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Drinking water treatment for underground low-redox water

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Drinking water treatment for underground low-redox water

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Prof. ing. Roberto Canziani

Drinking water treatment for underground low-redox water

By

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Thesis

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Dedication

In the Name of the Almighty Allah, the most Gracious, the most Merciful,

For my loving parents,
Md. Abdul Bari & Mrs. Sajeda Bari &
Dr. Afsana Ferdousy Akhee
Thank you for your love and inspiration &
For you're never ending supports and prayers
And for being there always………………

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Abstract

Drinking water treatment for underground low-redox water

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POLITECNICO DI MILANO, 2012
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Abstract: Water is a resource of prime importance. We cannot think of life without water. Life is said to have originated in water millions and millions year ago. Life on the earth would not have been evolved without water. Among various uses of water, drinking water is the most crucial issue. Although, it seems that ground water is more protected than surface water against pollution, it is still subjected to pollutants significantly whether it is natural or manmade. So the treat of water quality is also a serious concern. Increasing threat of pollution due to the man-made activities and natural phenomena, threat towards the quality of available fresh water is also rising at a faster rate. This is a warning to the world to start seriously thinking about water conservation and management and time delay in conservation and management aspects may create a tremendous treat on environment and social hazards originating from water.

Arsenic pollution in ground water is a global problem and not a new problem. Many countries, in the world had experienced danger of arsenic pollution in water and sacrificed many lives. Causes of arsenic pollution were different in different countries. However, the main source of arsenic occurrence in water had been thought to be due to the degradation of natural environment.

Iron and Manganese are not hazardous for the health but also they have tremendous bad effects on environment. Many countries in the world also had experienced for excess iron & manganese contamination in ground water. Sources of iron and manganese are also different in different countries.

This paper describes overall situation in ground water contamination by arsenic, iron& manganese globally mainly focuses on sources of contamination, mechanisms of mobilization of those pollutants in ground water, their effects on human health& environment and enlisting the existing technologies for removing those pollutants, their comparison, applicability, and effectiveness. It also describes arsenic contamination in Bangladesh as a most vulnerable country.

However, unless reasons and sources of arsenic, iron and manganese pollution are found out, and thereby an appropriate scientific management with a view to protect the spreading of those pollutants is thought, it would be difficult to combat the problem and the risk as well. All the available technologies are discussed in order to get idea about selecting the best treatment methods for removal of those pollutants. A combined design approach of the treatment plant also discussed in order to remove the arsenic, iron, manganese with excess ammonia and methane from ground water simultaneously to a desired limit.

As water is an integral part of life and has been well recognized by nectar, conservation and management of water both of its quantity and quality, on sound lines are necessary for the general well-being of all life. A proper water-shed management and conjunctions use of ground water may perhaps be an approach. But obviously it needs extensive research for solving these problems by improving the existing technologies and by innovation of new technology.

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CHAPTER 1: INTRODUCTION

Part 1: Arsenic

1.1 History of Arsenic

The word arsenic was borrowed from the Syriac word zarniqa and the Persian word Zarnikh, meaning "yellow orpiment", into Greek as arsenikon. It is also related to the similar Greek word arsenikos, meaning "masculine" or "potent". The word was adopted in Latin arsenicum and Old French arsenic, from which the English word arsenic is derived. Arsenic sulfides (orpiment, realgar) and oxides have been known and used since ancient times. Zosimos (circa 300 AD) describes roasting sandarach (realgar) to obtain cloud of arsenic (arsenious oxide), which he then reduces to metallic arsenic. As the symptoms of arsenic poisoning were somewhat ill-defined, it was frequently used for murder until the advent of the Marsh test, a sensitive chemical test for its presence. (Another less sensitive but more general test is the Reinsch test.) Owing to its use by the ruling class to murder one another and its potency and discreetness, arsenic has been called the Poison of Kings and the King of Poisons.

During the Bronze Age, arsenic was often included in bronze, which made the alloy harder (so-called "arsenical bronze". Albertus Magnus (Albert the Great, 1193–1280) is believed to have been the first to isolate the element in 1250 by heating soap together with arsenic trisulfide. In 1649, Johann Schröder published two ways of preparing arsenic.

Cadet's fuming liquid (impure cacodyl), often claimed as the first synthetic organometallic compound, was synthesized in 1760 by Louis Claude Cadet de Gassicourt by the reaction of potassium acetate with arsenic trioxide.

In the Victorian era, "arsenic" ("white arsenic" trioxide) was mixed with vinegar and chalk and eaten by women to improve the complexion of their faces, making their skin paler to show they did not work in the fields. Arsenic was also rubbed into the faces and arms of women to "improve their complexion". The accidental use of arsenic in the adulteration of foodstuffs led to the Bradford sweet poisoning in 1858, which resulted in approximately 20 deaths (1).

1.2 Sources of arsenic

Arsenic is found in the earth’s crust. Arsenic can also be found in the atmosphere as arsenic trioxide dusts, a by-product of industrial smelting operations. Arsenic compounds have also found their way into rivers, lakes and wells, sea waters, rain water and snow. Arsenic is also generated from different human activities (2).

1.2.1 Natural Sources

Arsenic is widely distributed in the environment and as a sequence of increased concern about environmental pollution; there is a growing demand for knowledge about arsenic contents in soils, water, air, foods, and beverages (3).

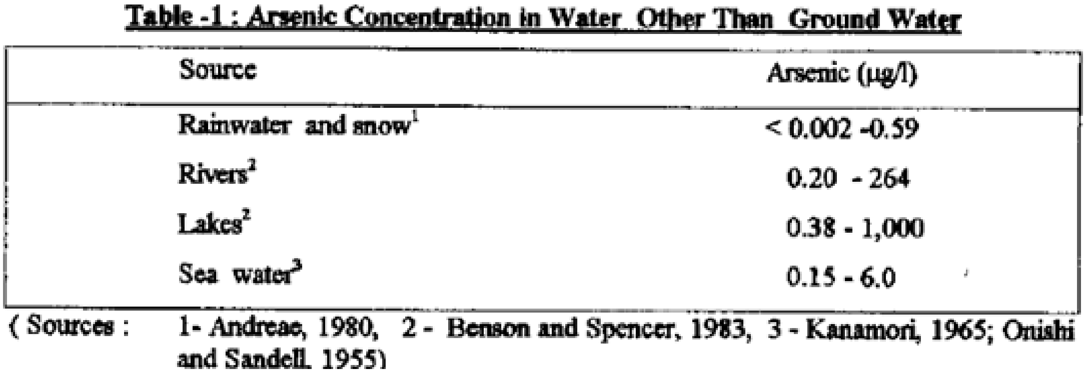


Table -1 : Arsenic Concentration in Water Other Than Ground Water

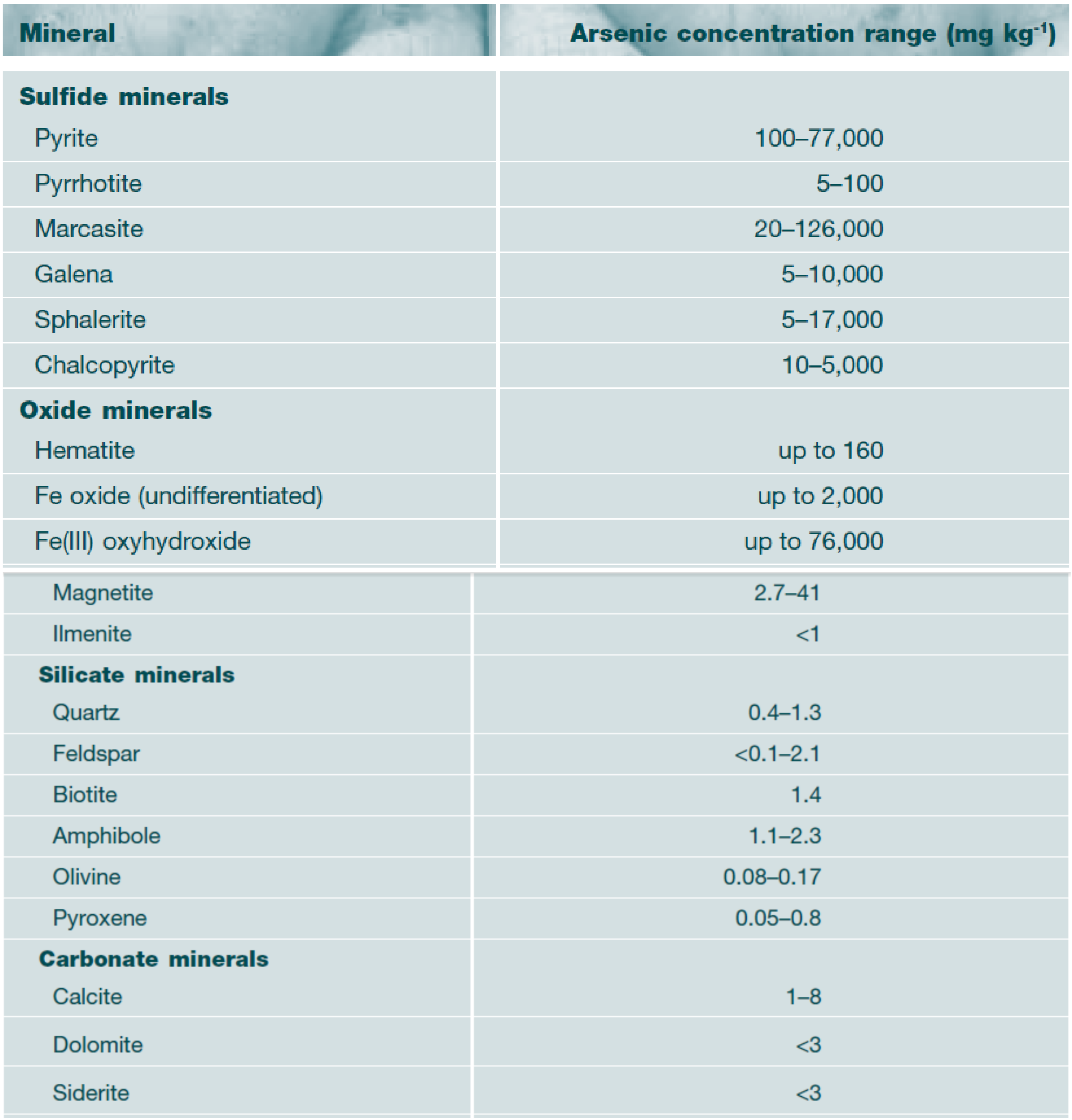
Source	Arsenic (μg/l)
Rainwater and snow[1]	< 0.002 -0.59
Rivers[2]	0.20 - 264
Lakes[2]	0.38 - 1,000
Sea water[3]	0.15 - 6.0

(Sources : 1- Andreae, 1980, 2 - Benson and Spencer, 1983, 3 - Kanamori, 1965; Onishi and Sandell. 1955)

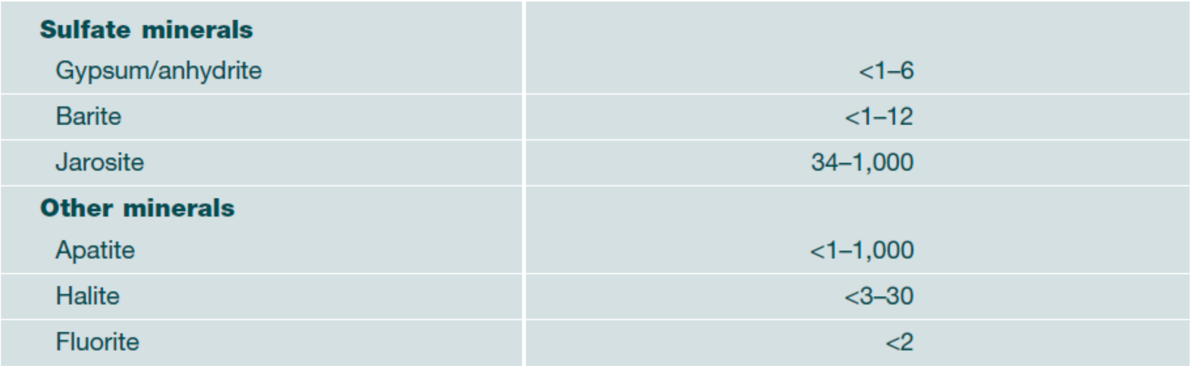
Arsenic occurs naturally in all minerals and rocks, although its distribution within them varies widely. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulfides, oxides, arsenates, and arsenites. Most are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment. The greatest concentrations of them occur in mineral veins. The most abundant arsenic ore mineral is arsenopyrite (FeAsS). This is often present in ore deposits, but is much less abundant than arsenian pyrite (Fe(S, As) 2), which is probably the most important source of arsenic in ore zones. Other arsenic sulfides found in mineralized areas are realgar (AsS) and orpiment (As2S3) (4).

Though not a major component, arsenic is also present in varying concentrations in common rock-forming minerals. As the chemistry of arsenic follows closely that of sulfur, the other, more abundant, sulfide minerals also tend to have high concentrations of arsenic. The most abundant of these is pyrite (FeS2). Concentrations of arsenic in pyrite, chalcopyrite, galena, and marcasite can be very variable but in some cases can exceed 10 weight percentages (**table 1.2**). Besides being an important component of ore bodies, pyrite is also formed in low-temperature sedimentary environments under reducing conditions. It is present in the sediments of many rivers, lakes, and oceans, as well as in a number of aquifers. Pyrite is not stable in aerobic systems and oxidizes to iron oxides with the release of sulfate, acidity, arsenic, and other trace elements. The presence of pyrite as a minor constituent in sulfide-rich coals is ultimately responsible for the production of acid rain and acid mine drainage, and for the presence of arsenic problems around coal mines and areas of intensive coal burning (4).

Table 1.2: Typical Arsenic Concentrations in Rock-Forming Minerals



Mineral	Arsenic concentration range (mg kg^{-1})
Sulfide minerals	
Pyrite	100–77,000
Pyrrhotite	5–100
Marcasite	20–126,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5,000
Oxide minerals	
Hematite	up to 160
Fe oxide (undifferentiated)	up to 2,000
Fe(III) oxyhydroxide	up to 76,000
Magnetite	2.7–41
Ilmenite	<1
Silicate minerals	
Quartz	0.4–1.3
Feldspar	<0.1–2.1
Biotite	1.4
Amphibole	1.1–2.3
Olivine	0.08–0.17
Pyroxene	0.05–0.8
Carbonate minerals	
Calcite	1–8
Dolomite	<3
Siderite	<3



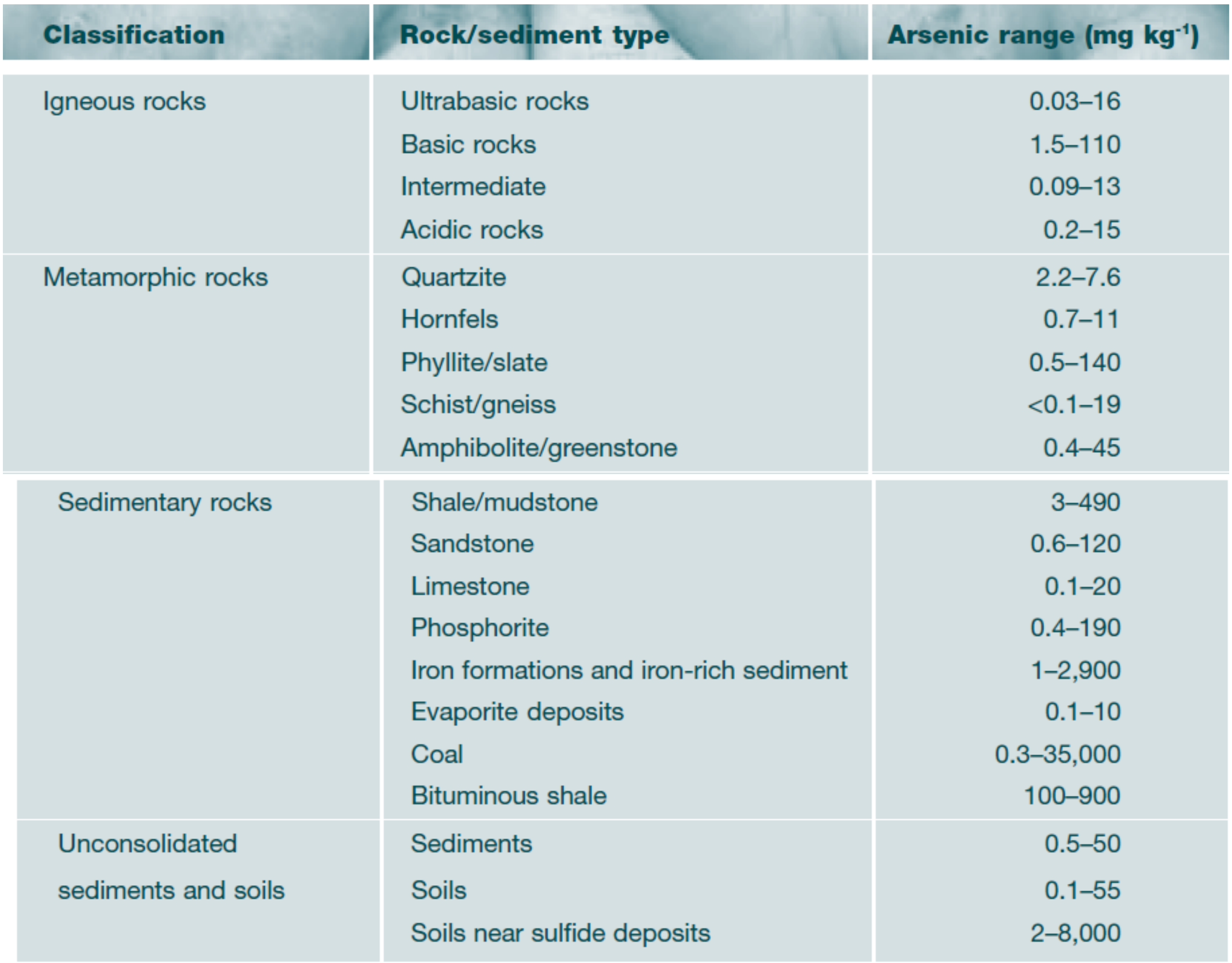
Sulfate minerals	
Gypsum/anhydrite	<1–6
Barite	<1–12
Jarosite	34–1,000
Other minerals	
Apatite	<1–1,000
Halite	<3–30
Fluorite	<2

(Source: Smedley and Kinniburgh 2002 and references therein) (4).

High concentrations of arsenic are also found in many oxide minerals and hydrous metal oxides, either as part of the mineral structure or adsorbed to surfaces. Concentrations in iron oxides can also reach weight percentage values (**table 1.2**), particularly where they form as the oxidation products of primary iron sulfides. Adsorption of arsenate to hydrous iron oxides is known to be particularly strong. Adsorption to hydrous aluminum and manganese oxides may also be important if these oxides are present in quantity (for example Peterson and Carpenter 1983; Brannon and Patrick 1987). Arsenic may also be adsorbed to the edges of clays and on the surface of calcite. However, the loadings involved are much smaller on a weight basis than for the iron oxides. Adsorption reactions are responsible for the low concentrations of arsenic found in most natural waters (4).

Arsenic is also present in many other rock-forming minerals, albeit at comparatively low concentrations. Most common silicate minerals contain around 1 mg kg-1 or less. Carbonate minerals usually contain less than 10 mg kg-1 arsenic (**table 1.2**). Rocks, sediments, and soils contain variable concentrations of arsenic but, not surprisingly, the highest concentrations tend to be found in materials with abundant sulfide and oxide minerals. Fine-grained sediments such as shale’s, mudstones, and their unconsolidated equivalents tend to contain the highest concentrations of arsenic. A summary of typical concentration ranges in common rocks, sediments, and soils is given in table 1.3 (4).

Table 1.3: Typical Arsenic Concentration Ranges in Rocks, Sediments, and Soils



Classification	Rock/sediment type	Arsenic range (mg kg^{-1})
Igneous rocks	Ultrabasic rocks	0.03–16
	Basic rocks	1.5–110
	Intermediate	0.09–13
	Acidic rocks	0.2–15
Metamorphic rocks	Quartzite	2.2–7.6
	Hornfels	0.7–11
	Phyllite/slate	0.5–140
	Schist/gneiss	<0.1–19
	Amphibolite/greenstone	0.4–45
Sedimentary rocks	Shale/mudstone	3–490
	Sandstone	0.6–120
	Limestone	0.1–20
	Phosphorite	0.4–190
	Iron formations and iron-rich sediment	1–2,900
	Evaporite deposits	0.1–10
	Coal	0.3–35,000
	Bituminous shale	100–900
Unconsolidated sediments and soils	Sediments	0.5–50
	Soils	0.1–55
	Soils near sulfide deposits	2–8,000

(Source: Smedley and Kinniburgh 2002 and references therein) (4).

1.2.2 Production of by human activities

Arsenic is also introduced to the environment through a number of human activities. Apart from mining activity and the combustion of fossil fuels, which involve redistribution of naturally occurring arsenic, concentrations in the environment can increase through the manufacture and use of arsenical compounds such as pesticides, herbicides, crop desiccants, and additives in livestock feed, particularly for poultry. The use of arsenical pesticides and herbicides has decreased significantly in the last few decades, but their use for wood preservation and feed additives is still common. The use of chromated copper arsonate (CCA) as a wood preservative may be banned in Europe in the coming years. The environmental impact of using arsenical compounds can be major and long lasting, although the effects of most are relatively localized. Most environmental arsenic problems recognized today are the result of mobilization under natural conditions (5).

Minerals with the formula MAsS and MAs2 (M = Fe, Ni, Co) are the dominant commercial sources of arsenic, together with realgar (an arsenic sulfide mineral) and native arsenic. An illustrative mineral is arsenopyrite (FeAsS), which is structurally related to iron pyrite. Many minor As-containing minerals are known. Arsenic also occurs in various organic forms in the environment. Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized to a less toxic form of arsenic through a process of methylation (5).

Other naturally occurring pathways of exposure include volcanic ash, weathering of arsenic-containing minerals and ores, and dissolved in groundwater. It is also found in food, water, soil, and air. The most common pathway of exposure for humans is ingestion, and the predominant source of arsenic in our diet is through seafood. An additional route of exposure is through inhalation. In 2005, China was the top producer of white arsenic with almost 50% world share, followed by Chile, Peru, and Morocco, according to the British Geological Survey and the United States Geological Survey. Most operations in the US and Europe have closed for environmental reasons. The arsenic is recovered mainly as a side product from the purification of copper. Arsenic is part of the smelter dust from copper, gold, and lead smelters (5).

On roasting in air of arsenopyrite, arsenic sublimes as arsenic (III) oxide leaving iron oxides, while roasting without air results in the production of metallic arsenic. Further purification from sulfur and other chalcogens is achieved by sublimation in vacuum or in a hydrogen atmosphere or by distillation from molten lead-arsenic mixture (5).

1.3 Effects of arsenic contamination

The use of Arsenic as a deadly poison has been known since long years back. Now-a-days naturally occurring arsenic and as well as human generated arsenic in drink water for drinking, cooking and irrigation is a catastrophe of global proportions, with enormous public health implications and has tremendous adverse effects on environment as a whole (6).

1.3.1 Effects on health

As a semi-metallic naturally occurring chemical, arsenic is all around us in the environment and we are all exposed to small doses on a regular basis. It is difficult to detect arsenic because at typical contamination levels it is odorless and flavorless, meaning people have little idea when it is around (7).

Arsenic has long been recognized as a toxin and carcinogen. This ubiquitous element can kill humans quickly if consumed in large amounts. Poisoning may result from a single large dose (acute poisoning) or from repeated small doses (chronic poisoning). Symptoms of acute poisoning from swallowing arsenic include nausea, vomiting, burning of the throat, and severe abdominal pains. Circulatory collapse may occur and be followed by death within a few hours (8).

Chronic exposure to arsenic can occur through various sources, both natural (e.g., weathering reactions and volcanic emissions) and man-made (e.g., mining related activities). Of the various sources of arsenic in the environment, drinking water probably poses the greatest threat to human life (9). The clinical manifestation due to chronic arsenic toxicity usually develops only after a prolonged latency period of several years. The most common effects of arsenic include gradual loss of strength, diarrhea or constipation, pigmentation and scaling of the skin, nervous system manifestations marked by paralysis and confusion, degeneration of faulty tissue, anemia, and the development of characteristic streaks across fingernails. A number of internal cancers (lung, bladder, liver, prostate, and kidney cancer) are also believed to be linked with chronic arsenic toxicity (10).

It is assumed that it may take two to twenty years for a person exposed to arsenic to develop the symptoms of arsenicosis, the name by which the disease is known (10). The period differs from patient to patient depending on the amount of arsenic ingested, nutritional status of the person, immunity level of the individual, and the total time period of arsenic ingestion (11). While the early symptoms of arsenicosis can be treated, many of the more advanced and most serious clinical symptoms are incurable (10).

In most cases, the victims initially do not have any complaint or symptoms until they are detected through a screening survey. The symptoms of arsenicosis are very difficult to differentiate from other clinical conditions. The present practice in diagnosing arsenicosis cases is by examination for external manifestation on the skin, called melanosis keratosis, in combination with a history of consuming arsenic-contaminated water (11).

Picture 1.1: Skin Lesions on Palm due to Arsenic Intake in Drinking Water (12);
Picture 1.2: Skin Lesions in Soles due to Arsenic Intake in Drinking Water (13)

Picture 1.3: Skin Lesions on Palm due to Arsenic Intake (14); **Picture 1.4: Skin Lesions on Palm due to Arsenic Intake** (15)

Picture 1.5: Skin Lesions on Palm due to Arsenic Intake (15)

Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer and lymphatic cancer. A very high exposure to inorganic arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions and brain damage with both men and women. Finally, inorganic arsenic can damage DNA. A lethal dose of arsenic oxide is generally regarded as 100mg. Organic arsenic can cause neither cancer, nor DNA damage. But exposure to high doses may cause certain effects to human health, such as nerve injury and stomachaches (2).

1.3.2 Effects on environment

The arsenic cycle has broadened as a consequence of human interference and due to this, large amounts of arsenic end up in the environment and in living organisms. Arsenic is mainly emitted by the copper producing industries, but also during lead and zinc production and in agriculture. It cannot be destroyed once it has entered the environment, so that the amounts that we add can spread and cause health effects to humans and animals on many locations on earth. Plants absorb arsenic fairly easily, so that high-ranking concentrations may be present in food. The concentrations of the dangerous inorganic arsenics that are currently present in surface waters enhance the chances of alteration of genetic materials of fish. This is mainly caused by accumulation of arsenic in the bodies of plant-eating freshwater organisms. Birds eat the fish that already contain eminent amounts of arsenic and will die as a result of arsenic poisoning as the fish is decomposed in their bodies (2).

Water and land-living plants and animals show a wide range of sensitivities to different chemical forms of arsenic. Their sensitivity is modified both by biological factors and by their surrounding physical and chemical environment. In general, inorganic forms of arsenic are more toxic to the environment than organic forms and, among inorganic forms, arsenite is more toxic than arsenate. This is probably because the way in which the various forms are taken up into the body differs and once taken up, they act in different ways in the body. The reason why arsenite is toxic is thought to be because it binds to particular chemical groups - Sulfhydryl groups - found on proteins. Arsenate, on the other hand, affects the key energy producing process that take place in all cells (16).

Arsenic compounds cause short-term and long-term effects in individual plants and animals and in populations and communities of organisms. These effects are evident, for example, in aquatic species at concentrations ranging from a few micrograms to milligrams per liter. The nature of the effects depends on the species and time of exposure. The effects include death, inhibition of growth, photosynthesis and reproduction, and behavioral effects. Environments contaminated with arsenic contain only a few species and fewer numbers within species. If levels of arsenate are high enough, only resistant organisms, such as certain microbes, may be present (16).

Aquatic and terrestrial biota shows a wide range of sensitivities to different arsenic species. Their sensitivity is modified by biological and biotic factors. In general, inorganic arsenicals are more toxic than organ arsenicals and arsenite is more toxic than arsenate. The mode of toxicity and mechanism of uptake of arsenate by organisms differ considerably. This may explain why there are interspecies differences in organism response to arsenate and arsenite. The primary mechanism of arsenite toxicity is considered to result from its binding to protein Sulfhydryl groups. Arsenate is known to affect oxidative phosphorylation by competition with phosphate. In environments where phosphate concentrations are high, arsenate toxicity to biota is generally reduced. As arsenate is a phosphate analogue, organisms living in elevated arsenate environments must acquire the nutrient phosphorous yet avoid arsenic toxicity (16).

Arsenic compounds causes acute and chronic effects in individuals, populations and communities at concentrations ranging from a few micrograms to milligrams per liter, depending on species, time of exposure and end-points measured. These effects include lethality, inhibition of growth, photosynthesis and reproduction, and behavioral effects. Arsenic-contaminated environments are characterized by limited species abundance and diversity. If levels of arsenate are high enough, only species which exhibit resistance may be present (16).

1.3.3 Effects on food chain

By now, the dangers of drinking arsenic-contaminated water have been well recognized. Consequently, research and studies are focusing on ensuring safe drinking water, either through mitigation techniques or through finding alternative sources of arsenic-safe drinking water. However, these studies do not discuss all potential arsenic exposure pathways that are important to animal and human systems. Even if an arsenic-safe drinking water is ensured, contaminated groundwater will continue to be used for irrigation purposes. Its use creates a risk of soil accumulation by the toxic element and eventual human exposure to it through the food chain via plant uptake and animal consumption. Between thirty and forty percent of the net cultivable area of the country is under irrigation and more than sixty percent of irrigation needs are met from groundwater, either through deep tube wells or through shallow tube wells (17).

The observation that arsenic poisoning amongst the population is not consistent with the level of arsenic in water has raised questions on potential pathways of arsenic ingestion. This necessitates an in-depth study on the bio-magnification of arsenic toxicity through the food chain (17).

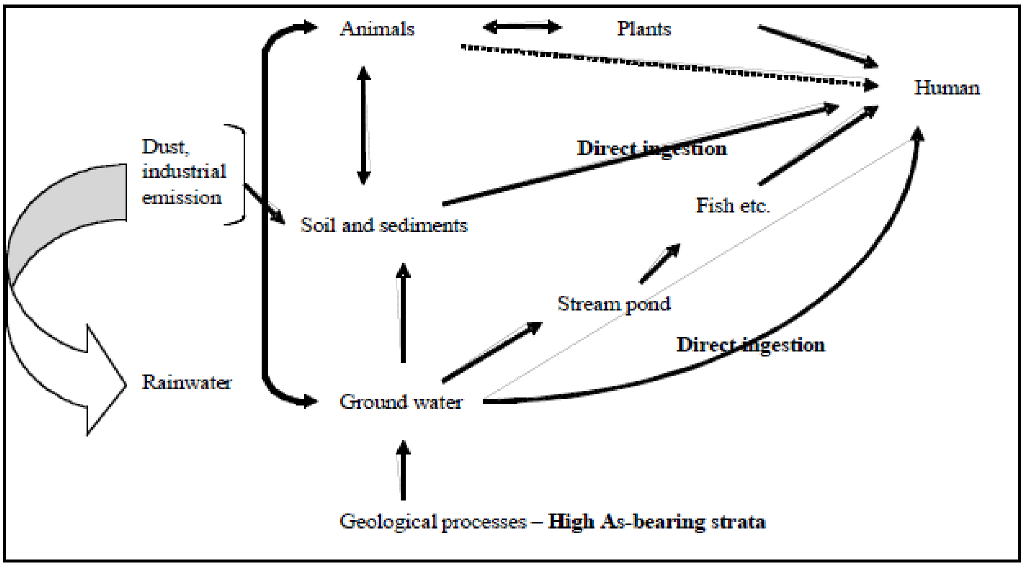


Figure 1.1: Total Exposure of Human Beings to Arsenic in Nature (17)

A recent study conducted by S. M. Imamul Huq of the Department of Soil, Water & Environment, Dhaka University, and Ravi Naidu of Commonwealth Scientific and Industrial Research Organization (CSIRO), Land and Water, Australia, demonstrates that apart from direct ingestion through drinking water, the major possible pathways of arsenic contamination are Soil-Crop-Food, as well as cooking water (31). The transfer could be schematized as Groundwater to Land Crop→Human Beings. The study by Huq and Naidu analyzed water, soil, and vegetables/crops growing on arsenic contaminated lands in fourteen districts (out of sixty-four in the country). Fish, cooked food, and grasses were also analyzed. The study concluded that there is a possibility of arsenic ingestion through consumption of different food materials (17).

Research is continuing into the impacts that irrigation with arsenic-contaminated water might have on food safety. According to the National Water Management Plan (December 2001), no firm conclusion can be drawn as yet. If it is shown to be unsafe, the implications will depend on whether the health hazards are applicable to some or all crops, and whether treatment is a viable option. However, if there were a need to ban irrigation from groundwater in these areas, the impacts would be moderated by the fact that most shallow tubewell irrigation is not in areas of high arsenic contamination (17).

1.4 Most affected areas in the world by arsenic contamination

The detrimental health effects of environmental exposure to arsenic have become increasingly clear in the last few years (18). The extent of the arsenic problem worldwide is as yet unknown. Before arsenic was identified as the unambiguous cause of wide-scale health problems in Bangladesh, such occurrences were considered relatively isolated. Although it is far too early to outline definitively the extent of the problem globally, it is clear that there are many countries in the world where arsenic in drinking water has been detected at concentrations greater than the WHO guideline value (10µg/L) or the prevailing national standard (4).

1.4.1 Global scale problem

The concentration of arsenic in natural waters, including groundwater, is typically below the WHO provisional guideline value for arsenic in drinking water of 10 µg/ L However, arsenic mobilization in water is favored under some specific geochemical and hydro geological conditions and concentrations can reach two orders of magnitude higher than this in the worst cases. Most of the extensive occurrences of high-arsenic groundwater are undoubtedly of natural origin, that is to say they involve the mobilization of arsenic naturally present in the ground and not the discharge of pollutants at the land surface, although the extent to which mobilization can be accelerated by groundwater pumping is still open to question (4).

Figure 1.2 shows the distribution of documented cases of arsenic contamination in groundwater and the environment worldwide. Many of these cases are related to areas of mineralization and mining activity and a few are associated with geothermal sources. While these cases can be severe, with high concentrations of arsenic in waters, sediments, and soils, their lateral scale is usually limited. Other areas with recognized high-arsenic groundwater are not associated with obvious mineralization and mining or geothermal activity. Some of these occur in major aquifers and may be potentially much more serious because they occupy large areas and can provide drinking water to large populations. This study deals with these areas rather than those where arsenic release is due to mining or geothermal activities (4).

Figure 1.2: World Distribution of Arsenic in Groundwater and the Environment (4)
Source: Modified after Smedley and Kinniburgh 2002.

Major alluvial plains, deltas and some inland basins composed of young sediments are particularly prone to developing groundwater arsenic problems. Several of these aquifers around the world have now been identified as having unacceptably high concentrations of arsenic. These include not only the alluvial and deltaic aquifers in parts of Asia, but also inland basins in Argentina, Chile, Mexico, the southwestern United States, Hungary, and Romania. Important differences exist between these regions, but some similarities are also apparent. The majority of the high-arsenic groundwater provinces are in young unconsolidated sediments, usually of Quaternary age, and often of Holocene deposition of less than 12,000 years in age. These aquifers do not appear to contain abnormally high concentrations of arsenic-bearing minerals but do have geochemical and hydro geological conditions favoring mobilization of arsenic and its retention in solution (4).

Many of the world's aquifers with high arsenic levels are located in those areas of Asia where large alluvial and deltaic plains occur, particularly around the perimeter of the Himalayan mountain range. In South Asia, naturally occurring arsenic in groundwater was initially identified in West Bengal, India, and in Bangladesh in the early 1980s and 1990s respectively. Since then governments, donors, international organizations, NGOs, and research institutions have increased testing of groundwater sources. As a result, naturally occurring arsenic has now been identified in the groundwater of the countries in South and East Asia that are the subject of this study.

Figure 1.3 shows the locations of high-arsenic groundwater provinces in the countries of South and East Asia. There may be other Quaternary aquifers with high groundwater arsenic concentrations that have not yet been identified, but since awareness of the arsenic problem has grown substantially over the last few years, these are likely to be on a smaller scale than those already identified (4).

Many of the health consequences resulting from contaminated groundwater have emerged in relatively recent years as a result of the increased use of groundwater from tube wells for drinking and irrigation. In terms of numbers of groundwater sources affected and populations at risk problems are greatest in Bangladesh, but have also been identified in India (West Bengal, and more recently Assam, Arunachal Pradesh, Bihar, Manipur, Meghalaya, Nagaland, Tripura and Uttar Pradesh), China, including Taiwan, Vietnam, Thailand, Cambodia, Myanmar, and Nepal. Occasional high-arsenic ground waters have also been found in Pakistan, although the occurrences there appear to be less widespread. (4)

Hence, much of the distribution is linked to the occurrence of young (Quaternary) sediments in the region's large alluvial and deltaic plains (Bengal basin, Irrawaddy delta, Mekong valley, Red River delta, Indus plain, Yellow River plain). Although groundwater arsenic problems have been detected in some middle sections of the Indus and Mekong valleys, such problems have apparently not emerged in the lower reaches (deltaic areas). Whether this represents lack of testing or whether arsenic problems do not occur there is as yet uncertain. However, the young Quaternary aquifers most susceptible to developing groundwater arsenic problems appear to be less used in these areas as a result of poor well yields or high groundwater salinity. Other Quaternary sedimentary aquifers in Asia have not been investigated and so their arsenic status is unknown. Some localized groundwater arsenic problems in South and East Asia relate to ore mineralization and mining activity (for example in peninsular Thailand and Madhya Pradesh, India) (4)

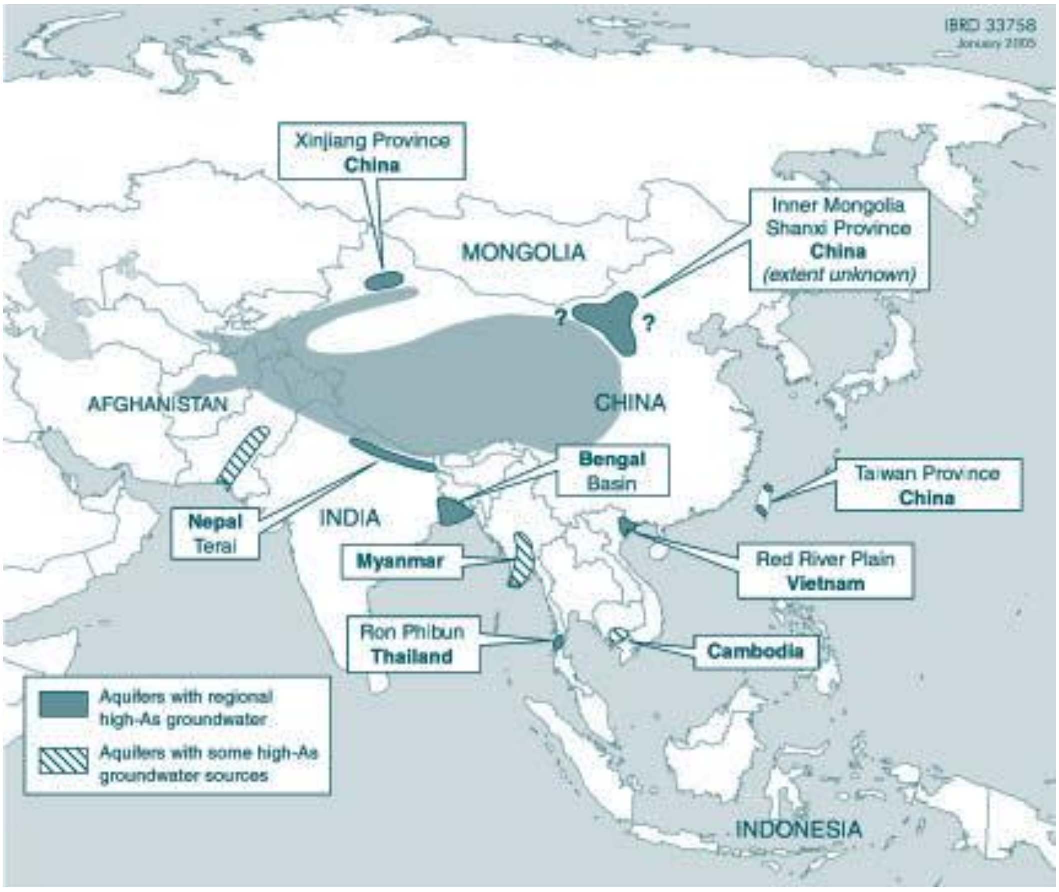


Figure 1.3: Locations of High-Arsenic Groundwater Provinces in South and East Asia (4)

Source: Modified after Smedley 2003

Wikipedia, the free encyclopedia, mentions ground water arsenic contaminated areas

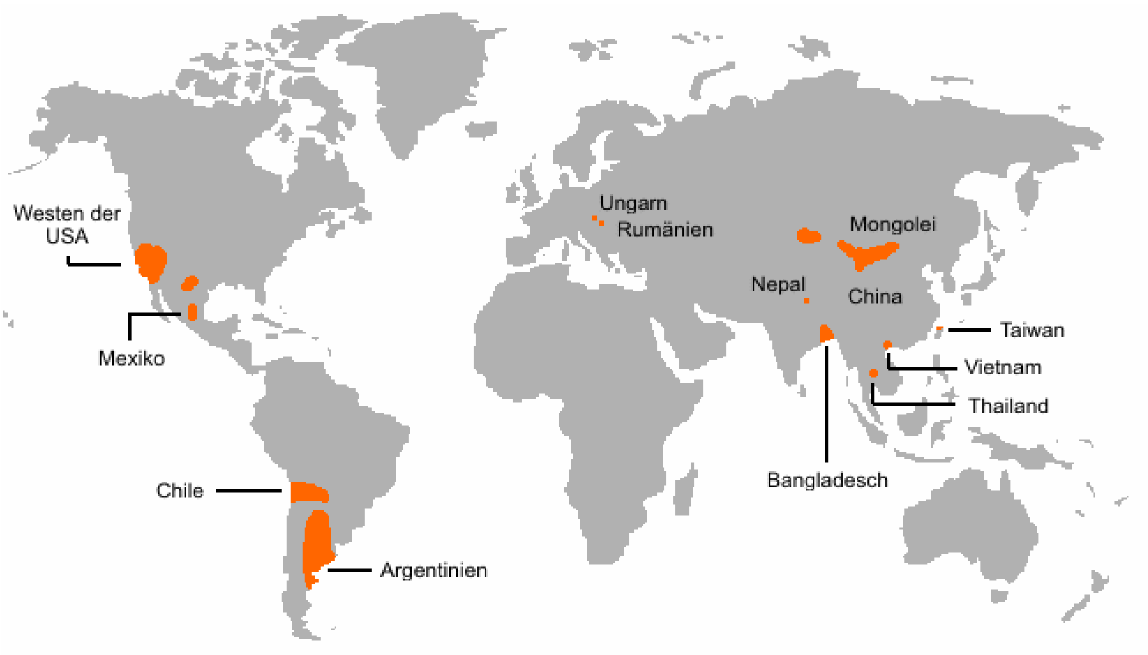


Figure 1.4: Ground water arsenic contaminated areas (19)

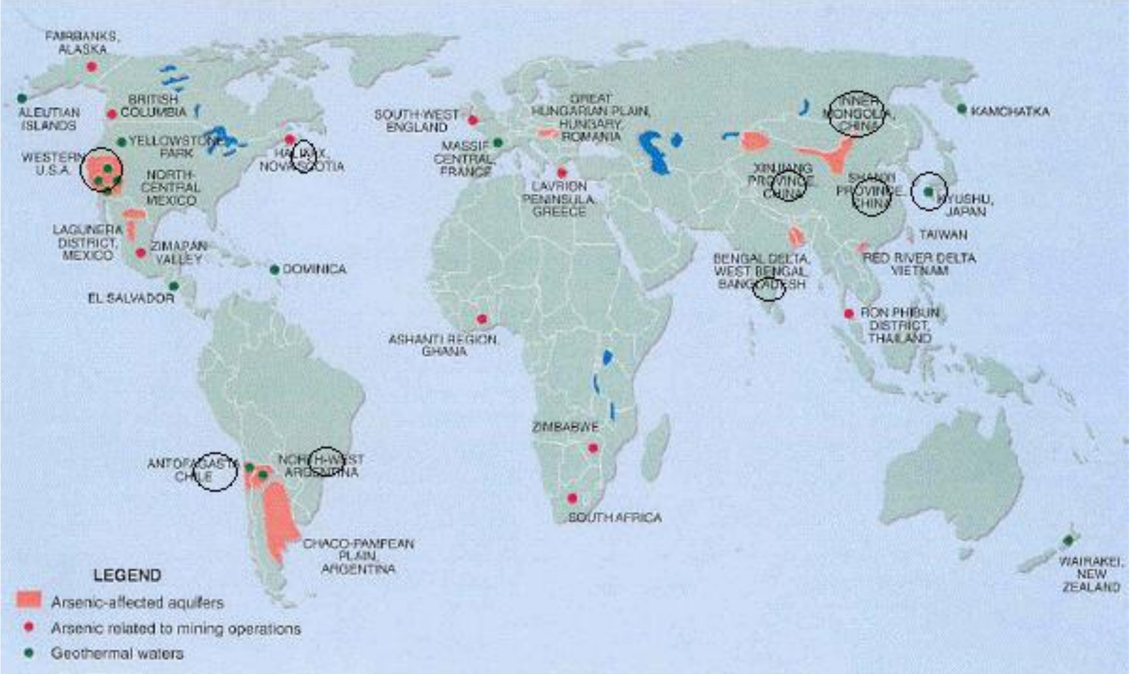


Figure 1.5: Ground water arsenic contaminated areas (20)

A map by Amini et al, Swiss Federal Institute of Aquatic Science and Technology, showing the modelled global probability of geogenic arsenic contamination can be found

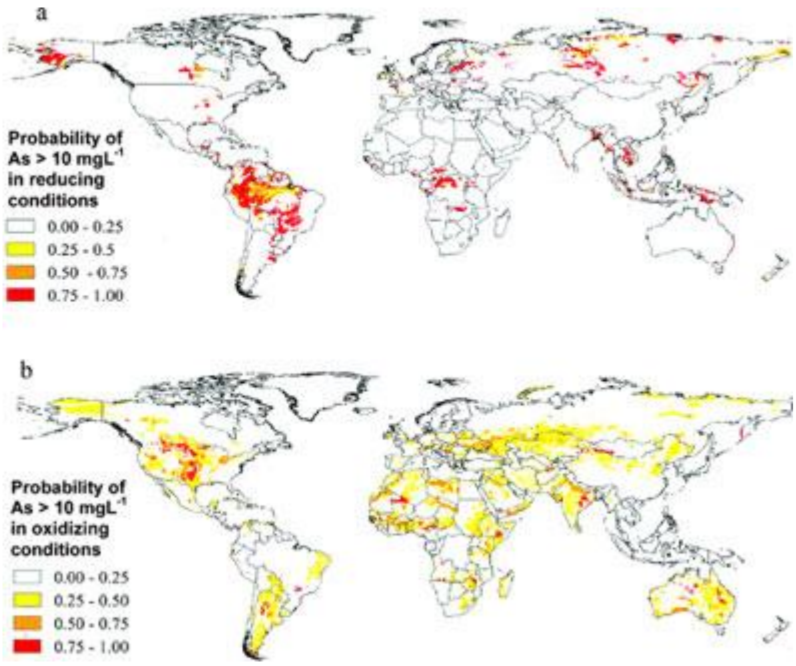


Figure 1.6: Ground water arsenic contaminated areas (21)

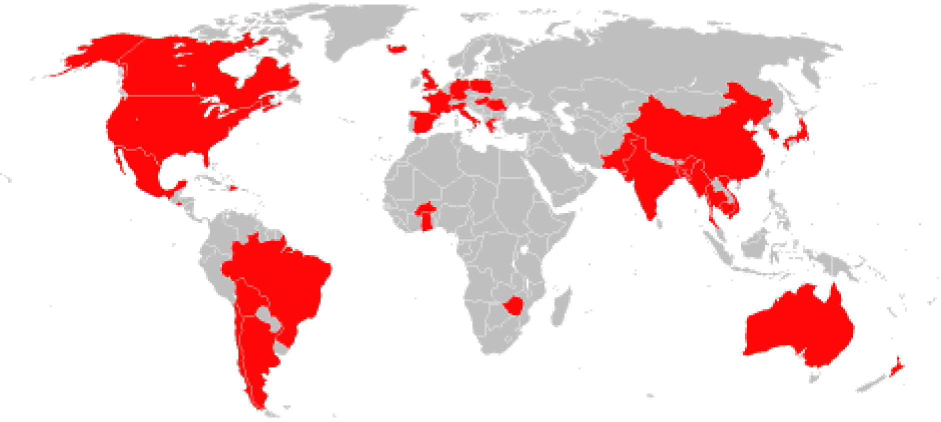


Figure 1.7: Arsenic-affected countries (red) of the world (Smedley and Kinniburgh, 2002; Apple yardet al., 2006; Smedley et al., 2007) (22).

1.4.2 Regional scale problem: Country to Country

Bangladesh: Widespread arsenic contamination of groundwater has led to a massive epidemic of arsenic poisoning in Bangladesh (19). Prior to the 1970s, Bangladesh had one of the highest infant mortality rates in the world. Ineffective water purification and sewage systems as well as periodic monsoons and flooding exacerbated these problems. As a solution, UNICEF and the World Bank advocated the use of wells to tap into deeper groundwater. Millions of wells were constructed as a result. Because of this action, infant mortality and diarrheal illness were reduced by fifty percent. However, with over 8 million wells constructed, approximately one in five of these wells are now contaminated with arsenic above the government's drinking water standard (23). The arsenic in the groundwater is of natural origin, and is released from the sediment into the groundwater, owing to the anoxic conditions of the subsurface. This groundwater began to be used after local and western NGOs and the Bangladeshi government undertook a massive shallow tube well drinking-water program in the late twentieth century. This program was designed to prevent drinking of bacteria-contaminated surface waters, but failed to test for arsenic in the groundwater (23).

India: West Bengal is the most affected state of India. So far, High concentration of Arsenic was detected in 8 districts of the state. As a result, 40 million people of the districts covering 38000 square kilometer are now at risk School of Environmental Studies (SOES) of Jadavpur University in Calcutta conducted a survey in the affected areas for the last 10 years. If identified 863 villages of the eight districts where Groundwater contains Arsenic more than the maximum permissible limit (0.05 mg/I). According to the SOES, 1.5 million people of the villages are taking Arsenic affected districts in West Bengal are: Malda, Murshidabad, Nadia, Bardhawan, North and South 24 Pargans, Hawra and Hoogli. In West Bengal Arsenic contamination in ground water was first detected in 1978. And the first Arsenic patient was found in West Bengal in 1983. A villager of Gangarampur in South 24 paragons came to physicians with infection in hands and legs in July, 1983 (24).

Italy: Some parts of Italy such as Romagna lower Po river valley has arsenic contamination problem. High arsenic (As) concentrations, >900 ug/L, were also measured in Ca-Mg-SO4 waters from springs and drainages in the village of Pesariis in the Carnic Alps (NE Italy) (25).

USA: Arsenic was found in groundwater throughout USA though the concentration is low. About 3 million people of the country are drinking Arsenic contaminated water. 0.045-mg/liter Arsenic was found in one of the county of California's groundwater while 0.092 mg/liter in two counties of Nevada (24). In the United States, arsenic is most commonly found in the ground waters of the southwest. Parts of New England, Michigan, Wisconsin, Minnesota and the Dakotas are also known to have significant concentrations of arsenic in ground water. Increased levels of skin cancer have been associated with arsenic exposure in Wisconsin, even at levels below the 10 part per billion drinking water standard. According to a recent film funded by the US Superfund, millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that exceed established limits. Some locations in the United States, such as Fallon, Nevada, have long been known to have groundwater with relatively high arsenic concentrations (in excess of 0.08 mg/L). Even some surface waters, such as the Verde River in Arizona, sometimes exceed 0.01 mg/L arsenic, especially during low-flow periods when the river flow is dominated by groundwater discharge (23).

Argentina: Arsenic contamination was detected in Argentina as early as the beginning of the country. The disease caused by Arsenic poisoning was known in the country as 'Bell will Disease'. In eastern and central Argentina, 0.1-2.0 Milligram Arsenic was found in every litter of groundwater. The deeper well water and the surface water showed almost Novell of Arsenic. Some 20000 people in Argentina suffered not take a severe shape as the numbers of affected people were less and essential cautionary measures were taken (24).

Nepal: Nepal is subject to a serious problem with arsenic contamination. The problem is most severe in the Terai region, the worst being near Nawalparasi District, where 26 percent of shallow wells failed to meet WHO standard of 10 ppb. A study by Japan International Cooperation Agency and the Environment in the Kathmandu Valley showed that 72% of deep wells failed to meet the WHO standard, and 12% failed to meet the Nepali standard of 50 ppb (24).

Mexico: Some 127,000 people in 11 counties of Northern Mexico have been drinking Arsenic contaminated water. Concentration of Arsenic of the contaminated area is by 0.1-0.5 mg/l. High concentration of Arsenic in groundwater was first detected in 1963. People of the country have been suffering from various diseases including cancer for drinking the contaminated water (24).

Chile: Arsenic contamination in water was first detected in 1957 in a province of Chile. And the first Arsenic patient was found in 1962. Later almost all the diseases caused by Arsenic were found in human bodies through various researches. From 1957-69 people of that province took drinking water containing Arsenic 0.8-1.3 mg/l liter by setting up a water treatment plant in 1970. But many people embraced death due to drinking Arsenic contaminated water since 1957. Arsenic was blamed for seven percent of total deaths in Chile from 1989 to 93 (24).

Taiwan: The Arsenic contamination in Taiwan was reported since 1968. A disease called 'black foot disease' spread in the county massively. Later it was known that the cause of the disease was Arsenic received through contaminated tube-well water. Water of 83000 tube-wells was annualized and 0.05 mg/liter Arsenic was found in 19 percent of the tube-wells. A water treatment plant was established in 1956. Supply of safe drinking water was able in 90 year of 1979. But every year new Arsenic patients are found as they drank Arsenic contaminated water earlier. At present, some 100,000 people are suffering from Arsenic problem (24).

Mongolia: The attack in Mongolia was in two ways. Flurried was also found in water along with Arsenic. The first Arsenic patient was found in Mongolia in 1988. A survey conducted in 1989 revealed that some 300,000 people of 627 villages of 11 counties were taking Arsenic contaminated water. Of them, 1774 were identified as Arsenic patients. Arsenic concentration above 0.05 mg/liter was detected in 90 percent tube-wells of Mongolia. It is thought that the problems arose due to continue irrigation for agriculture by ground water in arid region (24).

Thailand: The first Arsenic patient was found in Thailand in 1987. Some 18000 people of the country live under Arsenic threat. The situation is worst in Ronpibul district of Srithammarat province. In some places Arsenic was found even 5.0 milligram in every Arsenic contamination. A survey found that more than 1500 people with proven skin cancer. The country is trying to prevent Arsenic pollution through a community since 1993 (24).

The Philippines: Presence of Arsenic was found in human bodies living of both sides of Matingao and Marbol rivers after a geothermal power plant was set up of Mt. APO in 1992. The Geothermal plant is suspected as the cause of Arsenic contamination. The state- own Philippine national oil company, which installed the plan, has taken measures such as the installation of small water- supply system at various point of the affected area. A total of 39 Arsenic patients were detected in the affected area in September 1995 (24).

China: First Arsenic patient was found in a province of china in 1953. Medical surveys began in 1964. In 1992, about 3000 Arsenic patients ware identified. Another survey conducted in 1991 -93 examined 9202 people and found 1545 suffering from Arsenics. Of them, 88 percent received Arsenic from foods while 7 percent from water and 5 percent from water and 5 percent from air. In China, use of coal as fuel is considered as the main reason of arsenic contamination because some coal contains high Arsenic (24).

Japan: In Japan, Arsenic contamination was detected in water and air of two villages- Turoko and Matsu. It was proved that the two villages were affected by Arsenic for 50 years a total of 217 Arsenic patients were found in the two villages in 1995. Metal and coalmines are the sources of Arsenic pollution in the villages. The affected people sued the mine authorities and were compensated (24).

New Zealand: Presence of high level of Arsenic was found in several places of New Zealand recently (24).

1.5 Standards for Arsenic Concentrations in potable Water

Due to the carcinogenic nature of arsenic, the WHO has issued a provisional guideline for maximum permissible concentration of arsenic in drinking water of 10 μg L-1 (microgram per liter).WHO guidelines are intended as a basis for setting national standards to ensure the safety of public water supplies and the guideline values recommended are not mandatory limits. Such limits are meant to be set by national authorities, considering local environmental, social, economic, and cultural conditions (18).

The WHO-recommended maximum permissible value is usually related to acceptable health risk, defined as that occurring when the excess lifetime risk for cancer equals 10-5 (that is, 1 person in 100,000). However, in the case of arsenic, the United States EPA estimates that this risk would mean a standard as low as 0.17 μg L-1, which is considered far too expensive to achieve, even for industrial countries such as the United States. The EPA thus conducted an economic study with concentrations of 3, 5, 10, and 20 μg L-1 and concluded that for the United States a standard of 10μg/L represents the best trade-off among health risks, the ability of people to pay for safe water, and the availability of water treatment technology (18).

Most developing countries still use the former WHO-recommended concentration of 50 μg L-1 as their national standard for arsenic in drinking water, partially due to economic considerations and the lack of tools and techniques to measure accurately at such low concentrations. Here, it is important to note that even though the exact health effects of an arsenic concentration of 50 μg L-1 have not been quantified; many correlations between internal cancer and lower concentration of arsenic have also been found. Therefore, while the respective current national standards are valid and followed by international agencies such as the World Bank, epidemiological studies at these lower concentrations are of utmost importance in providing a better basis for decision makers in developing countries to understand the risks they are taking by adhering to their higher national standards and the trade-offs involved in investing in arsenic mitigation compared to other development needs (18).

Table 1.4: Current standards of selected organizations &countries for Arsenic in Drinking Water (18)

Parameter	WHO	EU	US EPA	Italy	Aus	Japan	China	Bangladesh	Canada
Arsenic (As)	0.01 mg/l	0.01 mg/l	0.01 mg/l	0.01 mg/l	0.05 mg/l	0.01 mg/l	0.05 mg/l	0.05 mg/l	0.025 mg/l

Part 2: Iron

1.6 History of Iron

Ancient Egyptians had learned how to use iron before the First Dynasty, which began in about 3400 B.C. The Egyptians probably found the iron in meteorites. Meteorites are chunks of rock and metal that fall from the sky. Some meteorites are very rich in iron. The Egyptians made tools and jewelry out of iron (26).

Iron was also known to early Asian civilizations. In Delhi, India, for example, a pillar made out of iron built in A.D. 415 still stands. It weighs 6.5 metric tons and remains in good condition after nearly 1,600 years (26).

Early Chinese civilizations also knew about iron. Workers learned to produce iron as early as 200 B.C. A number of iron objects, including cannons, remain from the Han period (202 B.C. to A.D. 221) (26).

The Bible also includes many mentions of iron. For example, a long passage in the book of Job describes the mining of iron. Other passages tell about the processing of iron ore to obtain iron metal (26).

By the time of the Roman civilization, iron had become an essential metal. The historian Pliny (A.D. 23-79) described the role of iron in Rome:

It is by the aid of iron that we construct houses, cleave rocks, and perform so many other useful offices of life. But it is with iron also that wars, murders, and robberies are effected, and this, not only hand to hand, but from a distance even, by the aid of weapons and winged weapons, now launched from engines, now hurled by the human arm, and now furnished with feathery wings (26).

Even from the earliest days, humans probably seldom used iron in a pure form. It was difficult to make iron that was free of impurities, such as carbon (charcoal) and other metals. More important, however, it became obvious that iron with impurities was a stronger metal that iron without impurities (26).

It was not until 1786, however, that scientists learned what it was in steel that made it a more useful metal than iron. Three researchers, Gaspard Monge (1746-1818), C. A. Vandermonde, and Claude Louis Berthollet (1748-1822) solved the puzzLe. They found that a small amount of carbon mixed with iron produced a strong alloy. That alloy was steel. Today, the vast amount of iron used in so many applications is used in the form of steel, not pure iron (26).

1.7 Sources of Iron

The most common sources of iron in groundwater are naturally occurring, for example from weathering of iron bearing minerals and rocks. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute iron to local groundwater (27).

Iron is a common metallic compound in the earth’s crust. Water percolating through soil and rock can dissolve minerals containing iron and hold them in solution. Occasionally human activities for instance using of iron materials like iron pipes also may be a source of iron in water (28).

The presence of iron in ground water is a direct result of its natural existence in underground rock formations and precipitation water that infiltrates through these formations. As the water moves through the rocks some of the iron dissolves and accumulates in aquifers which serve as a source for ground water (29).

Since the earth's underground rock formations contain about 5% iron it is common to find iron in many geographical areas around the globe (29).

1.7.1 Natural Sources

Iron is common metal found in soil and rocks. Water dissolves these elements while percolating through the ground, carrying them along as just two of many possible contaminants in groundwater. Deep wells and springs are more likely to have high concentrations of iron than surface streams or reservoirs. Groundwater pollution can increase the levels of both metals, with rusty pipes an additional possible source of excess iron (30).

In fact, the primary sources of iron in drinking water are natural geologic sources as well as aging and corroding distribution systems and household pipes. Iron-based materials, such as cast iron and galvanized steel, have been widely used in our water distribution systems and household plumbing (31).

1.7.2 Occurrence and production by human activities

Iron is the fourth most abundant element in the Earth's crust. Its abundance is estimated to be about 5 percent. Most scientists believe that the Earth's core consists largely of iron. Iron is also found in the Sun, asteroids, and stars outside the solar system (26).

The most common ores of iron are hematite, or ferric oxide (Fe_2O_3); limonite, or ferric oxide (Fe_2O_3); magnetite, or iron oxide (Fe_3O_4); and siderite, or iron carbonate ($FeCO_3$). An increasingly important source of iron is taconite. Taconite is a mixture of hematite and silica (sand). It contains about 25 percent iron (26).

Weathering processes release the element into waters. Both mineral water and drinking water contain iron carbonate. In deep sea areas the water often contains iron fragments the size of a fist, manganese and small amounts of lime, silicon dioxide and organic compounds (32).

Iron is applied worldwide for commercial purposes, and is produced in amounts of 500 million tons annually. Some 300 million tons are recycled. The main reason is that iron is applicable in more areas than possibly any other metal. Alloys decrease corrosivity of the metal. Steel producers add various amounts of carbon. Iron alloys are eventually processed to containers, cars, laundry machines, bridges, buildings, and even small springs. Iron compounds are applied as pigments in glass and email production, or are processed to pharmaceutics, chemicals, iron fertilizers, or pesticides. These are also applied in wood impregnation and photography (32).

Aluminum waste products containing iron were discharged on surface water in the earlier days. Today, these are removed and applied as soil fillers (32).

Iron compounds are applied in precipitation reactions, to remove compounds from water in water purification processes. The 59Fe isotope is applied in medical research and nuclear physics (32).

The largest iron resources in the world are in China, Russia, Brazil, Canada, Australia, and India. The largest producers of iron from ore in the world are China, Japan, the United States, Russia, Germany, and Brazil (26).

1.8 Effects of Iron contamination

In ground water such as wells and springs, iron is the most common dissolved chemical. Although not considered to cause health problems in humans, its presence in potable water is rather unpleasant due to the bad odors it spreads, its rusty taste and color, its feel on skin and hair, and its tendency to stain clothing (29).

In addition, the presence of dissolved iron enhances the growth of iron bacteria, which forms dark-colored slime layers on the inner side of a system's pipes. The slime is then released into the network through water flow fluctuations, leading to dirt build-up and damage to the plumbing (29).

At the same time, iron is an essential nutrient for humans, with a recommended daily intake of 5 milligrams. Therefore, the official water and environment agencies in many countries have established a secondary limit for iron in drinking water, which is based on aesthetic concerns (Secondary Maximum Contaminant Level – SMCL) (29).

1.8.1 Effects on health

The total amount of iron in the human body is approximately 4 g, of which 70% is present in red blood coloring agents. Iron is a dietary requirement for humans, just as it is for many other organisms. Men require approximately 7 mg iron on a daily basis, whereas women require 11 mg. The difference is determined by menstrual cycles. When people feed normally these amounts can be obtained rapidly. The body absorbs approximately 25% of all iron present in food. When someone is iron deficit feed iron intake may be increased by means of vitamin C tablets, because this vitamin reduces tertiary iron to binary iron. Phosphates and phytates decrease the amount of binary iron (32).

In food iron is present as binary iron bound to hemoglobin and myoglobin, or as tertiary iron. The body may particularly absorb the binary form of iron.

Iron is a central component of hemoglobin. It binds oxygen and transports it from lungs to other body parts. It transports CO2 back to the lungs, where it can be breathed out. Oxygen storage also requires iron. Iron is a part of several essential enzymes, and is involved in DNA synthesis. Normal brain functions are iron dependent (32).

In the body iron is strongly bound to transferring, which enables exchange of the metal between cells. The compound is a strong antibiotic, and it prevents bacteria from growing on the vital element. When one is infected by bacteria, the body produces high amounts of transferring (32).

When iron exceeds the required amount, it is stored in the liver. The bone marrow contains high amounts of iron, because it produces hemoglobin (32).

Iron deficits lead to anemia, causing tiredness, headaches and loss of concentration. The immune system is also affected. In young children this negatively affects mental development, leads to irritability, and causes concentration disorder. Young children, pregnant women and women in their period are often treated with iron (II) salts upon iron deficits (32).

When high concentrations of iron are absorbed, for example by haemochromatose patients, iron is stored in the pancreas, the liver, the spleen and the heart. This may damage these vital organs. Healthy people are generally not affected by iron overdose, which is also generally rare. It may occur when one drinks water with iron concentrations over 200 ppm (32).

Iron compounds may have a more serious effect upon health than the relatively harmless element itself. Water soluble binary iron compounds such as FeCl2 and FeSO4 may cause toxic effects upon concentrations exceeding 200 mg, and are lethal for adults upon doses of 10-50 g. A number of iron chelates may be toxic, and the nerve toxin iron penta carbonyl is known for its strong toxic mechanism. Iron dust may cause lung disease (32).

Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens (33).

1.8.2 Effects on environment

Iron is a dietary requirement for most organisms, and plays an important role in natural processes in binary and tertiary form. Oxidized tertiary iron cannot be applied by organisms freely, except at very low pH values. Still, iron usually occurs in this generally water insoluble form (32).

Adding soluble iron may rapidly increase productivity in oceanic surface layers. It might than play an important role in the carbon cycle. Iron is essential for nitrogen binding and nitrate reduction, and it may be a limiting factor for phytoplankton growth. Solubility in salt water is extremely low (32).

The iron cycle means reduction of tertiary iron by organic ligand (a process that is photo catalyzed in surface waters), and oxidation of binary iron. Iron forms chelating complexes that often play an important role in nature, such as hemoglobin, a red coloring agent in blood that binds and releases oxygen in breathing processes. Organisms take up higher amounts of binary iron than of tertiary iron, and uptake mainly depends on the degree of saturation of physical iron reserves (32).

Iron is often a limiting factor for water organisms in surface layers. When chelating ligand is absent, water insoluble tertiary iron hydroxides precipitate. This is not thought to be hazardous for aquatic life, because not much is known about hazards of water borne iron (32).

Mollusks have teeth of magnetite of goethite (32).

Green plants apply iron for energy transformation processes. Plants that are applied as animal feed may contain up to 1000 ppm of iron, but this amount is much lower in plants applied for human consumption. Generally plants contain between 20 and 300 ppm iron (dry mass), but lichens may consist up to 5.5% of iron. When soils contain little iron, or little water soluble iron, plants may experience growth problems. Plant uptake capacity strongly varies, and it does not only depend on soil iron concentrations, but also upon pH values, phosphate concentrations and competition between iron and other heavy metals. Limes soils are often iron deficit, even when sufficient amounts of iron are present. This is because of the generally high pH value, which leads to iron precipitation (32).

Iron usually occurs in soils in tertiary form, but in water saturated soils it is converted to binary iron, thereby enabling plant iron uptake. Plants may take up water insoluble iron compounds by releasing H+ ions, causing it to dissolve. Micro organisms release iron siderochrome, which can be directly taken up by plants (32).

Iron may be harmful to plants at feed concentrations of between 5 and 200 ppm. These cannot be found in nature under normal conditions, when low amounts of soil water are present (32).

A number of bacteria take up iron particles and convert them to magnetite, to apply this as a magnetic compass for orientation. Iron compounds may cause a much more serious environmental impact than the element itself. A number of LD50 values are known for rats (oral intake): iron (III) acetyl acetonate 1872 mg/kg, iron (II) chloride 984 mg/kg, and iron penta carbonyl 25 mg/kg (32).

1.9 Standards for Iron Concentrations in Water

The EPA secondary drinking water standard for iron is 300 ug/l (1 ug/l is equal to 1 part per billion). Above 300ug/l water may develop a red-orange color. As the amount of iron in the water increases, the color also increases. A public drinking water supply cannot be required to supply water with iron below any particular level.

However, drinking water systems are advised that iron over 300ug/l will cause their water to be discolored (34).

The Aesthetic Objective (AO) for iron in drinking water is less than or equal to 0.3 milligrams per liter (mg/L). The Illinois Environmental Protection Agency (IEPA) has established a maximum concentration for iron in drinking water of 1.0 mg/l.
The following levels of iron (Fe) are expressed in mg/l:

0 - 0.3	Acceptable
0.3 - 1.0	Satisfactory (however, may cause staining and objectionable taste)
Over 1.0	Unsatisfactory (35)

Table 1.5: Current standards of selected organizations &countries for Iron in Drinking Water (36 &37)

Parameter	WHO	EU	US EPA	Bangladesh	Canada
Iron(Fe)	0.3 mg/l	0.2mg/l	0.3mg/l	0.3-1.0mg/l	0.3 mg/l

Part 3: Manganese

1.10 History of Manganese

One of the main ores of manganese is pyrolusite. Pyrolusite is made up primarily of the compound manganese dioxide ($MnO2$). Early artists were familiar with pyrolusite. They used the mineral to give glass a beautiful purple color. They also used the mineral to remove color from a glass. When glass is made, it often contains impurities that give the glass an unwanted color. The presence of iron, for example, can give glass a yellowish tint. Adding pyrolusite to yellowish glass removes the color. The purple tint of pyrolusite balances out the yellow color of the glass. The glass ends up being clear and colorless (38).

By the mid-1700s, chemists began to suspect that pyrolusite might contain a new element. Some authorities credit German chemist Ignatius Gottfried Kaim with isolating the element in 1770. However, Kaim's report was not read by many chemists and was quickly lost (38).

During this period, some of the most famous chemists in Europe were trying to analyze pyrolusite, but none of them was successful. The problem was solved in 1774 when Gahn developed a method for removing the new element from pyrolusite. He heated pyrolusite with charcoal (pure carbon). The carbon took oxygen away from manganese dioxide, leaving behind pure manganese (39).

The origin of manganese's name is a bit confusing. Early chemists associated the new element with mineral called magnesia. That mineral got its name because it is magnetic. Magnesia does not contain manganese, but the name stuck (39).

1.11 Sources of Manganese

One may think of Manganese as initially being in metal form; however this is not the case. Manganese is not found in nature as the free metal we like to think of. Instead Manganese exists as minerals with the additions of oxides, silicates and carbonates added to the mix. Most Manganese is obtained from ores found in locations all over the world (38).

Manganese is another common metallic compound in the earth’s crust. Water percolating through soil and rock can dissolve minerals containing manganese and hold them in solution (28).

Manganese often occurs naturally. The most common sources manganese in groundwater is naturally occurring; for example, from manganese bearing minerals and rocks, such as amphiboles, ferromagnesian micas, oxides, carbonates, and manganese clay minerals (40).

Industrial effluent, acid-mine drainage, sewage, and landfill leachate may also contribute manganese to local groundwater (40).

1.11.1 Natural Sources

Manganese often occurs naturally in deeper wells where the groundwater may have little or no oxygen, and in areas where groundwater flows through soils rich in organic matter (40).

Iron is common metal found in soil and rocks. Water dissolves these elements while percolating through the ground, carrying them along as just two of many possible contaminants in groundwater. Deep wells and springs are more likely to have high concentrations of iron than surface streams or reservoirs. Groundwater pollution can increase the levels of both metals, with rusty pipes an additional possible source of excess iron (30).

1.11.2 Occurrence and production by human activities

In 1774, Gahn isolated manganese by reducing its dioxide with carbon. The metal may also be obtained by electrolysis or by reducing the oxide with sodium, magnesium, or aluminum. Manganese-containing minerals are widely distributed. Pyrolusite (MnO2) and rhodochrosite (MnCO3) are among the most common of these minerals (41).

Manganese never occurs as a pure element in nature. It always combines with oxygen or other elements. The most common ores of manganese are pyrolusite, manganite, psilomelane, and rhodochrosite. Manganese is also found mixed with iron ores (42).

Manganese also occurs abundantly on the ocean floor in the form of nodules. These nodules are fairly large lumps of metallic ores. They usually contain cobalt, nickel, copper, and iron, as well as manganese. Scientists estimate that up to 1.5 trillion metric tons of manganese nodules may lay on the floors of the world's oceans and large lakes. Currently, there is no profitable method for removing these ores. Up to 1.5 trillion metric tons of manganese nodules (large lumps of metallic ores) may lie on ocean floors (42).

Manganese is the 12th most abundant element in the Earth's crust. Its abundance is estimated to be 0.085 to 0.10 percent. That makes it about as abundant as fluorine or phosphorus (42).

Land-based resources are large but irregularly distributed. About 80% of the known world manganese resources are found in South Africa; other important manganese deposits are in Ukraine, Australia, India, China, Gabon and Brazil. In 1978, 500 billion tons of manganese nodules were estimated to exist on the ocean floor. Attempts to find economically viable methods of harvesting manganese nodules were abandoned in the 1970s (43).

Manganese is mined in South Africa, Australia, China, Brazil, Gabon, Ukraine, India and Ghana and Kazakhstan. US Import Sources (1998–2001): Manganese ore: Gabon, 70%; South Africa, 10%; Australia, 9%; Mexico, 5%; and other, 6%. Ferromanganese: South Africa, 47%; France, 22%; Mexico, 8%; Australia, 8%; and other, 15%. Manganese contained in all manganese imports: South Africa, 31%; Gabon, 21%; Australia, 13%; Mexico, 8%; and other, 27% (43).

For the production of ferromanganese, the manganese ore is mixed with iron ore and carbon, and then reduced either in a blast furnace or in an electric arc furnace. The resulting ferromanganese has a manganese content of 30 to 80%. Pure manganese used for the production of noniron alloys is produced by leaching manganese ore with sulfuric acid and a subsequent electro winning process (43).

1.12 Effects of Manganese contamination

At concentrations found in most natural waters, and at concentrations below the aesthetic objective, manganese is not considered a health risk. Water with a high concentration of manganese may cause the staining of plumbing fixtures or laundry. Manganese solids may form deposits within pipes and break off as black particles that give water an unpleasant appearance and taste. Manganese can increase the growth of unwanted bacteria that form a slimy coating in water pipes (27).

Manganese is one of the chemical elements that have both positive and negative effects on living organisms. A very small amount of the element is needed to maintain good health in plants and animals. The manganese is used by enzymes in an organism. An enzyme is a molecule that makes chemical reactions occur more quickly in cells. Enzymes are necessary to keep any cell operating properly. If manganese is missing from the diet, enzymes do not operate efficiently. Cells begin to die, and the organism becomes ill (42).

Fortunately, the amount of manganese needed by organisms is very small. It is not necessary to take extra manganese to meet the needs of cells. Manganous chloride ($MnCl_2$) is an additive in animal food .In fact, an excess of manganese can create health problems. These problems include weakness, sleepiness, tiredness, emotional disturbances, and even paralysis. The only way to receive such a large dose is in a factory or mine. Workers may inhale manganese dust in the air (42).

1.12.1 Effects on health

Manganese is a very common compound that can be found everywhere on earth. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances their health will decrease. But when the uptake is too high health problems will also occur (44).

The uptake of manganese by humans mainly takes place through food, such as spinach, tea and herbs. The foodstuffs that contain the highest concentrations are grains and rice, soya beans, eggs, nuts, olive oil, green beans and oysters. After absorption in the human body manganese will be transported through the blood to the liver, the kidneys, the pancreas and the endocrine glands (44).

Manganese effects occur mainly in the respiratory tract and in the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage. Manganese can also cause Parkinson, lung embolism and bronchitis. When men are exposed to manganese for a longer period of time they may become impotent (44).

A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia (44).

Because manganese is an essential element for human health shortages of manganese can also cause health effects. These are the following effects (44):
- Fatness
- Glucose intolerance
- Blood clotting
- Skin problems
- Lowered cholesterol levels
- Skeleton disorders
- Birth defects
- Changes of hair color
- Neurological symptoms

Chronic Manganese poisoning may result from prolonged inhalation of dust and fume. The central nervous system is the chief site of damage from the disease, which may result in permanent disability. Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in workers exposed to dust or fume of Manganese compounds. Manganese compounds are experimental equivocal tumorigenic agents (44).

1.12.2 Effects on environment

Manganese compounds exist naturally in the environment as solids in the soils and small particles in the water. Manganese particles in air are present in dust particles. These usually settle to earth within a few days (44).

Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese that derives from human sources can also enter surface water, groundwater and sewage water. Through the application of manganese pesticides, manganese will enter soils (44).

For animals manganese is an essential component of over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism. With animals that eat too little manganese interference of normal growth, bone formation and reproduction will occur (44).

For some animals the lethal dose is quite low, which means they have little chance to survive even smaller doses of manganese when these exceed the essential dose. Manganese substances can cause lung, liver and vascular disturbances, declines in blood pressure, failure in development of animal fetuses and brain damage (44).

When manganese uptake takes place through the skin it can cause tremors and coordination failures. Finally, laboratory tests with test animals have shown that severe manganese poisoning should even be able to cause tumor development with animals (44).

In plants manganese ions are transported to the leaves after uptake from soils. When too little manganese can be absorbed from the soil this causes disturbances in plant mechanisms. For instance disturbance of the division of water to hydrogen and oxygen, in which manganese plays an important part (44).

Manganese can cause both toxicity and deficiency symptoms in plants. When the pH of the soil is low manganese deficiencies are more common (44).

Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leafs and brown spots on leaves. Deficiencies can also cause these effects. Between toxic concentrations and concentrations that cause deficiencies a small area of concentrations for optimal plant growth can be detected (44).

1.13 Standards for Manganese Concentrations in Water

Manganese may become noticeable in tap water at concentrations greater than 0.05 milligrams per liter of water (mg/l) by imparting a color, odor, or taste to the water. However, health effects from manganese are not a concern until concentrations are approximately 10 times higher (45).

The CT Department of Public Health (DPH) recently set a drinking water action Level (AL) for manganese of 0.5 mg/l to ensure protection against manganese toxicity. This AL is consistent with the World Health Organization guidance level for manganese in drinking water. The CT AL provides guidance for prudent avoidance of manganese concentrations of potential health concern. Local health departments can use the AL in making safe drinking water determinations for new wells, while the homeowner in consultation with local health authorities makes decisions regarding manganese removal from existing wells (45).

Aesthetic Objective for manganese in drinking water is less than or equal to 0.05 mg/L. The taste and smell of manganese at concentrations above the drinking water guidelines may be noted by some water users (27).

Table 1.6: Current standards of selected organizations &countries for Manganese in Drinking Water (38 &39)

Parameter	WHO	EU	US EPA	Bangladesh	Canada
Manganese(Mn)	0.50mg/l	0.05mg/l	0.05mg/l	0.1mg/l	0.05mg/l

This fact sheet is intended to help individuals who have manganese in their water understand the health risks and evaluate the need for obtaining a water treatment system.

CHAPTER 2: CHEMISTRY OF THE POLLUTANTS

Part 1: Arsenic

Arsenic is a crystal-shape metalloid element, which is brittle in nature, and gray or tin-white in color. Arsenic is a Group-V element in the periodic chart. Arsenic cannot be found in nature as a free element. It exhibits a broad range of chemical reactivity with an ability to form alloys with other elements and covalent bonds. Arsenic precipitates readily in oxidation-reduction, methylation-demethylation and acid base reactions. Arsenic can not only create compounds with oxygen, chlorine, sulfur, carbon and hydrogen, but also with lead, mercury, gold and iron. It mainly remains as oxide, hydrate, sulfide, arsenate, and arsenide. As many as 150 species of arsenic bearing minerals exist in the earth. But only three of them are considered as arsenic ore. Because, the amount of arsenic is higher in these three compounds. Moreover, they are more available than other arsenic compounds. These three compounds are arsenic disulfide, orpiment or arsenic trisulfide, and arsenopyrite or ferus arsenic sulfide. There are differences in the physical properties of these three types of arsenic minerals. But a common feature of them is a garlic-like odor. When arsenopyrite oxidizes and mixes with water, no smell is found in the water. Arsenic burns in air giving off an odor of garlic and dense white fumes of arsenic trioxide. Arsenic can not only create compounds with oxygen, chlorine, sulfur, carbon and hydrogen, but also with lead, mercury, gold and iron. It mainly remains as oxide, hydrate, sulfide, arsenate, and arsenide. Gold, silver, copper, zinc, iron, and other metals exist with arsenic in these chemical compounds (6).

When heated in air, arsenic oxidizes to arsenic trioxide; the fumes from this reaction have an odor resembling garlic. This odor can be detected on striking arsenide minerals such as arsenopyrite with a hammer. Arsenic (and some arsenic compounds) sublimes upon heating at atmospheric pressure, converting directly to a gaseous form without an intervening liquid state at 887 K (614 °C).The triple point is 3.63 MPa and 1,090 K (820 °C). Arsenic makes arsenic acid with concentrated nitric acid, arsenous acid with dilute nitric acid, and arsenic trioxide with concentrated sulfuric acid (2).

2.1 Chemical reactions

With hydrogen: Arsenic trioxide can be reduced by hydrogen gas to form arsine. Arsine, AsH3, is a very toxic gas that is denser than air. When arsine is heated, it breaks down to arsenic and hydrogen

•Reaction of arsenic trioxide with hydrogen gas to form water and arsine

$$AS_2O_3(s) + 6H_2(g) \rightarrow 3H_2O(l) + 2AsH_3(g)$$

With oxygen: Solid arsenic is oxidized when exposed to oxygen. The surface of the metalloid becomes black. When heated in oxygen gas, arsenic binds with oxygen to form tetra arsenic decaoxide or arsenous oxide.

•Reaction of arsenic with oxygen gas to form arsenous oxide
4As(s) + 5O2 (g) → As4O10(s)
4As(s) + 3O2 (g) → As4O6(s)

With halogens: Arsenic reacts well with halogens with the exception of astatine. Arsenic pentafluoride is a highly toxic colorless gas. When liquid arsenic trichloride is cooled with free chlorine molecule, arsenic pentachloride can be formed. Solid arsenic with bromine gas forms a light yellow solid called arsenic tribromide.

•Reaction of arsenous oxide with hydrochloric acid to form water and arsenic trichloride
$As_4O_6 + 12HCl(aq) \rightarrow 4AsCl_3(l) + 6H_2O(l)$
•Reaction of arsenic trichloride with Cl2 to form arsenic pentachloride
$AsCl_3(l) + Cl_2(g) \rightarrow AsCl_5(s)$
•Reaction of solid arsenic with bromine gas
$2As(s) + I_2(g) \rightarrow 2AsI_3(s)$
Reacts with F2 (g): 2As(s) + 5F2 (g) → 2 AsF5 (g) [colorless]
2As(s) + 3F2 (g) → 2AsF3 (l) [colorless] (46)
Reactions with Halogens
2As(s) + 3Cl2(g) → 2AsCl3 (l) [colorless]
2As(s) + 3Br2 (g) → 2AsBr3(s) [pale yellow]
2As(s) + 3I2 (g) → 2AsI3(s) [red] (16)

With water: Arsenic does not react with water under normal conditions. It does not react with dry air, but when it comes in contact with moist air a layer is formed. The layer has a bronze color, and later develops a black surface (47). Pure arsenic is insoluble in water; however, many arsenic compounds dissolve easily in water. Arsenic in the form of arsenic trisulfide, and arsenic acid are examples of arsenic compounds that have found their ways into water supplies (46).

•Reaction of arsenic trisulfide with water to form hydrogen sulfide and arsenous acid (3)
$As_2S_3(s) + 6H_2O(l) \rightarrow 3H_2S(g) + 2H_3AsO_3(aq)$(3)
An example of arsenic compounds that reacts strongly with water is orpiment. This is an amorphous arsenic compound. Reaction mechanism (47):
As2S3 + 6 H2O -> 2 H3AsO3 + 3 H2S

In natural water arsenic participates in oxidation and reduction reactions, coagulation and adsorption. Adsorption of arsenic to fine particles in water and precipitation with aluminium or iron hydroxides causes arsenic to enter sediments. After some time arsenic may dissolve once again consequential to reduction reactions (47).

2.2 Biological reactions

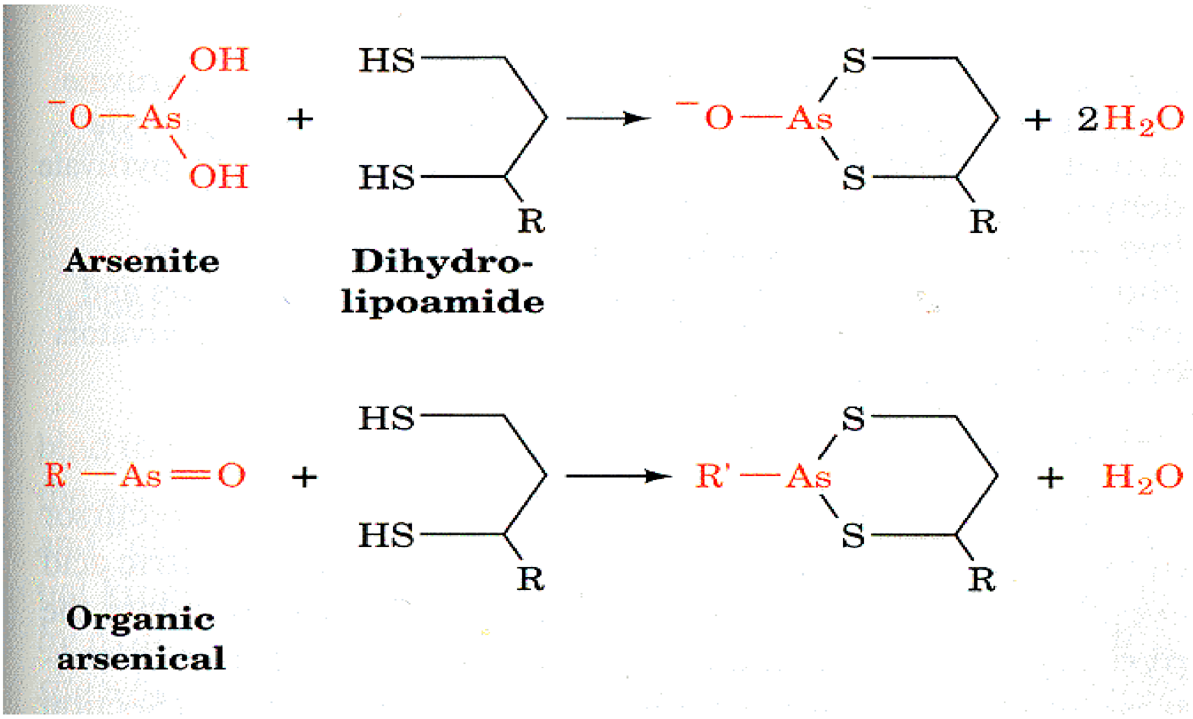
- Arsenic is an Allosteric Inhibitor of Enzymes

-This means that it modifies a regulatory site on an enzyme decreasing/preventing its function

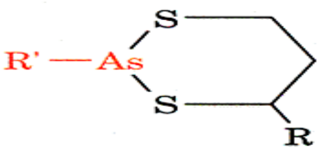
- It specifically targets Lipothiamide Pyrophosphatase and Dihydrolipoamide

-These enzymes are both important components of metabolism, specifically the Pyruvate Dehydrogenase complex

The reaction mechanism of inhibition is as follows:

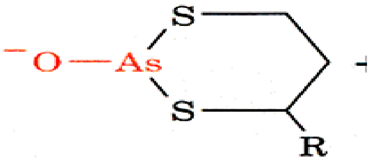


- The Reaction is one of Redox



-The Sulfhydryl groups are oxidized creating an Arsenic compound that prevents reduction of the Sulfur Groups

-This prevents metabolism from moving forward at the Pyruvate Dehydrogenase Complex



- Prevention of the Metabolic Breakdown of Pyruvate leads to Starvation on a Cellular Level

-There is also a build-up of compounds such as pyruvate that lead to neurological damage
-This leads to death from multi system organ failure (16)

2.3 Mechanism of Arsenic mobilization in ground water

One of the key hydro geochemical advances of the last few years has been in the better understanding of the diverse mechanisms of arsenic mobilization in groundwater, as well as its derivation from different mineral sources. The most important mineral sources in aquifers are metal oxides (especially iron oxides) and sulfide minerals (especially pyrite). Release of arsenic from sediments to groundwater can be initiated as a result of the development of highly reducing (anaerobic) conditions, leading to the desorption of arsenic from iron oxides with the breakdown of the oxides themselves. Such reducing conditions are usually found in recently-deposited fine-grained deltaic and alluvial (and some lacustrine) sediments.
Release of arsenic can also occur in acidic ground waters under oxidizing (aerobic) conditions. This tends to occur in arid and semiarid settings resulting from extensive mineral reaction and evaporation. High-arsenic ground waters with this type of association have not been reported in Quaternary aquifers in South and East Asia but are found in some arid inland basins in the Americas (western United States, Mexico, and Argentina). Analogous conditions could occur in some arid parts of the region, such as northern China or western Pakistan, but there is as yet no evidence for this.
Despite the improved understanding of the occurrences and distribution of arsenic in groundwater, there remains some uncertainty as to the precise nature of the source, mobilization, and transport of the element in aquifers. It is only in the last few years that detailed hydro geochemical investigations have been carried out in some of the affected regions (18).

Earlier responses to water-related arsenic problems typically involved engineering solutions or finding alternative water sources, with little emphasis on research. It is worthy of note that, despite the major epidemiological investigations that have been carried out in Taiwan since the discovery of arsenic-related problems there in the 1960s, there has been little hydro geochemical research carried out in the region.

Even today, the aquifers of Taiwan are poorly documented and the arsenic occurrence little understood (18).

One of the important findings of recent detailed aquifer surveys has been the large degree of spatial variability in arsenic concentrations in the affected parts of aquifers, even over lateral distances of a few hundred meters. This means that predictability of arsenic concentrations on a local scale is poor (and probably will always be so). Hence, blanket testing of individual wells in affected areas is necessary. This can be a major task in countries like Bangladesh where the contamination is extensive and the number of wells is very large (18).

There is also uncertainty regarding the temporal variability of arsenic concentrations in groundwater as very little groundwater monitoring has been carried out. Some studies have noted unexpectedly large temporal variations over various timescales but the supporting data are often sparse and inaccessible and so these reports cannot be relied upon. More controlled monitoring of affected ground waters is required to determine their variability in the short term (daily), in the medium term (seasonally), and in the long term (years, decades) (18).

2.4 Comparison between arsenic III arsenic IV

Arsenic is introduced into the aquatic environment from both natural and manmade sources. Typically however, arsenic occurrence in water is caused by the weathering and dissolution of arsenic bearing rocks, minerals and ores. Although arsenic exists in both organic and inorganic forms, the inorganic forms are more prevalent in water and are considered more toxic (48).

Total inorganic arsenic is the sum of particulate and soluble arsenic. A 0.45-micron filter can generally remove particulate arsenic (18).

Soluble, inorganic arsenic exists in either one of two valence states depending on local oxidation reduction conditions. Typically groundwater has anoxic conditions and arsenic is found in its arsenite or reduced trivalent form [As (III)]. Surface water generally has aerobic conditions and arsenic is found in its oxidized pentavalent form [As (V)] (18).

Both arsenite and arsenate exist in four different species. The speciation of these molecules changes by dissociation and is pH dependent. The kinetics of dissociation for each is nearly instantaneous. The pH dependences of arsenite and arsenate are depicted in **figure 2.1 and figure 2.2**, respectively.

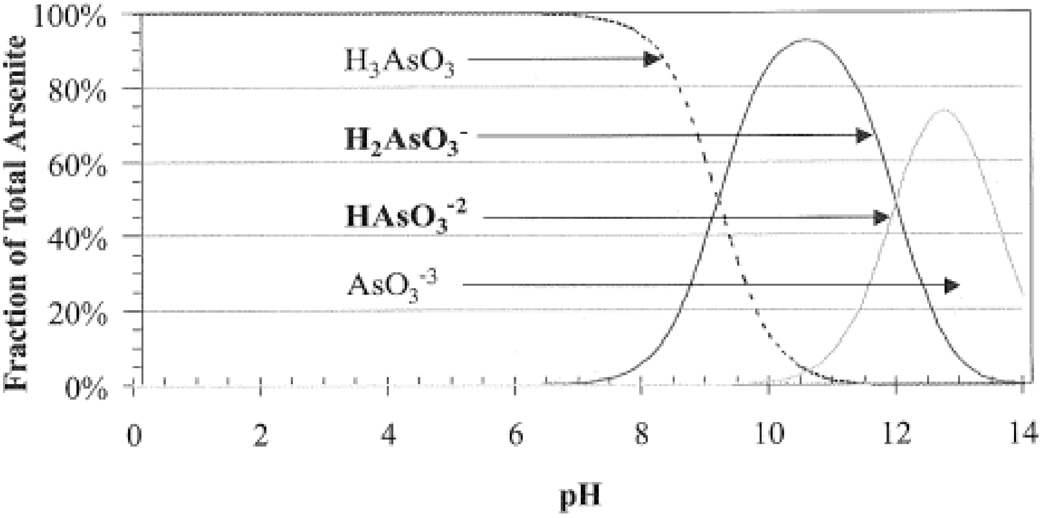


Figure 2.1: Dissociation of Arsenite [As (III)]

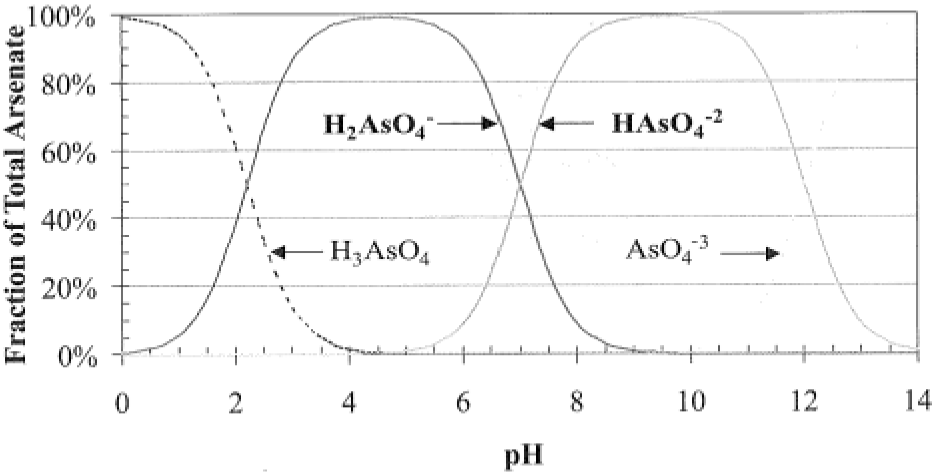


Figure 2.2: Dissociation of Arsenate [As (V)]

Chemical speciation is a critical element of arsenic treatability. Negative surface charges facilitate removal by adsorption, anion exchange, and co-precipitative process. Since the net charge of arsenite [As (III)] is neutral at natural pH levels (6-9), this form is not easily removed. However, the net molecular charge of arsenate [As (V)] is negative (-1 or -2) at natural pH levels, enabling it to be removed with greater efficiency. Conversation to As (V) is a critical element of most arsenic treatment processes. This conversion can be accomplished by adding an oxidizing agent such as chlorine or permanganate. Selection of the most appropriate oxidation technology should be based on several considerations, including cost, integration with existing treatment, disinfection requirements and secondary effects (48).

Part 2: Iron

Iron is probably the most precious of all metals, since man would certainly miss this element more than any other, even the so-called precious ones. In the beginning of the 14th century, when iron was rare, some iron kitchen utensils of Edward III where classified as jewelry and iron accessories were preferentially seek by robbers (49).

The period in human history beginning in about 1200 B.C. is called the Iron Age. It was at about this time that humans first learned how to use iron metal. But in some ways, one could refer to the current era as the New Iron Age. Iron is probably the most widely used and most important metal today. No other metal is available to replace iron in all its many applications (28).

Iron is a transition metal. The transition metals are the elements that make up Groups 3 through 12 in the periodic table. The periodic table is a chart that shows how elements are related to one another. The transition metals are typical metals in that they tend to be bright, shiny, silvery solids. They all tend to conduct heat and electricity well. And they usually have high melting points (28).

Iron is a lustrous, ductile, malleable, silver-gray metal (group VIII of the periodic table). It is known to exist in four distinct crystalline forms. Iron rusts in dump air, but not in dry air. It dissolves readily in dilute acids. Iron is chemically active and forms two major series of chemical compounds, the bivalent iron (II), or ferrous, compounds and the trivalent iron (III), or ferric, compounds (35).

Iron is the most used of all the metals, including 95 % of all the metal tonnage produced worldwide. Thanks to the combination of low cost and high strength it is indispensable. Its applications go from food containers to family cars, from screwdrivers to washing machines, from cargo ships to paper staples. Steel is the best known alloy of iron, and some of the forms that iron takes include: pig iron, cast iron, and carbon steel, and wrought iron, alloy steels, iron oxides (35).

Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5%. Elemental iron is rarely found in nature, as the iron ions Fe2+ and Fe3+ readily combine with oxygen- and sulfur-containing compounds to form oxides, hydroxides, carbonates, and sulfides. Iron is most commonly found in nature in the form of its oxides [1, 2] (50).

2.5 Chemical reactions

Reaction of iron with air:

Iron metal reacts in moist air by oxidation to give a hydrated iron oxide. This does not protect the iron surface to further reaction since it flakes off, exposing more iron metal to oxidation. This process is called rusting and is familiar to any car owner. Finely divided iron powder is pyrophoric, making it a fire risk (51).

On heating with oxygen, O_2, the result is formation of the iron oxides Fe_2O_3 and Fe_3O_4.

$4Fe(s) + 3O_2 (g) \rightarrow 2Fe_2O_3(s)$

$3Fe(s) + 2O_2 (g) \rightarrow Fe_3O_4(s)$ (13)

Reaction of iron with the halogens:

Iron reacts with excess of the halogens F_2, Cl_2, and Br_2, to form ferric, that is, Fe (III), halides.

$2Fe(s) + 3F_2 (g) \rightarrow 2FeF_3(s)$ (white)

$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$ (dark brown)

$2Fe(s) + 3Br_2(l) \rightarrow 2FeBr_3(s)$ (reddish brown) (51)

This reaction is not very successful for iodine because of thermodynamic problems. The iron (III) is too oxidizing and the iodide is too reducing. The direct reaction between iron metal and iodine can be used to prepare iron (II) iodide, FeI_2.

$Fe(s) + I_2(s) \rightarrow FeI_2(s)$ (grey) (51).

Reaction of iron with acids:

Iron metal dissolves readily in dilute sulphuric acid in the absence of oxygen to form solutions containing the aquated Fe (II) ion together with hydrogen gas, H_2. In practice, the Fe (II) is present as the complex ion $[Fe(OH_2)_6]^{2+}$.

$Fe(s) + H_2SO_4 (aq) \rightarrow Fe^{2+} (aq) + SO_4^{2-}(aq) + H_2 (g)$

If oxygen is present, some of the Fe (II) oxidizes to Fe (III).

The strongly oxidizing concentrated nitric acid, HNO_3, reacts on the surface of iron and passivates the surface (51).

Reaction of iron with water:

Air-free water has little effect upon iron metal. However, iron metal reacts in moist air by oxidation to give a hydrated iron oxide. This does not protect the iron surface to further reaction since it flakes off, exposing more iron metal to oxidation. This process is called rusting and is familiar to any car owner (51).

Iron does not clearly alter in pure water or in dry air, but when both water and oxygen are present (moist air), iron corrodes. Its silvery color changes to a reddish-brown, because hydrated oxides are formed. Dissolved electrolytes accelerate the reaction mechanism, which is as follows (34):

4 Fe + 3 O2 + 6 H2O -> 4 Fe3+ + 12 OH- -> 4 Fe (OH) 3 or 4 FeO (OH) + 4 H2O

Usually the oxide layer does not protect iron from further corrosion, but is removed so more metal oxides can be formed. Electrolytes are mostly iron (II) sulphate, which forms during corrosion by atmospheric SO2. In sea regions atmospheric salt particles may play an important role in this process. Iron (II) hydroxide often precipitates in natural waters (34).

2.6 Types of Iron

Iron is generally divided into two main categories:

1) Soluble or "Clear water" iron, is the most common form and the one that creates the most complaints by water users. This type of iron is identified after you've poured a glass, of cold clear water. If allowed to stand for a few minutes, reddish brown particles will appear in the glass and eventually settle to the bottom (52).

2) Insoluble: When insoluble iron or "red water" iron is poured into a glass, it appears rusty or has a red or yellow color. Although not very common in Wisconsin's water wells, insoluble iron can create serious taste and appearance problems for the water user (52).

Because iron combines with different naturally occurring acids, it may also exist as an organic complex. A combination of acid and iron, or organic iron, can be found in shallow wells and surface water. Although this kind of iron can be colorless, it is usually yellow or brown (52).

Finally, when iron exists along with certain kinds of bacteria, problems can become even worse. Iron bacteria consume iron to survive and leave a reddish brown or yellow slime that can clog plumbing and cause an offensive odor. You may notice this slime or sludge in your toilet tank when you remove the lid (52).

In other way Iron can be classified as:

Ferrous - This type of iron is often called "clear water iron" since it is not visible in poured water. It is found in water which contains no oxygen, such as water from deep wells or groundwater. Carbon dioxide reacts with iron in the ground to form water-soluble ferrous bicarbonate, which, in the water, produces ferrous ions (Fe++) (53).

Ferric - Ferric iron is also known as "red water iron". This type of iron is basically ferrous iron which has been exposed to oxygen (oxidized), usually from the air. As carbon dioxide leave the water, oxygen combines with the iron to form ferric ions (Fe+++). These oxidized particles are generally visible in poured water (53).

Bacterial Iron - Slime depositing in toilet tanks or fouling water filters and softeners is a good indication of the presence of bacterial iron. Better described as iron bio-fouling, the iron bacteria problem is both complex and widespread. It attacks wells and water systems around the world in all sorts of aquifer environments, both contaminated and pristine. In some places, it causes great damage; in others, it is considered a minor nuisance (53).

When iron exists along with certain kinds of bacteria, problems can become even worse. Iron bacteria consume iron to survive and leave a reddish brown or yellow slime that can clog plumbing and cause an offensive odor. You may notice this slime or sludge in your toilet tank when you remove the lid (52).

2.7 Mechanism of Iron in ground water

Iron is one of the earth's most plentiful resources, making up at least five percent of the earth's crust. Rainfall seeping through the soil dissolves iron in the earth's surface and carries it into almost every kind of natural water supply, including well water. Although iron is present in our water, it is seldom found at concentrations greater than 10 milligrams per liter (mg/1) or 10 parts per million (52).

Iron can be a troublesome chemical in water supplies. Making up at least 5 percent of the earth’s crust, iron is one of the earth’s most plentiful resources. Rainwater as it infiltrates the soil and underlying geologic formations dissolves iron, causing it to seep into aquifers that serve as sources of groundwater for wells. Although present in drinking water, iron is seldom found at concentrations greater than 10 milligrams per liter (mg/L) or 10 parts per million. However, as little as 0.3 mg/l can cause water to turn a reddish brown color (54).

Iron is mainly present in water in two forms: either the soluble ferrous iron or the insoluble ferric iron. Water containing ferrous iron is clear and colorless because the iron is completely dissolved. When exposed to air in the pressure tank or atmosphere, the water turns cloudy and a reddish brown substance begins to form. This sediment is the oxidized or ferric form of iron that will not dissolve in water (54).

The presence of iron in ground water is a direct result of its natural existence in underground rock formations and precipitation water that infiltrates through these formations. As the water moves through the rocks some of the iron dissolves and accumulates in aquifers which serve as a source for groundwater. Since the earth's underground rock formations contain about 5% iron it is common to find iron in many geographical areas around the globe (29).

The iron occurs naturally in the aquifer but levels in groundwater can be increased by dissolution of ferrous borehole and hand pump components. Iron dissolved in groundwater is in the reduced iron II form. This form is soluble and normally does not cause any problems by itself. Iron II is oxidized to iron III on contact with oxygen in the air or by the action of iron related bacteria. Iron III forms insoluble hydroxides in water. These are rusty red and cause staining and blockage of screens, pumps, pipes, reticulation systems etc. If the iron hydroxide deposits are produced by iron bacteria then they are also sticky and the problems of stain and blockage are many times worse. The presence of iron bacteria may be indicated by rusty slime inside headwork’s, reduced water flow from the bore and unpleasant odor from water pumped from the bore, slimy deposits blocking main and lateral lines, severe staining on pavements, walls foliage (55).

Biological iron removal is a means of removing iron from groundwater within water filters. Microbiologists have known for many years that certain bacteria are capable of oxidizing and immobilizing iron. The bacteria responsible for the process appear to be natural inhabitants of the well environment (55).

Part 3: Manganese

Manganese is a transition metal. The transition metals are the large block of elements in the middle of the periodic table. The periodic table is a chart that shows how chemical elements are related to each other. The transition metals make up Rows 4 through 7 in Groups 3 through 12 of the periodic table. Many of the best known and most widely used metals are in this group of elements (44).

It took chemists some time to discover the difference between manganese and iron. The two metals have very similar properties and often occur together in the Earth's crust. The first person to clearly identify the differences between the two elements was Swedish mineralogist Johann Gottlieb Gahn (1745-1818) in 1774 (44).

Manganese is the twelfth most abundant transition element (1,060 parts per million of Earth's crust) with twenty-three known isotopes. Large nodules of manganese ore have been discovered on the ocean floor. The pure metal can be obtained by reduction of the oxide with sodium or by electrolysis (38).

Manganese metal is used in many alloys. In conjunction with aluminum and copper it forms strong ferromagnetic alloys. Ninety-five percent of all manganese ores are used in the production of steel. The element improves the strength and toughness of steel by acting as a scavenger of sulfur, preventing the formation of FeS, which induces brittleness (56).

2.8 Chemical reactions

Manganese is very chemically active and it has the ability to react with various elements in chemistry which we see on a day to day basis that allow for its diversity in function and uses. Because of its valence electron configuration, it allows us to use it in different and unique ways that typically other elements cannot be used in (57).

Reaction of manganese with air (with $N2$ & $O2$):

Manganese is not particularly reactive to air, despite it being a little more electropositive than its neighbors in the periodic table. The surface of manganese lumps oxidize to a minor extent. When finely divided, manganese metal burns in air. It burns in oxygen to form the oxide $Mn3O4$ and in nitrogen to form the nitride $Mn3N2$.

$3Mn(s) + 2O2 (g) \rightarrow Mn3O4(s)$

$3Mn(s) + N2 (g) \rightarrow Mn3N2(s)$ (47)

Reaction of manganese with water:

Manganese does not react with water under normal conditions (58).

Reaction of manganese with the halogens:

Manganese burns in chlorine to form manganese (II) chloride, $MnCl_2$. It also reacts with bromine or iodine to form respectively manganese (II) bromide, $MnBr_2$, or manganese (II) iodide, MnI_2. The corresponding reaction between the metal and fluorine, F_2 affords the fluorides manganese (II) fluoride, MnF_2 and manganese (III) fluoride, MnF_3.

$Mn(s) + Cl_2 (g) \rightarrow MnCl_2(s)$

$Mn(s) + Br_2 (g) \rightarrow MnBr_2(s)$

$Mn(s) + I_2 (g) \rightarrow MnI_2(s)$

$Mn(s) + F_2 (g) \rightarrow MnF_2(s)$

$2Mn(s) + 3F_2 (g) \rightarrow 2MnF_3(s)$ (58)

Reaction of manganese with acids:

Manganese metal dissolves readily in dilute sulphuric acid to form solutions containing the aquated Mn (II) ion together with hydrogen gas, H_2. In practice, the Mn (II) is present as the virtually colorless complex ion $[Mn (OH_2)_6]^{2+}$.

$Mn(s) + H_2SO_4 (aq) \rightarrow Mn^{2+} (aq) + SO_4^{2-}(aq) + H_2 (g)$ (24)

2.9 Biological role of Manganese

- Manganese is an essential trace element.
- Manganese activates the enzyme alkaline phosphates' in bone formation and the enzyme organase in urea formation.
- Manganese deficiency can cause deformation of the skeleton and sterility.
- In plants manganese ions activate carboxylase. (59)
- It accumulates in mitochondria and is essential for their function. The manganese transport protein, transmanganin, is thought to contain Mn (III). Several metalloenzymes are known: arginase, pyruvate carboxylase and superoxide dismutase (60).
- Humans excrete roughly 10 kg of urea per year, these results from the hydrolysis of arginine by the enzyme arginase found on the liver which is the final step of the urea cycle (60).
- The oxygen-evolving complex (OEC) is a part of photosystem II contained in the thylakoid membranes of chloroplasts; it is responsible for the terminal photooxidation of water during the light reactions of photosynthesis (45)

2.10 Mechanism of manganese in ground water

Manganese (Mn) is a metal that occur naturally in soils, rocks and minerals. In the aquifer, groundwater comes in contact with these solid materials dissolving them, releasing their constituents, including Mn, to the water. At concentrations approaching 0.05 mg/L Mn, the water’s usefulness may become seriously impacted, e.g., there may be a metallic taste to the water and staining of plumbing fixtures may become common. At these concentrations, however, the health risk of dissolved Mn in drinking water is insignificant. The extent to which Mn dissolve in groundwater depends on the amount of oxygen in the water and, to a lesser extent, upon its degree of acidity, i.e., its pH (61)

If the groundwater is oxygen poor, manganese will dissolve more readily, particularly if the pH of the water is on the low side (slightly more acidic). Dissolved oxygen content is typically low in deep aquifers, particularly if the aquifer contains organic matter. Decomposition of the organic matter depletes the oxygen in the water .Under these conditions, dissolved manganese may form blackish particulates in the water and cause similar colored stains on fixtures (61).

Treatment for dissolved manganese takes advantage of the natural process of oxidation, through the use of aeration, i.e., injecting air into the water prior to the tap to precipitate manganese from the water. Chlorine is also an effective oxidizer and will cause manganese to precipitate, plus it provides protection from microbial contaminants. Usually a physical filter follows the treatment so that the particles will not exit through the tap. Additional treatment methods include greensand filters and water softeners (61).

The amount of dissolved manganese in groundwater may vary seasonally for a given well. Usually this is associated with an influx of oxygenated water from the surface during periods of high recharge. This oxygenated water will prevent the manganese from dissolving and the water pumped from the well will have low concentrations of this metal. After the oxygen in the recharge water has been consumed, manganese will again be dissolved and the water will have dissolved manganese characteristics (61).

The reducing conditions found in groundwater and some lakes and reservoirs favor high manganese levels; concentrations up to 1300 µg/l in neutral groundwater and 9600 µg/l in acidic groundwater have been reported (ATSDR, 2000). The National Water Quality Assessment Program data indicate that the 99th-percentile level of manganese in groundwater (5600 µg/l) is generally higher than that in surface waters (62).

CHAPTER 3: ARSENIC CONTAMINATION IN BANGLADESH

Arsenic poisoning has emerged as a fresh blow to Bangladesh, a country of 130 million populations, known as a land of frequent natural calamities. Recent surveys showed that about 80 million people of the country are living under the risk of Arsenic poisoning as the groundwater of a vast region contaminated with Arsenic the Arsenic pollution is not only causing serious health hazard to the people, but also affecting the environment and creating social problems (63).

Arsenic poisoning was first detected in Bangladesh in 1993 by the Department of Public Health Engineering (DPHE). But the fact remained behind the screen till 1996. According to the latest surveys conducted at both Government levels, at least 53 out of the total 64 districts of Bangladesh are affected with Arsenic pollution (63).

More than 2 million Tube-wells are presently being used as the source of drinking water in Bangladesh. Out of those, only 50,000 have so far been brought under investigation by various Government and non-Government agencies. The rest are still beyond the survey. The actual picture of the severity of Arsenic pollution is yet to be revealed as the entire country could not be surveyed till now (63).

The Arsenic poisoning has mainly been detected through testing samples of tube-well water and human tissues-hair, nail, skin and urine. Regular intake of Arsenic at higher level through food and drinking water causes various diseases, especially skin diseases. Arsenic causes both physical and intellectual damage to the human beings.

Since the very beginning, Dhaka Community Hospital (DCH) has been playing the leading role in school of Environmental Studies (SOES) of Jadavpur University, Calcutta is actively collaborating with the DCH in the survey and research works in this field. On the part of Government, National Institute of Preventive and Social Medicine (NIPSOM), an organization engaged in health related activities, and the Department of Public health Engineering (DPHE) has taken the key role to identify the Arsenic patients and determine the extent and severity of the problem. In 1994, a national committee was formed to deal with Arsenic problem. Country's leading experts and the representatives of Environment Department, water Development Board, universities, WHO and UNICEF. In 1996 the Government abolished the national committee and formed three new committees. These are the national steering committee headed by Health Minister, Arsenic Technical Commute and Scientific Research Committee. But the Progress of Government activities to check Arsenic pollution is not satisfactory. Millions of people are facing the danger of Arsenic pollution and a large number of them are still in darkness about the problem (63).

3.1 Water supply scenario

Bangladesh is located in the midst of one of the world's largest river systems. Bangladesh has a large area of surface water in the form of the major Padma (Ganges), Jamuna (Brahmaputra) and Meghna Rivers and their tributaries (64). Although this vast amount of water provides a living for almost 1/3 of the country's population, the water quality is poor and the abundance of this water does little to meet the drinking needs of the people. Drinking water in Bangladesh is not largely a river based water purification system but instead, the most crucial source of drinking water remains groundwater (65).

Availability of water resources in Bangladesh has an enormous excess of surface water during the summer monsoon (June to October) and relative scarcity towards the end of the dry season in April and May. Internal renewable water resources are about 105 km^3 per year, while inflowing trans- boundary rivers provide another 1,100 km^3 annually (average 1977-2001) (66).

3.1.1 Aquifer types and hydrological situation

The surface geology of Bangladesh is dominated by young (Holocene) alluvial and deltaic sediments deposited by the major river systems of the Bengal Basin, much of it deposited within the last 6000–10000 years. These deposits are several hundreds of meters thick and the Basin has been one of the most rapidly accreting delta systems in the world. Surface sediments in the north include mainly Coarse-grained mountain-front alluvial fan deposits (the 'Tista Fan'). Sediments in much of lowland central Bangladesh is alluvial sands and silts, while in the south closest to the coast, the sediments are predominantly deltaic silts and clays (**figure 3.1**). The deposits become generally more fine-grained towards the lowland south.

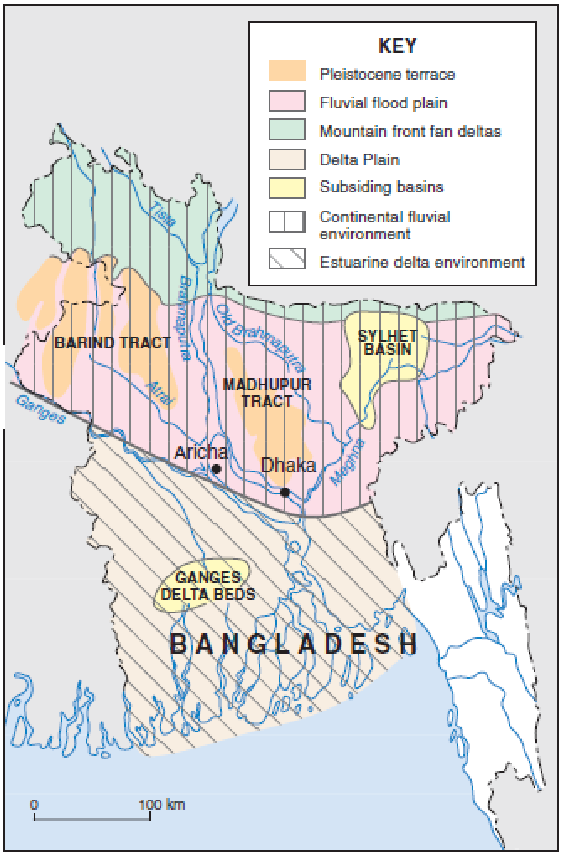


Figure- 3.1: Simplified geology and geomorphology of Bangladesh (BGS and DPHE, 2001) (67)

The surface geology of north-central Bangladesh comprises the so-called ‘Barind and Madhupur Tracts’ (**figure 3.1**). These are up-faulted terraces of older (Pleistocene) sediments which are more strongly weathered than the surrounding alluvium. The sediments present within the Barind and Madhupur Tracts (which include at depth the Dupi Tila Formation, a productive sandstone aquifer) also underlie much of the younger alluvial sediment at depths of the order of 150–200 m or more. However, the distribution and extent of the older sediments at depth is as yet poorly known. The geology of the Chittagong Hill Tracts in south- east Bangladesh is distinctive: sediments exposed in this region are dominantly older (Tertiary) folded and indurate deposits of sandstone, silt and limestone (67).

A baseline study of aquifers was conducted by Bangladesh Water Development Board under the UNDP assistance on groundwater survey and investigation in the country (UNDP, 1982). The study included drilling of deep (300 m) and shallow (100 m) exploratory boreholes, aquifer tests, and periodic monitoring of groundwater level and quality at selected locations in the country. **Figure 3.2** shows E-W cross section of the southern part of the country. Geological formations show significant variations and lateral continuity cannot easily be established. Based on the subsurface litho logical, water level, and water quality information, the UNDP report identified three aquifers in the present area of study (this classification is reconsidered later in this report based on the isotopic results) (68).

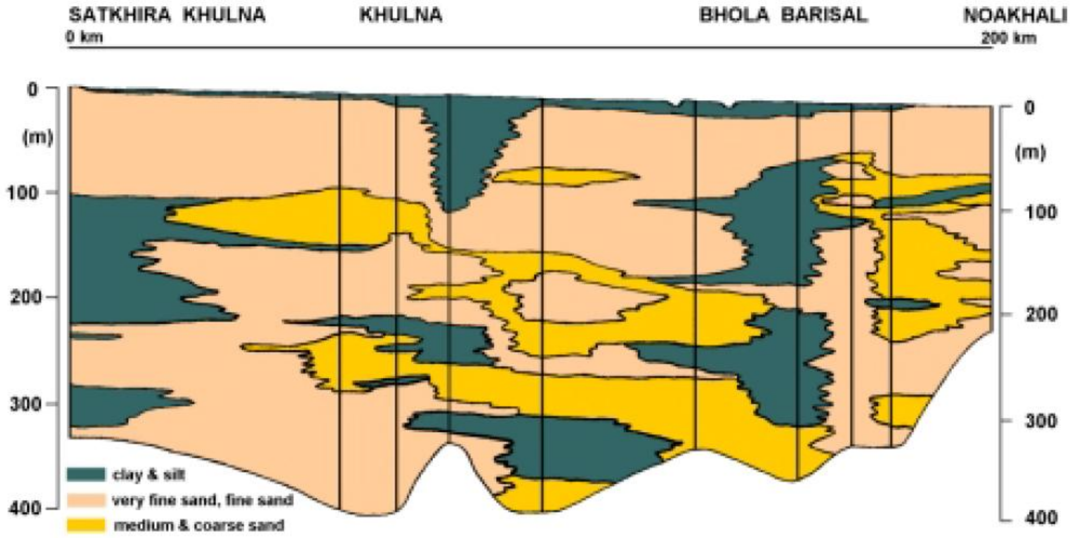


Figure -3.2: E-W litho logical cross section across the coastal areas of Bangladesh

(a) First or Composite Aquifer

This aquifer exists within 50 m below ground level (bgl). It consists of very fine to fine sand occasionally inter bedded with silt and clay. The thickness of such shallow, unconfined aquifer varies from 2 - 6 m. Dug wells and hand pumped wells are generally used to withdraw water from these aquifers (68).

(b) Second or Shallow Aquifer

This aquifer exists between approximately 50 - 150 m bgl and consists of medium to coarse sand with occasional fine sand and silt. The aquifer thickness varies from 20 to 80 m. Thin beds of clay occur infrequently within this aquifer. The estimated transmissivity of this main aquifer ranges from 820 m2/d in the southeastern parts to 3200 m2/d in the northwestern parts (68).

(c) Third Aquifer

This aquifer occurs at or more than about 200 m bgl. It generally consists of fine to medium sands and is mostly confined to semi-confined in nature. This aquifer is exploited mainly in the coastal zone. Beneath Potuakhali, Barisal and Pirojpur district, an aquifer of coarse to medium sand is encountered at depth. The thickness of this fresh aquifer is variable. So far limited numbers of tube wells are installed in this aquifer to cater to the needs of Pouroshava water supply and rural water supply (68).

High-Arsenic Shallow Aquifers

The aquifers affected by arsenic are quaternary, largely Holocene, alluvial and deltaic sediments associated with the Ganges-Brahmaputra-Meghna river system. These occur as the surface cover over a large part of Bangladesh (4). Groundwater from the Holocene aquifers contains arsenic at concentrations up to around 2,300 µg L-1, though concentrations span more than four orders of magnitude (BGS and DPHE 2001) (67). Van Geen, Zheng, and others (2003) (8) found concentrations in the range <5-860 µg L-1 in groundwater's from Araihazar, east of Dhaka.

Several surveys of the groundwater have shown a highly variable distribution of arsenic, both laterally and with depth. This means that predictability of arsenic concentrations in individual wells are poor and each well used for drinking water needs to be tested. Nonetheless, on a regional scale, trends are apparent, and the worst-affected areas with the highest average arsenic concentrations are found in the southeast of the country, to the south of Dhaka (**figure 3.3**). Here, in some districts, more than 90% of shallow tube wells tested had arsenic concentrations >50 µg L-1. Some areas with low overall arsenic concentrations have localized hotspots with locally high arsenic concentrations. That of the Chapai Nawabganj area of western Bangladesh is a notable example (**figure 3.4**), where the median concentration in groundwater from Holocene sediments was found to be 3.9 µg L-1 but with extremes up to 2,300 µg L-1 concentrated in a small area of around 5 x 3 km. Overall, the BGS and DPHE survey of shallow ground waters found that 27% exceeded 50 µg L-1 and 46% exceeded 10 µg L-1 (4).

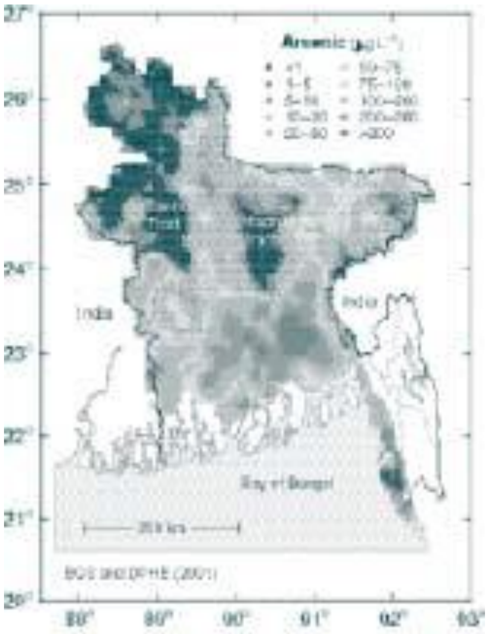


Figure- 3.3: Smoothed Map of Arsenic Distribution in Groundwater from Bangladesh

Note: Samples are from tube wells <150 m deep. (BGS and DPHE 2001) (67).

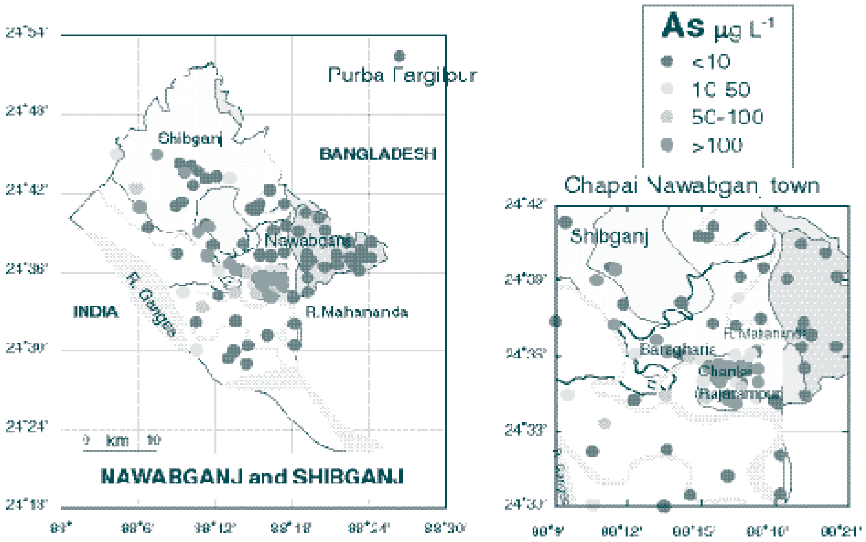


Figure- 3.4: Maps of the Distribution of Arsenic in Shallow Groundwater from the Chapai Nawabganj Area, Northwest Bangladesh

Note: Samples are from tube wells <150 m deep (BGS and DPHE 2001) (67)

Investigation of the depth ranges of affected tube wells suggests that concentrations are low in Ground water from the top few meters of the aquifers close to the water table, but that they increase markedly over a short depth range. This is demonstrated by the profile of groundwater compositions in a piezometer (10 cm diameter, 40 m deep) in Chapai Nawabganj, northwest Bangladesh. Arsenic concentration was relatively low (17 µg L-1) at 10 m depth but increased to values in the range 330-400 µg L-1 over the depth interval 20-40 m (BGS and DPHE 2001) (**figure 3.5**) (67)

The largest range and highest concentrations of arsenic are typically found at around 15-30 m depth below surface, although the depth ranges of the peaks vary from place to place. **Table 3.1** shows the frequency distribution of arsenic concentrations with depth for all analyzed samples from the BGS and DPHE (2001) survey (67).

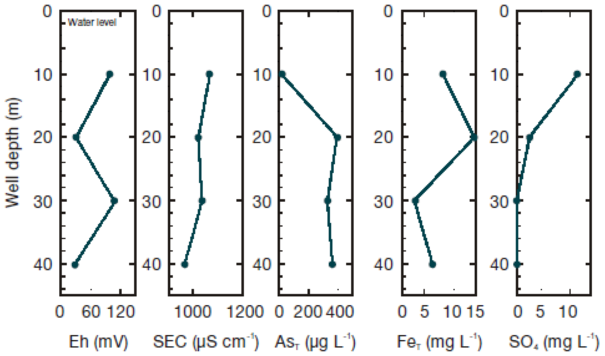
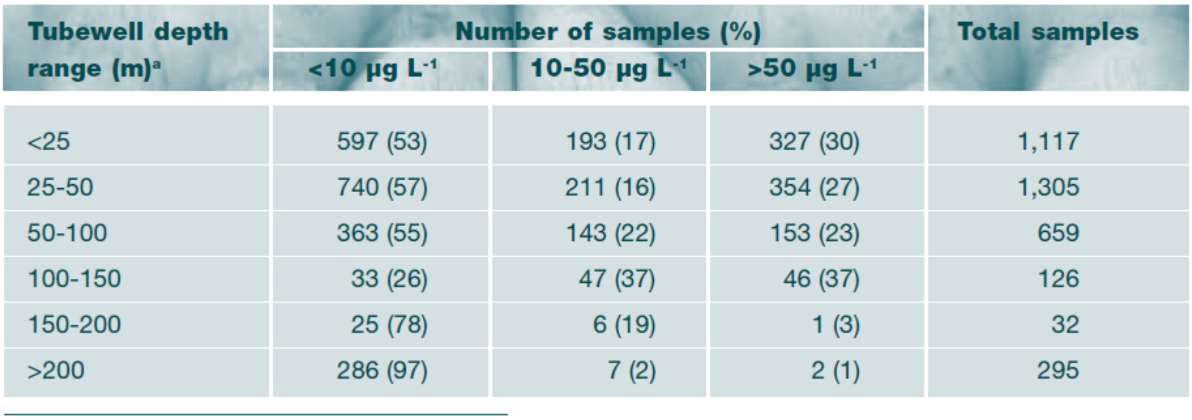


Figure-3.5: Variation in Concentration of Arsenic and Other Elements with Depth in a Purpose-Drilled Piezometer in Chapai Nawabganj, Northwest Bangladesh (BGS and DPHE 2001) (67).

Table -3.1: Frequency Distribution of Arsenic in Groundwater from Tube wells from Quaternary Alluvial Aquifers in Bangladesh



Tubewell depth range (m)[a]	Number of samples (%)			Total samples
	<10 $\mu g\ L^{-1}$	10-50 $\mu g\ L^{-1}$	>50 $\mu g\ L^{-1}$	
<25	597 (53)	193 (17)	327 (30)	1,117
25-50	740 (57)	211 (16)	354 (27)	1,305
50-100	363 (55)	143 (22)	153 (23)	659
100-150	33 (26)	47 (37)	46 (37)	126
150-200	25 (78)	6 (19)	1 (3)	32
>200	286 (97)	7 (2)	2 (1)	295

Depth of intake of groundwater is difficult to determine and may be from several horizons at differing depths. (BGS and DPHE 2000) (67).

Low-Arsenic Aquifers

The BGS and DPHE (2001) (67) map (**figure 3.3**) demonstrates the low overall arsenic concentrations of groundwater from coarser sediments in the Tista Fan of northern Bangladesh. Low concentrations are also found in ground waters from aquifers in the older (Pleistocene) uplifted plateaux of the Barind and Madhupur tracts (north-central Bangladesh). These usually have concentrations less than 10 µg L-1 and often significantly less. Similar results for these areas have also been obtained by other workers (for example van Geen, Zheng, and others 2003) (69). Groundwater from these areas is therefore expected to be normally safe from the point of view of arsenic (4).

Arsenic concentrations also appear to be mostly low in groundwater from older ("deep") aquifers which occur in some areas below the Holocene deposits. The stratigraphy of the deep aquifers of Bangladesh is poorly understood at present, but where studied, the aquifers with low-arsenic groundwater appear to be of Pleistocene age (BGS and DPHE 2001; van Geen, Zheng, and others 2003) (5&8). Limited investigations indicate that they are miner logically distinct from the overlying Holocene deposits. They are typically browner in color and relatively oxidized. The deep aquifer sediments are likely to be akin to the aquifers below the Barind and Madhupur tracts, which occur at shallower depths because of tectonic uplift (4).

Although these sediments are often referred to as the "deep aquifer", the definition of "deep" varies from place to place and between organizations and the subject has become rather confused. However, depth ranges for the low-arsenic groundwater are usually at least 100-200 m. Recent data produced by the BAMWSP for groundwater samples from 60 upazilas across Bangladesh found that out of 7,123 samples from tube wells >150 m deep, 97% had arsenic concentrations <50 μg L-1 (percentage <10 μg L-1 unspecified; BAMWSP website(4).

3.1.2 Drinking water supply scenario

Even though Bangladesh is famous, from ancient times, for its abundance of water from various sources, one of the major problems that the country has been suffering for decades is the scarcity of safe drinking water. Prior to independence in 1971, surface waters from ponds, lakes, and rivers, and to a lesser degree, groundwater from dug wells, were the traditional sources of drinking water for the people of Bangladesh. In coastal areas, rainwater for drinking has also been used on a limited scale for a long time. Despite the abundance of surface water, there has always been the question of quality. The surface water sources are being misused as a sink for highly polluting wastewaters from domestic as well as industrial sources. Pollution loads far exceeding dispersion capacities cause severe degradation of water quality. This microbiologically unsafe surface water, with its bacteriological and fecal contamination, extracted a heavy toll on human lives. Every year, hundreds of thousands of people, particularly children, died of cholera, diarrhea, dysentery, typhoid, and other water-borne diseases (70).

3.1.3 Evolution of groundwater as the main source of potable water

Sources of drinking water supply in Bangladesh rely mainly on groundwater. In rural areas, more than 97% of the population relies on groundwater for its drinking water supply. In Dhaka, 82% of the water supply is abstracted from groundwater that is free of arsenic, while three surface water treatment plants provide the remaining 18%.Groundwater is being severely depleted in Dhaka where the groundwater levels are dropping at two to three meters every year. The city’s water table has sunk by 50 meters in the past four decades and the closest underground water is now over 60 meters below ground level. The Asian Development Bank estimated in 2007 that by 2015 a severe supply shortage would occur if the utility did not reduce groundwater abstraction (66).

The poor surface water quality compelled the water supply authorities and agencies to develop a groundwater supply system in Bangladesh. After the independence of the country, in the early 1970s, the Department of Public Health Engineering (DPHE) of the government of Bangladesh, with assistance from the United Nations Children’s Fund (UNICEF), embarked on a massive program to bore holes to tap into groundwater they believed would not be contaminated. The program sought to install hundreds of thousands of groundwater wells, known as tube wells, to provide safe drinking water for the people of Bangladesh. Initially, the community did not share any cost for sinking of tube wells; but in the course of time, to ensure improved maintenance, cost sharing principles were adopted for the program (71). At present, there are approximately 4.5 million public tube wells (installed by government departments) as part of the total of 9 million tube wells in Bangladesh (72).

Bangladesh achieved a remarkable success, at least initially, through this tube well initiative. An estimated 97 percent of the rural population received access to this bacteriologic ally safe tube well water. This made a significant contribution to decreasing the infant mortality rate, halving it over a period of thirty-six years, from 151 per thousand in 1960 to 83 per thousand in 1996 (73). The under-five mortality rate also decreased significantly.

3.1.4 Existing water supply system from sources to users in rural areas

The type of hand pump technology suitable for a particular area depends on the groundwater level, water quality and hydro geological conditions. Arsenic safe groundwater is generally found in shallow aquifers in north-western region, and in pockets/strata in arsenic contaminated areas where conventional shallow tube wells are producing arsenic-safe water. Deep aquifers separated from shallow contaminated aquifers by impermeable layers can be a dependable source of arsenic safe water. The deeper aquifers without any separating aquiclude/clay layer may initially produce arsenic safe water but vulnerable to contamination. The important alternative water supply technologies include (74):

- Shallow shrouded tube well (SST) and Very shallow shrouded tube well (VSST)
- Deep Tube well;
- Dug Well; and
- Infiltration galley (74)

<u>Shallow Shrouded Tube well (SST) and Very Shallow Shrouded Tube well (VSST)</u>
In many areas, groundwater with low arsenic content is available in shallow aquifers composed of fine sand at shallow depth. This may be due to accumulation of rainwater in the topmost aquifer or dilution of arsenic contaminated groundwater by fresh water recharging each year by surface and rain waters. However, the particle size of soil and the depth of the aquifer are not suitable for installing a normal tube well. To get water through these very fine-grained aquifers, an artificial sand packing is required around the screen of the tube well. This artificial sand packing, called shrouding, increases the yield of the tube well and prevents entry of fine sand into the screen (74).

These low-cost hand pump tube well technologies have been designed and installed in the coastal areas to collect water from very shallow aquifers formed by displacement of saline water by fresh water. The SST/VSSTs can be convenient methods for withdrawal of fresh water in limited quantities. Over-pumping may yield contaminated water. Installation of low capacity pumps may prevent over exploitation of shallow aquifers. The systems may be considered suitable for drinking water supply for small settlements where water demand is low. A shallow/Very shallow tube well is shown in **figure 3.6** (74). The department of Public Health Engineering has sunk a total of 5,904 VSST/SST to provide water to 0.44 million people in coastal areas (DPHE, 2000) (37).

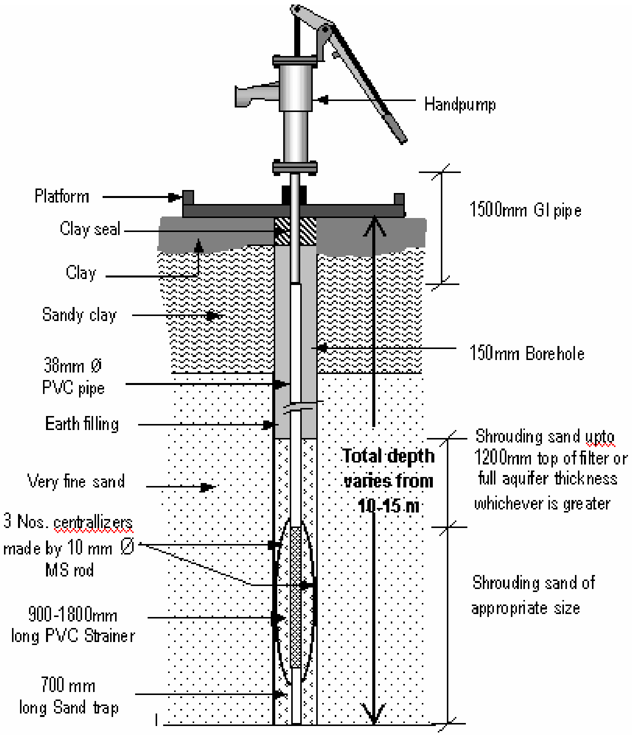


Figure- 3.6: Shallow and Very Shallow Shrouded Tubewell (37)

In the high salinity coastal areas it has been found that fresh water is available in small pockets of shallow aquifers composed of fine sand at 15 to 20m depth. This is due to accumulation of rainwater in the upper aquifer. However, the particle size of soil and the thickness of the aquifer are not suitable for installing a normal tube-well. To get water through these very fine-grained aquifers, an artificial sand packing is required around the screen of the tube well. This artificial sand packing is called shrouding increase the yield of the tube well and prevents entry of fine sand into the screen. The 15 to20m deep tube wells, installed as above are called Shallow Shrouded Tube well (SST) (13). The SSTs are fitted with No. 6 hand pumps operating under suction mode (DPHE, 2000) (37).

Very shallow shrouded tube well (VSST) is a low-cost hand pump tube well about 8m in depth with a short strainer depending on the aquifer thickness and shroud with coarse sand. The VSST is designed to collect water from very shallow aquifers formed by displacement of saline water by a continuous flow of accumulated fresh water. The lenses of fresh water formed by this process are found beneath old ponds in coastal areas. In many places, ponds dry up but fresh water in shallow aquifers remains beneath the pond. Immobile preserved aquifers are also found at shallow depths at various locations in the coastal area. A VSST is a convenient method for withdrawal of fresh water in limited quantities. In many places, the water produced by VSSTs becomes saline due to rising of water caused by over-pumping. Installation of low capacity pumps may prevent over exploitation of shallow aquifers. The system is considered suitable for drinking water supply for small settlements where water demand is low (74). A VSST is not different from an SST except in the depth of well (DPHE, 2000) (37).

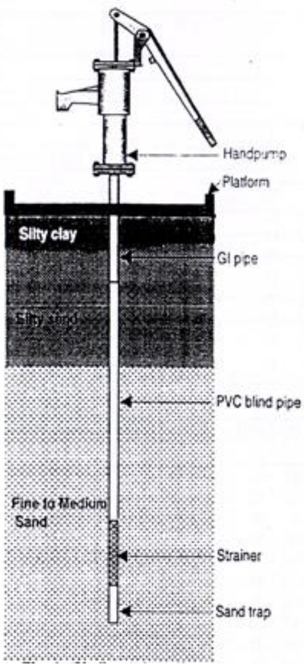
Deep Tube well

The deep aquifers in Bangladesh have been found to be relatively free from arsenic contamination. The aquifers in Bangladesh are stratified and in some places the aquifers are separated by relatively impermeable strata. In Bangladesh two types of deep tube wells are constructed, manually operated small diameter tube well similar to shallow tube wells and large diameter power operated tube wells called production well. Deep tube wells installed in those protected deeper aquifers are producing arsenic safe water. The BGS and DPHE study has shown that only about 1% deep tube well having depth greater than 150 m are contaminated with arsenic higher than 50m g/L and 5% tube well have arsenic content above 10m g/L (BGS and DPHE, 2001). Sinking of deep tube wells in arsenic affected areas can provide safe drinking water but replacement of existing shallow tube wells by deep tube wells involves huge cost. Some of the deep tube wells installed in acute arsenic problem areas have been found to produce water with increasing arsenic content. Post-construction analysis shows that arsenic contaminated water could rapidly percolate through shrouded materials to produce elevated levels of arsenic in deep tube well water (74).

Shallow Tubewell : In shallow Tubewell technology, handpumps are operated in a suction mode. A suction pump draws water from a shallow depth by creating a vacuum in the suction pipe. The suction handpump can practically extract water from a depth of 7.5m from ground level.

Conventional Deep-set Hand Pump : Shallow tubewells operated under the suction mode are not able to withdraw water in low water table areas. The low water table area is increasing with the excessive withdrawal of groundwater for different purpose.

Water can be abstracted from a depth beyond the suction limit using intermediate technology. Conventional Deep-set handpumps can abstract water from depth of 30 m from the ground level, depending on the technological advancement of the handpump. Usually Conventional Deep-set hand pump are designed to draw water from 20m from ground level in the country.



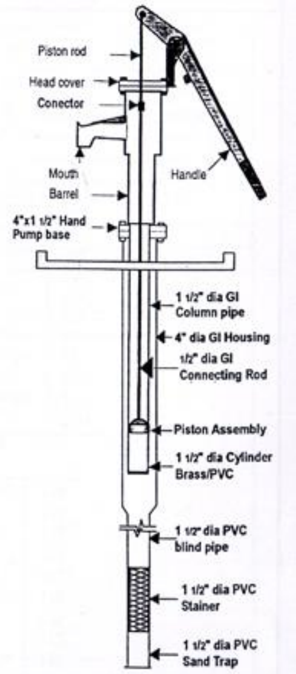
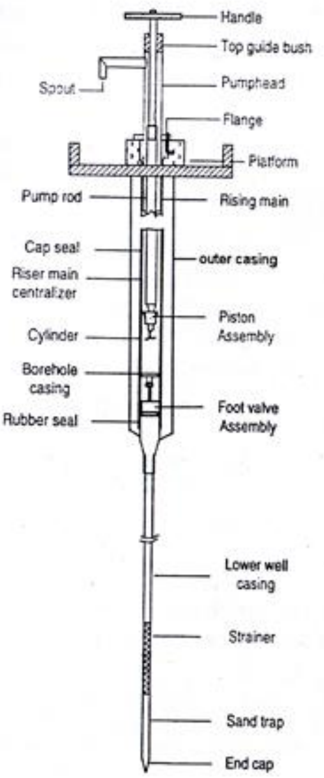


Figure-3.7: Shallow tube well (37) **Figure-3.8: Conventional deep-set pimp** (37)

Tara handpump Tubewell : In Bangladesh, the groundwater table during monsoon in most places remains within the suction limit. But due to extensive use of groundwater for irrigation, the groundwater table is falling & in the dry season it goes beyond the suction limit in many part of the country. As a result Shallow Tubewell is inoperable in dry season. To overcome the problems Conventional Deep-set Hand Pump was developed and used. But due to cumbersome maintenance problem and corrosion of GI an MS connecting rod under research and development activities the Tara handpump has been developed in Bangladesh to tap water from up to 15 m below ground surface. The Tara handpump is a force mode pump in which the piston of the pump operates below the static water level to eliminate the limitation of suction mode handpumps to operate in low water table areas. The cylinder of the pump is set at 18m below the ground surface and a PVC hollow pump rod set vertically operates the piston. The pump is operated by a person holding the handle fitted at the top end of the pump rod and pulling and pushing the pump rod vertically. Due to leakage in the PVC column pipe, the tubewell become permanently chocked within shorter time frame. To overcome the problem, extractable Tara Hand Pumps have been introduced.



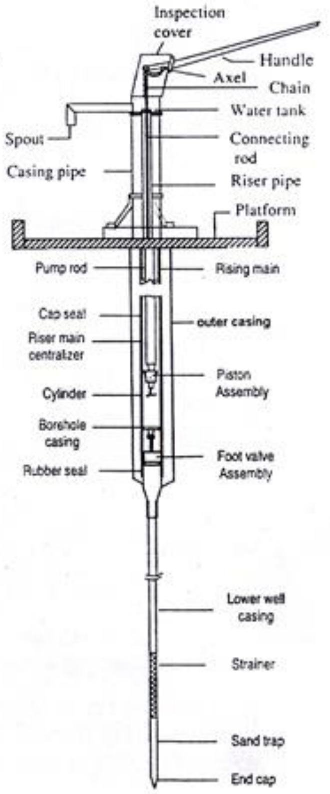
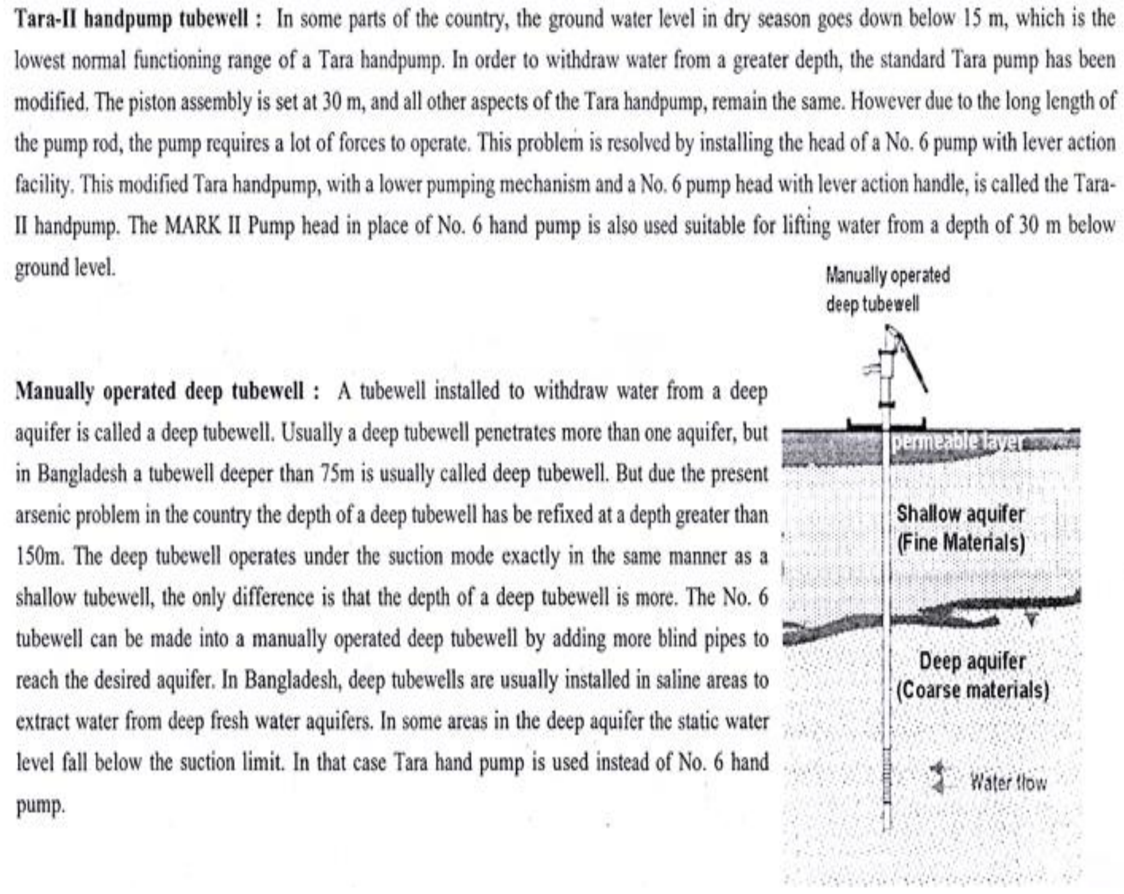


Figure-3.9: Tara hand pump tube well (extractable mode) (37), **Figure-3.10: Tara-II hand pump tube well** (37)



Tara-II handpump tubewell : In some parts of the country, the ground water level in dry season goes down below 15 m, which is the lowest normal functioning range of a Tara handpump. In order to withdraw water from a greater depth, the standard Tara pump has been modified. The piston assembly is set at 30 m, and all other aspects of the Tara handpump, remain the same. However due to the long length of the pump rod, the pump requires a lot of forces to operate. This problem is resolved by installing the head of a No. 6 pump with lever action facility. This modified Tara handpump, with a lower pumping mechanism and a No. 6 pump head with lever action handle, is called the Tara-II handpump. The MARK II Pump head in place of No. 6 hand pump is also used suitable for lifting water from a depth of 30 m below ground level.

Manually operated deep tubewell : A tubewell installed to withdraw water from a deep aquifer is called a deep tubewell. Usually a deep tubewell penetrates more than one aquifer, but in Bangladesh a tubewell deeper than 75m is usually called deep tubewell. But due the present arsenic problem in the country the depth of a deep tubewell has be refixed at a depth greater than 150m. The deep tubewell operates under the suction mode exactly in the same manner as a shallow tubewell, the only difference is that the depth of a deep tubewell is more. The No. 6 tubewell can be made into a manually operated deep tubewell by adding more blind pipes to reach the desired aquifer. In Bangladesh, deep tubewells are usually installed in saline areas to extract water from deep fresh water aquifers. In some areas in the deep aquifer the static water level fall below the suction limit. In that case Tara hand pump is used instead of No. 6 hand pump.

Figure-3.11: Manually operated deep tube-well (37)

However, there are many areas where the separating impermeable layers are absent and aquifers are formed by stratified layers of silt and medium sand. The deep tube wells in those areas may yield arsenic safe water initially but likely to increase arsenic content of water with time due to mixing of contaminated and uncontaminated waters. Again the possibility of contamination of deep aquifer by inter-layer movement of large quantity of groundwater cannot be ignored. If the deep aquifer is mainly recharged by vertical percolation of contaminated water from the shallow aquifer above, the deep aquifer is likely to be soon contaminated with arsenic. However, recharge of deep aquifer by infiltration through coarse media and replenishment by horizontal movement of water are likely to keep the aquifer arsenic free even after prolong water abstraction. Since many people in the rural area still use surface water for cooking, installation of deep tube well in an area can be a source of drinking water supply for a large number of people (74).

In general, permeability, specific storage capacity and specific yield usually increase with depth because of the increase in the size of aquifer materials. Experience in the design and installation of tube wells shows that reddish sand produces best quality water in respect of dissolved iron and arsenic. The reddish color of sand is produced by oxidation of iron on sand grains to ferric form. Which will not release arsenic or iron in groundwater, rather ferric iron coated sand will adsorb arsenic from ground water. Dhaka water supply, in spite of arsenic contamination around is probably protected by its red colored soil. Hence, installation of tube well in reddish sand, if available, should be safe from arsenic contamination (74).

Some areas of the coastal region of Bangladesh are very suitable for construction of deep tube well. Department of Public Health Engineering has sunk a total of 81,384 deep tubes well mainly in the coastal area to provide safe water to 8.2 million people (DPHE, 2000). The identification of areas having suitable deep aquifers and a clear understanding about the mechanism of recharge of these aquifers are needed to develop deep tube well based water supply systems in Bangladesh (74).

Dug Well

Dug well is the oldest method of groundwater withdrawal for water supplies. The water of the dug well has been found to be free from dissolved arsenic and iron even in locations where tube wells are contaminated. The mechanism of producing water of low arsenic and other dissolved minerals concentration by dug wells are not fully known. The following explanations may be attributed to the low arsenic content of dug well water (74):

- The oxidation of dug well water due to its exposure to open air and agitation during water withdrawal can cause precipitation of dissolved arsenic and iron.
- Dug wells accumulates groundwater from top layer of a water table which is replenished each year by arsenic safe rain and surface waters by percolation through aerated zone of the soil. The fresh recharges also have diluting effects on contaminated groundwater.
- The presence of air and aerated water in well can oxidize the soils around dug wells and infiltration of water into wells through this oxidized soil can significantly reduce the concentration of arsenic in well water (74).

Dug wells are widely used in many countries of the world for domestic water supply. The flow in a dug wells is actuated by lowering of water table in the well due to withdrawal of water. Usually no special equipment or skill is required for the construction of dug wells. For construction by manual digging, the wells should be at least 1.2 meters in diameter. Large diameter wells may be constructed for community water supplies. The depth of the well is dependent on the depth of the water table and its seasonal fluctuations. Wells should be at least 1m deeper than the lowest water table. Community dug wells should be deeper to provide larger surface area for the entry of water to meet higher water demand. Private dug wells are less that 10m deep but dug wells for communal use are usually 20-30 meters deep (74).

It is very difficult to protect the water of the dug well from bacterial contamination. Percolation of contaminated surface water is the most common route of pollution of well water. The upper part of the well lining and the space between the wall and soil require proper sealing. The construction of an apron around the well can prevents entry of contaminated used water at the well site by seepage into the well. Water in a dug well is very easily contaminated if the well is open and the water is drawn using bucket and rope. Satisfactory protection against bacteriological contamination is possible by sealing the well top with a watertight concrete slab. Water may be withdrawn by installation of a manually operated hand pump. Water in the well should be chlorinated for disinfection after construction. Disinfection of well water may be continued during operation by pot chlorination. A conventional dug well and a dug well with sanitary protection sunk in most common soil strata in Bangladesh are shown in **figure 3.12.** (74)

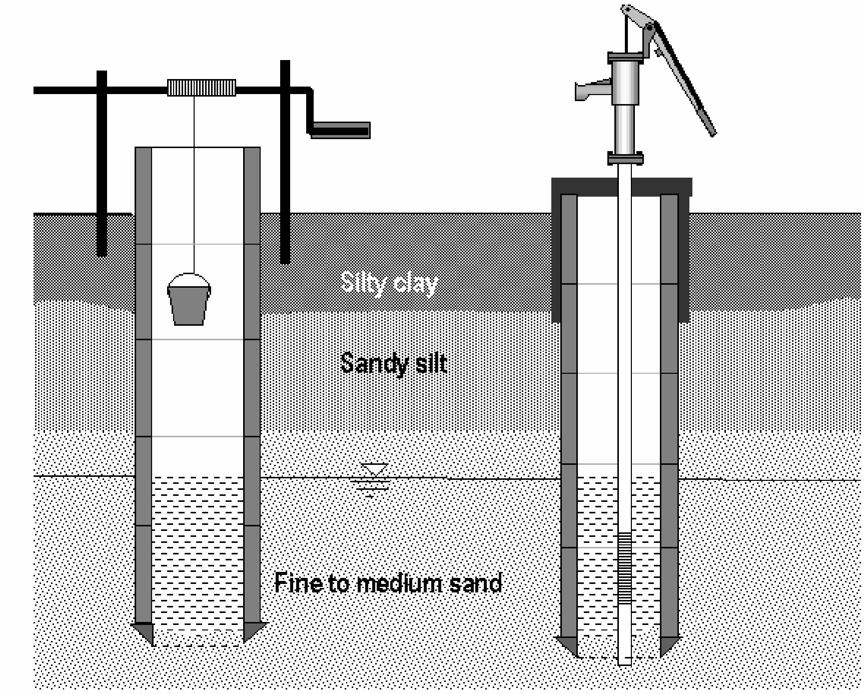


Figure-3.12(a): Conventional Dug well **Figure-3.12(b): Well with sanitary protection**

Figure-3.12: Conventional sanitary protected dug well (74)

In a completely closed dug well, the inflow of water is actuated by suction created due to withdrawal of water from the well. If aeration is controlling process of decontamination of well water, sanitary protection may affect the quality of well water. Extensive research to understand the mechanism of deracination of well water and the effects of sanitary protection of well on chemical quality of water is needed.

An open dug well and a closed dug well with a tube well for water collection are shown in **Figures 12(a) and 12(b)** respectively.

Picture-3.1: Water collection from a closed dug well by tube well (74)

Picture-3.2: Water collection from open dug well (74)

In the Chittagong hilly areas, Sylhet and northern parts of Bangladesh, construction of hand pump tube wells is not always possible due to adverse hydro-geological and stony soil conditions. Construction of protected dug wells can be a good option for water supply in these areas. A large number of dug wells are found operating in those areas. Dug wells are not successful in many areas of Bangladesh having thick impermeable surface layer. In areas with thick clayey soil, dug wells do not produce enough water to meet the requirements. Again in areas having very low water table, there may be difficulty in construction as well as withdrawal of water. Although tube wells in Bangladesh have replaced traditional dug wells in most places, still about 1.3 million people in both urban and rural areas are still dependent on dug well for drinking water supply in Bangladesh (74).

Infiltration Gallery / Well

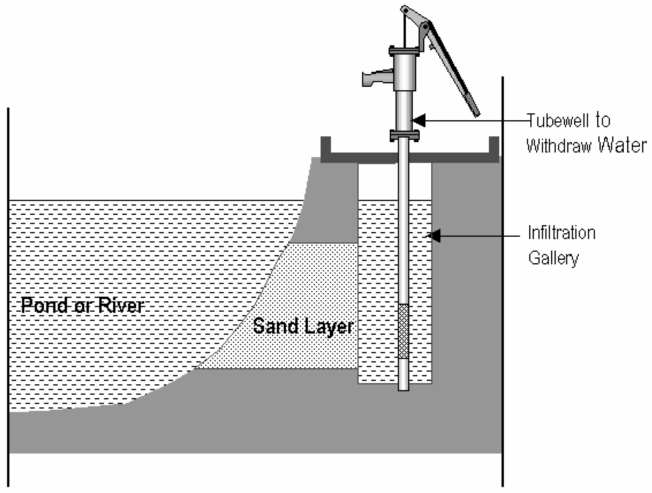


Figure-3.13: An Infiltration Gallery by the Side of a Surface Water Source (74)

Infiltration Galleries (IG) or wells can be constructed near perennial rivers or ponds to collect infiltrated surface waters for all domestic purposes. Since the water infiltrate through a layer of soil/sand, it is significantly free from suspended impurities including microorganisms usually present in surface water. Again, surface water being the main source of water in the gallery/well, it is free from arsenic. If the soil is impermeable, well graded sand may be placed in between the gallery and surface water source for rapid flow of water as shown in **figure 3.13** (74).

Experimental units constructed in the coastal area to harvest low saline surface waters show that water of the open infiltration galleries is readily contaminated. The accumulated water requires good sanitary protection or disinfection by pot chlorination. Sedimentation of clayey soils or organic matters near the bank of the surface water source interfere with the infiltration process and require regular cleaning by scrapping a layer of deposited materials (74).

Surface waters

Protected Ponds

A protected pond in a community can provide water for drinking purpose with minimal treatment and for other domestic uses without treatment. Traditionally, rural water supply, to a great extent, was based on protected ponds before and during early stage of installation of tube well. Sinking of tube wells under community water supply schemes in rural Bangladesh began in 1928. There are about 1,288,222 nos. of ponds in Bangladesh having an area of 0.114 ha per ponds and 21.5 ponds per mauza (BBS, 1997). About 17% of these ponds are derelict and probably dry up in the dry season. The biological quality of water of these ponds is extremely poor due to unhygienic sanitary practices and absence of any sanitary protection. Many of these ponds are made chemically and bio-chemically contaminated for fish culture. In order to maintain good quality water, a protected pond shall not receive surface discharges or polluting substances and should only be replenished by rain and groundwater infiltration (74).

Pond Sand Filters

A prospective option for development of surface water based water supply system is the construction of community type Slow Sand Filters (SSFs) commonly known as Pond Sand Filters (PSFs). It is a package type slow sand filter unit developed to treat surface waters, usually low-saline pond water, for domestic water supply in the coastal areas. Slow sand filters are installed near or on the bank of a pond, which does not dry up in the dry season. The water from the pond is pumped by a manually operated hand tube well to feed the filter bed, which is raised from the ground, and the treated water is collected through tap(s). It has been tested and found that the treated water from a PSF is normally bacteriologically safe or within tolerable limits. On average the operating period of a PSF between cleaning is usually two months, after which the sand in the bed needs to be cleaned and replaced. The drawing of a typical PSF is shown in **figure 3.14** (74).

The program initiated by DPHE with the construction of 20 experimental units in 1984 to utilize low saline pond water for water supply in the coastal area. Pond Sand Filters serve 200-500 people per unit. The PSF is being promoted as an option for water supply in arsenic affected areas (74).

The problems encountered are low discharge and difficulties in washing the filter beds. Since these are small units, community involvement in operation and maintenance is absolutely essential to keep the system operational. A formal institutional arrangement cannot be installed for running such a unit, community involvement in operation and maintenance is the key issue in making the system work. By June 2000, DPHE has installed 3,710 units of PSF, a significant proportion of which remains out of operation for poor maintenance (74).

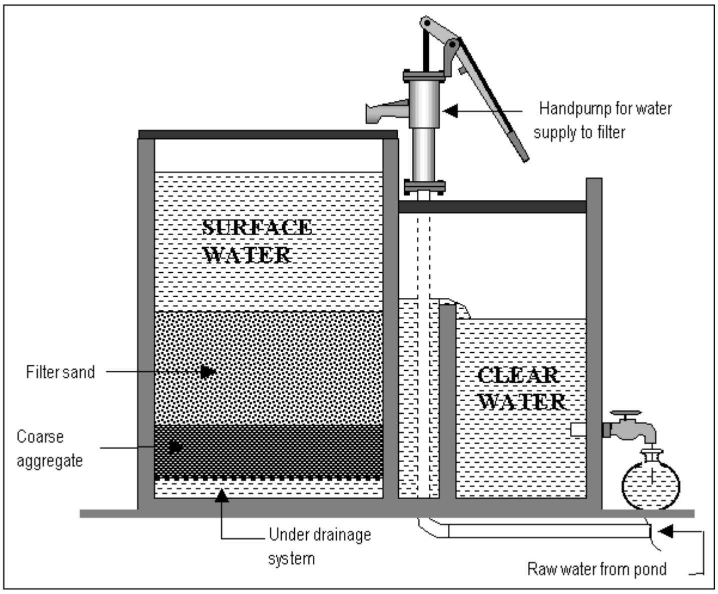


Figure-3.14: Pond Sand Filter for Treatment of Surface Water (74)

The PSF is a low-cost technology with very high efficiency in turbidity and bacterial removal. It has received preference as an alternative water supply system for medium size settlements in arsenic affected areas and areas. Although PSF has very high bacterial removal efficiency, it may not remove 100% of the pathogens from heavily contaminated surface water. In such cases, the treated water may require chlorination to meet drinking water standards (74).

Combined Filters

A combined filter consists of roughing filters and a slow sand filter. It is introduced to overcome some of the difficulties encountered in PSF. The PSF cannot operate effectively when the turbidity of surface water exceeds 30 mg/l. The low discharge and requirement of frequent washing of the filter beds are common in Bangladesh. This is due to high turbidity and seasonal algal bloom in pond water. The situation can greatly be improved by design modifications particularly by the construction of roughing filters for pretreatment of water. The roughing filters remove turbidity and color to acceptable level for efficient operation of the slow sand filter installed in sequential order following roughing filters. A diagram of a combined filtration unit is shown in **figure 3.15** (74).

The roughing and slow sand filter units have been constructed in many parts of the world with success in reduction of very high turbidities and coli form counts. Operation and maintenance are relatively easy and less frequent attention is needed for longer duration of operation between cleaning. A combined unit of such filter has been constructed in Samta Village in Jessore district by Asian Arsenic Network

(AAN) and it functions well in rural condition but remains idle in dry season when there is no water in the pond (AAN, RGAG and NIPSOM, 1999) (74).

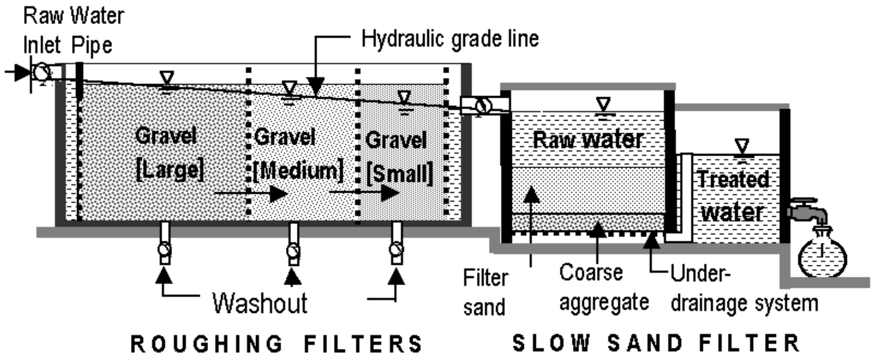
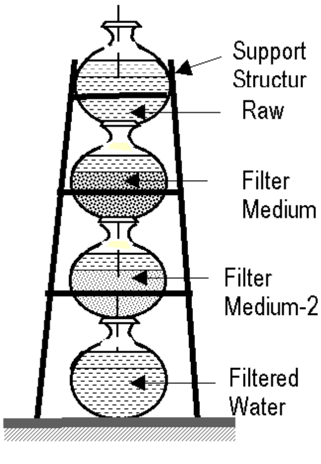


Figure-3.15: A combined filtration unit for surface water treatment (74)

<u>Household Filters</u>

Surface water containing impurities can be clarified by a pitcher filter unit or a small sand filter at the household level. It is an old method of water purification, once widely used in rural areas of Bangladesh. These processes of water treatment at household level have been phased out with the introduction of tube wells for village water supply. Pitcher filters are constructed by stacking number pitchers (Kalshis), one above the other, containing different filter media as shown in **figure 3.16**. Raw water is poured in the top Kalshi and filtered water is collected from the bottom one. In this process, water is mainly clarified by the mechanical straining and adsorption depending of the type of filter media used (74).



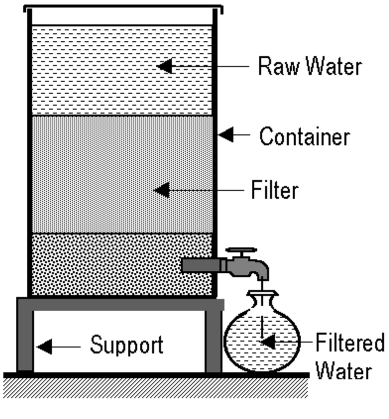


Figure-3.16: Pitcher (Kalshi) filters (74)

Figure-3.17: Small household filter (74)

Small household filters can be constructed by stacking about 300-450 mm thick well graded sand on a 150-225 mm thick coarse aggregate in a cylindrical container as shown in **figure 3.17**. The container is filled with water and the filtered water is collected from the bottom. It is essential to avoid drying up of the filter bed. Full effectiveness of the filtration process is obtained if the media remain in water all the time. The pitcher and other small household filters cannot completely remove micro-organisms if these are present in large numbers in raw water. Experimental units constructed in Bangladesh and in other countries show that the residual coli form bacteria present in the filtered water may vary from a few to several hundred. However, improvement of water quality by household filters is remarkable (74).

3.1.5 Existing water supply system from sources to users in urban areas

Public health requirements are those associated with meeting all drinking water regulations and as well as customers' satisfaction regarding aesthetic quality. In summary, the reliability of the distribution system may be gauged by its ability of deliver a sufficient quantity of safe and good quality water under adequate pressure to the customers at all times (DPHE, BD) (37).

Urban water infrastructure typically includes water collection and storage facilities at source sites, water transport via aqueducts (canals, tunnels and/or pipelines) from source sites to water treatment facilities; water treatment, storage and distribution systems; wastewater collection (sewage) systems and treatment; and urban drainage works (75).

The most convenient water supply system, in terms of collection and use, is undoubtedly piped water supply. In Bangladesh, only piped water can replace the existing vast system of tubewell water supply. It is the most convenient because water can be delivered to the close proximity of the consumers, piped water is safe from external contamination of any kind, and better quality control is possible in such a system. The arsenic-free and bacteriological contamination-free water for such a piped supply can be collected from any source like deep tubewell, treated surface, or arsenic-contaminated (but properly treated) water, and from community dug wells. In some areas of Bangladesh, for example, urban piped water supplies distributing treated river water are being installed in some arsenic-affected areas (70). A water distribution system is not just pipes and valves, but rather like a living organism — a dynamic, sensitive, complex entity that must be operated properly to maintain safe and good quality water at the customer's tap. To be reliable, a water distribution system should be designed, maintained and operated to meet both public safety and public health requirements. Public safety requirements are those associated with sufficient quantity (peak demands) and adequate pressure for normal use (76).

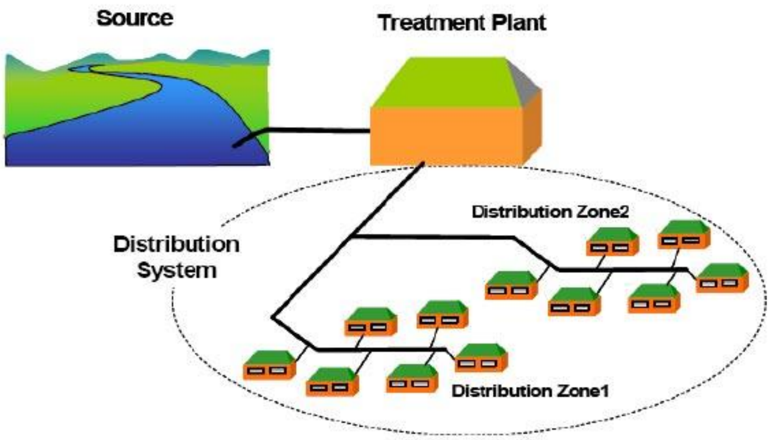
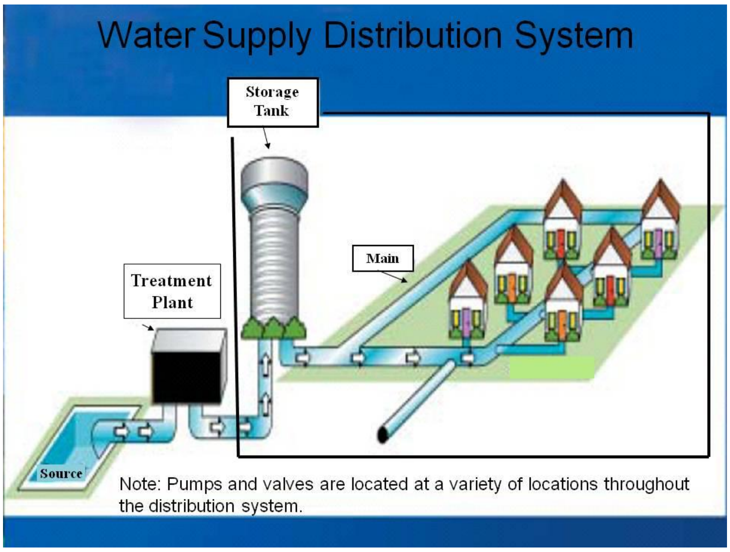


Figure-3.18: Water supply and distribution system in urban areas (76)



Note: Pumps and valves are located at a variety of locations throughout the distribution system.

Figure-3.19: Water supply and distribution system in urban areas (77)

Water distribution systems consist of an interconnected series of pipes, storage facilities, and components that convey drinking water and meeting fire protection needs for cities, homes, schools, hospitals, businesses, industries and other facilities. Public water systems depend on distribution systems to provide an uninterrupted supply of pressurized safe drinking water to all consumers. It is the distribution system mains that carry water from the treatment plant (or from the source in the absence of treatment) to the consumer (77).

This is a very expensive system and not suitable immediately for many large, dispersed communities in Bangladesh. It requires huge initial cost and moreover, piped water supplies for all domestic supplies may be too expensive for low-income groups of people. It is also technically inconvenient because of the scattered settlement patterns of the urbanization in Bangladesh. It is only feasible as a potential solution to the arsenic problem only for urban fringe areas (70).

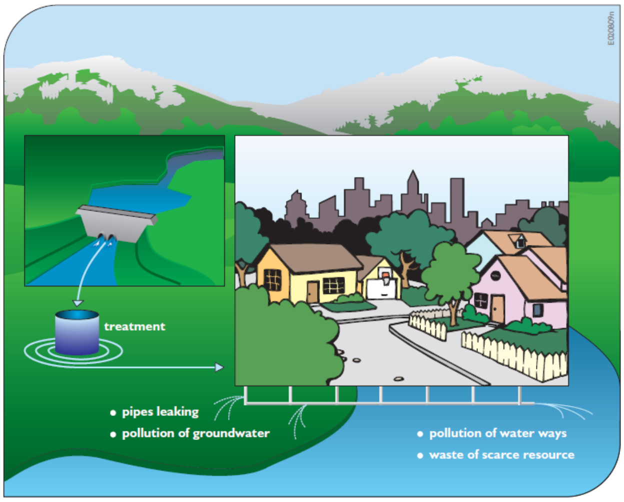


Figure- 3.20: Schematic showing urban surface water source, water treatment prior to urban use, and some sources of nonpoint urban drainage and runoff and its impacts (75)

3.2 Ground water poisoning

The serious arsenic contamination of groundwater in Bangladesh has come out recently as the biggest natural calamity in the world. The people in 59 out of 64 districts comprising 126,134 km2 of Bangladesh are suffering due to the arsenic contamination in drinking water. Seventy five million people are at risk and 24 million are potentially exposed to arsenic contamination. Most of the recognized stages of arsenic poisoning have been identified in Bangladesh and the risk of arsenic poisoning in the population is increasing every day (78).

Severe arsenic contamination of groundwater in Bangladesh has disrupted the idea of using shallow Tube wells for safe drinking water throughout the country. Millions of tube-wells that had been sunk in various parts of the country are now dispensing arsenic contaminated drinking water. As a result, thousands of people are suffering from arsenic related diseases (79).

3.2.1 Discovery of arsenic contamination in ground water

Until recently the arsenic problem was almost unknown in Bangladesh, although in neighboring West Bengal it became evident in the mid-eighties. Arsenic specialists in Calcutta however, predicted that as the younger deltaic deposition stretched from West Bengal into Bangladesh, the latter might also have arsenic contamination of ground water. The prediction held true as they found patients from the bordering districts of Bangladesh with arsenical skin lesion going to Calcutta for treatment. They warned the government of Bangladesh and the WHO about the presence of arsenicosis patients in Bangladesh in the early nineties and accordingly Bangladesh government began some investigations in this direction, however it was kept more or less unpronounced and neither the physician community, nor the public knew anything about it until 1996 when Dhaka Community Hospital came into the scene (80).

In June 1996, Dhaka Community Hospital held a health camp at Pakshi in the western part of the country in which several skin patients were suspected of having arsenical skin lesions. Tube-well from that area was tested and was found to have high content of arsenic. DCH informed the local officials and made newspaper reports. Following this news on arsenic began flowing from other districts, there were rumor and tales, and however nobody seemed to know how real the arsenic threat was. DCH felt the need to respond to the interest of the public health and send a fact finding team consisting of 8 members including 3 skin specialists and 3 other senior doctors to that area. They collected water samples from 41 tube-wells and biological samples (nail, hair, skin and urine) form 95 patients. Water samples were tested at the BCSIR Laboratories, Dhaka, while biological samples were tested at the School of Environmental Studies, Jadavpur University, Calcutta 66% of the water samples and more than 90% of the biological samples water found to have higher than normal concentration of arsenic. DCH made the results public in a national seminar held with the participation of Dr. Dipankar Chakraborty of the SOES, Jadavpur University, Calcutta in January 1997 and urged the government and other concerned organizations to take immediate steps to face the problem (80).

3.2.2 Causes of arsenic contamination

Intermittent incidents of arsenic contamination in groundwater can arise both naturally and industrially. The natural occurrence of arsenic in groundwater is directly related to the arsenic complexes present in soils. Arsenic can liberate from these complexes under some circumstances. Since arsenic in soils is highly mobile, once it is liberated, it results in possible groundwater contamination (78).

The alluvial and deltaic sediments containing pyrite has favored the arsenic contamination of groundwater in Bangladesh. Most regions of Bangladesh are composed of a vast thickness of alluvial and deltaic sediments, which can be divided into two major parts – the recent floodplain and the terrace areas. The floodplain and the sediments beneath them are only a few thousand years old. The terrace areas are better known as Madhupur and Barind Tracts and the sediments underlying them are much older than the adjacent floodplain. Most of the arsenic is occurring in the younger sediments derived from the Ganges Basin. The investigators found that there is a layer containing arsenic compound at a depth of 20 to 80 meters (79). This layer is rich in arseno-pyrite, pyrite, iron sulfate, and iron oxide as revealed by the geological investigation. The researchers also inferred that, although arsenic is occurring in the alluvial sediments, the ultimate origin of arsenic is perhaps in the outcrops of hard rock's higher up the Ganges catchment. These outcrops were weather-beaten in the recent geological past and then the eroded soil was deposited in West Bengal and Bangladesh by the ancient courses of the Ganges (81). Arsenic in sediment or water can move in adsorbed phase with iron, which is available in plenty in the Himalayas. Here about 100 to 300 mg/kg arsenic combined with iron oxides can be found in the sediments under aerobic conditions (83). When these sediments were deposited in Bengal basin under tidal environment, it came under anaerobic condition. The sulfate available in Bengal basin was reduced to hydrogen sulfide in presence of sulfur reducing bacteria. Iron minerals and hydrogen sulfide rapidly tie together to form iron sulfide. Arsenic had been absorbed on the surface of iron sulfide and produced arsenopyrite. This mineral usually remains stable unless it is exposed to oxygen or nitrate. In aerobic environment, arseno-pyrite is oxidized in presence of oxygen and arsenic adsorbed with iron sulfide becomes mobilized (82).

The groundwater in Bangladesh has declined progressively due to the excessive extraction of water for irrigation and domestic water supply, lack of water management and inadequate recharge of the aquifer. The groundwater declined beyond 8 meters in 12% areas of Bangladesh in 1986. This extent rose to 20% areas in 1992 and 25% areas in 1994 (86). The study on forecasting groundwater level fluctuation in Bangladesh indicated that 54% areas of Bangladesh are likely to be affected up to 20 meters in some areas particularly in northern part of the country (82). Excessive groundwater extraction may be the vital reason for creating a zone of aeration in clayey and peaty sediments containing arseno-pyrite. Under aerobic condition, arseno-pyrite decomposes and releases arsenic that mobilizes to the subsurface water. The mobilization of arsenic is further enhanced by the compaction of aquifers caused by groundwater withdrawal.

3.2.3 Mechanisms of arsenic contamination

Presently, there are two well-known theories about the mechanism of arsenic contamination in groundwater. These are oxidation and oxy-hydroxide reduction theory. The oxidation theory is so far the accepted theory. According to this theory, arsenic is released from the sulfide minerals (arseno-pyrite) in the shallow aquifer due to oxidation (85). The lowering of water table owing to over exploitation of groundwater for irrigation has initiated the release of arsenic. The large-scale withdrawal of groundwater has caused rapid diffusion of oxygen within the pore spaces of sediments as well as an increase in dissolved oxygen in the upper part of groundwater. The newly introduced oxygen oxidizes the arseno-pyrite and forms hydrated iron arsenate compound known as pitticite in presence of water. This is very soft and water-soluble compound. The light pressures of tube-well water break the pitticite layer into fine particles and make it readily soluble in water. Then it seems like drops of tea from the teabag and percolates from the subsoil into the water table. Hence, when the tube-well is in operation, it comes out with the extracted water. This mechanism is portrayed in **figure 3.21** (78).

The alternative hypothesis on the arsenic contamination is the oxy-hydroxide reduction theory proposed by Nickson et. Al (86). This theory has been accepted recently by some scientists and researchers as main the process for mobilization of arsenic in groundwater. According to this theory, arsenic is derived by desorption from ferric hydroxide minerals under reducing conditions. Ferric hydroxide minerals are present as coatings in the aquifer sediments. In anaerobic groundwater, these sedimentary minerals release its scavenged arsenic (78).

The oxidation of arseno-pyrite could be the main mechanism for the groundwater arsenic contamination in Bangladesh but there is not enough hydrological and geochemical data to validate the process completely. The validity of oxy-hydroxide reduction theory is also questionable due to the lack of comprehensive sampling and systematic analysis of iron oxy-hydroxides in the affected areas (78).

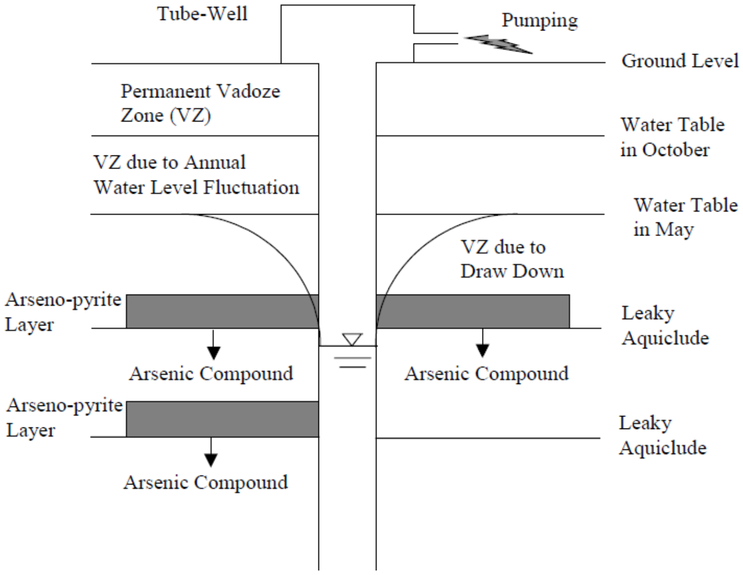


Figure- 3.21: Aerobic Condition in Groundwater around a Heavy-Duty Tube-Well (84)

3.2.4 Sources of arsenic: A natural origin or human process

It is now generally agreed that the arsenic contamination of groundwater in Bangladesh is of natural origin, deriving from the geological strata underlying Bangladesh (87). It is also suggested that this arsenic is transported by rivers from the sedimentary rocks in the Himalayas (88).

The arsenic is thought to be closely associated with iron oxides. Arsenic occurs in two oxidation states in water. In reduced (anaerobic) conditions, it is dominated by the reduced form: arsenite. In oxidizing conditions the oxidized form dominates: arsenate. The release mechanism of arsenic from the sediment is not yet clearly understood, but two major theories for the release of arsenic are put forward (89):

Pyrite oxidation: This associates the release of arsenic with oxidation due to draw-down of the water table, particularly by irrigation extraction. In response to the pumping of water, air or water with dissolved oxygen penetrates into the ground, leading to decomposition of sulphide minerals and release of arsenic (89).

Oxy hydroxide reduction: Arsenic naturally transported in the river systems of Bangladesh is adsorbed onto fine-grained iron or manganese oxy hydroxides. These were deposited in flood plains and buried in the sedimentary column. Due to the strong reducing conditions that developed in the sediments and groundwater of certain parts of Bangladesh, the arsenic continues to be released into groundwater (89).

The second theory is thought to be the more likely explanation. However, some other hypotheses like microbial activity and the effects of deposition via arsenic contaminated fertilizer have also been hypothesized (89).

Natural processes of groundwater flushing will eventually wash the arsenic away but this will take thousands or ten thousands of years. The flushing is particularly slow in the Bengal Basin in general because it is so large and flat (89).

The majority of tests to date have been carried out on shallow tube wells used for drinking water. A significant number of tests have also been carried out on deep tube wells down to 300 meters or more, used for drinking water, and other wells (also referred to as deep tube wells) down to 100 meters used for agriculture. The tests show that at depths below 200 meters the incidence of contamination falls off and at 250 meters or more it is rare. In general, it appears that water drawn from depths greater than 250 meters is, and will remain, arsenic-free provided that irrigation wells do not start using the same aquifer (89).

However, according to Islam and Uddin (2002), the distribution of arsenic in the groundwater is related to the geology of the country rather than just the depth of the water table. According to them, the division of the aquifer system from the geological point of view—like the Upper Holocene aquifer, Middle Holocene aquifer, Upper Pleistocene-Early Holocene aquifer, Plio-Pleistocene aquifer, and older aquifers—is more logical when applied to the depth of the tube well pumping system as is customarily adopted in Bangladesh. They conclude that most of the arsenic-contaminated tube wells are drawing water from the Middle and Upper Holocene sediments (90).

3.2.5 Most affected areas & average concentration

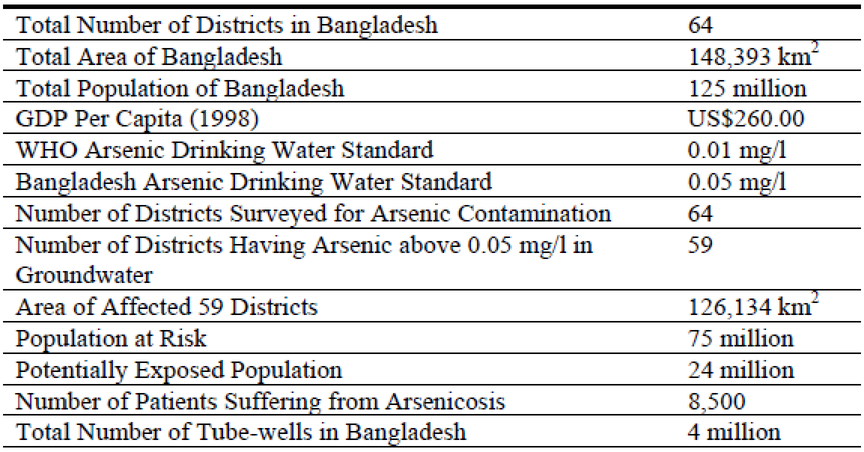
Groundwater arsenic contamination in Bangladesh is reported to be the biggest arsenic calamity in the world in terms of the affected population (91). The Government of Bangladesh has addressed it as a national disaster (92). The millions of shallow and deep wells that had been sunk in various parts of the country are dispensing their own special brand of poison. In consequence, a large number of populations in Bangladesh are suffering from the toxic effects of arsenic contaminated water (93). Recent studies in Bangladesh indicate that the groundwater is severely contaminated with arsenic above the maximum permissible limit of drinking water. In 1996, altogether 400 measurements were conducted in Bangladesh (94). In 1998, British Geological Survey (BGS) collected 2022 water samples from 41 arsenic-affected districts (94). Laboratory tests revealed that 35% of these water samples were found to have arsenic concentrations above 0.05 mg/l. The survey results are shown in **table 3.2**.

Table 3.2: Percentage of Groundwater Surveyed in 1998 by British Geological Survey with Arsenic Levels above 0.05 mg/l (94)

District	Percentage of Groundwater Surveyed	District	Percentage of Groundwater Surveyed
Bagerhat	66	Madaripur	93
Barisal	63	Magura	19
Brahmanbaria	38	Manikganj	15
Chandpur	96	Meherpur	60
Chittagong	20	Moulvibazar	12
Chuadanga	44	Munshiganj	83
Comilla	65	Narail	43
Cox's Bazar	3	Narayanganj	24
Dhaka	37	Nawabganj	4
Faridpur	66	Noakhali	75
Feni	39	Pabna	17
Gopalganj	94	Pirojpur	24
Jessore	51	Rajbari	24
Jhalakati	14	Rajshahi	6
Jhenaidah	26	Satkhira	73
Khulna	32	Shariatpur	80
Kushtia	28	Syllhet	19
Lakshmipur	68		

NIPSOM and SOES conducted a study in Rajarampur village of Nawabganj district in 1996. The report shows that 29% of the 294 tube-wells tested had arsenic concentrations greater than 0.05 mg/l (95). Between September 1996 and June 1997, DCH also conducted a field survey in Samta village of Jessore district in collaboration with SOES (96). In total, 265 tube-wells were examined and it was found that about 91% of the tube-wells had arsenic concentrations higher than 0.05 mg/l. Further studies by SOES and DCH in the Ganges delta exhibited that 59% of the 7800 groundwater samples had arsenic concentrations greater than 0.05 mg/l (97). So far from August 1995 to February 2000, SOES and DCH had jointly analyzed 22003 tube-well water samples collected from 64 districts in Bangladesh (98). Five years sampling results indicate that out of 64 districts in Bangladesh, arsenic in groundwater is above 0.01 mg/l in 54 districts and above 0.05 mg/l in 47 districts. The experts from Bangladesh Council for Scientific and Industrial Research (BCSIR) have been found the highest level of arsenic contamination, 14 mg/l of shallow tube-well water in Pabna (99). The recent statistics on arsenic contamination indicate that 59 out of 64 districts of Bangladesh have been affected by arsenic contamination (93). Approximately, arsenic has contaminated the ground water in 85% of the total area of Bangladesh and about 75 million people are at risk (98). It has been estimated that at least 1.2 million people are exposed to arsenic poisoning. The reported number of patients seriously affected by arsenic in drinking water has now risen to 8500 (98). As the people are getting arsenic also from food chain such as rice, fish and vegetables, the problem is growing more severe. The current statistics of arsenic calamity given in **table 3.3** and the arsenic crisis map shown in **figure 3.22** present the severity of arsenic contamination in Bangladesh.

Table 3.3: Statistics of Arsenic Calamity in Bangladesh (98)



Total Number of Districts in Bangladesh	64
Total Area of Bangladesh	148,393 km^2
Total Population of Bangladesh	125 million
GDP Per Capita (1998)	US$260.00
WHO Arsenic Drinking Water Standard	0.01 mg/l
Bangladesh Arsenic Drinking Water Standard	0.05 mg/l
Number of Districts Surveyed for Arsenic Contamination	64
Number of Districts Having Arsenic above 0.05 mg/l in Groundwater	59
Area of Affected 59 Districts	126,134 km^2
Population at Risk	75 million
Potentially Exposed Population	24 million
Number of Patients Suffering from Arsenicosis	8,500
Total Number of Tube-wells in Bangladesh	4 million

Total Number of Affected Tube-wells **1.12 million**

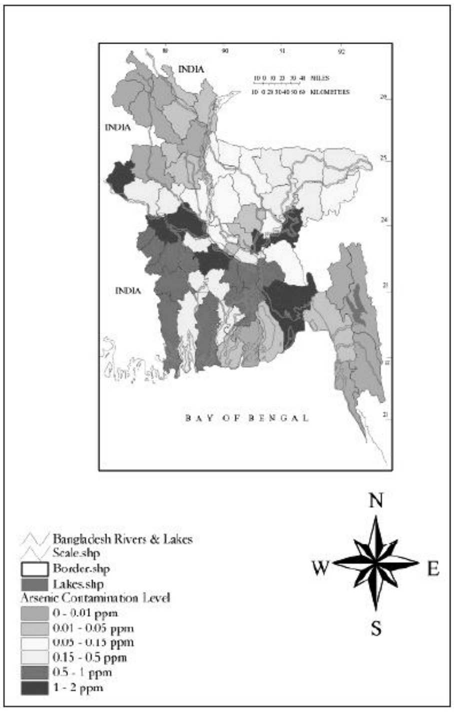
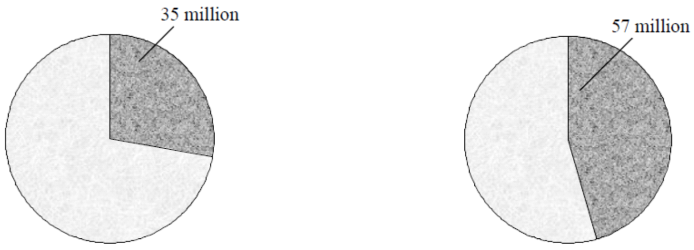


Figure-3.22: Arsenic Crisis Map of Bangladesh (98)

In fact, the severity of arsenic contamination has caused a serious panic for the people in Bangladesh. It is felt that the magnitude of arsenic problem in Bangladesh surpasses the aggregate problem of all the twenty countries of the world where groundwater arsenic contamination has been reported. This is the worst case of mass poisoning the world has ever experienced. Alarm bells are now ringing in Bangladesh since arsenic in groundwater has emerged as a serious problem across the country. The problem is made more complex by the fact that the contamination is occurring below the ground where it cannot be easily identified (98).



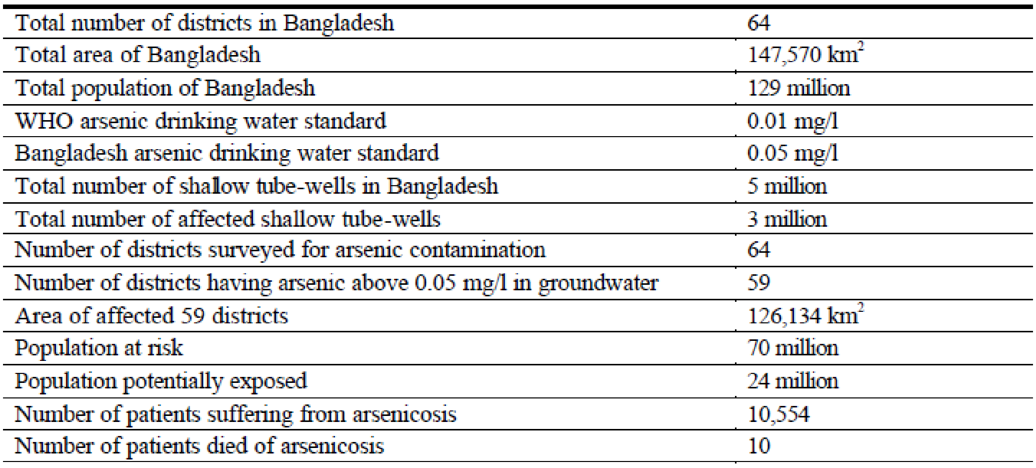
Number of people drinking arsenic contaminated water according to the Bangladesh standard of 50 µg/ L

Number of people drinking arsenic contaminated water according to the WHO Guideline value of 10 µg/ L

Figure-3.23: Number of People Drinking Arsenic Contaminated Water in Bangladesh (Source: British Geological Survey and the Department of Public Health Engineering (DPHE) of Bangladesh in 2001) (67)

The arsenic contamination of Bangladesh’s groundwater with its genesis and toxic effects on humans has already been reported (Dhar et al. 1997 (105), DCH 1997 (104), Karim et al. 1997, Nickson et al. 1998 (109), Ahmed 2000 (100), Karim 2000) (107). Recent studies in Bangladesh indicate that the groundwater is severely contaminated with arsenic above the maximum permissible limit of 0.05 mg/l for drinking water. Altogether 400 measurements were conducted in Bangladesh in 1996 (Smith et al. 2000). Arsenic concentrations in about half of the measurements were above the maximum permissible limit. In 1998, British Geological Survey (BGS) collected 2,022 tube-well water samples from 41 arsenic affected districts (Smith et al. 2000) (99). Laboratory tests revealed that 35% of these water samples had arsenic concentrations above 0.05 mg/l. Moreover, School of Environmental Studies (SOES), Jadavpur University, India and Dhaka Community Hospital (DCH), Bangladesh had jointly analyzed 22,003Tube-well water samples collected from 64 districts of Bangladesh between August 1995 and February 2000 (SOES and DCH 2000) (104). Five years of sampling indicated that arsenic concentration in groundwater was above 0.01 mg/l in 54 districts and above 0.05 mg/l in 47 districts. Furthermore, a recent study of World Bank reports, "With more than an estimated 20 million of its 126 million people assumed to be drinking contaminated water and another 70 million potentially at risk, Bangladesh is facing what has been described as perhaps the largest mass poisoning in history. High concentrations of naturally occurring arsenic have already been found in water from thousands of tube-wells, the main source of potable water, in 59 out of Bangladesh's 64 districts" (World Bank 2000) (110). The contemporary statistics given in **table 3.4** reveal the severity of arsenic contamination in

Table 3.4: Current Statistics of Arsenic Calamity in Bangladesh (Begum and Karim 2000, World Bank 2000, Safiuddin and Karim 2001, Meng et al. 2001) (100,103&110)

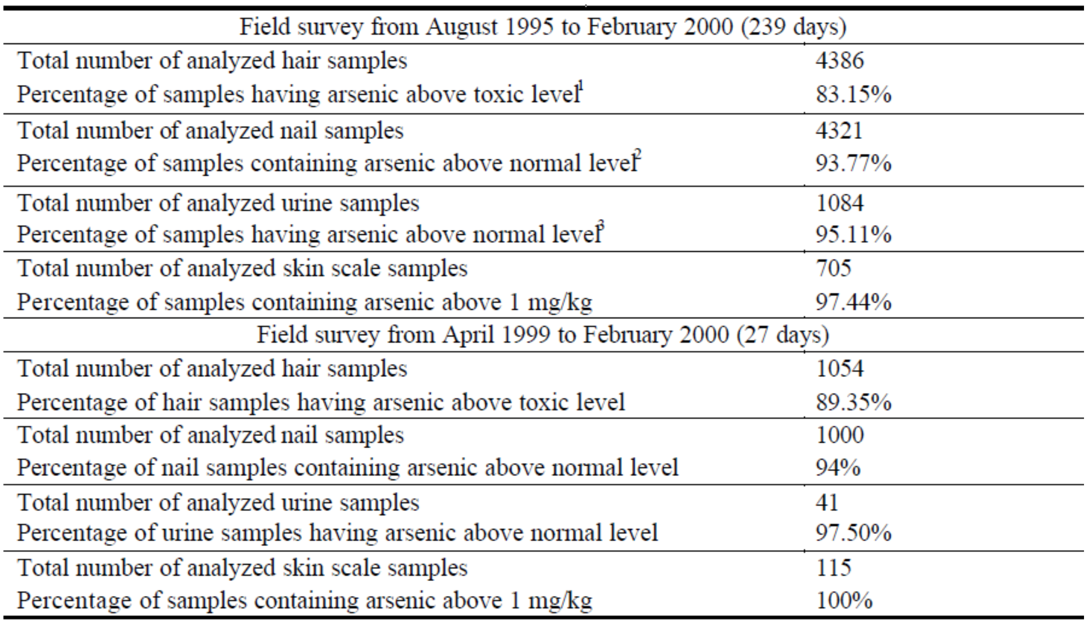


Total number of districts in Bangladesh	64
Total area of Bangladesh	147,570 km^2
Total population of Bangladesh	129 million
WHO arsenic drinking water standard	0.01 mg/l
Bangladesh arsenic drinking water standard	0.05 mg/l
Total number of shallow tube-wells in Bangladesh	5 million
Total number of affected shallow tube-wells	3 million
Number of districts surveyed for arsenic contamination	64
Number of districts having arsenic above 0.05 mg/l in groundwater	59
Area of affected 59 districts	126,134 km^2
Population at risk	70 million
Population potentially exposed	24 million
Number of patients suffering from arsenicosis	10,554
Number of patients died of arsenicosis	10

Bangladesh. In fact, arsenic contamination has become a serious problem in 16 districts of the country affecting 15 million people (Safiuddin and Karim 2000) (107). The groundwater of Kushtia, Meherpur, Chuadanga, Jhenidah, Nawabganj, Naogaon, Khulna, and Rajshahi has been badly contaminated by arsenic (99).

Since 95% of the population of Bangladesh is drinking groundwater, arsenic contamination has evolved into a serious health hazard. Arsenic is accumulating in humans through the intake of arsenic contaminated drinking water (102). As the people are also getting arsenic from the food chain, the problem is growing more severe. SOES and DCH performed a field survey for arsenic patients in 32 districts of Bangladesh (SOES and DCH 2000). The researchers analyzed a total of 5440 hair, 5321 nail, 1125 urine, and 820 skin scale samples collected from 210 arsenic affected villages. The results analysis given in **table 3.5** shows that over 80% hair samples were found to contain arsenic above the level indicating toxicity. Arsenic concentrations were also above the normal ranges in more than 90% nail and 95% urine samples. The normal concentration of arsenic in hair is 0.08-0.25 mg/kg. Levels above 1 mg/kg indicate toxic exposure (Arnold et al. 1990) (101). The normal arsenic content in nails is 0.43-1.08 mg/kg (Dhar et al. 1997) and the normal amount of arsenic in urine ranges from 0.005 to 0.040 mg/day (Farmer and Johnson 1990) (106). Obviously, the arsenic contents in hair, nails, and urine and skin scales of the affected people in Bangladesh are very high. This indicates that arsenic is being ingested in humans at a rate faster than it can be excreted. Therefore, many people in Bangladesh are suffering from arsenic driven diseases (108).

Table 3.5: Arsenic Contents in Hairs, Nails, Skin Scales and Urines of the Patients in the Affected Regions of Bangladesh (SOES and DCH 2000) (107)



Field survey from August 1995 to February 2000 (239 days)	
Total number of analyzed hair samples	4386
Percentage of samples having arsenic above toxic level[1]	83.15%
Total number of analyzed nail samples	4321
Percentage of samples containing arsenic above normal level[2]	93.77%
Total number of analyzed urine samples	1084
Percentage of samples having arsenic above normal level[3]	95.11%
Total number of analyzed skin scale samples	705
Percentage of samples containing arsenic above 1 mg/kg	97.44%
Field survey from April 1999 to February 2000 (27 days)	
Total number of analyzed hair samples	1054
Percentage of hair samples having arsenic above toxic level	89.35%
Total number of analyzed nail samples	1000
Percentage of nail samples containing arsenic above normal level	94%
Total number of analyzed urine samples	41
Percentage of urine samples having arsenic above normal level	97.50%
Total number of analyzed skin scale samples	115
Percentage of samples containing arsenic above 1 mg/kg	100%

Patients with arsenical skin-lesions have been identified in 30 districts. Melanosis and keratosis are the most common manifestations among the arsenic affected people, although patients of leuco-melanosis and hyperkeratosis have also been found. A few cases of skin cancer, gangrene a Bowen's disease have also been identified. In brief, the majority of the people in Bangladesh are grappling with an arsenic driven health crisis. Indeed, the magnitude of the arsenic problem in Bangladesh surpasses the aggregate problem of all the twenty countries of the world where groundwater arsenic contamination had been reported. This is the worst case of arsenic contamination the world has ever experienced. According to Department of Public Health Engineering (DPHE) of Bangladesh the worst affected Districts: Chandpur (90%), Noakhali (69%), Shriatpur (65%), Munsiganj (83%), Satkhira (67%), Meherpur (60%), Gopalganj (79%), Comilla (65%), Bagerhat (60%), Madaripur (69%), Faridpur (65%), and Laxmipur (56%) (67)

3.2.6 Socioeconomic effects of arsenic contamination

While addressing the problem of arsenic contamination, emphasis is being put on the identification, mitigation, and supply of safe drinking water. Arsenic is not only a physical but also a social phenomenon; the social fallout of arsenicosis is enormous. The arsenic hazard has a strong social dimension, affecting issues such as relationships within the family and the village, as well as the mental health of the sick (111).

Dr. Mahbuba Nasreen from the Department of Sociology, University of Dhaka, observed the social costs of arsenic contamination in the following forms: social instability, superstition, ostracism, marital problems, discrimination against women, increased poverty, diminished working ability, and death (112).

Social Instability: Lack of proper knowledge about arsenic contamination and unavailability of arsenic safe drinking water as well as proper treatment are creating extreme instability in the social life of the people in the arsenic-prone areas of Bangladesh. Moreover, social conflict over contaminated water contributes to destruction of social harmony and network relationships (112).

Superstition: Superstitions and prejudices are constructed surrounding arsenic patients. For example, in the north-eastern district of Kushtia, arsenic is considered as a "curse of Allah" or the work of evil spirits (53). People stay away from arsenic victims, neglect them, or become scared of them because of these superstitions (112).

Ostracism: Arsenic patients are often identified by the society as patients of leprosy and as a result they remain ostracized, at either the household or the village level.

Children of arsenic patients are not allowed to attend social or religious functions. The patients as well as their close relatives are not allowed to use public tube wells and village ponds. Often family members, like husbands or wives, abandon the arsenicosis victims (112).

The problem is more serious in the case of children (114). The entry of arsenic affected children into schools becomes restricted. Some may be denied the opportunity to go to school. They also are subject to social ostracism by their friends and classmates (112).

Diminished working ability: Arsenic is a silent killer. The black spots on a victim's body slowly become nodules and even grow if the victim remains exposed to arsenic contamination. Limbs and internal organs like the liver, kidney, and lungs may be affected. Gangrene cripples the victim and makes him or her unable to do hard labor. Arsenic is carcinogenic (112).

Marriage related problems: Arsenic has an adverse impact on marital relationships. People are reluctant to develop marital relationships with families whose members suffer from arsenicosis. This has caused serious anxiety for parents of unmarried adult children. Many women are divorced or abandoned by their husbands due to arsenicosis (112).

Increased poverty: Those in poverty are the main victims of arsenic contamination as they are compelled to drink contaminated tube well water. Researchers believe that the severity of arsenicosis is very much related to nutritional deficiency. Malnutrition makes them easy victims. Due to poverty, victims are deprived of proper treatment. When seeking treatment, the costs become a burden to them. As arsenicosis decreases the victim's ability to work, he or she often suffers from a reduced income. Due to ostracism, arsenic patients lose their jobs. Thus, arsenic negatively contributes to the poverty situation in Bangladesh (112).

Gender implications of arsenic contamination: In Bangladesh women perform the majority of the household work. Arsenic contamination in nearby drinking water often compels them to collect and carry water from a long distance, imposing an additional burden on them. However, they are not properly aware of the danger of arsenic. This makes arsenic mitigation activities difficult. Women are frequent victims of ostracism due to arsenicosis. They are doubly vulnerable: from the disease itself and by being divorced, abandoned, or even forced out of the society. As gender discrimination exists in many forms in the patriarchal society of Bangladesh, women suffer more from these things than men (113).

CHAPTER 4: TECHNOLOGIES FOR ARSENIC, IRON & MANGANESE REMOVAL FROM POTABLE WATER

4.1 Overview of technologies use in arsenic removal

4.1.1 Conventional methods for arsenic removal

According to USEPA best available technologies for arsenic removal:

- Precipitation
- Membrane filtration
- Adsorption
- Ion exchange
- Permeable reactive barriers (48)

Generally the most common arsenic removal technologies can be grouped into the following four categories:

- Oxidation and sedimentation
- Coagulation and filtration
- Sorptive filtration
- Membrane filtration (4)

Detailed description of common methods for removing arsenic from drinking water is given by Petrusevski et al. (2007). These methods are based on the following processes:

- Precipitation processes, including coagulation/filtration, direct filtration; coagulation assisted microfiltration, enhanced coagulation, lime softening, and enhanced lime softening
- Adsorptive processes, including adsorption onto activated alumina, activated carbon and iron/manganese oxide based or coated filter media
- Ion exchange processes, specifically anion exchange
- Membrane processes, including nano-filtration, reverse osmosis and electro dialysis (115).

The principal mechanisms and technologies for arsenic removal using the above technological options are described in detail in the following sections:

<u>Precipitation processes</u>

Adsorption co-precipitation with hydrolyzing metals such as Al3+ and Fe3+ is the most common treatment technique for removing arsenic from water. Sedimentation followed by rapid sand filtration or direct filtration or microfiltration is used to remove precipitate. Coagulation with iron and aluminium salts and lime softening is the most effective treatment process. To improve efficiency of this method, a priory oxidation of As (III) to As (V) is advisable. Hypochlorite and permanganate are commonly used for the oxidation. Atmospheric oxygen can also be used, but the reaction is very slow (115).

Adsorptive processes

Adsorptive processes involve the passage of water through a contact bed where arsenic is removed by surface chemical reactions. Activated alumina, activated carbon, iron oxide coated or based filter media are used for these processes (115).

Activated alumina, Al2O3, having good sorptive surface is an effective medium for arsenic removal. When water passes through a packed column of activated alumina, the impurities including arsenic present in water are adsorbed on the surfaces of activated alumina grains. Eventually the column becomes saturated, first at its upstream zone and later the saturated zone moves downstream towards the bottom end and finally the column gets totally saturated (74).

Regeneration of saturated alumina is carried out by exposing the medium to 4% caustic soda, NaOH, either in batch or by flow through the column resulting in high arsenic contaminated caustic waste water. The residual caustic soda is then washed out and the medium is neutralized with a 2% solution of sulfuric acid rinse. During the process about 5-10% alumina is lost and the capacity of the regenerated medium is reduced by 30-40%. The activated alumina needs replacement after 3-4 regeneration. Like coagulation process, pre-chlorination improves the column capacity dramatically (74).

Ion exchange processes

In these processes, ions held electro-statically on the surface of a solid phase are exchanged for ions of similar charge dissolved in water. Usually, a synthetic anion exchange resin is used as a solid. Ion exchange removes only negatively charged As (V) species. If As (III) is present, it is necessary to oxidize it (115).

Membrane processes

Microfiltration (MF), ultra-filtration (UF), nano-filtration (NF), reverse osmosis (RO) and electro-dialysis reversal (EDR) can remove arsenic through filtration, electric repulsion, and adsorption of arsenic-bearing compounds. The use of MF and

UF membranes is dependent on the size distribution of arsenic bearing particles in water. To increase removal efficiency with a low percentage of particulate arsenic content, MF can be combined with coagulation processes. Nano-filtration membranes are capable of removing significant portions of the dissolved arsenic compounds in natural waters. Reverse Osmosis (RO) is very effective in removing dissolved arsenic. Electro-dialysis reversal (EDR) can also be used for removal of arsenic. A water recovery of 85% is achievable. Reported arsenic removal varies from 28% to 86% (EPA, 2000). In general, membrane filtration is more effective for removal As (V) than for As (III) (115).

4.1.2 Prospective technologies for arsenic removal

Several new methods have been studied recently that are shortly described below:

- Fe-Mn-Oxidation
- Green sand filtration
- Coagulation assisted Microfiltration
- In situ (sub-surface) arsenic immobilization
- Passive Sedimentation
- Enhanced coagulation (aka electro-coagulation, electro-flotation)
- Biological arsenic removal
- Phytoremediation
- Electro-kinetic treatment
- IOCS (iron oxide coated sand
- Memstill
- Water Pyramid
- Solar Dew Collector (115)

Fe-Mn Oxidation

Conventional iron and manganese removal can result in significant arsenic removal, through co-precipitation and sorption onto ferric or manganese hydroxides (Johnston, R. and Heijnen, H., 2001). Most low-cost methods for arsenic and manganese removal rely on aeration and filtration through porous media such as sand and gravel. Any method that effectively removes iron and manganese could be evaluated to see if arsenic is also removed effectively (115).

Manganese Greensand

Greensand is a granular material composed of the mineral glaciate, which has been coated with manganese oxide. It is a natural zeolite (micro-porous mineral), and has strong ion exchange properties, and will remove iron, manganese, arsenic, sulphide, and many other anions (Water & Wastes, 2003). Like manganese dioxide coated sand, greensand surface is strongly oxidizing, and is thus able to remove both arsenite and arsenate (115).

This method is especially interesting to utilities where Fe and Mn are already being removed using a manganese greensand filter. It is possible that a small pH adjustment from 8+ to 6.5 may be all that is required to bring the facility into compliance (115).

Coagulation assisted Microfiltration

In coagulation assisted microfiltration technology, microfiltration is used in a manner similar to a conventional gravity filter. The advantages of MF over conventional filtration are a more effective microorganism barrier, removal of smaller flock sizes and an increased plant capacity (EPA, 2000; Wachinski et al., 2006). The microfiltration membrane system works to remove arsenic from water by the addition of an iron-based coagulant, such as ferric chloride, to the water. The arsenic is adsorbed onto positively charged ferric hydroxide particles, which are then removed by microfiltration. In pilot studies, the removal of arsenic to below 2μg/l is reported in waters with a pH between 6 and 7 (115).

In situ (sub-surface) arsenic immobilization

When arsenic is mobilized in groundwater under reducing conditions, it is also possible to immobilize the arsenic by creating oxidized conditions in the subsurface. In Germany, in order to remediate an aquifer containing high arsenite, high ferrous iron, low-pH groundwater, potassium permanganate was injected directly into contaminated wells, oxidizing arsenite, which coprecipated with ferric oxides as ferric arsenate. Arsenic concentrations were reduced by over 99%, from 13,600 to 60μg/l. In another project atmospheric oxygen was used to reduce arsenic concentrations in situ from approximately 20 to 5 μg/l, while iron and manganese levels were also lowered (Johnston and Heijnen, 2001). However, this oxidation is a slow process. Under reducing conditions, and in the presence of sulphur, arsenic can precipitate out of solution and form relatively insoluble arsenic sulphides. However, arsenic sulphides like all metal sulphides are not stable when in contact with acidic conditions (low pH values). In situ immobilization has the great advantage of not producing any wastes that must be disposed of. However, experience is limited, and the technique should be considered with caution (115).

Passive sedimentation

Passive sedimentation received considerable attention because of rural people's habit of drinking stored water from pitchers. Oxidation of water during collection and subsequent storage in houses may cause a reduction in arsenic concentration in stored water (Bashi Pani). Experiments conducted in Bangladesh showed no to high reduction in arsenic content by passive sedimentation. Arsenic reduction by plain sedimentation appears to be dependent on water quality particularly the presence of precipitating iron in water. Ahmed et al. (2000) showed that more than 50% reduction in arsenic content is possible by sedimentation of tubewell water containing 380-480 mg/l of alkalinity as CaCO3 and 8-12 mg/L of iron but cannot be relied to reduce arsenic to desired level. Most studies showed a reduction of zero to 25% of the initial concentration of arsenic in groundwater. In rapid assessment of technologies passive sedimentation failed to reduce arsenic to the desired level of 50µg/L in any well (BAMWSP, DFID, Water Aid, 2001) (74).

Enhanced coagulation (aka electro-coagulation, electro-flotation)

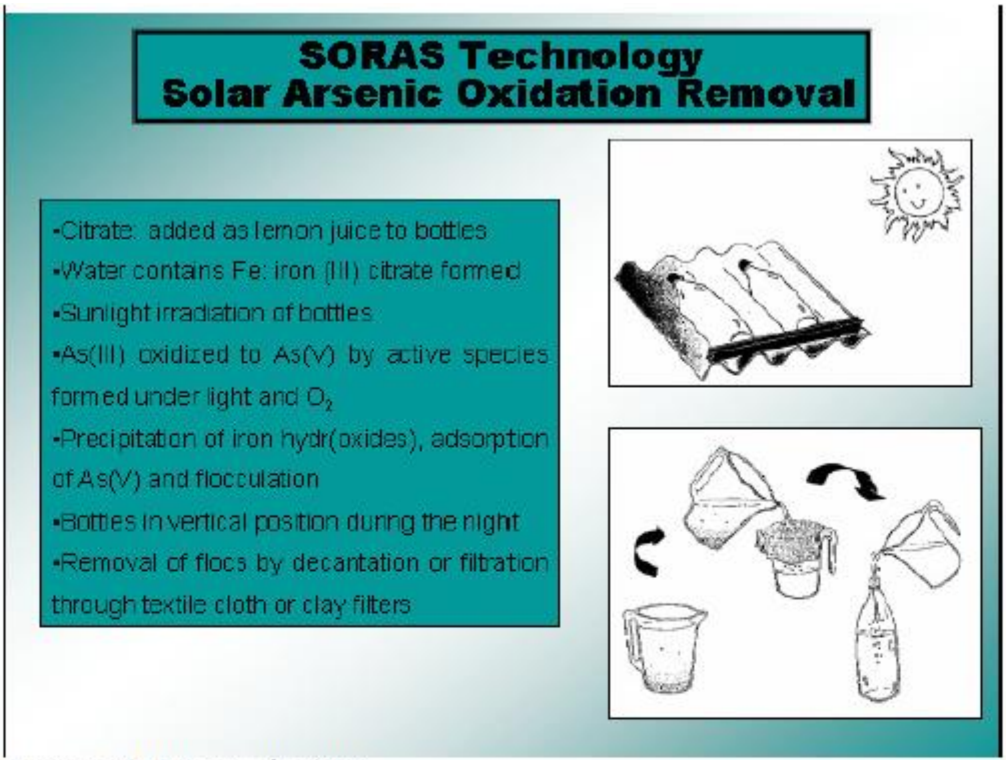
With enhanced coagulation, aka electro-coagulation or electro-flotation, soluble anodes made from iron or aluminium is used. Reported advantages mentioned in laboratory studies are the in-situ oxidation of As (III) tot As (V), and better removal efficiencies than with classical coagulation. Also organic arsenic, fluoride and dissolved metals are removed by this method. Final As concentrations in groundwater are below 10µg/l, even with high initial concentrations (Kumar et al., 2004). An additional advantage of enhanced coagulation is the reported removal of natural organic matter (NOM). Recent studies showed two to three times better effects on the removal of humic substance (NOM) than required by US EPA (Perisic, 2006). The method has many advantages for purification of highly humic waters. It simply and efficiently neutralizes molecules to form flocs and coagulates. The coagulation evolves at a high specific reduction of the coagulant, which makes the method suitable from a techno-economic viewpoint and with respect to environmental aspects. The efficient flocs separation allows a long safe operation of sand filter without washing (115).

Biological arsenic removal

Arsenic in water can be removed by microbiological processes (Rahman and Ravenscroft, 2003). Two main types of metal-microbe interactions can be potentially used for the removal of arsenic from ground water. They are (a) microbial oxidation of arsenic (III) to arsenic (V) to facilitate its removal by conventional arsenic removal processes, and (b) bioaccumulation of arsenic by microbial biomass (115).

The Biological Activated Carbon (BAC) system, developed by the Mainstream BMS Ltd., Vanscoy, Saskatchewan and Davnor Water Treatment Technologies Ltd., Calgary, Alberta, is a biologically active filtration unit. In this system a granular activated carbon (GAC) filter is used, which are continuously aerated to enhance the growth of biological activity within the filter media. This system has been used in rural Saskatchewan on experimental basis for seven years with consistent arsenic removal exceeding 90% (Pokhrel et al., 2005). This system could also remove more than 99% of iron and also dissolved organic material (115).

Solar Oxidation and Removal of Arsenic (SORAS) is a simple method that uses irradiation of water with sunlight in PET or other UV transparent bottles to reduce arsenic level from drinking water. The process is developed by Swiss Federal Institute of Environmental Science and Technology, Switzerland (EAWAG) and Swiss Agency for Development and Cooperation (SDC) (Wegelin et al., 2001). The method is based on photochemical oxidation of As (III) followed by precipitation or filtration of As (V) adsorbed on Fe (III) oxides. Field tests in Bangladesh show removal efficiency between 45-78% with an average of 67%. Concerning the Bangladesh guideline value of 50μg/l, SORAS can treat raw water having an arsenic concentration below 100 – 150 μg/l (Weling et al., 2001) (115).



SORAS Technology
Solar Arsenic Oxidation Removal

- Citrate: added as lemon juice to bottles
- Water contains Fe: iron (III) citrate formed
- Sunlight irradiation of bottles
- As(III) oxidized to As(V) by active species formed under light and O_2
- Precipitation of iron hydr(oxides), adsorption of As(V) and flocculation
- Bottles in vertical position during the night
- Removal of flocs by decantation or filtration through textile cloth or clay filters

Source: D'Hiriat et al., 2006

Figure 4.1: Solar arsenic oxidation removal (115)

Phytoremediation

Some aquatic plants have capacity to accumulate arsenic. Among these aquatic plants, Azolla and Spirodella (duckweed) species have the highest efficiency of arsenic absorption. A study on duckweed in removing arsenic from contaminated water was carried out by Dr. Abdul Aziz of the Department of Botany of Dhaka University (Rahman and Ravenscroft, 2003). This study revealed that Sirodella polyrhiza species was found to absorb arsenic very efficiently. The results indicated that a complete cover of Spirodella polyrhiza could accumulate about 175 g of arsenic from a pond of one hectare area per day (115).

Permeable reactive barriers

Permeable reactive barriers (PRBs) are used to treat groundwater in situ. This method tends to have lower operation and maintenance costs than ex situ (pump and treat) methods. On the other hand it typically requires a treatment time of many years. PRBs are already commercially available and are being used to treat groundwater containing arsenic at a full scale at two sites in the USA, although arsenic is not the primary target component for treatment by the method at either site (EPA, 2002). Permeable reactive barriers are walls containing reactive media that are installed across the path of a contaminated groundwater plume to intercept the plume. The barrier allows water to pass through while the media remove the components by precipitation, degradation, adsorption, or ion exchange (115).

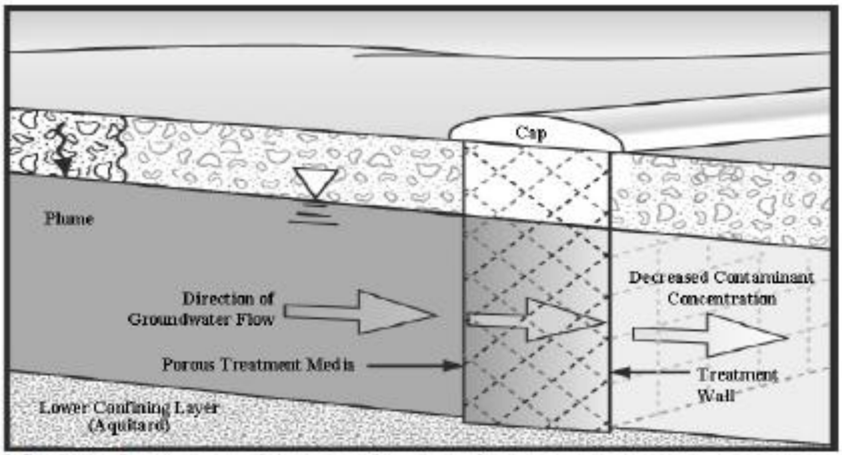


Figure 4.2: Model of a permeable reactive barrier (Source: US-EPA) (115)

Electro-kinetic treatment

Electro-kinetic treatment is an emerging remediation method designed to remove heavy metal contaminants from soil and groundwater. The method is most applicable to soil with small particle sizes, such as clay. However, its effectiveness may be limited by a variety of components and soil and water characteristics. Electro-kinetic remediation is based on the theory that a low current density will mobilize components in the form of charged species. A current passed between electrodes is intended to cause water, ions, and particulates to move through the soil, waste, and water. Components arriving at the electrodes can be removed by means of electroplating or electrode-position, precipitation or co-precipitation, adsorption, complexion with ion exchange resins, or by pumping of water (or other fluid) near the electrode (EPA, 2002). Electro-kinetic treatment is a method with relatively few applications for arsenic treatment. It is an in situ treatment method, and therefore does not require excavation of contaminated soil or pumping of contaminated groundwater. Its effectiveness may be limited by a variety of soil and contaminant characteristics. In addition, its treatment depth is limited by the depth to which the electrodes can be placed (115).

Iron oxide coated sand (IOCS)

UNESCO-IHE developed an arsenic removal method based on adsorption on iron oxide coated sand (IOCS). IOCS is a by-product from groundwater treatment plants and consequently very cheap. This technique is efficient for both As (III) and As (V). Different family scale removal filters were tested in Bangladesh (2004) and also a large scale centralized application was tested in Greece and Hungary (Petrusevski et al., 2007) (115).

Figure 4.3: Arsenic removal Family Filter; Figure 4.4: Iron oxide coated sand
(Source: UNESCO-IHE) (115)

Memstill® technology

The Netherlands Organization of Applied Scientific Research (TNO) has developed a membrane based distillation concept which radically improves the economy and ecology of existing desalination technology for seawater and brackish water. This so-called "Memstill® technology" combines multistage flash and multi-effect distillation modes into one membrane module (Hanemaaijer et al., 2007) (115).

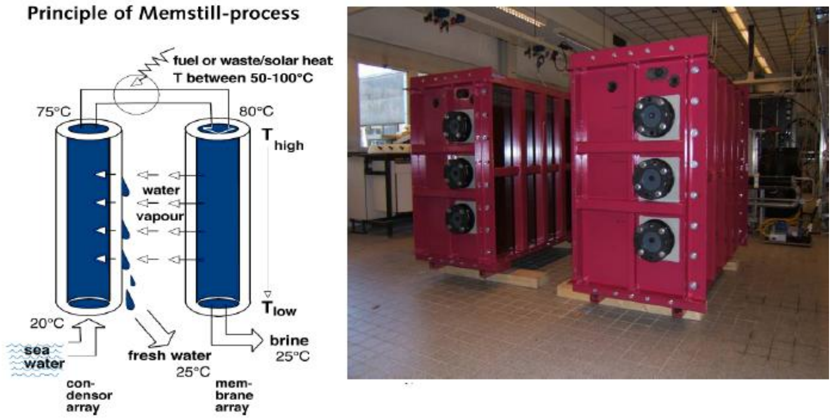


Figure 4.5: Memstill MD modules (*Source: TNO)* (115)

Cold feed water takes up heat in the condenser channel through condensation of water vapor, after which a small amount of (waste) heat is added, and flows counter currently back via the membrane channel. Driven by the small added heat, water evaporates through the membrane, and is discharged as cold condensate. The cooled brine is disposed, or extra concentrated in a next module. The Memstill® technology can produce (drinking) water at a cost well below that of existing methods like reverse osmosis and distillation. With the Memstill® technology also anions like fluoride and arsenic are removed. It is expected that the Memstill® technology will also be developed for small scale applications using solar heat (115).

The Water Pyramid® solution

Aqua-Aero Water Systems has developed the Water Pyramid® concept for tropical, rural areas (Aqua- Aero Water systems, 2007). The Water Pyramid makes use of simple method to process clean drinking water out of salt, brackish or polluted water. One of the pollutants could be fluoride. Most of the energy needed to clean the water is derived from the sun. Water Pyramid® with a total area of 600 m2 and situated under favorable tropical conditions, can produce up to 1.250 litres of fresh water a day. The production rate depends on site specific factors such as climate and temperature, cloudiness and wind activity. Desalination is driven by the sun and the energy needed for pressuring the Water Pyramid® is obtained using solar cells in combination with a battery back-up system. Intermittent peak demands in electricity, related to e.g. (borehole) pumping and maintenance, are covered using a small generator system (115).

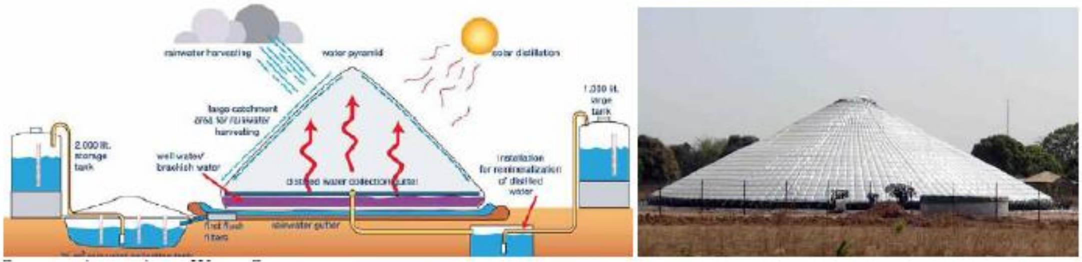


Figure 4.6: The Water Pyramid® solution; (Source: Aqua-Aero Water Systems) (115)

The Solar Dew Collector system

Solar Dew purifies water uses a new porous membrane to purify water using solar energy (Solar Dew, 2007). The technique is similar to the Water Pyramid®. Water sweats through the membrane, evaporates on the membrane's surface and increases the air humidity in the evaporation chamber. Based on a temperature difference, pure water condenses on the cooler surfaces of the system (115).

The product water quality is very constant and similar to that of distilled water. The quantity depends on the intensity of the solar radiation. To avoid crystallization, the brine has to be drained periodically. The system is able to process: sea-, brackish or contaminated waste water (e.g. with heavy metals, oil residue, boron, fluoride) with an allowable pH range of 5-11 (115).

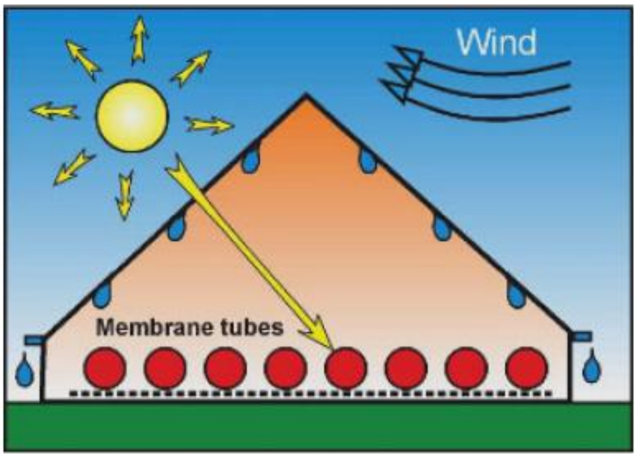


Figure 4.7: The Solar Dew Collector system (115)
(Source: Solar Dew)

4.1.3 Some low cost technologies for developing countries

Bucket Treatment Unit

The Bucket Treatment Unit (BTU), developed by DPHE-Danida Project is based on the principles of coagulation, co-precipitation, and adsorption processes. The unit consists of two bucket, each 20 liter capacity, placed one above the other. Chemicals are mixed manually with arsenic contaminated water in the upper red bucket by vigorous stirring with a wooden stick for 30 to 60 seconds and then flocculated by gentle stirring for about 90 second. The mixed water is then allowed to settle for 1- 2 hours. The water from the top red bucket is then allowed to flow into the lower green bucket via plastic pipe and a sand filter installed in the lower bucket. The flow is initiated by opening a valve fitted slightly above the bottom of the red bucket to avoid inflow of settled sludge in the upper bucket. The lower green bucket is practically a treated water container (74).

The DPHE-Danida project in Bangladesh distributed several thousand BTU units in rural areas of Bangladesh. These unist are based on chemical doses of 200 mg/L aluminum sulfate and 2 mg/L of potassium permanganate supplied in crushed powder form. The units were reported to have very good performance in arsenic removal in both field and laboratory conditions (Sarkar et al., 2000 and Kohnhorst and Paul, 2000). Extensive study of DPHE-Danida BTU under BAMWSP, DFID, and Water Aid (2001) rapid assessment program showed mixed results. In many cases, the unit under rural operating conditions fails to remove arsenic to the desired level of 0.05 mg/L in Bangladesh. Poor mixing and variable water quality particularly pH of groundwater in different locations of Bangladesh appeared to be the cause of poor performance in rapid assessment (74).

Bangladesh University of Engineering and Technology (BUET) modified the BTU and obtained better results by using 100 mg/L of ferric chloride and 1.4 mg/L of potassium permanganate in modified BTU units. The arsenic contents of treated water were mostly below 20 ppb and never exceeded 37 ppb while arsenic concentrations of tubewell water varied between 375 to 640 ppb. The BTU is a promising technology for arsenic removal at household level at low cost. It can be built by locally available materials and is effective in removing arsenic if operated properly (74).

Stevens Institute Technology

This technology also uses two buckets, one to mix chemicals (reported to be iron sulphate and calcium hypo-chloride) supplied in packets and the other to separate flocs by the processes of sedimentation and filtration. The second bucket has a second inner bucket with slits on the sides as shown in **figure 4.8** to help sedimentation and keeping the filter sand bed in place. The chemicals form visible large flocs on mixing by stirring with stick. Rapid assessment showed that the technology was effective in reducing arsenic levels to less than 0.05 mg/L in case of 80 to 95% of the samples tested (BAMWSP, DFID, Water Aid, 2001). The sand bed used for filtration is quickly clogged by flocs and requires washing at least twice a week (74).

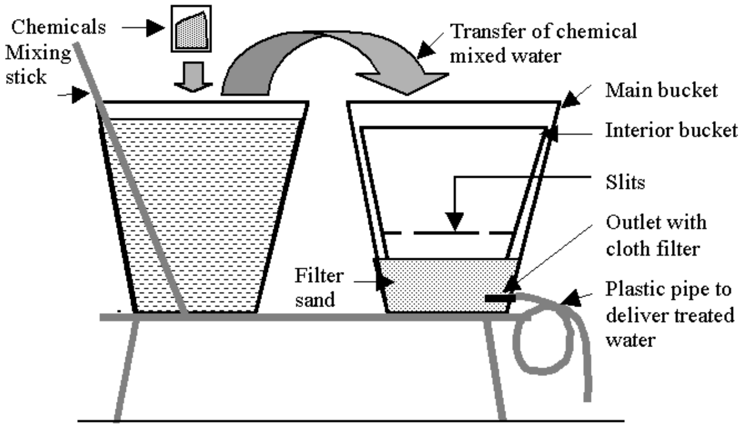


Figure 4.8: Stevens Institute Technology (74)

BCSIR Filter Unit

Bangladesh Council of Scientific and Industrial Research (BCSIR) have developed an arsenic removal system, which uses the process of coagulation/co-precipitation with a iron based chemical followed by sand filtration. The unit did not take part in a comprehensive evaluation process (74).

DPHE-Danida Fill and Draw Units

It is a community type treatment unit designed and installed under DPHE-Danida Arsenic Mitigation Pilot Project. It is 600L capacity (effective) tank with slightly tapered bottom for collection and withdraws of settled sludge. The tank is fitted with a manually operated mixer with flat-blade impellers. The tank is filled with arsenic contaminated water and required quantity of oxidant and coagulant are added to the water. The water is then mixed for 30 seconds by rotating the mixing device at the rate of 60 rpm and left overnight for sedimentation. The water takes some times to become completely still which helps flocculation. The flocs formation is caused by the hydraulic gradient of the rotating water in the tank. The settled water is then drawn through a pipe fitted at a level few inches above the bottom of the tank and passed through a sand bed and finally collected through a tap for drinking purpose as shown in **figure 4.9**. The mixing and flocculation processes in this unit are better controlled to effect higher removal of arsenic. The experimental units installed by DPHE-Danida project are serving the clusters of families and educational institutions (74).

The principles of arsenic removal by alum coagulation, sedimentation and filtration have been employed in a compact unit for water treatment in the village level in West Bengal, India. The arsenic removal plant attached to hand tubewell as shown in **figure 4.10** has been found effective in removing 90 percent arsenic from tubewell water having initial arsenic concentration of 300 m g/l. The treatment process involves addition of sodium hypo-chloride (Cl2), and aluminium alum in diluted form, mixing, flocculation, sedimentation and up flow filtration in a compact unit (74).

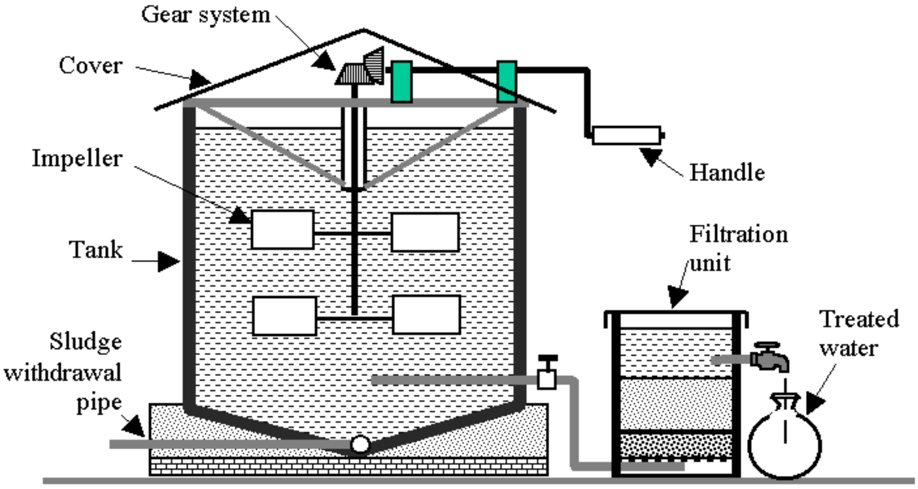


Figure 4.9: Stevens Institute Technology (74)

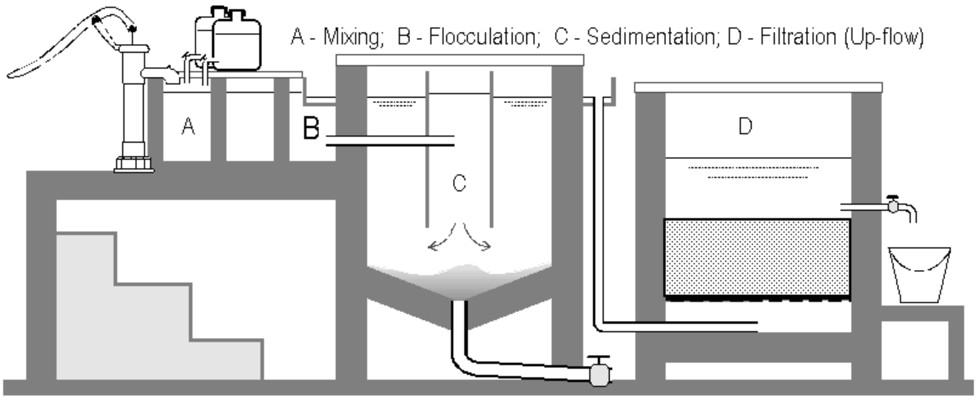


Figure 4.10: Arsenic Removal Plants Attached to Tubewell (74)
(Designed and Constructed in India)

Naturally Occurring Iron

The use of naturally occurring iron precipitates in groundwater in Bangladesh is a promising method of removing arsenic by adsorption. It has been found that hand tubewell water in 65% of the area in Bangladesh contains iron in excess of 2 mg/l and in many acute iron problem areas; the concentration of dissolved iron is higher than 15 mg/l. Although no good correlation between concentrations of iron and arsenic has been derived, iron and arsenic have been found to co-exist in groundwater. Most of the Tubewell water samples satisfying Bangladesh Drinking Water Standard for Iron (1 mg/l) also satisfy the standard for Arsenic (50 m g/l). Only about 50% of the samples having iron content 1 - 5 mg/l satisfy the standard for arsenic while 75% of the samples having iron content > 5 mg/l are unsafe for having high concentration of arsenic (74).

The iron precipitates [Fe (OH)3] formed by oxidation of dissolved iron [Fe(OH)2] present in groundwater, as discussed above, have the affinity for the adsorption of arsenic. Only aeration and sedimentation of tubewell water rich in dissolved iron has been found to remove arsenic. The Iron Removal Plants (IRPs) in Bangladesh constructed on the principles of aeration, sedimentation and filtration in small units have been found to remove arsenic without any added chemicals. The conventional community type IRPs, depending on the operating principles, more or less work as Arsenic Removal Plants (ARPs) as well. A study suggests that As (III) is oxidized to As (V) in the IRPs to facilitate higher efficiency in arsenic removal in IRPs constructed in Noakhali (Dahi and Liang, 1998). The Fe-As removal relationship with good correlation in some operating IRPs has been plotted in **figure 4.11**. Result shows that most IRPs can lower arsenic content of tubewell water to half to one-fifth of the original concentrations. The efficiency of these community type Fe-As removal plants can be increased by increasing the contact time between arsenic species and iron flocs. Community participation in operation and maintenance in the local level is absolutely essential for effective use of these plants (74).

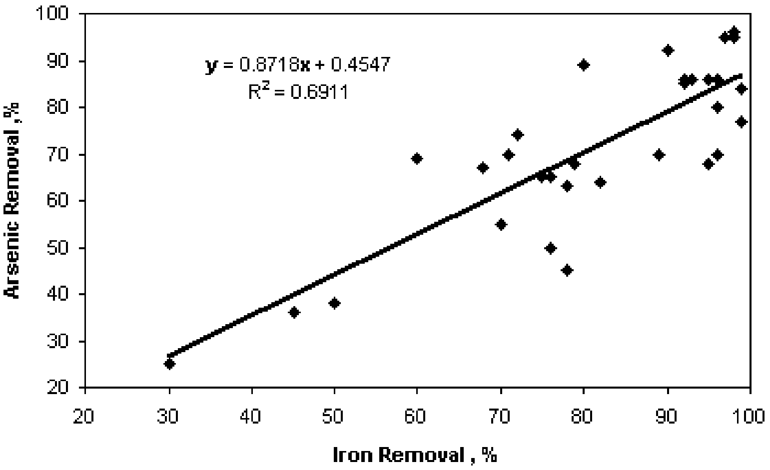


Figure 4.11: Correlation between Fe and As Removal in Treatment Plants (74)

Some medium scale Fe-As removal plants of capacities 2000-3000 m3/d have been constructed for water supplies in district towns based on the same principle. The treatment processes involved include aeration, sedimentation and rapid sand filtration with provision for addition of chemical, if required. These plants are working well except that treated water requirement for washing the filter beds is very high. Operations of small and medium size IRP-cum-ARPs in Bangladesh suggest that arsenic removal by co-precipitation and adsorption on natural iron flocs has good potential (74).

Granular Ferric Hydroxide

M/S Pal Trockner (P) Ltd, India and Sidko Limited, Bangladesh installed several Granular Ferric Hydroxide based arsenic removal units in India and Bangladesh. The Granular Ferric Hydroxide (Adsorb As®) is arsenic selective abdsorbent developed by Technical University, Berlin, Germany. The unit requires iron removal as pre-treatment to avoid clogging of filter bed. The proponent of the unit claims to have very high arsenic removal capacity and produces non-toxic spent granular ferric hydroxide (74).

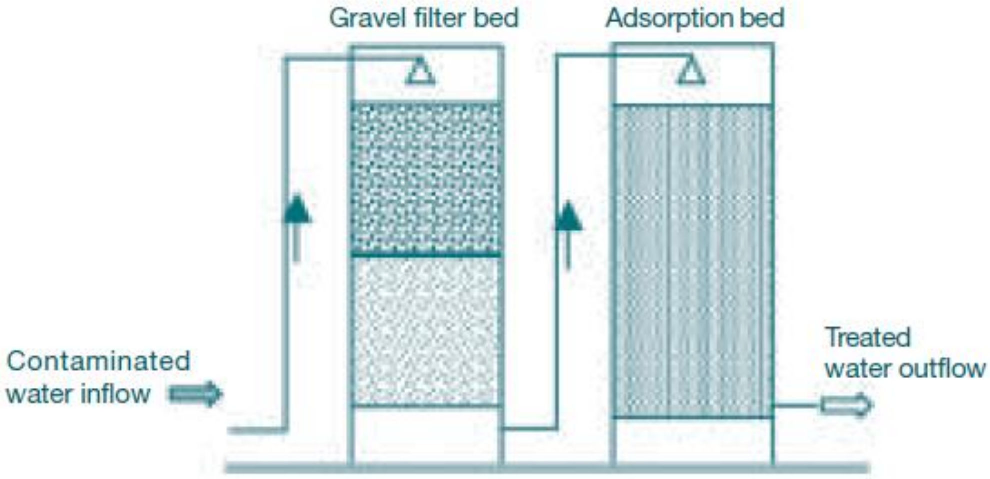


Figure 4.12: Granular Ferric Hydroxide-Based Arsenic Removal Unit (Pal, 2001) (4)

Read-F Arsenic Removal Unit

Read-F is an adsorbent produced and promoted by Shin Nihon Salt Co. Ltd, Japan for arsenic removal in Bangladesh. Read-F displays high selectivity for arsenic ions under a broad range of conditions and effectively adsorbs both arsenite and arsenate without the need for pretreatment. The Read-F is Ethylene-Vinyl Alcohol Copolymer (EVOH) -borne hydrous cerium oxide in which hydrous cerium oxide ($CeO2 \cdot n H2O$), is the adsorbent. The material contains no organic solvent or other volatile substance and is not classified as hazardous material. Laboratory test at BUET and field testing of the materials at 4 sites under the supervision of BAMWSP showed that the adsorbent is highly efficient in removing arsenic from groundwater (SNSCL, 2000) (74).

Shapla Filter

Shapla filter, a household arsenic removal unit, has been designed with iron coated brick dust as an adsorption medium and works on the same principles as iron coated sand described above. The unit is effective in removing arsenic from drinking water (74).

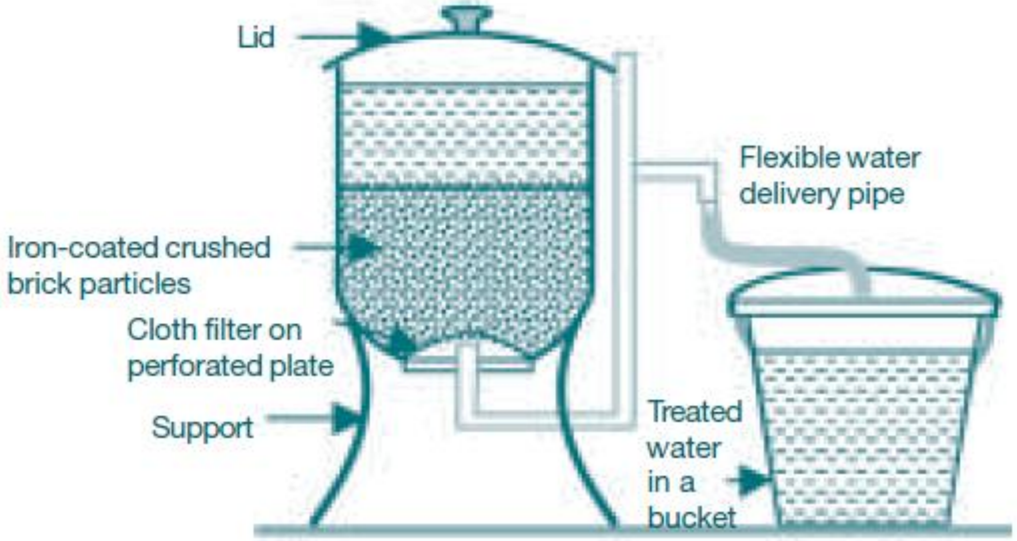


Figure 4.13: Shapla Filter for Arsenic Removal at Household Level by IDE
(Ahmed, 2003) (4)

Indigenous Filters

There are several filters available in Bangladesh that use indigenous material as arsenic adsorbent. Red soil rich in oxidized iron, clay minerals, iron ore, iron scrap or fillings, processed cellulose materials are known to have capacity for arsenic adsorption. Some of the filters manufactured using these materials include:

- Sono 3-Kolshi Filter
- Granet Home-made Filter
- Chari Filter
- Adarsha Filter
- Shafi Filter and
- Bijoypur Clay/Processed Cellulose filters (37).

The Sono 3-Kolshi filter uses zero valent iron fillings and coarse sand in the top Kolshi, wood coke and fine sand in the middle Kolshi while the bottom Kolshi is the collector of the filtered water (Khan et al., 2000). Earlier Nikolaidis and Lackovic (1998) showed that 97 % arsenic can be removed by adsorption on a mixture of zero valent iron fillings and sand and recommended that arsenic species could have been removed through formation of co-precipitates, mixed precipitates and by adsorption onto the ferric hydroxide solids. The Sono 3-Kolshi unit has been found to be very effective in removing arsenic but the media harbor growth of microorganism (BAMWSP, DFID and Water Aid, 2001). The one-time use unit becomes quickly clogged, if groundwater contains excessive iron (37).

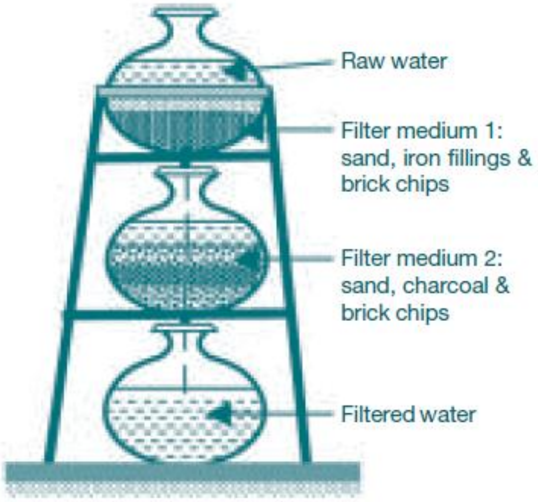


Figure 4.14: Three Kalshi Filter for Arsenic Removal (Drawn by Ahmed, 2003 based on Khan and Others, 2000) (4)

The Garnet home-made filter contains relatively inert materials like brick chips and sand as filtering media. No chemical is added to the system. Air oxidation and adsorption on iron-rich brick chips and flocs of naturally present iron in groundwater could be the reason for arsenic removal from groundwater. The unit produced inadequate quantity of water and did not show reliable results in different areas of Bangladesh and under different operating conditions. The Chari filter also uses brick chips and inert aggregates in different Chairs as filter media. The effectiveness of this filter in arsenic removal is not known (74).

The Shafi and Adarsha filters use clayey material as filter media in the form of candle. The Shafi filter was reported to have good arsenic removal capacity but suffered from clogging of filter media. The Adarsha filter participated in the rapid assessment program but failed to meet the technical criterion of reducing arsenic to acceptable level (BAMWSP, DFID and Water Aid, 2000). Bijoypur clay and treated cellulose were also found to adsorb arsenic from water (Khair, 2000) (74).

Cartridge Filters

Filter units with cartridges filled with sorptive media or ion-exchange resins are readily available in the market. These units remove arsenic like any other dissolved ions present in water. These units are not suitable for water having high impurities and iron in water. Presence of ions having higher affinity than arsenic can quickly saturate the media requiring regeneration or replacement. Two household filters were tested at BUET laboratories, these are:

- Chiyoda Arsenic Removal Unit, Japan
- Coolmart Water Purifier, Korea (4)

The Chiyoda Arsenic Removal Unit could treat 800 BV meeting the WHO guideline value of 10µg/L and 1300 BV meeting the Bangladesh Standard of 50µg/L when the feed water arsenic concentration was 300µg/L. The coolmart Water Purifier could treat only 20L of water with an effluent arsenic content of 25µg/L (Ahmed et al., 2000). The initial and operation costs of these units are high and beyond the reach of the rural people (4).

Some of the activated alumina based sorptive media used in Bangladesh include:

- BUET Activated Alumina
- Alcan Enhanced Activated Alumina
- ARU of Project Earth Industries Inc., USA
- Apyron Arsenic Treatment Unit (4)

The BUET and Alcan activated alumina have been extensively tested in field condition in different areas of Bangladesh under rapid assessment and found very effective in arsenic removal (BAMWSP, DFID, Water Aid, 2001). The Arsenic Removal Units (ARUs) of Project Earth Industries Inc. (USA) used hybrid aluminas and composite metal oxides as adsorption media and were able to treat 200-500 Bed Volume (BV) of water containing 550g/L of arsenic and 14mg/L of iron (Ahmed et al., 2000). The Apyron Technologies Inc. (ATI) also uses inorganic granular metal oxide based media that can selectively remove As (III) and As (V) from water. The Aqua-Bind TM arsenic media used by ATI consist of non-hazardous aluminium oxide and manganese oxide for cost-effective removal of arsenic. The proponents claimed that the units installed in India and Bangladesh consistently reduced arsenic to less than 10µg/L (4).

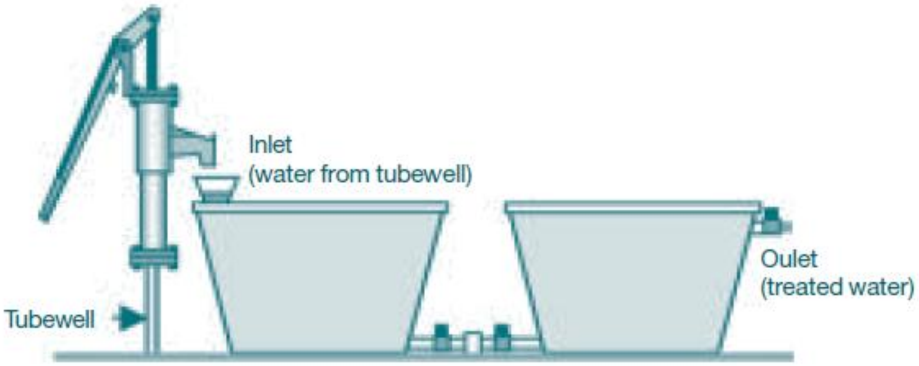


Figure 4.15: Alcan Enhanced Activated Alumina Unit (Drawn by Ahmed, 2003) (4)

Water System International (WSI) India has developed and patented an ion exchange process for arsenic removal from tubewell water. The so-called bucket of resin unit is encased in a rectangular container placed adjacent to the tubewell. There are three cylinders inside the container. Water in the first cylinder is mixed with an oxidizing agent to oxidize As(III) to As(V) while As(V) is removed in the second cylinder, which is filled with WSI patented processed resin. The treated water is then allowed to flow through a bed of activated alumina to further reduce residual arsenic from water. Ion Exchange (India) Ltd. Has also developed and marketed an arsenic removal community-level plant based on ion exchange resin (4).

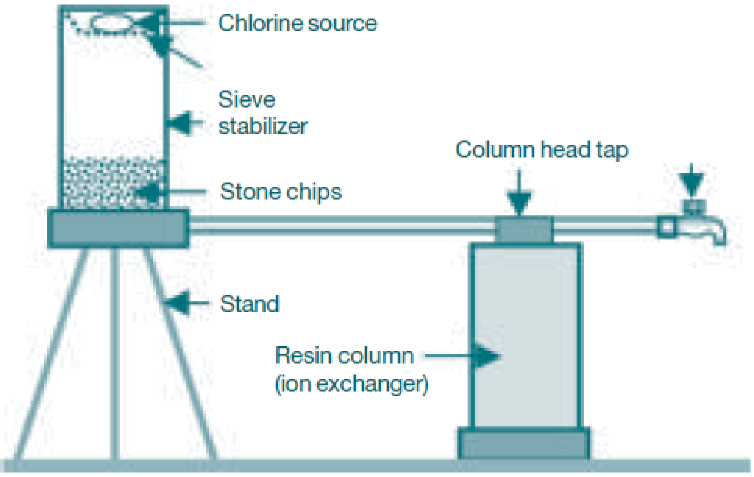


Figure 4.16: Tetrahedron Arsenic Removal Technology (Drawn by Ahmed, 2003) (4)

4.2 Centralized arsenic removal systems

Conventional coagulation-separation and adsorption are the most common methods used in centralized removal systems both in industrialized and developing countries (115).

a. <u>Coagulation-separation arsenic removal system</u>

In these systems, aluminium or iron based salts are used as a coagulant. After flocculation, flocs are separated in a floc separation unit, usually using sedimentation and rapid sand filtration. An example of a compact conventional coagulation based treatment unit is given in the figure below (115):

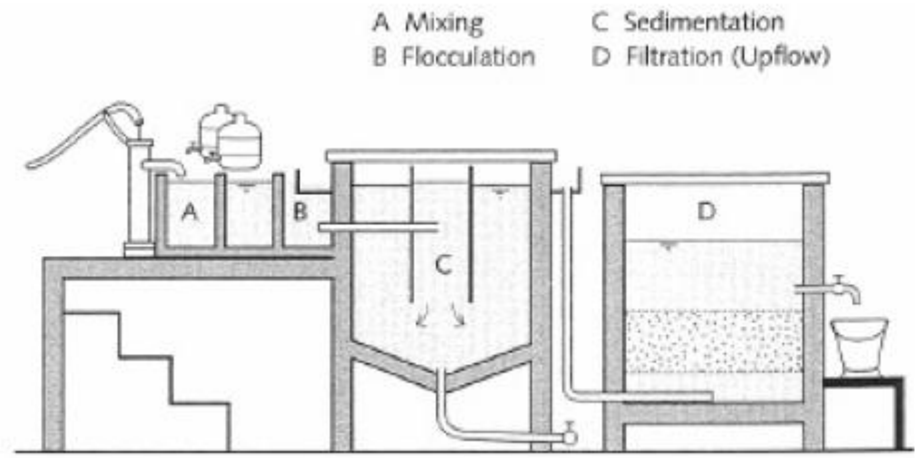


Figure 4.17: Conventional coagulation based treatment unit attached to a tube well (Source: IRC) (115)

Aeration (cascade, plate aerator, aeration tower, etc.) can be used before adding the coagulant. In groundwater containing high iron concentrations, aeration can considerably reduce the coagulant dosage. Aeration and filtration used in a conventional iron removal system (see figure below) will always remove some arsenic (3).

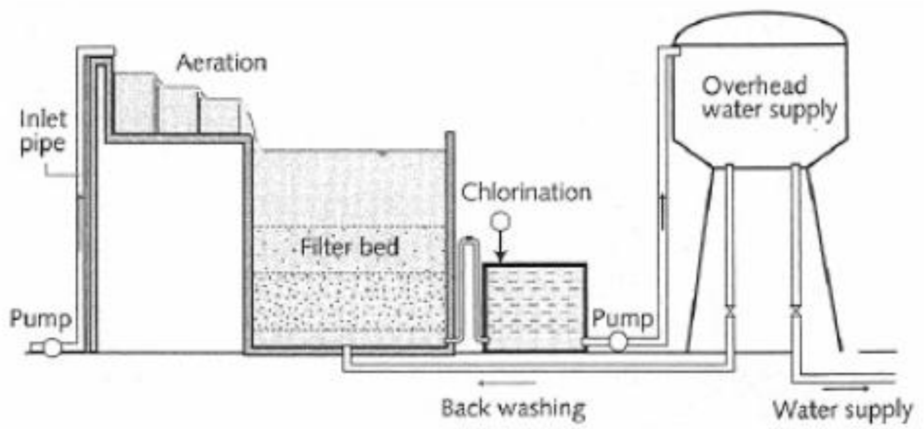


Figure 4.18: Conventional iron removal treatment unit (Source IRC) (115)

Aeration combined with rapid sand filtration is promising for iron-rich groundwater areas in Bangladesh. Chemical pre-oxidation (chlorination or ozonation) is required for removal of As (V). Production of a large volume of toxic liquid waste is the major disadvantage of the coagulation based systems (115).

b. Adsorption based arsenic removal systems

Traditionally, these systems use activated alumina (AA) as an adsorbent. This absorbent is cheap, but its efficiency strongly depends on pH, salinity and presence of competing ions (e.g. fluoride or sulphate) (115).

Recently, iron based adsorbents are used. Commercial available adsorbents are relatively expensive but have high adsorption capacity. The systems using these adsorbents are simply to operate. Such systems typically comprise one or a series of adsorptive filters without need for chemical addition (BASF, 2007) (115).

Iron oxide coated sand (IOCS) from groundwater treatment plants is an innovative and cheap alternative for commercially available adsorbents (115).

4.3 Household level point-of-use (POU) treatment systems

Household level arsenic removal systems use adsorptive filtration or coagulation, ion exchange treatment or combination of coagulation and adsorption. Oxidation is sometimes used to improve As (III) removal efficiency (115).

A comprehensive survey of POU arsenic removal systems based on a short-term performance test in terms of flow rate, storage capacity, breakthrough time, bacteriological performance, chemical use, costs, and user acceptability has been made by WaterAid. The results of this survey are presented in two reports (WaterAid, 2001a, and b). UNESCO-IHE has developed a POU filter for arsenic removal with iron oxide coated sand (IOCS) as an adsorbent. The filter is simple, easy-to-use and does not require any chemicals (115).

Alcan, Sidko (a granular ferric hydroxide filer system), READ-F and Sono are four commercial methods recently approved by the Government of Bangladesh for sale. Good back-up and accepted methods for sludge disposal are essential for the operation of the POU systems (Arsenic project, 2007). Alcan and Sono filters are shown in figure below (115).

Figure 4.19: An Alcan filter (left) under testing in Azimpur village, Manikgonj district, Bangladesh and **Figure 4.20: A Sono arsenic removal filters** (right) (Source: IRC) (115)

4.4 Comparative study between the different technologies

Table 4.1: Removal methods for Arsenic from groundwater/drinking water (based on Johnston and Heijnen, 2001and Ahmed, 2001) (115)

Techniques	**Household**	**Community level**	**Removal efficiency As (III)**	**As (V)**	**Working pH**	**Interferences**	**Operator skill**	**Relative costs**	**Advantages**	**Disadvantages**	**Remarks**
Oxidation/Precipitation											
Air oxidation	x	x	-	-					relative simple, low-cost	partial removal of arsenic slow process	
chemical oxidation	x	x	-	+					relative simple and rapid proces oxidizes other impurities and kills microbes		
Coagulation/Co-precipitation			-	+++		little		low	no monitoring of break through is requir low costs and simple chemicals	toxic sludge is produced operation requires training	most effective process to meet the regulations standard wide-range of arsenic contaminated influent concentrat
Alum coagulation	x	x	-	+++	6.0 - 8.0		medium	low	chemicals normaly available low capital costs	pre-oxidation is a must (low removal of As (III) produces toxic sludges	proven at central level piloted at community and household level silica and phosphate may reduce As removal
Iron coagulation	x	x	++	+++	< 8		medium	low	efficient at low costs simple operation common chemicals	medium removal of As (III) pre-oxidation may be required	well proven at all three levels. silica and phosphate may reduce As removal
Lime softening	x	x	+	+++	> 11,5		medium	low-medium	common chemicals	re-adjustment of pH is required large waste	proven in lab and pilot scale
Enhanced Coagulation	x	x	++	+++	5.0-9.0		meduim	low-medium	high removal efficiency of As also removal of organic matter and metal hydroxides	emerging technique, not proven on practical scale	
Sedimentation	x	x	-	-			low	low	simple	low reduction	relies on passive coagulation with iron
Oxidation/Filtration	x	x	-	++	5.5-8.5		medium	medium			
Adsorption			+	+++		average			no daily sludge problem	requires monitoring break through requires periodical regeneration or medium shift	
Activated Alumina	x	x	++	+++	5.5 - 6		low	medium	well known, commercially available very efficient removal low maintenance, no daily sludge	re-adjustment of pH required toxid solid waste monitoring is difficult	pilot scale in community and household level in indus. countries arsenite removal is poorly understood
Iron based Sorbents (IBS)	x	x	+	+++	6.0-8.5		low	low-medium	plenty possibilities well defined technique no regeneration	requires pH control requires replacement of media after exhausting reuqires regular testing to provide safe operation	

Techniques	Household	Community level	Removal efficiency		Working pH	Interferences	Operator skill	Relative costs	Advantages	Disadvantages	Remarks
			As (III)	As (V)							
Ion exchange											
Anion resin	x	x	-	+++	6.5-9.0	many	high	medium	well defined medium no pH correction	only As (V) removal interference from sulfate, nitrate and TDS adding of salt monitoring is difficult high costs	pilot scale in central and household systems, mostly in indus. countries
Membrane/Reverse Osmosis								high	high removal efficiency no solid waste capable of removal of other contaminant	high running costs high tech operation and maintenance re-adjustment water quality is required	shown effective at lab scale in industrial countries pretreatment required research needed on removal of arsenite
Reverse osmosis	x	x	-/++	++			medium	high	easily monitoring no chemicals required no toxic wastes	removal of Arsenite (III) lower than Arsenate (V) removal high investment costst high tech operation/maintenance	
Electrodialysis		x	-/++	+++			medium	high	removal of other contaminants	interference by oxidizing agents toxic waste water	
Nanofiltration			-/++	++			medium	high	well defined, high removal efficiency	very high capital and running costs	
CAMP (Coagulation Assisted Membrane Process)		x	-/+++	+++				high		pre-treatment required high costs	
Biological											
Other											
In-situ Oxidation/immobilizatio		x	++	+++				medium	no arsenic-rich wastes	possibility of aquifer clogging	very limited experience

*)
: +++ = > 90% removal
: ++ = 60 - 90% removal
: + = 30 - 60% removal
: - = < 30% removal

Table 4.2: Overview of small scale (household) arsenic removal methods (based on WaterAid, 2001 and Rahman and Ravenscroft, 2003) .Most of them are small scale (household) methods practiced in rural areas (115).

Technology	Method	Removal Efficiency		Flow rate	Cost (US$)	User	Agency/promotor
		As (III)	As (V)				
Passive sedimentation	sedimentation	-	0	20 litres in 12 hours	5 (20 litre aluminium kolhsi)	Household	DPHE
in-situ sedimentation	sedimentation	-	0			Community	DPHE/Danida
Ardasha Filter (AR)	sedimentation + adsorption			13 litres in 12 hours	11 (installation)	Household	CRS-Ardasha filter Ind., Chagalnaya, Feni
Solar Oxidation (SORAS)	oxidation	-	-	not adequate		Household	Swiss Federal Institute for Environmental Science and technology
UNESCO-IHE IOCS-technology	adsorption	++	+++	100 litres in 12 hours		Household (Fam. filter)	UNESCO-IHE, Vitens and Selor
UNESCO-IHE IOCS-technology	adsorption	++	+++	> 200 M3/day	0,25/m3 (total costs)	Large scale application	UNESCO-IHE, Vitens and Selor
Alcan Activated Alumina (AL)	adsorption			> 3600 litres in 12 hours	170 (installation)	Household/comm.	MAGC Technologies Ltd., Dhaka
BUET Activated Alumina	oxidation + adsorption		+++	100 litres in 12 hours	20 (installation)	Household	Department of Civil Engineering, BUET
Two Bucket System	coagulation + adsorption		++	43 litres in 12 hours	7 (installation)	Household	DPHE/Danida
GARNET-filter	coagulation		0	13 litres in 12 hours	12 (installation)	Household	GARNET
Sono 3-kolski method	coagulation + adsorption		+++	60 litres in 12 hours	6 (installation)	Household	Prof. Khan/University of Dhaka
Stevens Institute Method	coagulation + filtration		++	240 litres in 12 hours	40 (installation)	Household/community	Stevens Institute
Rice Husk Arsenic Unit	coagulation + flocculation	-	+	not adequate		household	DPHE/Danida
ARU (Arsenic Removal Unit)	adsorption	-	+	sufficient		Community	DPHE/Danida
Harbauer Technology	adsorption	0	+++	sufficient	low	Community	German-Sidko Ltd.
Safi filter	oxidation + filtration	-	+	not adequate		Household	Prof. Safiullah, Safiullah University
Tetrahedron	Ion exchange		+	1800 litres in 12 hours	250 (installation)	Household/comm.	Tetra hedron@prodigy.net
Bio-solution to Arsenic Problem	micro-biological		0	sufficient		Community	Prof. Aziz, Department of Botany Dhaka University
Microbiological process	micro-biological	0	0	not adequate		Community	Paknikar

Based on available information, a matrix is composed to give an idea about the applicability of the methods for some given situations (115).

Table 4.3: Applicability of arsenic removal methods for specific conditions (115)

Methods	domestic + low costs	community + low costs	domestic + high As removal	community + high As removal	domestic + brackish water	community + brackish water
alum coagulation	🟩	🟩	🟩	🟩	🟥	🟥
Iron coagulation	🟩	🟩	🟩	🟩	🟥	🟥
Enhanced coagulation (EC)	🟩	🟩	🟩	🟩	🟩	🟩
Activated alumina	🟧	🟧	🟩	🟩	🟥	🟥
Iron coated sand (IBS)	🟩	🟩	🟩	🟩	🟥	🟥
Ion exchange	🟧	🟧	🟩	🟩	🟥	🟥
membrane processes	🟥	🟥	🟩	🟩	🟩	🟩
conventional Fe-removal technique	🟩	🟩	🟥	🟥	🟥	🟥
memstill®	🟧	🟧	🟩	🟩	🟩	🟩
waterpyramid/solar dew	🟧	🟧	🟩	🟩	🟩	🟩
UNESCO-IHE IOCS	🟩	🟩	🟩	🟩	🟥	🟥
Alcan Activated Alumina	🟩	🟧	🟩	🟩	🟥	🟥
BUET Activated Alumina	🟩	🟥	🟩	🟥	🟥	🟥
Sono 3-kolski method	🟩	🟥	🟩	🟥	🟥	🟥
Stevens Institute Method	🟩	🟧	🟩	🟩	🟥	🟥
Tetrahedron	🟩	🟧	🟧	🟧	🟥	🟥
Two bucket System	🟩	🟥	🟧	🟥	🟥	🟥

The colors in the matrix correspond with the appropriateness of the method for the given situation:

- Green color means that the method is very suitable
- Orange color means average suitability
- Red color means that the method is unattractive or not applicable for the given situation (115).

The methods marked in italic are household level arsenic removal methods, which have been tested by WaterAid in Bangladesh (WaterAid, 2001b). From the matrix it is evident that all the mentioned household methods are low cost methods. For community scale, iron and alum coagulation and Iron coated sand (IBS/IOCS) adsorption are low cost methods. A promising emerging technique is Enhanced Coagulation (EC). With this technique a very efficient removal of As (III) and As(V) is possible to below the recommended WHO-value of 10 µg/l. With EC also the removal of fluoride, humic substances and other harmful or toxic matters is realized (metal hydroxides). For groundwater with high iron content, also conventional iron removal techniques, like aeration and filtration, can be used to remove arsenic at low costs. However, the efficiency of these techniques for As-removal is not very high (115).

In situations where high arsenic removal efficiency is necessary, several methods can be used. With the mentioned household methods an arsenic concentration reduction to well below 50µg/l can be achieved. This concentration is still applied as a drinking water standard in many developing countries. It must be stressed that these household methods were tested under field conditions in rural Bangladesh with no or limited monitoring involved. Under optimal conditions and with the required monitoring, a reduction of the arsenic concentration to below the WHO guideline value of 10µg/l can be achieved by using advanced methods like membrane processes and adsorption1. Most of the methods do not remove arsenite (arsenic III) as efficient as arsenate (arsenic V). Therefore an oxidation of arsenite to arsenate is recommended (115).

For brackish water membrane processes like reverse osmosis and electro-dialysis reversal are available. The emerging techniques Memstill® and the Water Pyramid®/Solar Dew are also suitable. Again, enhanced coagulation is a very promising technique for this application (115).

4.5 Overview of technologies use in iron& manganese removal

4.5.1 Common methods for iron & manganese removal

There are some methods of treating water containing these two contaminants:
1) Ion exchange water softeners
2) Oxidation and filtration

- Oxidizing with aeration followed by filtration
- Chemical oxidization followed by filtration

i) Chlorine

ii) Potassium permanganate
iii) Ozonation
3) Sequestration- use of such materials as polyphosphates
(a) "Pot" feeders
(b) Solution feeders
4) Oxidizing Filtration Media

- Manganese Greensand
- Birm
- Pyrolox

5) Reverse osmosis
6) Biological removal (116)

1) Ion exchange water softeners

Ion exchange should be considered only for the removal of small quantities of iron and manganese. For practical purposes in an everyday working softener, the upper limit is about 5 to 7 parts per million. Ion exchange involves the use of synthetic resins where a pre-saturate ion on the solid phase (the "adsorbent," usually sodium) is exchanged for the unwanted ions in the water. One of the major difficulties in using this method for controlling iron and manganese is that if any oxidation occurs during the process, the resulting precipitate can coat and foul the media. Cleaning would then be required using acid or sodium bisulfate where the concentration of iron is above 5 or 6 parts per million, or when there is both dissolved and precipitated iron and manganese in the water, a different approach is needed (53).

2) Oxidation and filtration

Oxidation followed by filtration is a relatively simple process. The oxidant chemically oxidizes the iron or manganese (forming a particle), and kills iron bacteria and any other disease-causing bacteria that may be present. The filter then removes the iron or manganese particles (53).

Before iron and manganese can be filtered, they need to be oxidized to a state in which they can form insoluble complexes. Oxidation involves the transfer of electrons from the iron, manganese, or other chemicals being treated to the oxidizing agent. Oxidation methods fall into two groups: those using additives like chlorine, ozone or air; or those using an oxidizing filter media (53).

Oxidizing with aeration followed by filtration

Air is also used to convert dissolved iron into a form that can be filtered. This approach mimics what happens when untreated dissolved iron comes into contact with the air after leaving a faucet. Aeration methods can be of a two-tank or a single-tank variety. In a two-tank system, air is introduced into the first tank using a pump or other injection device. The dissolved iron precipitates in the first tank and is carried into the second tank where it is filtered in a Birm or multi-media filter. One drawback to this system is that water bearing the precipitated iron goes through the head of the first unit and the piping between the units. Particularly at lower flow rates, the sticky ferrous hydroxide tends to foul the valve on the first unit and may require cleaning every 6-24 months. A single-tank system essentially combines the two tanks of a single tank system into one. The iron is oxidized at the top of the tank before falling into the filter medium at the bottom. There is no potential fouling of the head. The iron is filtered before it goes through the outlet port of the valve. For very high levels of iron, chlorination with continuous regeneration is the only practical approach (53).

Operation of the aeration process requires careful control of the flow through the process. If the flow becomes too great, not enough air is applied to oxidize the iron and manganese. If the flow is too small and the aeration is not cut back, the water can become saturated with dissolved oxygen and, consequently, become corrosive to the distribution system. Corrosive water may lead to increased lead and copper levels at customers' taps (117).

There are many ways to provide the aeration. Either the water being treated is dispersed into the air or else air is bubbled into the water. Other aeration methods include cascade trays, cone aerators, and porous air stones (117).

During aeration, slime growths may be created on the aeration equipment. If these growths are not controlled, they could produce taste and odor problems in the water. The growth of slime can be controlled by the addition of chlorine at the head of the treatment plant. The process should be inspected regularly to catch the problems in their early development (117).

A reaction basin can be provided after the aeration to allow the oxidation to proceed to completion. The detention time is commonly provided by a head on the filters rather than by providing a separate tank. The detention time before filtration should be at least 20 minutes, more if possible. The pH of the water influences how much time is needed for the reaction to be completed (117).

If the reaction basin is separate from the filters, the basin must, on a regular schedule, be cleaned and monitored for sludge accumulation (117).

After the oxidation of the iron and manganese is completed, the water must be filtered to remove the precipitated material. The filters used are generally of pressure type (117).

The oxidation of iron and manganese with air is by far the most cost-effective method since there is no chemical cost; however, there are disadvantages. If there are high levels of manganese, the oxidation process can be slowed and the reaction tank has to be quite large. In addition, small changes in the water quality may affect the pH of the water and the oxidation rate may slow to a point where the plant capacity for iron and manganese removal is reduced (117).

Chemical oxidization followed by filtration

- ### Oxidization with chlorine

Iron and manganese in water can be oxidized by chlorine, converting them to ferric hydroxide and manganese dioxide. The flocculated material can then be removed by filtration. The higher the amount of chlorine fed, the more rapid the reaction. Some plants have been designed for an initial chlorine residual of 5 to 10 ppm. After filtration the chlorine is removed by the addition of sodium bisulfide, sulfur dioxide, or sodium bisulfide (117).

When using this process on water containing high organic color, the likelihood of generating disinfection by-products is greatly increased (117).

When de-chlorinating, the operator must be careful that the chemical used for de-chlorination is not overdosed. This could result in inadequate disinfection in the system since any chemical left in the water could also remove the necessary chlorine in the distribution lines (117).

- ### Oxidization with potassium permanganate

The use of potassium permanganate for the oxidization of iron or manganese is common in Minnesota. Potassium permanganate oxidizes iron and manganese into their insoluble states. The dose must be great enough to oxidize all of the manganese, but not too great as this will produce a pink color in the water in the distribution system. Observing water being treated will indicate if any adjustments of the feeders are needed. Use of permanganate is more effective at oxidizing manganese than aeration or chlorination (117).

When oxidizing with permanganate, the operation of the filters becomes important since the reaction also continues to take place in the filter media. The normally-used filter media will remove iron and manganese if the combined concentration is below 1 ppm. Higher concentrations require different type of filter materials and different methods of operation (117).

Potassium permanganate treatment is often done by the use of manganese greensand, a granular material that is charged with potassium permanganate after the backwashing process. This method allows the oxidation process to be completed in the filter itself. After the filter is backwashed, it will be allowed to regenerate for a period of time with a high level of permanganate before it is put back into operation (117).

A common modification of the manganese greensand process is the adding of permanganate on a continuous basis. The permanganate is fed at the head of the filter so that the greensand is continuously recharged. The permanganate addition has to be carefully controlled; if the chemical is overfed, the effluent from the filter turns pink (117).

- **Ozonation**

An ozone generator is used to make ozone that is then fed by pump or by an air injector into the water stream to convert ferrous iron into ferric iron. Ozone has the greatest oxidizing potential of the common oxidizers. This is followed by a contact time tank and then by a catalytic medium or an inert multilayered filter for removal of the ferric iron (53).

2) Sequestration- use of such materials as polyphosphates

Sometimes a polyphosphate is added at the source to mask the effects of high iron concentrations in the distribution system. This is effective in cases in which the water contains up to 0.3 ppm of iron and less than 0.1 ppm of manganese. The phosphate delays the precipitation of oxidized manganese and iron, thereby greatly reducing the layer of scale that forms on the pipe. The effect is called sequestration. The iron or manganese ion is surrounded by a chain of phosphate molecules and is not allowed to precipitate in the water (117).

Pyrophosphate, tripolyphosphate, and metaphosphate may all be effective as iron and manganese sequestering agents. The most effective one, however, seems to be sodium phosphate in low concentrations. The proper dose and type of phosphate should be selected only after bench-scale testing is performed by a qualified technician or consultant (117).

The amount of phosphates required sequestering iron and manganese varies, the amount generally has to be approximately two parts actual phosphate (as product) for one part of iron and manganese to accomplish the desired result. It is important to remember that chlorine residual must be maintained throughout the distribution system to control bacterial growth. This residual should be greater than 0.2 ppm at the most distant part of the system (117).

If the total detention time in the distribution system exceeds 72 hours, the phosphates may break down and release the iron and manganese in the outer portions of the system. It is important for the operators to know if the detention time will be exceeded and that the iron or manganese problem may not be resolved with polyphosphate treatment (117).

3) Oxidizing Filtration Media

Manganese Greensand - the most common chemical oxidant used, it has a relatively high capacity for iron removal and can operate at high flow rates with moderate backwash requirements. Greensand is a processed material consisting of nodular grains of the zeolite mineral glauconitic. The material is coated with manganese oxide. The ion exchange properties of the glauconitic facilitate the bonding of the coating. This treatment gives the media a catalytic effect in the chemical oxidation reduction reactions necessary for iron and manganese removal. This coating is maintained through regeneration with potassium permanganate – about 1.5 to 2 oz. per cubic foot of greensand (53).

Birm - acts as a catalyst to promote the reaction between the oxygen and iron dissolved in the water. It requires no regeneration but needs a relatively high level of dissolved oxygen and works best at a pH above 6.8 (53).

Pyrolox - a natural ore that oxidizes and then filters the resulting insoluble iron. It does not need to regenerate; therefore, it doesn't need other chemicals. However, it needs, ideally, to backwash at 25 to 30 gallons per sq. ft (53).

4) Reverse osmosis

Reverse osmosis (R.O.) is a membrane separation technology that is very effective in removing almost all inorganic contaminants and dissolved solids in fluids. The membranes for R.O. can be able to remove up to 99,8% of substances present in water, ranging from inorganic chemicals to organic and biological contaminants. Reverse osmosis can remove contaminants and dissolved solids using a semi-permeable membrane that permits only water and not dissolved ions (such as sodium and chloride) to pass through it. Contaminated water is forced through the membrane by high pressure, leaving contaminants and dissolved solids behind. Membranes are available in a variety of pore sizes and characteristics (118).

Where only a small volume of treated water is needed, approximately 0-10 gallons per day (gpd), RO is typically the most flexible and cost efficient treatment process available for private home use (119).

Devices treating small volumes of water are often called "under-the-sink" or "point-of-use" (POU) sized treatment devices. Treatment devices which purify all water used in a home are commonly called "whole house" or "point-of-entry" sized water treatment devices (119).

These naturally occurring contaminants often create particles which will clog RO membranes by rust particles, Fe/Mn bacteria and silt and cannot be regenerated. New membranes would be required frequently and even a particle filter is critical where iron or manganese concentrations are high (119).

5) Biological removal

There are some bacteria which take their energy from the oxidation of iron and manganese and which require water with specific conditions to have an optimal activity of micro-organisms. In fact, the iron and manganese specific bacteria need different environmental conditions (120).

Iron bacteria can be controlled by periodic well chlorination or it can be treated in the building. The treatment involves the following: Chlorination, retention, filtration. Activated carbon is usually used as the filter material so the excess chlorine can also be removed (53).

The most common approach to control iron and manganese bacteria is shock chlorination. This involves introducing a concentration of chlorine solution into the entire water distribution system, letting the system remain idle for at least two to three hours, and then flushing the system to remove the chlorine. It is almost impossible to kill all the iron and manganese bacteria in a system. The shock chlorination procedures will most likely need to be repeated from time to time (121).

Multistage treatment

If water has high levels of iron and manganese in both dissolved and solids forms, a multistage treatment operation is necessary. For instance, the water could be chlorinated to oxidize dissolved iron and kill iron bacteria and filtered through a mechanical device to remove particles. This can be followed by activated carbon filtration to remove excess chlorine and water softener for hardness control as well as removal of any residual, dissolved iron or manganese (121).

4.5.2 Comparative study between different iron and manganese removal technologies

Table 4.4: Comparative study of different iron& manganese removal technologies

Symptom	Cause	Treatment
Water clear when drawn, reddish-brown or black particles appear as water stands; reddish-brown or black stains on fixtures or laundry.	Dissolved iron or manganese.	Water softener (less than 5 mg/L of iron) Aeration (less than 25 mg/L of iron). Oxidation/Filtration (less than 15 mg/L of iron plus manganese). Chlorination-Filtration (greater than 10 mg/L of iron).
Water contains reddish-brown particles when drawn; particles settle out as water stands.	Iron particles from corrosion of pipes and equipment.	Raise pH with neutralizing filter that also filters particles.
Water contains reddish-brown or black particles when drawn; particles settle out as water stands.	Oxidized iron, manganese, or both due to exposure of water to air prior to tap.	Particle filter (if quantity of oxidized material is high, use larger filter than in line, e.g. sand filter).
Reddish-brown or black slime appears in toilet tank or from faucet.	Iron bacteria. Manganese bacteria.	Kill bacteria masses by shock treatment with chlorine or potassium permanganate, then filter; may require continuous feed of chlorine or potassium permanganate, then filter.
Reddish or black color that remains after 24 hours.	Colloidal iron, manganese, or both. Organic-complexed iron, manganese, or both.	Chemical oxidation with chlorine or potassium permanganate.

(122)

Table 4.5: Applicability of iron & manganese removal methods for specific conditions

	To control discoloration without removal of Fe/Mn	To control discoloration, by removal of Fe/Mn	
Fe/Mn Condition	Dissolved Fe/Mn	Dissolved Fe/Mn Only	Precipitated/Dissolved
Water's Appearance	Clear water	Clear water	Rust or blackish color
Appropriate Fe/Mn Treatment Method	**Sequestering** Add sequestering chemicals, typically phosphate, to prevent staining. Not normally a homeowner approach.	**Water softening** (cation exchange)	**Oxidation/Filtration** Chlorine, potassium permanganate, aeration, followed by filtration, using greensand, Birm, cartridge or bag filters.

(119)

CHAPTER 5: DESIGN OF A SYSTEM TO REMOVE As, Fe, Mn, NH3& CH4 FROM POTABLE WATER

The concentration of dissolved arsenic, iron and manganese and gases like ammonia and methane have collected from sample test of well 23 that is shown in the table below with target value of the pollutants after treatment (123).

Table 5.1: Design parameter for well 23

Parameter	Influent water (mg L^{-1})	Regulatory limit (mg L^{-1})	Effluent after treatment (average value) (mg L^{-1})
Ammonia	1.25	<0.50	0.2
Iron	0.650	<0.2	0.1
Manganese	0.09	<0.05	0.03
Arsenic	0.05	<0.01	0.005
Methane	10	<10	2

As for methane, safety issues should be addressed such as the explosion potential of the off-gas during aeration (123).

5.1 Flow-sheet of the project schemes

In order to have economical, efficient and environmentally friendly treatment system there are three alternatives systems are presented here for removing those pollutants effectively.

Option A:

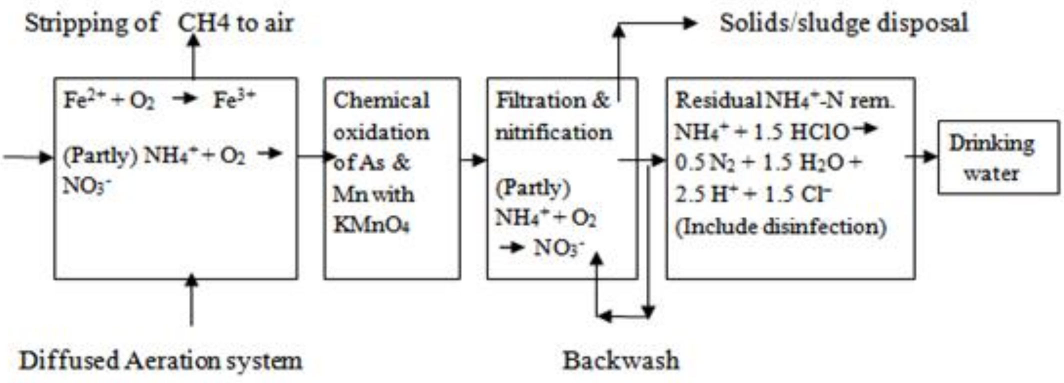


Figure 5.1: Flow-sheet of the project schemes-1

Option B:

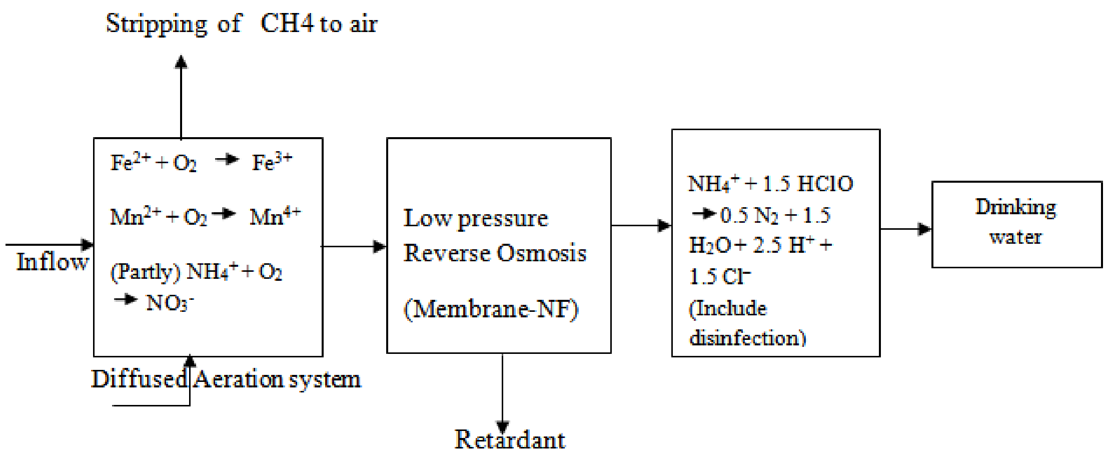


Figure 5.2: Flow-sheet of the project schemes-2

Option C:

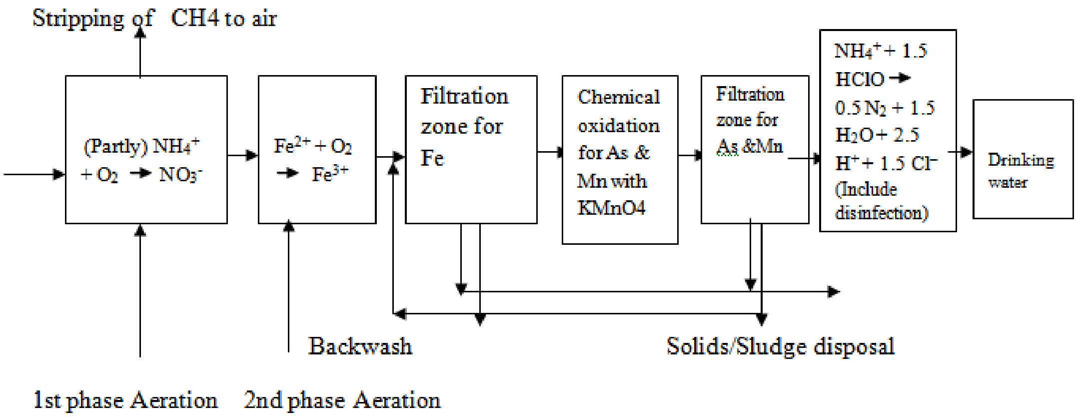


Figure 5.3: Flow-sheet of the project schemes-3

5.2 Feasibility study of the project schemes

Each system is different from each other from design point of view, installation, operating& maintenance. There are some specific features and characteristics of each system. **Table 5.2** describes briefly the feasibility of all those systems.

Table 5.2: Feasibility study of the projects schemes

Project scheme	**Description**	**Comments**
Option-A	1.This system can be easily applicable for our work; 2. Environmentally friendly as less chemical used and we can treat the system almost as a natural treatment method; 3. Cost effective as it removes methane & iron and most part of ammonia in a natural way; 4. Most common method and very easy to operate since the components are not too much complicate and less labor cost for operating and maintenance.	All the three systems have some common process and all the three systems have efficiency to remove those pollutants to the target level. But for cost efficient, space efficient, environmentally friendly and in order to remove those pollutants effectively to the target value, it's very useful and realistic to use the system-A for our work.
Option-B	1.Using of reverse osmosis does not fit to our work as flow rate is high and reverse osmosis is useful for less flow rate, high concentrations and for private home use; 2. As the concentrations are not so high, it is not realistic to design this system which is very expensive for installing, operating and maintenance.	
Option-C	It is applicable for high concentration of pollutants especially for Fe, Mn and As. So this case it also doesn't fit to our work.	

5.3 Process flow diagram of the system

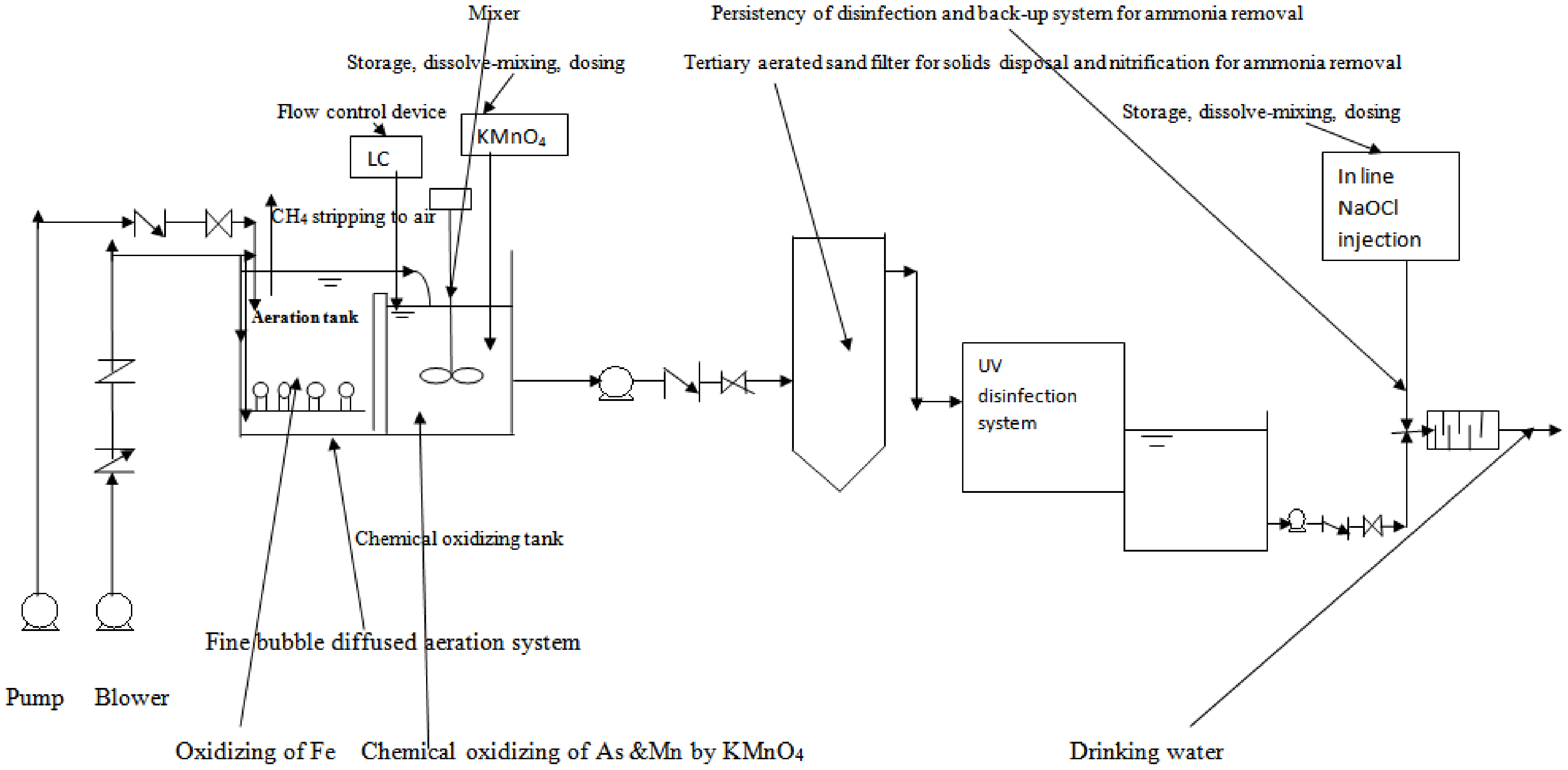


Figure 5.4: Process flow diagram of the system

5.4 Design consideration

For aeration methane will be extracted to the open air and iron will be oxidized easily. In order to oxidize ammonia and manganese to the very low level target, we need to increase pH and high aeration, but we will not increase pH and we also consider normal aeration but still there will be a possibility of oxidizing of partly ammonia and manganese.

By using potassium permanganate ($KMnO_4$), it is very effective to oxidize arsenic and manganese to the target values. In filtration and nitrification unit, we will remove the oxidized precipitation of arsenic, iron and manganese effectively (124). It is also possible to remove ammonia partly if the biological system works properly during operation. For any accidental failure of biological nitrification, still we have back-up for ammonia removal by using sodium hypochlorite with break point chlorination which is useful system as an emergency back-up for biological nitrification (125).

We can reasonably assume that ammonium has been removed below regulatory limits after the filtration unit. Then, disinfection can be performed by UV irradiation. Disinfection persistency can be achieved by a minimum dosage of sodium hypochlorite (<0, 2 mgCl/L) (125).

5.4.1 Diffused aeration system

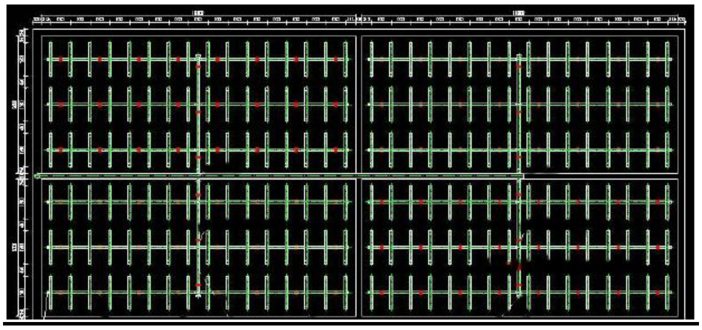


Figure 5.5: Layout of diffused aeration system (126)

Figure 5.6: Fine bubble disc diffused aeration system (126)

Diffused Aeration system is a subsurface from of diffusion in which air is introduced in the form of very small bubbles to aid or enhance the treatment of wastewater. Air from pipe into diffusers located at the bottom of aeration tank. These diffusers have numerous small openings (known as pores) through which air flows into the raw water in the tank. Diffused Aeration technology includes a major reduction in energy coasts, significantly higher oxygen transfer rates per hour, higher dissolved oxygen (DO) levels and an improved bottom line (126). The diffuser produces fine bubbles that carry the methane through a vent system to the outside air. The more and small fine bubbles, the system have the greater air-to-water contact and have greater efficiency (127).

Ensure the system is installed and operated according to the manufacturer's instructions. After installation, retest both the raw water (prior to treatment) and the treated water at a state certified laboratory to ensure the system is working properly and removing the contaminants. Continue to test the quality of both the raw and treated water annually or more frequently (quarterly or semi-annually) if high levels of contaminants is present in the raw water. Frequent testing will help determine how well the treatment system is working and whether maintenance or replacement of components may be necessary (127).
Another consideration is the length of time the treatment is required which is very important for effective aeration (127).

Design of aeration tank & diffuser

Design flow rate = 1000m^3/d = 42m^3/h
Assume, hydraulic retention time for aeration= 20 min
Volume of aeration tank = 14 m^3
Considering, length = 2.5 m
Width = 2.5m
Height = 3.0 m
Total net volume = 18.75 m^3
Free board = 0.5 m
Total height of the tank = 3.5 m

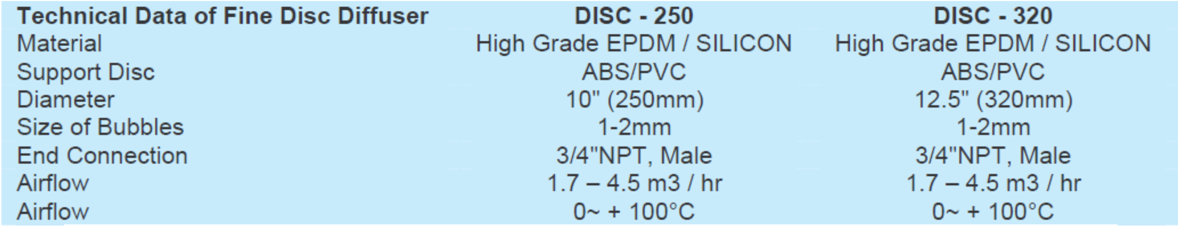
Effective hydraulic retention time = 26.67 min, but it's not a problem for our work. Moreover, it'll be effective for aeration of methane and oxidizing of iron and partly of ammonia and manganese.

According to Prof. Nurizzo we can consider air ratio = 0.5 ≈1.0 m^3 of air/ m^3 of water for this kind of operation (128). This case we consider 1.0 m^3 of air/ m^3 of water.

So we need 42 m^3 of air/h, considering factor 1.2, the design air will be 50 m^3/h
Air-volume ratio=3 > 1.8, so theoretically we don't need mixture, but practically it's better to use at least 1 mixture if possible.

Generally, the capacity of a single standard high efficient diffuser varies from 1.7m^3/h to 4.5 m^3/h. Considering 4 m^3/h, we can consider 12 diffuser.

Table 5.3: Technical specification of fine disc diffuser (126)



Technical Data of Fine Disc Diffuser	**DISC - 250**	**DISC - 320**
Material	High Grade EPDM / SILICON	High Grade EPDM / SILICON
Support Disc	ABS/PVC	ABS/PVC
Diameter	10" (250mm)	12.5" (320mm)
Size of Bubbles	1-2mm	1-2mm
End Connection	3/4"NPT, Male	3/4"NPT, Male
Airflow	1.7 – 4.5 m3 / hr	1.7 – 4.5 m3 / hr
Airflow	0~ + 100°C	0~ + 100°C

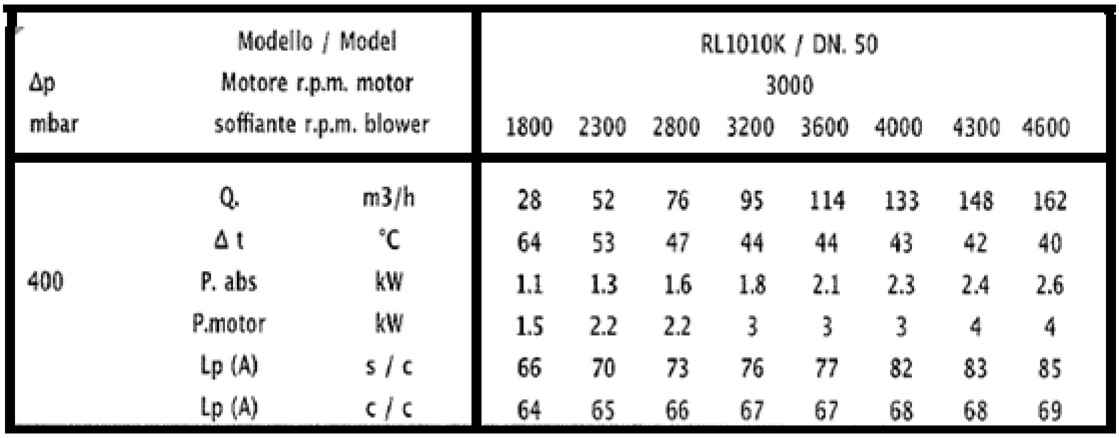
Specification of blowers

Table 5.4: Design head calculation

Static head	3.0m = 300 mbar
Control valve	20.00 mbar
Air diffuser	40.00 mbar
Silencer	4.0 mbar
Air Filter	7.6 mbar
Net Diffuser Drop	0.0 mbar
Line pressure drop (assume)	20.0 mbar
Total head	391.60 mbar
	39.16kPa
Design head	40kPa
Inlet pressure	101kPa
Discharge pressure	141.00kPa
Compression ratio	1.39604

So from the above data and from the table 5.4 we can select the blower specification:

Table 5.5: Performance table pressure operation (129)



Δp mbar	Modello / Model Motore r.p.m. motor soffiante r.p.m. blower		RL1010K / DN. 50 3000							
			1800	2300	2800	3200	3600	4000	4300	4600
400	Q.	m3/h	28	52	76	95	114	133	148	162
	Δ t	°C	64	53	47	44	44	43	42	40
	P. abs	kW	1.1	1.3	1.6	1.8	2.1	2.3	2.4	2.6
	P.motor	kW	1.5	2.2	2.2	3	3	3	4	4
	Lp (A)	s / c	66	70	73	76	77	82	83	85
	Lp (A)	c / c	64	65	66	67	67	68	68	69

Absorbed power of the blower = 1.3 kW
Installed power of the blower = 2.2 kW

Table 5.6: Summary of the design data (aeration tank & aeration system)

Particulars	Aeration lane
No. of tank	1
Length	2.5 m
Width	2.5 m
Water depth	3.0m
Design air flow	50 m3/h
Number of diffuser	12
Design head	45kPa
Absorbed power of the blower	1.7 kW
Installed power of the blower	2.2 kW
Temperature of water	12 degree Celsius
pH	7

5.4.2 Chemical oxidizing of arsenic & manganese by potassium permanganate

$KMnO_4$ is supplied in bulk quantities in solid form in either drums or tanker truck deliveries. Since the $KMnO_4$ is stored as a dry solid, it is typically dissolved in water prior to application. In small system like our work the material can be scooped into the solution tank. Typically, the dry solid is removed using a water-driven eductor to makeup a 3% $KMnO_4$ solution in batch sequence. Two storage tanks are typically required so that one tank can be applied while the other is being refilled. The $KMnO_4$ solution is stored and pumped from these storage tanks to the point of application.

Figure 5.7 presents a typical process schematic for the dissolution and application of $KMnO_4$ using either drum or silo dry storage (124).

Based on the oxidization reaction, the mass stoichiometric ration of permanganate to arsenic is 0.8. The expected conversion of arsenite to arsenate with permanganate is expected to be greater than 95%, although the dose may be as high as 10-times the stoichiometric dose in the presence of interfering reductants (124).

Potassium permanganate ($KMnO_4$) is typically used from IG5-lb or 330-1b drums. Bulk dry shipments arc transferred to steel silos for storage. $KMnO_4$ absorbs moisture from the air and will harden inside the storage container. Drums of $KMnO_4$ should not be opened until they are ready to be used and $KMnO_4$ silos should be purged with a small volume of dry air continuously (124).

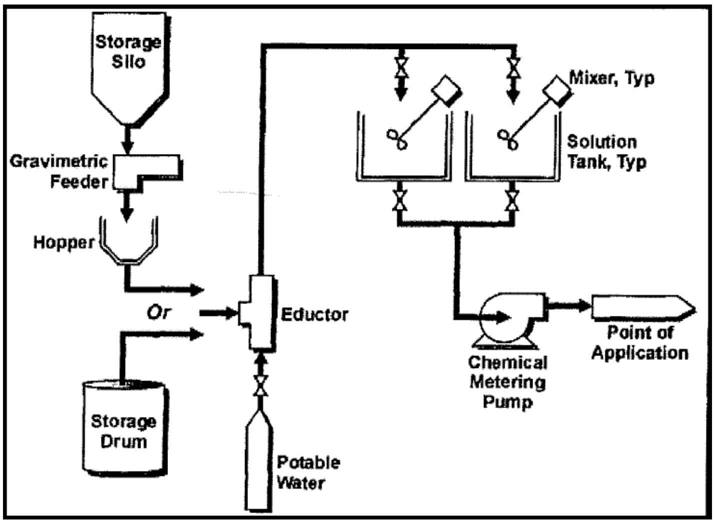


Figure 5.7: Potassium permanganate feed system schematic (124)

$KMnO_4$ is removed from the drums manually using a vacuum created by a water-driven eductor (similar to chlorine gas withdrawal). Each drum is emptied into a fixed amount of water such that a 3% $KMnO_4$ is created. Similarly, the silo can have a gravimetric feeder to measure out a fixed weight of $KMnO_4$ to make up batches of 3% solution. The storage tanks holding the solution should be mixed to avoid stratification of the $KMnO_4$ solution. Stratification will lead to varying doses of permanganate addition (124).

The $KMnO_4$ solution is pumped into the process water using a chemical metering pump. Diaphragm, peristaltic or progressive cavity pumps can all be used to meter $KMnO_4$ solution. Typically, the $KMnO_4$ solution is flow-paced for control. In situations where the flow does not change on a daily basis, manual control can be used (124).

Design of chemical oxidation tank

Design flow rate = 1000m^3/d = 42m^3/h
Usually, hydraulic retention time for oxidizing of arsenic and manganese is recommended from 5 mins to 15 mins (130) Sank, 1980
We consider hydraulic retention time for maximum oxidization that is 15 mins
Volume of aeration tank = 11 m^3
Considering, length = 2.0 m
Width = 2.0 m
Height = 3.0 m
Total net volume = 12 m^3
Free board = 0.5 m
Total height of the tank = 3.5m
Effective hydraulic retention time = 17.17 min, but it's not a problem for our work. Moreover, it'll be effective for complete oxidizing of arsenic and manganese.

Computations of the consumptions of chemical reagents

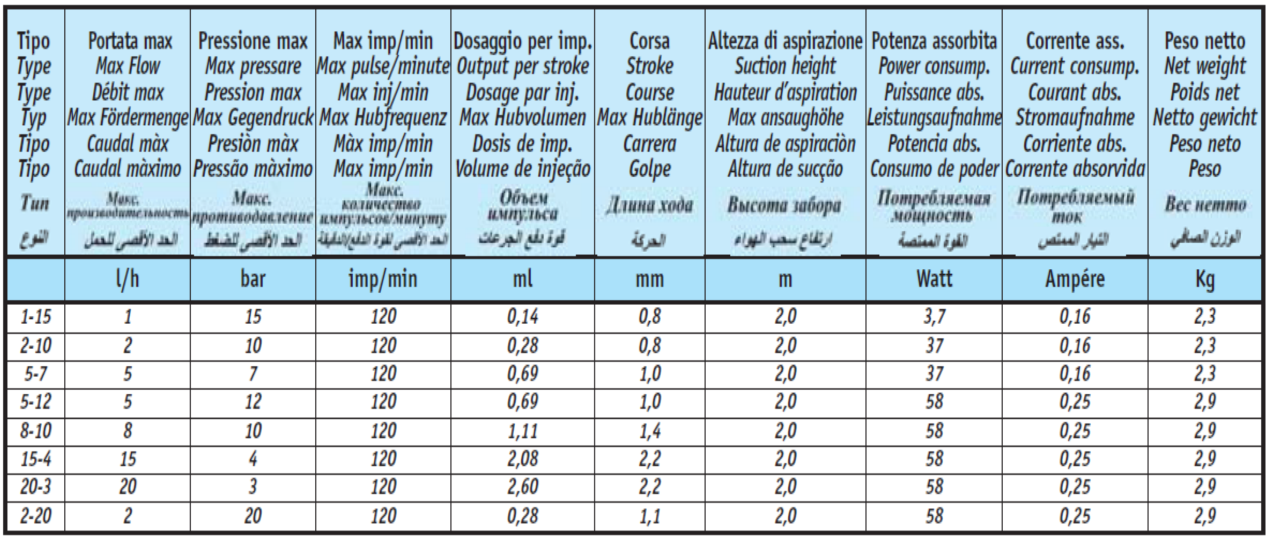
Table 5.7: Computations of consumptions of potassium permanganate and dosing pump specification

		Manganese	Arsenic	
	MnO_4 dose =		0.8	mg/l
	Flow rate =	1000	1000	m^3/d
	MnO_4 dose =		0.8	mg/l
	Safety Factor =		1.0	
	MnO_4 dose =		0.8	mg/l
	M.W. MnO_4 =	119	119	
	M.W. $KMnO_4$ =	158.1	158.1	
	$KMnO_4$ =	1.92	1.06	mg/l
		1.92	1.06	kg /d
		0.080	0.044	kg/h
	Concentration =	3%	3%	w/w
	$KMnO_4$ solution =	64.000	35.429	kg /d
		2.667	1.476	kg/h
	SG (solution) =	1.02	1.02	kg/Lit

	$KMnO_4$ solution =	0.06	0.03	m^3/d
		0.10		m^3/d
		0.0026	0.0014	m^3/h
		0.0041		m^3/h
		2.61	1.45	Lit/h
	TOTAL DOSE =	4.06		Lit/h
		10%	100%	
	Dosing pump =	***0.8***	***8.0***	***Lit/h***
	Storage =		7	d
	Volume to storage =		0.682	m^3
	Diameter =		1	m
	Height =		1	m
	Net Volume =		0.79	m^3
	Quantity =		2	
	Total Volume =		1.57	m^3

Note: Two vessel of 1m3 volume each. One is operating and another one is for standby

Table 5.8: Catalogue of DLX &DLX (B) solenoid dosing pumps series (131)



Tipo Type Type Typ Tipo Tipo Тип النوع	Portata max Max Flow Débit max Max Fördermenge Caudal màx Caudal màximo Макс. производительность الحد الأقصى للحمل	Pressione max Max pressare Pression max Max Gegendruck Presiòn màx Pressão màximo Макс. противодавление الحد الأقصى للضغط	Max imp/min Max pulse/minute Max inj/min Max Hubfrequenz Màx imp/min Max imp/min Макс. количество импульсов/минуту الحد الأقصى لقوة الدفع/الدقيقة	Dosaggio per imp. Output per stroke Dosage par inj. Max Hubvolumen Dosis de imp. Volume de injeção Объем импульса قوة دفع الجرعات	Corsa Stroke Course Max Hublänge Carrera Golpe Длина хода الحركة	Altezza di aspirazione Suction height Hauteur d'aspiration Max ansaughöhe Altura de aspiraciòn Altura de sucção Высота забора ارتفاع سحب الهواء	Potenza assorbita Power consump. Puissance abs. Leistungsaufnahme Potencia abs. Consumo de poder Потребляемая мощность القوة الممتصة	Corrente ass. Current consump. Courant abs. Stromaufnahme Corriente abs. Corrente absorvida Потребляемый ток التيار الممتص	Peso netto Net weight Poids net Netto gewicht Peso neto Peso Вес нетто الوزن الصافي
	l/h	bar	imp/min	ml	mm	m	Watt	Ampére	Kg
1-15	1	15	120	0,14	0,8	2,0	3,7	0,16	2,3
2-10	2	10	120	0,28	0,8	2,0	37	0,16	2,3
5-7	5	7	120	0,69	1,0	2,0	37	0,16	2,3
5-12	5	12	120	0,69	1,0	2,0	58	0,25	2,9
8-10	8	10	120	1,11	1,4	2,0	58	0,25	2,9
15-4	15	4	120	2,08	2,2	2,0	58	0,25	2,9
20-3	20	3	120	2,60	2,2	2,0	58	0,25	2,9
2-20	2	20	120	0,28	1,1	2,0	58	0,25	2,9

For our work we can consider the IST one since we have dosing rate 1l/h, so installed power will be 3.7 watt which is 0.0037Kw

Figure 5.8: DLX &DLX (B) solenoid series dosing pump (131)

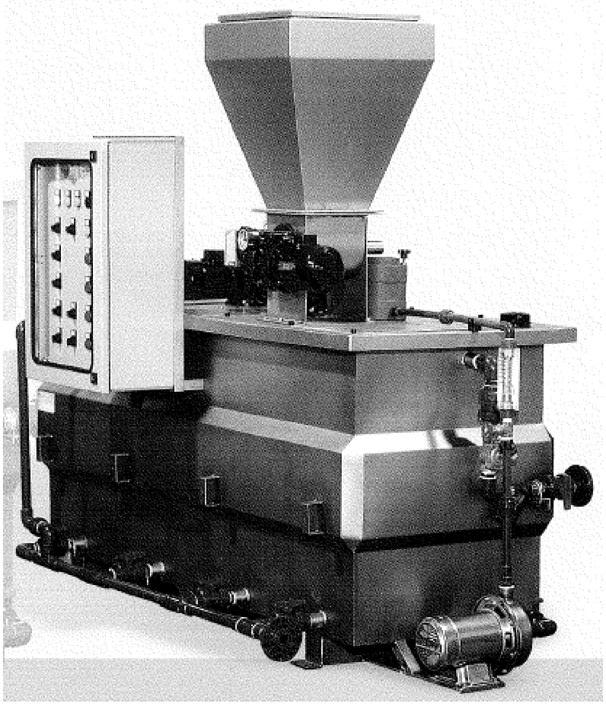


Figure 5.9: Typical dosing piston pump assembly with hopper and storage vessel (132)

5.4.3 Tertiary aerated sand filter with nitrification

Tertiary aerated sand filters, combining the solids removal aspects and self cleaning properties of continuously backwashed up-flow filters (CoUF's) with the ammonia conversion capabilities of an attached growth filter (133). It is an alternative solution for ammonia removal along with solids filtration is to install up flow vertical tank biological sand filters, which require typically one-tenth of the space required by the conventional basin alternative. The DynaSand filter removes ammonia from wastewater by creating favorable conditions for treatment bacteria to flourish within the sand filter, providing a highly effective process to reduce ammonia pollution in the environment (134).

The DynaSand system filters solid particles from wastewater travelling up through a granular media bed, trapping them in the bed. The bed moves down through the filter as a result of the action of an air lift pump removing 'dirty' media from the base for 'washing' and subsequent return to the bed surface. The process is therefore 'continuous'. The trapped solids act as part of the filtration process causing higher solids capture than would be achieved in a totally clean bed (133).

Figure 5.10 provides a schematic sectional view through a DynaSand filter. Its operations are described below:

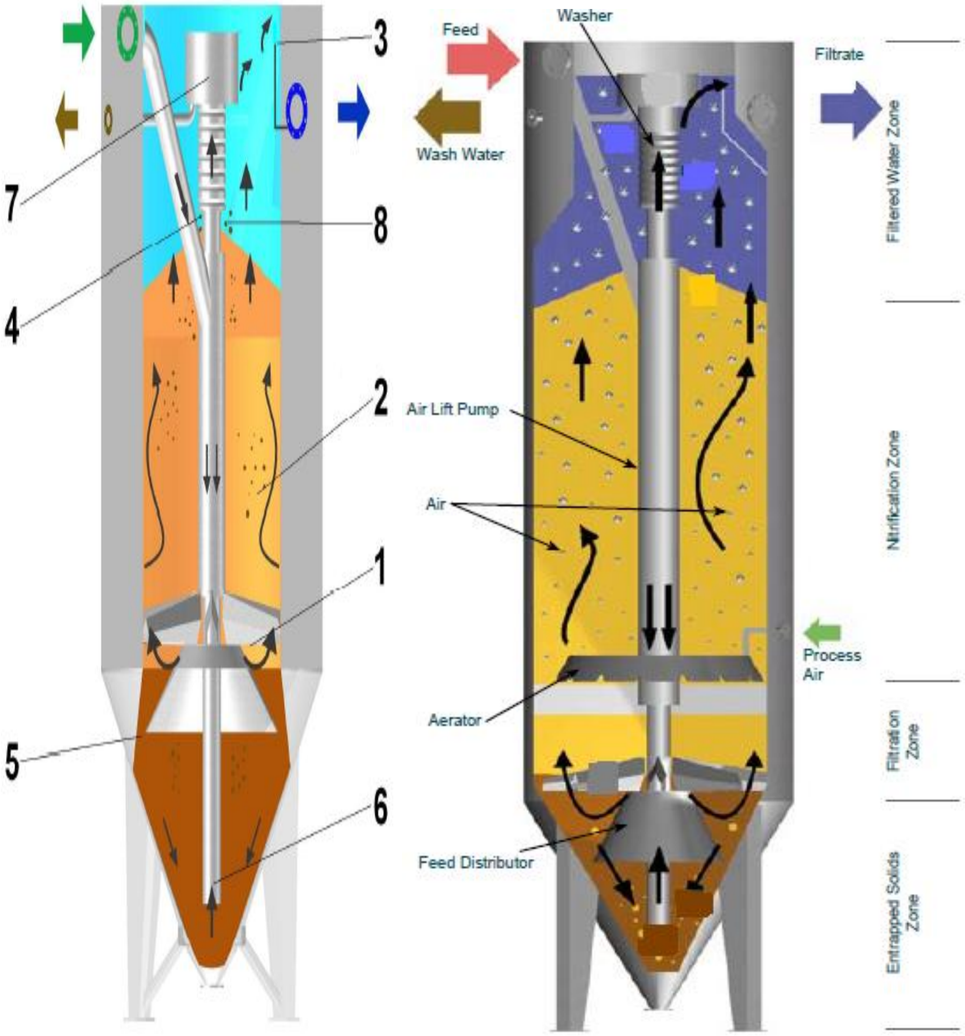


Figure 5.10: Sectional view through a DynaSand filter, showing effluent flow paths (133)

1. Wastewater is introduced at the bottom of the filter and spread across the available surface area by a number of distribution arms.
2. The water flows up through the sand bed where solid particles are captured.
3. Most of the cleaned water (filtrate) passes over the fixed final filtrate weir
4. A small percentage travels up through the sand-washing labyrinth, where entrained solid particles are released from the sand grains as they fall down through the washer.
5. The sand bed moves down the filter and over the sand distribution cone as a result of the action of an air-lift pump.
6. Sand, trapped solid particles and water are pulled up through the air-lift pump to the washing section.
7. The sand particles, because of their greater size and density, fall through the sand washer, against the countercurrent of process filtrate, which carries the lighter effluent particles over the wash water weir and out of the system.
8. The clean sand is return to the top of the bed (133)

By adjusting the air flow rate to the air-lift pump it is possible to increase and decrease the amount of sand lifted, and therefore the sand movement rate through the filter. By adjusting the wash water weir height (and therefore its relationship with the filtrate weir), the amount of wash water generated can be increased or decreased. For optimal performance, the wash water is typically set to be 1.5 to 2 times the sand volume lifted (133).

Continuous sand cleaning also maintains the health of the bacterial population. Bacteria remain in the sand as the water flows up through the sand and through an undisturbed upper volume in water to cascade over a weir. This feature eliminates the need for additional settling tanks to remove bacteria from the water (134).

Thus, for a small power input, cleaning of both the water and the sand is continuous and the filter need never be shut down. The diagram shows the operating principle that has been used for tertiary filtration (134).

As the biomass and sand are continuously moved through the filter and the most favorable conditions for growth, the filters are also very tolerant of ammonia surges. Aeration hoods fed by process air are sited within the upper layer of sand to ensure that the autotrophic nitrifying bacteria - Nitrosamonas and Nitrobacter spp. - have sufficient oxygen to convert ammonia to nitrates. This mixing action provides sufficient aeration and the resultant nitrates are dissolved in the water (134).

Table 5.9: General specification for loading rate (134)

Typical data	**Loading rate**	**Influent solids**	**Filtrate solids**
Tertiary filtration	3-5gpm/ft^2	20-50ppm SS	5-10ppm SS
Tertiary filtration	0.13m/min to 0.21m/min	20-50mg/l SS	5-10mg/l SS

The size and shape of DynaSand vessels is determined by both hydraulic loading rate and ammonia removal considerations. The loading rate will determine the surface area, while ammonia removal targets will govern media bed volume requirements. Given these two parameters, the nearest best fit in terms of standard units can be selected (134).

Given that the basic operating costs for pumping to the filters and providing the compressed air for the air-lift pump are not going to change in any given system as the size and shape are set, this leaves the air required for the nitrification process as the main variable in terms of power usage (134).

After computation it is found that the solids that is produced after oxidizing is very low and it is easily removed by this filtration without any problem. Even it is effectively remove the low concentration of ammonia. So it is recommended to ask the manufacturer for the smallest tertiary sand filter unit for this work.

5.4.4 Disinfection by ultraviolet radiation

A UV disinfection system transfers electromagnetic energy from a mercury arc lamp to an organism’s genetic material (DNA and RNA). When UV radiation penetrates the cell wall of an organism, it destroys the cell’s ability to reproduce (135).

An effective dose is measured as a product of the lamp’s intensity (the rate at which photons are delivered to the target), including radiation concentration, proper wavelength, exposure time, water quality, flow rate, and the microorganism’s type, and source, as well as its distance from the light source and the reactor configuration (14). For any one treatment plant, disinfection success is directly related to the concentration of colloidal and particulate constituents in the water (135).

The main components of a UV disinfection system are mercury arc lamps, a reactor, and ballasts. The source of UV radiation is either the low-pressure or medium-pressure mercury arc lamp with low or high intensities (135).

At a minimum, drinking water systems should install two UV units, which are both capable of carrying the amount of water the system was designed to handle. Having two units in place assures continuous disinfection when one unit is being serviced. Two units also can ensure operation during low-flow demand periods (136).

Modular units designed for small drinking water systems are easy to install and operate (two plumbing connections per unit and one electrical hook-up). They should be equipped with automatic cleaners and remote alarm systems. For systems in isolated areas, operators should maintain and store a set of spare parts onsite, and consider a telemetry system for monitoring treatment (136).

Figure 5.11 & 5.12 show isometric cut-away views of typical UV disinfection systems with cover grating removed

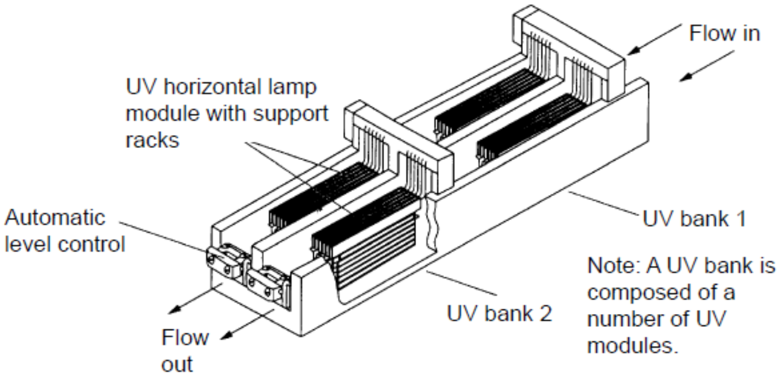


Figure 5.11: Horizontal lamp system parallel to flow (adapted from Trojan Technologies, Inc.) (135).

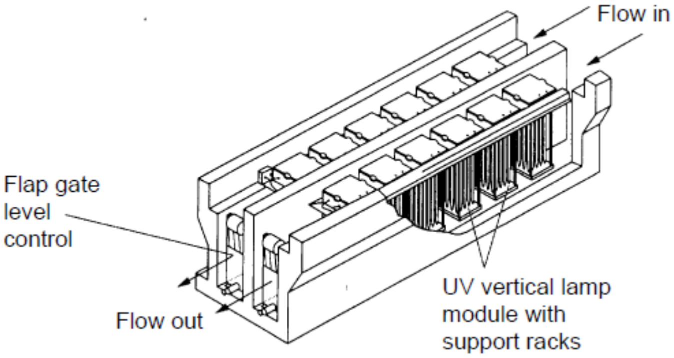


Figure 5.12: Vertical lamp system perpendicular to flow (adapted from Infilco Degremont, Inc.) (135)

Two types of UV disinfection reactor configurations exist: contact types and noncontact types. In both the contact and the noncontact types, water can flow either perpendicular or parallel to the lamps (135).

In the contact reactor, a series of mercury lamps are enclosed in quartz sleeves to minimize the cooling effects of the water. **Figure 5.11 & 5.12** show two UV contact reactors with submerged lamps placed parallel and perpendicular to the direction of the water flow. Flap gates or weirs are used to control the level of the water. In the noncontact reactor, the UV lamps are suspended outside a transparent conduit, which carries the water to be disinfected. However, this configuration is not widely used. In both types of reactors, a ballast—or control box— provides a starting voltage for the lamps and maintains a continuous current (135).

The following are three critical areas to be considered when choosing a UV disinfection system. The first is primarily determined by the manufacturer; the second, by design and O&M; and the third has to be controlled at the treatment facility:

1. Hydraulic properties of the reactor: Ideally, a UV disinfection system should have a uniform flow with enough axial motion (radial mixing) to maximize exposure to UV radiation. The path that an organism takes in the reactor determines the amount of UV radiation it will be exposed to before inactivation. A reactor must be designed to eliminate short-circuiting and/or dead zones, which can result in inefficient use of power and reduced contact time (135).
2. Intensity of the UV radiation: Factors affecting the intensity are the age of the lamps, lamp fouling, and the configuration and placement of lamps in the reactor (135).
3. Wastewater characteristics: These include the flow rate, suspended and colloidal solids, initial bacterial density, and other physical and chemical parameters. Both the concentration of TSS and the concentration of particle-associated microorganisms determine how much UV radiation ultimately reaches the target organism. The higher these concentrations, the lower the UV radiation absorbed by the organisms (135).

5.4.5 Persistency of disinfection by sodium hypochlorite

Disinfection persistency can be achieved by a minimum a minimum dosage of sodium hypochlorite (≤ 0.2 mg Cl/l).

This case we don’t need to chlorination basin but only inline chlorination with good mixing system is enough for getting persistency.

Table 5.10: Computation of consumptions of sodium hypochlorite

	Cl dose =		0.2	mg/l
	Flow rate =		1000	m^3/d
	Cl dose =		0.2	mg/l
	Safety Factor =		1.0	
	Cl dose =		0.2	mg/l
	M.W. Cl =		35.45	
	M.W. NaOCl =		74.45	
	NaOCl =		0.42	mg/l
			0.42	kg /d
			0.018	kg/h
	Concentration =		15%	w/w
	NaOCl solution =		2.800	kg /d
			0.117	kg/h
	SG (solution) =		1.20	kg/Lit
	NaOCl solution =		0.10	m^3/d
			0.0041	m^3/h
			4.05	Lit/h
	TOTAL DOSE =	4.05		Lit/h
		10%	100%	
	Dosing pump =	***0.8***	***8.0***	***Lit/h***
	Storage =		7	d
	Volume to storage =		0.681	m^3
	Diameter =		1	m
	Height =		1	m
	Net Volume =		0.79	m^3
	Quantity =		2	
	Total Volume =		1.57	m^3

Note: Two vessel of 1m3 volume each. One is operating and another one is for standby but the storage vessel, dosing pumps and mixing assembly will be different from the above system as mentioned for potassium permanganate.

5.4.6 Electrical consumptions of the system

Considering only the operating devices
3 pumps (1.1kW each) = 3*1.1=3.3kW
2 blowers (1.3kW each) = 2*1.3=2.6kW
4 Dosing pumps (37Watt each) = 0.5 kW
Control room & miscellaneous = 1kW
Total = 7.4kW≈8 kW

5.5 Possible effects on environment and public and government satisfaction level

The end products of a water treatment plant are sludge and treated water. From the environmental standpoint the most important aspect of a water treatment plant is the proposed disposal or use of the sludge and the treated water (137).

Improperly constructed or operated treatment plant and improper disposal or use of sludge and treated water may become a most serious public health problem. Therefore, whatever level of treatment and method of disposal and use is approved, it should strictly comply with national standards and internationally accepted environmental quality criteria, taking into account the recipient environment and the biological targets which may be affected (137).

Elements specifically recommended for inclusion in the follow-up monitoring and re-evaluation programs are: regular compliance with methods approved for treatment and disposal, including for use of treated water; seepage of contaminants from the treatment plants or sludge disposal sites into trash water aquifers or coastal waters (137).
Fundamental environmental issues should be discussed on the identification and evaluation, during the design phase, during construction and during operation & maintenance (138).

The environmental impact analysis of a plant should be prepared considering of the following aspects:

- Legal and other requirements applicable to the project concerning environmental protection considered during the design phase;

- Identification of the environmental aspect connected to the different plant sections;
- Identification and evaluation of those environmental aspects that have or can have significant environmental impacts;
- Identification of the actions for the prevention and mitigation of the environmental impacts;
- Description of any environmental monitoring systems provided by the project (138).

Environmental Preliminary Analysis

The preliminary environmental analysis includes the individuation of the measures for the prevention and mitigation of the environmental impacts (138).

- Element of the organization's activities, products or services that can interact with the environment;
- Environmental aspect that has or can have a significant environmental impact;
- Any change to the environment, whether adverse or beneficial, wholly or partially resulting from the organization's environmental aspects;
- Normal conditions: ordinary conditions, with regular activities/plant functioning;
- Abnormal conditions: conditions diverging from normal conditions, but predictable, for example shut-down and start-up conditions etc;
- Emergency conditions: emergency situations, for example failure of plant "equipment" as defined in the design phase (138).

Identification of possible environmental impacts

- **Energy consumption**- The main energy consumption is due to dosing pumps and the blowers and operating for DynaSand filter. In order to provide the electrical power, the authority needs some operational works and it has some environmental impacts in terms of constructions, maintenance, fuel consumptions, economy and producing more electricity;
- **Air Pollution & explosion**- Possibility of odors and air pollution from the plant and from the disposal of sludge. We should keep in mind that in a 5 percent to 15 percent concentration in air, methane can become explosive and present a health hazard. Again, methane is lighter than air and has the potential of concentrating into pockets — this is why proper ventilation is necessary; (139)

- **Soil/underground water**-Using of chemical substances ($KMnO_4$ & NaOCl, there is a possibility of infiltration in soil and groundwater especially during the maintenance of dosing pumps, storage vessel and so on;
- **Discharge in to sewer system** (surface water bodies contamination)-If any how the sludge that is produced discharge in to sewer system, possibility of contaminated surface water bodies;
- **Sludge and waste generation**- Possibility of environmental pollution from sludge produced by the plant and waste generation;
- **Noise**- Plant should be equipped with suitable silencing features, so that the noise emitted will not exceed the value guarantee. The system is foreseen designed in such a way that neither the operating personnel nor the neighborhood of the site will be annoyed by abnormal noise related with the process. Obviously it can be stopped completely specially during construction works and transport of construction materials and plant equipments;
- **Aesthetic**- Possible impacts on tourist and recreation areas such as nature reserves, forests, parks, monuments, sport centers, beaches, and other open areas
- **UV radiation-** Dealing with UV radiation is always risky as it is really difficult to install, operation and maintenance. So possible failure of the UV system have great negative impacts on environmental;
- **Plant failure**- any possible plant failure has tremendous impact on the environment as it is designed for drinking water supply facility (137).

The ultimate goal of this water treatment system is installed for providing drinking water facilities to the municipality. If the system has maintained the best efficiency considering minimum level negative impact on environment, of course the plant will be gained the government and public satisfaction level.

5.6 General overview of the operation and maintenance of the system

Aeration system

Regardless of the quality of the equipment purchased, it will not perform satisfactorily unless maintained in accordance with the manufacturer's recommendations for maintenance, cleaning, and part replacement. Blowers must be maintained by periodically lubricating the motor and changing the air filters. Use a log book to record water test results, equipment maintenance, and repairs. Proper, adequate ventilation is must when operating an aeration system. The tanks and trays need occasional cleaning for precipitated substances. A valve controlled drain line to the ground surface makes flushing the storage tank once or twice each year easier (140).

A methane removal system involving sanitation should be checked once a year at a very minimum. Other water issues may require more frequent checks of the system anyway. Of course, when sourcing drinking water systems, look for those in which all components are of food-grade quality and are NSF-certified (141).

It should be noted that the aeration process requires careful control, as insufficient air flow will not properly oxidize. At the same time, if the air flow is too high, the water may become saturated with dissolved oxygen and become corrosive (142).

It is important to ensure successful completion of the aeration process by allowing at least 20 minutes of detention time before filtration. This is regularly done by installing a reaction tank downstream of the aeration basin. The water pH affects the reaction time and therefore it is necessary to monitor and correct the pH during the detention process (142).

Chemical oxidizing with potassium permanganate

Regular maintenance of this system is required. Solution tanks must be routinely refilled and mechanical filters need to be backwashed to remove accumulated iron, manganese and arsenic particles. The frequency of maintenance is primarily determined by the concentration of the metals in the raw water and the amount of water treated. For potassium permanganate careful calibration, maintenance and monitoring of the water treatment equipment is necessary. Also exercise caution with potassium permanganate, as it is both poisonous and a skin irritant (12).

The operator should frequently determine whether all the iron, arsenic& manganese in the water entering the filter have been oxidized. The operator collects a water sample, passes it through a filter paper, and runs test on the clean, filtered water, the filtrate. If no dissolved form is present, it has all been oxidized and it should be removed in the filtration process. If dissolved form is found in the filtrate, oxidation has not been complete. Some of the pollutant will then pass through the filter and end up in the treated water. In this case, the operator should consider adjustments in the oxidation process (8).

Most such removal filters are designed so that the filters are backwashed based on head loss through the filter. If pollutants breakthrough is a problem, the filters will have to be backwashed more frequently. Accurate records will reveal when breakthrough is expected so that the operator can backwash before it is likely to occur (8).

Potassium permanganate is considered a strong oxidizer. Care must be taken to keep dry $KMnO_4$ from oxidizable organic materials such as lubricating grease or asphalt paving. Local fire and building codes typically regulate the storage and use of potassium permanganate. Storage regulations for $KMnO_4$ solutions typically require separation from incompatible materials and containment of spills, Local and state codes must be considered during the design and operation of $KMnO_4$ facilities at a water treatment plant (126).

When using $KMnO_4$ in water treatment, caution should be taken to prevent overdosing. Excess permanganate will pass through the treatment plant and can cause a pink color to appear in the finished water, Also when using $KMnO_4$, the result of oxidizing arsenite is the formation of manganese dioxide, which forms a precipitate. Therefore, $KMnO_4$ addition must occur before filters so these solids are removed. If residual permanganate is reduced downstream of the filters the resulting solids can turn the finished water a brown/black color and precipitate in the distribution system and consumer's homes. Although the secondary MCL for manganese is 0.05 mg/L, it is an aesthetic concern at concentrations greater than 0.02 mg/L (126).

The use of $KMnO_4$ can also be a source of manganese in the finished water, which is regulated in drinking water with a secondary maximum contaminant level of 0,05 mg/L. The release of soluble manganese can occur when manganese dioxide solids accumulated in filter backwash and settling basins are placed under reducing conditions. Soluble manganese can also be returned to the head of the plant from settling water dewatering facilities and filter backwash recycle facilities (126).

Tertiary aerated sand filters (DynaSand Filters)

This filter needs very low maintenance with great performance. It is an up flow, deep bed; granular media filter with continuous backwash. The filter media is cleaned by a simple internal washing system that does not require backwash pumps or storage tanks. The absence of backwash pumps means low energy consumption. The Filter’s deep media bed allows it to handle high levels of suspended solids. This heavy-duty performance may eliminate the need for pre-sedimentation or flotation steps in the treatment process in some applications. It is recommended to follow the operating and maintenance manual for effective operation (143).

Disinfection by UV

The proper O&M of a UV disinfection system ensures that sufficient UV radiation is transmitted to the organisms to render them sterile. All surfaces between the UV radiation and the target organisms must be clean, and the ballasts, lamps, and reactor must be functioning at peak efficiency. Inadequate cleaning is one of the most common causes of a UV system's ineffectiveness. The quartz sleeves or Teflon tubes need to be cleaned regularly by mechanical wipers, ultrasonic's, or chemicals. The cleaning frequency is very site-specific, with some systems needing to be cleaned more often than others. Chemical cleaning is most commonly done with citric acid. Other cleaning agents include mild vinegar solutions and sodium hydrosulfite. Noncontact reactor systems are most effectively cleaned by using sodium hydrosulfite. A combination of cleaning agents should be tested to find the agent most suitable for the wastewater characteristics without producing harmful or toxic by-products (144).

To ensure continued system operation, a maintenance schedule needs to be in place. This schedule should include periodic site inspections; changing lamps annually or when light transmission efficiency has decreased to 70 percent; inspecting and cleaning surfaces; inspecting or cleaning the UV chamber interior every six months; and inspecting and replacing ballasts, O-rings, valves, and switches (145).

Furthermore, the operator should monitor water turbidity and color since they are natural barriers to UV light transmission. And some dissolved minerals, such as calcium, have a tremendous negative effect on UV absorbance. Since it may not be practical to provide instantaneous stand-by power during power outages, the system should be designed to automatically stop water flow or provide an alternate means of disinfection as a backup. Where the system is dependent on electrically powered pumps, this measure may not be necessary because the pumps will shut off when the power goes out. However, gravity flow systems may be vulnerable (145).

UV disinfection should have the following minimum operational controls and procedures:

- A central display indicating alarms for power failure, lamp failure, hours of lamp operation, low UV dosage, high lamp temperature, high ballast temperature, and high system flows;
- Methods that monitor lamp temperature, ballast temperature, and system water flows;

- A minimum of two photodiode sensors per unit to monitor UV dosage at 254 nm. These sensors must be calibrated using approved standards each time the lamps are cleaned or replaced or the UV chamber is serviced;
- Automatic UV system by-pass or shutoffs, which are activated whenever the system exceeds peak design flow rates, when UV dosage is low, or when lamp or ballast temperatures are high; and
- Two UV units should be installed so flow is not interrupted when one unit is out of service (145).

A routine O&M schedule should also be developed and followed according to manufacturer's instructions for using sodium hypochlorite for achieving the persistency of the disinfection system by ultraviolet radiation. Regular O&M involves disassembling and cleaning the various components, such as meters and floats, once every 6 months. Valves and springs should also be inspected and cleaned annually. All manufacturers' O&M recommendations should be followed, and equipment must be tested and calibrated as recommended by the equipment manufacturer (146).

5.7 General overview of the costing of the system

The costs associated with owning and operating an aeration system is significant. Maximize return on investment with a present-worth analysis considering initial and long-term operating costs. Repair frequency, labor, chemicals and replacement parts vary based on the selected technology. As a percent of initial cost, annual maintenance varies from 5% to 10% for a fine bubble diffuser system (147).

Price of potassium permanganate solution and sodium hypochlorite varies from w/w% and location. Generally pre-packaged potassium permanganate solution price starts from US dollar 180 for 4liter (37 Euro/liter). On the other hand price of sodium hypochlorite start from 19US dollar to 22 per for 5 gallons (5 Euro per liter) (148).

The DynaSand® Filter is available as either stand alone package units or in a modular concrete design. The package units are constructed of either 304 SST or FRP. Materials of construction for the internal components of both package and concrete units are SST and/or FRP. Filters are available in 40" standard bed or 80" deep-bed design depending on the nature of the application (143).

The cost of UV disinfection systems is dependent on the manufacturer, the site, the capacity of the plant, and the characteristics of the wastewater to be disinfected. The annual operating costs for UV disinfection include power consumption; cleaning chemicals and supplies; miscellaneous equipment repairs (2.5% of total equipment cost); replacement of lamps, ballasts, and sleeves; and staffing requirements (144).

Medium-pressure lamps cost four to five times as much as low-pressure lamps. However, the reduced number of lamps necessary for adequate disinfection could make medium-pressure lamps cost-effective. Listed in Tables 5.11 and 5.12 are the results of a study conducted by the Water Environment Research Federation in 1995 for secondary effluents from disinfection facilities at average dry weather flow rates of 1, 10, and 100 mgd (2.25, 20, and 175 mgd peak wet weather flow, respectively) (144).

Table 5.11: Capital Costs for UV Disinfection Systems (144)

Item	**Range**	**Typical**
UV lamps	($/lamp)	($/lamp)
1-5 mgd	397-1,365(€ 320-1100)	575 (€ 463)
5-10mgd	343-594 (€ 276-478)	475 (€ 383)
10-100mgd	274-588 (€221-474)	400 (€323)
Construction cost for physical facilities	(% of UV lamp cost 75-200(€ 61-162)	(% of UV lamp cost) 150(€ 121)

Table 5.12: O&M Costs for UV Disinfection Systems (144)

Item	**Unit cost ($)**	**Cost/Year, $/lamp**
Power (per kWh)	0.08 (€0.06)	29.78 (€ 24)
Replacement		
Lamp	40each (€)	14.60 (€ 12)
Ballast	80each (€)	4 (€ 3.5)
Sleeve	5 (€)	4 (€ 3.5)
Chemicals (lamp/year)	36 (€)	5 (€ 4)
Staffing (per hour)		18-27 (€ 15-22)
Misc. Equipment repair		10-14.38 (€8 -12)
Total		85.38-98.76 (€ 69-80)

Table 5.13: Approximated investment cost

Description of work	Quantity	Unit price	Total	Installation	Total	Note
General Civil works					€ 10,000.00	
Soil preparation					€ 15,000.00	
Basin construction(Big)	3	€ 20,000.00	€ 40,000.00	€5,000.00	€ 65,000.00	
Control house	1	€ 20,000.00	€ 20,000.00	€ 2,000.00	€ 22,000.00	
Environmental impact mitigation works	1	€ 7,000.00	€ 7,000.00	€2,000.00	€ 9,000.00	
Consultancy/Engineering					€20,000.00	
Miscellaneous labor cost					€ 5,000.00	
Equipment cost						
Diffuser	15	€ 40.00	€ 600.00	€500.00	€1,100.00	
Blower	2	€ 4,000.00	€ 8,000.00	€1,000.00	€ 9,000.00	
Centrifugal pump	4	€ 6,000.00	€24,000.00	€1,000.00	€25,000.00	
Dosing pump assembly with storage vessel	2	€ 10,000.00	€20,000.00	€2,000.00	€22,000.00	
Mixer for chemical oxidation	2	€ 5,000.00	€ 10,000.00	€2,000.00	€12,000.00	
UV disinfection system (complete package)	1	€ 40,000.00	€ 40,000.00	€5,000.00	€45,000.00	
Tertiary aerated sand filter(complete package)	1	€ 40,000.00	€ 40,000.00	€5,000.00	€45,000.00	
Sludge dewatering, storage & handling	1	€ 2,000.00	€ 2,000.00	€ 500.00	€ 2,500.00	
Electrical Installations	1	€ 20,000.00	€ 20,000.00	€ -	€ 20,000.00	
Instrumentation	1	€ 20,000.00	€ 20,000.00	€ -	€ 20,000.00	
Piping	1	€ 20,000.00	€ 20,000.00	€ -	€ 20,000.00	
Total cost (excluding taxes)					**€ 367,600.00**	

Table 5.14: Approximated operating cost

Description of work	Quantity	Unit price	Total	Installation	Total	Note
Operator					€50,000.00	€/year
1/2 Technical person						
1 Worker						
Power consumptions	45000kWh	€ 0.13	€ 5,850.00	€ -	€5,850.00	€/year
Chemical consumptions						
Potassium permanganate	1100Kg	€ 37.00	€ 40,700.00	€ -	€40,700.00	€/year
Sodium hypochlorite	1050 Kg	€5.00	€ 5,250.00	€ -	€5,250.00	€/year
Connecting utilities	1	€ 10,000.00	€10,000.00	€ -	€ 10,000.00	€/year
Goodwill and train operators	1	€10,000.00	€10,000.00	€ -	€ 10,000.00	€/year
Charges for the safety	1	€10,000.00	€10,000.00	€ -	€ 10,000.00	€/year
ANALYSIS						
Annual inspection					€10,000.00	€/year
Different analyzes for testing the water quality					€10,000.00	€/year
MAINTENANCE						
Cleaning, lubrication, oil change & so on					€20,000.00	€/year
Total cost (excluding taxes)					**€171,800.00**	€/year

Table 5.14: Summary of the approximated total cost

Total investment cost	22,481.21	Euro/year
Total operating cost	171,800.00	Euro/year
Total cost	194,281.21	Euro/year
Cost per m^3 of water (excluding taxes)	0.532	Euro/m^3

Considering bank interest = 2% and life span of the project= 20 years

Note: This is just an approximation for having an idea about the cost per $m^3$of water. Even if the bank interest varies from 2-5%, the cost per m^3 varies from 0.532-0.551 €/m^3.

CHAPTER 6: CONCLUSION AND RECOMMENDATION

This system is designed by combination of physical-chemical way and has efficiency enough to remove the pollutants effectively to the desire level but still have drawbacks in the system. **Table 6.1** describes the advantages and disadvantages of the system.

Table 6.1: Advantages and disadvantages of the designed system

	Description
Advantages	• Methane and iron is completely removed by natural way; • No free chlorine in the drinking water; • Less chemical used for treatment process; • UV radiation also have very high efficiency and also natural process; • No special unit for ammonia removal; • Ammonia can be removed by natural process by using the same tertiary aerated sand filter used for solids extraction; • Back-up system (break-point chlorination) for ammonia removal if any failure of ammonia removal from tertiary aerated filtration unit; • Environmentally friendly as less chemical used and space efficient and effective system; • Less labor cost as installation, operating and maintenance is much easier and flexible than other system like membrane, ion exchange; • No need for backwashing.
Disadvantages	• Possibility of methane explosion if it is high volume; • Air stripping of methane to the open air could be controversial issue for environmental agency; • Tertiary aerated sand filter has very high capacity for solids removal, but very small amount of solids produced this case. So small filtration unit and separate ammonia removal unit could be another good option; • Break-point chlorination could be the good alternative rather than nitrification.

Efficiency of any system depends on proper installation, operations & maintenance and performance of the system itself. So it is recommended to the operators to ensure the proper installation, operation and maintenance of single equipment and treatment unit according to the manufacturer manual. The system has great importance since it is designed for drinking water facilities so extra care must be taken for all aspects in order to fulfill the purposes and preventive measures must be applied for any possible system failure. In order to make the system simpler especially for tertiary sand filtration unit that has capacity more than the requirement, we can think about the exact filtration unit to achieve the purpose.

APPENDIX A: CHEMISTRY OF ARSENIC

A.1 Physical Properties

The three most common allotropes are metallic grey, yellow and black arsenic, with grey being the most common. Grey arsenic (α-As, space group R3m No. 166) adopts a double-layered structure consisting of many interlocked ruffled six-member rings. Because of weak bonding between the layers, grey arsenic is brittle and has a relatively low Mohs hardness of 3.5. Nearest and next-nearest neighbors form a distorted octahedral complex, with the three atoms in the same double-layer being slightly closer than the three atoms in the next. This relatively close packing leads to a high density of 5.73 g/cm3. Grey arsenic is a semimetal, but becomes a semiconductor with a band gap of 1.2–1.4 eV if amorphized. Yellow arsenic is soft and waxy, and somewhat similar to tetra phosphorus (P4). Both have four atoms arranged in a tetrahedral structure in which each atom is bound to each of the other three atoms by a single bond. This unstable allotrope, being molecular, is the most volatile, least dense and most toxic. Solid yellow arsenic is produced by rapid cooling of arsenic vapor, As4. It is rapidly transformed into the grey arsenic by light. The yellow form has a density of 1.97 g/cm3. Black arsenic is similar in structure to red phosphorus (1).

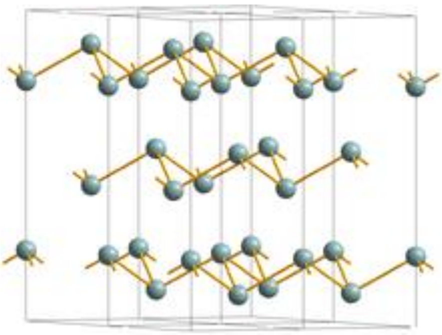


Figure-A.1: Crystal structure common to Sb, AsSb and grey As (1)

A.2 Isotopes

Naturally occurring arsenic is composed of one stable isotope, 75As. Therefore, Arsenic is a mono-isotopic element. As of 2003, at least 33 radioisotopes have also been synthesized, ranging in atomic mass from 60 to 92. The most stable of these is 73As with a half-life of 80.3 days. Isotopes that are lighter than the stable 75As tend to decay by β+ decay, and those that are heavier tend to decay by β- decay, with some exceptions. At least 10 nuclear isomers have been described, ranging in atomic mass from 66 to 84. The most stable of arsenic's isomers is 68mAs with a half-life of 111 seconds (1). Arsenic has five valence electrons. In group five, Arsenic is most closely related to antimony, both being metalloids. Since nitrogen and phosphorus are non metal, they share very little commonalities with arsenic and antimony. As with bismuth being a P-block metal, they too share very little similarities. Arsenic is used as the group 5 element in the III-V semiconductors gallium arsenide, indium arsenide, and aluminium arsenide. The valence electron count of GaAs is the same as a pair of Si atoms, but the band structure is completely different, which results distinct bulk properties. Other arsenic alloys include the II-IV semiconductor cadmium arsenide (46).

A.3 Chemical Properties

Atomic number	- 33
Atomic mass	74.9216 g.mol -1
Electro negativity according to Pauling	2.0
Density	5.7 g.cm-3 at 14°C
Melting point	814 °C (36 atom)
Boiling point	615 °C (sublimation)
Vanderwaals radius	0.139 nm
Ionic radius	0.222 nm (-2) 0,047 nm (+5) 0,058 (+3)
Isotopes	8
Electronic shell [Ar]	3d10 4s2 4p3
Energy of first ionization	947 kJ.mol -1
Energy of second ionization	1798 kJ.mol -1
Energy of third ionization	2736 kJ.mol -1
Standard potential	- 0.3 V (As3+/ As)
Discovered by	The ancients (2)

A.4 Compounds

Arsenic compounds resemble in some respects those of phosphorus, which occupies the same group (column) of the periodic table. Arsenic is less commonly observed in the pentavalent state, however. The most common oxidation states for arsenic are: −3 in the arsenide's, such as alloy-like inter-metallic compounds; and +3 in the arsenites, arsenates (III), and most organic arsenic compounds. Arsenic also bonds readily to itself as seen in the square As3− 4 ions in the mineral skutterudite. In the +3 oxidation state, arsenic is typically pyramidal, owing to the influence of the lone pair of electrons (1).

A.4.1 Organic compounds

A large variety of organic arsenic compounds are known. Several were developed as chemical warfare agents during World War I, including vesicants such as lewisite and vomiting agents such as adamsite. Cacodylic acid, which is of historic and practical interest, arises from the methylation of arsenic trioxide, a reaction that has no analogy in phosphorus chemistry. Organic arsenic compounds also include monomethyl arsenic acid, sodium cacodylet, atoxyl, stovarsol, sulpharsinamine etc. Arsenic is used as the group 5 element in the III-V semiconductors gallium arsenide, indium arsenide, and aluminium arsenide. The valence electron count of GaAs is the same as a pair of Si atoms, but the band structure is completely different, which results distinct bulk properties. Other arsenic alloys include the II-IV semiconductor cadmium arsenide (1).

Figure A.2: Trimethylarsine (1)

A.4.2 Inorganic compounds

Inorganic arsenic is divided into two types- trivalent and pentavalent arsenic. Inorganic arsenic is more toxic than the organic ones. The trivalent arsenic is 60 times more toxic than pentavalent arsenic. Trivalent arsenic compounds are known as arsenide and the pentavalents are as arsenate. Usually there are four types of arsenic compounds existing in water. These are arsenide, arsenate, monomethyl arsenic acid and dimethyl arsenic acid. But in the groundwater arsenic predominantly occurs in the tri- and pentavalent form. The name of some inorganic arsenic compounds can be mentioned here- arsenous oxide or arsenic trioxide, sodium arsenide, potassium arsenide, copper arsenide, copper aceto-arsenite, arsenic acid, sodium arsenate, potassium arsenate, arsenic disulfide or realgar, orpiment or arsenic trisulfide, arsenopyrite, arsine, arsenic triiodide, etc (6).

A.4.3 Identity of some arsenic compounds

Arsenic exists in oxidation states of −3, 0, 3 and 5. It is widely distributed throughout Earth's crust, most often as arsenic sulfide or as metal arsenates and arsenides. In water, it is most likely to be present as arsenate, with an oxidation state of 5, if the water is oxygenated. However, under reducing conditions (<200 mV), it is more likely to be present as arsenite, with an oxidation state of 3 (IPCS, 2001).

Compound	*Chemical Abstracts Service No.*	*Molecular formula*
Arsenic	7440-38-2	As
Arsenic trioxide	1327-53-3	As_2O_3
Arsenic pentoxide	1303-28-2	As_2O_5
Arsenic sulfide	1303-33-9	As_2S_3
Dimethylarsinic acid (DMA)	75-60-5	$(CH_3)_2AsO(OH)$
Monomethylarsonic acid (MMA)	124-58-3	$(CH_3)AsO(OH)_2$
Lead arsenate	10102-48-4	$PbHAsO_4$
Potassium arsenate	7784-41-0	KH_2AsO_4
Potassium arsenite	10124-50-2	$KAsO_2HAsO_2$

(149)

A.4.4 Physicio-chemical properties of some arsenic compounds
(IARC,1980, Lide, 1992-1993)

Compound	*Melting point (°C)*	*Boiling point (°C)*	*Density (g/cm^3)*	*Water solubility (g/l)*
As	613	–	5.727 at 14 °C	insoluble
As_2O_3	312.3	465	3.738	37 at 20 °C
As_2O_5	315 (decomposes)	–	4.32	1500 at 16 °C
As_2S_3	300	707	3.43	5×10^{-4} at 18 °C
$(CH_3)_2AsO(OH)$	200	–	–	829 at 22 °C
$CH_3AsO(OH)_2$	–	–	–	–
$PbHAsO_4$	720 (decomposes)	–	5.79	very slightly soluble
KH_2AsO_4	288	–	2.867	190 at 6 °C
$KAsO_2HAsO_2$	–	–	–	soluble

(150)

APPENDIX B: CHEMISTRY OF IRON

B.1 Physical Properties

Iron is a silvery-white or grayish metal. It is ductile and malleable. Ductile means capable of being drawn into thin wires. Malleable means capable of being hammered into thin sheets. It is one of only three naturally occurring magnetic elements. The other two are nickel and cobalt (28).

Iron has a very high tensile strength. Tensile means it can be stretched without breaking. Iron is also very workable. Workability is the ability to bend, roll, hammer, cut, shape, form, and otherwise work with a metal to get it into a desired shape or thickness (28).

The melting point of pure iron is 1,536°C (2,797°F) and its boiling point is about 3,000°C (5,400°F). Its density is 7.87 grams per cubic centimeter. The melting point, boiling point, and other physical properties of steel alloys may be quite different from those of pure iron (28).

B.2 Isotopes

There are four naturally occurring isotopes of iron, iron-54, iron-56, iron-57, and iron-58. Isotopes are two or more forms of an element. Isotopes differ from each other according to their mass number. The number written to the right of the element's name is the mass number. The mass number represents the number of protons plus neutrons in the nucleus of an atom of the element. The number of protons determines the element, but the number of neutrons in the atom of any one element can vary. Each variation is an isotope (28).

Six radioactive isotopes of iron are known also. A radioactive isotope is one that breaks apart and gives off some form of radiation. Radioactive isotopes are produced when very small particles are fired at atoms. These particles stick in the atoms and make them radioactive (28).

Two radioactive isotopes of iron are used in medical and scientific research. They are iron-55 and iron-59. These isotopes are used primarily as tracers in studies on blood. A tracer is a radioactive isotope whose presence in a system can easily be detected. The isotope is injected into the system. Inside the system, the isotope gives off radiation. That radiation can be followed by detectors placed around the system.

Iron-55 and iron-59 are used to study the way in which red blood cells develop in the body. These studies can be used to tell if a person's blood is healthy (28).

B.3 Chemical Properties

Iron is a very active metal. It readily combines with oxygen in moist air. The product of this reaction, iron oxide (Fe 2 O 3), is known as rust. Iron also reacts with very hot water and steam to produce hydrogen gas. It also dissolves in most acids and reacts with many other elements (28).

Atomic number	26
Atomic mass	55.85 g.mol -1
Electro negativity according to Pauling	1.8
Density	7.8 g.cm-3 at 20°C
Melting point	1536 °C
Boiling point	2861 °C
Vanderwaalsradius	0.126 nm
Ionic radius	0.076 nm (+2); 0.064 nm (+3)
Isotopes	8
Electronic shell	[Ar] 3d6 4s2
Energy of first ionization	761 kJ.mol -1
Energy of second ionization	1556.5 kJ.mol -1
Energy of third ionization	2951 kJ.mol -1
Standard potential	- o.44 V (Fe2+/ Fe); 0.77 V (Fe3+/ Fe2+)
Discovered by	The ancient (33)

B.4 Organoleptic properties

Iron (as Fe2+) concentrations of 40 µg/liter can be detected by taste in distilled water. In mineralized spring water with total dissolved solids content of 500 mg/liter, the taste threshold value was 0.12 mg/liter. In well-water, iron concentrations below 0.3 mg/liter were characterized as unnoticeable, whereas levels of 0.3–3 mg/liter were found acceptable (E. Dahi, personal communication, 1991) (50).

In drinking-water supplies, iron (II) salts are unstable and are precipitated as insoluble iron (III) hydroxide, which settles out as a rust-colored silt. Anaerobic ground waters may contain iron (II) at concentrations of up to several milligrams per liter without discoloration or turbidity in the water when directly pumped from a well, although turbidity and color may develop in piped systems at iron levels above 0.05–0.1 mg/liter. Staining of laundry and plumbing may occur at concentrations above 0.3 mg/liter. Iron also promotes undesirable bacterial growth ("iron bacteria") within a waterworks and distribution system, resulting in the deposition of a slimy coating on the piping (50).

B.5 Compounds

Iron forms compounds mainly in the +2 and +3 oxidation states. Traditionally, iron (II) compounds are called ferrous and iron (III) compounds ferric. Iron also occurs in higher oxidation states, an example being the purple potassium ferrate (K_2FeO_4) which contains iron in its +6 oxidation state. Iron (IV) is a common intermediate in many in biochemical oxidation reactions. Numerous organometallic compounds contain formal oxidation states of +1, 0, −1, or even −2. The oxidation states and other bonding properties are often assessed using the technique of Mössbauer spectroscopy. There are also many mixed valence compounds that contain both iron(II) and iron(III) centers, such as magnetite and Prussian blue ($Fe_4(Fe[CN]_6)_3$. The latter is used as the traditional "blue" in blueprints (151).

The iron compounds produced on the largest scale in industry are iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron (III) chloride ($FeCl_3$). The former is one of the most readily available sources of iron (II), but is less stable to aerial oxidation than Mohr's salt ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$). Iron (II) compounds tend to be oxidized to iron (III) compounds in the air (151).

Unlike many other metals, iron does not form amalgams with mercury. As a result, mercury is traded in standardized 76 pound flasks (34 kg) made of iron (151).

Some iron is made into compounds. The amount is very small compared to the amount used in steel and other iron alloys. Probably the fastest growing use of iron compounds is in water treatment systems. The terms ferric and ferrous refer to two different forms in which iron occurs in compounds. Some of the important iron compounds are (28):

The U.S. Recommended Daily Allowance (USRDA) for iron is 18 milligrams.
Ferric acetate ($Fe(C_2H_3O_2)_3$): used in the dyeing of cloth
Ferric ammonium oxalate ($Fe(NH_4)_3(C_2O_4)_4$): blueprints
Ferric arsenate ($FeAsO_4$): insecticide
Ferric chloride ($FeCl_3$): water purification and sewage treatment systems; dyeing of cloth; coloring agent in paints; additive for animal feed; etching material for engraving, photography, and printed circuits
Ferric chromate ($Fe_2(CrO_4)_3$): yellow pigment (coloring) for paints and ceramics

Ferric hydroxide ($Fe(OH)_3$): brown pigment for coloring rubber; water purification systems
Ferric phosphate ($FePO_4$): fertilizer; additive for animal and human foods
Ferrous acetate ($Fe(C_2H_3O_2)_2$): dyeing of fabrics and leather; wood preservative
Ferrous gluconate ($Fe(C_6H_{11}O_7)_2$): dietary supplement in "iron pills"
Ferrous oxalate (FeC_2O_4): yellow pigment for paints, plastics, glass, and ceramics; photographic developer ferrous sulfate ($FeSO_4$): water purification and sewage treatment systems; catalyst in production of ammonia; fertilizer; herbicide; additive for animal feed; wood preservative; additive to flour to increase iron levels (28).

B.5.1 Binary compounds

Iron reacts with oxygen in the air to form various oxide and hydroxide compounds; the most common are iron (II, III) oxide (Fe_3O_4), and iron (III) oxide (Fe_2O_3). Iron (II) oxide also exists, though it is unstable at room temperature. These oxides are the principal ores for the production of iron (see bloomery and blast furnace). They are also used in the production of ferrites, useful magnetic storage media in computers, and pigments. The best known sulfide is iron pyrite (FeS_2), also known as fool's gold owing to its golden luster (151).

The binary ferrous and ferric halides are well known, with the exception of ferric iodide. The ferrous halides typically arise from treating iron metal with the corresponding binary halogen acid to give the corresponding hydrated salts (151).
$Fe + 2\,HX \rightarrow FeX_2 + H_2$
Iron reacts with fluorine, chlorine, and bromine to give the corresponding ferric halides, ferric chloride being the most common:
$2\,Fe + 3\,X_2 \rightarrow 2\,FeX_3$ ($X = F, Cl, Br$) (151)

B.5.2 Coordination and organometallic compounds

Several cyanide complexes are known. The most famous example is Prussian blue, ($Fe_4(Fe[CN]_6)_3$). Potassium ferricyanide and potassium ferrocyanide are also known; the formation of Prussian blue upon reaction with iron (II) and iron (III) respectively forms the basis of a "wet" chemical test. Prussian blue is also used as an antidote for thallium and radioactive caesium poisoning. Prussian blue can be used in laundry bluing to correct the yellowish tint left by ferrous salts in water (151).

Several carbonyl compounds of iron are known. The premier iron (0) compound is iron pentacarbonyl, $Fe(CO)_5$, which is used to produce carbonyl iron powder, a highly reactive form of metallic iron. Thermolysis of iron pentacarbonyl gives the trinuclear cluster, triiron dodecacarbonyl. Collman's reagent, disodium tetracarbonylferrate, is a useful reagent for organic chemistry; it contains iron in the −2 oxidation state. Cyclopentadienyliron dicarbonyl dimer contains iron in the rare +1 oxidation state. Also known is the iron carbonyl ligand, Fp (151).

Ferrocene is an extremely stable complex. The first sandwich compound, it contains an iron (II) center with two cyclopentadienyl ligand bonded through all ten carbon atoms. This arrangement was a shocking novelty when it was first discovered, but the discovery of ferrocene has led to a new branch of organometallic chemistry. Ferrocene itself can be used as the backbone of a ligand, e.g. dppf. Ferrocene can itself be oxidized to the ferrocenium cation (Fc+); the ferrocene/ferrocenium couple is often used as a reference in electrochemistry (151).

APPENDIX C: CHEMISTRY OF MANGANESE

C.1 Physical Properties

Manganese is a steel-gray, hard, shiny, brittle metal. It is so brittle, in fact, that it cannot be machined in its pure form. Machining refers to the bending, cutting, and shaping of a metal by mechanical means. The melting point of manganese is 1,245°C (2,273°F) and its boiling point is about 2,100°C (3,800°F). Its density is 7.47 grams per cubic centimeter (42).

Manganese exists in four allotropic forms. Allotropes are forms of an element with different physical and chemical properties. The element changes from one form to another as the temperature rises. The form that exists from room temperature up to about 700°C (1,300°F) is the most common form (42). It is difficult to fuse, but easy to oxidize. Manganese metal and its common ions are paramagnetic (45).

C.2 Isotopes

Naturally occurring manganese is composed of one stable isotope, 55Mn. Eighteen radioisotopes have been characterized, with the most stable being 53Mn with a half-life of 3.7 million years, 54Mn with a half-life of 312.3 days, and 52Mn with a half-life of 5.591 days. All of the remaining radioactive isotopes have half-lives that are less than three hours and the majority of these have half-lives that are less than one minute. This element also has three Meta states (45).

Manganese is part of the iron group of elements, which are thought to be synthesized in large stars shortly before the supernova explosion. 53Mn decays to 53Cr with a half-life of 3.7 million years. Because of its relatively short half-life, 53Mn occurs only in tiny amounts due to the action of cosmic rays on iron in rocks. Manganese isotopic contents are typically combined with chromium isotopic contents and have found application in isotope geology and radiometric dating. Mn–Cr isotopic ratios reinforce the evidence from 26Al and 107Pd for the early history of the solar system. Variations in 53Cr/52Cr and Mn/Cr ratios from several meteorites indicate an initial 53Mn/55Mn ratio that suggests Mn–Cr isotopic composition must result from in situ decay of 53Mn in differentiated planetary bodies. Hence 53Mn provides additional evidence for nucleosynthetic processes immediately before coalescence of the solar system (45).

The isotopes of manganese range in atomic weight from 46 u (46Mn) to 65 u (65Mn). The primary decay mode before the most abundant stable isotope, 55Mn, is electron capture and the primary mode after is beta decay (45).

Only one naturally occurring isotope of manganese exists, manganese-22. Isotopes are two or more forms of an element. Isotopes differ from each other according to their mass number. The number written to the right of the element's name is the mass number. The mass number represents the number of protons plus neutrons in the nucleus of an atom of the element. The number of protons determines the element, but the number of neutrons in the atom of any one element can vary. Each variation is an isotope (42).

Nine radioactive isotopes of manganese are known also. A radioactive isotope is one that breaks apart and gives off some form of radiation. Radioactive isotopes are produced when very small particles are fired at atoms. These particles stick in the atoms and make them radioactive. None of the radioactive isotopes of manganese has any important commercial uses (42).

C.3 Chemical Properties

Manganese is a moderately active metal. It combines slowly with oxygen in the air to form manganese dioxide (MnO2). At higher temperatures, it reacts more rapidly. It may even burn, giving off a bright white light. Manganese reacts slowly with cold water, but more rapidly with hot water or steam. It dissolves in most acids with the release of hydrogen gas. It also combines with fluorine and chloride to make manganese difluoride (MnF2) and manganese dichloride (MnCl2) (42).

Atomic number	25
Atomic mass	54.9380 g.mol -1
Electro negativity according to Pauling	1.5
Density	7.43 g.cm-3 at 20°C
Melting point	1247 °C
Boiling point	2061 °C
Vanderwaals radius	0.126 nm
Ionic radius	0.08 nm (+2); 0.046 nm (+7)
Isotopes	7
Electronic shell	[Ar] 3d5 4s2
Energy of first ionization	716 kJ.mol -1
Energy of second ionization	1489 kJ.mol -1
Standard potential	- 1.05 V (Mn2+/ Mn)
Discovered	Johann Gahn in 1774 (44)

C.4 Organoleptic Properties

At concentrations exceeding 0.1 mg/l, the manganese ion imparts an undesirable taste to beverages and stains plumbing fixtures and laundry (Griffin, 1960). When manganese (II) compounds in solution undergo oxidation, manganese is precipitated, resulting in encrustation problems. At concentrations as low as 0.02 mg/l, manganese can form coatings on water pipes that may later slough off as a black precipitate (Bean, 1974). A number of countries have set standards for manganese of 0.05 mg/l, above which problems with discoloration may occur (62).

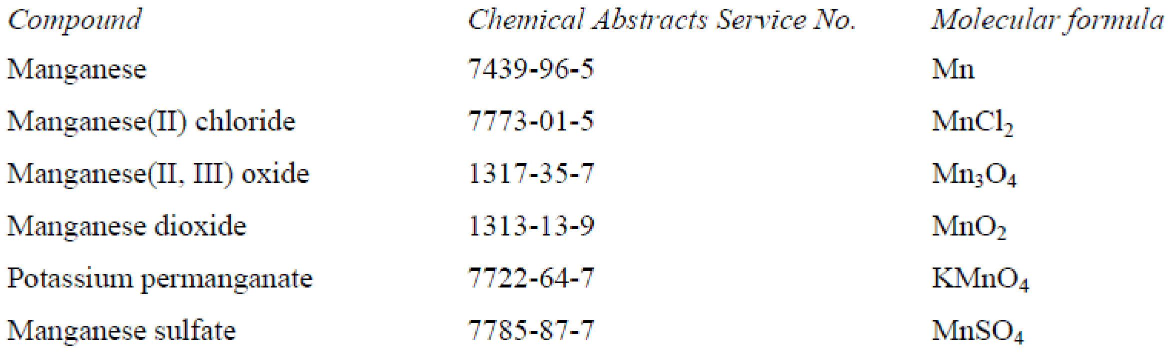
C.5 Compounds

Less than 10 percent of all the manganese used in the United States goes to the production of manganese compounds. Perhaps the most important commercial use of these compounds is manganese dioxide (MnO2). Manganese dioxide is used to make dry-cell batteries. These batteries are used in electronic equipment, flashlights, and pagers. Dry cell batteries hold a black pasty substance containing manganese dioxide. The use of manganese dioxide in a dry cell prevents hydrogen gas from collecting in the battery as electricity is produced (42).

Another manganese compound, manganous chloride (MnCl2), is an additive in animal food for cows, horses, goats, and other domestic animals. Fertilizers also contain manganous chloride so that plants get all the manganese they need (42).

Finally, small amounts of manganese compounds are used as coloring agents in bricks, textiles, paints, inks, glass, and ceramics. Manganese compounds can be found in shades of pink, rose, red, yellow, green, purple, and brown (42).

C.5.1 Identity of some compounds



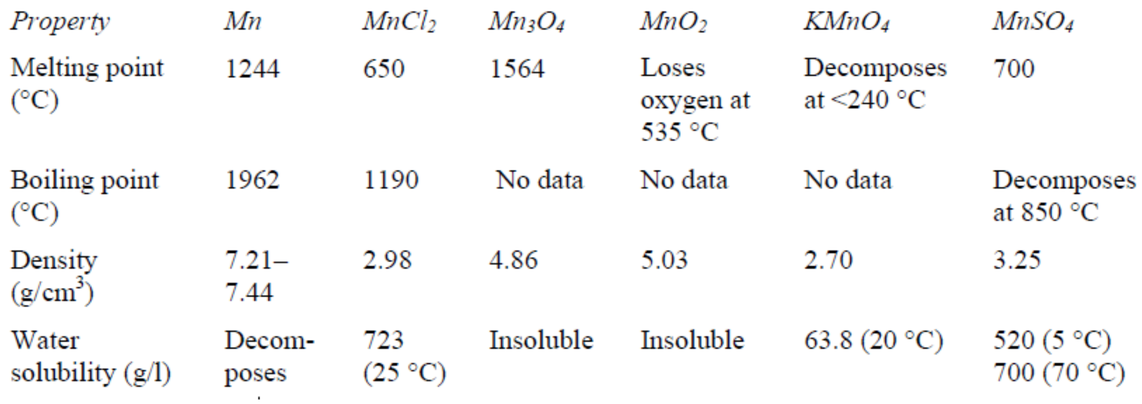
Compound	*Chemical Abstracts Service No.*	*Molecular formula*
Manganese	7439-96-5	Mn
Manganese(II) chloride	7773-01-5	$MnCl_2$
Manganese(II, III) oxide	1317-35-7	Mn_3O_4
Manganese dioxide	1313-13-9	MnO_2
Potassium permanganate	7722-64-7	$KMnO_4$
Manganese sulfate	7785-87-7	$MnSO_4$

Source: ATSDR (2000) (62).

Manganese is one of the most abundant metals in Earth's crust, usually occurring with iron. It is a component of over 100 minerals but is not found naturally in its pure (elemental) form (ATSDR, 2000). Manganese is an element essential to the proper functioning of both humans and animals, as it is required for the functioning of many cellular enzymes (e.g. manganese superoxide dismutase, pyruvate carboxylase) and can serve to activate many others (e.g. kinases, decarboxylases, transferases, hydrolases) (IPCS, 2002). Manganese can exist in 11 oxidative states; the most environmentally and biologically important manganese compounds are those that contain Mn2+, Mn4+ or Mn7+ (USEPA, 1994) (61).

C.5.2 Physicio-chemical properties of some manganese compounds

The physical and chemical properties of different manganese compounds vary substantially. These characteristics in turn determine the environmental behavior and fate, exposure potential and subsequent toxicological potential of each compound.



Property	*Mn*	$MnCl_2$	Mn_3O_4	MnO_2	$KMnO_4$	$MnSO_4$
Melting point (°C)	1244	650	1564	Loses oxygen at 535 °C	Decomposes at <240 °C	700
Boiling point (°C)	1962	1190	No data	No data	No data	Decomposes at 850 °C
Density (g/cm^3)	7.21–7.44	2.98	4.86	5.03	2.70	3.25
Water solubility (g/l)	Decom-poses	723 (25 °C)	Insoluble	Insoluble	63.8 (20 °C)	520 (5 °C) 700 (70 °C)

Source: ATSDR (2000) (62).

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