

## **In Situ Arsenic Removal in Groundwater for Rural Communities by Iron Sorption and Arsenic Immobilization**

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**Abstract.** Arsenic in drinking water is a worldwide problem that is not limited to just developing countries. Rural communities, including U.S., where sophisticated treatment systems are not available, residents often consume water with arsenic concentrations higher than 10 ppb (0.01 mg/l), and most of the water sources with arsenic problem are groundwater. In this study, we propose an innovative “treat-and-pump” method (in situ iron precipitation and arsenic immobilization) that is a simple, inexpensive, and readily available technology that may be used to mitigate arsenic in groundwater. The process includes three major steps: (1) Hydrous ferric oxide (HFO) is precipitated in groundwater aquifer by injection of ferric ion and NaOH into a well; (2) Arsenic in groundwater is adsorbed onto HFO and thus be immobilized in situ. The sorption will significantly reduce dissolved arsenic concentration in groundwater and “clean” water will be produced thereafter; (3) Arsenic is remobilized when HFO reaches maximum sorption capacity by either aquifer acidification or alkalization. When arsenic is released back into the water phase again, the arsenic rich groundwater is then pumped out and arsenic is therefore removed from the groundwater aquifer permanently. The arsenic laden water can be pumped into an evaporation pond to precipitate out the arsenic that can be collected later for disposal or as an industrial feedstock.

**Keywords:** hydrous ferric oxide, HFO, arsenic, removal, sorption, desorption, immobilization

### **1. Introduction**

Arsenic occurs naturally in water and has been recognized as a worldwide problem [1], especially in groundwater. High arsenic concentrations (10-50 ppb, parts per billion) in groundwater have been detected in many regions of the United States, and the concentrations can reach higher than 50 ppb in Texas and many western states [2]. Worldwide, many countries are affected by having drinking water from subsurface aquifers with concentrations higher than 10 ppb, they include Argentina, Australia, Bangladesh, Chile, China, Hungary, India, Mexico, Peru, Thailand, and the U.S., among which Bangladesh, China, and India (West Bengal) are the countries that have As concentrations that can induce adverse health effects [3].

USEPA had recently reduced the drinking water maximum contaminant level (MCL) of As to 10 ppb, water utilities in the country had to comply with this standard by January, 2006 [4]. WHO (World Health Organization) has established also 10 ppb as a provisional guideline value for As, it states that the guideline value for As in drinking water should be less than 10 ppb based on health criteria; but the guideline value was restricted by measurement limitations, thus the realistic limit is set to be 10 ppb.

Although some studies have suggested that As at very low doses can send some forms of cancer into remission and help thin blood, and is perceived as an essential element for human, animals, and plants. But for centuries, As is better known to be a poison: Numerous toxicological and epidemiological studies have shown that ingestion of inorganic arsenic can result in cancer and/or non-cancer health concerns [5]. Arsenic also interferes with a number of essential physiological activities, including reactions of enzymes and

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essential cations, and transcriptional events in cells. Natural Resources Defense Council (NRDC) estimated that lifetime risks of dying of cancer from arsenic in tap water (assuming 2 liters/day consumed) based on the 1999 risk estimates from National Academy of Sciences that the total cancer risk is 1 in 5,000, 1 in 500, and 1 in 100 for arsenic concentrations of 1, 10 and 50 ppb, respectively [6].

Bangladesh perhaps is a country that has the highest fraction of population affected by As contamination in drinking: It was estimated that the number of people exposed to arsenic concentrations above 50 ppb is 28-35 millions and the people exposed to more than 10 ppb is 46-57 millions [7]. Unfortunately, most of these people who are at risk are also the people who can ill afford using high tech treatments for their drinking water.

It is the motivation of this study to develop a technology that is simple but effective to remove As from groundwater in rural and developing areas that people can utilize this technology to obtain safe drinking water without incurring high operating expenses.

## 2. Background

### 2.1. Sources

Natural arsenic is introduced into the groundwater by water rock interactions. Arsenic content within minerals and rocks, either as a primary structural component or an impurity, is released into groundwater when those minerals and rocks are dissolved. Arsenic can also be adsorbed to and co-precipitated with metal hydroxides (such as iron, aluminum, manganese oxides) and clay mineral, or be associated with sulfide minerals and organic carbon. Hence, these oxides, clays, and sulfur minerals are both sinks and sources (secondary) for arsenic in groundwater. Welch et al. [8] analyzed natural arsenic sources for groundwater supplies in the United States and indicated that Fe oxide, sulfide minerals, black shale, and geothermal water are the major sources for arsenic, with iron oxides as the most prevalent sources.

### 2.2. Arsenic Speciation and Transport in Groundwater

Arsenic speciation is affected by both redox potential and pH. Generally speaking, groundwater environment is usually suboxic to anoxic with typical Eh (redox potential) ranges vary from -200 to 100 millivolts, and typical pH ranges from 7 to 9 in groundwater [9]. In the general ranges of Eh and pH conditions of groundwater environment, both arsenite (trivalent arsenic or As(III)) and arsenate (pentavalent arsenic or As(V)) exist [10] (Fig. 1), with  $\text{HAsO}_4^{2-}$  predominant at oxidizing conditions and  $\text{H}_3\text{AsO}_3$  predominant at reducing conditions.

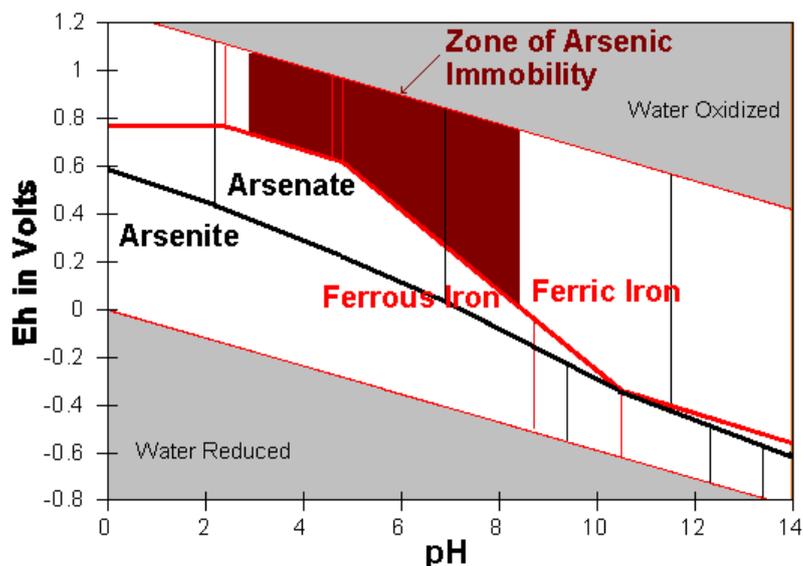


Fig. 1: Arsenic immobilization zone in groundwater as controlled by the effect of Eh/pH conditions (Modified from Vance [21]) (Red thick line represents Fe(III)-Fe(II) equilibrium line and the thick black line represents equilibrium line between arsenate and arsenite)

Under oxidizing conditions,  $\text{H}_2\text{AsO}_4^-$  is dominant at low pH (less than about pH 6.9); while at higher pH,  $\text{HAsO}_4^{2-}$  becomes dominant. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species,  $\text{H}_3\text{AsO}_3$ , dominates.

Hinkle et al. [11] found that arsenite species was always predominant in well water and accounted for 68 to 99% of total arsenic. Changes in pH, however, may reverse the arsenate/arsenite ratio. Mok et al. [12] studied arsenic speciation and ratio in acidic groundwater (pH between 2.7 and 6.4) in a lead-zinc mine; they found that arsenite dominated in groundwater when pH was less than 3, while arsenate dominated when pH was higher than 3.

Arsenic mobility in aquifers is largely controlled by two types of reactions [11], [13]: precipitation and dissolution reaction, and adsorption and desorption reaction. For example, sulfide minerals generally are unstable under oxidizing conditions and may release arsenic when they are oxidized and dissolved, but may co-precipitate with arsenic under reducing conditions and remove arsenic from the water phase. Also, arsenic adsorbs strongly to iron hydroxide surfaces in slightly acidic and near neutral pH water; when the hydroxide dissolves under reducing conditions, adsorbed arsenic will be released into solution phase. These reactions are dependent of pH, redox potential, and competing anions in groundwater [11].

### 2.3. Arsenic Adsorption onto and Desorption from Hydrus Ferric Oxide (HFO)

Arsenic adsorbs strongly onto hydrous ferric oxides (HFO). HFO (also called ferric hydroxide, ferrihydrite, or iron oxyhydroxide) is formed by rapid hydrolysis of ferric iron in solutions at 20 to 30 °C. It is amorphous when it precipitates, and slowly transforms to a crystalline iron compound, usually goethite ( $\text{FeOOH}$ ), and the rate of transformation depends on pH, temperature, and ferric iron concentration. It was reported that about 2 to 10% of HFO is transformed to goethite after 12 to 15 days of aging [14].

Although the HFO adsorption capacity of As is high from most reports, there are discrepancies: For example, Raven et al. [15] found that the adsorption capacity of HFO for arsenate and arsenite to be 0.60 and 0.25 mol As/mol Fe at pH 4.6, and 0.58 and 0.16 at pH 9.2 respectively; Dzombak et al. [13] reported that the adsorption capacity of HFO for arsenite and arsenate to be 0.16 and 0.05 – 0.18 mol As/mol Fe at pH 7.0 respectively, and for arsenate to be 0.1 – 0.13 mol As/mol Fe at pH 4.0. The As adsorption rate on HFO is reported to be fast, from 2 to a few hours, to reach equilibrium [15], [16].

Generally, the optimal adsorption of As on HFO occurs at pH 7 to 9 for arsenite and 4 to 8 for arsenate at concentrations normally found in natural waters. Adsorption of arsenite and arsenate on HFO as a function of pH was summarized by Drever [10] and is modified as shown in Fig. 2.

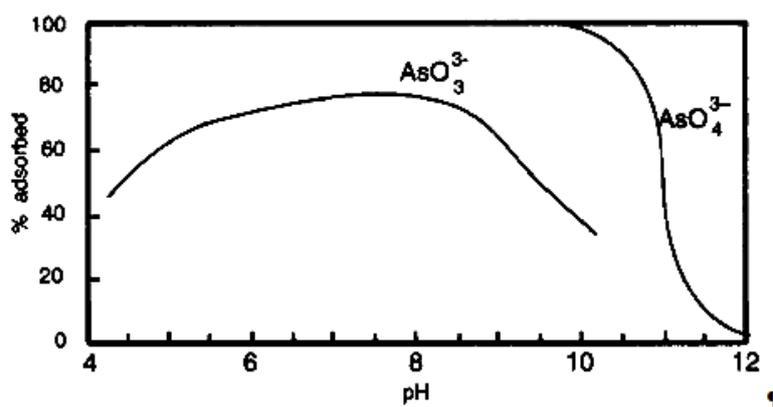


Fig. 2: Adsorption of arsenate and arsenite on hydrous ferric oxide (HFO) as a function of pH (modified from Drever and [14]).

Direct experimental research on arsenic desorption associated with HFO chemical dissolution has not yet been found, but research on arsenic desorption and remobilization due to microbial ferric hydroxide reduction has been reported [16]-[20]. However, Fig. 2 indicates that both arsenite and arsenate are desorbed by HFO and dissolved into the aqueous solution at pH 12 or higher.

Vance [21], [22] explored the chemical characteristics of arsenic and iron in groundwater and superimposed the Eh/pH diagrams for the arsenic and iron phase diagrams. Fig. 1 is a modified summary of the results of Vance [21] that shows the conditions under which arsenic can be immobilized due to adsorption onto HFO in a groundwater system, and how arsenic adsorbed onto HFO can be released if pH and/or Eh conditions change. Therefore, by manipulating pH and/or Eh, we can immobilize or remobilizing arsenic in groundwater.

## 2.4. Scheme of in situ Iron Precipitation and Arsenic Mitigation

According to the geochemical behavior of arsenic and iron in groundwater, an in situ iron precipitation and arsenic mitigation technique is proposed in this study: First, ferric iron solution and NaOH is injected into a well with arsenic contamination (Fig. 3, top left). Ferric iron will hydrolyze and precipitate out as amorphous ferric hydroxide (HFO) in the local aquifer surrounding the well. Arsenic species, including arsenite ( $\text{AsO}_3^{3-}$ ) and arsenate ( $\text{AsO}_4^{3-}$ ) in the groundwater, will be intercepted and sorbed onto HFO in the immobilization zone where “clean” water are produced (Fig. 3, top right).

After a certain period of “clean” water production, HFO reaches its maximum sorption capacity and will no longer be able to sorb more arsenic. In order to remove arsenic permanently from the local aquifer, either HCl or NaOH is injected into the precipitation zone, where As species have been accumulated, to desorb and mobilize the absorbed arsenic. This process will create a high arsenic plume (and perhaps with iron also depending on the method used) around the well (Fig. 3, bottom right). The groundwater with high arsenic and iron concentrations can then be pumped out (Fig. 3, bottom left). The accumulated arsenic in the local aquifer will thus be removed permanently. After that, a new cycle of precipitation-sorption-desorption process may be repeated when necessary and in situ arsenic remediation of groundwater is thus accomplished.

The viability of this new technique for As mitigation in groundwater is demonstrated in the following sections by batch and column experiments to support the theory outlined above.

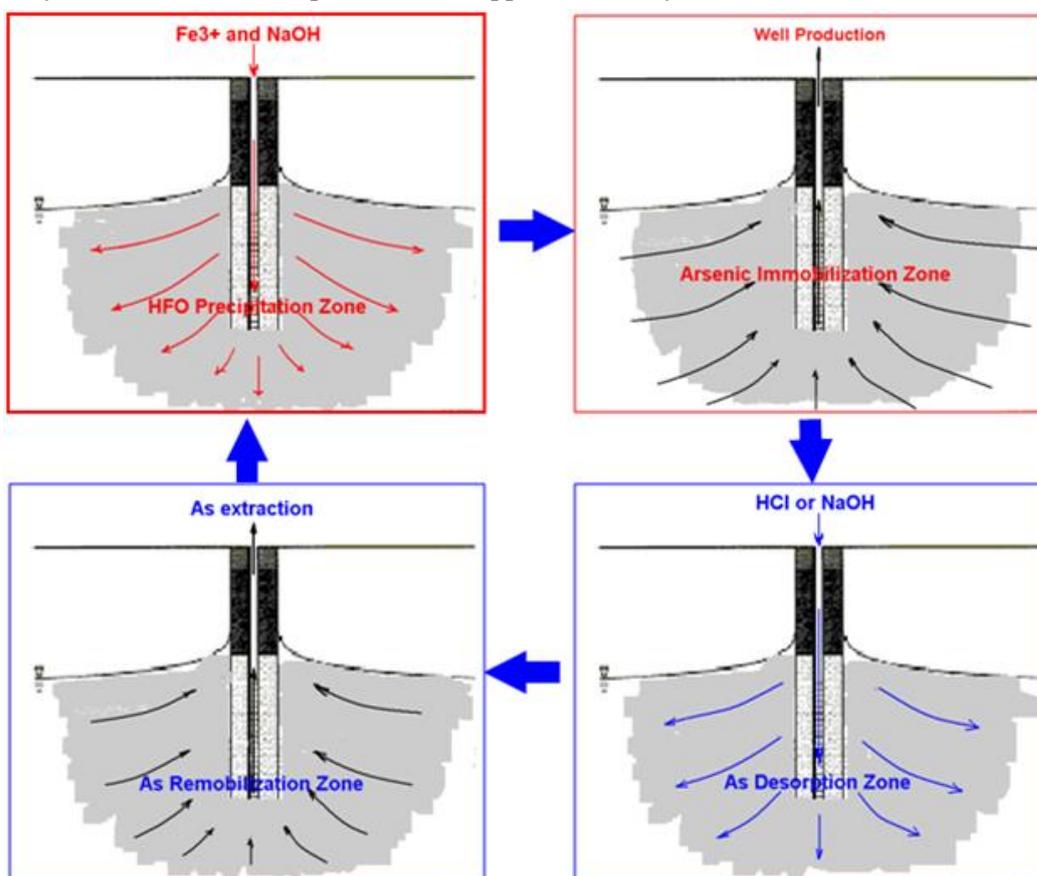


Fig. 3: Schematic of ferric iron precipitation and arsenic immobilization in groundwater (top), and arsenic (and iron) desorption and extraction from groundwater (bottom).

Although many in situ chemical oxidation approaches to remove As from groundwater have been suggested and discussed [23]-[26], however, no detailed results are currently available. The intent of this study is to provide detailed information of an in situ treatment approach to the public domain, policy makers and engineers can then use this information to assess specific situations to decide if this approach would be feasible for the local needs.

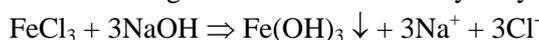
### 3. Methodology

#### 3.1. Batch Experiments for Theory Testing

Batch experiments were conducted in this study to understand and verify the kinetics of ferric hydrolysis to form HFO, HFO dissolution by HCl, As sorption rate and capacity with HFO, and As desorption rate from HFO with HCl or NaOH at different concentrations and temperatures (5-17 °C) as follows: These experiments were conducted in a series of 125 ml Erlenmeyer flasks as reactors, aluminum foil was used to cover the flasks to prevent light exposures in As sorption/desorption experiments. Continuous stirring was not used in the reaction process to simulate natural diffusion in groundwater.

##### 3.1.1. HFO formation from ferric iron hydrolysis

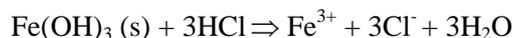
Ferric chloride (FeCl<sub>3</sub>) was weighed and dissolved to prepare for 0.05, 1, 5, 10, and 20 ppm (parts per million) of Fe<sup>3+</sup> solution, NaOH of 0.5 or 5 mg/ml were used for the hydrolysis reaction to form HFO:



Excess amount of NaOH was used to accelerate the reaction process. Water samples were collected from the reactors at 1, 2, 4, 8, and 24 hours after mixing once, samples were then filtered with 0.45 μm of nitrocellulose membrane and stored in 4 °C refrigerator before analysis.

##### 3.1.2. HFO dissolution by HCl

After the HFO formation was 100% completed in 24 hours or more, more than stoichiometric amount of 10% HCl (by weight) was added into the HFO solutions for the HFO dissolution according to the following reaction:



Likewise, water samples from the reactors were collected from the reactors at 1, 2, 4, 8, and 24 hours after mixing, samples were then filtered and stored in 4 °C refrigerator before analysis.

##### 3.1.3. Arsenic sorption onto HFO

Samples of 50 and 100 ppb of arsenate, arsenite, and arsenic 1:1 mixture of arsenate and arsenite (e.g., 25 ppm of arsenate and 25 ppm of arsenite for a total of 50 ppm of As) were employed separately to 50 ml solution containing 10 ppm of HFO precipitate to observe the sorption capacity of HFO for 24 hours. HFO precipitate was prepared by mixing 50 ml of 10 ppm of FeCl<sub>3</sub> solution with 0.3 ml of 5 mg/ml NaOH for 24 hours. The final solution was prepared by adding 0.5 ml of 5 ppm or 0.1 ml of 50 ppm of arsenic solution(s) into the 50 ml solution containing 0.5 mg of HFO precipitate as Fe. Initial pH of the final solutions after mixing of As solution with HFO varied from 7.35 to 6.37.

Supernatant of the batch solutions were collected and filtered with 0.45 μm pore size of nitrocellulose membranes at 1, 2, 4, 8, and 24 hour period after mixing and then stored in plastic containers at 4 °C for As analysis.

##### 3.1.4. Arsenic desorption from HFO with HCl or NaOH

One mg of HFO as Fe in 50 ml was made by the same method described in 3.1.3 except the concentration of Fe was doubled and then equivalent of 100 ppb of arsenate, arsenite, and arsenic 1:1 mixture solution was employed in the 50 ml solution containing the HFO. The solution was idled for 24 hours to ensure that all the As were sorbed by the HFO, then either 1ml of 10% HCl or 0.7 ml of 50 mg/ml of NaOH was added to the HFO sorbed with As; samples were then taken and filtered at 0, 2, 4, 8 and 24 hours. Filtered sample solutions were then stored at 4 °C before analysis.

#### 3.2. Column Simulations of in Situ Treatment of As Removal in Groundwater

To simulate As remediation in a more realistic environment and study factors that may affect the feasibility of in situ treatment, such as groundwater flow velocity, chemical dosage, etc., column experiments were conducted. Major parameters monitored in the column simulations were pH, total As, and Fe concentrations in the effluent so that mass balance could be performed to understand the As and Fe retention and release in the column, which is a good reassembly of a tube well. The major steps in the column experiments included the characteristics of water flow, As sorption capacity of pure sand with apparatus, in situ HFO precipitation, As sorption onto HFO (immobilization), and As desorption and remobilization.

An one-dimensional flow device (sand column) was built to model the groundwater flow in an aquifer and to examine the effect for arsenic stabilization and remobilization. The column was constructed by a 20-cm long transparent Plexiglas with a diameter of 5 cm, 650 g of medium to fine white sand (Fisher Scientific, Inc., Pittsburg, PA, USA) was used to fill the column, rubber stoppers were used to seal the column. A variable speed low flow mini pump (Control Company, Friendswood, TX, USA) was used to connect a solution reservoir to the bottom of the column, and the top of the column was connected to a graduate cylinder for measuring the effluent flow.

The column was predetermined to be about 345 ml, with a void volume of about 135 ml, thus total porosity of the column was about  $0.38 \pm 1.3\%$ . Furthermore, the column setup could handle Darcy velocity between 2 to 500 cm/day. For all the column experiments, different concentrations of As 1:1 As mixture solutions were used for testing and simulations. A schematic diagram of the batch and column apparatus for the in situ simulations is shown in Fig. 4.

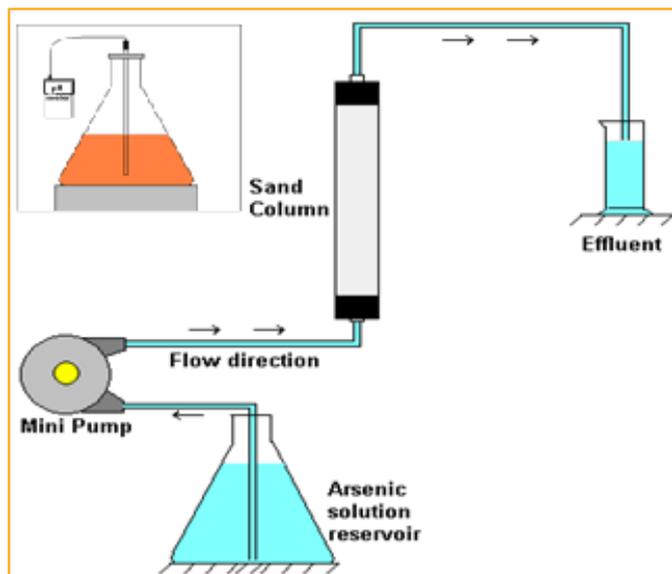


Fig. 4: Schematic diagram of the batch and sand column for the in situ simulations.

### 3.2.1. Column pump test

To understand how the sand column behaved with different flow rates, As 1:1 solutions of 100 and 1000 ppb were pumped through the sand column. Effluent samples were collected and analyzed to find out if the column setup behaved as an ideal plug-flow reactor and the threshold of flow limit before excessive mixing occurred within the column. A plug-flow type of reactor would be the most efficient for the As immobilization and remobilization process.

### 3.2.2. Arsenic sorption capacity with sand and the column apparatus

For better mass balance calculations and to make sure that pure sand and the apparatus would not contribute to a major factor in the retention of As, As 1:1 solutions of 100 and 1000 ppb were pumped through the sand column with various flow rate (Darcy velocity of 5 to 100 cm/day) that are typical flow velocities in groundwater. Then, after a pause period (8 to 48 hours) that the solution remained stagnant in the column to allow the sand and apparatus to have enough time to establish sorption equilibrium, de-ionized water was pumped into the column to flush out all the soluble As in the column. Effluent samples were

collected and analyzed. Sorption capacity of the “naked” sand and apparatus could then be determined by the difference of total As going in and out of the column.

### **3.2.3. In situ arsenic immobilization followed by remobilization with HCl**

HFO colloidal slurry injection, or Fe and NaOH sequential injection could both be used to coat a layer of HFO on the surface of sand in the test column. It was found in pre-testing that the HFO colloidal slurry injected into the column could easily adhere onto the sand, even though it was immediately followed by flushing of As solution, less than 0.5% of HFO would be eluting out from the effluent of the column. Thus the HFO colloidal slurry method was adopted in the column experiments.

One mg of HFO as Fe slurry was quickly injected into the sand column and immediately followed by pumping 53 ppb of 1:1 As solution into the column at a Darcy velocity of 22 cm/day for 30 hours. Then, 10 ml of 10% HCl was quickly injected into the column followed by continuous As solution feeding at a Darcy velocity of 21 cm/day for another 60 hours. Iron, As, and pH in the effluent of the column were monitored and analyzed.

### **3.2.4. In situ arsenic immobilization followed by remobilization with NaOH**

In this section of experimentation, 10 mg of HFO slurry instead of 1 mg of HFO was quickly introduced into the sand column, immediately followed by 83 ppb 1:1 arsenic solution pumping with an average Darcy velocity of 17 cm/day for 84 hours.

Then, 5 ml of 50 mg/ml of NaOH was quickly injected into the column followed by continuous As solution feeding at a Darcy velocity of 15 cm/day for another 48 hours. Iron, As, and pH in the effluent of the column were monitored and analyzed.

This portion of experimentation was to find out if excessive amount of HFO would be more effective to remove As and the efficacy of As remobilization on the surface of HFO by NaOH.

## **3.3. Chemicals and Analysis**

Arsenate solutions were prepared from  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , arsenite solutions were prepared from  $\text{NaAsO}_2$ , and  $\text{Fe}^{3+}$  solutions were prepared from  $\text{FeCl}_3$ . All reagents including NaOH, HCl were reagent grade or the highest grade available from Fisher Scientific, Inc. (Pittsburg, PA, USA), water used for solution preparation was double deionized water.

Total As analysis was conducted with either a JY-70C simultaneous - sequential ICP – AES (Longjumeau, France) which has a detection limit of 10 ppb with an ultrasonic nebulizer, or an Agilent 7500 cx ICP-MS (Palo Alto, CA, USA) which had the detection limit of lower than 5 ppb (1-5 ppb). Total Fe was measured by the JY-70C ICP-AES with the detection limit of 5 ppb. All elemental analyses were software controlled, reported values were at least an average of 10 measurements. pH was monitored in all batch samples and column effluents with a Hach 10 pH meter.

## **4. Results and Discussion**

This paper would mostly concentrate on the results of the in-situ groundwater treatment, thus, results from the batch experiments are not shown here, but the details can be viewed from a previous publication [27]. However, results of the batch experiments were used for the design of the column experiments herein, the pump test showed that the column apparatus maintained to be plug-flow up to an average Darcy velocity of 135 cm/day with a residence time of 1.2 hours, with which the in-situ treatment system would not exceed in this study.

### **4.1. Arsenic Sorption Capacity with Sand and the Column Apparatus**

Table 1 showed the results of the column test where various Darcy velocities were applied to the column system with an 1 ppm of 1:1 As solution (50 ppm of arsenite and arsenate each) for a period of time, then after a pause period of 8 to 48 hours, de-ionized water was pumped into the column to recover the As in the solution. It was determined that the total sorption of As by the sand and the apparatus was between 0.7 to 2.8%. Therefore, it is reasonable to assume that “naked” sand does not have very strong affinity with As.

Table 1: Test of As sorption capacity for sand and the column apparatus at different Darcy velocities.

Darcy velocity, cm/day	Total As (in), mg	As (in) concentration, ppm	Total As (out), mg	Time, hr	Pause time, hr	Sorbed amount, ppm	Sorption %
10	0.4323	1.0	0.4254	96.0	48	0.0069	1.6
50	0.2351	1.0	0.2286	12.0	14	0.0065	2.8
100	0.4150	1.0	0.4121	9.0	8	0.0029	0.7

#### 4.2. In Situ Arsenic Immobilization Followed by Remobilization with HCl

For this continuous column experiment, the total As pumped into the column (containing 1 mg of HFO) in 30 hours was 0.0336 mg (636.5 ml x 53 ppb) while the total As coming out from the effluent was 0.0196 mg, thus the amount of As sorbed by 1 mg of HFO was 0.0141 mg (1.4 mg As/100 mg HFO), that greatly exceeded the As sorption capacity predicted by the batch experiments (0.8 mg As/100 mg HFO) [27].

At the remobilization stage of operation after the 10% HCl injection, 0.0574 mg (1083 ml x 53 ppb) of As was pumped into the column while 0.0666 mg of As was collected from the effluent of the column. In summary, total As entered the column during the immobilization/remobilization operation in 90 hours was 0.091 mg, while the total As left the column was 0.086 mg, that amounted to 94.5% of the As recovery from desorption.

Mass balance from the effluent of the column indicated that 1 mg of the HFO was completely dissolved and eluted out from the sand column 26 hours after the HCl injection. HFO would be needed to replenish the column if a new cycle of simulation was to be conducted. Fig. 5 in the following is the composite diagram with the 4 stages (Fig. 3) of simulation of the in situ HFO precipitation and As immobilization/remobilization with HCl.

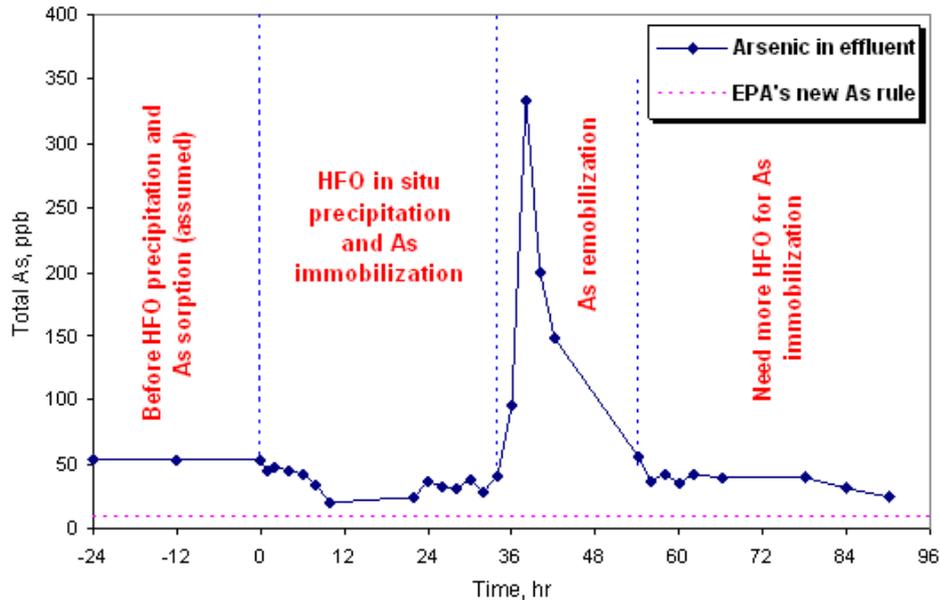


Fig. 5: Combination diagram of in situ As immobilization with HFO sorption followed by As desorption with HCl. The initial As concentration at the influence of the column was 53 ppm and 1 ppm of HFO was injected in the column.

#### 4.3. In Situ Arsenic Immobilization Followed by Remobilization with NaOH

In this section of column experiment, the total As pumped into the column in 84 hours was 0.1008 mg (1214 ml x 83 ppb) while the total As coming out from the effluent was 0.0129 mg, the amount of As sorbed by 10 mg of HFO was 0.0879 mg. In terms of sorption capacity of HFO, it was 0.88 mg As /100 mg HFO, that was slightly exceeded the As sorption capacity predicted by the batch experiments but was less than that the results obtained from similar experiment above with 1.0 mg of HFO in the column initially.

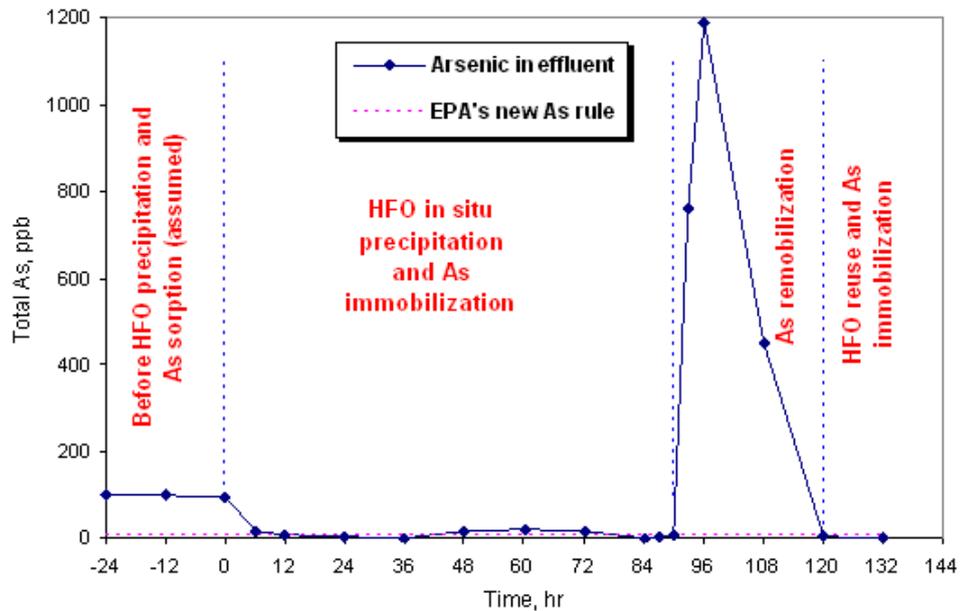


Fig. 6: Combination diagram of in situ As immobilization with HFO sorption followed by As desorption with NaOH. The initial As concentration at the influence of the column was 83 ppm and 10 ppm HFO was injected in the column.

At the remobilization stage of operation after the NaOH injection in this simulation, 0.0511 mg (615.5 ml x 83 ppb) of As was pumped into the column while 0.1403 mg of As was collected from the effluent of the column. In summary, total As entered the column during the immobilization/remobilization operation in 132 hours was 0.152 mg, while the total As left the column was 0.153 mg, that indicated total As desorption. The combination diagram of the 4-stage simulation of the in situ HFO precipitation and As immobilization/remobilization with NaOH is shown in Fig. 6.

Mass balance from the effluent of the column indicated that 10 mg of the HFO was almost 100% conserved with the injection of NaOH during the As remobilization stage (with only 0.275 mg of HFO loss), that was less than 3% of the original HFO. Thus, frequent addition of HFO is not necessary with the NaOH approach to remobilize As. Fig. 7 in the following shows the HFO dissolution in the sand column at the effluent due to NaOH addition that was almost negligible.

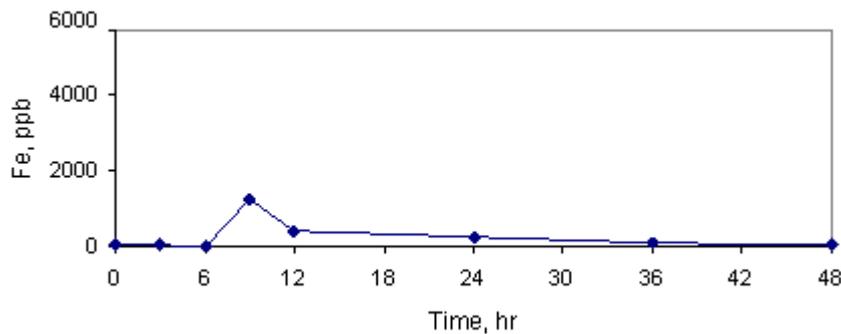


Fig. 7: HFO dissolution in the sand column due to NaOH addition as monitored from the effluent of the column.

A potential industrial utility of the waste solution coming out of the column from desorption, that is laden with high concentration of As, can be pumped into a lined lagoon. After the water content in the solution is evaporated, the residual As can be harvested as industrial or pharmacological feedstock.

## 5. Conclusions

For the in situ treatment, solution alkalization (NaOH remobilization) would be a better alternative: it desorbs As from HFO more completely and preserve the HFO precipitate on the sand, thus frequent HFO replenishment is not necessary for the next treatment cycle. On the other hand, the acidification approach

would dissolve all the HFO on the sand into the surrounding solution and the HFO would be flashed away in situ.

This simple “treat-and pump” approach to remove As from groundwater was demonstrated to be technically feasible, its operation is simple and requires low initial investment, the high As concentration solution during As remobilization/desorption actually can be collected as industrial feedstock. However, since chemical is needed to inject into the groundwater aquifer to create HFO precipitation and an As immobilization/remobilization zone, it may generate unexpected bio/geochemical effects for the subsurface system. If this operation is to be conducted in the U.S., a permit would be required. Therefore, for real-time application, one should also consider the local environmental and socioeconomic factors before this technology is employed.

## 6. Acknowledgements

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