

## Chapter- 6

# A Critical Appraisal- Future Risk, Scope to Remediate, Technological Competence, etc.

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### 6.1 Appraisal on Source and Mobilization in the Bengal Basin

After the first detection of arsenical dermatitis and its causal connection with the drinking of high-As groundwater by the affected agglomerations of population, in a few districts of West Bengal (1983-84), it was only natural that the initial systematic studies on the problem were clinical, epidemiological and chemical-analytical in technique and orientation (Chakraborty et al., 1982; Saha, 1984; Chakraborty and Saha, 1987; Chatterjee et al., 1995; Das et al., 1996; Mondal et al., 1996). One fallout of this initial perception of the looming threat was the formulation of the question as to whether this arsenic contamination has been caused and is being caused by anthropogenic factors (e.g., large-scale use of chemical fertilizers, pesticides, herbicides, and excessive withdrawal of groundwaters) or by natural (geogenic) factors. It is now generally agreed that the source is of geological origin, being the top strata of the Bengal Basin, underlying the Bengal Delta Plain (WHO, 2008). The percolation of fertilizer residues can have only a modifying role on a limited scale, that too in the very upper strata. The question of the possible role of excessive withdrawal of groundwater, however, continues to divide the opinion.

Initial studies of this natural source and pathways of the metalloid came to centre on delineation of spatial extents of the contamination (reported, till the 1990s, as confined to the regions east of the Bhagirathi-Hugly River), and the stratigraphic level of occurrence (reported as confined to the Meander Belt of the Upper Delta Plain of the Late Quaternary). Based on the argument that the contamination occurs in the pore-waters of the terrigenous sediments of the Ganga-Brahmaputra-Meghna (GBM) delta, it was naively felt that the contaminant (arsenic) has an inland source. The chief interest has been put in locating the possible inland source. And the speculations have ranged from the sulphide belts of Bihar, Uttar Pradesh, North Bengal to the coal seams of the neighbouring Godwana Basins, the basic rocks of the Rajmahal Traps, the metamorphic schists of the Lesser Himalaya, even as far to a common source as in the Qamdo-Siman volcanic and ophiolite province in China for the whole mosaic of arsenic show-ups in the entire south-east Asia (e.g., PHED, 1991; Chakraborty et al., 1994; Das et al., 1996; Bhattacharya et al., 1997; Dhar et al., 1997; Saha, 1998; Nickson et al., 1998; Acharya et al., 1999; Stanger, 2005). The main thrust of these studies was, however, on the chemical characterization of groundwater, with elevated levels of arsenic concentration, redox state, arsenic speciation, age of waters, depth control, etc. All of this leads to the conclusion that the contaminated water is enriched by Fe, Mn, Ca, Mg, bicarbonates, and depleted in sulphate, fluoride, chloride. The pH, in this water ranges from 6.5 to 8. The redox condition is usually reducing. It is high on organic matter content; lodged mostly in sand coatings, or sorbed on clays, HFOs, and organic matters. As-concentration, in this water, is diminishing down-depth.

Widening and deepening of the knowledge base has now pushed forth the question as to how does arsenic mobilize into the aqueous phase from the aquifer solid phase. Early opinions are divided into two schools: oxidation model and reduction model. Kinniburgh et al. (1994) have postulated that the high quantum of groundwater withdrawal in Bangladesh and India has been causing the widening of the zone of aeration, resulting in oxidation of the source arsenian sulphides (pyrite and arsenopyrite, especially), in the aquifer sediments. And the acid so released has been reacting to liberate cations, including arsenic, into the aqueous phase. Soon, however, the euphoria subsided when (i) search for source clastic (detrital) arsenian sulphides proved elusive; (ii) any pyrites present were found to have framboidal structure, indicative of their diagenetic origin; (iii) aqueous phase was bicarbonate- enriched (alkaline), not acidic (e.g., Maynard et al. 1997; McArthur, 1999; BGS, 1999).

The favor of support has now tilted to the reduction model, with a host of workers proposing that arsenic is initially sorbed on HFOs, clays, ferromagnesian phyllosilicates, organic matter, or is lodged in the lattices of some crystalline oxide phases (magnetite, haematite, etc.), carbonates (siderite, rhodochrosite, etc.), and silicates (grunerite, etc.). Under appropriate reducing conditions, especially with Fe-3 reducing to Fe-2 and release to the aqueous phase, the sorbed arsenic (now reduced) desorbs and dissolves, in the aqueous phase in amounts, controlled by equilibrium conditions. It co-precipitates with Fe-2, or if the crystalline oxides and/or carbonates and/or silicate phases dissolve, it comes along into the aqueous phase. If and when the redox state of the aqueous phase reverses, with changing micro- environment, precipitation occurs back to the solid phases. It is warranted that the cycle may repeat, in space and time, or should change in the micro-environment. The presence of arsenical pyrite shows that sulphate reduction occurred after, or at the same time as, Fe reduction, in micro-environments. The latter yield arsenic, for incorporation into diagenetic pyrite, which is a sink for, not a source of, arsenic (Jekel, 1994; McArthur, 1999). With significant corroboration coming from field, laboratory and theoretical studies, this reduction origin of arsenic has now gained the status of the standard model among workers in this field (Matisoff et al., 1982; Saha, 1984; Welch et al., 1988; Belzile and Tessier, 1990; Saha and Chakraborty, 1995; Sullivan and Aller, 1996; Chen et al., 1997; Dutta and Subramaniam, 1997; Manning and Goldberg, 1997; McArthur 1997; CGWB, 1999; Jain et al., 1999; Nickson et al., 2000; Chowdhury et al., 2000; Gotkowitz et al., 2000; Acharya et al., 2001; BGS and DPHE, 2001; Pal et al., 2001; Ravi Shankar et al., 2001; Achyuthan and Baker, 2002; Harvey et al., 2002; Price and Picher, 2002; Rowland et al., 2002; Smedley and Kinniburgh, 2002; Ta TKO et al., 2002; Bhattarchyia et al., 2003; McArthur et al., 2004; Pal et al., 2003; Swartz et al., 2004; Adel Miah, 2005; Stanger et al., 2005; Gurung et al., 2006; Lipfert et al., 2006; Mukherjee, 2007; Hasan et al., 2007; Rowland et al., 2007; Banning et al., 2008; Hoque et al., 2008; Purakait and Mukherjee, 2008; Sengupta et al., 2008). On the other hand, the oxidation model is considered relevant only locally, occasionally and insignificantly.

The major controls of arsenic mobilization have thus been specified. The question of source has been relegated to the backburner. Briefly put, arsenic is present initially in the solid phase. Under reducing conditions, it mobilizes. It is being largely mediated, perhaps, by microbial

activity. In presence of high concentrations of S, it precipitates as sulphides. That is, only the general conditions of mobilization have been defined. The more intriguing questions of the mechanism of mobilization are yet to be understood i.e., the nature of specific reactions involved and the micro-environmental controls of these reactions, in terms of aquifer sedimentary lithic properties (physical and geometrical), mineralogical attributes, organic matter contents and microbial activities, groundwater flux, and so forth. And, if this is true, then the mineralogical-phase form (s) of the source of arsenic, the initial pattern of dispersal of the source-assemblage(s), and, especially, the relation of this dispersal pattern to the geological evolutionary history of the delta, must be taken into account alongside and in full measure. Due to the lack of knowledge base, neither we can explain the specificities of the observable pattern of distribution of arsenic in the aqueous phase at present, nor the variance for concentration values in time series in a given region, e.g., in the Bengal Basin. More importantly, the real reason of the alarming fact of gradual spread-out and newer show-ups of arsenic in groundwater, over time in newer tracts of this deltaic basin, will remain elusive to undermine all mitigation programmes, in not distant future. Accumulating reports on widespread occurrence of arsenic, its potential health hazards, have drawn worldwide attention. As a result, arsenic research has been accorded recognition as a thrust area. The focus has been turned on to the specifics of microbially mediated reduction, sorption mechanism, reaction kinetics, hydrostratigraphic and hydrochemical modeling, laboratory simulation, effects of groundwater flux, site specificity, thermodynamics of arsenic incorporation in pyrite, isotopic probe, besides mitigation. That is, all ramifications but the vital of a natural holistic approach.

In this backdrop, the present arsenic research group of the School of Fundamental Research of Kolkata conducted a two-year investigation into the problem of arsenic presence, in Nadia district of West Bengal, and reached the definitive conclusions that: (i) presently observable distribution-pattern of arsenic, in aqueous phase in the Bengal Basin, defines the picture, obtaining at the present stage of an ongoing hydrochemical evolutionary process, modified by anthropogenic interventions; (ii) specifics of this pattern become evident, only if and when, considered with reference to a natural frame of reference; (iii) there exists a definite and regional correlation, both positive and negative, between arsenic (total) and iron (total). It demonstrates that other than desorption reactions, there must have been more reaction; (iv) memories of the micro-environmental Eh and pH states of some of the preceding evolutionary stages, at least, are preserved in the diagenetic-phase mineral parageneses present in the aquifer sediments (Berner, 1981); (v). study of the aquifer solid phase arsenic and iron by sequential extraction (Keon, et al., 2001), along with studies on oxidation states of As and Fe and on the diagenetic phases and their parageneses, will yield the basic information to making possible the reconstruction of the past and present reaction regimes, the ones that induced arsenic and iron mobilization--- in short, the mechanism and triggers; (vi) nature of initial source of arsenic, in the deltaic sediments-in terms of pattern of distribution (whether dispersed throughout or concentrated in thin bands), reactive forms, and mineral association --- definitely bears on the evolutionary changes, leading to the present picture, i. e., the question of source pertains, it needs to be addressed (Chatterjee et al., 2005; Basu et al., 2007; Ghatak, 2007; Roy et al., 2007).

## **6.2 Appraisal on Arsenic Removal Technologies**

Widespread variations, in the projected costs of arsenic removal, are partially attributed to the large number of possible arsenic removal technologies. All of the methods are intended to remove arsenic in the As (V) state. As (III) can be oxidized to As (V) by using ferric chloride, potassium permanganate, or chlorine. Ferric sulfate coagulation works well, for removing arsenic at nearly neutral pH values, but sludge disposal can be a problem. Lime softening is effective, especially at  $\text{pH} > 10.5$ . This could initially be a good step, but extremely low arsenic concentrations cannot be achieved. Activated aluminum is very good for water, with high total dissolved solids (TDS) concentrations, but ion competition and regeneration difficulties must be overcome. Ion exchange drawbacks include ion competition and iron precipitate clogging. Reverse osmosis can remove 95% of the arsenic; however, a significant amount of water is concentrated with arsenic and, therefore, is wasted. Nano filtration can be  $> 90\%$  effective, but 80% of the water is wasted. Iron coagulation and filtering work well, given tight control of parameters, most notably iron content, time, and pH. Arsenic often is bound to iron or manganese, so traditional Fe/Mn removal methods work well for some waters (Water World, 2000). In 1978, Jones and others suggested Fe (II) and lime, for the removal of As (V) from acidic solutions (Prasad, 1994). At present, lime softening and iron co-precipitation appear to be the most effective removal technologies, barring the wasteful membrane separation methods. Arsenic removal methods and their effectiveness are shown in Table 6.1. The approaches of arsenic removal from contaminated water can be summarized as follows:

### **6.2.1 Arsenic Removal Technologies**

- (i) It is proved that arsenic has affinity with iron. Under restricted Eh-pH conditions, arsenic dissolved in water, gets adsorbed onto iron and precipitates as oxyhydroxide. So if a volume of oxygenated water is injected into arseniferous aquifers, the concentration of arsenic in water may be proportionately depressed. This technique would work effectively in areas, where arsenic in groundwater correlates positively with iron, and prior knowledge of arsenic distribution pattern and flow direction has been gathered to facilitate grids for sinking injection wells.
- ii) The second alternative is to remove arsenic from arsenic-contaminated water by suitable filtration techniques. If we can solve the related problems of sludge disposal effectively, and maintenance is ensured locally, this appears to be the indigenously viable practical solution. There are various kinds of filter manufacturers, who claim their success in making arsenic contaminated water into water of standard potable type. These are:

**Oxidation of As (III) to As (V)** by free Cl, ferric chloride, potassium permanganate, ozone, hydrogen peroxide. Each process of oxidation has its limitation and drawbacks.

**Coagulation-precipitation process:** Aluminum and ferric salts are commonly used in drinking water treatment, for coagulation of particles and colloids in the water. If the As content in water is in the range of 0.1 to 1 ppm, under optimized condition of Fe dosage and pH, precipitation efficiency and the elimination process may be as high as 99%.. With change in Eh / pH ratio efficiency varies appreciably.

**Lime softening:** This treatment is used for reducing hardness of water, and is also an effective process for As (V) removal. The use of activated charcoal powder increases the efficiency as it induces oxidation of As (III). But effectiveness decreases in alkaline condition.

The biggest problem of the above three processes is concerned with the separation of the precipitate and disposal of arsenic contaminated coagulated sludge.

**Ion exchange:** It can remove As (V) more efficiently than As (III). In some recent studies, it has been established that by this process, As<sup>5+</sup> level can be reduced to 2 mg/L and the brine regeneration can be done several times without any adverse impact on As removal. TDS, selenium, sulphate, fluoride and nitrate, present in water, affect the life of resin adversely. Suspended solid and precipitated iron cause clogging of resin bed. Another disadvantage is that As (III) is hardly removed.

**Activated alumina:** It is a porous oxide with large surface area and it adsorbs As<sup>5+</sup> under favorable pH condition of 5.5 to 6, but it is also susceptible to various interfering chemicals as in the case of ion exchange process.

The great advantage of activated alumina is its simple operation, with regeneration operation at intervals of one to three months. Unfortunately, activation efficiency decreases fast. As (III) cannot be removed efficiently. The biggest problem is disposal of highly concentrated sludge with high contents of toxic dissolve solid.

**Granular ferric hydroxide:** It is poorly crystallized B-FeOOH, with very large specific surface of 250-300 m<sup>2</sup>/g and porosity of 75-80%, which is capable of high adsorption. The grain size ranges from 0.2 to 2 mm. It also acts as fixed bed absorbers, with best efficiency between pH ranges of 5.5 to 9.

In addition to As (V), As (III) can also be adsorbed by granular ferric hydroxide. The presence of sulphates in raw water has little influence on adsorption capacity. Depending on As concentrations, the treatment efficiency ranges from 5 to 25g/m<sup>3</sup> of water. The residue is solid and the spent absorbent is non-toxic and can withstand temperature of 950°C without release of As from the granules. So disposal is less problematic. Phosphate, in raw water, reduces the arsenate adsorption due to interference.

**Activated carbon:** It may be helpful, to some extent, in removing arsenate, specially As (V) from water, but its efficiency is very low and cost inhibitive.

**Conventional Fe-Mn removal process:** It is effective only in case of raw water, with less concentration of As.

**Natural oxides:** Crushed hematite and feldspar can be used for adsorption of arsenic, in the particle size, range of 200  $\mu\text{m}$ ; but the maximum capacity is only 2.6  $\mu\text{mol/g}$ .

There are some other plausible methods of separation of As in laboratory scale.

**Reverse osmosis and nano-filtration:** Efficiency may be as high as 95% in ideal situations, but water rejection is very high, 25-40%, and discharge of large volume of reject-water, with higher concentrations of As. This may pose a problem.

**Electro dialysis reversal:** Removal efficiency of As (V) crosses 80%, but As (III) can hardly be removed.

**Table 6.1:** Arsenic removal methods and their effectiveness (from Torrens, 1999)

**Arsenic removal in drinking water: summary of available data**

Treatment technology	Arsenic in (ppb)	Arsenic out (ppb)	% removal
<b>Chemical precipitation</b>			
Oxidation/iron co-precipitation	110	10-85	23-91
Oxidation/iron co-precipitation	200	80-200	0-60
Oxidation/iron co-precipitation	1100	<5	>99
Lime softening	220	30	86
Lime softening (pH>10.5)	75	<5	>95
Lime softening	100	<5	>95
Oxidation/iron co-precipitation	50	<5	>90
Oxidation/iron co-precipitation	21	<2	>90
Oxidation/iron co-precipitation	377	11	95

### Adsorption

Activated alumina	88	<50	>43
Activated alumina	103	<50	>51
Ion exchange	92	<50	>45
Ion exchange	103	<50	>51
Manganese green sand	110	6.8-37.7	64-94

### Membrane separation

Reverse osmosis	91	1	99
Electrodialysis	85	23	73
Reverse osmosis	260	2.6	99
Coagulation/micro-filtration	50	<5	>90

## 6.3 Future of Remediation Approaches

### 6.3.1 *In-situ Treatment of Arsenic in Aquifer by Removing Dissolved Iron*

There is wide-scale report of the presence of dissolved iron, in arsenic contaminated groundwater in many countries, and of co-precipitation of iron and arsenic under oxidizing condition. In the investigated region of Nadia District, West Bengal, it has been found that As correlates with Fe in groundwater both positively and negatively, depending upon the condition. This raises the hope of a plausible way of *in situ* remediation of the problem of As contamination by removal of Fe from groundwater before withdrawal.

*In situ* Fe removal has proved to be a viable technique for diminishing Fe concentration in groundwater. The technique involves a cyclic injection of oxygenated water, in which Fe and Mn concentrations are lower than in the native groundwater. It is applied in a number of European countries and in the US (Hallberg and Martinell, 1976; Rott et al. 1978; Booch and Barovich, 1981; Van Beek, 1983; Rott and Lamberta, 1993; Meyerhoff, 1996). The reaction involves the displacement of ferrous iron exchange and sorption sites and subsequent oxidation by oxygen. Clogging has not been observed and appears to be unimportant, by virtue of self-regulatory nature of Fe<sup>2</sup> exchange and sorption mechanism. (Appelo et al., 1999) Increasing oxygen concentration in injected water is useless, because efficiency is limited by exchangeable Fe<sub>2</sub>, capable of consuming the oxidant during the injection stage.

Quantification of the reaction mechanism allows assessment of operational conditions. The gross mechanism of *in situ* oxidation appears to be simple as a given amount of oxidant is injected and is consumed by reduced substances in the aquifer. The problem is how the dissolved oxidant, such as O<sub>2</sub>, in injected water reaches the dissolved reductant, Fe<sup>2</sup>, in groundwater, while

the latter is being displaced during injection. The essence of *in situ* treatment is, in fact, the iron removal, and hence, arsenic removal, it continues even after the complete withdrawal of the injected water. The resulting ferric iron is highly insoluble and precipitates as an oxyhydroxide. It has been found that clogging does not occur, even in the case of systems, operating for more than 30 years. The lack of clogging suggests that precipitation takes place at a distance away from the well and possibly at varying locations in time.

In the aquifer, the fronts spread out due to dispersion and the combined effects of transport and reaction. When a new run is started with the injection of oxygenated water, the concentration of iron increases gradually in the well on pumping, and its efficiency depends on the limiting concentration of  $\text{Fe}^{2+}$ . With each cycle 1000 cubic meter of oxygenated water may be injected and 7000 cubic meter pumped out. The ensuing runs show a delayed rise of iron concentration, in the pumped water. In other words, the efficiency increases with the number of runs. The efficiency can better be improved, by optimizing the well arrangement, for example, by installing separate injection and pumping wells, to prevent the last part of oxygenated water, being withdrawn without reaction.

Groundwater pH should be above 6 for *in situ* iron removal, because rapid decrease of oxidation rate of  $\text{Fe}^{2+}$  occurs when pH is below 6. Moreover, if the aquifer contains lot of sulphides, the oxidation acidifies the system. And aquifers should be as homogeneous as possible. And this should be without extremely coarse layers to prevent preferential flow of injected water, through the most permeable parts, which generally have low exchange capacity. Thus, planning for *in situ* remediation, with injection of oxygenated water (pH ~7.5), four times a year, is a plausible long lasting mitigation technique for decontamination of arsenic in groundwater.

Researchers in the Queens University, Belfast, claimed to have developed a low-cost technology, which offers chemical-free groundwater arsenic treatment technology to provide arsenic-free water to rural communities for drinking and farming needs. The technology is based on recharging a part of the groundwater, after aeration, into a subterranean aquifer (permeable rock), which is able to hold water. Increased levels of oxygen, in the groundwater, slow down the arsenic release from the soil. At higher dissolved oxygen levels, soil micro organisms as well as iron and manganese reduce the dissolved arsenic level significantly. Based on this concept, a trial plant in Kasimpoore near Kolkata was planted and its performance was found satisfactory.

### **6.3.2 Limestone-based Arsenic Removal Methods**

Experiments have been performed, using Limestone to remove arsenic from water. This approach is supported by previous research, regarding the removal of arsenic by the formation of calcium arsenate (Bothe and Brown, 1999). Mobilization of arsenic, from sediment, is most likely when the sediment is low in iron and calcium carbonate (Brannon and Patrick, 1987). A reasonable conclusion is that arsenic is immobilized in iron and/or calcium compounds. Work on



arsenic-rich mine drainage and the subsequent decrease of arsenic content, down gradient from where discharges crossed limestone outcrops, indicated that limestone is a possible arsenic removal medium (Davis et al., 1999). Surface area of the limestone is a key parameter, controlling the efficiency of the process. The smaller grain sizes have provided a greater surface area per unit weight. Thus, better arsenic removal has been demonstrated.

The areas of major concern, regarding feasibility of a limestone-based arsenic removal process, are ionic interference, the stability and disposal of arsenic-saturated limestone, and the rate at which the process can treat water. Each of these concerns should be addressed. The process should be studied at the molecular level, regarding what compound is formed on or within the limestone. A better understanding of the entire process and the composition of the arsenic-rich limestone waste product would likely result from such a study. Perhaps a material, other than limestone, needs to be added to the process to enhance waste product stability. Based on previous research, iron oxide seems an appropriate choice. Other lime stones should be tested. A rock unit can contain various constituents and still qualify for classification as limestone. One of these minor constituents could greatly enhance the process. Various other natural waters should be used in upcoming work with a batch reactor. Chemical analyses of these natural waters should be done in an attempt to identify as to which ions preferentially interfere. Column experiments, using a constant flow rate, are needed. Understanding the flow mechanics of the process will be essential to the development of a prototype.

A prototype cartridge must be designed. Experimental data regarding mass adsorption ratios and necessary residence times, indicating an appropriate cartridge size and flow rate, would assist in the design of a prototype. The intent of any design should be to maximize the efficiency of the limestone-based arsenic removal process, with regard to both limestone mass and water volume or flow rate. This assumes the use of 58 smallest feasible limestone grain sizes. Cost and availability factors could affect that assumption. Initial experimental work has been successful in demonstrating the use of limestone to reduce the arsenic concentrations of a prepared standard solution. Prototype design and arsenic-rich limestone disposal must be addressed, before the ultimate feasibility of applying limestone-based arsenic removal systems, can be determined. Further work should focus on expanding the applications of the process, namely, to include removing arsenic from natural waters as well as standard solutions.

### **6.3.3 Remediation of Arsenic contaminated Soils by *in situ* Chemical Fixation**

Subsurface soils, from several industrial facilities, are contaminated with arsenic because of the application of arsenic containing herbicide. Low cost *in situ* chemical fixation treatment is designed to react with contaminated soils directly, against the treatment solutions to cause the formation of insoluble arsenic-bearing phases, and thereby, decreases the environmental leachability of arsenic (Xang, Li *et al*). Combinations of ferrous sulfate, potassium permanganate and calcium carbonate are used as major reagents for the chemical fixation

solutions. Sequential leaching, with an extraction fluid described in the EPA synthetic precipitation leaching procedure (SPLP), has been used to simulate the long-term leaching behavior of treated soils under natural conditions. The results indicate that the fixation solution, with only ferrous sulfate, have the best effect among all the reagent combinations, reducing SPLP-leachable arsenic by as much as 90%.

A modified 4-step sequential extraction procedure can be used to further study the chemical fractionation of soil As, before and after chemical treatment. Sequential extraction data would likely show that the soil treatment has greatly reduced the most readily labile portion of arsenic which is extracted in the 1st step of the sequential extraction, with its value lowered to less than one tenth than that of untreated soil. The potentially mobile fraction of soil arsenic, extracted in the 2nd step of the sequential extraction, is also considerably smaller. It is shown that after treatment; most of the As in the soil is transferred to amorphous Fe oxyhydroxides which are the major phases extracted in the 3rd step. X-ray absorption near edge spectra show As is present as As (V) in the treated soil. Extended X-ray absorption fine structure (EXAFS) spectral analysis indicates that a large portion of the total soil arsenic is co-precipitated and incorporated into newly formed amorphous Fe oxides after treatment.

#### **6.4 Experiences during Arsenic Removal Technology Evaluation in Technology Park**

School of Fundamental Research has been entrusted to conceptualize, execute and manage the evaluation programme of Arsenic Removal Technologies, using an Arsenic Technology Park during August 2001 to September 2003. It has gained some knowledge about the problems and genesis of arsenic mitigation in dynamic field conditions. Some of which are mentioned below.

- (i) **Tube-well:** The probable scenario has been in operation for more than a decade, with most of the tube-wells, which have been selected, based on their contamination level, and has practically concluded their critical life span. These have been found to be the same in all cases. Re-sinking of all the tube wells, due to sudden heavy drawl of water, becomes a necessity.

Since most of the lift pumps are used to pump water for gravitational drawdown through the media column natural system, resistance seems to affect the performance of the tube wells, which are otherwise meant for free lifting of water without any resistance in the path. Thus, difference in pull-push process interaction within the tube well generates a resultant back-pressure. Continuous over use disturbs the performance of the lift pumps as well as creates an impact on the interface mechanism. It is one of the critical issues that seem to affect the overall performance of ARPs.

- (ii) **Fluctuation:** Some of the major issues for fluctuation are high level of arsenic fluctuation in raw water in subsequent weeks, fine silvery colloidal sand, pollution due to unstabilised sub-surface condition and old under-used tube-wells. They have created many initial problems for the technology park programme and are a common scenario in most of the sites in lower deltaic region. Operation and maintenance have, thus, become quite a difficult task for obvious reasons. Erratic behaviour of arsenic, in raw water, is quite baffling as observed in each week and even on daily fixed time study. The fluctuation ranges from 11% to 35.6%, as observed. Some units tend to increase the pH and conductivity in the filtered water. Some units also show increase in hardness in the filtered water. All are capable of lowering Iron to permissible level. Backwashing is quite a regular feature for all the units. The suppliers of devices shall have to take note of the high level of arsenic fluctuation and *in situ* sub-soil condition for future device making as they seem to affect and alter the performance of media in both short term and long term interest.
- (iii) **As (III) & As (V) speciation:** Although it is generally felt that As (V) is better removed in the adsorption approach, for which in the design concept of most of the ARPs a primary oxidizing-interface for converting As(III) species to pentavalent status is ensured. The speciation studies have observed that all the As (III) species, present in the raw water, get converted or removed through the media interface. This may not be essentially true for the removal or adsorption in the process for As (V). In fact, whatever Arsenic remains after filtration is of As (V) species. Besides, it is to be noted, with interest, that this phenomenon is also repeated with even non-oxidant interface like the units with only Activated Alumina. One of such units has been installed by Oxide India.
- (iv) **Sludge:** Apparently sludge disposal, management and detoxification have not received due priority in the plan of actions, initiated along with the device installation by the ARP manufacturers. Even no discernible programme is seen for the backwash which contains high level of As in media-washed water. It needs high priority in the installation programmes. Both the raw water, pumped out for ordinary use, and back washed water; require to be passing through a soak pit type of arrangement, to avoid surface contamination.
- (v) **Operation & Maintenance:** The maintenance of the systems requires double attention for the ARPs and the tube wells. Majority of the operation and maintenance issues are related to tube wells, that have nothing to do with the ARP or its chemical media. In the resultant scenario, whole programme of operation and maintenance shall continue to suffer till design changes are ensured for the lift pumps. This can be done by releasing the back pressure through an outlet before it can exert cumulative pressure on the inlet valve.

In fact, without adequate in-built maintenance arrangements apparently, the performance of all the devices would suffer. Proper training and mobilization of the user community, in the operation and maintenance aspect, would be an essential task before any future installation programme can be envisaged. This aspect holds good for the best performing devices too.

- (vi) **People's Participation:** In a scenario, rural community has come to believe that getting free water is their fundamental right and getting pipe supply water at the door step is a matter of priority expectations. This poses serious concerns to planners of community based systems in maintenance and fund mobilization for the upkeep of the facilities at the time of media replacement. A fundamental change in community perception can only ensure the success of these endeavors. Although it will continue to suffer but the chances of getting *free* water from governmental agencies are still quite bright. *By executing the programme of establishing the Technology Park and evaluating the critical performance parameters, it was understood that beyond fund mobilization through motivation, the community participation, in a programme of high technical nature, requires continuous physical involvement of manufacturers' representative at site, otherwise quality of filtered water cannot be ensured. This matter needs to be appreciated in reality.*
- (vii) **Sludge Treatment :** Treatment of the slurry, obtained from arsenic removal process (from groundwater), is essential to make the slurry arsenic free so that it can be disposed without any hazard of the arsenic re-entering the aquifer system. The slurry may be transferred to plastic tanks and clear water from top drained off, further slurry added and top clear water drained off. In this way a large amount of slurry is obtained in concentrated form for treatment.

The slurry can be dissolved in hydrochloric and/or sulphuric acid. Then it can be treated with metal scraps and/or other suitable reducing agents to convert arsenic of the slurry solution into arsine gas, which can be allowed to escape in the atmosphere (as a primary tentative measure). As a future research, depending on the total amount of arsenic to be treated and availability of fund, the arsenic generated may be absorbed in oxidative alkaline medium to produce sodium arsenate or calcium arsenate. The compounds may be consumed by glass industries.

## **6.5 Alternate approach for ensuring supply of arsenic-free water**

It is important to note that in most of the areas, the arsenic contaminated zone is at the shallow/intermediate depth ranged largely between 20m and 50m. The groundwater in deeper aquifer  $\geq 100$  m has been reported arsenic-free, and has potential prospect of tapping. Though our studies at School of Fundamental Research in Nadia district showed tube wells up to 250

meters are affected. In alluvial formations, possibility of having confined aquifer is a chance phenomenon, and if at all, it would be on a very limited local scale. The aquifers are normally of unconfined to semi-confined types. Therefore, threat of downward mobilization of arsenic, from shallow to deeper zones over the years always, prevails. Further, the source being *in-situ* at localized pockets, a large part in a spatially distributed groundwater domain has uncontaminated groundwater reserves, which may not be under the influence of arsenic groundwater mobilization due to some obvious chemical portioning leading to self-purging, etc.. Areas barring large scale fluvial deposits, accumulated formations of clays, shifted river courses, already exposed by arsenic mobilization, etc. are normally expected to have uncontaminated reserves or accumulations. Modeling studies of arsenic contamination transport by various researchers showed that judicious and scientific management of fresh zones of aquifer, both shallow and deep, can sustain withdrawal of fresh groundwater resources for a long period without much aggravation of arsenic contaminated zones. For identification and design of safe locations of groundwater withdrawal, wells modeling studies can be the right tool. The caution that one has to take is analysis of post groundwater development scenarios, particularly with respect to transformed groundwater direction and movement.

Watershed is considered to be the basic unit of land-water management practices. From hydrological point of view, watershed possesses all characteristics generally required for conservation and development of water resources. Surface water is arsenic-free, and it is more so when rainwater is harvested as surface storage. Harnessing, developing and appropriate management of surface water, on a watershed basis, in arsenic affected areas and their usages in irrigation and other domestic purposes, can be a potential alternative. This can be noted that the major application of watershed based approaches and harnessing surface was not a traditional practice in alluvial tracts in Bengal, - major part of which is scourged with Arsenic contamination. On the contrary, in the western part of Bengal and mostly in drier zones and hard rock areas, use of surface water, was a natural option and practice.

Supply and usage of surface water exclusive from other sources, particularly due to distributive rain fall pattern, are no doubt a viable alternative, when availability of water from the source is assured and sustainable. The demand management of some areas from resources of other areas is linked to certainty of many factors. Creation of alternate surface water system may involve considerable money. Conjunctive use of surface water (either from watershed development or from other sources) and *in-situ* groundwater can be another potential alternative. A technical feasibility study, considering risk, cost and benefit of each alternative, would form an important task.

Whatever technological options we adopt, the success and effectiveness of that task can not be achieved unless end-users and beneficiaries of the schemes are debugged from concern and responsibility. No strategic planning of availability of safe and wise use of water can

be sustained by delinking user community and their effective participation in the management of traditional and new resources. Obviously, for the success of the program, people's awareness, regarding importance of water, its know-how on 'dos and don'ts and rightful uses, need to be tagged as a mandatory task.

## **6.6 Summary**

There exist a number of opinions about causes of arsenic induced groundwater contamination, in the Gangetic and Brahmaputra plains, in Indian sub-continent. However, it is now generally accepted that the source is of geological origin and percolation of fertilizer residues may have played a modifying role in its further exaggeration. Identification of parental rocks or outcrops is yet to be recognized, including their sources, routes, transport, speciation and occurrence in Holocene aquifers along fluvial tracks of the Ganga-Brahmaputra-Barrak valley and in scattered places, adjoining to it, in their basins. The speculation of sources in the Gangetic plains ranged from the sulphide belts of Bihar, Uttar Pradesh, and North Bengal to the coal seams of the neighboring Godwana Basins, the basic rocks of the Rajmahal Traps, the metamorphic schists of the Lesser Himalaya. The question of the possible role of excessive withdrawal of groundwater for its triggering, however, has continued to have divided opinions. The chemical processes such as, Redox potential, sorption, precipitation-dissolution, pH, influence of other competing ions, biological transformation, etc under different soil-water environmental condition; influence the perturbation of arsenic in a system, having presence of source material and/or conditions of enrichment. Whether the processes of physicochemical transformation were only influenced by excessive groundwater exploitation or there were other coupled actions of a number of hydro-geological and geo-environmental disturbances, over the periods, are yet to be recognized. Surfacing new arsenic affected areas, in every additional survey, is a matter of concern. It was reported that the contaminated waters are enriched in Fe, Mn, Ca, Mg, bicarbonates, and depleted in sulphate, fluoride, chloride; pH ranged from 6.5 to 8; redox condition usually in reducing; high on organic matter content; lodged mostly in sand coatings, or sorbed on clays, HFOs, and organic matters; As-concentration diminishing down-depth, which brings out a generalized geochemical perception that could help develop *in-situ* remediation of arsenic.

It has been proved that arsenic has affinity with iron. The relationship between As-Fe can be interpreted as signifying that in these instances iron played the scavenger role, adsorbing arsenic from water as it precipitated out, again desorbing arsenic into water as it re-dissolved in response to appropriate change of Eh-pH conditions. It appears that the reductants and oxidants were transported / accumulated / diagenetically precipitated components of the process of build-up of the sediment sequence of the delta. The oscillations owe their origin either to resetting of oxidants / reductants as a result of diffusion-dispersion-flux, or combined with, initial variation of As-Fe contents of the solid phases in the aquifer sediments.

It is also to be understood that the arsenic contamination of groundwater in the BDP is the result of interaction of the aquifer lithology and aquifer waters in flux in a complex evolutionary sequence in the mid-Holocene to the present times. Studying the morphologic and lithologic makeup of the area, its water drawal level pattern, aquifer water chemistry, mineral phases, and arsenic-and-iron concentration variation pattern, have provided basic insights into the problem.

Towards the mechanism of mobilization of **As**, the oxidation model is considered relevant only locally, while the reductive dissolution model of **As** from soils is largely acknowledged as the dominant processes of **As** mobilization in the Gangetic plains.

Removal of **As** from arsenic-contaminated water by suitable filtration techniques, to ensure supply of arsenic-free water, appears to be a viable practical solution for potable water if the related problems, such as sludge disposal and operation & maintenance, are resolved effectively. But the agricultural requirement is much more than potable water. Supply of treated groundwater to meet agricultural requirement by *ex-situ* arsenic removal technologies would not be a sustainable option or approach.

A variety of arsenic removal devices have been developed, based on different working principles, and have been extended to fields. Many of those could not produce satisfactory performance or failed due to lacks in O & M or due to sludge disposal problems. Among the various removal technologies, lime softening and iron co-precipitation have been reported to be the most effective removal technologies, and observed running satisfactorily, where operation and maintenance problems were taken care of by public-private partnership. Majority of the operation and maintenance is linked to tube wells and day-to-day care, which has nothing to do with the ARP or its chemical media. Without adequate in built maintenance arrangements apparently the performance of all the devices would suffer. Proper training and mobilization of the user community in the operation and maintenance aspect would be an essential task before any future installation of ARP programme can be envisaged. Thus, future emphasis should be oriented around in-situ remediation at the source-aquifer level and also chemical fixation of the contaminant at the source should be properly explored through proper calibrated and configured studies and experimentations.

