisms with chronic exposure to high levels.

2.2 Natural Occurrence

Natural arsenic contamination has been observed all over the globe. Two types of environments have shown high levels of arsenic in groundwaters: inland or closed basins in arid or semi-arid areas and strongly reducing aquifers often derived from alluvium. Minimal flushing and slow groundwater flow is characteristic of both environments, thus arsenic that becomes mobile will accumulate in the aquifers. Geothermal, mining and sulfide oxidation areas may also contain arsenic. There is an ongoing debate as to the specific mechanism of arsenic mobilization, but some indications have been emerging. Mineral weathering and high evaporation in semi-arid or arid conditions causing increased pH greater than 8.5, leads to desorption of arsenic from oxides and prevents resorption. Another scenario involves strong reducing conditions near neutral pH leading to desorption from oxides and dissolution of manganese and iron oxides, which also releases arsenic. Competition of arsenic with other compounds such as phosphate, bicarbonate, silicate and organic matter for sediment oxide adsorption sites also results in mobility (Smedley and Kinniburgh 2002). Figure 2.1 shows the possible pathways for arsenic mobility in high concentrations in groundwaters.

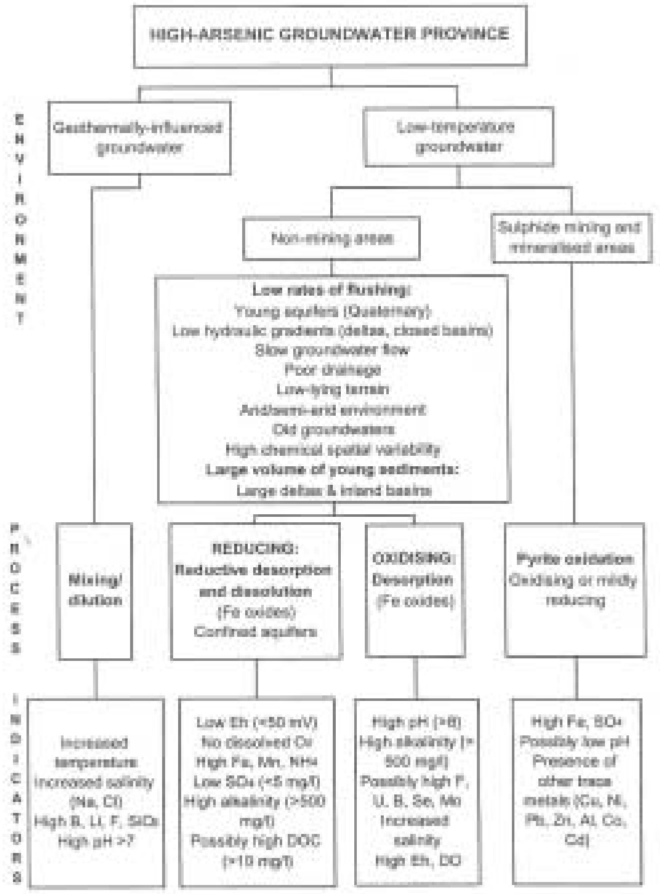


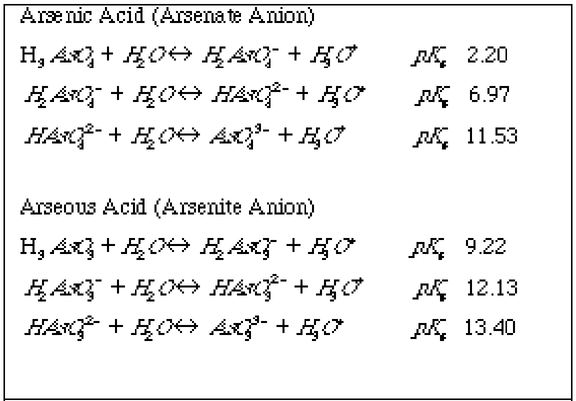
Figure 2.1 Flow diagram to aid locating possible high-arsenic groundwaters (Smedley and Kinniburgh 2002).

2.3 Source in Groundwater of Nepal

The Himalayan Mountains which serves as Nepal's northern boarder with China, are the source of sand, silt and mud to the southern lands of the Terai, and the Ganges Plain. Effects from natural elements, wind, rain, glacial movements have weathered mountains, breaking solid rocks into tiny particles causing chemical changes. From these processes, iron present in these rocks has turned to iron oxide, coating the particles. As arsenic is abundantly found in many rocks and adsorbs to iron oxides, it has been transported with the rocks as they were washed into rives and swept down stream. These rocks were deposited in the sea or in soils of the land, to become buried as the process repeated itself. When buried, iron oxide and arsenic are stable due to the small amount of dissolved oxygen supplied via percolated rainwater.

2.4 Speciation

Arsenic speciation in groundwater is an important factor in determining mobilization, toxicity, and general water chemistry. Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Natural waters have been recorded between pH 4-10, and typical Eh values range between 0.295V-0.472V. Figure 2.2 shows the prevalence of arsenic species as these two factors vary and Figure 2.3 shows the acid dissociation constants of inorganic arsenic. In the pH range of natural waters, $H_2AsO_4^-$ is dominant below pH 6.97, in oxidizing conditions while $HAsO_4^{2-}$ is dominant above that particular pH. In reducing environments $H_3AsO_3^0$ dominates. This species is uncharged thus its mobility is increased. There exists a correlation between speciation and the presence of reduced sulfur compounds. At elevated concentrations of the latter, reducing acidic conditions favor precipitation of sulfide minerals containing co-precipitated arsenic. For this reason, one would not predict high concentrations of arsenic in the presence of high concentrations of free sulfide. At neutral and alkaline pH's, thioarsenite species will be more important with high sulfide concentrations (Smedley and Kinniburgh 2002). Arsenic speciation is also affected by other chemical and microbial pathways such as oxidation and reduction by microorganisms and oxidation of arsenite by sediments like manganese and iron oxyhydroxides.



Arsenic Acid (Arsenate Anion)

$H_3AsO_4 + H_2O \leftrightarrow H_2AsO_4^- + H_3O^+$ pK_a 2.20

$H_2AsO_4^- + H_2O \leftrightarrow HAsO_4^{2-} + H_3O^+$ pK_a 6.97

$HAsO_4^{2-} + H_2O \leftrightarrow AsO_4^{3-} + H_3O^+$ pK_a 11.53

Arseous Acid (Arsenite Anion)

$H_3AsO_3 + H_2O \leftrightarrow H_2AsO_3^- + H_3O^+$ pK_a 9.22

$H_2AsO_3^- + H_2O \leftrightarrow HAsO_3^{2-} + H_3O^+$ pK_a 12.13

$HAsO_3^{2-} + H_2O \leftrightarrow AsO_3^{3-} + H_3O^+$ pK_a 13.40

Figure 2.2 Acid dissociation constants for both arsenic and arsenous acid (Linge 2002).

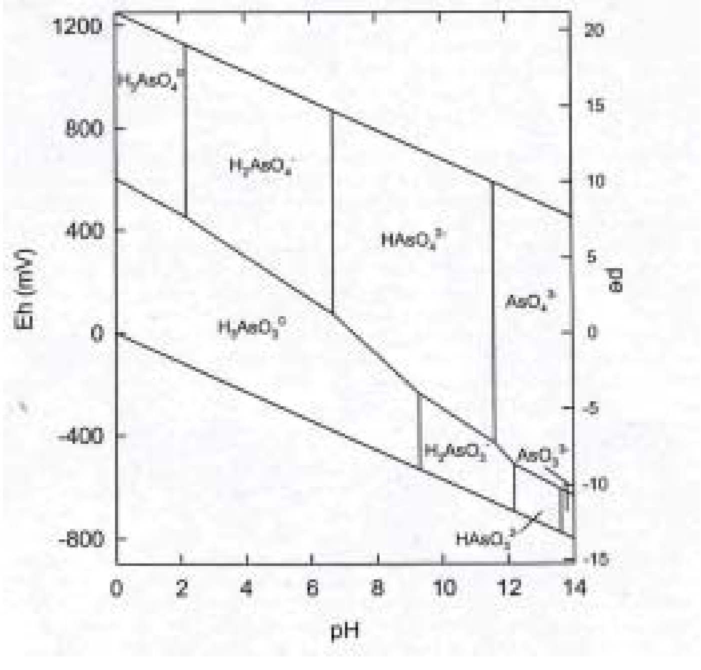


Figure 2.3 Eh vs. pH diagram for arsenic species. (Smedley and Kinniburgh 2002).

2.5 Mobilization of Arsenic

The pH values typically found in groundwaters are between 6.5 and 8.5. The mobility of arsenic at these levels and in both oxidizing and reducing environments sets it apart from other heavy metalloids and oxyanion-forming elements (Smedley and Kinniburgh 2002). Many studies have been conducted that indicate the release of arsenic from sediments and soils occurs under reducing conditions, though the mechanisms under which it happens are still being debated. Some have found reductive desorption of arsenate, reductive dissolution of iron oxides thus releasing adsorbed arsenic, and/or changes in mineral structure producing conditions where adsorption is no longer possible (Smedley and Kinniburgh 2002). Figure 2.4 shows a schematic of arsenic transport with iron oxides and mobilization under reducing conditions.

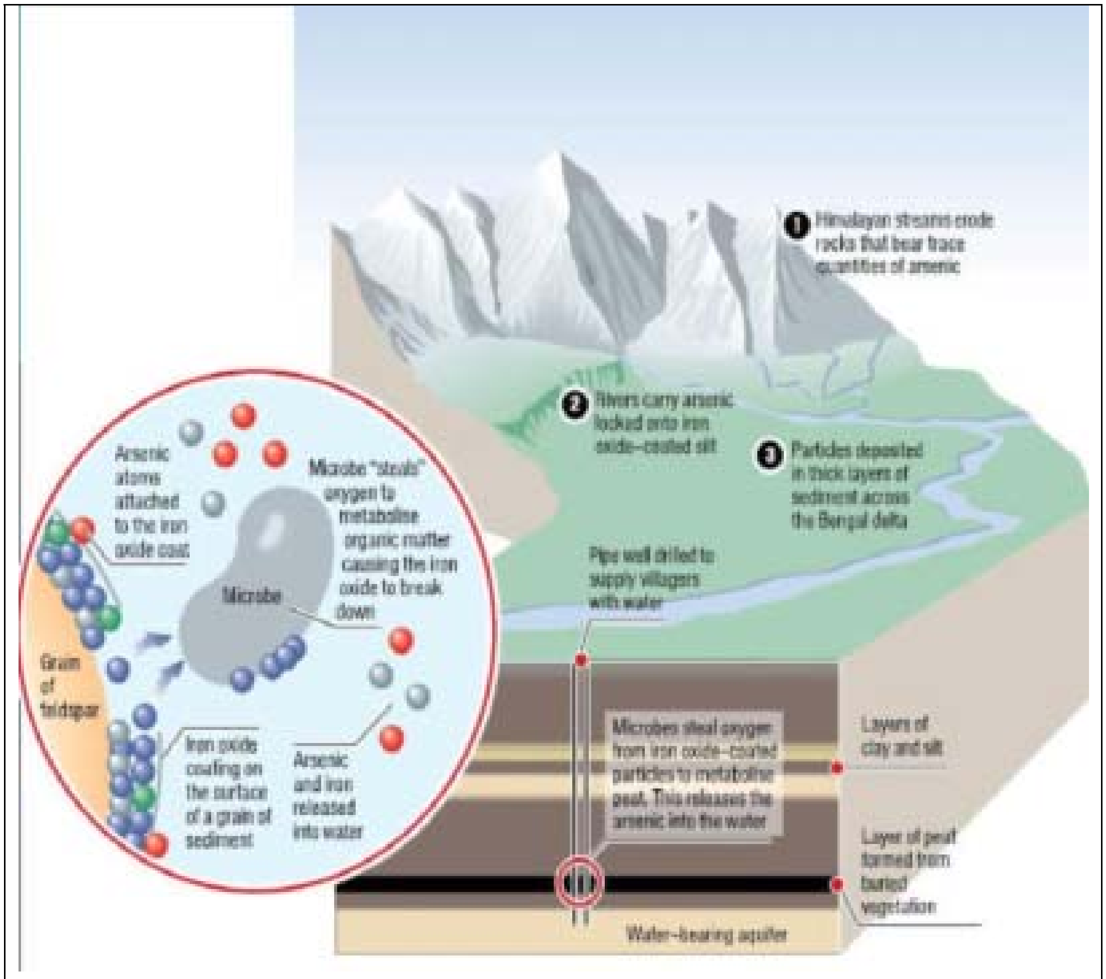


Figure 2.4 Source of arsenic deposition and desorption from sediments (McArthur, 2002).

2.6 Toxicity and Health Effects

Due to the high concentrations in groundwater compared with other media, such as air or food, ingestion of arsenic from drinking water is a major source of exposure. The process of arsenic uptake and distribution in organisms adapts the pathway of the essential element phosphorus. Phosphorus and arsenic have similar oxidation states and ability to form covalent bonds with sulfur. These characteristics contribute to arsenic's toxicity. Arsenate (H_3AsO_4) is an analogue of phosphate and is taken up via the phosphate transport system by most organisms. Arsenate has been postulated to replace phosphate in energy transfer phosphorylation reactions (Smedley and Kinniburgh 2002). The comparison of arsenic and phosphorus is partly illustrated by comparing dissociation constants for arsenic and phosphoric acid in Figure 2.5 (Linge 2002).

Phosphoric Acid

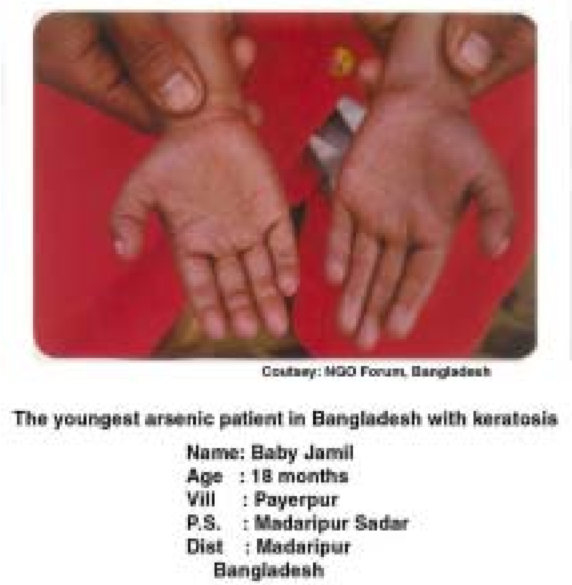
$H_3PO_4 + H_2O \leftrightarrow H_2PO_4^- + H_3O^+$ pK 2.15 (2.20)

$H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$ pK 7.20 (6.97)

$HPO_4^{2-} + H_2O \leftrightarrow PO_4^{3-} + H_3O^+$ pK 12.38 (11.53)

Figure 2.5 Acid dissociation constants for phosphoric acid (arsenic acid in brackets) (Linge 2002).

Arsenite (As (III)) has a high affinity for thiol groups of proteins, inactivating many enzymes and tissue proteins such as keratin in skin, nails, and hair, and has a longer half-life than other arsenic species in mammalian systems. Common symptoms of toxicity include chronic intoxication with decreased motor coordination, nervous disorders, respiratory distress, and damage to kidneys and respiratory tract. Acute toxicity leads to gastrointestinal irritation, accompanied by difficulty in swallowing, thirst, abnormally low blood pressure and convulsions; death follows from cardiovascular collapse. The lethal dose (LD_{50}) to humans is 1-4 mg As/kg for an adult (Pontius et al. 1994). Dermal and vascular changes are the main symptoms of chronic exposure. Skin pigments, hyperkeratosis and ulcerations of the hands and feet are the visible initial effects, while organ cancer follows (Figure 2.6 and Figure 2.7). Due to the bioaccumulation of arsenic in the body, these effects are irreversible.

	
Figure 2.6 Cancerous lesions on feet. (Wilson 2002)	Figure 2.7 Youngest sufferer to date. (Wilson 2002)

Chapter 3 IRON OXIDE FORMATION AND ADSORPTION THEORY

3.1 Nature of Iron Oxide

There are sixteen different iron oxides in the environment. The compounds are oxides, hydroxides or oxide hydroxides, composed of Fe with O and/or OH. Hydrous ferric oxides naturally coat suspended sediments, minerals and bacteria. Most consist of trivalent iron (Cornell and Schwertmann, 1996). The general formation of iron oxides begins with the oxidation of Fe (II) bound to sediments to Fe (III) and subsequent hydrolysis to form trivalent iron oxides. The iron oxide cycle is shown in Figure 3.1. The major oxide forms are represented in Table 3.1.

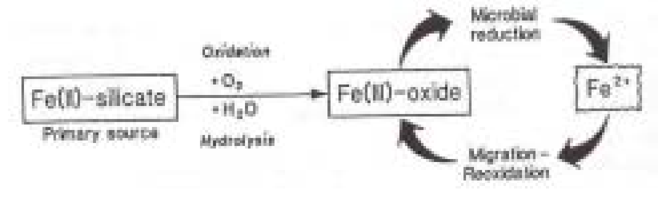
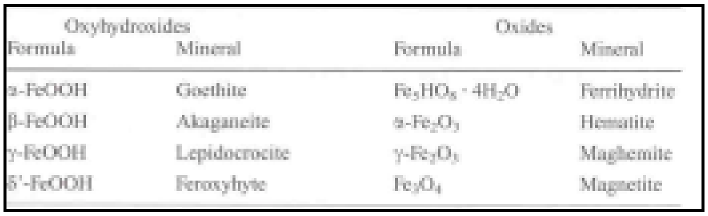


Figure 3.1 Basic process of Fe oxide formation in Nature (Schwertmann and Cornell, 2000)

Table 3.1 The Major Iron Oxides and Oxide Hydroxides (Schwertmann and Cornell, 2000)



Oxyhydroxides		Oxides	
Formula	Mineral	Formula	Mineral
α-FeOOH	Goethite	$Fe_5HO_8 \cdot 4H_2O$	Ferrihydrite
β-FeOOH	Akaganeite	α-Fe_2O_3	Hematite
γ-FeOOH	Lepidocrocite	γ-Fe_2O_3	Maghemite
δ'-FeOOH	Feroxyhyte	Fe_3O_4	Magnetite

These iron oxides differ in color, structure and adsorption capacity. The conditions under which they are formed play an important role in their structural orientation. Changes in the environment, such as pH or temperature, are capable of converting some iron oxides from one type into another form. Figure 3.2 through Figure 3.4 show the characteristic relationships between iron oxides. Each iron oxide has a distinct color, which can be used in identification of a form present, though chemical identification should validate the previous approximation. Figure 3.2 displays the different colors of iron oxides present in our environment, which can also be made in the laboratory.

Figure 3.2 Colors of Iron Oxides (Schwertmann and Cornell, 2000)

The crystalline structures of major iron oxides are shown in Figure 3.3. Differences exist in their compositions and the number of exposed faces of iron available for adsorption. More crystalline structures have less surface area for chemical interactions.

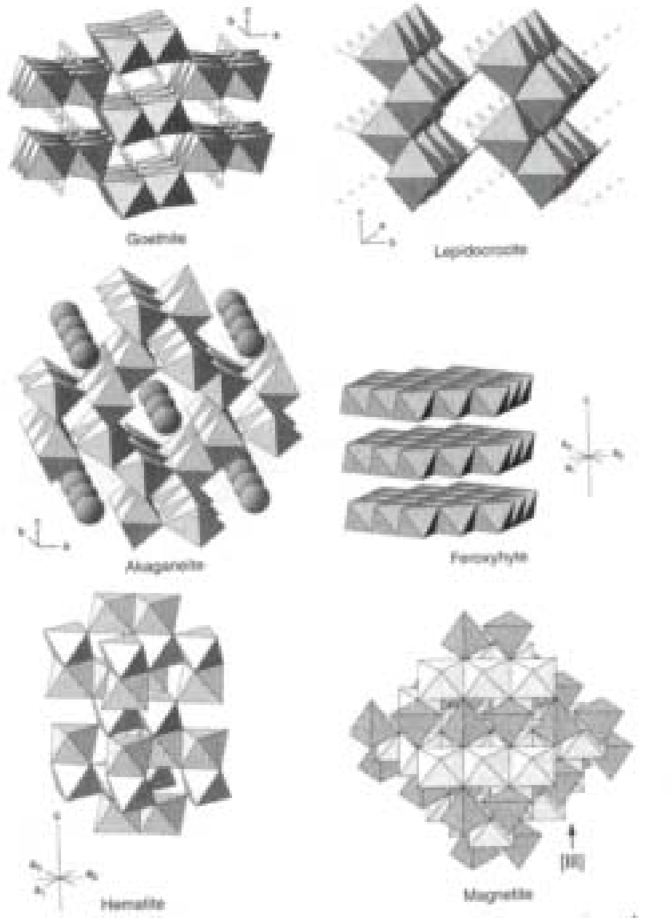


Figure 3.3 Structural models of goethite, akaganite, lepidocrocite, feroxyhyte, hematite, and magnetite. Small, open circles indicate H atoms. (Schwertmann and Cornell, 2000)

Figure 3.4 is a schematic presentation of frequent formation and transformation pathways of common iron oxides together with the approximate formation conditions (Schwertmann, Cornell, 2000). Iron oxides formed from Fe (III) and Fe (II) are linked through chemical and thermal processes as transformations in physical form and composition occur.

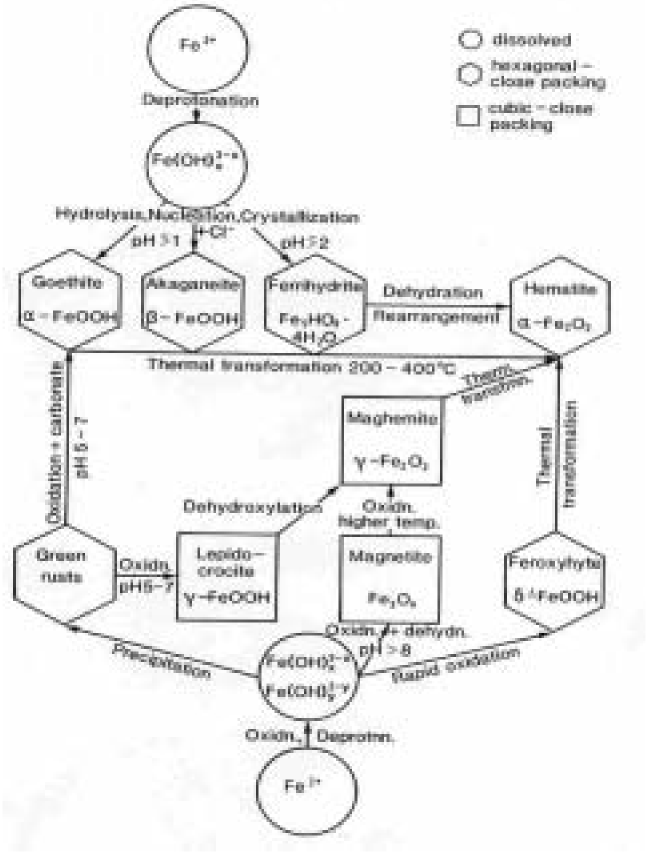


Figure 3.4 Conversions of iron oxides due to pH, temperature, and other chemical processes. (Schwertmann and Cornell, 2000)

The specific iron oxides that resulted from the various methods employed by the author have not yet been identified. It is believed that precipitation with 10M NaOH initially produces ferrihydrite. This supposition is based on the color of the colloid solution, the reagents used and the titration pH. The effects of increasing pH, and drying temperature are unclear from the methods used, when compared to those used in Schwertmann and Cornell, 2000. One can speculate at the presence of goethite and hematite on the basis color and extremely high drying temperature. Further analysis of the specific particles attached to the sand would have to be undertaken in order to conclude which form of iron oxide is present. Determining the iron oxide coated on the sand is important because the characteristics of each iron oxide give different adsorption capacities due to their crystalline structure and the attachment strength to the sand. While this project sought to evaluate iron oxide, in general, as an appropriate technology to remove arsenic, knowing which iron oxide has the maximum binding and adsorption ratio is necessary future work if implementation of this technology is desired.

The numerous methods employed to make iron-oxide coated sand outlined in Chapter 4 and Appendix A, do not specify which type of iron oxide is made nor is there any analysis as to maximizing the sand attachment or adsorption strength. Some analysis has been done as to the amount of iron oxide that actually coated the sand grains and measurements of coated surface areas. The distribution of the iron oxide particles on the sand surface shows a marked dependence on ionic strength, iron oxide to sand ratio and temperature (Schwertmann and Cornell, 2000). Electrostatic interactions between the SiO_2 and iron oxides promote adsorption, where the charge of the adsorbed iron oxide neutralizes the charge of the SiO_2 surface. Increases in pH cause the negative charge on the surface to increase also. The point of zero charge (PZC) is the pH where the surface has a net zero charge. At pHs greater than the PZC, the net surface charge changes from positive to negative. The extent of sand coating increases with increasing pH up to the PZC of the iron oxide, and decreases quickly above the PZC. The pH_{zpc} of silica (SiO_2), hematite (α-Fe_2O_3) and goethite (α -FeOOH) are 2, 6.7 and 7.8 respectively (EPA, 1999).

3.2 Adsorption of Arsenic to Iron Oxides

Arsenic adsorption onto iron oxides has been characterized as the Langmuir type, limited by surface site saturation (Wilkie and Hering, 1996). The diagram below is an example of a Langmuir isotherm. The maximum adsorbed arsenic per unit mass of solid is reached when all surface sites are occupied. Dissolved equilibrium solution concentration of arsenic goes to infinity. The sorption concentration is represented by the equation in Figure 3.5. The rate constant K depends on pH, competing ions (SO_4^{2-}, PO_4^{2-}, etc.) and the nature of the iron oxide related to the energy of adsorption (Voelker, EPA, 1999).

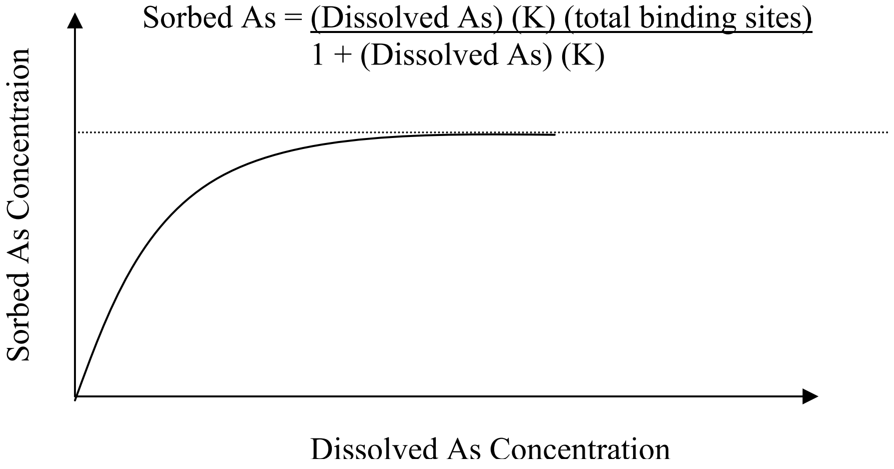


Figure 3.5 Langmuir Isotherm for Arsenic adsorption on to iron oxides. (Voelker)

Arsenic adsorption on ferrihydrite, hydrous ferric oxide (Hfo) and goethite have been examined. Basic adsorption reactions of arsenate and arsenite are shown below; oxide surface sites are represented by [≡FeOH°].

Arsenite on oxy-hydroxides surface (Elizalde-González et al. 2001)

$$\equiv FeOH^\circ + H_3AsO_3 \rightarrow \equiv FeH_2AsO_3 + H_2O \qquad (3.1)$$

Reactions of arsenate with hydrous iron oxide (Herring, 1996)

$$Fe(OH)_3\,(s) + H_3AsO_4 \rightarrow FeAsO_4{\cdot}2H_2O + H_2O \qquad (3.2)$$

$$\equiv FeOH^\circ + AsO_4{}^{3-} + 3H^+ \rightarrow \equiv FeH_2AsO_4 + H_2O \qquad (3.3)$$

$$\equiv FeOH^\circ + AsO_4{}^{3-} + 2H^+ \rightarrow \equiv FeHAsO^{4-} + H_2O \qquad (3.4)$$

Both arsenate and arsenite form inner sphere complexes with the iron oxide surface, characterized by monodentate and bidentate, binuclear bridging complexes as surface coverage increases (Fendorf et al. 1997, Manning et al. 1998). It has been noted that uncharged arsenite molecules are adsorbed less efficiently than negatively charged arsenate species. Also, in the presence of arsenate (As (V)), arsenite (As(III)) adsorption decreases (Jain and Loeppert1999). Adsorption of arsenate and arsenite is pH dependant.

Arsenate is adsorbed more readily at low pHs ≤ 7 due to repulsion between more negatively charged species and surface sites at high pHs (Raven et al. 1998). Arsenite is adsorbed optimally at pHs ≥ 8 or 9.

Chapter 4 IRON OXIDE SAND FOR ARSENIC REMOVAL

Arsenic adsorption onto iron oxides has been observed in various studies, and is one of several mechanisms believed to contribute to the presence of arsenic in groundwater and its subsequent mobilization due to dissolution of the oxides. Many researchers have previously used iron oxide coated sand to treat metal bearing wastes from industrial processes and contaminated groundwater containing elements such as cadmium, strontium and chromium.

Scientists at Bangladesh University of Engineering and Technology (BUET) have been investigating arsenic removal technologies in response to the overwhelming number of afflicted people affected with arsenicosis, keratosis, and other health problems associated with arsenic poisoning. BUET researchers found iron oxide coated sand to be an improvement over iron filings or chips due to the increased surface area and binding sites. Two iron oxide coated sand units have been assembled and installed in homes in two villages in Bangladesh, the Adda village in Barura thana of the Comilla district and Bejgaon village in Srinagar, Munshigong. One unit achieved removal below 15 µg/L from an initial concentration of 226 µg/L. Over eight months in operation, the unit had not reached the breakpoint of 50 µg/L, at which point the sand would be regenerated for further use. With minimum maintenance required, the user was very pleased with its performance. With these limited but promising results and advice from Borhan Badruzzaman of BUET, the author undertook the production of iron oxide coated sand as a possible arsenic removal technology to be applied in Nepal. The history of the iron oxide coated sand filter in Bangladesh, the production process and detailed description of the unit follow.

4.1 History in Bangladesh from Ali et al. 2001

The removal capability of iron oxide coated sand was tested in the laboratory at BUET in glass burettes. Groundwater spiked with As (III) and As (V) at a concentration of 300 µg/L was used as the influent water. With a contact time of 1 minute in a sand depth of 20 cm, the sand was able to treat 200 to 225 bed volumes before reaching the breakpoint of 50 µg/L, the Bangladesh arsenic drinking water standard. No flow rate information was provided. In a 40 cm bed depth contact time was 3-3.5 minutes, the initial flow rate fluctuated from 10 to 15 mL/min, and 350 to 400 bed volumes were treated before breakthrough. Arsenic concentrations were measured after each liter of water passed through the sand. Based on these results, it was determined that removal increased significantly with contact time. Also there was no discrepancy in removal efficiency between As (III) and As (V). Figure 4.1 below shows effluent concentrations as a function of bed volume for As (III) and (V).

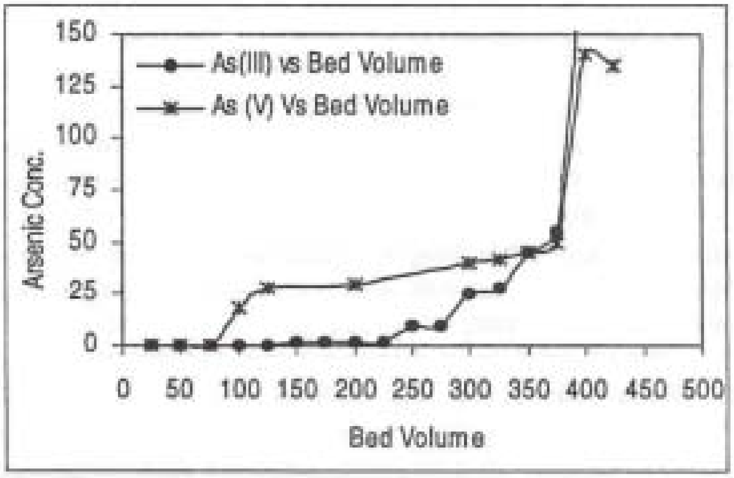


Figure 4.1 Effluent Arsenic concentration as a function of bed volume in the 40 cm sand bed. Initial As concentration 300µg/L. (Ali et al. 2001).

Once the breakthrough concentration was reached, the sand was regenerated. Three different procedures were tested in order to determine optimal recovery of arsenic and subsequent removal efficiency after regeneration. The methods used follow:

Method 1. Remove sand from burette and soak in 0.2N NaOH for several hours, followed by washing with 3 liters of distilled water.

Method 2. Pass 1.5 liters of 0.2N NaOH through the column, followed by washing with 3 liters of distilled water.

Method 3. Soak sand inside burette in 50 mL of 0.2N NaOH for 2 days, followed by washing with 3 liters of distilled water.

Method 1 reduced the depth of the sand bed by 2-3 cm when added back to the burette for reuse another time. Subsequent poor removal was attributed to this reduction. The methods 2 and 3 achieved arsenic removal to the same level as the original iron coated sand. An average of 300 to 350 bed volumes were treated with the regenerated iron oxide coated sand; this performance lasted up to five regeneration cycles. Treated bed volumes reduced to 275 to 300 after the sixth regeneration. The results in Figure 4.2 show regeneration efficiencies using Method 2.

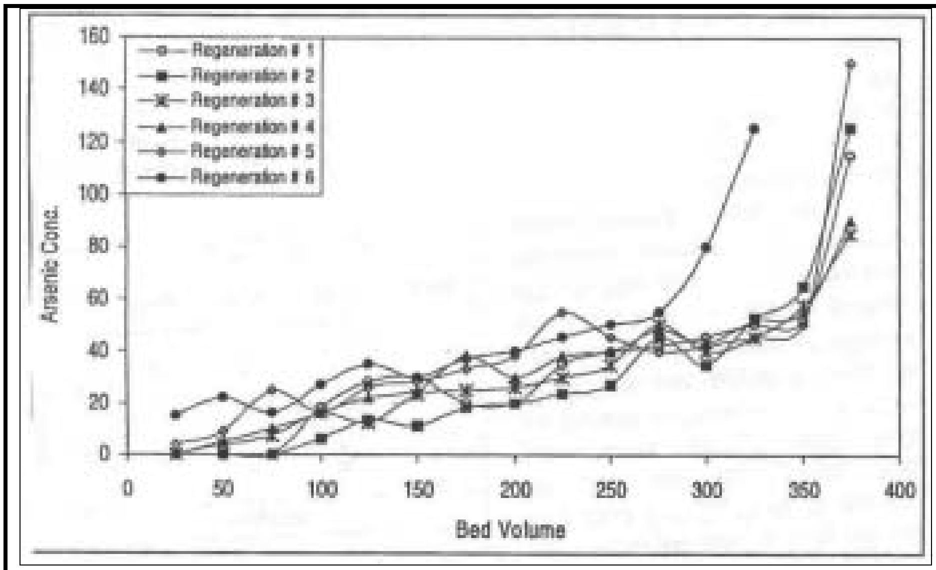


Figure 4.2 Effluent Arsenic concentration as a function of bed volume in the 40 cm regenerated sand bed. (Ali et al. 2001)

In August of 2000, BUET researchers installed an iron oxide coated sand unit in a household in the Adda village in Barura thana of the Comilla district of Bangladesh. The unit setup is described in Section 4.3.2. The household was given verbal instructions for use and a simple instruction sheet explaining operation and maintenance of the unit. The household collected one bottle of effluent a day for seven months, then one bottle a week for the research team members to collect during field visits. Results from these samples indicate that arsenic concentration decreased from 226µg/L to below 15µg/L.

Maintenance of this unit includes periodic washing (about once a month) of the upper sand bed to wash away precipitated iron, and to maintain an adequate flow rate. The flow rate of this unit was 1-2 L/min. At the time of publication, regular monitoring indicated that in more than eight months in operation the breakthrough concentration of 50 μg/L had not been reached. An additional unit was installed in the Bejgaon village in Srinagar, Munshigong; results are being evaluated.

4.2 Iron Oxide Coated Sand Production

Over the course of an extensive literature review, the author uncovered a plethora of methods, 10 to be specific, previously employed to produce iron oxide coated sand. Researchers have used a wide variety of methods which vary from the reagents used to the actual coating, drying temperatures and pH of the coating. Several methods adapt previous methods used with slight variations. The majority of these methods do not use iron oxide coated sand to remove arsenic, but instead to remove other heavy metals such as cadmium, chromium and aluminum. A general procedure is outlined below, followed by a step-by-step description of the previous methods in chronological order which contributed to and influenced the author's procedures. The methods adapted by the author are described in the next section.

The text that follows describes 4 different methods. Some of which were directly followed to produce and iron oxide coated sand (IOCS), others of which were not directly followed to produce and IOCS but which directly influenced the author's final procedure. Additional methods that were not directly followed to produce and IOCS or which did not directly influence the author's procedure are given in Appendix A.

4.2.1 General Coating Method

Step 1: Acid wash sand for 24 hours. Rinse sand with distilled water and dry in oven.

Figure 4.3 Author rinsing sand in ENPHO lab.

Step 2: Precipitate iron oxide from a ferric salt solution titrated with strong base.

Figure 4.4 Precipitated colloids in hood.

Step 3: Coat the sand with colloids and dry.

Figure 4.5 Dried sand after heating at 550°C.

Step 4: Rinse sand with clean water a few times.

Figure 4.6 Author rinsing sand of non-attached iron oxide colloids.

Step 5: Dry sands once again in oven.

Figure 4.7 Sands drying overnight.

Step 6: Store finished product in capped bottles.

Figure 4.8 Finished product

4.2.2 Methods Utilized in Production of Iron Oxide Coated Sands

During the 2001-2002 academic year, the author produced 7 different iron oxide coated sands. These are referred to in the text under Poole (2002). The methods leading up to Poole (2002) are those in which Poole (2002) is based upon.

4.2.2.1 Bailey, Bennet and Benjamin (1992)

Materials:

Ottawa sand (quartz) 20-30 mesh (0.60 to 0.85 mm diameter)

50% sulfuric acid

De-ionized water

2 M ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) solution

2.47M ferric chloride ($FeCl_3$)

10M and 1M sodium hydroxide (NaOH)

Method:

IOCS- Bailey1: Ferric Nitrate

1. Acid wash 200 mL of sand for 24 hours with 50% sulfuric acid.
2. Rinse sand with de-ionized water and dry sand.
3. Mix 10M sodium hydroxide with 80 mL of 2M ferric nitrate solution.
4. Pour solution over 200 mL of sand in Pyrex glass baking dish.
5. Loosely cover dish and place in oven at 110°C for 14 hours.
6. Remove from oven, separate grains and pass through a #16 sieve (1.18 mm).
7. Store in capped polystyrene bottles until use.

IOCS- Bailey 2: Ferric Chloride

1. Acid wash 200 mL of sand for 24 hours with 50% sulfuric acid.
2. Rinse sand with de-ionized water and dry sand.
3. Place 200 mL of sand in a Pyrex glass baking dish.
4. Add 80 mL of 2.47M ferric chloride and 1.85 mL of 10M sodium hydroxide.
5. Heat dish uncovered at 110°C, and stir each hour until the sand is dry (3-4hrs).
6. Heat sand to 550°C for 3 hours.
7. After cooling, sieve 100 mL batches through a #16 sieve (1.18 mm) and mix with 40 mL of 2.47M ferric chloride.
8. Loosely cover and heat at 110°C for 10 hours.
9. Once cool, sieve again and place under a hood for 20 hours.
10. Sand will be hygroscopic upon exposure to air. Begin a “rest and dry” cycle-let the sand become damp, then dry at 110°C for 3 hours. Repeat 5-7 times until sand no longer dampens when exposed to laboratory air.

IOCS-Bailey1&2 Laboratory testing: Rigid acrylic and polycarbonate tubing 0.63 cm ID, packed with 6 mL of media was used.

4.2.2.2 Joshi and Chandhuri (1996)

Procedure similar to that of Bailey et al. (1992).

Materials:

River sand of geometric mean size 0.49 mm

80 mL of a 2M ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) solution

Sodium hydroxide (NaOH)

Distilled water

Method:

1. Wash 200 g of sand and dry.
2. Titrate ferric nitrate solution to pH 11 with sodium hydroxide.
3. Add sand to solution and mix for 2 minutes.
4. Place mixture in drying oven at 110°C for 14 hours.
5. After drying, wash sand with distilled water until the runoff is clear.
6. Dry sand at 105°C.
7. Store in capped bottles.

Laboratory Testing:

Column Test: Glass column 11mm ID was packed with 75 g (50 mL) of coated sand (bed depth 52.5 cm; porosity 0.36). Empty bed contact time (EBCT) 50 min. Medium was regenerated by backwashing with 2 L of a 0.2 N sodium hydroxide solution, followed by rinsing with distilled water until influent and effluent pH were comparable.

Table 4.1 Groundwater Composition used in Joshi and Chandhuri (1996) Laboratory Experiment.

Parameter	Concentration
pH	7.5-7.8
Alkalinity	250-260 mg $CaCO_3$/L
Hardness	190-200 mg $CaCO_3$/L
Conductivity	780-840 µmhos/cm
Spiked with:	
Sodium arsenite ($NaAsO_2$), As(III)	100 µg/L
Sodium arsenate (Na_2HAsO_4), As(V)	100 µg/L

The natural Indian groundwater used in the experiments by Joshi and Chandhuri was spiked with arsenic concentrations listed in the table above.

4.2.2.3 Lo, Jeng and Lai (1997)

Materials:

Quartz sand 16-25 mesh (0.99 to 0.67 mm)

Ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$

Milli-Q water

pH 1.0 hydrochloric acid (HCl)

Deionized water

6N or 0.1N sodium hydroxide (NaOH)

Magnetic agitator

Method: This method utilizes various coating pHs, heating temperatures, and Fe concentrations.

1. Soak sand in pH 1.0 HCL for 24 hours.
2. Rinse sand with deionized water and dry at 103°C.
3. Make a 0.25M Fe(III) stock solution by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in Milli-Q water.
4. Add stock solution and Milli-Q water to a 1200 mL beaker to obtain a 1 L solution with the required concentration of iron ions.

5. Add NaOH (6N or 0.1N) drop wise until desired pH is reached.
6. Mix solution for approximately 15 minutes with magnetic agitator (when colloids begin to form, keep agitator at 300 rpm to provide required velocity gradient for colloid formation).
7. Allow the colloids to settle for two hours, and then discard the supernatant.
8. Mix 120 g of sand with the colloids.

IOCS-Lo1: Temperatures <200°C

9. Place beaker in oven, heat for 15 hours to evaporate water, then agitate.

IOCS-Lo2: Temperatures >200°C

9. Place beaker in a high temperature oven for 5 hours.
10. Wash sand with deionized water until runoff is clear.
11. Re-dry in high temperature oven for 5 hours, store in polystyrene bottles until use.

<u>Laboratory testing:</u> Adsorption studies were carried out in Pyrex vessels with 20 g of coated sand, and agitation provided by magnetic stirrers. The temperature was controlled at 20°C by circulating water from a temperature bath through the vessels. Carbon-dioxide-free nitrogen was bubbled though the vessels.

4.2.2.4 M. Ashraf Ali, A.B.M. Badruzzaman, M.A., Jalil, M. Delwar Hossain, M.M. Hussainuzzaman, M. Badruzzaman, O.I. Mohammad, N. Akter (2001)

(Procedure similar to that by Joshi and Chandhuri (1996))

<u>Materials</u>:

Sand passing through a #30 sieve and retained on #40 sieve

20% commercial grade hydrochloric acid (HCL)

2M ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$

10 N sodium hydroxide (NaOH)

Distilled water

Method:

1. Wash sand in HCL for 24 hours.
2. Dry sand.
3. Mix sand with 2M ferric nitrate and 10 N sodium hydroxide solution (80 mL for ferric nitrate solution and 4 mL of sodium hydroxide solution is required for each 200 cm^3 of sand).
4. Heat the mixture in oven at 110°C for 14 hours.
5. Wash with distilled water a number of times then dry again.

Laboratory testing: Glass burettes with a cross sectional area of 1 sq. cm. and a sand bed depth of 20 cm and 40 cm were used. Groundwater was spiked with both As (III) and As(V) at a concentration of 300 μg/L. Contact time for the 20 cm and 40 cm beds were 1 minute and 3-3.5 minutes, respectively. The media was regenerated 3 ways: 1) by taking the iron coated sand from the burette and soaking it in 0.2N NaOH for several hours, followed by washing with 3 liters of distilled water; 2) by passing 1.5 liters of 0.2 N NaOH through the column, followed by washing with 3 liters of distilled water; and 3) by soaking the sand (inside the burette) in 50 mL of 0.2 N NaOH for 2 days, followed by washing with 3 liters of distilled water. Regeneration by the first method reduced the bed depth and removal was poor. Regeneration by the second and third methods achieved removal efficiency similar to the original iron oxide coated sand.

The characteristics of the background Bangladesh groundwater used are listed in Table 4.2. This water was spiked with As (III) and As(V) at a concentration of 300 μg/L.

Table 4.2 Original Groundwater Composition used in Ali et al. 2001 Laboratory Experiment

Parameter	**Concentration**
pH	6.0
Color	15 Pt.-Co.
Turbidity	0.90 NTU
Alkalinity as $CaCO_3$	242 mg/L
Carbon-dioxide	203 mg/L
DO	2.97 at 26°C 2.03 at 26.1°C
Conductivity	1054 µs/cm
Chloride	165 mg/L
Hardness as $CaCO_3$	338 mg/L
Sulfate	35.1 mg/L
Nitrate	0.4 mg/L
Phosphate	0.14 mg/L
Chromium	0.0049 mg/L
Fluoride	0.35 mg/L
Iron	0.07 mg/L
Manganese	0.01 mg/L
Potassium	25.4 mg/L
Sodium	131.9 mg/L
Arsenic	< 1 µg/L
Lead	0.0214 mg/L
Cadmium	0.0018 mg/L
Zinc	0.0372 mg/L
Copper	0.0467 mg/L
Nickel	0.0074 mg/L
Mercury	Nil mg/L
Silica	32 mg/L

The methods adapted by the author are summarized below.

4.2.2.5 Poole (2002)

Seven IOCS were made by varying concentration, colloid treatment, and drying temperature. Methods were adapted from Ali et al. 2001, Joshi and Chandhuri, 1996, Bailey et al. 1992, and Lo et al., 1997.

Materials:

3 Sands- 1.Ace Hardware fine grained, 2.Passed #30 retained #40 sieve, 3. Local Nepal medium-fine

0.826 $Fe(NO_3)_3 \cdot 9H_2O$ and crystalline ferric nitrate

Anhydrous sodium hydroxide (NaOH)

6 N (20%) commercial grade hydrochloric acid (HCL) and concentrated hydrochloric acid (HCL)

Distilled water

Deionized water

Methods:

IOCS1- Hardware fine grained sand

1. Wash sand in 6 N HCL for 24 hours.
2. Rinse with distilled water until free of HCL.
3. Place sand in oven to dry at 103°C.
4. Slowly dissolve anhydrous NaOH in 80 mL 0.25 M ferric nitrate to a pH of 12.4 while mixing continuously.
5. Let colloids settle for 12 hours.
6. Discard the supernatant, and let excess liquid evaporate in hood.
7. Add 200g of sand to the colloids and mix well.
8. Heat sand in oven at 170°C-200°C for 10 hours.
9. Rinse sand with distilled water till runoff is clear.
10. Dry sand in oven.
11. Store in capped bottle.

IOCS2- Passed #30 sieve retained on #40 sieve sand

1. Wash sand in 6 N HCL for 24 hours.
2. Rinse with distilled water till free of HCL.
3. Place sand in oven to dry.
4. Titrate 2 M ferric nitrate (80 mL/ 200 mL of sand) with 10 M NaOH to a pH of 11 while mixing continuously.
5. Add sand to colloid solution and mix well.
6. Heat sand in oven at 120°C for nine hours, then ramp to 550°C for six hours.
7. Once sand is cool, rinse with distilled water several times.
8. Dry sand in oven.
9. Store in capped bottles.

IOCS3- Local Nepal medium-fine grained sand

1. Wash sand in concentrated HCL for 24 hours.
2. Rinse with deionized water until free of HCL.
3. Place sand in oven to dry at 200°C.
4. Titrate 500mL of 2M ferric nitrate with 1L of 1M NaOH, and 500 mL of 10 M NaOH to pH of 12.3 while mixing continuously.
5. Let colloids settle overnight.
6. Discard the supernatant and mix colloids with sand (200 mL/80 mL ferric nitrate).
7. Put sand in ceramic pot and place in kiln at 100-110°C overnight.
8. Increase temperature to 550°C and hold for 12 hours.
9. Rinse sand with deionized water a few times, then with clean tap water.
10. Dry in oven.

IOCS4, IOCS6- Passed #30 sieve retained on #40 sieve sand, air dried and heated colloids

1. Wash sand in 6 N HCL for 24 hours.
2. Rinse with distilled water till free of HCL.
3. Place sand in oven to dry.
4. Titrate 2 M ferric nitrate (80 mL/ 200 mL of sand) with 10 M NaOH to a pH of 11.44 while mixing continuously.
5. Let the colloids settle for 4 hours.

6. Remove the supernatant and discard.
7. Let the colloids sit in hood for 24 hours.
8. Heat colloids in oven at 105-110°C to evaporate liquid remaining liquid.
9. Mix sand and colloids thoroughly.
10. Divide sand in half, heat one half at 110-150°C for 17 hours (IOCS4) and the other half at 550°C for 15 hours (IOCS6).
11. Wash sands three times with distilled water, then with tap water.
12. Dry in oven at 170°C.

IOCS5, IOCS7- Passed #30 sieve retained on #40 sieve sand, air dried colloids

1. Wash sand in 6 N HCL for 24 hours.
2. Rinse with distilled water till free of HCL.
3. Place sand in oven to dry.
4. Titrate 2 M ferric nitrate (80 mL/ 200 mL of sand) with 10 M NaOH to a pH of 11.44 while mixing continuously.
5. Let the colloids settle for 4 hours.
6. Remove the supernatant and discard.
7. Let the colloids air dry in hood.
8. Mix sand and colloids thoroughly.
9. Divide sand in half, heat one half at 110-150°C for 17 hours (IOCS5) and the other half at 550°C for 15 hours (IOCS7).
10. Wash sands 3 times with distilled water, then with tap water.
11. Dry in oven at 170°C.

The characteristics of the sands are summarized in

Table **4.3**. The major differences between the sands are the mixture with which the sands were coated, either an aqueous colloidal solution or a colloidal paste after the liquid had evaporated; and the temperature of the drying oven for after the sand was coated with the colloids. More detailed explanations follow in Section 4.4, and possible effects of the differences are discussed in Chapter 6 , Section 6.3.

Table 4.3 Summary of Sands Produced

IOCS	Sand Grain Size	$Fe(NO_3)_3$ Conc.	Coating Procedure	Drying Temp.
1	Medium-Fine grain	0.25 M	Supernatant removed, Air dried colloids	~170-200ºC 10 hrs
2	Pass #30 sieve retained on #40 sieve	2.0 M	Aqueous colloidal suspension	Held at 120ºC for 9hr, then ramped to 550ºC for 6hrs.
3	Local Nepal Medium-Fine grain	2.0 M	Supernatant removed	Held at 100-110ºC overnight then ramped to 550ºC held for 12 hrs.
4	Pass #30 sieve retained #40 sieve	2.0 M	Supernatant removed, colloids partially air dried, and dried at 105-110°C	~ 110-150ºC for 17 hrs
5	Pass #30 sieve retained #40 sieve	2.0 M	Supernatant removed, Air dried colloids	~ 110-150ºC for 17 hrs
6	Pass #30 sieve retained #40 sieve	2.0 M	Supernatant removed, colloids partially air dried, and dried at 105-110°C	550ºC for 15 hrs
7	Pass #30 sieve retained #40 sieve	2.0 M	Supernatant removed, Air dried colloids	550ºC for 15 hrs

Field Testing:

Field Test Sites: The author tested these 7 iron oxide coated sands, contained in treatment columns, in Parasi, Nepal, Pepperell, MA, USA and Salem, NH, USA. The field site in Parasi, Nepal was at the house in which the author was staying. A work space was set up on the front porch, and source water was drawn from the tubewell in the backyard of the house. In Salem, NH the field site was also at a private residence. The field site in Pepperell was a private residence. A work space was created on the back concrete patio. Due to the connection of a water softener to the distribution system, water was collected in a bucket from a valve before the softener and brought outside for testing. The author worked along the front walkway of the house, drawing water from a garden hose.

Testing Parameters: The author tested source water for various water quality parameters in addition to arsenic, including iron, manganese, pH, hardness, alkalinity and redox potential (ORP). Not all parameters were tested in each field site due to equipment limitations. The water chemistry of each source water is found in Table 4.4 through Table 4.6 .

Table 4.4 Parasi, Nepal January 10, 2002

Parameter	Concentration
pH	7.0
Hardness	250 mg/L as $CaCO_3$
Alkalinity	180-240 mg/L
Iron	2.5 mg/L
Manganese	0 mg/L
ORP	-045 mV
Arsenic (Test Kit)/ (GFAAS)	300 µg/L/242 µg/L
Arsenic III (GFAAS)	220µg/L

Table 4.5 Pepperell, NH March 27, 2002

Parameter	Concentration
pH	6.6
Iron	0.3 mg/L
As	101 µg/L

Table 4.6 Salem, NH March 28, 2002

Parameter	Concentration
pH	7.0
Iron	0.7 mg/L
Hardness	80
Alkalinity	80-120
Manganese	0-0.3 mg/L
Arsenic (GFAAS)	1020 µg/L

Test Apparatus: Polycarbonate tubing 3.7 cm ID was packed with 10 cm of medium sized sand, followed by a 2 cm gravel layer, plus mesh screening to separate the gravel from the IOCS, packed to a depth of 40 cm. A porous pad prevented the IOCS from entering the spigot. Figure 4.9 and Figure 4.10 show the field testing prototypes used to test each sand.

Figure 4.9 Test apparatus with IOCS1 and IOCS2 in Parasi, Nepal

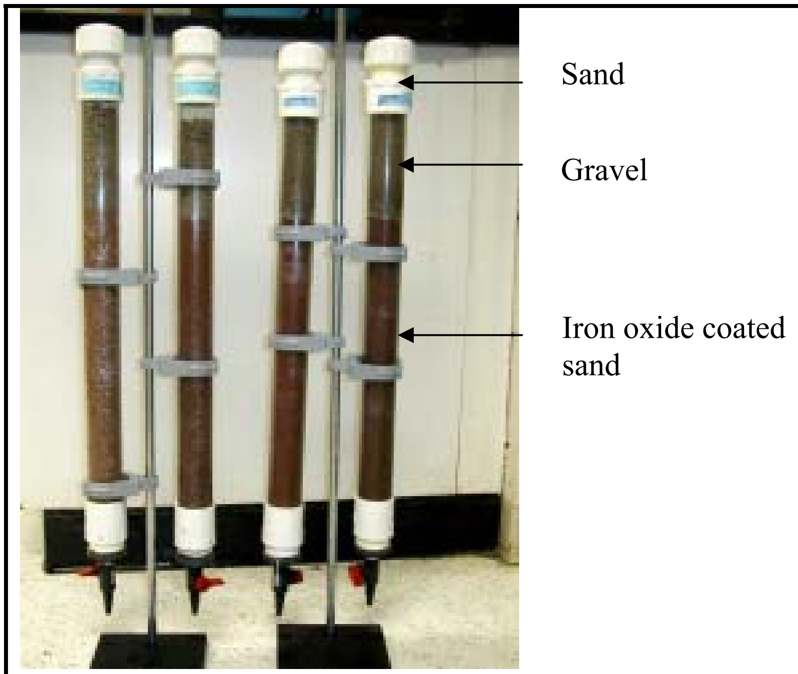


Figure 4.10 Test apparatus with IOCS 4,5,6, 7 in lab at MIT

Testing Procedure: Source water was allowed to flow freely from the hose or was pumped for approximately 3 minutes to extract fresh groundwater. Sands were flushed with two bed volumes of the sample water, or until outflow was free of visible particulate iron. Once the system was flushed, contaminated water was aerated either by addition to a bucket, and stirred for approximately 5 minutes, or by high a flow from a hose, to allow precipitation of iron. Sample collection followed.

Sample Collection: When sample was source water, samples were collected in plastic bottles, which were rinsed with sample water prior to collection when the sample was source water. Outflow from the IOCS units were collected directly into clean sample bottles. Samples collected in November 2001 in Pepperell, MA and in Parasi, Nepal in January 2002, were collected from sequential bed volumes after flushing. Of the samples collected in Pepperell in March 2002, samples 1 and 2 were collected sequentially after flushing, sample 3 was collected after passing five bed volumes of source water through the column after collection of sample 2. Sample collection in Salem, NH went as follows: after flushing, samples 1 and 2 were collected, and then 1 bed volume of source water was allowed to flow though, with the exception of IOCS1 where five bed volumes were allowed to pass. Samples 3 and 4 were then collected. A speciation sample was collected next, followed by samples 5 and 6. Ten mL samples were brought back to MIT from Nepal to be analyzed on the GFAAS, and were preserved by adding 1 drop of concentrated HCL within 24 hours of collection. Samples collected in the United States were preserved in the lab by adding one drop of 6M HCL/20 mL of water to reduce the pH below 2.

All results are presented in Chapter 6

4.3 Household Units Developed for Utilizing IOCS for Drinking Water

Joshi and Chandhuri, as well as Ali et al., have designed household units to implement IOCS for arsenic removal. The unit by Joshi and Chandhuri was only tested in the lab however, while Ali et al.'s unit was implemented in households in Bangladesh. The author assembled a household system based on that by Ali et al. but due to size constraints with airline luggage, was unable to bring the unit to Nepal for testing. Below are descriptions of the 3 units presently designed, 1. Joshi and Chanduri unit, 2. Ali et al. unit, and 3. Poole unit.

4.3.1 Joshi and Chandhuri (1996)

Apparatus Materials:

628.3 mm x 660 mm galvanized iron sheet
1 tap
Brass disc, with a 1.5 mm diameter orifice
Perforated splash plate

Apparatus construction:

1. Cut galvanized iron sheet to make one chamber of 200 mm ID x 380 mm ~ 1193.81 cm^3 (top chamber) and one of 200 mm ID x 280 mm ~ 879.65 cm^3 (bottom chamber).
2. Fit the tap to the bottom chamber.

3. Fit the brass disc to the bottom of the top chamber.
4. Stand the top chamber on top of the bottom chamber and fill with 6 kg (4L) of iron oxide coated sand medium up to a height of 125 mm.
5. Cover sand bed with perforated splash plate.

Two units were constructed and tested in the lab, assessing removal of 100µg/L of arsenic (III) and (V) separately. Runs continued until effluent arsenic concentration exceeded the WHO guideline of 10 µg/L in drinking water. EBCT was 40 minutes. The medium was regenerated with 10 L of a 0.2 N sodium hydroxide solution followed by washing with 10 L of clean water. The arsenic (III) unit treated 625 L of water before regeneration and 610 L after one regeneration. The arsenic (V) unit treated 780 and 760 L of water respectively.

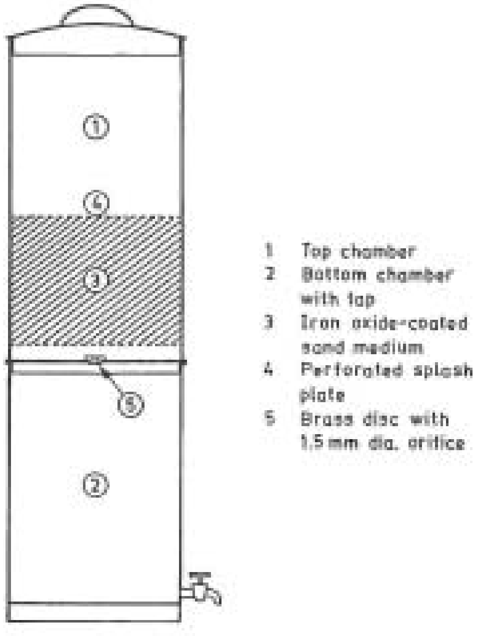


Figure 4.11 Household arsenic removal unit (From Joshi and Chandhuri, 1996)

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Apparatus Materials:

2 water collection buckets with spigots
1 15-cm diameter PVC pipe, at least 12 cm in length, perforated at its base
1 15-cm diameter PVC pipe, at least 40 cm in length, with tap 4 cm from bottom
Plastic tubing to fit bucket spigot
1.5 inch diameter strainer connected to a plastic pipe

Apparatus Description:

A pre-treatment system of a bucket is provided in order to stir the water for sometime to accelerate precipitation of naturally present iron. From the pre-treatment bucket the water flows through a sand filter where the excess iron is removed. Plastic tubing connects the spigot of the bucket to the top of the shorter PVC column, where the sand filter resides to a depth of 10 cm below which is a 1-2 cm gravel bed to prevent sand from passing through the bottom of the perforated PVC chamber. Next, in the second PVC column the water passes through the IOCS of 40 cm depth, (7100 cm^3 of sand). A plastic pipe connects a 1.5 inch diameter strainer to a tap 4 cm from the bottom of the chamber. BUET researchers assumed that this unit would be able to treat at least 2500 liters of arsenic contaminated water with a concentration of about 300 µg/L of water (assuming 350 bed volumes) before regeneration of the sand media is required.

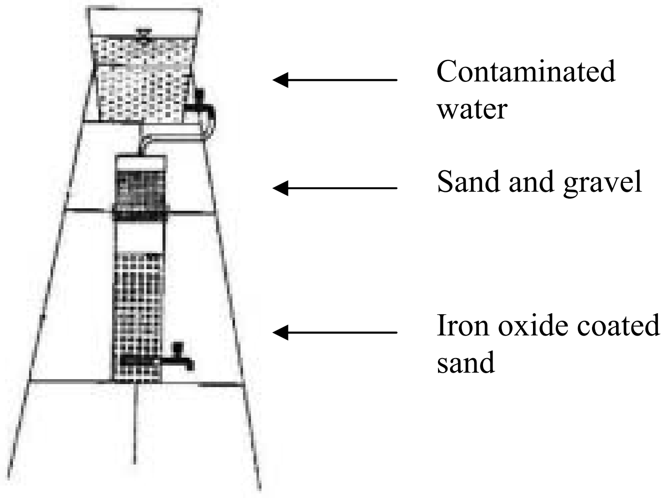


Figure 4.12 Household arsenic removal unit based on iron-coated sand.

Performance results for this unit are described in Section 4.1.

4.3.3 Poole (2002)

Apparatus Materials:

6- inch diameter PVC pipe with fittings on either end (top with a hole, bottom with a spigot)
2 water collection buckets, one with spigot
Plastic stopper
Plastic tubing to fit bucket spigot and stopper

Apparatus Description:

A household unit was designed by the author but not tested in the field. The design was an adaptation of that by Ali. et al. 2001. The unit consists of a 6-inch ID PVC pipe equipped with an inflow hose connecting the bucket to the top of the chamber, and an outflow spigot. The setup would be the same as the field testing system, keeping depths constant. The system would hold approximately 7 L of iron oxide coated sand. Once the system reaches the desired breakthrough concentration of 50µg/L or 10µg/L the media would be regenerated by passing approximately 17.5L of a 0.2M NaOH solution through the system in order to release the arsenic adsorbed to the iron oxide sand grains.

Subsequently, one would pass and equal volume of clean water through the unit or until the outflow concentration equals that of the inflow water, in order to re-equilibrate the media.

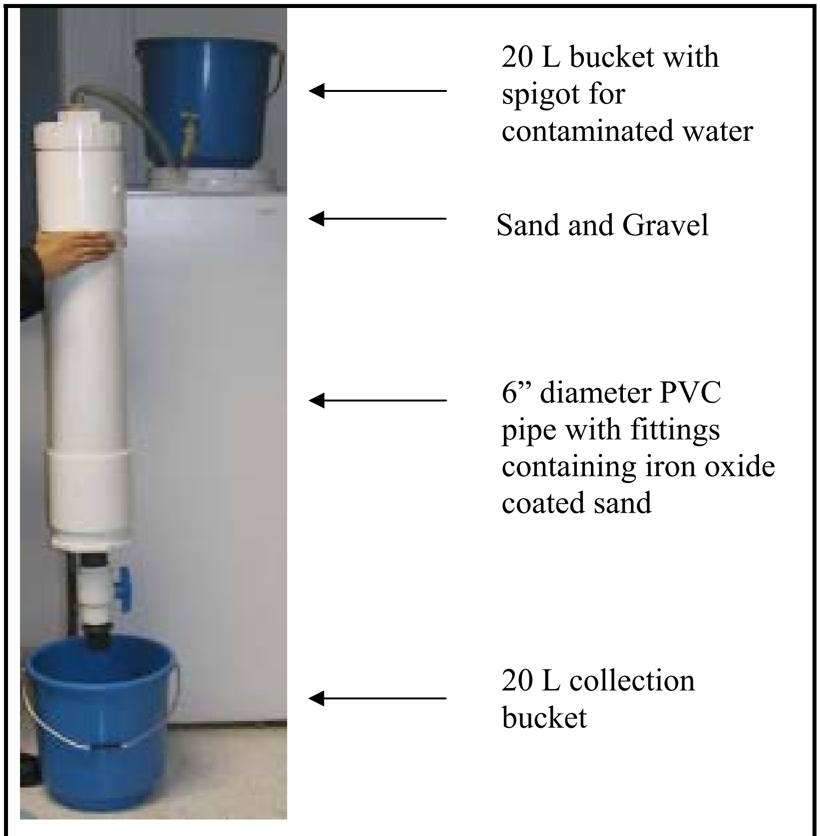


Figure 4.13 Household unit for arsenic removal.

4.4 Progression of Iron Oxide Coated Sand Production

Comments on the Preparation of IOCS1

The author began a literature investigation on the methods available to produce iron oxide coated sand. The first articles uncovered were by Ali et al., Lo et al. and Joshi and Chandhuri. Due to the unavailability of the reference article for the other two articles in the MIT library, Bailey et al. 1992, it had to be requested. In the meantime, the method described in Lo et al. was the most clear so IOCS1 was prepared using the article as a guideline. A mix of medium to fine sand was used, liquid ferric nitrate at a concentration of 0.25M made from 0.826M stock solution, to which NaOH pellets were added due to a lack of concentration information, until pH of 12.3. The colloids were left to settle and the supernatant was removed. The colloids were left to sit in the hood for 2 days, while other preparations were being made. Upon returning to the colloids, the author found them only slightly moist; most of the remaining liquid had evaporated. The colloids were paste-like and coated the sand easily. Only 200g of sand were used in coating as this was the initial attempt. The sand was heated at approximately 200°C. Upon consultation with Borhan Badruzzaman, who produced and implemented this technology in the field in Bangladesh, a higher temperature was needed to dry the sand. Due to the high cost of ferric nitrate, the author also inquired if cheaper ferric chloride could be used. Mr. Badruzzaman indicated that ferric chloride becomes hygroscopic, thus is not recommended. With further literature review the author uncovered other articles which reiterate the same findings. The first field tests with this media were successful in total arsenic removal from contaminated water in Pepperell, MA. This finding was surprising due to Mr. Badruzzaman's advice.

Comments on the Preparation of IOCS2

Next, the Bailey et al. 1992 reference was obtained and it was discovered that the high temperature recommended was 550°C. The author decided to use Ali et al. as the basis for her IOCS experiments due to its successful implementation in Bangladesh. The size of the sand grains became important to maintain a reasonable flow rate while retaining arsenic removal. The author searched extensively for a sand and gravel operation or building supplies outlet that could provide sand grains passing #30 sieve and retained on #40 sieve. An extensive volume of coated sand was required (7 L) for the household unit, which added more difficulty to the process. In the meantime, the author attempted to sort through bags of coarse and medium to fine sand, crushing larger sand grains with a mallet and using a sieving machine. In the end, the author sieved most of the 7 L required herself, and was provided with approximately 2L from Ricci Bros. Co. of Port Norris, New Jersey.

In preparation for bringing iron oxide coated sand media to Nepal, the author began coating the sand sieved according to Ali et al.. Crystalline ferric nitrate was used to prepare a 2 M solution and anhydrous NaOH to prepare a 10 M solution. Because Ali et al. did not specify settling of the colloids and removal of the supernatant, approximately 3L of sand was added to the aqueous solution. Despite the addition of the sand, the mixture remained aqueous. This proved a problem when trying to heat the sand at 550°C in the high temperature oven in The Ralph M. Parsons Lab of MIT, for fear of boiling over thus ruining the oven and causing an electrical disaster. The oven was therefore ramped to 120°C and cooked for 4 hours. The oven was then turned up to 550°C, but before it reached that temperature, brown steam began billowing from the oven thus it was turned back down and held at 120°C for another 3 hours, at which point the oven temperature was raised to 550°C and cooked for 6 hours. This was IOCS2.

Comments on the Preparation of IOCS3

Once in Nepal, the author made iron oxide coated sand in the ENPHO lab. One liter of local medium to fine sand was used with crystalline ferric nitrate. All chemicals were available and obtained locally with ease thanks to the assistance from ENPHO. Not wanting to repeat the hazards of heating an aqueous solution as had occurred with the preparation of IOCS2, the author let the colloids settle and removed the supernatant. Upon combining with the sand, the author found this mixture to be aqueous also, though not to the same degree as with IOCS2. In order to obtain a high heating oven temperature, the sand was taken to a ceramist in Thimi, Nepal. There, the sand was put in a clay pot, warmed at 100°C overnight, then the kiln was fired up 550°C and the iron oxide coated sand was cooked for 12 hours. This was IOCS3. This sand was left in Nepal with ENPHO for testing. Results are pending.

Comments on the Preparation of IOCS4,5,6 and 7

Upon returning to MIT, the author continued testing IOCS1 and IOCS2 in arsenic contaminated field sites in Massachusetts and New Hampshire, and in addition made four different types of iron oxide coated sand. Throughout her literature review, the author came across articles indicating the first round of heating for the coated sand was done at

110°C or slightly higher, and produced media which gave effective removals. In order to begin to test the effect of heating on iron oxide the author made two batches of colloids which were halved and heated at different temperatures. The colloids were made with 2 M aqueous ferric nitrate and titrated with 10 M NaOH. In the first batch, the colloids were left to settle, the supernatant removed and partially air dried in the hood. In order to speed drying, the author placed the colloids in the oven at 105-110°C. The colloids changed color to a light orange indicating a possible change in the form of iron oxide to goethite (refer to Chapter 3). Once the solution evaporated, the colloids were cooled, halved and mixed with sand. One half was heated at 110-150°C for 17 hours, this was IOCS4. The other half was heated at 550°C for 15 hours in a programmable electric oven in the lab of Professor Michael Cima of the MIT Material Science Department. This was IOCS6. The oven's temperature was increased to 550°C over 1.5 hours, then held for 15 hours, then cooled. Due to the small capacity of the oven, heating had to be done in stages. The oven fit four crucibles holding approximately 300 mL each. The sand that could not be heated the first day was sealed tightly in a plastic bottle so as to not dry out. The second batch of colloids was initially prepared the same way, except the remaining liquid from the aqueous mixture was allowed to evaporate in the hood over two days. The colloids were then halved and mixed with sand. Half accompanied IOCS4 at 110-150°C as IOCS5, and the other half was subjected to the same drying as IOCS6. This was IOCS7.

1 liter was made of each IOCS4-7.

Chapter 5 WATER QUALITY TEST METHODS

In addition to arsenic, water quality parameters tested included pH, alkalinity, hardness, iron and manganese. pH and alkalinity gave insights on the possible forms of arsenic present in the water. The hardness, iron and manganese were indications of competing ions for arsenic adsorption on to iron oxide sights.

5.1 Arsenic Test Methods

Two arsenic test methods were used to quantify arsenic in samples collected and analyzed in the field and the lab. Both methods were easy to use in their respective environments.

5.1.1 Industrial Test Systems Inc. Arsenic Check^{TM} Field Test Kit

This arsenic field test kit provides a safe, simple, and reliable method to test for aqueous inorganic arsenic. It requires no electricity or refrigeration. The detection range is between 0 and 800 μg/L. The upper detection limit can be extended to 4,000 μg/L with a simple 1 to 5 dilution. With the exception of a timer, all components are supplied in the kit, including a detailed description of the test method, a color chart, three chemical reagents with material safety data sheets,3 measuring spoons for the reagents, test strips, 2 reaction bottles, 4 bottle caps, a thermometer, and a zip-loc disposal bag for test strips. The chemistry of reaction is based on the conversion of inorganic arsenic compounds in water to arsine gas (AsH_3) by the reaction of zinc dust and tartaric acid. Reagent 1 is composed of L-tartaric acid 98.9% and 1.1% of iron (II) sulfate$\cdot 7H_2O$. The second reagent is composed of 43% potassium peroxymonosulfate, 23% potassium bisulfate, 29% potassium sulfate, 3% potassium peroxydisulfate, and 2% magnesium carbonate. Reagent 3 contains >99% zinc. The test results are determined by colorimetry. The arsine gas reacts with mercuric bromide contained in the test strip forming mixed mercury halogens (such as AsH_2HgBr). It is recommended that the water sample temperature be between 15°C and 40°C, (preferably between 20°C and 30°C) for accurate reading off the color chart. The color chart is standardized at 25°C. This test tolerates up to 2 mg/L hydrogen sulfide and 0.5 mg/L antimony without test result interference. No interference from iron or sulfate was found by the manufacturer. Because hydrogen may cause an explosion, and arsine gas is toxic, it is highly recommended the test be conducted in a well-ventilated area away from fire and other sources of ignition.

Figure 5.1 Industrial Test Systems Arsenic Test Kit.

Procedure as per Instructions:

1. Fill a clean reaction bottle with raw water to the 100 mL mark. Verify the temperature is between 15°C with the thermometer.
2. Add three level pink spoons of reagent 1. Close the bottle with yellow cap and shake vigorously upright for 15 seconds to dissolve the tartaric acid.
3. Add three level red spoons of reagent 2. Cap and shake vigorously upright for 15 seconds. Allow the contents to sit for 2 minutes undisturbed.
4. Add three level white spoons of reagent 3, zinc dust. Cap and shake vigorously upright for 15 seconds.
5. Switch caps to the white cap with the turret up (open).
6. Remove a test strip from the Arsenic test strip storage bottle and recap.

7. Insert test strip into the turret with the pad down and facing the back of the cap until the red line is even with the top of the turret.
8. Close the turret securing the test strip in place. Leave bottle undisturbed for 30 minutes. Both hydrogen gas and arsine gas will bubble from the solution. The arsine gas then reacts with mercuric bromide on the test strip producing a color change from white to yellow or brown.
9. At the end of 30 minutes, take the test strip out of the bottle and compare to the color chart to determine the arsenic concentration.

5.1.2 Graphite Furnace Atomic Adsorption Spectrometry (GFAAS)

GFAAS is one of the USEPA methods for measuring arsenic in drinking water. Atomic adsorption is based on the principle that atoms will absorb light at some characteristic wavelength. These wavelengths are related to the atomic structure of an element and the energy required for the promotion of its electrons from one quantum level to another. Therefore, each element has its own characteristic wavelength. A wavelength of 193.7 nm is characteristic for arsenic. The amount of light absorbed by an element at a certain wavelength can be correlated to the concentration of the element within the linear calibration range. The reliable calibration range is as low as 1-5 μg/L, and as high as 200 μg/L. Dilution of samples with higher arsenic concentrations may be required. A mixture of palladium and magnesium nitrate ($Pd/MgNO_3$) is used as a matrix modifier to permit temperatures to effectively remove other components without loss of arsenic. This method is not suitable for field use because of its large size and the sensitivity of the delicate components to transportation. The GFAAS requires electricity, but no refrigeration. A GFAAS instrument is available for use in the R.M. Parsons Laboratory at MIT.

To begin the GFAAS analysis, water samples from Nepal were first preserved by adding a drop of strong hydrochloric acid (HCl) per 10 mL of sample at the time of collection. The acidification prevents the precipitation of aqueous iron and other chemicals that would adsorb arsenic. In the laboratory, 1 mL of the water sample is pipetted into a specially made plastic vial for GFAAS analysis. The instrument then takes a small amount of the sample and volatilizes the arsenic atoms by intense heating. Once the atoms are excited, a monochrome lamp at 193.7 nm sends an optical beam through the headspace above the sample. The instrument measures the absorption and reports it as a peak focused around the 193.7 nm wavelength. The area under the peak is numerically integrated. By comparing the area under the peak of the sample water with standard arsenic solutions, the concentration of the sample can be determined. Because variability associated with the instrument, a standard calibration curve was developed for every ten samples analyzed in order to maintain accurate readings. Chloride is known to cause matrix interference in the GFAAS, but due to the unavailability of nitric acid in Nepal, hydrochloric acid (HCL) had to be used. This interference was checked by adding the equivalent concentration of HCL as contained in the samples to Milli-Q water and comparing the result on the GFAAS with that of 5% nitric acid. The output concentrations were almost identical, thus it was concluded that the concentration of HCL used did not interfere with instrument readings.

5.2 Iron Test Methods

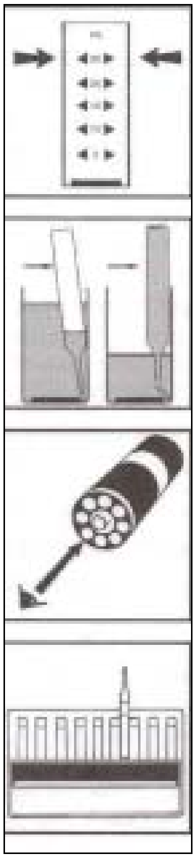
5.2.1 CHEMetrics, Inc. Iron CHEMets® Test Kit

The Iron CHEMets® test method employs phenanthroline chemistry. Ferrous iron reacts with 1,10-phenanthroline to form an orange colored complex in direct proportion to the ferrous ion concentration. Both total and soluble iron can be measured, however, in our case, only the soluble iron was measured. The kit measures iron in two ranges from 0-1 and 1-10 mg/L. The kit includes a sample cup, self-filling ampoules, 1 color comparator for each of the two concentration ranges, instructions and MSDS sheets, and A-6000

Activator Solution for the Total Iron Procedure. Each ampoule contains approximately 0.5 mL of liquid reagent sealed under a vacuum. The liquid is composed of <0.5% 1,10-phenanthroline, 0.5% isopropyl alcohol, 0.5% hydroxylamine hydrochloride, 4% ammonium hydroxide, 14% acetic acid, glacial, and >80% deionized water.

Figure 5.2 Iron CHEMets® Test Kit

Soluble Iron Procedure as per Instructions:



1. Rinse sample cup with sample. Fill with sample to the 25 mL mark.

2. Place the CHEMet ampoule in the sample cup. Snap the tip by pressing the ampoule against the wall of the sample cup. The ampoule will fill leaving a small bubble to facilitate mixing. Invert ampoule several times to mix. Wait one minute for color development.

3. Use the appropriate comparator to determine the concentration of iron in the sample. If the color is between two standards estimate the concentration.

a. Place the CHEMet ampoule in the center of circular comparator flat end down, if color is light. Hold up to white light and rotate the comparator until the color standard below the CHEMet ampoule shows the closest match.

b. Hold the high range comparator in a nearly horizontal position while standing directly beneath a bright source of light. Place the CHEMet ampoule between the color standards moving it from left to right along the comparator until the best color match is found.

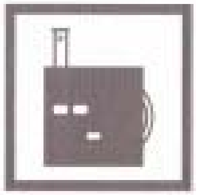
5.2.2 HACH Iron Test Kit

The HACH Iron Test Kit 0-5 mg/L FE Model IR-18 was used to measure total iron (soluble + precipitate) in samples gathered from Pepperell, MA and Salem, NH in March 2002. The test kit can measure accurately from 0-5mg/L of iron; samples thought to contain more should be diluted with deionized water. The kit is comprised of 2 sample viewing tubes with caps, one color comparator disc and holder, instructions and FerroVer® Iron Reagent powder pillows. The powder pillows contain 1, 10-phenanthroline-p-toulenesulfonic acid salt, sodium citrate, sodium hydrosulfite, sodium metabisulfite and sodium thiosulfate. Samples should be shaken prior to testing if they contain rust or precipitated iron.

Figure 5.3 HACH Iron Test Kit

Testing Procedure as per Instructions:

1. Rinse viewing tube with sample water, and then fill a viewing tube to the first (5 mL) line with sample water. This is the blank.

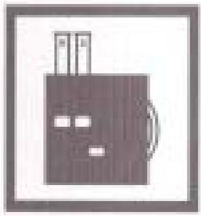


2. Place this tube in the top left opening of the color comparator, and place the color disc in the comparator with the color side facing the openings.

3. Fill another viewing tube to the first (5 mL) line with sample water.

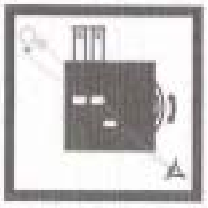
4. Add the contents of one FerroVer® Iron Reagent Powder Pillow to the second tube. To open Powder Pillow, tap the bottom on a hard surface then tear along the dotted line. Open the pillow and form a spout by squeezing the side edges. Pour the contents into the sample.

5. Swirl to mix. An orange color will develop if iron is present. If iron is present as dissolved iron, color will develop almost instantly. If iron is present as rust, wait two to five minutes for complete color development.



6. Place the second tube in the top right opening of the color comparator.

7. Hold comparator up to a light source such as the sky, a window or a lamp. Look through the openings in front.



8. Rotate the color disc until the color matches in the two openings.

9. Read the mg/L iron in the scale window.

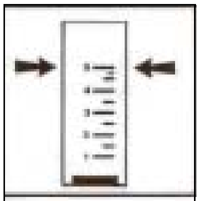
5.3 Manganese Test Method

5.3.1 CHEMetrics, Inc. Manganese CHEMets® Test Kit

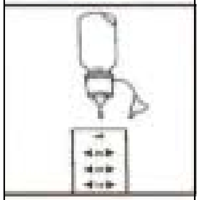
The Manganese CHEMets® test method employs periodate oxidation chemistry. Soluble manganous compounds are oxidized by periodate in a slightly acidic solution to form permanganate ion. The resulting pink color is proportional to the manganese concentration in the sample. The test kit comes with self-filling ampoules, instructions, Material Safety Data Sheets, color comparator, reaction reagent and sample cup. The self-filling ampoules are for determination of manganese in water from 0-2 mg/L. Each CHEMet™ contains approximately 0.5 mL of liquid reagent sealed under vacuum. The liquid is composed of <5% sodium meta periodate and >95% deionized water. The manganese activator solution is an accessory solution used in conjunction with reagent ampoules in the determination of manganese in water. Each bottle contains approximately 10 mL of accessory solution, composed of <5% citric acid, monohydrate, 6% sodium sulfate, 10% sodium phosphate, dibasic, and >79% deionized water. The manganese concentration is determined by colorimetry.

Figure 5.4 Manganese CHEMets® Test Kit

Testing Procedure as per Instructions:



1. Rinse the snap cup with sample water, and then fill to the 5mL mark.



2. Add five drops of the reagent to the sample cup and stir with the tip of an ampoule.

3. Immerse the ampoule and snap the tip against the side. Vacuum pulls the sample in automatically, leaving a small bubble.

4. Invert the ampoule a few times to mix. Wait one minute for full color development. Place ampoule in center of color comparator flat end down and hold up to white light. Rotate the comparator until the color standard below the CHEMet ampoule shows the closest match. If the color is between two standards, estimate. Record the manganese concentration.

5.4 pH, Total Alkalinity and Hardness Test Methods

5.4.1 Industrial Test Systems, Inc. pH and Total Alkalinity Test Kit

The pH and total alkalinity test kit is comprised of test strips with two pads each; upper for total alkalinity, lower for pH. When in contact with the solution, the pads change colors which can be matched to the color coded concentrations on the test strip bottle. pH ranges from 6.0-9.0, and total alkalinity is measured in milligrams per liter- mg/L and ranges from 0 to 360.

Test Procedure as per Instructions:

1. Remove test strip from bottle and recap.
2. Dip test strip into water sample for ten seconds without any motion.
3. Remove strip and match pH color (bottom pad) within 15 seconds, then match Total Alkalinity color before 30 seconds have elapse.

5.4.2 WaterWorks™ Total Hardness (As Calcium Carbonate)

Total hardness is a measure of the total amount of calcium and magnesium that has naturally leached into the water during its journey through the watershed. The test kit contains strips with one pad which changes color when in contact with water, producing a color change which can be compared to the color chart provided. Total Hardness is measured in milligrams per liter-mg/L and ranges form 0-425.

Test Procedure as per Instructions:

1. Remove test strip from packaging.
2. Dip strip into water sample for 3 seconds, remove and immediately match with the closest color. Color is stable for one minute.

Figure 5.5 pH and Total Alkanilty Test Kit (left) and Total Hardness Test Kit (right).

Chapter 6 RESULTS AND DISCUSSION

6.1 Iron Oxide Coated Sand Removal Results

Iron oxide coated sand units were tested in 3 different field locations for removal of arsenic. The results obtained indicate that iron oxide coated sand does remove arsenic though its effectiveness depends on source arsenic concentrations and characteristics of the iron oxide present, such as surface area, a factor of crystalline structure. Percent removal efficiencies varied widely among the prepared sands, and on a smaller scale between the samples tested for each sand, with the exception of IOCS5. The effects of the composition of the colloidal mixture and drying temperature most likely contributed to these differences as well as the concentration of arsenic in the source water. Table 6.1 below summarizes the effluent results obtained from the treated water sample analysis using GFAAS. Samples are listed in the table in the order in which they were collected. Testing of IOCS2 was discontinued due to its poor performance. Testing of IOCS3, prepared and left at the ENPHO lab in Kathmandu is being performed later this year. Raw data results and standardized curves used to analyze the data are contained in Appendix B.

Table 6.1 Results analyzed by the GFAAS of effluent samples.

IOCS1	IOCS2	IOCS4	IOCS5	IOCS6	IOCS7
Pepperell, Ma November, 2001 As~ 95µg/L					
BDL	--	--	--	--	--
BDL	--	--	--	--	--
BDL	--	--	--	--	--
Percent Removal					
99%	--	--	--	--	--
Parasi, Nepal January, 2002 As~ 242µg/L					
17	176	--	--	--	--
37	145	--	--	--	--
Percent Removal					
97-85%	27-40%	--	--	--	--
Pepperell, Ma March, 2002 As~ 101 µg/L					
BDL	72	32	BDL	--	--
BDL	81	58	BDL	--	--
33	73	69	BDL	--	--
Percent Removal					
67-98%	20-29%	32-68%	93-99%	--	--
Salem, NH March, 2002 As~1020 µg/L					
565	--	496	BDL	710	551
565	--	710	13	620	682
623	--	661	126	570	412
533	--	646	186	540	631
386	--	514	162	907	404
386	--	723	194	887	805
Percent Removal					
39-62%	--	29-51%	81-99%	11-47%	21-60%
Overall Average Percent Removal					
67%	29%	42%	90%	31%	43%

BDL= Below Detection Limit= ≤ 10 µg/L

6.2 Discussion of Major Variables Contributing to IOCS Arsenic Removal

Over the course of this investigation, the author was able to determine several variables which contributed to the adsorption of arsenic onto iron oxide coated sand. These variables concern two major properties of the system, the number and availability of adsorption sites, and contact time within the sand bed.

6.2.1 Number and Availability of Adsorption Sites

The variables concerning the number and availability of adsorption sites include: the concentration of iron attached to the sand, the surface area of the coated sand, the position of iron ions in the crystalline structure, and the concentration of the influent raw water. The adsorption threshold of the sands seems to be on the order of hundreds of µg/L, although due to lack of testing of raw water samples in the 100 and 1000 µg/L range, results are inconclusive.

The non-optimal overall removal rates of 67% and 29% for IOCS1 and IOCS2 respectively, can be explained in part by the amount of iron ions attached to the sand. Coating the sand with a colloidal paste or an aqueous solution would increase or decrease the amount of iron oxide available for attachment to the sand respectively. The more liquid present in the mixture, the more colloids are evaporated away during heating. IOCS1 was coated with a colloidal paste with an initial ferric nitrate concentration of 0.25M, compared to 2M used for the other sands tested, thus less iron ions were available for adsorption of arsenic in IOCS1. IOCS2 was made from an aqueous colloidal solution, therefore colloid particles were transported with the liquid from the mixture during evaporation in the oven, and thus iron was lost.

The surface area of the coated sand depended on the grain size, the extent of iron oxide coating on the sand, and the form of iron oxide present. Adsorption in all sands was affected by these variables. IOCS1 had a larger surface area than the other sands, due to the combination of smaller grain size and in some cases, a possibly more amorphous form of iron oxide present. These two effects on surface area however, could not overcome the impact of a smaller concentration of iron ions to elevate its performance beyond that of IOCS5, which achieved removal on the order of 90%.

The type of iron oxide present directly affects the surface area and available number of adsorption sites, the position of iron ions in the crystalline structure, as well as the attachment strength of the iron oxide to the sand particles. The more crystalline structures are formed at high temperatures and have high attachment strengths to the sand, but less binding sites for arsenic due to their decreased surface area.

IOCS6 and IOCS7, 31% and 43% removal respectively, are thought to contain highly crystallized forms of iron oxides with these low adsorption characteristics. The poor performance of these sands was unexpected, contrary to the advice and experience of Mr. Badruzzaman with iron oxide coated sand in Bangladesh (personal communication). The poor performance of IOCS4, only 42% removal, could also be attributed to the presence of a less amorphous form of iron oxide than IOCS5, due to the colloid heating in the oven in order to evaporate the liquid from the mixture.

The concentration of the influent raw water is another variable that affects adsorption. The higher the concentration of influent water, the quicker the sites are utilized, and the rate of adsorption slows as surface sites are occupied. If the number of arsenic ions exceeds the number of readily available iron adsorption sites within the contact time between the water and the sand, breakthrough will occur. This most likely contributed to the high effluent concentrations obtained from the Salem, New Hampshire tests in all sands, except IOCS5 which preformed quite well at 90% arsenic removal, but which still did not get below the Nepali 50 µg/L standard. Arsenic ions exceeding the number of adsorption sites is best demonstrated in IOCS5, as the first two effluent samples of IOCS5 were BDL and 13µg/L. The next sample jumped to over 100µg/L indicating a decrease in adsorption due to an increase in surface site occupation. This quick change likely resulted from the high influent concentration. IOCS1 achieved good removal at lower influent arsenic concentrations of 95-242 µg/L but not at the higher arsenic concentrations of 1020µg/L.

6.2.2 Contact Time within the Sand Bed

The contact time between the arsenic present in the influent water and the iron oxide on the sand is also important for adsorption. The rate of the adsorption reaction must be shorter than the contact time to acquire removal of arsenic from the water.
Figure 6.1 represents the effluent samples obtained from the Salem, NH sample water as a function of bed volume. With an overall removal rate of 90%, IOCS5 consistently achieved the highest total arsenic removal of all 6 IOCSs, and exhibited a predictable trend of increasing effluent arsenic concentration with increasing number of bed volumes

as surface sites became occupied. The fluctuations in effluent total arsenic concentration results for IOCS1-4, 6, and 7 could be attributed to varied contact times between the contaminated water and the iron oxide coated sand, i.e. different short-circuiting paths or delays through the sand. Increasing contact time between sand and arsenic would generally increase removal as long as the surface sites are unoccupied and the pH_{zpc} (zero point of charge) has not been reached. Because of the limited number of tests that could be performed under the time constraints of this thesis research, equilibrium was not reached between the iron oxide and the arsenic adsorption, thus the Langmuir isotherm could not be demonstrated. Additional differences between IOCS5 and IOCS1, other than those mentioned above; the grain size, the sand bed depth, and the flow rate, could contribute to IOCS1's decreased performance at higher source water concentrations. Only 200g of IOCS1 was used, which could cause the sand to reach breakthrough sooner. Despite the measurement of the number of bed volumes as a constant variable, as noted before, adsorption is not linear.

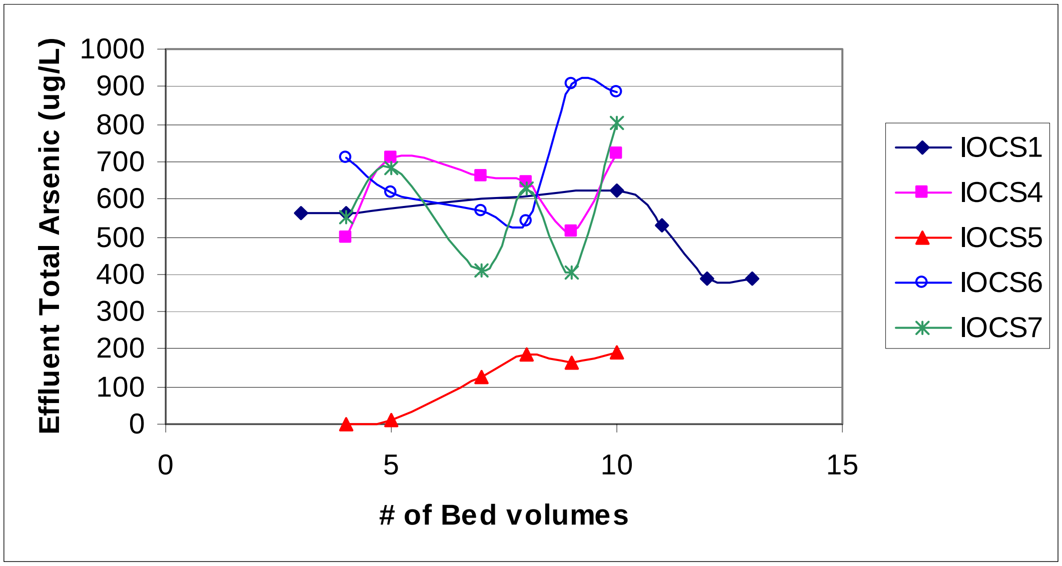


Figure 6.1 Adsorbed arsenic concentration as a function of bed volume for Salem, NH samples.

The flow rates for all test units are presented in Table 6.2, and were on average, 103mL/min with a constant head of 3.7 inches. The flow rates were approximately the same through IOCS1 and IOCS5 with 200g and ~1L of sand respectively, therefore IOCS1 had an overall slower flow rate, as would be expected with smaller grain sizes.

Table 6.2 FTS Flow Rates

IOCS	Flow Rate mL/min	Constant Head inches
1	98	5.5
2	N/A	N/A
4	98	3
5	113	3.5
6	103	3.25
7	103	3.25

Analysis of the iron oxides present, the amount of iron attached to the sand, the attachment strength and a more in depth study of the conditions and variables under which different iron oxides form are necessary next steps in determining the appropriateness of this technology for implementation to remove arsenic. Further evaluation of the sands with a wider range of source water arsenic concentrations should also take place before any conclusive statements on the overall effectiveness of the sands is made.

6.3 Accuracy of Test Methods

6.3.1 Accuracy of Test Kits

The accuracy of the various test methods used to analyze sample water is important. Since the Industrial Test Systems Arsenic Check^{TM} Field Test Kit (ITS) and the other water quality test kits, but not the GFAAS, employed colorimetry as the analytic method, human interpretation of the sample color compared to the reference color is a constant source of error. Though all test kits were easy to use, distinguishing one color from another is up to the user.

6.3.2 Correlation Between the GFAAS and ITS Industrial Test Systems Arsenic Check^{TM} Field Test Kit

The most important correlation in the analysis of the water samples is that between the ITS and the GFAAS. In November, 2001 the test kit results correlated very well with the results from the GFAAS, as seen in Table 6.3. Of 22 samples collected in Pepperell, MA, 11 showed non-detect level (less than 5 μg/L) of arsenic by the ITS. The same 11 samples also showed non-detect level (less than 5 μg/L) by the GFAAS. The other 11 water samples tested positive for arsenic by the field test kit. Ten of these 11 results were verified by the GFAAS. Therefore, taking the GFAAS as the more accurate measurement, it was concluded that the field test kit gives highly reliable results.

Table 6.3 Agreement between the ITS kit and the GFAAS for Total Arsenic for November 2001 Pepperell samples.

Sample #	Test Kit Results	GFAAS Results	Correlation ?
	Total Arsenic (μg/L)	Total Arsenic (μg/L)	
1	0	0	Yes
2	0	0	Yes
3	20	18	Yes
4	0	0	Yes
5	0	0	Yes
6	100	78	Yes
7	100-200	32	No
8	0	0	Yes
9	0	0	Yes
10	0	0	Yes
11	0	0	Yes
12	20	26	Yes
13	5-10	5	Yes
14	5-10	7	Yes
15	10-20	20	Yes
16	5	9	Yes
17	5-10	5	Yes
18	0	0	Yes
19	50-100	78	Yes
20	0	0	Yes
21	0	0	Yes
22	20-50	29	Yes

Upon returning from Nepal for the spring 2002 semester and analyzing the samples collected both in Nepal and the samples from Pepperell, MA and Salem, NH, the accuracy of the GFAAS results became more questionable. Replicate consistency was not found and the standard curves varied greatly over time. Detection in the 0-10µg/L range showed large background and non-linearity. As has already been mentioned, the interference of chloride present in the HCL preserved samples could be ruled out due to the adsorption consistency of Milli-Q water and 6N HCL with Milli-Q water and 5% nitric acid. Standard curves were run every ten samples to monitor the output of the GFAAS. Curves were averaged to compute the arsenic concentrations for the samples run between them. Appendix B gives the spreadsheet of all the GFAAS and ITS test results.

Table **6.4** and Table 6.5 show examples of differences in the results obtained from the GFASS and the ITS in April 2002.

These differences could be contributed to user and machine error, contamination of standards, adsorption of arsenic to the plastic bottles and possible iron scavenging. Although adsorption to particulate iron should not be a problem, since the pH was reduced to 2 or below with the addition of HCL, the presence of a pinkish tint in some samples caused concern that perhaps this did occur. This tint was present in some samples from IOCS4, 5 and 6. The excellent performance of IOCS5 was re-checked by the GFAAS and the ITS to verify the effluent arsenic concentrations.

In addition, the total iron concentration was measured with the HACH Iron Test Kit. Due to the quick color change, indicating presence of mostly soluble iron, it was determined that the pinkish color was not a result of particulate iron. The iron concentrations were not significant to cause such adsorption, thus the results were not considered to be invalid on account of the presence of iron.

Table 6.4 Comparison of GFAAS and ITS Results, (Analyzed in April, 2002)

Sample	Total Arsenic µg/L	
	GFAAS	ITS
Parasi, Nepal January, 2002 As~ 242µg/L		
IOCS1-A	17	5-10
IOCS1-B	37	10-20
IOCS2-A	176	100
IOCS2-B	145	100-200
Pepperell, Ma March, 2002 As~ 101 µg/L		
IOCS1-B	BDL	5
IOCS2-B	81	50
IOCS4-B	58	20-50
IOCS5-B	BDL	0

Table 6.5 ITS Re-check of Salem, NH Samples Due to Pinkish Color and High Concentration, (Analyzed in April, 2002)

Sample	Total Arsenic µg/L		Total Iron mg/L
	GFAAS	ITS	
IOCS4-D	646	500-800	---
IOCS5-A	BDL	0-5	1.2
IOCS5-B	13	5	0.3
IOCS5-C	126	50	0.5
IOCS5-D	186	100	0.2
IOCS5-F	194	~ 100	0.25
IOCS6-C	570	---	0.45
IOCS6-D	540	~ 800	---

6.4 Availability and Cost

As originally discussed in Chapter 1, Section 1.5, one major assessment criteria of this project was to investigate a system that would be affordable to the local Nepali people and which could be locally manufactured with local materials. With a per capital annual

Nepali income of $230 (World Bank, 2001), the system must be less than 10% of a user's earned yearly income, preferably less than $15. The system used in field testing in Nepal was assembled in the United States and made of materials available in the United States (Figure 4.9). The Field Testing System (FTS) was a small-scale version adapted from the BUET system using approximately 1/7 the media of the prototype household system (HHS). The cost of this prototype system was quite high, so it was necessary to determine its adaptability to Nepal. Once in Nepal, the author was able to find all the materials to construct the iron oxide coated sand arsenic removal technology on a household scale. Local buckets were able to be purchased for the collection vessel (10L) and the sand container (20L) for 36NRs and 75NRs respectively (1USD=75NRs). Table 6.6and Table 6.7 show the breakdown in cost for materials, and media for systems built in the US and Nepal.

Table 6.6 Raw Material Costs in the United States for Analytical Grade: Solution/Crystalline Chemical Reagents and Treatment Unit Components

Reagent	Quantity/200mL of sand	Unit Cost	Cost/200mL of sand
0.826M Ferric Nitrate Solution	193.7 mL	$61.36/L	$11.89
Crystalline Ferric Nitrate	52.1g	$21.70/kg	$1.13
6N Hydrochloric Acid	66 mL	$30.31/4L	$0.50
Sodium Hydroxide Pellet-Coating	38.4g	$90.00/2.5kg	$1.38
Sodium Hydroxide Pellet-Regeneration	4g	$90.00/2.5kg	$0.15
Subtotal	**Using 0.826 M Ferric Nitrate Solution**		**$13.92**
	Using Crystalline Ferric Nitrate		**$3.16**
Item	Quantity	Unit Cost	Cost
Polycarbonate tubing + fittings (FTS)	2	$54.43	$108.86
6" PVC chamber + fittings (HHS)	1	$192.93	$192.93
Grand Total-HHS-7L of sand: Subtotal*35+ HHS unit cost	**Using 0.826 M Ferric Nitrate Solution**		**$680.13**
	Using Crystalline Ferric Nitrate		**$303.53**

Exchange rate US$1.00= NRs 75 (January 2002)

The material costs for producing iron oxide coated sand in the United States is very high to be supplied for developing countries like Nepal. At $192.93, the treatment unit accounts for a little more than half the cost alone. One could possibly construct a treatment unit from cheaper materials, and use commercial grade crystalline ferric nitrate, though both were not readily found during preparations and set-up for this project.

Table 6.7 Raw Material Costs in Nepal -Analytical Grade (AG)/Commercial Grade (CG) Chemical Reagents and Treatment Unit Components

Reagent		Quantity/200mL of sand	Unit Cost	Cost/200mL of sand
Crystalline Ferric Nitrate	AG	52.1g	NRs250/500g	NRs26
	CG		NRs125/kg	NRs6.5
Conc. Hydrochloric Acid	AG	66 mL	NRs660/25L	NRs1.7
	CG		NRs15/L	NRs1
Sodium Hydroxide Pellet-Coating	AG	38.4g	NRs204/500g	NRs15.7
	CG		NRs35/kg	NRs1.3
Sodium Hydroxide Pellet-Regeneration	AG	4g	NRs204/500g	NRs1.6
	CG		NRs35/kg	NRs0.1
Subtotal-1	**AG**			**NRs45/ US$0.60**
	CG			**NRs9/ US$0.12**
Item		Quantity	Unit Cost	Cost NRs/USD$
10L bucket		1	NRs36	NRs36
20 L bucket		1	NRs75	NRs75
Subtotal-2				NR111s
Grand Total-HHS-7L of sand: Subtotal*35+ HHS unit cost	**AG**			**NRs1686/ $22.48**
	CG			**NRs426/ $5.68**

Exchange rate US$1.00= NRs 75 (January 2002)

The costs for producing iron oxide coated sand in Nepal differ significantly between analytical and commercial grade chemicals. These costs would be reduced if the chemicals were manufactured in Nepal as opposed to being imported from Indian companies. The household unit components are quite different than those available in the United States. The setup would be adapted to using a bucket to hold the media, as these buckets are readily available in local markets. A column type container may be available, but hard to find.

With a raw material cost of 426NRs ($5.68) using commercial grade materials, the iron oxide coated sand unit meets the affordability criteria for household removal units for Nepal. However, due to the nature of the media preparation, ongoing monitoring, regeneration and disposal of the arsenic contaminated sodium hydroxide solution, an added time and labor cost might well need to be included in the final cost to the user.

Ideally this cost would be negligible, as the organization, agency or business promoting the arsenic removal system would incorporate this O&M cost in the annual salaries of its employees.

6.5 CONCLUSIONS AND RECOMMENDATIONS

6.5.1 Conclusions

In this study the author hypothesized that iron oxide coated sand could be:

1) Effective in removing total arsenic (As (III) and As (V)), minimally, below the Interim Nepali Standard of 50 µg/L, but ideally below the WHO standard of 10 µg/L;
2) Manufactured with locally available materials;
3) Affordable to the Nepali citizens affected by arsenic contamination;
4) Socially acceptable in terms of maintenance, operation and water demand.

The author performed and extensive literature review, found 10 papers using different IOCS methods, and adapted 4 of these methods to produce 7 different IOCSs. The author also adapted a treatment unit designed by Ali et al. 2001 for field testing units and a household removal unit. The performance of the 7 IOCSs showed that iron oxide sand is capable of removing arsenic from groundwater, but there was variability in performance of the sands, as their differences revealed significant impact on adsorption properties which led to only 27% of the effluent sample concentrations to fall below the Nepali Interim Standard of 50µg/L. Previous success of arsenic removal from natural waters with iron oxide coated sand media suggested that this technology could be effective in removing arsenic from raw waters with arsenic concentrations up to at least 300 µg/L (Ali et al. 2001). Removal at concentrations of 1000 ±100 µg/L does not seem viable without further detailed investigation and maximization of the relations between several variables such as form of iron oxide, surface area, binding strength, iron concentration, and contact time in the sand bed.

Considering the evaluation criteria such as cost, availability of materials, and local production, iron oxide coated sand technology successfully meets these requirements. In this study social acceptability has not been determined, as data for only one household was available to the author.

6.5.2 Recommendations

Based on this investigation of iron oxide coated sand for arsenic removal from groundwater, the author's experiences have uncovered many questions as well as ideas for future investigations. Recommendations based on her observations follow:

- The coating process of the sand is quite involved, spanning several days and requiring high temperatures, thus a large oven or kiln would have to be acquired to mass produce this technology.
- Due to the chemicals involved and required monitoring of the unit for regeneration, this technology would have to be implemented with a sustainable program through a lab or NGO or business with the proper knowledge and resources.
- Detailed analysis of the iron oxide sand grains should be performed for each sand made:
    1) Determine the iron oxide crystal structure
    2) Determine the type of iron oxide present
    3) Measurement of surface area
    4) Measurement of attachment strength of iron oxide to the sand
    5) Measurement of the coating extent
    6) Measurement of the average amount of iron ions attached to the sand
    7) Determine the effect of colloid size on coating and adsorption
    8) Measure the overall charge of the coated sand
    9) Determine how the iron coated sand charge changes with the pH of natural waters and as adsorption of arsenic increases.

  The results of these analyses will provide some insight into the properties of iron oxides, such as their adsorption capability, the stability of attachment to the sand, some factors that effect adsorption of arsenic in natural waters, and the effects of the physical coating process such as mixture composition, and how to maximize sand coating extent and concentration of iron present.
- A literature review on the methods to make different forms of iron oxides should be conducted and their previously demonstrated adsorption properties investigated, in light of the present research.

- Possible addition of an arsenic oxidizing step (oxidize As (III) to As (V)) prior to iron oxide coated sand, such as flow through a permanganate layer, or use of manganese green sand or manganese dioxide coated sand (Subramanian 1997, Bajpai 1999).

Detailed testing and evaluation of the iron oxide properties, as well as sufficient resources allocated to production of the media, is crucial before iron oxide coated sand technology could be implemented for point-of-use arsenic removal in Nepal or other developing countries. In addition, social acceptability studies would need to be conducted.

Chapter 7 DIGITIZED MAP OF NEPAL REPRESENTING ARSENIC CONTAMNIATION IN THE TERAI

7.1 Introduction

In addition to her study of iron oxide coated sand technology for arsenic removal from groundwater, the author also made a preliminary attempt to map arsenic contaminated tubewell sites in three districts in the Terai region of Nepal. Accurate maps of the geographic locality of both the arsenic and microbial contamination of tubewell and surface waters are needed for Nepal. Paper maps of Nepal exist that represent different data sets, but many are hand drawn, without distance scales and boundaries and land features are not accurate or consistent from map to map. Also, these maps are not readily upgradeable as changes occur, such as in district, VDC, or village boundaries.

7.1.1 Survey Maps

Survey maps are also available as upgraded hand-drawn maps generated in the traditional manner by the use of surveyor tools. Survey maps provided to the author by the Finnish Aid Organization, FINNIDA in Butwal, Nepal have the following description:

> The contours, roads and river systems of this map have been traced from 1:50000 maps published under the authority of the Surveyor General of India, 1959 and 1:25000 aerial photographs prepared by Topographic Survey Branch, Nepal, 1987. The international and local administrative boundaries have been compiled from various maps available from the district officials and should not be used as an authorized reference. Temples, schools, settlement and numbers of households in each settlement have been collected during the settlement data collection by the Rural Water Supply and Sanitation Project, HMG/ FINNIDA, Lumbini Zone Western Region, Nepal, July 1993.

These survey maps are an improvement over hand-drawn interpretations. They incorporate aerial photographs to verify boundary lines and feature locations. Survey maps, however, are just as limited as hand drawn maps insofar as both are presented on paper. This limits the amount of data that can be represented. While paper maps can give some helpful information, digital maps can be manipulated and represented in various formats using multiple boundary and elevation layers, such as land use, geologic soil layers or watershed boundaries.

World Wars I and II caused a significant advance in the art and science of mapping, as multi-spectral scanners and airborne and satellite radar incorporating remote sensing could rapidly collect data and update map-making information (encyclopedia.com). Developed in the 1960s, computerized map-making through Geographic Information Systems (GIS) allowed information databases to be linked to maps. GIS is a useful tool in analyzing and integrating multiple data sets. Today, this mapping tool is used in business, law enforcement, emergency response planning, population growth analyses and a variety of other applications.

7.1.2 Geographical Information Systems (GIS)

Presently, there are efforts by national and international organizations in Nepal to represent existing data sets using GIS. With the increase in information technology developments, these maps are in great demand to permanently replace their non-referenced paper versions. Digital maps can also be presented as hard copy with the ability to quickly modify a feature and instantly upgrade information. In order to be useful, digital maps have to be geo-referenced; features must physically exist in the world and be identified with coordinates, whether in latitude-longitude, or some other map projection. This allows data to be combined with existing or future data sets that other researchers develop.

7.2 Project Background

As has already been presented in Section 1.4 "Arsenic in Nepal", arsenic has been found in the groundwater of some districts in the Terai region. In 1999, the Department of Water Supply and Sewerage prepared a draft report entitled "Research Study on Possible Contamination of Groundwater with Arsenic in Jhapa, Morang, and Sunsari Districts of Eastern Terai of Nepal". In this report, representation of arsenic concentrations in these districts was done with hand drawn maps and symbols (these maps are located in Appendix C). The Nepal Red Cross and ENPHO have recently gathered tubewell data for arsenic contamination in several central Terai districts including Nawalparasi, Bara and Parsa . Wanting to increase the standard of representation of this new data, ENPHO and the NRC began recording the exact locations of each tubewell monitored using GIS. However to the present civil unrest in the country, Global Positioning System (GPS) coordinate gathering for the tubewells sampled for possible arsenic contamination has been delayed. Integrating the tubewell data into GIS is quite difficult without these data, but a general map of the distribution of arsenic within each affected district can be produced with the aid of a geo-referenced digitized map, this was the intention of the author. These geo-referenced digitized maps are not readily available for Nepal however, nor are non-referenced digitized maps that detail VDC's and villages. If such maps were available, they are expensive. The next option was to use a scanner to produce an image of a paper map, manually digitize the boundaries, and then link the tubewell data to the general area of its location. In order to geo-reference this type of map, one would need to know the coordinates of a few features. This data manipulation can get quite complicated, thus the necessity of obtaining an accurate map as a starting point becomes apparent.

7.3 Production Process

ENPHO provided the author with hand-drawn maps of four arsenic contaminated districts for her to bring back to the United States in order to produce a general representation of arsenic contamination in the form of a digitized map. Several of the maps were without scales and all were without legends. Work from maps without scales or legends proved completely untenable, so the next attempt was to obtain existing digital maps of Nepal. The search for digitized data of Nepal was lengthy but conclusive as to the scarcity of available digitized maps and useful data in Nepal. The author proceeded to manually digitize the hand-drawn maps using ArcView GIS 3.2 software created by Esri. Due to the uncertainty of feature identification on the hand-drawn maps provided, the author attempted to make correlations between these maps and other paper maps and digital data, such as hydrologic features and roads. Unfortunately, very few correlations were found. Furthermore, when examining the VDCs for which tubewell data was gathered and the VDCs represented on the maps, the author found discrepancies in the names as well as missing locations. This problem arises from inconsistent and multiple naming of areas as well as the difficulty of transcribing letters from Nepali to English, as well as from the fact that the author does not write or speak Nepali. Therefore an attempt was made to match the VDC names phonetically.

The author was able to use ArcView GIS 3.2 and CartaLinx by Clark Labs to roughly geo-reference the hand-digitized maps and link the arsenic data provided by ENPHO and the NRC, produce a simple electronic representation of arsenic contamination in the Terai. Below, is a visual representation of the production process and the quality of data used to produce the final digitized, geo-referenced maps.

Step 1: Obtained Hand-drawn Maps from ENPHO.

Step 2: Found a large scanner (not an easy task), and scanned maps into computer.

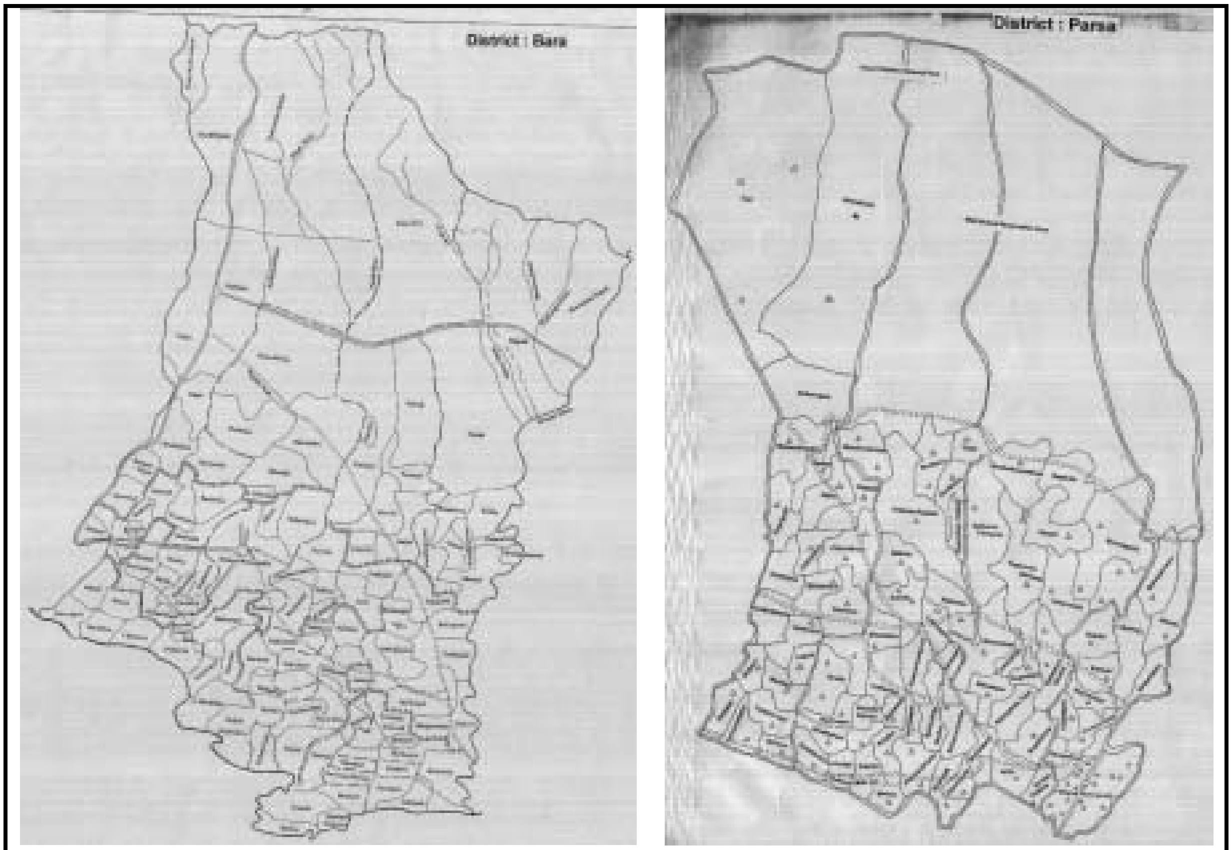


Figure 7.1 Jpeg images of scanned maps for Bara and Parsa districts.

Figure 7.2 demonstrates the inconsistency in VDC boundaries from one map to another. The top map is the hand-drawn map provided by ENPHO. Features are indistinguishable, and many lines end in empty space. VDC boundaries are more clearly defined in the bottom map, which includes a legend. This map was extracted from the Micro-Enterprise Development Programme (www.medp.org.np) website.

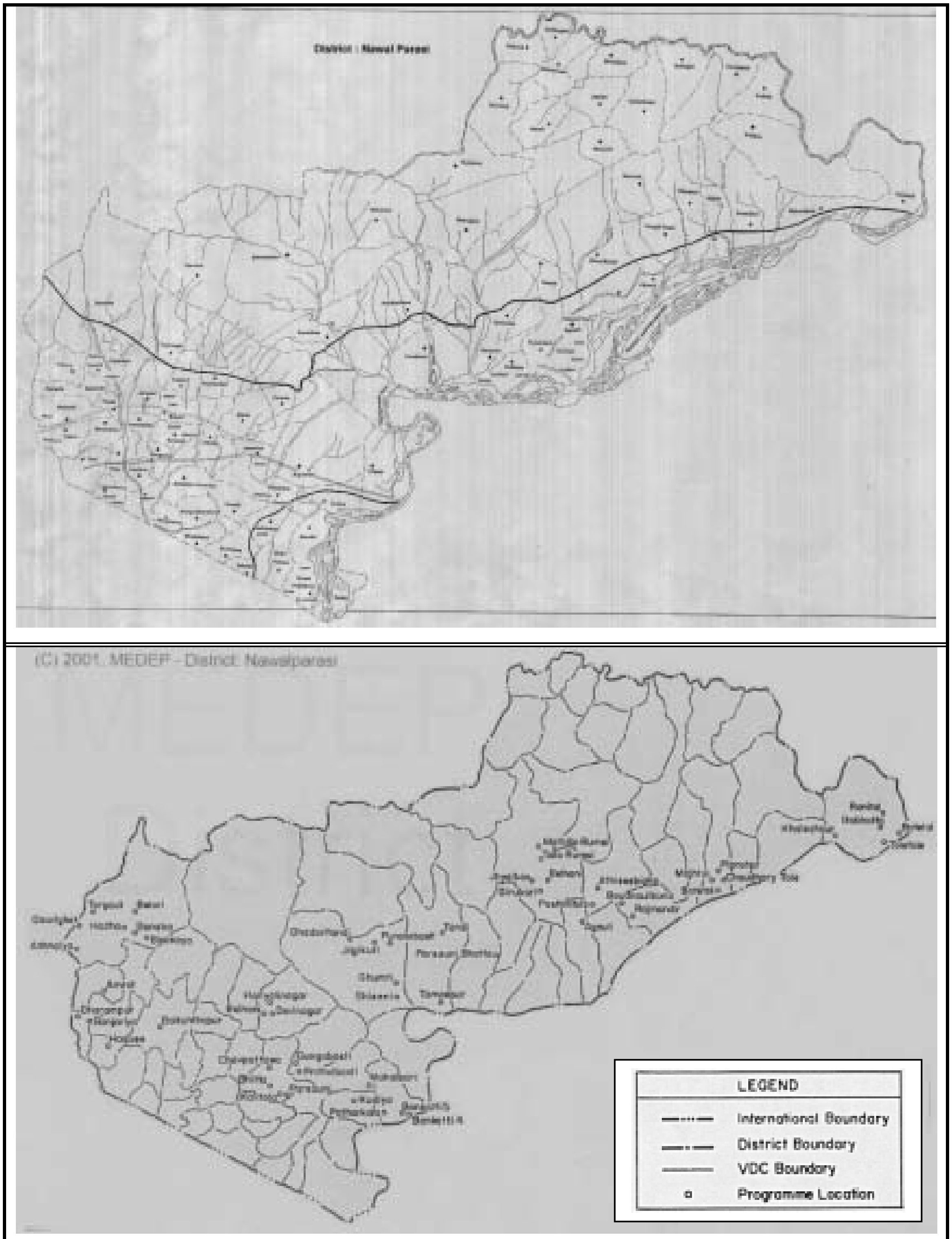


Figure 7.2 Hand-drawn map (top), image map from MEDEP 2001 (bottom).

Step 3: Hand digitized maps in ArcView 3.2 by tracing lines on scanned image.

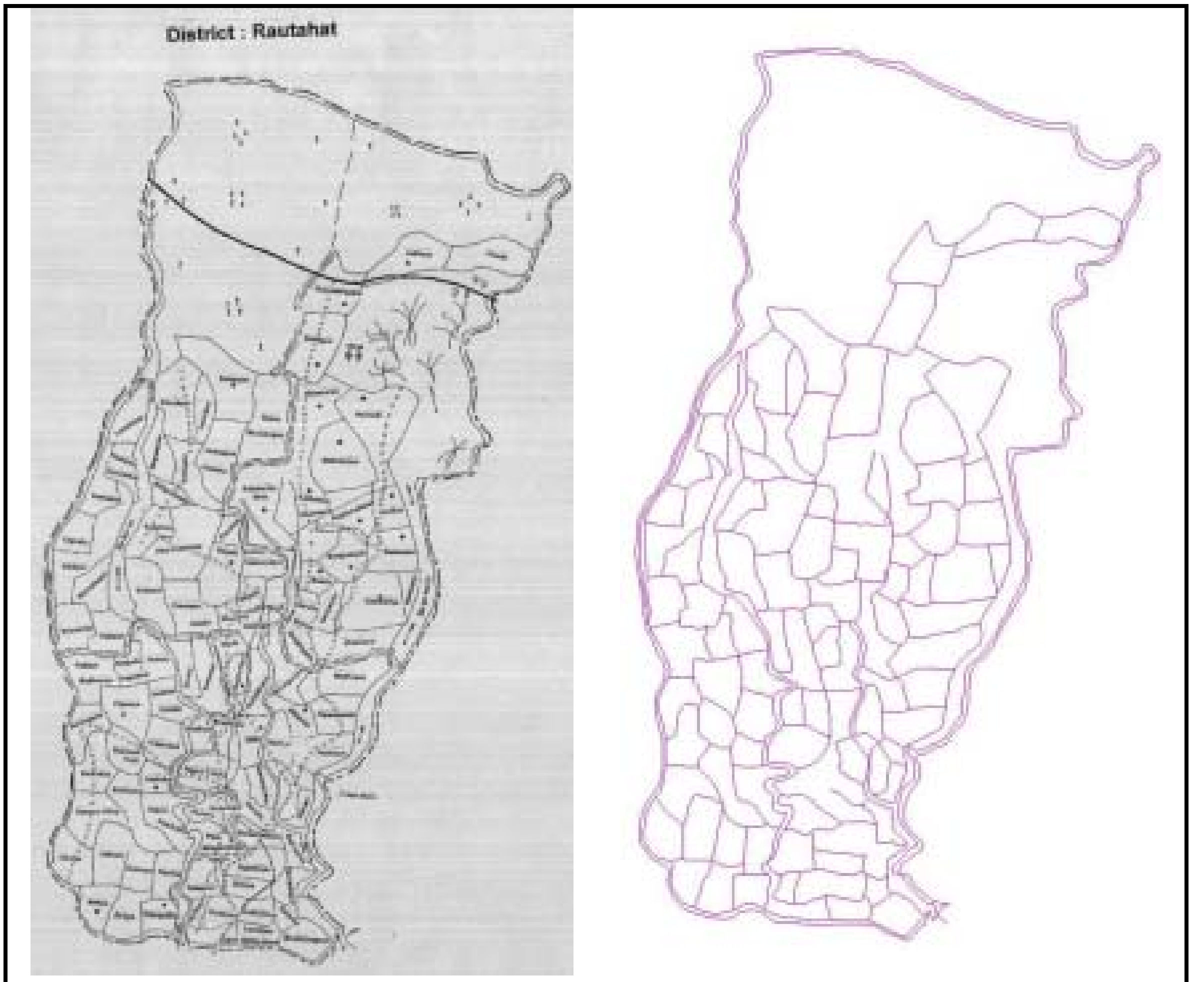


Figure 7.3 Scanned hand-drawn map (left) and hand-digitized map (right) of Rautahat district.

Step 4: Roughly matched VDC names on paper maps with those in ENPHO/NRC arsenic database.

Step 5: Marked location of VDCs on hand digitized map.

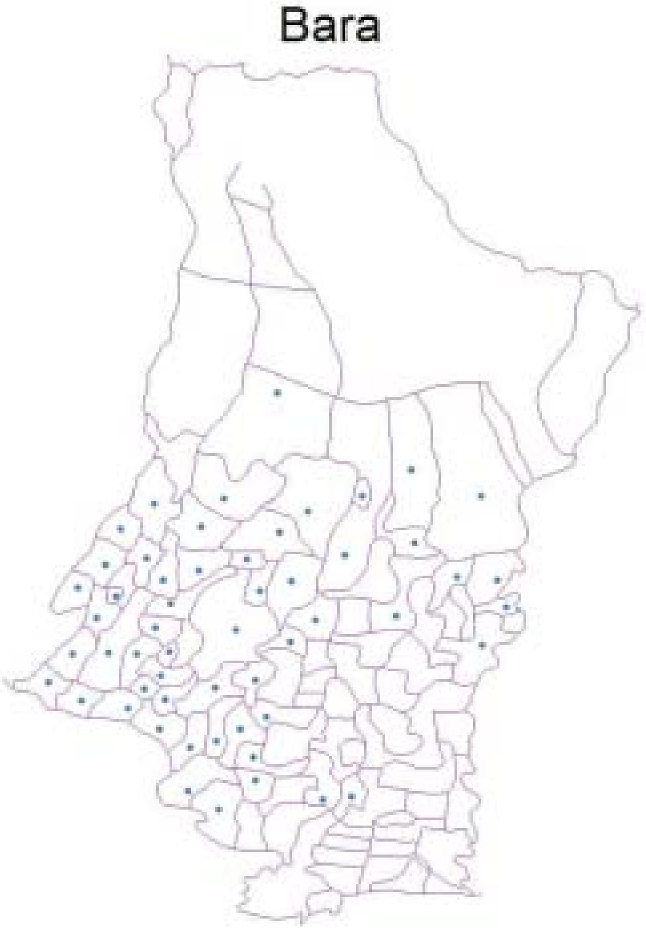


Figure 7.4 Points mark arsenic contaminated VDCs.

Step 5: Searched for and found two digitized maps of Nepal districts, one in unknown coordinates, and one in latitude-longitude. Figure 7.5 shows the two files, notice slightly different distortions between the two. The map represented in latitude-longitude was used for the remainder of the analysis.

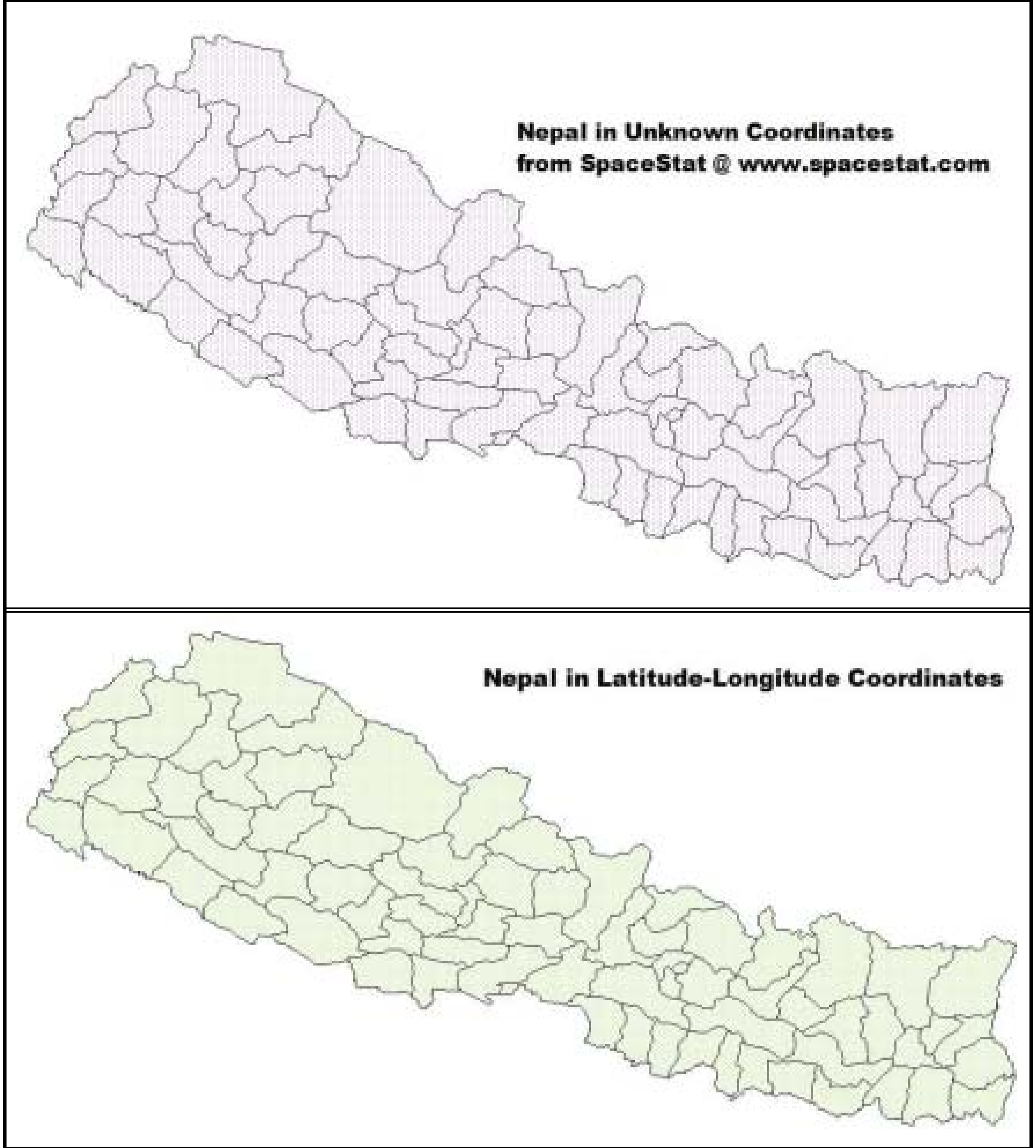


Figure 7.5 Nepal in ArcView formats, represented in unknown coordinates (top) and lat-long (bottom).

Step 7: Used Cartalinx to geo-reference hand digitized files with latitude-longitude digitized files.

Step 8: Convert ENPHO/NRC arsenic database Microsoft Excel files to dbf format, and import into ArcView.
Step 9: Enter latitude-longitude coordinates for VDC markings on newly geo-referenced digitized map, in dbf files, and link to map.

This representation was quite limited due to the available data and resources. The final product will be provided to ENPHO.

7.4 Present Progress in Nepal

One organization, Finnmap, a Finnish consultant/contractor, launched a mapping project in an effort to produce digitized maps of Nepal. Finnmap maps are owned by the Nepal Survey Department, and were produced as a development cooperation between Nepal and Finland. Mr. Jukka Koivisto, the director of Finnmap/Kathmandu, provided the author with information on the maps to be produced, located in Appendix C. The Survey Department currently sells digital material of 1:25000 base maps. All the maps are not available at the present time. There are 3 categories of price depending on the buyer. The lowest fee is NRs 5 per sheet, for governmental agencies and Nepalese NGOs. Donors and foreign companies have to pay a considerably higher price. ENPHO can obtain maps at the low rate, but was seeking funding in order to purchase these maps. Recently, ENPHO hired a consultant to gather GIS data for Nepal. They will conduct a geospatial investigation with ENPHO's data and are now responsible for producing a map. Completion is scheduled for the end of July, 2002.

7.5 Conclusion

Data representation has evolved from hand-drawn maps, to survey maps, to digitized maps. Countries like Nepal still operate on all three levels, which leads to inconsistency in the usefulness and analysis of the represented data. Through the author's experience of data transfer, from very primitive sources of hand-drawn maps to sophisticated representation in digital format through GIS, one can see the difficulty of the process when the correct tools are unavailable. The potential analysis that can be carried out with digital data is immense. When unable to generate a simple, accurate and coherent digitized data representation of arsenic contamination in the Terai, one is handicapped in the depth of analysis that is capable with GIS.

APENDICIES

APPENDIX A

Iron Oxide Coated Sand Procedures Reviewed by Author

A literature review was conducted to determine a method for producing iron oxide coated sand. This review uncovered many different methods and techniques utilized by researchers. The methods adapted by the author to produce the iron oxide coated sand used for testing arsenic removal are detailed in Chapter 4, Section 4.2. The methods outlined in this appendix are the additional procedures uncovered in the literature review.

A.1 Edwards and Benjamin (1989)

Materials:

Ottawa sand (quartz) 20-30 mesh

0.1M $Fe(NO_3)_3$

Concentrated base

pH 1 Acid

De-ionized water

Method:

1. Wash sand in acid of pH 1 for 24 hours.
2. Rinse sand with deionized water and dry at 105°C.

IOCS-Edwards1: Precipitation

3. Add 300 mL of water to 500g of sand
4. Mix in 20 mL of a 0.1M $Fe(NO_3)_3$ solution
5. Titrate solution with concentrated base for ten minutes to a pH of 8.0.
6. Wash and drain sand with water until runoff is clear.
7. Repeat steps 3-6, 14 times for a total of 15 cycles.

IOCS- Edwards2: Heating

3. Place 200 g of sand, 20 g of $Fe(NO_3)_3 \cdot 9H_2O$, and enough water (about 50 mL) to cover sand in a 1L glass flask.
4. Gently agitate for 2 minutes to dissolve the $Fe(NO_3)_3 \cdot 9H_2O$.

5. Place uncovered in drying oven at 110 ± 10°C for 20 hours, until all visible water evaporates.
6. Wash sand with deionized water until runoff is clear.

Laboratory testing: Polymethylmethacrylate column 2.0 cm ID was packed with media to a depth of 15 0.5 cm. Empty bed volume was 43.2mL, porosity of 0.33, yielding a detention time in the bed of 5 minutes.

A.2 Stenkamp and Benjamin (1994)

Materials:

Graded Ottawa sand (Filtersil 0.25, 99.8% silica dioxide)
25% Nitric acid (HNO_3)
2.7 M $Fe(NO_3)_3$
10 M NaOH

Method:

1. Sieve sand to 0.297-0.420 mm in diameter.
2. Soak in Nitric acid at 70°C for 8-10 hours before use.
3. Add 1.2 mL of NaOH to 80 mL of $Fe(NO_3)_3$ solution.
4. Pour mixture over 200mL of bulk, clean sand in a heat-resistant glass baking dish.
5. Loosely cover and place in oven at 110°C for 14-16 hours.
6. Once cooled, separate grains by mild grinding.
7. Sieve and reheat at 110°C for 3 hours to remove residual liquid.
8. Store in polyethylene bottles.
9. Before initial use, backwash with deionized water until the pH of backwash water is near 7

Laboratory testing: Acrylic columns 25.4 mm ID packed to a depth of 10 cm with coated sand.

A.3 Satpathy and Chaudhuri (1995)

Procedure outlined by Edwards and Benjamin (1989)

Materials:

Locally available sand
pH 1 acid
Triple distilled water
$Fe(NO_3)_3 \cdot 9H_2O$

Method:

1. Sieve sand to a geometric mean size of 0.71 mm.
2. Acid wash sand for 24 hours.
3. Rinse in triple distilled water and dry at 105°C.
4. Place 200g of dried sand and 20g of $Fe(NO_3)_3 \cdot 9H_2O$ in a conical flask.
5. Add enough water (approximately 50 mL) to cover the sand.
6. Gently agitate for 2 minutes.
7. Place in a drying oven at 110° ± 10°C for 20 hours.
8. Wash with triple-distilled water until runoff is clear.
9. Dry overnight at 105°C, and store in capped bottles.

Laboratory testing: Column test conducted in a glass column (5 cm ID) with 100cm depth (2.83 kg) of coated sand.

A.4 Benjamin, Sletten, Bailey, Bennett (1996)

Materials:

Ottawa sand 20-30 mesh

2.5M Ferric chloride ($FeCl_3$)

2.1M Ferric nitrate ($Fe(NO_3)_3$

10M Sodium hydroxide (NaOH)

Method:

1. Pour 80 mL of a 2.5 ferric chloride solution over 200 mL of sand.
2. Heat mixture at 110°C and stir every hour for 3 hours (till appears dry).
3. Raise temperature to 550°C for 3 hours.
4. After cooling sand to room temperature in air, rinse sand with water till black coating rinses away.

IOCS- Benjamin1: Recoated with ferric nitrate

5. Place 40 mL of the above sand in a heat-resistant dish in a layer 1-3 cm deep.
6. Mix with a solution of 80 mL of 2.1M ferric nitrate and 0.6 mL of 10M sodium hydroxide.
7. Cover loosely and heat at 110°C until dry (10-14 hours).
8. After cooling, mechanically break crust around sand grains, and sieve the sand.
9. Reheat at 110°C for 3 hours to ensure all grains are dry.

IOCS- Benjamin2: Recoated with ferric chloride

5. Place 40 mL of the above sand in a heat-resistant dish in a layer 1-3 cm deep.
6. Mix with a solution of 80 mL of 2.5M ferric chloride.
7. Cover loosely and heat at 110°C until dry (10-14 hours).
8. After cooling, mechanically break crust around sand grains, and sieve the sand.
9. Begin seven drying cycles, each consisting of 3 hours of drying at 110°C followed by 21 hours at room temperature, to relieve hygroscopic nature.

Laboratory testing: Acrylic columns 1.8 cm ID, packed with IOCS- Benjamin2 to a depth of 88cm (250 mL packed volume) were used. The pH was adjusted to 9.5. Water passed through a pre-treatment column packed with plain sand. Next, it passed through the iron coated sand column, then through a vessel which lowered pH to 3.5. Finally, flowing through a second column with iron coated sand. Detention times in the two pH steps were 70 and 5 min respectively, and empty bed contact time (EBCT) in each column was 5 min. Arsenite recovery with 1M NaOH at pH 2 and 12 solutions was not successful. The characteristics of the water used in testing are displayed in Table A.1 below.

Table A.1 Water Chemistry of Source Used for Tests.

Parameter	Concentration
Ca	200 mg/l
Mg	20 mg/l
Na	10 mg/l
SO_4	800 mg/l
Cl	10 mg/l
Se	75 µg/l
Zn	900 µg/l
Cu	200 µg/l
Ni	300 µg/l
Cd	100 µg/l
As	75 µg/l

A.5 Thirunavukkarasu, Viraraghavan, Subramanian, and Tanjore (2000)

Materials:

Red flint sand (Watergroup Canada Ltd., Regina)

1M $FeCl_3 \cdot H_2O$

2M $Fe(NO_3)_3 \cdot 9H_2O$

Tap water

pH 1 acid

Distilled water

Method:

IOCS- Thirunavukkarasu1: Ferric Chloride

1. Add 40 mL of 1M $FeCl_3 \cdot H_2O$ solution per 500 g of sand in column, let stand for 12 hours.
2. Backwash column for a short duration before starting run.

IOCS- Thirunavukkarasu2: Ferric Nitrate (prepared as per Benjamin et al. 1996)

1. Sieve sand to geometric mean size of 0.6mm to 0.8mm.
2. Acid wash sand for 24 hours.
3. Rinse with distilled water three times and dry at 110°C for 20 hours.
4. Put 200g of sand in a heat resistant dish, and add 80 mL of 2M $Fe(NO_3)_3 \cdot 9H_2O$.
5. Heat at an elevated temperature, cool and wash with distilled water.
6. Take 100g and add 80mL of 2M $Fe(NO_3)_3 \cdot 9H_2O$ and heat for a desired duration.
7. Subject sand to six drying cycles- heat at 110°C for 4 hours let sit at room temperature for 20 hours.
8. Store in capped bottles.

Laboratory testing: IOCS- Thirunavukkarasu1- A column 10 cm ID and 180 cm high was used. Water was pumped into column using a submersible pump (model # 3E-12N Little Giant Pump Co. Oklahoma). Packed volume of media was 4681 mL and EBCT was 5.64 minutes.

IOCS- Thirunavukkarasu2- A column 16mm ID and 400 mm long with suitable stoppers was used. Mesh was placed inside stopper to prevent the escape of adsorbent during filtration. Flow rate, packed volume, and EBCT were 17.5 mL/min, 23mL, and 2.64 minutes respectively.

A.6 Thirunavukkarasu, Viraraghavan, Subramanian (2001)

According to Edwards and Benjamin (1989)

Materials:

Natural water from Kelliher Water Treatment Facility, Kelliher, Saskatchewan

Red flint sand, geometric mean size 0.6 mm to 0.8 mm (Watergroup Canada Ltd., Regina)

Distilled water

$Fe(NO_3)_3 \cdot 9H_2O$ (BDH Inc., Toronto)
pH 1 acid

Method:

1. Acid wash sand in pH 1 for 24 hours.
2. Rinse sand with distilled water three times and dry at 100°C for 20 hours.
3. Place 200 g of dried sand in a wide mouth beaker with 20 g of $Fe(NO_3)_3 \cdot 9H_2O$ and enough distilled water to cover.
4. Gently agitate for 3 minutes.
5. Dry at 110°C for 20 hours.
6. Rinse sand with distilled water till runoff is clear (approx. 4 times), and dry at 110°C for 12 hours.
7. Place in capped bottles.

Laboratory testing: 0.5-1.2 g of coated sand was placed in a 250 mL Erlenmeyer flask containing 100 mL of raw water. The flasks were sealed with parafilm and shaken at 125 rpm for a contact time of 5 hours.

The characteristics of the water used in testing are listed in Table A.2. below. Natural arsenic concentration was 325 µg/L.

Table A.2 Natural water from Kelliher Water Treatment Facility, Kelliher, Saskatchewan.

Water Composition	Concentration
pH	7.4
Iron	2.1 mg/L
Nitrate	2.9 mg/L
Copper	0.04 mg/L
Lead	0.002 mg/L
Aluminum	<0.005 mg/L
Cadmium	<0.001 mg/L
Arsenic	325 µg/L
Manganese	1.2 mg/L
Sulfate	518 mg/L
Zinc	0.01 mg/L
Selenium	<0.001 mg/L
Barium	0.011 mg/L
Chromium	<0.001 mg/L

APPENDIX B

APPENDIX C

C.1 Maps Showing Arsenic Contamination in Morang, Sunsari and Jhapa Districts

C.3 FINNMAP Mapping Summary

Provided by Jukka Koivisto

1. Topographic Maps 1:25 000 (Terai and mid-mountain) and 1:50 000 (high mountain areas) are in printed format (paper, 6 colors). All above maps are for sale in the Survey Department Map Sale Office in New Baneshwore. Coverage of 1:25 000 and 1:50 000 maps is as indicated in attached index.
2. Topographic Maps, same as above, in digital format. Digitization work is going on and all maps will be digitized before end of 2002. All 1:25 000 maps are digitized by now and work continues in High Himalayas. Maps are available from Survey Department, Tel 482 393

FM-International Oy FINNMAP in cooperation with Survey Department, New Baneswore:

1. Orthophoto mosaics with up to 1mx1m ground resolution and +/- 5m horizontal accuracy in true map scale. Orthophoto products are corrected for terrain relief through the use of DTM (digital terrain model) and geo-referenced to local coordinate system by using Ground Control Points (GCP). Above products can be provided for any part of Nepal. Source material used for production is Black & White aerial photography at scale 1:50 000. Photographs have been taken in 1989 (Lumbini district) 1992 Eastern and Central Regions, 1996 Western, Mid Western and Far Western Regions. Digital Terrain Model (DTM) from the whole country. Delivery in digital format and media, as agreed.

2. Orthophoto mosaics with up to 0,3mx0,3m ground resolution and +/- 2m horizontal accuracy in true map scale. Produced as above, but using Black & White aerial photographs at scale 1:15 000 taken late1998- early1999. These products can be provided from all urban areas, total 39 blocks and approx. 13.000 km2 all over Nepal. Delivery in digital format and media, as agreed.
3. Large scale digital maps using professionally approved photogrammetric production methods, large scale map specifications and 1:15000 aerial photography as source material.

APPENDIX D

ARSENIC TREATMENT PLANT

ENPHO, with funding from the Japan Red Cross, has installed five community based arsenic removal plants (ARP) in the Nawalparasi district of Nepal, where high levels of arsenic have been previously detected. Each treatment plant was built in the center of the village around an existing community tubewell. The villagers were trained by ENPHO staff in the operation and maintenance of the treatment plant and one villager was appointed overseer of the plant. The community is responsible for upkeep of the tubewell and the plant components, while ENPHO personnel test the effectiveness of the operation and removal of arsenic on a periodic basis. Each treatment plant cost roughly NRs 16,000 (US$213). Figure D.1 and Figure D.2 show the external schematic of the ARPs. See below for specifications and cost analysis done by ENPHO.

Figure D.1 ENPHO Community Arsenic Removal Plant (ATP).

Figure D.2 Operating the ARP

The three different removal media using the same principle were instituted in the treatment plants. The first component of each was an aeration chamber to oxidize and precipitate naturally occurring ferrous species to ferric species. This employs the same theories of iron oxide and arsenic adsorption previously discussed. The precipitated ferric-arsenic compounds then flow to the filtration chamber where they are filtered out with other impurities through a maze of gravel, charcoal and sand in one type of plant. Clean water flows into the storage chamber ready for use. Effective removal of these systems can only be achieved when naturally occurring iron concentrations are high, so that adsorption of arsenic is maximized. In Baluwa, where the iron concentration is only 2 mg/L, the ARP does not achieve effective removal. Learning from the Baluwa case, researchers added cast iron chips on top of gravel in the aeration chamber to promote iron oxide adsorption, to the next treatment plant built in Ranipakad. In Laxmipur, iron oxide coated gravel was used to a depth of 10 inches, to adsorb arsenic in the filtration chamber. All ARP's had a bag of bleaching powder in the aeration chamber to oxidize arsenic (III) to arsenic (V) at one time, but by the time of observation, the supply had been exhausted a long time ago. The villagers were responsible for replenishing the supply, but did not because they did not like the taste.

Observations taken in the field:

Rupauliya- mud hut village, visible livestock-cows. ARP next to cauliflower garden. Houses nearby. When removed filter top-lots of small ants. ARP made of concrete. 6 months in operation. Tubewell 52ft. deep. Used by 52 houses for drinking and cooking. Question: where to dispose of iron and arsenic waste that is going into the fields at the moment?

Baluwa- small town, tiled roofed huts, some concrete buildings. Visible livestock-cows, ducks. When removed filter top-lots of small ants. Aeration chamber made out of brick. Tubewell depth 95 ft. Five months in operation. Used by 20 households for cooking and drinking. Questions: how often should the chamber and filter media be washed so it does not clog? Where should the ARP drain and how to dispose of waste?

Ranipakad- small village like Rupauliya, but brick houses made with mud, with tiled roofs. Livestock-cows, oxen, ducks. When removed filter top-lots of small ants. Four months in operation.

Badera- Nine or 10 months in operation. Not used very much due to installation of gravity flow source provided by the government. When removed filter top-lots of small ants. Used for drinking. Tubewell 40 ft. Question: How to improve pumping mechanism?

Laxmipur- Small mud hut village-straw and tiled roofs. ARP was wedged in between a house and a cabbage and taro plot. Visible livestock- ducks. ARP made of brick. Leak from tubewell to aeration chamber. When removed filter top-lots of small ants. Four months in operation. Tubewell 50 ft. Used by 50 households. Question: What method could be used for regeneration of the iron oxide coated gravel?

Influent and effluent samples were collected by the author from each ARP in January, 2002. Samples were brought back to the field laboratory and analyzed for total arsenic and soluble iron. Table D.1 shows the results for these samples.

Table D.1 Influent and Effluent Samples for Each ARP.

Village ARP	Total As Source		Total As Treated		Soluble Iron mg/L Source	Soluble Iron mg/L Treated
	GFAAS	Test Kit	GFAAS	Test Kit		
Rupauliya aeration + sand, charcoal, gravel in filter	109	200	16	10	6.5	0.7
Baluwa aeration + sand, charcoal, gravel in filter	73	50-100	41	50	2	0.7
Ranipakad aeration + big cast iron chips on gravel;; sand, charcoal in filter	75	100	66	100	1.5	0.7
Badera aeration + sand, charcoal, gravel in filter	130	200	16	20	6	0.4
Laxmipur aeration + iron coated gravel in filter	37	50-100	35	50	1.5	0

Figure D.3 Iron oxide coated gravel in Laxmipur ARP (top view as seen through water).

As one can see from Table D.1 the majority of the ARPs are not working. More investigation into community level ARPs should be undertaken before any more are constructed. In the meantime alternative methods for removal of arsenic such as the ENPHO Arsenic Removal System (Hwang, 2002) or the A/M media (Ngai, 2002) should be implemented in those villages with non-functioning ARPs.

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