

# Removal of Dissolved Arsenic from Contaminated Groundwater and Its Consequent Safe Containment: Serving to Answer a Global Conundrum

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**Abstract-** Arsenic (At.no:33) occurs as a metalloid and is positioned in group no.VA. As useful the element might be, it serves for the presence of threats to human health and the environment as well. Although silvery white in colour, the presence of this element does not show any characteristic properties in its dissolved stage in case of water. Hence, it becomes all the more important in order to study its properties, accordingly work out an effective plan for the prevention of health disorders and also test for the presence of arsenic in groundwater or fresh water bodies like lakes and ponds in its nascent stages. Arsenic may potentially occur in both of its trivalent ( $As^{+3}$ ) or its pentavalent form ( $As^{+5}$ ), the former being relatively more difficult to remove. Once the consumed water having dissolved arsenic gets in contact with human skin or organs, it may cause blisters, skin deformations and even fatal diseases like cancer. Removal methods may include Chemical precipitation-coagulation/flocculation, Fixed bed adsorption, Ion exchange, Membrane filtration, Phytoremediation and Electro coagulation.

**Keywords:** Well-Head Units, sorbents, sorption, adsorption, adsorbents, sludge, community-heads, monodentate, bidentate.

## INTRODUCTION

Arsenic (at no. 33), is a chemical element, more specifically a metalloid, occurring in many minerals, especially in combination with sulphur but can also exist in its pure elemental crystal state and is proven to be quite toxic in its inorganic form. Arsenic, eventually, has been found to be naturally present at high levels in the groundwater of countries like India, Cambodia, Vietnam, Bangladesh, Pakistan and even parts of The United States. Of all the naturally occurring contaminants in groundwater, arsenic is by far the most toxic. The contaminated groundwater, when used for adverse purposes such as drinking, bathing, irrigation, etc. poses a great threat to human health depending upon the duration of exposure of health to these contaminants. Arsenic has been known for being one of the chief causes for diseases like cancer and also cognitive problems such skin lesions, cardiovascular diseases, diabetes and so on.

The greatest threat of arsenic exposure is posed by contaminated groundwater. Same hindrances caused by different types of sources include fish, shellfish, meat, poultry and dairy products. However, cases reported due to such products has relatively a very lower instance of causing arsenic related diseases in the recent times. Long-time effects of being exposed to this jeopardy results in visible changes in the skin pigmentation and soles of the feet (hyperkeratosis) which can evidently prove to be the precursor to fatal diseases like cancer.

Acute effects include acute arsenic poisoning thereby causing vomiting, diarrhoea, numbness and tingling in the extremities, muscle cramping and even death in extreme cases. Magnitude of the problem can easily be seen from the fact that The International Agency on Cancer (IARC) has classified arsenic and its consequent compounds as carcinogenic to humans. Current research and studies are still in progress eliminate the jeopardy or at least, moderate its effects. Despite such strong initiatives, an estimated 140 million people in about 70 countries have been found to still have been adversely affected and exposed to arsenic contaminated drinking water. WHO has set the provisional guideline value of  $10\mu\text{g/L}$  (4-5) which is consistent with the fact that about 220 million people have still been found to have the risk of being exposed to elevated arsenic concentrations in groundwater.

Many methods are available in order to provide relaxation from this problem. Further research continues to find a solution. Some of the methods include Coagulation and Flocculation, Adsorption mechanisms, Electrocoagulation, Membrane filtration, Ion Exchange resin, etc. This report further includes certain newly developed ideas from recent study and also some ideas which can be used for the enhancement and bettering the effects, thereby making it more efficient. One of the most important things to be kept in mind before devising any large-scale plan for arsenic removal from groundwater is the consideration of safe containment of the removed arsenic with no adverse ecological and environmental impacts whatsoever.

Adsorption techniques such as fixed adsorption or sorption mechanisms are widely used in parts of the Indian subcontinent. Currently, as many as 150,000 villagers are affected by these well headed units for a particular adsorption technique. What is more impressive is the presence of regeneration technique of the arsenic removal adsorbents by certain trained personnel, which also reduces the volume of the arsenic laden solids by as much as 2 orders of magnitude. Hence, the continued safe operation of these units indicates the success of the study to say the least. This report further focuses on the presence of both viable and non-

viable techniques along with the new implementable ideas in creating a safe environment, an arsenic free environment and transforming the most important resource for human lives, from, what perhaps can be called “Water of Death” to “Water of Life and Prosperity”.

### What Exactly Is Arsenic and Why is It Considered to be a Potential Threat to the Human Environment?

Arsenic is a metalloid having atomic number 33 occurs as a metalloid and is sometimes found in combination with either inorganic or organic substances to form many compounds of different type. As far as occurrence goes, it has been noticed that the presence of inorganic arsenic is found more often in soils, sediments and groundwater. These compounds may emerge from naturally occurring substances or artificial processes like mining, ore smelting, industrial usage of arsenic and so on. This inorganic form of arsenic was successful in finding its usage as pesticides and paint pigments and a lot of many other products which has now been restricted due to safety reasons.

*Structure and Occurrence:* Arsenic, being a metalloid, also has various allotropes. However, only the grey form having a metallic appearance is important to the industry. It exists in its grey, yellow and black allotropic form. It also has a characteristic atomic

weight of about 74.921595 and occupies the 4<sup>th</sup> period and 15<sup>th</sup> group in the periodic table.

Physical properties include:	
Phase at STP:	solid
Density (near r.t)	5.727 g/cm <sup>3</sup>
when liquid:	5.22 gm/cm <sup>3</sup>
Triple point:	1090 K, 3628kPa
Critical point:	1673K
Heat of fusion:	grey:24.44 kJ/mol
Molar heat capacity:	24.64J/(mol-K)

Atomic properties include:	
Oxidation states:	-3, -2, -1, 0, +1, +2, +3, +4, +5
Electronegativity:	Pauling scale: 2.18
Ionization Energies:	1 <sup>st</sup> : 947.0 kJ/mol
	2 <sup>nd</sup> : 1798kJ/mol
	3 <sup>rd</sup> : 2735 kJ/mol
Atomic radius:	empirical: 119 pm
Covalent Radius:	119 +_4 pm
Van der Waals radius:	185pm

Other properties include:	
Natural occurrence:	primordial
Crystal structure:	rhombohedral
Thermal conductivity:	50.2W/ (m.K)
Thermal expansion:	5.6μm/ (m.K)
Electrical resistivity:	333 nΩ.m (at 20C)
Magnetic ordering:	diamagnetic
Molar magnetic susceptibility:	-5.5*10 <sup>-6</sup> cm <sup>3</sup> /mol
Youngs modulus:	8Gpa
Bulk modulus:	22Gpa
Mohs hardness:	3.5
Brinell hardness:	1440 MPa
*CAS Number:	7440-38-2

The spectral diagram is given as:



\*A CAS Registry Number is a unique identification number assigned by the Chemical Abstracts Service, US to every chemical substance described in the open scientific literature, from 1957 to present, while some substances ranging back to as far as the early 1800s.



Figure 1: Nascent Arsenic.

In addition to these properties, arsenic finds its uses in alloys of lead and also acts as a common n-type dopant in semiconductor devices. However, the previous uses of arsenic as different types of herbicides and pesticides are finding their way difficult in the recent times due to the increased awareness spread about the toxicity of this element.

According to The United States' Environmental Protection Agency, almost all forms of arsenic have been classified as harmful to not only to human health and usage but also as an environmental and ecological intoxicant.

It must be also mentioned here that arsenic can exist in the following two forms: Trivalent form ( $As^{+3}$ ) and Pentavalent form ( $As^{+5}$ ). Both of them are considered harmful as both of these elements have almost the equal probability of being present in groundwater, the former being more difficult to remove due to its stable nature.

### Inorganic Arsenic vs Organic Arsenic: Are Both of Them Same?

Before going into the details regarding the differences in physical, chemical and structural properties between the organic and inorganic form arsenic, let us first understand that why is arsenic considered a pathogen, especially in its inorganic form.

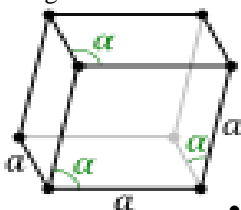


Figure 2: Rhombohedral Crystal Structure of Arsenic.

- Arsenic, being an exclusively mobile component, refers that it cannot be found at a particular site. This is actually a good thing; however, it also means that arsenic pollution can easily be spread to other parts of lakes, ponds and other freshwater bodies because of its naturally mobile nature and high usage of water as a daily component.
- Relatively high exposure to inorganic arsenic may lead to miscarriages and infertility in women and also can potentially damage DNA.
- Organic arsenic, though, is not as toxic and does not cause cancer, but still can affect human skin in miserable ways if it comes in human contact for a longer period.
- We have already discussed, that the trivalent form is more toxic than the pentavalent form. So, what might be the possible reason behind that? Current vitro studies have shown that the cellular uptake of the trivalent form is greater as compared to that of the pentavalent form. This is probably because of the

greater mobility of +3 ions.

Now, lets us see the key differences in the physical properties of organic and inorganic arsenic ions:

<u>INORGANIC ARSENIC:</u>	<u>ORGANIC ARSENIC:</u>
Occurs mainly in nature in inorganic substances.	Occurrence is more in plants, animals, sea foods, etc.
Causes adverse effects like cancer, skin deformations. Bigger doses can be fatal.	Not known to produce such adverse effects due to its less toxicity.
Examples include arsenic acid, arsenic trioxide.	Arsanilic acid, cacodylic acid, are the examples.
High toxicity: For arsenic trioxide, the LD50 in rats is 20mg/kg	Less toxicity: In mice, no toxicity is observed even after a dose of 10mg/kg of arsenobetaine and is excreted in humans within days.
Is mainly found in terrestrial foods, water, etc. 25% - 100% of the total terrestrial foods comprises of inorganic arsenic.	Mainly found in sea foods like shellfish, crustaceans, seaweed, etc.
Refers to the pure metallic form of the element.	Refers to the arsenic having covalent bonds with carbon atoms, thereby becoming an organic compound.

### Uses of Arsenic and Its Compounds

Arsenic, howsoever knave, as it is being portrayed, does not necessarily mean that is of no absolute use or of benefits to humanity. Its presence on the earth itself, is the biggest evidence of its utility value and benefits, only we know the methods of using it, or, more specifically, knowing three parameters: "*HOW, WHEN and WHERE?*"

Therefore, let us take a quick look at the advantages that Arsenic provides us with:

It is important to know that, from a biological and toxicological perspective, Arsenic and its corresponding compounds can widely distribute into the following three classes:

- Inorganic arsenic compounds
- Organic arsenic compounds
- arsine gas.

Examples of inorganic arsenic compounds, as mentioned previously, includes: arsenic trioxide, sodium arsenate and arsenic trichloride amongst trivalent forms and arsenic pentoxide, arsenic acid and other arsenates (e.g., calcium arsenate) amongst pentavalent forms of the element.

Common organic compounds, again, as discussed earlier, include arsanilic acid, methylarsonic acid, dimethylarsonic acid (cacodylic acid) and arsenobetaine (WHO, 2000).

The following uses of the abovementioned agents can be listed:

- Arsenic has been traditionally in commercial use since past few centuries and is still in use for purposes such as pharmaceuticals, wood preservatives, agricultural chemicals, applications in mining, glass-making, metallurgy and also in semiconductor industries.
- Until 1970, inorganic arsenic used to find its uses in the treatment of diseases like leukaemia, psoriasis, chronic bronchial asthma whereas organic arsenic was used for treatment of spirochaetal and protozoal diseases (ATSDR, 2007).
- Inorganic arsenic acts as an active component of chromated copper arsenate, an antifungal wood preservative. However, it is no longer in use, courtesy of a voluntary ban on chromated copper by the Canadian and the USA government by the end of 2003.
- Arsenic and its compounds are also used in making pigments, sheep-dips, leather preservatives and other poisonous baits. They are also used in different catalytic purposes, in pyrotechnics, antifouling agents in paints, pharmaceutical substances, ceramics, alloys, etc.
- As far as Industrial application is considered, arsenic and a variety of its compounds are used in the manufacture of alloys, particularly with lead, as in the case of lead acid batteries. Gallium arsenide and arsine are widely used in semiconductor and electronics industries. Because of its high electron mobility, light-emitting, photovoltaic and electromagnetic properties, gallium arsenide finds its usage in semiconductor devices, millimetre-wave devices, optoelectronic devices such as fibre optic sources and detectors (IARC,2006) whereas arsine is used as a doping agent to manufacture crystals for computer chips and fibre optics.
- Arsenic and its compounds were earlier in use for different agricultural uses before being banned in 1993 in the USA. It had a range of applications, including applications like pesticides, herbicides, insecticides, defoliants and also as soil sterilant. The organic forms of arsenic, however, were constituents of some agricultural pesticides in the USA till 2009, when the US Environmental Protection Agency issued an order ruling out the use of organic arsenic pesticides by 2013(EPA,2009). An exception to the order was monosodium methane arsonate (MSMA), a broadleaf weed herbicide which is applied on cotton. The aforementioned US EPA 2009 also prohibited the use of organic arsenic products using disodium methane arsonate (DSMA, also known as cacodylic acid). Further applications include organic arsenicals such as roxarsone, arsanilic acid and its derivatives, widely used as feed additives for poultry and also to increase the rate of weight gain pigmentation, disease treatment and prevention (EPA, 2000, 2006; FDA, 2008a, b).

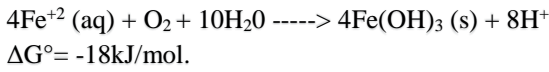
### **Removal Techniques for Dissolved Arsenic in Groundwater and Corresponding Techniques for Its Safe Containment**

We have already discussed in great detail about the threats of dissolved oxygen. However, being already aware of the fact of the presence of the dissolved arsenic, the immediate question which may arise is: *How does arsenic get collected beneath and why does this level vary from one region to another?* Well, it is due to the fact of natural geo chemical weathering of subsurface soil which has caused a gigantic and unimaginable level of dissolved arsenic in regions of the Indian subcontinent. Despite the presence of heavy rainfall, the surface water proves to be quite unfit for drinking purposes for the villagers due to poor sanitation practises in an area which is under the jeopardy of different water-borne diseases. Thousands of well-head units were attached to manual hand pumps were sunk during the last four decades, which are continuing to provide safe drinking water to the residents of these villages. This suddenly appeared and came as a mitigation to the solution of purifying the arsenic laden groundwater. Now, in certain geographical regions, arsenic levels in groundwater have been seen to exceed as much as 100µg/L and over 100 million people in Bangladesh and in eastern part of India have been adversely affected by a widespread of arsenic poisoning caused by contaminated groundwater being used for drinking purposes. Around 2008, this problem has also been noticed in regions of Vietnam and Cambodia.

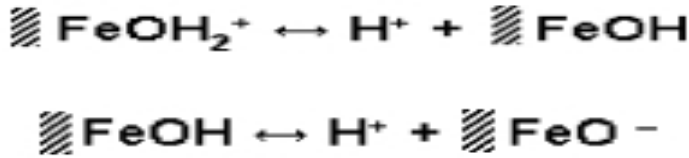
During the last 24-25 years, Bengal Engineering and Science University (BESU) in Howrah, India, in association with Lehigh University in Pennsylvania have joined hands and installed around 175 community based well-head arsenic removal units (ARUs) in villages of Bangladesh and West Bengal, India. Now, during the first two years of this project, after being inaugurated in 1997, both, point of use (PoU) household units and the above-mentioned well-head arsenic removal (ARUs) were in use. However, the PoUs demanded personal and time-taking attention from each family or household in the village as it served only one family at a time. Further, the disposal of the arsenic laden sludge from each family seemed a very complex job and hence the plan of PoUs had to be disposed of. Subsequently, only the community-based units (ARUs) were kept in use which has the potential to serve the whole village and still remains in use.

**Role of Dissolved Iron:** Although a fixed bed sorption mechanism is effective for removal of trace contaminants of arsenic due to the fact that it forgives towards fluctuations in the influent quality and can also be started or stopped momentarily without any such complex procedures involved in its operation, the role of dissolved iron (Fe(II)) in the groundwater cannot be ignored and should be taken into consideration. Keeping in mind a sorption process is nothing but a combination of adsorption and absorption

mechanisms. The dissolved iron concentration was observed around 2.0mg/L or greater in certain cases. Observations were almost similar in cases of research in parts of Vietnam, Cambodia and Mexico. This Fe(II) can be, however, oxidised to insoluble Fe(III) hydroxide at near neutral pH as it is a thermodynamically stable process due to its high negative free energy at the reaction site at the standard state.



Now, the freshly prepared hydrated Fe(III) oxide (HFO) particle surfaces are considered to be a diprotic acid with two dissociation constants:



Here, the shaded lines represent the solid phase. Now, at circumneutral pH,  $\text{FeOH}_2^+$  and  $\text{FeOH}$  serve as the predominant HFO species and have the ability of binding both the trivalent and pentavalent arsenates through the formation of bidentate and/or monodentate inner-sphere complexes where Fe(III), a transition metal serves as an electron pair acceptor or more specifically, a Lewis Acid.

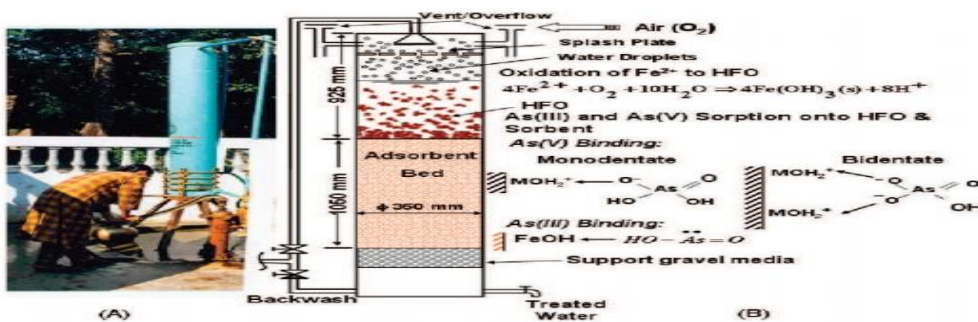
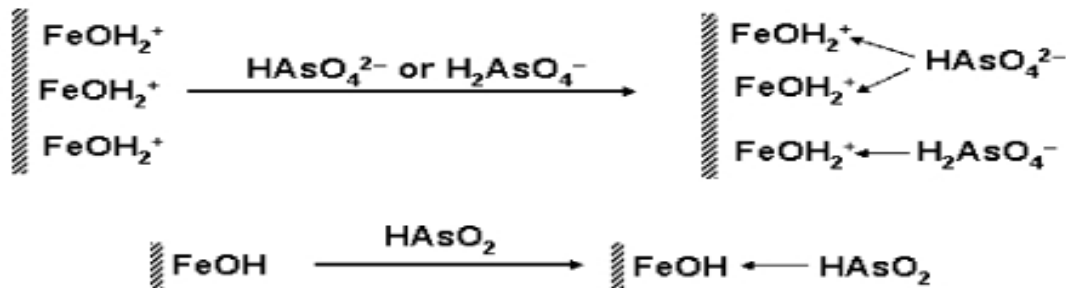


Figure 3: (A) Photograph showing the easy-to-operate community based arsenic removal unit and (B) reactions taking place at various parts of the unit

The other commonly existing anions which are at relatively high-levels include chloride, sulphate and bicarbonate, which are, however weak ligands due to which they exhibit poor sorption affinity to the above-mentioned HFO particles. However, dissolved phosphate and silica do compete for the sorption sites along with arsenic. Although phosphate concentrations in the contaminated groundwater rarely exceeds 1.2mg/L, silica concentration may vary between 20 and 35 mg/L as  $\text{SiO}_2$ . The top part of the gravity-flow column can be seen with a large void space and open vent to the atmosphere. This is because the handpumps are manually operated and the groundwater entering the column forms small water droplets having larger surface area per unit volume and is aided by something known as a splash plate. These droplets first get oxygenated thereby bringing reaction I near completion. The top most chamber consists of regenerative sorbent material i.e., activated alumina and/or arsenic-selective hybrid anion exchanger (HAIX). The figure represents the photograph(original) well-head arsenic removal unit which is in use and demonstrates how simple it is to actually operate these units as a village woman can unilaterally operate the handpumps to collect the arsenic-free safe groundwater. The adjacent(1B) figure further depicts the salient process steps at different section of the well-head column.

**Containment of the subsequent Arsenic-laden Residuals/Wastes: Role of Redox Condition:** Now, as mentioned earlier, since the arsenic is being removed from the groundwater to a safe level, something must be done for the safe containment of the removed arsenic gangue. These arsenic wastes can consequently evolve from the following two methods/locations:

- 1) Firstly, the pressure drops or head-loss in the well-head column is gradually increases due to the precipitation of ferric hydroxide or the HFO particulates, which thereby, reduce the flowrate. It, therefore, becomes very important in order to back wash the full column and the subsequent arsenic loaded HFO particulates get collected on top of a coarse sand filter located in the same premise.
- 2) Secondly, the adsorbents that are regenerated periodically in the central regeneration facility and following treatment in the spent regenerating agents further produce the arsenic laden wastes.

Now, these two wastes are of the similar type, both rich in iron and arsenic, as discussed earlier. The local laws for the type of methodology to be used in these remote villages for the removal of these arsenic laden sludge is either non-existent or not enforceable. Hence, the containment of these removed arsenic laden wastes become as important as the removal of these contaminants to sustain a safe ecological environment. These wastes are routinely disposed of safely in the developed countries. However, recent investigations have revealed the leaching of arsenic is a possible hazard in these land-fills or such other hazardous waste site environments. The arsenic leachability is controlled by both the pH and redox conditions of that particular site. The below given figure shows the composite predominance or the pe-pH diagram for various arsenic and iron species using equilibrium relationships is shown.

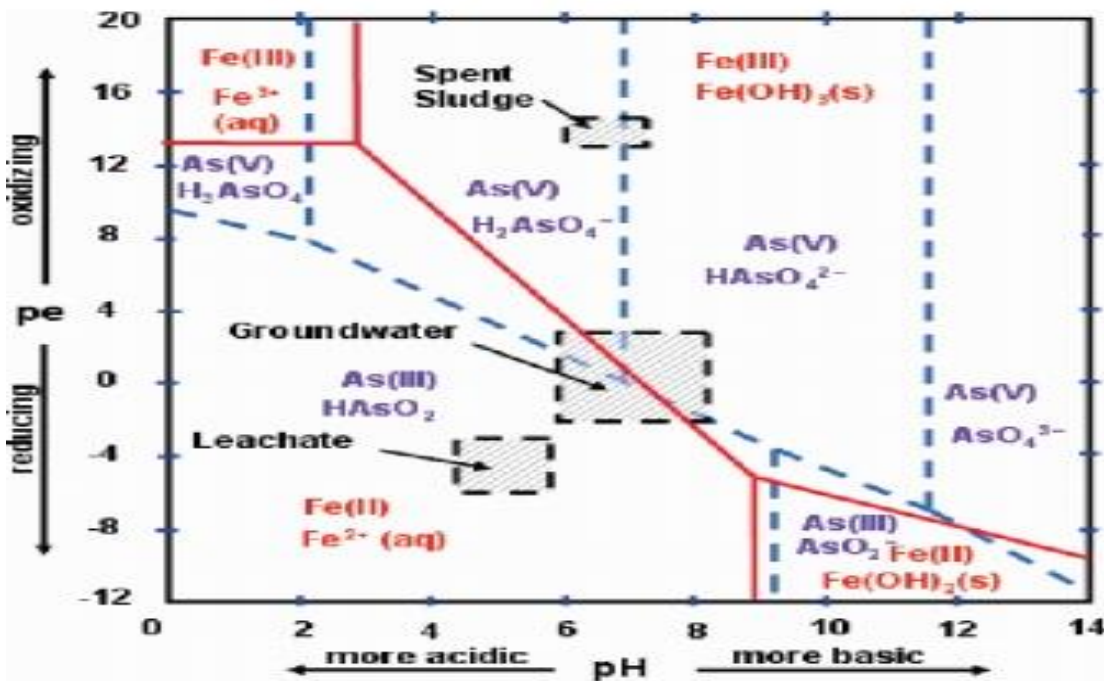


Figure4: Figure showing superimposed predominance of pe-pH diagram of major As (III)/As (V) and Fe (II)/Fe (III) species.

The figure shows and highlights (the shaded rectangles) the three separate predominance zones of survey/interest: neutralized HFO laden sludge where Fe(III) is also insoluble in contrast to the sole species of Fe (II) and As(III) which are practically the sole species in reducing landfill environment. However, the high solubility of Fe(II) and low sorption affinity of As(III) would always lead to the iron-laden sludge to be more susceptible to rapid leaching under an non-aerated environment of the disposal site, if it is a landfill or a ground of such type. Leaching is minimized under an aerated(oxidising) environment.

**Objectives of the Study:** Different removal for these kind of arsenic removal methods are available from the contaminated groundwater as discussed earlier which include processes like Adsorption, Electrocoagulation, Ion-Exchange, Coagulation and Flocculation. The objective of this paper is the primary objective of giving and increasing awareness about the increasing rate of arsenic poisoning in remote villages of different parts of India, Cambodia, Bangladesh, Vietnam, Mexico, USA, etc. Firstly, the removal of the unimaginable and unacceptable levels pf arsenic from the groundwater in an ecological, simple and cheap way has been discussed in this paper along with stats and also new alternatives that can and should be applied in order to better the conditions people living in the remote villages. Secondly, one of the most important parts of these kinds of solutions which are easily missed out from normal human observation, is the safe containment of the arsenic and iron laden sludge which, if not disposed of safely, can have the same adverse effects that arsenic laden groundwater affects the people in different parts of the world. Thirdly, the appropriate control of redox and the consequent pH conditions can result to being an effective solution to this

problem of arsenic containment. One of the benefits of the system includes the presence of regenerative adsorbents, which has the capability of reducing the arsenic laden waste amount by some proportion.

### Materials and Methods

The main adsorbent material uses, as shown earlier, was activated alumina (AA) having nearly spherical physical configuration. This item was produced from an indigenous chemical company (Oxide India Ltd., Durgapur, West Bengal) for the already made units. This was done consequently after carrying out various laboratory tests to confirm its amenability for regeneration and reuse. In addition to these, hybrid anion exchanger (HAIX) or ArsenX having specific affinity towards dissolved As(V) and As(III) was used in various places and locations where the community units were used and planted. This increases the regenerative abilities of the adsorbent. Each such unit consists of about 100L of AA or HAIX while the average sizes of the adsorbent particles vary between 600 and 900 $\mu$ m.

In order to contain the arsenic-laden wastes or solids from the treated spent regenerant to avoid anoxic conditions, aerated coarse-sand filters have been used in the central regeneration facility as shown in the below figure. Primary materials needed for the construction of these units include indigenously available bricks, cement, PVC pipes, gravels and coarse sands.

The existing sand filters can safely store the arsenic laden wastes for as many as 20 years. Each of these units are also provided with a similar aerated but smaller coarse-sand filter to collect and contain the HFO particulates. However, these units need backwashing and rinsing on almost a regular basis as seen earlier and it requires almost 2-3 volumes of water on an average.

**TABLE 1. Steps of Regeneration and Spent Regenerant Treatment**

chemical:	volume(L)	time of contact/agitation (min )	approximate pH
sodium hydroxide 2%	140	60	12-13
rinse	100	15	12
acid rinse	140	15	5-6
treated spent regenerant	$\approx$ 520	$\approx$ 60	6-7 <sup>a</sup>

<sup>a</sup> pH adjusted and FeCl<sub>3</sub> added to bring to bring down total arsenic concentration in the supernatant to less than 200 $\mu$ g/L.

A cylindrical stainless steel (SS-304) tank containing two compartments, namely Fe(II) oxidation and adsorption has been used on top of the existing well-head hand pump. The gravity-flow unit has been designed for almost a flowrate of about 12-15L per minute after consequent rinsing and backwash. The process of Regeneration is carried out in several steps in the central regeneration unit in a stainless-steel batch reactor. The above given table provides with the salient features and steps of the units' regenerative abilities and processes.

Arsenic was analysed using an atomic adsorption spectrometer having a graphite furnace accessory (Perkin-Elmer, SIMAA 6000). For As(III) analysis, a technique developed by Clifford et al. (1983) was used.

### Results

**Performance of the Well-Head Units:** The attached figure shows the dissolved the dissolved arsenic concentrations in both contaminated groundwater (i.e., influent) and the treated water for a well-head unit Sangrampur village, West Bengal near the Bangladesh border for two consecutive runs. Although the arsenic concentration in the influent water was found to be well over 200 $\mu$ g/L, the concentration of the same was found to be around 50 $\mu$ g/L after its consequent treatment through the unit, which is the maximum permitted arsenic concentration level in the groundwater, in India. The activated alumina used was regenerated in April,2000 and was reused.

However, during the second run of the procedure, the arsenic concentration of the treated water was seen to be a little more than that of the first run but the overall length remained quite comparable. Arsenic breakthrough from the column is due to the intraparticle diffusion-controlled kinetics.

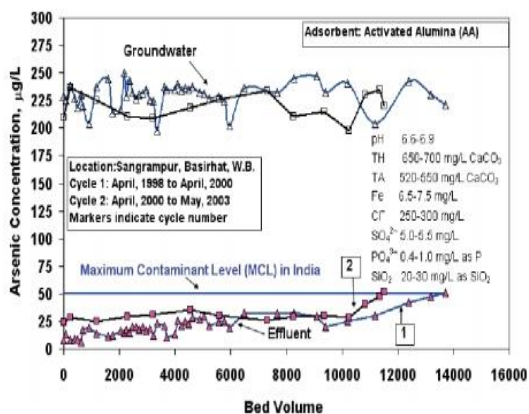


Figure 5: Arsenic concentration histories involving influent and treated water at Sangrampur village using activated alumina over two consecutive cycles as depicted (1 bed volume= 100L; TH= total hardness; TA= total alkalinity).

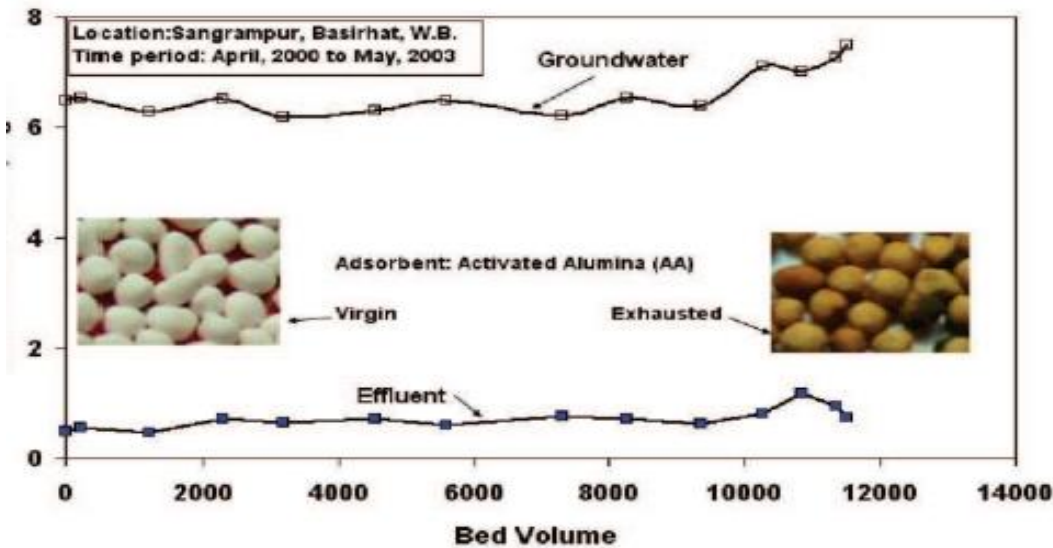


Figure 6: Depicting Iron breakthrough history of removal unit at Sangrampur village in West Bengal (1 bed volume= 100L). Virgin and used activated alumina beads (~18\* magnification) are shown above.

The above figure shows that the iron concentration, too, dropped from greater than 6µg/L in the influent to about less than 0.5µg/L when the water is treated through the units during the entire column run. From the inset of the figure, the near-spherical configurations and the presence of brown iron oxide precipitates on the surface of the used particles can be noted.

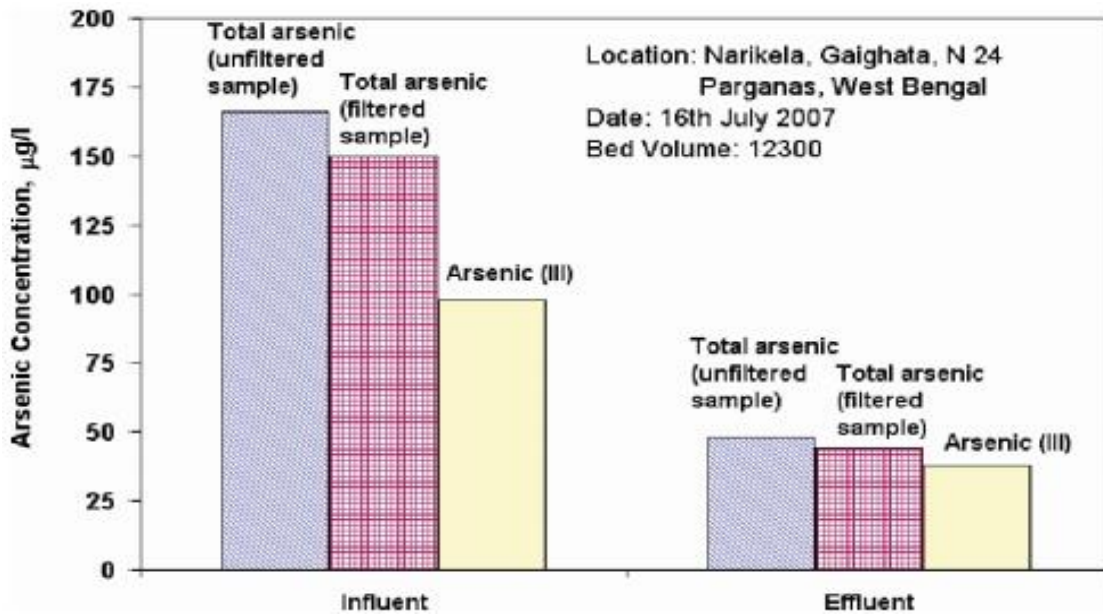


Figure 7: Distribution of arsenic species in the influent and effluent in the unit of Narikela village.



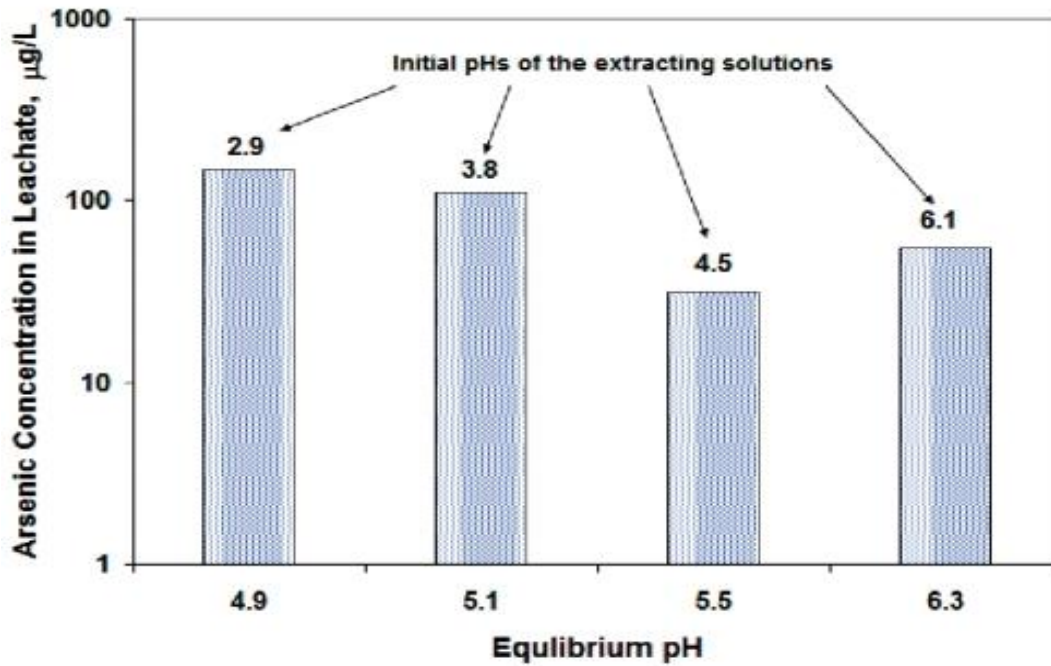


Figure 8: Arsenic concentrations in the leachate during an extended-TCLP test for a spent regenerant sludge collected from the coarse sand filter.

The above figure shows three different arsenic concentrations in the groundwater (unfiltered, filtered, and As(III) in the influent and also in the treated water samples for a well-head unit based in Narikela Village through the passage of as many as 12,300 bed volumes of contaminated groundwater. The filtered samples were obtained after vacuum filtration was done through a 0.45µm membrane. It is to be noted that As(III) has been significantly removed from 90 to 35mg/L despite the fact that activated alumina does not possess the removal ability of As(III) to a high amount. The difference in the filtered and unfiltered water turned out to be very marginal in not only here but also parts where other well-head units were used, probably insisting that arsenic in the groundwater is only present in the dissolved state.

**Regeneration and consequent fate of the removed arsenic:** The regeneration is carried on by a steel batch reactor for regeneration in the central facility. The regeneration steps have generalised in table 1. The dissolved arsenic in the used arsenic varies between 30 to 100mg/L and is solely present in the form of arsenate or As(V). However, after adding waste regenerants and the consequent addition of Fe (III) chloride and also the constant effort for maintaining the pH between 6.5-7.0, the residual arsenic concentration has been observed to reduce considerable to about below 200µg/L. Now, the entire amount of arsenic has been converted into solid phase along with ferric hydroxide as precipitate.

The arsenic-laden solids in the central regeneration facility are kept on top of the well-aerated sand filter as shown in the earlier representation. To validate the low arsenic leachability, an extended TCLP test has been performed for a small sludge sample collected from the top of the well-aerated coarse sand filter. While the sludge had approximately 32 mg As/g of dry solids the arsenic concentration in the leachate was constantly found to be less than 200µg/L in the approximate pH range of about 4.3-6.3.

## Discussion

**Sustainability Issues: Developed vis-à-vis Developing Nations.** The consequences of two consecutive cycles performed with these ARU units in a particular village in which the experiment is formed reveals the effectiveness of the system and hence its' success is clearly visible. According to our survey, around 150,000 villagers are in current methodology of consuming safe and almost arsenic free water from about 175 of these well-head arsenic-based units. The more notable part of this venture is the fact that which how much ease the villagers are handling the well-head-based units by themselves. Three of the most salient features include: Firstly, the adsorbent media chosen is quite robust and regenerated frequently. Secondly, a central regeneration facility is equipped adequately to collect and event regenerate the exhausted media with quite effective methodology and with ease. Finally, the removed arsenic is also stored as defenestrated solids on the aerated sand filters mentioned above, with minimum potentiality for arsenic leaching. The figure below somewhat depicts the global scheme for overall process of arsenic removal present along with its' consequent management.

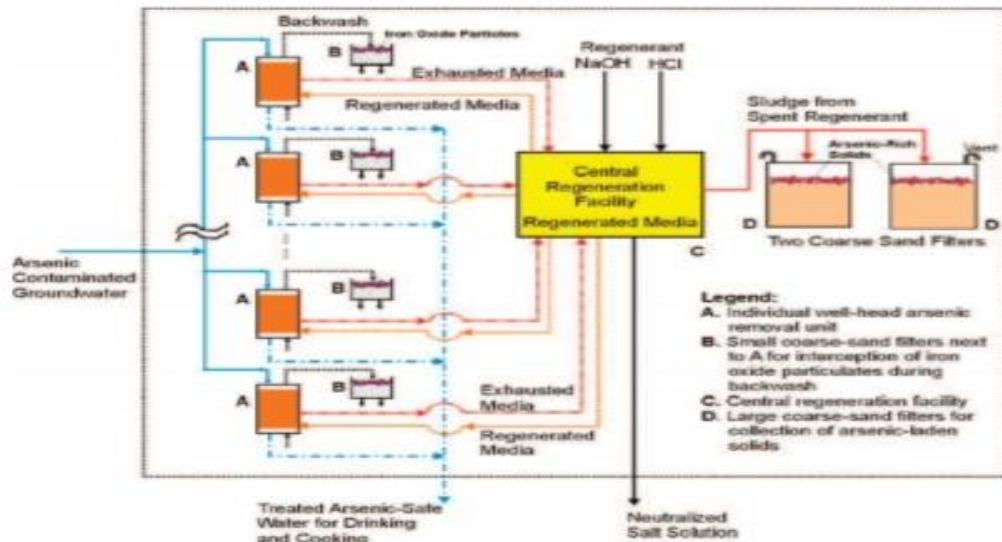
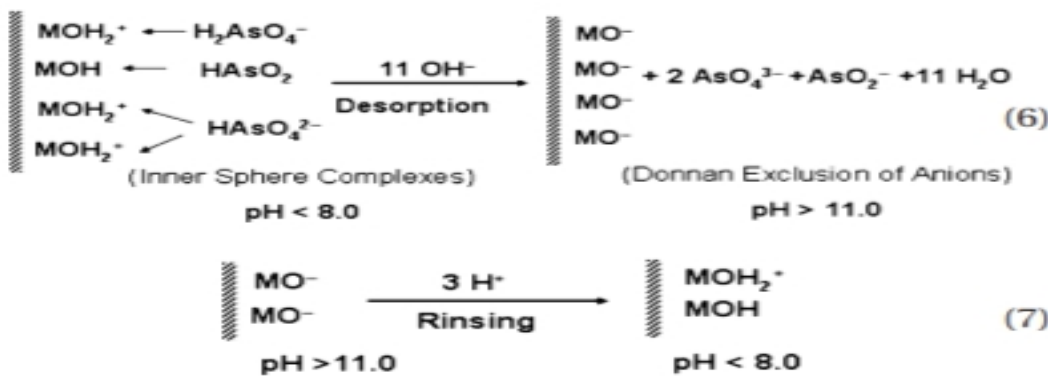


Figure 9:Figure depicting global arsenic treatment protocol with the presence of a central regeneration facility with safe containment.

The primary reactions during regeneration of the already exhausted adsorbents with 2% NaOH and rinsing along with dilute acid are given below where *M* represent Al(III) or Fe(III) in AA or HAIX:

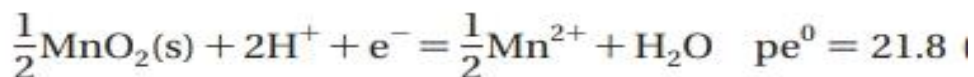
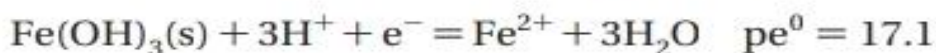
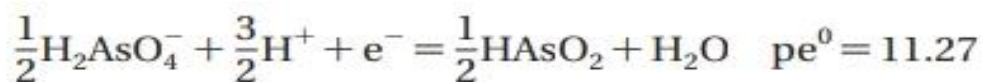


The demonstrated surface hydroxyl groups get deprotonated and thus get negatively charged, thereby causing desorption of the negatively charged arsenic species with high efficiency. However, this procedure takes place only under high alkaline pH. The rinsing procedure later followed with the corresponding dilute acids allows reuse of adsorbent media and also helps in reducing the volume of arsenic-laden sludge by over a particular order of magnitude. However, it also must be noted that mostly non-regenerable adsorbent media is used in most parts of the western world. After a cycle of replication, such high-volume adsorbent media needs to be duly disposed off in time in hazardous waste sites. Such types of disposable sites are lying unused in different parts of the world, thereby leading to increased environmental pollution and production of hazardous sites.

It should also be noticed that the chronic toxicity caused by the presence of lower concentrations of arsenic (<1 mg/L) in the consumed or even ingested water does not have any considerable effects depending upon the presence of either As(III) or As(V) in it. Such lower concentrations lead to the conversion of the pentavalent compound into its consequent trivalent form which is probably one of the most important reasons why various health organisations such as the World Health Organisation (WHO), the United States Environmental Protection Agency (USEPA), and European Union (EU), always specify only total arsenic for the maximation contamination level (MCL) in drinking water.

Subsequently during the survey, it was also observed that the proposed ARUs remove both the arsenites and arsenates with equal efficiency.

Lastly, the corresponding stability of both As(III) and As(V) redox pair and the consequent hierarchy it is associated with in relation to two other redox pairs of the environmental significance, namely Mn(IV) or Mn(III) along with Fe(III) or Fe(II) are represented in the already attached figure given above and the equilibrium relationships include:



It should be noted that even at slight anoxic condition ( $\text{pe} \approx 0$ ),  $\text{MnO}_2(\text{s})$  and  $\text{Fe}(\text{OH})_3(\text{s})$  serve to be thermodynamically unstable and hence  $\text{Mn}^{2+}(\text{aq})$  and  $\text{Fe}^{2+}(\text{aq})$  states predominate. Therefore, an adsorbent which is doped with  $\text{MnO}_2(\text{aq})$  and Fe (III) oxide-based sorbent will eventually leach away under the reducing environment of a landfill. However, activated alumina is thermodynamically stable under anoxic conditions but soon after As(V) gets reduced to As(II), it results in being poorly adsorbable onto AA (27). A reducing environment therefore serves as non-conductive to disposal of commercially available sludge laden adsorbents after use. Hence, the project demonstrates that the proposed method is quite effective and also serves to be scientifically sound as a process.

### Acknowledgments

Thankful wishes should be extended to Dr Pratap Mukherjee, from the Department of Chemistry in the Institute of Engineering and Management. Also, sincere gratitude to Mr. Jaydip Sengupta and Mrs. Sumana Sengupta, coordinator for the conduction of laboratory experiments. Sincere gratitude to Prof Arup K Sengupta, Department of Civil and Environmental Engineering, Lehigh University, who provided to be the central source of all our information and guidance. Also, special gratitude should be extended to prof. Sudipta Sarkar, prof Lee M. Blaney, prof. Anirban Gupta, prof. Debabrata Ghosh, for providing us with all related and required information.

### Supporting Information available

The abandoned arsenic removal units having the non-regenerable adsorbent media are also shown in one of the attached photographs above whereas another table provides corresponding arsenite and arsenate removal data for some units present in certain villages. The material can be accessed free of cost via the internet at <http://pubs.acs.org>.

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