1. Proposal Title: *In Situ* Groundwater Arsenic (As) Removal using Iron Oxide-Coated Sand

2. USGS Project #: 2009TX329B

3. Principal Investigator

Thomas S. Abia II, EIT
Ph.D. Graduate Student
Dept. of Bio and Ag. Engineering (BAEN)
230 Scoates Hall, Texas A&M University
College Station, TX 77843-2117
(805) 215-8816, tabia@tamu.edu

4. Co-Principal Investigator

Yongheng Huang, PE, Ph.D.
Assistant Professor
Dept. of Bio and Ag. Engineering (BAEN)
303E Scoates Hall, Texas A&M University
College Station, TX 77843-2117
(979) 862-8031, yhuang@tamu.edu

5. Abstract

Iron oxide-bearing minerals have long been recognized as an effective reactive media for arsenic (As) remediation. A simple iron oxide coating process was developed to employ a sustainable and cost-effective *in situ* coating technique for treating contaminated groundwater. To *in situ* emplace iron oxide coatings on soil particles, ferrous salt and dissolved oxygen solutions were periodically injected into a sand matrix following a specially designed injection scheme. The resulting adsorption, diffusion, and redox reactions could continuously deposit large quantities of ferric oxide onto the surface of soil particles, thus creating a constantly-refreshed reactive surface for the continuous adsorption and co-precipitation of arsenic and other heavy metals.

6. Statement of Critical Regional Water Problems and Current Solutions (Need for Research)

Arsenic, a naturally-occurring groundwater toxicant, has been linked to illnesses such as liver dysfunction, gangrene, and skin tumors (Hutton, 1978). Furthermore, a study focusing on the carcinogenic risks associated with arsenic-laden water concluded that cancers in the lung, kidney, bladder, and liver may result from consumption (Smith et al., 1992). There are many sources of arsenic in the environment that are transported by water. Soil erosion and leaching are suspected of depositing dissolved and suspended arsenic into the oceans (Mackenzie et al., 1979). Industrial effluents from metallurgy, petroleum, fertilizer, glassware, pesticides, chemical, and coal-power facilities are major causes of point source As pollution. On January 23, 2006, the United States Environmental Protection Agency (USEPA) lowered the maximum concentration level (MCL) of As in drinking water to 10 micrograms per liter (µg/L) (USEPA, 2006). The American Water Works Association (AWWA) conducted a survey for inorganic contaminants in water supply regions in the United States that identified 34 cases where As levels exceeded the MCL (American Water Works Association Committee, 1985) and the USEPA identified 541 superfund sites with As being the contaminant of concern in groundwater (USEPA, 2009). The majority of the violations were documented in New Mexico, Oklahoma, and Texas while separate cases were reported in Alaska, Illinois, New Hampshire, North Carolina, and Virginia (Viraraghavan et al., 1999).

Interest in the development of dissolved metal removal technology has been triggered by USEPA regulation of inorganic contaminants in drinking waters. Some volatile metals in the water are highly hydrophilic and cannot be easily removed through oxidation, precipitation, or biological treatment while maintaining low operating costs and environmental sustainability. Major problems with the treatment technology for dissolved metals are complex operations, mono-functionality, use of expensive and dangerous chemicals, and lack of re-usability.

7. Objective and Scope of Research

Objective

With an emphasis on economics and sustainability, this study aims to develop and optimize the iron coating of sand under submerged conditions to simulate an aquifer environment. Lab-scale column tests will be performed to verify feasibility and assess iron oxide-coated sand regeneration capabilities. Dissolved oxygen will be used as the only Fe^{2+} oxidant.

Scope of Work (Methodology)

The range of work for this applied research encompasses coating design, coating optimization, and coating regeneration of iron oxide-coated sand. Contaminant treatment will only be analyzed as part of the regeneration assessment.

- **Stoichiometry, Calculations, and Chemical Preparation**
  - ***Stoichiometry*** - The basis of the calculations and chemical preparation in this experiment resulted from the following oxidation-reduction reactions between Fe^{2+} and dissolved oxygen:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \qquad (1)$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \qquad (2)$$

where the resulting equation below represents the overall production of ferric oxide:

$$4Fe^{2+} + O_2 + 4H^{+} \rightarrow 4Fe^{3+} + 2H_2O \qquad (3)$$

The formation of ferric oxide by oxygen requires the addition of alkalinity (OH^-) to resist the significant reduction in pH caused by the hydrogen ion (H^+). The source of alkalinity used in this study to maintain a high Fe^{2+} oxidation rate was NaOH. To compensate for the fixed elevated temperature, the rate of oxygen flow into the system was adjusted to exceed the stoichiometric requirements.

  - ***Calculations*** – Fe^{2+} source: anhydrous ferrous chloride 4-hydrate ($FeCl_24H_2O$), $MW_{FeCl24H2O}$ = 198.81 grams per mole
    Fe^{2+} oxidant: compressed oxygen (O_2) dissolved in tap water @ 21 ^{o}C, MW_{O2} = 32 grams per mole
    O_2 saturation = 8.24 mg/L in ambient air @ 21 ^{o}C (21% composition of air)
    Alkalinity (OH^-) source: sodium hydroxide (NaOH), MW_{NaOH} = 40.00 grams per mole
    Acid (H^+) source: hydrochloric acid (HCl), MW_{HCl} = 36.46 grams per mole
    Water source: **tap water**, ~~V~~$_{Fe(II)}$ = 10 L, ~~V~~$_{O2}$ = 10 L, ~~V~~$_{water\ buffer}$ = 20 L

O_2 (mM) = $\dfrac{8.24\frac{mg}{L}}{(21\%)*\left(32\frac{mg}{mmole}\right)}$ = **1.226 mM O_2** (39.24 mg/L) dissolved in 10 L tap H_2O

Alkalinity (O_2) = [1.226 mM O_2]*[10 L]*[0.040 $\frac{g\ NaOH}{mM\ NaOH}$]*[4 $\frac{g\ NaOH}{mM\ NaOH}$] = 1.962 g NaOH dissolved in 10 L tap H_2O

$M_{Fe(II)}$ (g) = [1.226 mM O_2]*[4 $\frac{mM\ Fe(II)}{mM\ O2}$]*[10 L H_2O]*[0.19881 $\frac{g\ Fe(II)}{mM\ Fe(II)}$] = 9.75 g Fe^{2+} dissolved in 10 L tap H_2O

[Fe^{2+}] (mM) = [1.226 mM O_2]*[4 $\frac{mM\ Fe(II)}{mM\ O2}$] = **4.905 mM Fe^{2+}** dissolved in 10 L tap H_2O

  - ***Preparation of sand cleaning agents***

Acid water: 20 L of de-ionized water (DI H_2O) was acidified to 0.5 mM HCl.
Base water: 0.5 mM NaOH was made by mixing 10 L DI H_2O with 5 mL of 1 M NaOH.
Salt water buffer: 3 L of DI H_2O was fortified to 0.5 mM NaCl

  - ***Preparation of iron oxide coating agents***

Dissolved Oxygen: 10 L of tap H_2O was oxygenated under ambient conditions to 1.23 mM (39.2 mg/L) using a compressed oxygen tank. The oxygenated water was supplied with 4.92 mM of NaOH to provide extra alkalinity.

Iron source: Equation 3 was used to determine the proper amount of Fe^{2+} sufficient for DO saturation in water in a submerged environment. 9.75 g of $FeCl_2{\cdot}4H_2O$ was dissolved in 10 L of tap H_2O to produce a stock solution of 4.92 mM Fe^{2+} (274.7 mg/L Fe^{2+}). 0.3 mM HCl was used to adjust the pH and prevent Fe^{2+} precipitation in the storage tank.

Acid water buffer: 20 L tap H_2O was used as a buffer between the Fe^{2+} and the oxygen water to prevent precipitation in the conveyance system in the coating procedure. The pH of the acid water was adjusted using 0.5 mM of HCl.

- **Iron Oxide-Coated Sand (IOCS) Research Approach (page 4)**
  - ***Phase 1: In Situ Coating*** – wet-pack and pre-clean sand, determination of optimum coating pH range, ascertain applicable *in situ* injection schematic, optimize coating procedure through the control of the pH and acid water buffer, and assess iron oxide accumulation through Fe^{2+} breakthrough curves and concentration profiles. Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) for describing iron oxide crystallization. Chemical production costs will be compared to conventional IOCS production costs.

  - ***Phase 2: In Situ Treatment and Regeneration*** – filter design via As batch isotherms from Phase 1 IOCS, synthetic pollutant (As of various species and concentrations) removal and iron oxide regeneration, evaluate for feasibility of regeneration using Fe^{2+} and pollutant breakthrough curves. Re-dissolution of iron oxides and pollutant will be explored and analyzed via SEM. Iron oxide-coated sand usage rates (IOCSUR) and specific throughputs (ST) for each contaminant will also be estimated. Repeat phase 2 for real groundwater spiked with targeted toxicant.
  - ***Phase 3: In Situ Pilot Study*** – construction of simulated sub-surface groundwater aquifer with gravity-driven injection wells incorporating data and details from Phases 1 and 2, evaluate using real groundwater spiked with As.

- **Iron Oxide-Coated Sand (IOCS) Analytical Process (Figure 1)**
  - ***Characterization*** – collect sand samples before wet-packing, after pre-cleaning, and after iron oxide coating for SEM imaging. Obtain Fe^{2+} breakthrough curves to assess the distribution of the iron oxide crystals on the sand surface throughout the filter. Air-dry sand samples for 5 days before undergoing imaging. Mix 6 5-gram samples of dried, coated sand placed in separate vials with 9.5 mL strong acid for 48 hours to obtain aqueous iron oxide solutions. Analyze for Fe^{2+} and total Fe to quantify the Fe^{3+} accumulation on the sand at various depths of the filter.

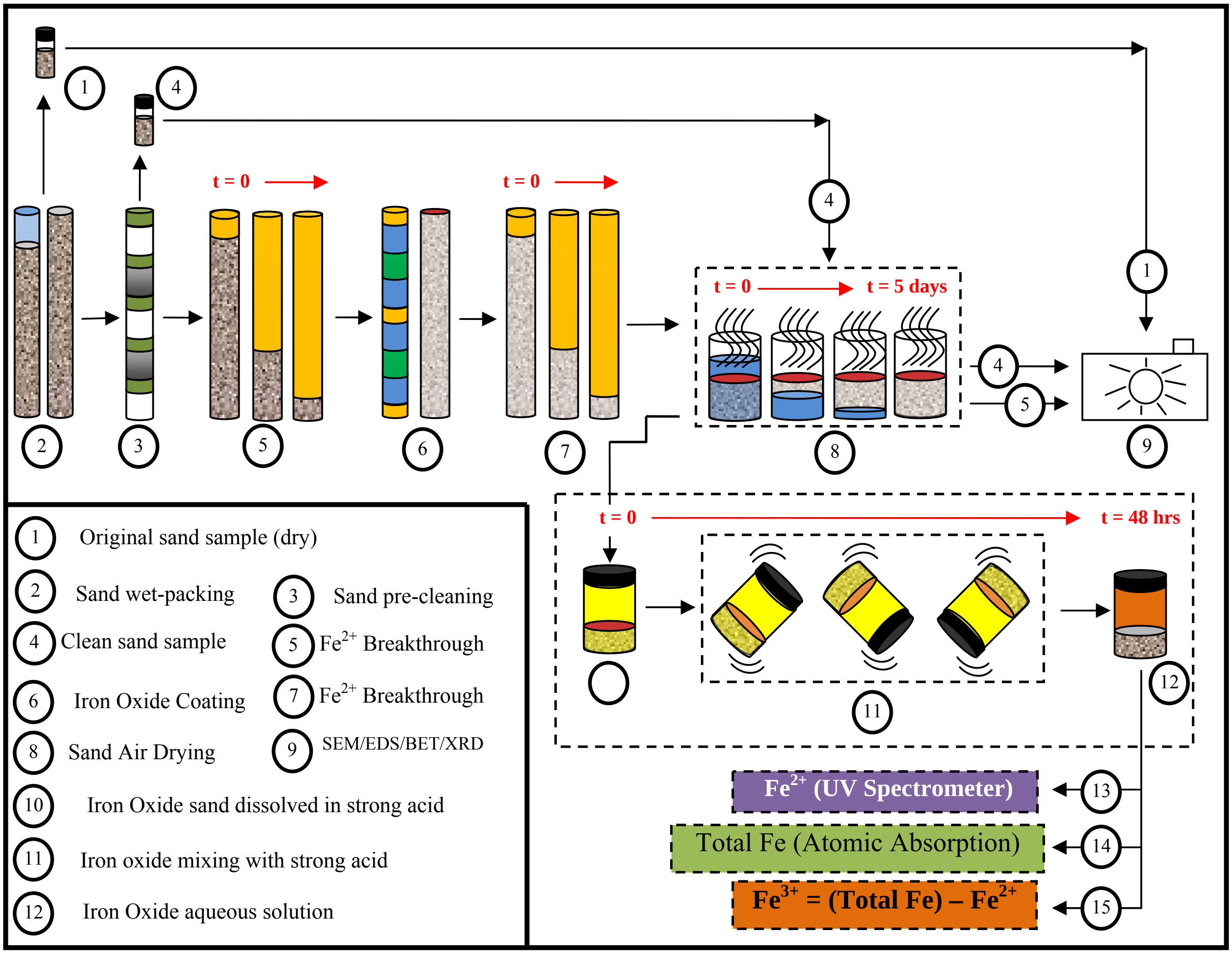
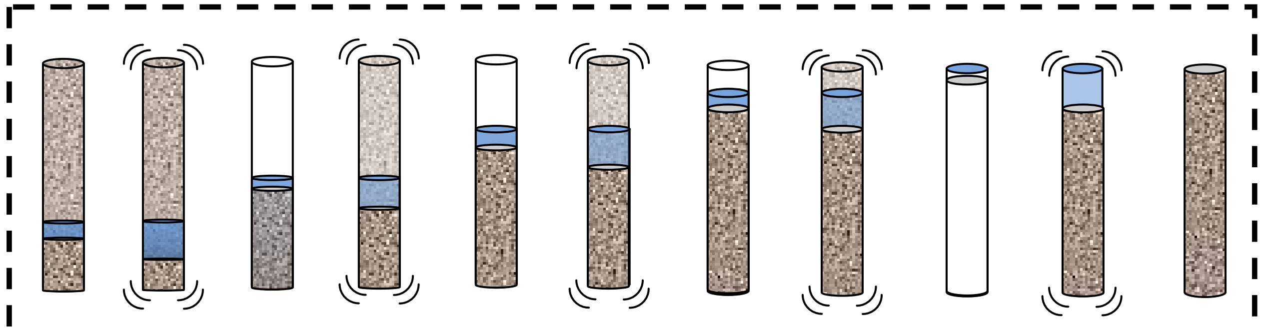
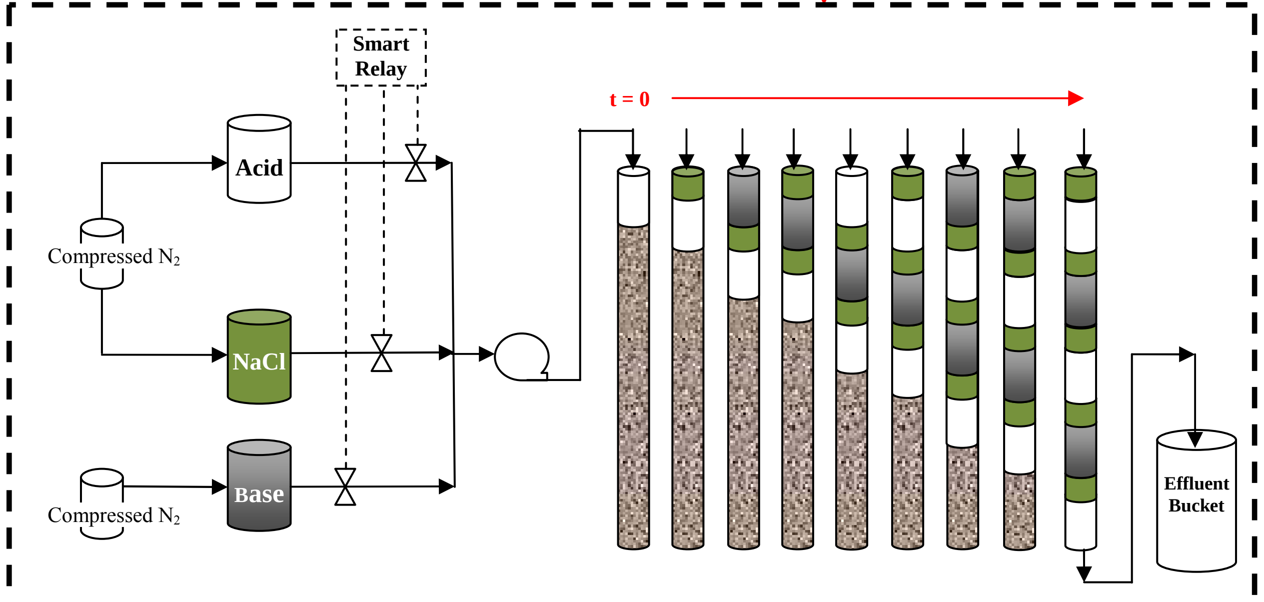


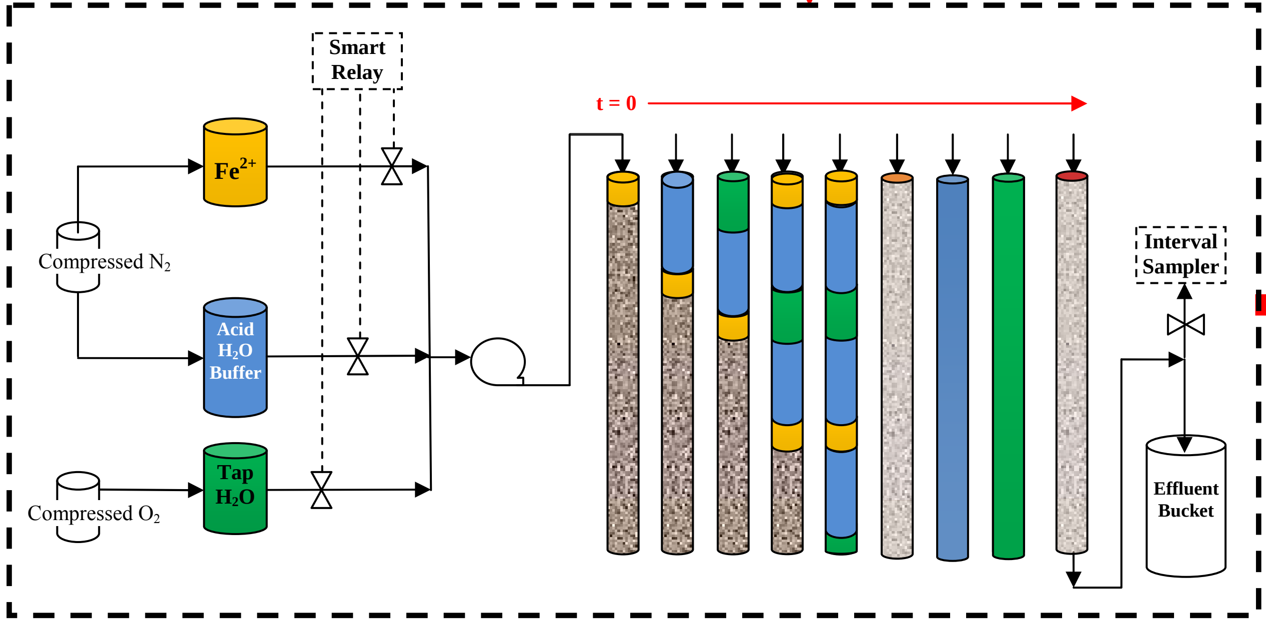
Figure 2: IOCS Analytical Process Diagram



Step 1: Sand Wet-packing

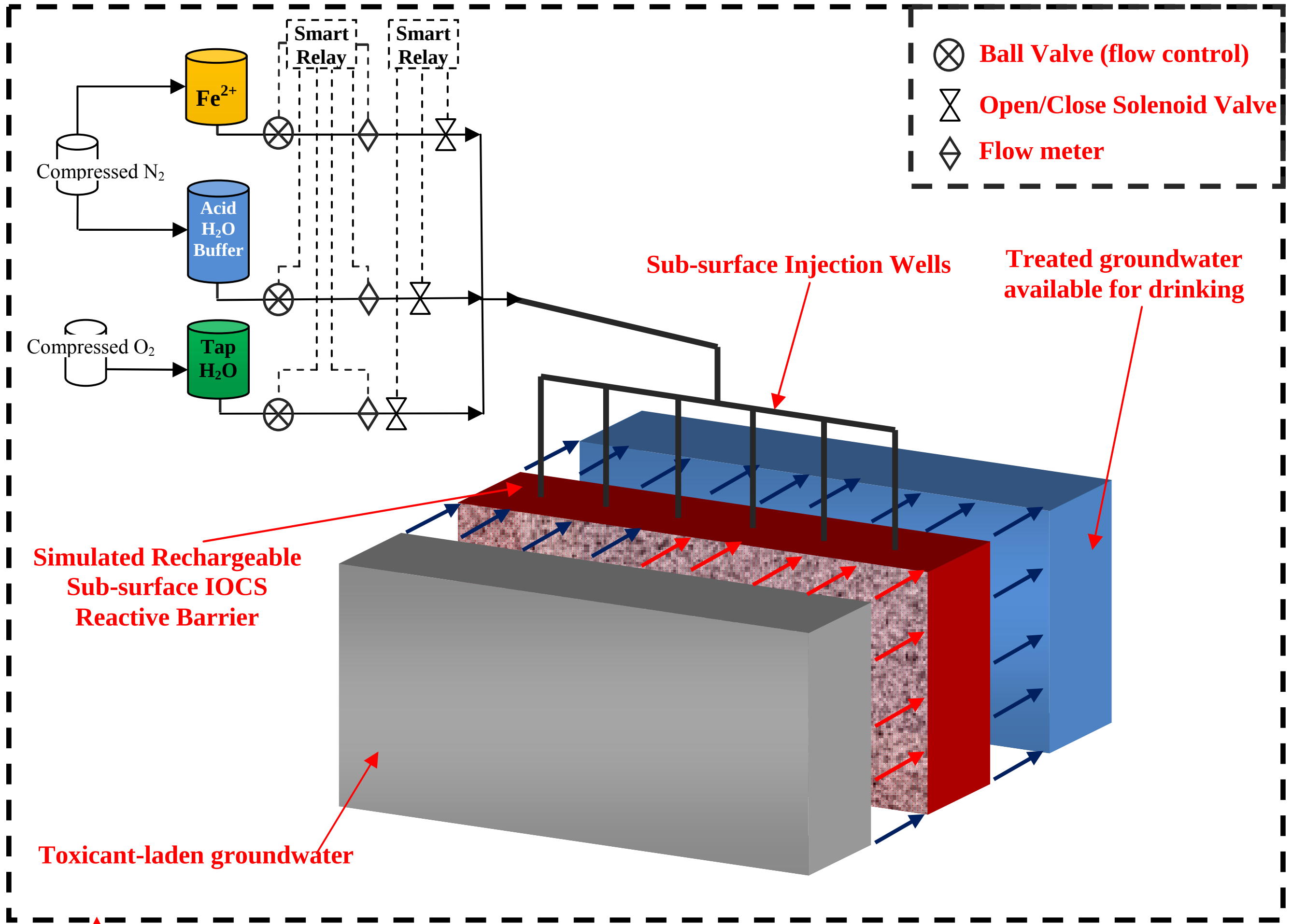


Step 2: Sand Pre-cleaning



Step 3: Iron Oxide Coating

PHASE 1: *In Situ* Coating (June 2009 – March 2010)



PHASE 3: *In Situ* Pilot Study (September 2010 – April 2011)

RESEARCH STATUS

PHASE 1

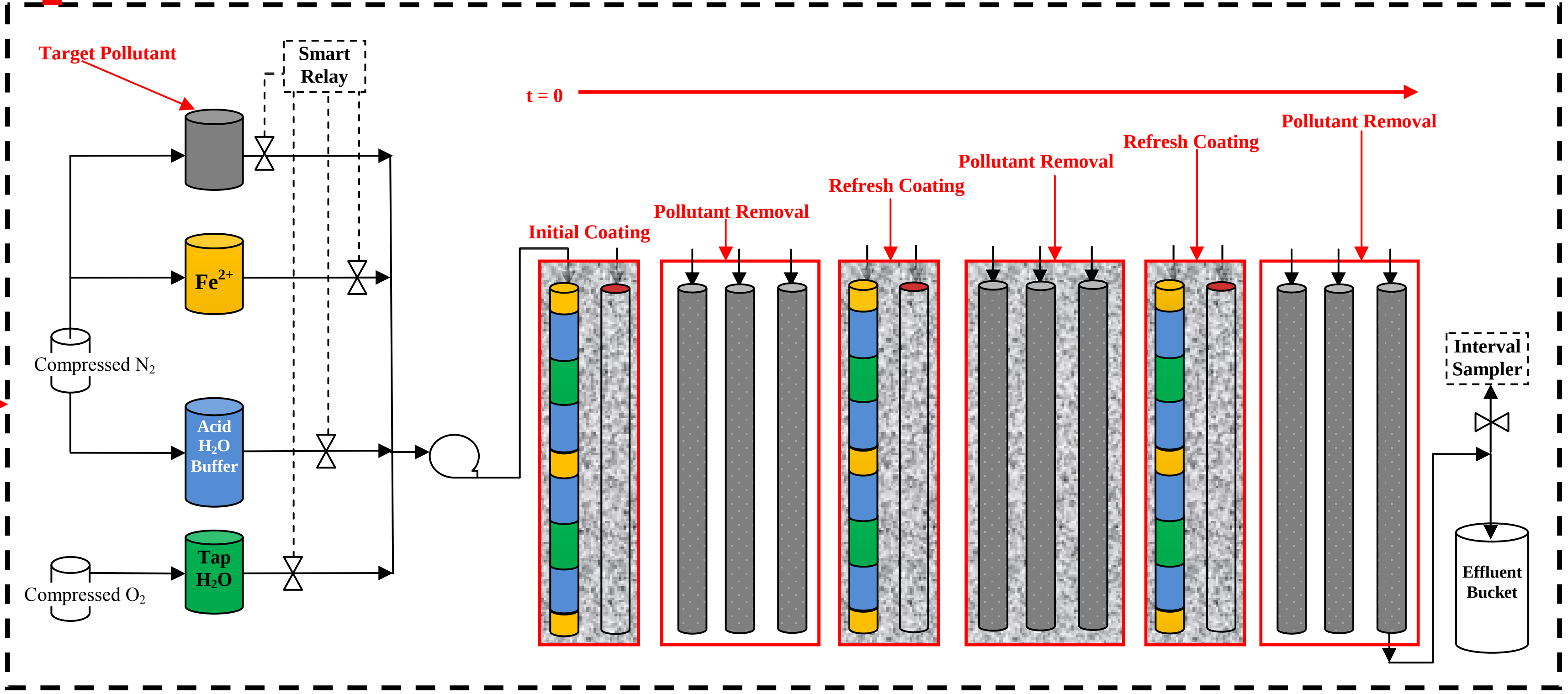
- Step 1: Complete
- Step 2: Complete
- Step 3: Complete
- Publication: **In Progress**

PHASE 2

- 1st run: **In Progress**
- 2nd run: Stand-by
- 3rd run: Stand-by
- Publication: **In Progress**

PHASE 3

- Design: Stand-by
- Construction: Stand-by
- Operation: Stand-by
- Publication: **In Progress**



PHASE 2: *In Situ* Treatment & Regeneration (March 2010 – August 2010)

8. Analytical Equipment

Effluent samples were collected using a Spectrum Chromatography IS-95 Interval Sampler, Model 141200, Houston, Texas, United States. pH measurements were made on a pH meter, Model Thermo Scientific No. 5000, Singapore. Arsenic and total iron analyses were performed using an Atomic Absorption Spectrometer; Model PerkinElmer No. B3150080, Shelton, Connecticut, United States. The spectrometer was also used to analyze ions and metals that were believed to be detected at the parts per billion (ppb or ppm x 10^{-3}) level. Fe^{2+} was analyzed using a UV/IVS Spectrometer; Model PG Instruments T80+, Wibtoft Lutterworth, Leicestershire, United Kingdom via Standard Methods 3500-Fe (Standard Methods, 1998).

9. Significant Findings

The injection schematic designed in the Research Approach accommodates the demand for numerous trials using a variety of configurations to determine the best feed sequence. Tables 1 and 2 provide the operations for sand cleaning and Fe-O coating.

Table 1 - Sand Pre-cleaning Operation[a]

Agent	Strength	Units	Time[b, c]	Units
HCl	0.5	10^{-3} mol/L	180	minutes
NaCl	0.5	10^{-3} mol/L	60	minutes
NaOH	0.5	10^{-3} mol/L	180	minutes
NaCl	0.5	10^{-3} mol/L	60	minutes

[a] 7-day operation
[b] injection time during a single cycle
[c] hydraulic retention time of 60 minutes

Table 2 - Iron Oxide Coating Operation[a]

Agent	Strength	Units	Time[b, c]	Units
Fe^{2+}	4.92	10^{-3} mol/L	4 - 5	minutes
HCl	0.5	10^{-3} mol/L	8 - 10	minutes
O_2	1.23	10^{-3} mol/L	6 - 7	minutes
HCl	0.5	10^{-3} mol/L	8 - 10	minutes

[a] 3-day operation
[b] injection time during a single cycle
[c] hydraulic retention time of 30 minutes

Figure 3 depicts a scanning electron method (SEM) angled view of a sand particle surface before and after acid/base cleaning. The acid treatment degraded the bonds between the impurities, colloids, and the sand surface while the base removed the impurities and colloids from the sand filter. The saltwater buffer was used to keep the acid and base from reacting with each other in the conveyance system prior to sand application.

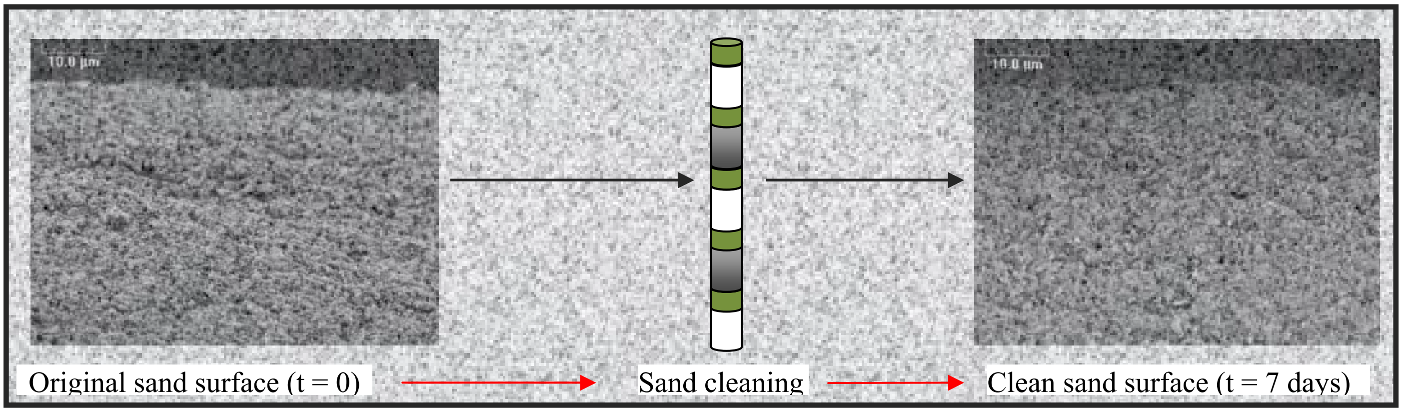


Figure 3 – Sand Pre-cleaning Results

There was a great deal of speculation during the pre-planning stages of this project that the sand cleaning would provide a more uniform sand surface for the iron oxide to form; thus promoting a uniform coating process throughout the filter rather than coating one specific region at a time. Furthermore, this process has slightly improved the porosity of the sand by, minimizing the effect of significant head loss induced by clogging. The removal of the impurities and colloids on the sand surface increased the space between the sand particles; allowing water to flow through the filter with less resistance.

As a result of the improved sand surface from the acid/base treatment, the iron oxide coating was successful. After 40 hours of intermittent injection with the chemicals described in Table 2, uniform coating was observed (Figure 4). The coating sequence was employed for a little while longer in an attempt to accumulate more iron oxide on the sand. The acid water buffer was then injected for 30 minutes to flush the filter of excess solids and suspended Fe^{2+} before applying a 9-hr oxygen blanket to strengthen the iron oxide crystallization on the sand. This method was intended to oxidize any excess Fe^{2+} that was adsorbed onto the sand surface. An x-ray diffraction analysis (XRD) revealed that the iron oxide crystals were consistent with hematite and lepidocrocite.

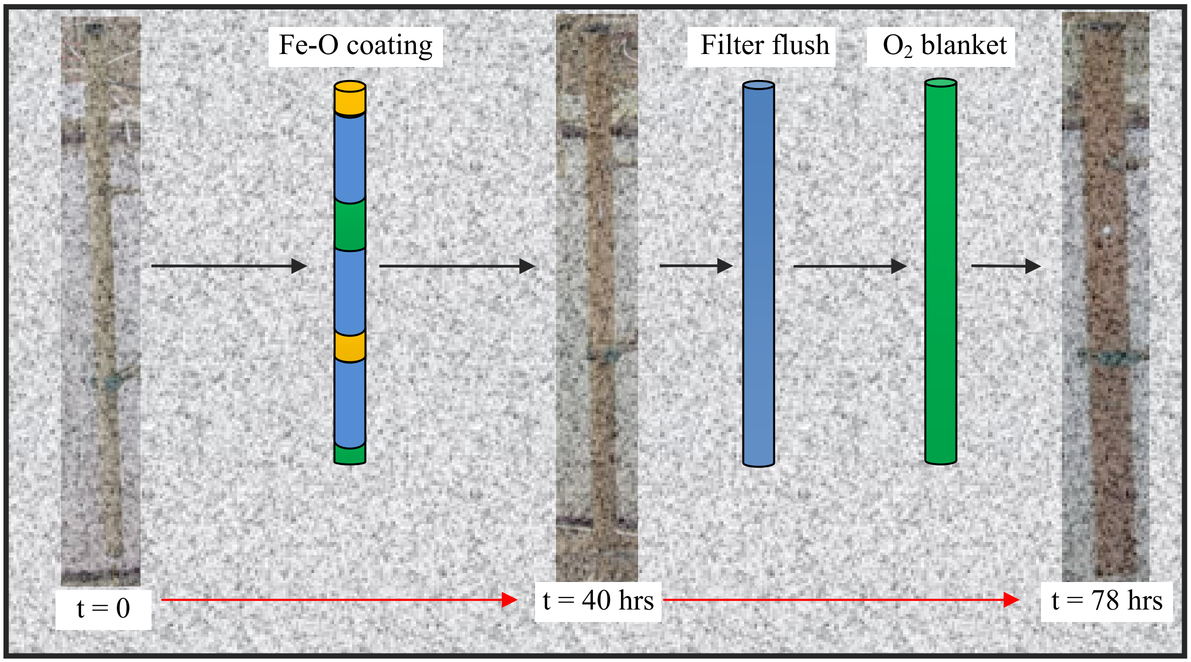


Figure 4 – Iron Oxide Coating

Two trials were performed to evaluate the performance of the coating method by quantifying the iron oxide accumulation on the sand surface. The sand was broken into six segments when coating was complete after it was assumed that the accumulation was not homogeneous throughout the filter. The second trial shows more accumulation after elongating the coating procedure and applying the oxygen blanket (Figure 5). The second trial resulted in clogging and it was determined that the suspended particles were not flushed out of the system and produced a thick slurry in the top 18" of the filter that induced significant head loss. The coating procedure was then modified to intermittently flush the filter with acid water to prevent any excess solids from being suspended between the sand particles.

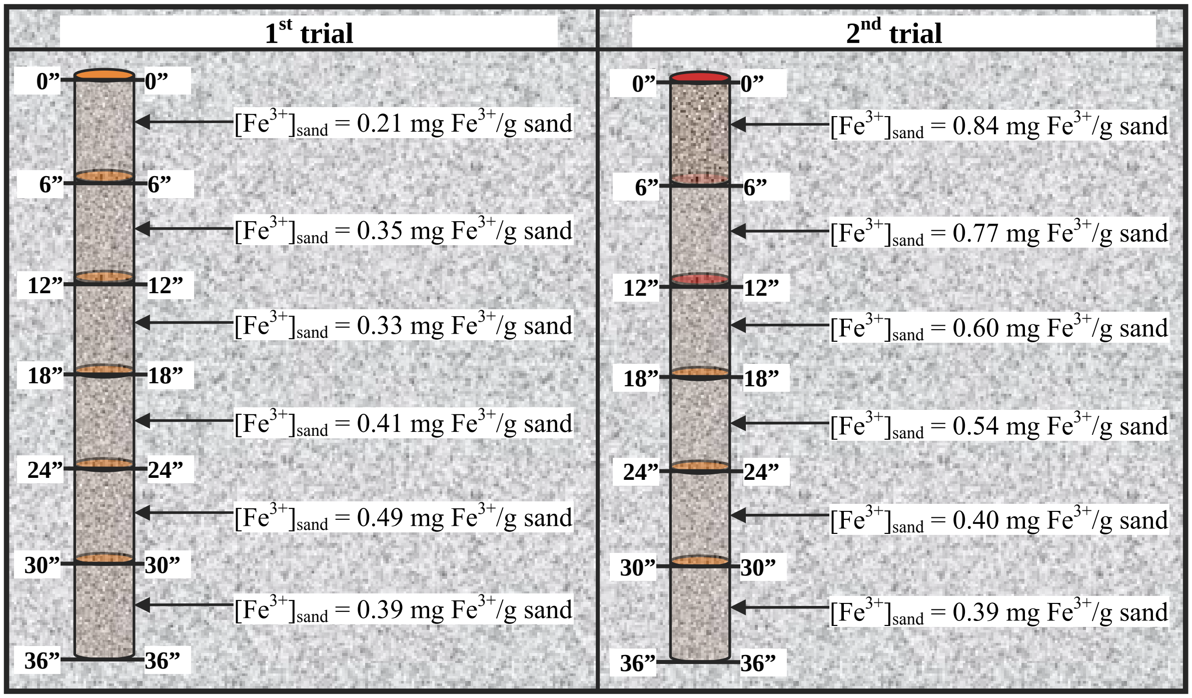


Figure 5 - Iron Oxide Accumulation Profiles

10. Intentions of the Research

1) Establish a sustainable and inexpensive *in situ* emplacement of iron oxides onto sand matrices with dissolved metal treatment and re-usability capabilities that can be employed for large-scale groundwater applications. This study has immense potential to be an applicable removal technology for arsenic and other metals in rural groundwater treatment.
2) Evaluate and re-use the devised research approach to develop reactive barriers for mercury (Hg), cadmium (Cd), chromium (Cr), and cobalt (Co) removal as mandated by the USEPA priority industrial pollutants (USEPA, 2009).
3) Expand the research to devise a large-scale IOCS manufacturing process that will accommodate the demand for industrial water treatment. The design of this research can be retrofitted to produce an IOCS sub-surface reactive barrier (as described in Phase 3) for a variety of applications; making this product a highly versatile technology.

11. REFERENCES

American Society of Testing and Materials (ASTM). Standard Test Method for Determination of the Particle Size of Powdered Activated Carbon by Air Jet Sieving. West Conshohocken, PA: ASTM, 1998.

American Water Works Association Committee (1985). “An AWWA Survey of Inorganic Contaminants in Water Supplies.” Journal American Water Works Association 77(5), 67 - 72

Hutton M. (1987) “Human Health Concerns of Lead, Mercury, Cadmium, and Arsenic.” Lead, Mercury, Cadmium, and Arsenic in the Environment. New York: John Wiley and Sons, 53-68.

MacKenzie F.T., Lanzy R.J., and Paterson V. (1979). “Global Trace Metal Cycles and Predictions.” Journal of International Association of Mathematics and Geology **6**, 99 – 142.

Smith A.H., Hopenhayn-Rich C., Bates M.N., Goeden H.M., Picciotto I.H., Duggan H.M., Wood R., Kosnett M.J., and Smith M.T. (1992) "Cancer risks from Arsenic in Drinking Water." Environmental Health Perspectives **97**, 259–267.

US Environmental Protection Agency (2006). Drinking Water Standards and Health Advisories. EPA 822-R-06-013. Washington, D.C.: USEPA.

US Environmental Protection Agency (2009). Steam Electric Power Generating Point Source Category. EPA Title 40, Part 423. Electronic Code of Federal Regulations. Washington D.C.: USEPA.

USEPA Office of Emergency and Remedial Response (2009). Environmental Response Comprehensive and Liability Information System database (CERCLIS 3).

Viraraghavan T., Subramanian K.S., and Aruldoss J.A. (1999). "Arsenic in Drinking Water: Problems and Solutions." Water Science and Technology, **40**(2), 69-76.