PILOT-TESTING AN ION EXCHANGE TECHNOLOGY FOR SELECTIVE AND REGENERATIVE ARSENATE REMOVAL AND AN ENGINEERED APPROACH FOR STABILIZING ARSENIC-LADEN PROCESS WASTE RESIDUALS

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PILOT-TESTING AN ION EXCHANGE TECHNOLOGY FOR SELECTIVE AND REGENERATIVE ARSENIC REMOVAL AND AN ENGINEERED APPROACH FOR STABILIZING ARSENIC-LADEN PROCESS WASTE RESIDUALS

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Date of Graduation

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Chunhui Luo, son of Zhiping Luo and Xiaoying Lai, was born in Longnan City, Jiangxi Province, China on March 14, 1980. He received a B.S. and a M.S. degree of Environmental Engineering in 2001 and 2004, respectively, both from Dong Hua University (former China Textile University) in Shanghai, China. After graduation, he served as Laboratory Team Leader in Engelhard Environmental Technologies, Inc. (now BASF Catalyst LLC) for one year. Starting from August 2006, He has been pursuing his graduate degree at Auburn University.

THESIS ABSTRACT

PILOT-TESTING AN ION EXCHANGE TECHNOLOGY FOR SELECTIVE AND REGENERATIVE ARSENIC REMOVAL AND AN ENGINEERED APPROACH FOR STABILIZING ARSENIC-LADEN PROCESS WASTE RESIDUALS

Chunhui Luo

Master of Science, December 19, 2008
(M. S. Donghua University, China, 2004)
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Directed by Dongye Zhao

Pilot-scale tests of a regenerable and selective polymeric ligand exchanger (PLE) were conducted to remove As(V) at the well field of El Paso Water Utilities (EPWU) in El Paso, TX, USA. The PLE was prepared by immobilizing Cu(II) onto a commercially available chelating resin of a uniform particle size of ~0.41 mm. For a period of three months, we tested the breakthrough behaviors of fresh and regenerated PLE for removal of arsenate in a pilot-scale column configuration and under various operating conditions (empty bed contact time (EBCT) and column size) and raw water characteristics (pH). Column runs were also carried out to study the PLE's performance under conditions of the NSF international standard 53 arsenic challenge water (NSF, 2006). The results confirmed that the PLE's affinity for various anions follows the sequence: $HAsO_4^{2-}$

>>HCO_3^->SO_4^{2-}>Cl^-. The PLE bed can be regenerated efficiently using 6-8% (w/w) NaCl at pH 9.0, and more than 90% of As(V) recovery can be repeatedly achieved within ~25 BV's of regeneration with the brine, and the same spent brine can be reused for multiple runs with only pH adjustment. The regeneration was controlled by bicarbonate, which was completely eluted with ~10 BV's of the regenerant, indicating the level of groundwater alkalinity can be an important factor for the process design. Lowering the influent water pH from 8.3 to 6.5 increased the treatment capacity by 30%, confirming that slightly acidic pH is more favorable for arsenic removal. When the influent As(V) was increased from 50 to 300 μg/L, the treatment capacity was nearly proportionally decreased from 3000 BVs to 500 BVs. Mass balance calculation of copper eluted from the PLE column indicated that the copper leakage per operation cycle (saturation and regeneration) was less than 0.077% of the total copper loaded in the resin. The selective and regenerable ligand exchange process may serve as a viable alternative to remove trace levels of arsenate from drinking water.

The arsenic-laden process waste residues can be effectively stabilized using either ferric chloride or iron-based nanoparticles at Fe/As ratio of 10-20, pH in the range of 6-8. The stabilized sludge can pass leaching tests (either TCLP or WET) after sufficient air drying period (~2 weeks) and the resulted sludge would not be characterized as hazardous wastes.

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Style manual or journal used Water Research

Computer software used Microsoft Word & Excel 2003; SigmaPlot 8.0.

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CHAPTER 1. INTRODUCTION

1.1 Overview

Arsenic in groundwater has emerged as a global problem due to the toxicity and the potential health effects of arsenic. Naturally occurring arsenic in groundwater has been reported in 21 countries exceeding the World Health Organization (WHO) guideline of 10 μg/L (Mohan and Pittman, 2007). Triggered by the risk concern of arsenic contamination, the US EPA lowered the maximum contamination level (MCL) for arsenic in drinking water from 50 to 10 μg/L, effective in January, 2006.

Arsenate (As(V)) and arsenite (As(III)) are the most common species of arsenic in natural waters (Edwards, 1994). The occurrence of natural arsenic in groundwater is usually associated with weathered volcanic rocks, sedimentary rocks of marine origin, fossil fuels, geothermal areas, and mineral deposits (Korte and Fernando, 1991). Arsenic speciation in aquatic systems is dependent upon pH, redox potential, co-ions, the presence of Fe(II/III), dissolved organic matter (DOM), and microbial activity (Ferguson, 1972; Smedley, 2002; Islam, 2004). Arsenite is commonly present in natural waters as a neutral molecule $As(OH)_3$ (pKa_1=9.2), while arsenate is present as anions, $H_2AsO_4^-$ and $HAsO_4^{2-}$ (pKa_2=6.9) (Dean, 1979). This difference in the oxidation states results in disparate sorption affinities, and is the basis for anion exchange methods that separate As(III) and As(V).

In recent years, a number of technologies have been tested at the pilot- or full-scale to meet the 10 ppb MCL. Brandhuber and Amy (1998) pilot-tested reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) membranes for arsenic removal at a California utility, and they observed that RO membrane exhibited the highest (>95%) arsenic rejection. Chwirka et al. (2004) pilot-tested a coagulation/microfiltration (C/MF) technique, and showed that microfiltration membranes can be effectively used to remove As with the addition of ferric chloride. Arora et al. (2007) demonstrated that a coagulation/filtration (C/F) process with a ferric chloride dose of 3.75 mg/L and a hydraulic loading rate of 8 gpm/ft^2 was able to the acceptable effluent arsenic levels. Khandaker et al. (2005) carried out field tests at Well 15 located at Kirtland Air Force Base, Albuquerque, New Mexico, to evaluate the performance of two arsenic removal media, ferric coated activated alumina and granular ferric hydroxide and showed that both media were able to meet the tightened MCL. Lytle et al. (2007) demonstrated a microbial filtration technique at an Ohio treatment plant, where natural bacteria concentrated in the filters were able to oxidize As(III). Siegel et al. (2007) pilot-tested five commercial adsorptive media under ambient flow conditions, including granular ferric oxides, titanium oxide, and ion exchange (IX) resin impregnated with iron oxide nanoparticles and a zirconium oxide. They observed that the sorption performances of the different media depended on the physical and chemical nature of the media and the test methodology. As current technologies are still rapidly evolving, the following general challenges remain: a) it is hard to meet the new MCL cost effectively; b) costly pre-treatment or pH adjustments are often required; c) current sorbent sot ion exchange media lack selectivity for arsenic, especially in the presence of competing anions; d) frequent regeneration or replacement of sorbents is required; And e) large volumes of As-laden process residuals are produced.

Ion exchange has been currently an EPA-identified best available technology (BAT) for removal of As(V) (EPA, 2000a). However, standard ion exchangers have been held back by their poor selectivity, and thus, low sorption capacity for arsenate. To overcome this limitation, a arsenic-selective resin, known as polymeric ligand exchanger (PLE), was tested by An et al. (2005). Based on their extensive bench-scale column investigations, An et al. (2005) reported that the PLE was able to treat ~8,000 bed volumes (BVs) of typical arsenic-containing water before breakthrough at 10μg/L. It also observed that the PLE was amenable to highly efficient regeneration with brine and can be reused for multiple cycles of operations.

1.2 Objetives

This study aimed to pilot-test this PLE-based ion exchange process to acquire information essential for field applications of the technology. The specific objectives were to: 1) demonstrate the effectiveness of the PLE process for arsenate removal with a pilot-scale column system and under various conditions of As(V)-laden field water and modified groundwater, including the NSF international standard 53 arsenic challenge water (NSF, 2006); 2) Pilot-test the regeneration efficiency of arsenate-laden PLE under various conditions; 3) Pilot-test the effects of various field operating conditions (pH, flowrate, and TDS) and 4) Develop an engineering approach for treating exhausted regenerant brine and stabilizing arsenic-laden process waste residues. The pilot tests were carried out at the well field of El Paso Water Utilities (EPWU), which has been tremendously impacted by the recent tightening of the arsenic MCL rule.

1.3 Summary of Following Chapters

The thesis consists of three major parts. Part I (chapters 2 and 3) provides the background and research premise. Part II (chapters 4-7) presents details on the pilot-scale testing. In the last part, Chapters 8 and 9 provide scale up analysis & cost estimation and conclusions & future research recommendations, respectively.

Chapter 2 gives the master plan and field groundwater quality at the pilot testing site, Well 303 in EPWU. All the testing equipment and materials are listed. In addition, we provide analytical methods used for various water quality parameters. Chapter 3 presents detailed procedures for preparation of PLE and experimental setup. In particular, we constructed a mobile and stand alone ion exchange system for the pilot scale testing. Hydraulic head loss testing through the PLE bed was performed using a small column.

In Chapter 4, we conducted a series of preliminary pilot scale testing of the PLE technology and obtained important information necessary to finalize our experimental protocols for the field tests at the site of EPWU. Various recipes of As(V)-laden synthetic groundwater are used in this stage. Chapter 5 focuses on initial setup of the testing facilities and demonstration of pilot operations. At this stage, two column runs were conducted under different bed heights and flowrate using the actual contaminated groundwater from Well 303 at the EPWU site. Chapter 6 continues the pilot-scale field tests under various operating conditions outlined in our master plan. Finally, in Chapter 7 we confirmed the effect of brine pH on the PLE's regeneration efficiency and determined the optimal conditions and processes for treating the exhausted arsenic-laden regenerant brine used for regenerating the PLE.

In order to dertermine the cost impacts of arsenic treatment using PLE, a full process design was developed in Chapter 8. A cost estimate was prepared based on this design scheme. Finally, Chapter 9 summerizes the conclusions of this research.

CHAPTER 2. MASTER PLANNING AND FIELD GROUNDWATER QUALITY

The primary objective for the work in this stage was to plan and prepare for the pilot tests at a field site in El Paso, TX. Major activities include: 1) Designing an ion exchange (IX) testing system for the proposed pilot-scale experiments; 2) Assembling the major pieces of equipment and materials; and 3) Carrying out a comprehensive water quality analysis of raw water samples from three wells at the testing site. Experimental details and main results are summarized as follows.

2.1 Design of the experimental set-up

The objectives of this sub-task are to 1) finalize treatment schematic, 2) size the treatment units for the experiments, and 3) select equipments.

Figure 2-1 shows the proposed schematic for the pilot experiments. Based on our prior bench scale results, we assumed an empty bed contact time (EBCT) of 4-8 minutes for service runs and up to 30 minutes for regeneration runs.

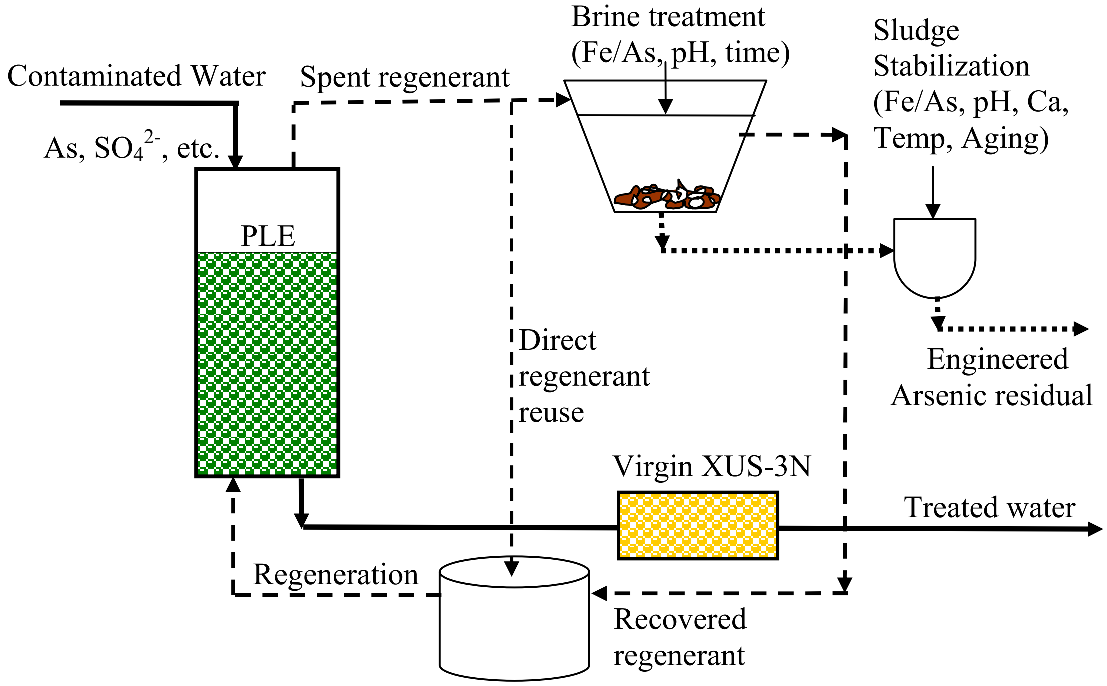


Figure 2.1. A schematic of the proposed IX technology for selective removal of arsenic from drinking water with engineered treatment of spent brine and sludge stabilization.

An ion exchange vessel of 0.8 ft×2 ft (inner diameter D× length L) with adjustable headspace was constructed, which was to be filled with up to ~1 ft^3 (bulk volume) of a PLE for the experiments. A peristaltic pump with adjustable flow rate (up to 10 L/min) was used for feeding the column during service runs. Another peristaltic pump with a lower flowrate (up to 2.3 L/min) was used for regeneration uses. An on-line pH meter will be placed at the exit to monitor the product water pH. In addition, a smaller column 0.4 ft×0.5 ft (D×L) was connected right after the pH probe. Virgin (no copper loaded) XUS 3N at ~10% of the XUS 3N-Cu in the primary column was packed in the column. The small column serves for two purposes: 1) to trap any possible copper leaked from the primary column over long runs; and 2) to quantify copper leakage as a function of time and water quality parameters. Over long runs (months to years), when the virgin XUS 3N is saturated by copper, a new XUS 3N-Cu is made online, which can be used to supplement the capacity drop in the primary PLE column. The column set up will be operated in the down flow mode; however, the system can be operated in both down and up flow modes.

2.2 Equipment, materias and supplies

We are grateful that DOW Chemical volunteered to provide us with 1 ft^3 XUS 3N resin with no charge for this pilot test, which allows us for more column runs.

Table 2-1 shows the list of all the testing equipment purchased, and **Table 2-2** lists major chemicals or ion exchange resins obtained to date. All other chemicals were purchased from Fisher Scientific, USA.

Table 2-1. Major equipment or facilities for the pilot experiments

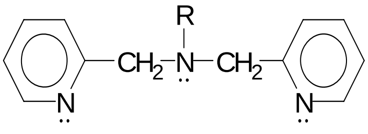
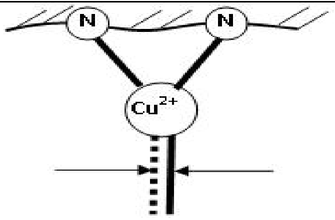
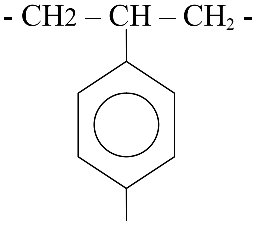
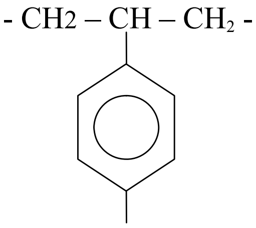
No.	Item	Manufacturer	Note
1	AP85 pH/Conductivity Meter	Fisher Scientific, Fair Law, NJ	
2	pH/CON510 Bench Meter	Oakton Instruments, Williston, VT	
3	Tank CYL W/CV-SPGT	Fisher Scientific, Fair Law, NJ	55 Gallon
4	Tank CYL W/CV-SPGT	Fisher Scientific, Fair Law, NJ	35 Gallon
5	FPU500 Peristaltic Pump	Omega Engineering, Inc., Stamford, CT	
6	FPU5-MT Pump Motor	Omega Engineering, Inc., Stamford, CT	
7	Vial AMB W/TFE 40mL	Fisher Scientific, Fair Law, NJ	72/Cs
8	Bottle NM HDPE 20oz	Fisher Scientific, Fair Law, NJ	12/PK×16

Table 2-2. Major chemicals or materials purchased for the pilot experiments

No.	Item	Manufacturer	Note
1	Sodium Chloride (Certified ACS)	Fisher Scientific, Fair Law, NJ	10kg
2	Sodium Hydroxide (certified ACS)	Fisher Scientific, Fair Law, NJ	5kg
3	Copper (II) Chloride Dihydate	Fisher Scientific, Fair Law, NJ	3kg
4	XUS 3N	Dow Chemical, Midland, MI	1 ft^3
5	DOW 3N	Dow Chemical, Midland, MI	0.5 ft^3

Two commercial chelating IX resins were obtained from DOW Chemical (Midland, MI, USA). Accordingly, two PLE's are prepared by loading Cu^{2+} ions onto these resins. Table 2-3 provides key properties of the resin matrices.

Table 2-3. Salient properties of ion exchange resins used in this study

Sorbent	DOW 3N or XFS 4195	XUS 3N or XUS 43578	DOW 3N-Cu	XUS 3N-Cu
Manufacturer	DOW Chemical, Midland, MI, USA		Copper-loaded XUS 3N	
Functional Group				
Matrix (R or R')	 - CH2 – CH – CH_2 - Polystyrene, Macroporous		 - CH2 – CH – CH_2 - Polystyrene, Macroporous	
Particle Size (mm)	0.2-1.2[a]	0.41[a]	N/A	N/A
BulkDensity (lbs/ft^3)	42[a]	43.1	45.5	47.3
Capacity (meg/g-dry)	2.61 (copper form)	3.04 (copper form)	N/A	N/A

[a]From the manufacture's manual, other information was taken from our lab data.

2.3 Water quality analysis

To gain updated information on the water quality at the target test site, water samples from three wells (Well 303, Well 308, and UVWTP) of the El Paso Water Utilities were shipped within 24 hours to Auburn University and analyzed for a number of key water quality parameters. **Table 2-4** gives the well water quality data for Well 303 (the targeted well for the pilot experiments) provided by our host El Paso Water Utilities based on their long-term water quality monitoring. For comparison, **Table 2-5** summarizes the resultant water quality based on our laboratory data. (Note: Data are given as mean of triplicates ± Standard Error except SC, Ca, and Mg which are single measurements).

Table 2-4. Prior water quality data for Well 303, El Paso Water Utilities (01/27/1998-11/01/2004 Average)

Unit	As (mean±SD)	Copper (mean±SD)	Iron (mean±SD)	Phosphate (mean±SD)	pH (mean±SD)
(mg/L)	0.0309±0.0058	0.13±0.32	0.082±0.19	0.0708±0.093	8.28±0.42
	NO_3-N	SO_4^{2-}	Turbidity	Alkalinity	Hardness
(mg/L)	0.20±0.16	87.65±5.52	0.13±0.058	63.80±0.26	35.10±13.01
	Cl^-	SiO_2	TDS		
(mg/L)	44.3±4.93	7.5±8.5	343±22		

Source: (El Paso Water Utilities, El Paso, TX)

Table 2-5. Key water quality data from three wells at the El Paso site

Parameter	Well 303	Well 308	UVWTP
Arsenic, Total (ppb)	27.65 ± 1.85	20.16 ± 2.90	17.54 ± 0.42
Copper, Total (ppb)	7.3 ± 0.3	<5	<5
Chloride (mg/L)	51.9 ± 0.6	252.0 ± 2.0	114.0 ± 2.0
Fluoride (mg/L)	0.98 ± 0.01	0.27 ± 0.04	0.56 ± 0.01
Iron (mg/L)	0.303 ± 0.003	0.006 ± 0.005	<0.006
Sodium (mg/L)	96.99 ± 1.57	253.4 ± 0.97	138.7 ± 1.76
Nitrate as N (mg/L)	Not detected	Not detected	Not detected
Ortho-phosphate as PO_4^{3-} (mg/L)	Not detected	Not detected	Not detected
pH	8.82 ± 0.02	7.89 ± 0.04	8.58 ± 0.02
SiO_3^{2-}	24.90 ± 0.17	25.02 ± 0.09	25.00 ± 0.08
Sulfate (mg/L)	127.6 ± 3.8	329.0 ± 5.0	149.0 ± 3.0
TDS	337	1074	565
TOC (mg/L)	0.93 ± 0.05	2.76 ± 0.04	1.22 ± 0.05
DO (mg/L)	7.5 ± 0.1	7.7 ± 0.2	7.8 ± 0.1
SC (µs/cm)	519	1653	869
Total alkalinity (mg/L)	64 ± 0.0	155 ± 0.0	72 ± 0.0
Calcium (mg/L)	11.2	93.8	24.4
Magnesium (mg/L)	0.22	10.5	1.4
Turbidity (NTU)	0.31 ± 0.00	16.98 ± 0.00	0.10 ± 0.00
Hardness(mg/L as $CaCO_3$)	46 ± 0.0	252 ± 0.0	68 ± 0.0

2.4 QC procederes and analytical methods

Water samples from the three wells were collected and shipped immediately to the environmental engineering laboratory at Auburn University, and stored at 4 ^{o}C before the analyses. Chemicals of analytical reagent grade or higher were used for all analytical purposes. All data were obtained by analyzing triplicate samples and are reported as mean± standard deviation (SD).

Table 2-6 gives a list of major analytical instruments. **Table 2-7** summarizes various standard analytical methods that were employed for various water quality parameters.

Table 2-4. Major analytical instruments used for chemical analysis

No.	Item	Manufacturer	Note
1	pH/CON510 Bench Meter	Oakton Instruments, Williston, VT	
2	2100AN laboratory turbidimeter	Hach Company, Loveland, CO	
3	3110 Atomic Absorption Spectrometer	Perkin Elmer, Waltham, MA	HGA-600 graphite furnace and EDL
4	DX-120 ion chromatograph	Dionex, Sunnyvale, CA	IonPac AS14 column; IonPac CS12A column
5	AB30 conductivity meter	Fisher Scientific, Fair Law, NJ	
6	PHOENIX 8000 TOC analyzer	UF – PERC, Gainesville, FL	
7	Spectr AA 220FS	Varian Inc., Palo Alto, CA	

Table 2-5. Analytical methods used for various water quality parameters

Parameter	Instrumentation	EPA Method	SM (20th Ed.)	Others
Arsenic, Tot		200.9	3113 B	
Arsenite	AA; Furnace		3500-As B	
Arsenate			3500-As B	
Copper	AA; Furnace		3113 B	
Chloride	Ion Chromatography	300.0; 300.1		
Sulfate	Ion Chromatography		4110 B	
Fluoride	Ion Chromatography	300.0; 300.1		
Iron	AA; Flame	7380		
Sodium	AA; Flame		3111 B	
Ca, Mg	Ion Chromatography			See a)
Nitrate	Ion Chromatography		4110 B	
Ortho-PO_4^{3-}	Ion Chromatography		4110 B	
pH	Electrometric			See b)
SC				See c)
TDS				See d)
TOC				See e)
DO				See f)
Alkalinity			2320 B	
Turbidity				See g)
Silica	Colorimetric, Molybdate Blue			I-1700-85
Hardness		215.1; 242.1		

* Water sample was collected on August 28, 2006; Water sample was delivered to our environmental engineering lab on August 29, 2006.

a). Cation analysis: Sodium, calcium and magnesium were analyzed using a DX-120 ion chromatograph (IC) equipped with an IonPac CS12A column. All of the samples were first filtered using 0.45 μm syringe filters before being injected to the IC.

b). pH measurement: An ORION 520A pH meter was used in this experiment. The pH meter was calibrated using pH 4.0, pH 7.0 and pH 10.0 buffer solutions.

c). Specific Conductance (SC) testing: An ACCUMET AB 30 conductivity meter was used for measuring water conductivity. The meter was calibrated with a 1000 µs/cm KCl solution.

d) TDS: The calculation used is: TDS = SC × 0.65. Where, TDS = total dissolved solids in mg/L; SC = specific conductance (temperature corrected) in µs/cm.

e). TOC: A PHOENIX 8000 TOC analyzer was used for TOC measurements.

f). DO: A model YSI 57 Dissolved Oxygen Meter was used for the DO measurements. (Note: Water samples were shipped from site to our lab, the DO values reported may not reflect the real time DO levels, which will be re-measured during our field tests)

g). Turbidity: A model 2100AN Laboratory turbidity meter was used for measuring turbidity. A HACH turbidity standard kit was used to standard the turbidity meter.

CHAPTER 3. PREPARATION OF THE PLE AND EXPERIMENTAL SETUP

Our work in this stage focused on design, construction and test operation of the experimental setup. Major task include: 1) Preparing the polymeric ligand exchanger, PLE or XUS 3N-Cu; 2) Constructing the pilot test setup including ion exchange columns, pumps and plumbing; 3) Carrying out some test runs; 4) Developing a standard curve for measuring the hydraulic head loss as a function of flow rate through the PLE bed. Detailed experimental procedures and main results are summarized as follows.

3.1 Preparation of the PLE

About 0.8 ft^3 of Cu (II)-loaded PLE was prepared based on the commercially available chelating resin XUS-3N. **Figure 3-1** shows a photograph of the original XUS 3N resin received from Dow Chemical Company, Midland, MI, USA.

Figure 3-1. The parent chelating resin XUS 3N (1 ft^3) received from Dow Chemical.

The raw XUS resin was first conditioned according to the following procedure: First, rinse the resin once to remove any residual impurities from the manufacturing process using 5% (v/v) methanol solution and at a resin-to-solution ratio of 1 g/100 mL. Then, thoroughly rinse the resin using plenty of deionized (DI) water. Then, the resin was treated with 1 N HCl solution for 4 hours at a resin-to-solution ratio of 1 g/100 mL. Then, rinse the resin thoroughly again with plenty of DI water. Finally, the resin was treated with 1N NaOH solution for 4 hours and at a resin-to-solution ratio of 1 g/100 mL. The treated XUS 3N is in its free base form and is ready for Cu(II) loading.

The copper(II) loaded PLE or XUS 3N-Cu was then prepared by loading Cu(II) onto the conditioned XUS 3N resin following the protocols below. First, the resin was added in a solution containing ~1,000 mg/L Cu(II) at pH 4.0-4.5, and equilibrated under shaking (**Figure 3-2**) for two weeks. The resin-to-solution ratio was approximately 1 g: 200 mL. To enhance copper loading, the resin-solution mixture was intermittently heated at 70 °C for ~4 hours (**Figure 3-3**) every other day and then placed back at ambient temperature (~21 °C). The mild heating is expected to swell the resin matrix, and thus, favors the Cu(II) loading. Nitrogen gas was blown in the solution during heating to avoid oxidation damage of the resin. During the loading, the high concentration of Cu(II) was maintained by intermittent addition of $CuCl_2$ in the solution. Upon Cu(II) loading, the resin color turned to blue-green (**Figure 3-4**). The copper-loaded PLE was either thoroughly rinsed using DI water and air dried, or remained soaked in Cu(II) solution for future uses.

Figure 3-2. Loading Cu(II) onto XUS 3N under shaking.

Figure 3-3. Heating the resin-Cu(II) solution In a water bath during copper loading.

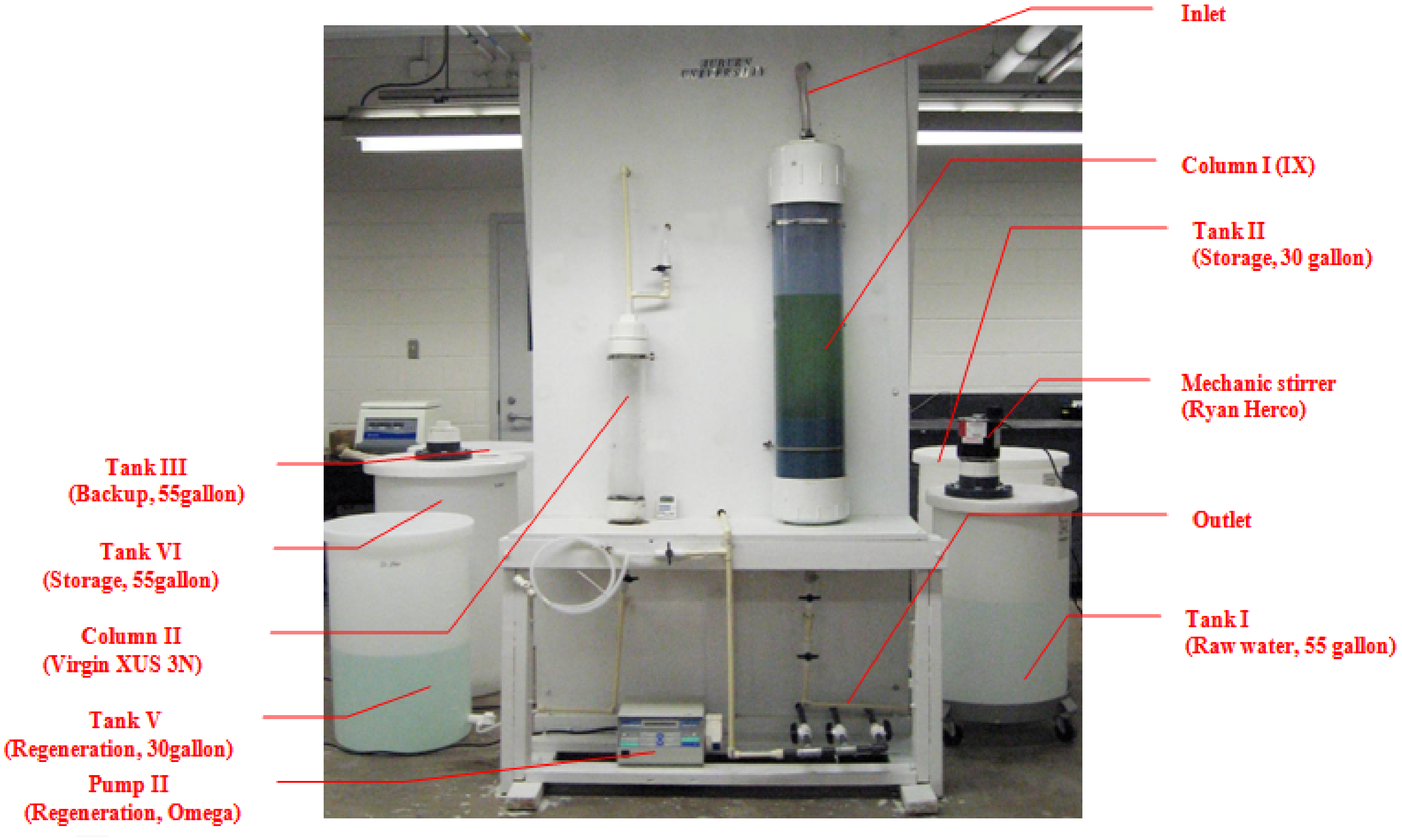
(a) **(b)**

Figure 3-4. Conditioned parent chelating resin XUS 3N (**a**) and the resultant copper-loaded PLE, XUS 3N-Cu (**b**).

To determine the maximum Cu capacity of XUS 3N-Cu, 50 mL of ~6% (w/w) of ammonia solution was mixed with 0.1 g of XUS 3N-Cu (under shaking) for ~2 hours to completely desorb Cu(II) from the PLE. The extracted solution was analyzed using a Flame AA and the Cu capacity for the PLE was determined to b e 97.2 ± 0.5 mg/g resin, which is close to the value of maximum Cu-loading capacity (95 mg/g) provided by the manufacturer.

3.2 Construction of the Pilot-Test Setup

A mobile and stand alone experimental test system was built on a 2x4 (mxm) wood board. The key components of the test setup includes a primary ion exchange column, a service run pump, a regeneration run pump, a secondary small column, various containers, a mechanical stirrer, and tubing. **Figure 3-5** shows the details of the pilot-test setup.


Inlet
Column I (IX)
Tank II
(Storage, 30 gallon)
Mechanic stirrer
(Ryan Herco)
Outlet
Tank I
(Raw water, 55 gallon)
Tank III
(Backup, 55gallon)
Tank VI
(Storage, 55gallon)
Column II
(Virgin XUS 3N)
Tank V
(Regeneration, 30gallon)
Pump II
(Regeneration, Omega)

(a)

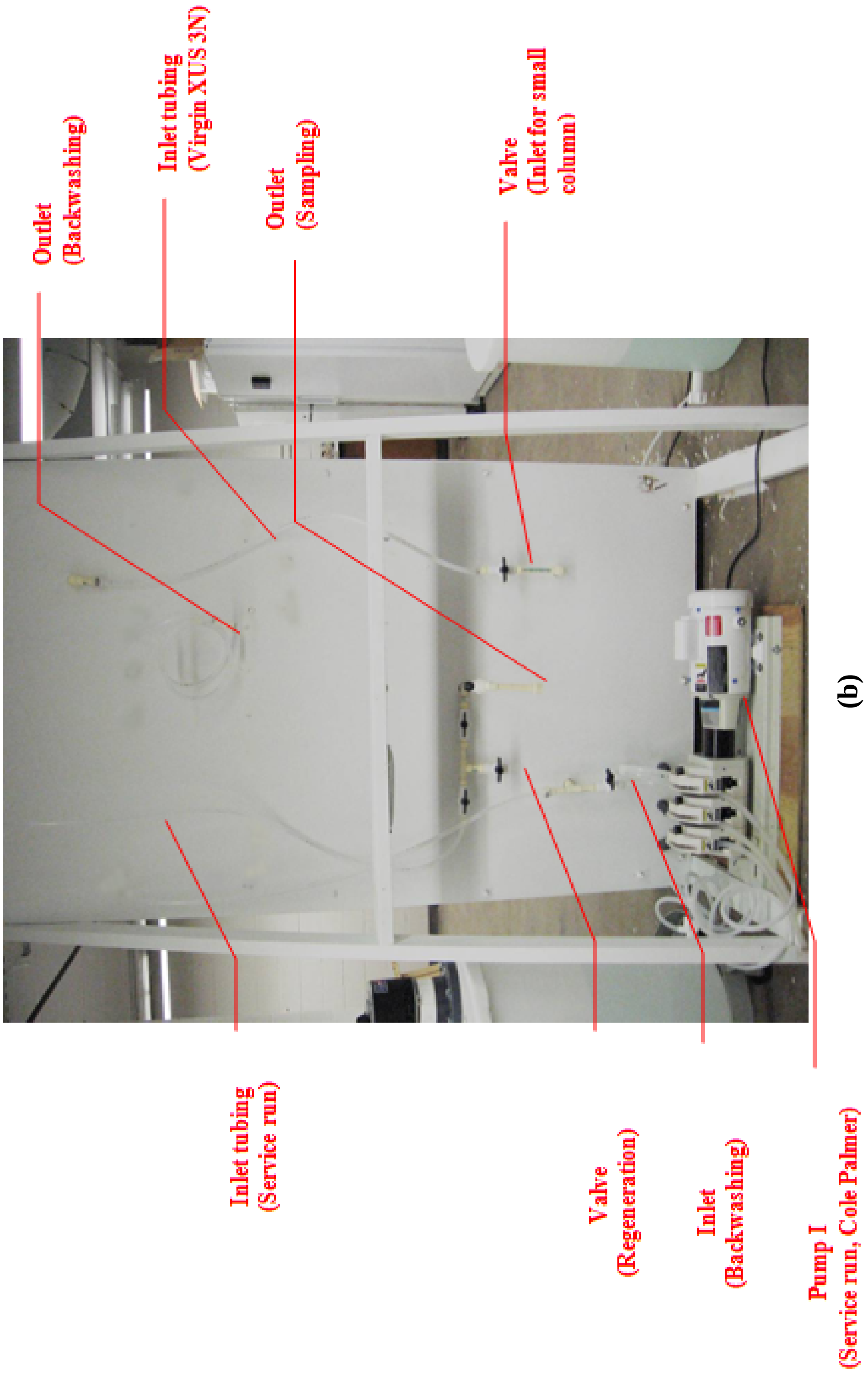


Figure 3-5. A front view **(a)** and rear view **(b)** of pilot test setup.

Pump I (Cole Palmer, USA) is a three-channel peristaltic pump. Each channel generates a fixed flow rate of 2.2 L/min. Thus, three levels of flow rates (2.2, 4.4, and 6.6 L/min) can be achieved by use of a ball valve and according to the desired empty bed contact time (EBCT) of 10 min, 5 min, and 3 min, or a superficial liquid velocity (SLV) of 4.0m/h, 8.0m/h, and 12.0m/h, respectively. Pump II (Omega, USA) is a variable-speed peristaltic pump, which serves for the regeneration uses. It can deliver flow rates in the range of 0.2-2.3 L/min.

Each inlet line is equipped with a filter screen, which consists of a fine woven polypropylene mesh (0.0159" or 0.04cm opening, McMaster, USA) to remove larger (>0.4 mm) objects in the influent. A precision woven polypropylene mesh (0.0083" or 0.021cm opening, McMaster, USA) is placed at the inlet as well as the outlet of the column to support the resin bed or to prevent larger particles from entering into the column. In addition, a layer of glass wool is also placed on top of the resin bed to facilitate even distribution of the influent water. The column was designed to be operated in the downflow mode.

In addition, a smaller (2x0.33, ftxft, LxD) PVC column was constructed. This small column is placed right after the primary PLE column to catch any Cu(II) possibly leaked during the operations. Virgin XUS 3N of ~10% of the XUS 3N-Cu bed will be placed in the small column.

Tank I is to store the influent water contaminated with arsenate. In addition to the planned field experiments, some test runs were conducted in the lab using NSF standard 53 arsenic challenge water (NSF, 2006). For the field tests, raw well water was first aerated by stirring to convert As(V) to As(III) before it is introduced into the PLE column.

Tank VI is to store and treat spent regenerant brine, which will minimize the volume and arsenic leachability of the process waste residuals, and allows for reuse of the treated brine. Tank V is used for regeneration purpose, in which fresh and/or recovered regenerants are stored.

Two primary ion exchange columns (4x0.67 ftxft, length (L) x inner diameter (D)) were assembled using clear polyvinyl chloride columns (CPVC) (only one column is shown in **Figure 3-5**). **Figure 3-6** shows a close up of the IX columns and its dimensions.

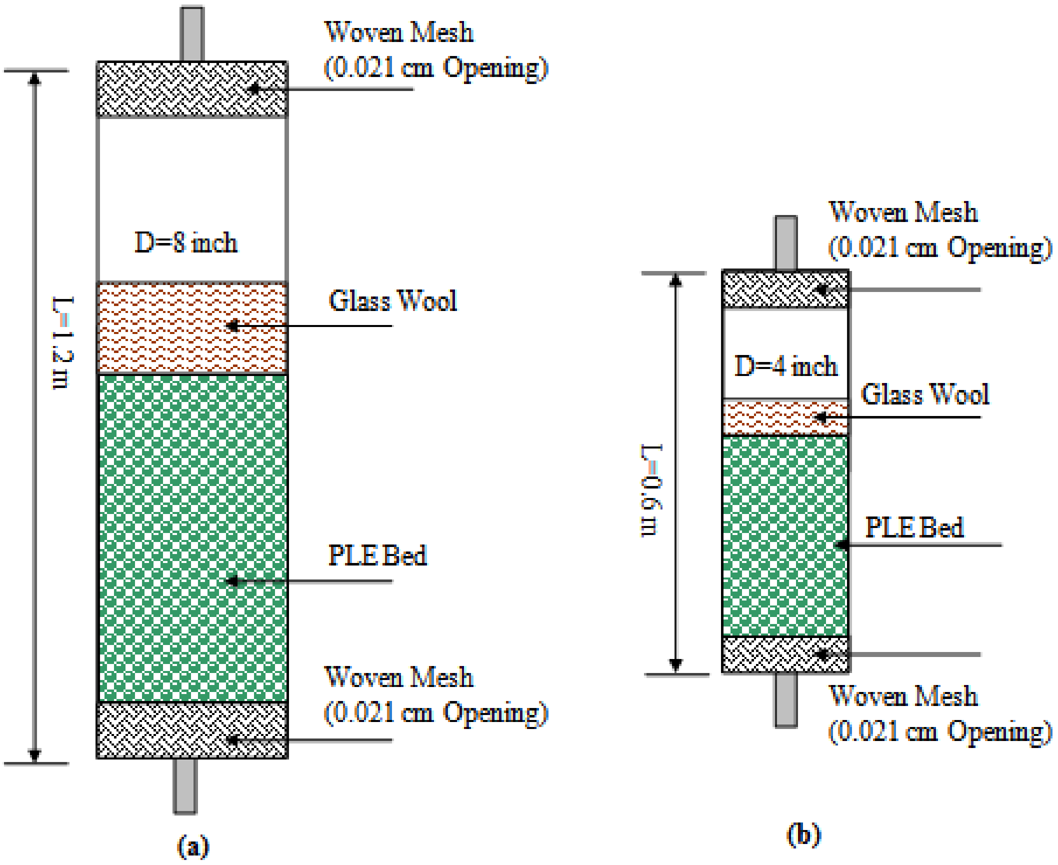


Figure 3-6. A close up of the 8-inch PLE column (a) and the 4-inch PLE column (b).

Based on the constructed mobile and stand alone experimental test system, **Figure 3-7** shows the schematic of a whole pilot test system.

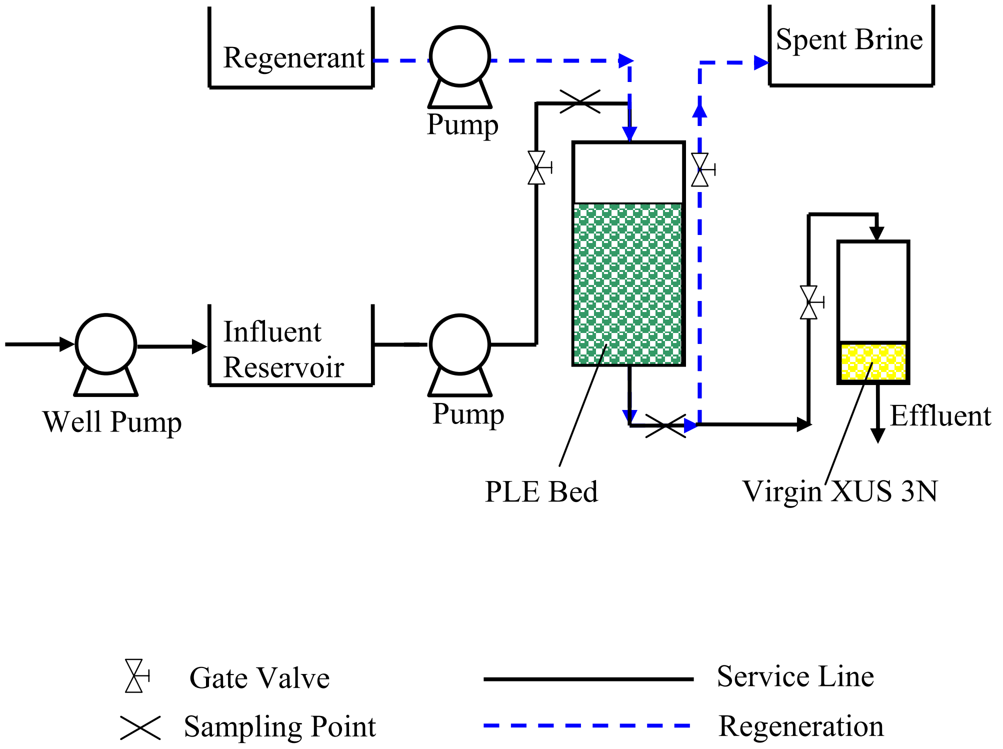


Figure 3-7. Schematic of the pilot-scale ion exchange system.

3.3 Hydraulic Head Loss through the PLE Bed

Hydraulic head loss through ion exchange media is an important parameter in practical applications. To determine the head loss as a function of the superficial liquid velocity (SLV), a series of laboratory scale experiments were conducted using a small column (2ftx0.33ft, LxD) over a broad range of SLV (0.28-5.8 m/h). **Figure 3-8** shows an overview of the experimental setup for measuring the head loss. Hydraulic head loss was measured in duplicate. DI water was introduced by a peristaltic pump (Omega, USA) at a flowrate ranging from 38 mL/min to 2,200 mL/min. A digital differential pressure gauge with reading precision of 2% was used to measure the pressure difference between the inlet (point A) and outlet (point B).

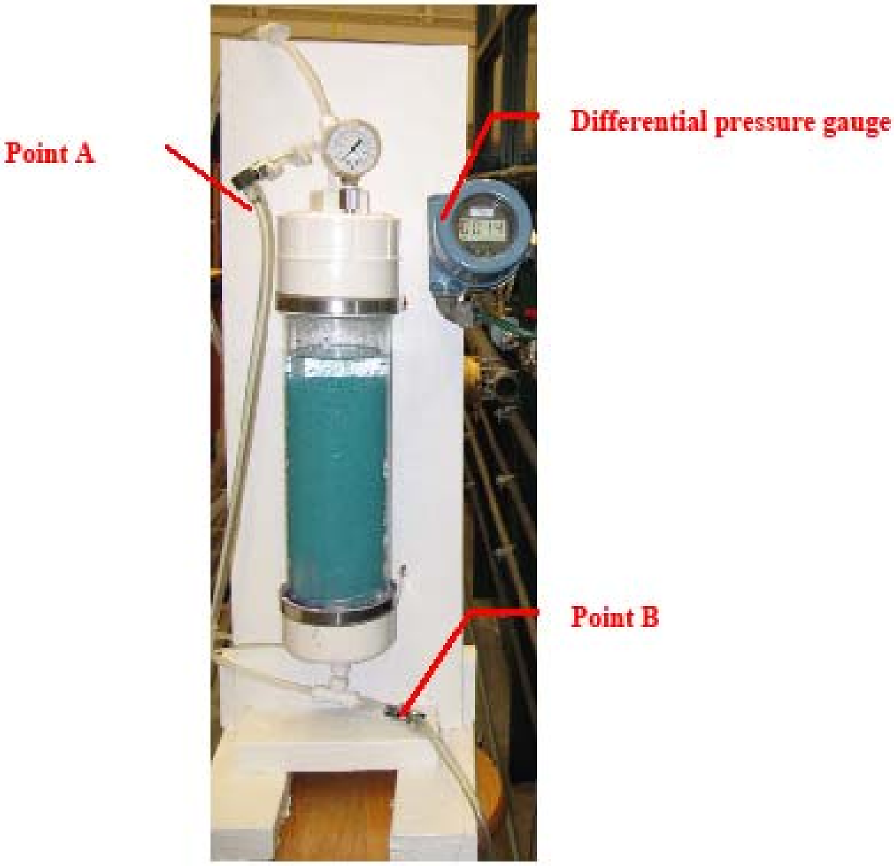


Figure 3-8. Experimental setup for measuring hydraulic head loss through the PLE bed.

CHAPTER 4. PRELIMINARY PILOT SCALE TESTING OF THE PLE TECHNOLOGY

The primary objective for the work in this stage was to preliminarily test the pilot-scale experimental setup for both service and regeneration runs under various operating conditions. These testing runs provided important information on the mechanical durability of the setup, breakthrough behaviors, and operating times under a given set of influent water compositions. The information is important for us to finalize our experimental protocols for the upcoming field experiments at the site of El Paso Water Utilities (EPWU).

Major activities for this quarter include: 1) Conducting two column runs for As(V) removal using various recipes of As(V)-laden synthetic groundwater, including the NSF international standard 53 arsenic challenge water (NSF, 2006), and simulated groundwater based on the water quality data from the intended pilot test site at El Paso Water Utilities (EPWU); 2) Carrying out one regeneration run and tested the regeneration efficiency; and 3) Developing and testing a simple approach to convert As(III) to As(V) in water. Detailed experimental procedures and main results are summarized as follows.

4.1 Methods and procedures

4.1.1 Preparation of synthetic water

In an effort to compare the arsenic removal performance of various media materials, NSF/ANSI 53 (NSF, 2006) prescribed two sets of influent water recipes, where the influent As(V) concentration was set at 50 μg/L and 300 μg/L, respectively, but both targeting at an effluent concentration of 10 μg/L.

In our preliminary tests, two types of NSF standard waters were prepared with a local tap water from Auburn, AL. In addition, we prepared simulated water based on the water quality data (Well 303, EPWU, El Paso, TX). **Table 4-1** gives the water quality data for the tap water used for preparing the test water.

Table 4-1. Water quality data for tap water of Auburn, AL

Primary Detected Contaminants			
Contaminant	MCL	Amount Detected	
Bacteriological			
Turbidity	TT	0-0.16	NTU
Inorganic Chemicals			
Barium	2	0.00-0.053	mg/L
Copper	AL=1.3	0-1.3	mg/L
Fluoride	4	0-0.67	mg/L
Lead	AL=15	0-3.00	μg/L
Nitrate	10	0-0.12	mg/L
Nitrite	1	0.00-0.01	mg/L

Organic Chemicals			
Chlorine	4 MRDL	0.55-2.4	mg/L
TOC	TT	1.79-5.57	mg/L
Other Detected Constituents/Contaminants			
Aluminum	-	0-0.073	µg/L
Calcium	-	0-17.8	mg/L
Sodium	-	0-1.65	mg/L
Iron	300	0-0.021	µg/L
Hardness	-	47.7-64	mg/L
Magnesium	-	0-2.73	mg/L
Alkalinity	-	21-24	mg/L
Carbon Dioxide	-	0.4-18.7	mg/L
pH	-	6-8.01	-
TDS	500	0-111	mg/L
Chloride	250	0-7.5	mg/L
Sulfate	250	16.89-27.6	mg/L

Tables 4-2 and 4-3 give the characteristics of the two NSF/ANSI challenge waters prepared for our tests. Each of the water was prepared at pH 6.5 and pH 8.3, respectively.

Table 4-2. Influent and effluent concentrations of As(V) for NSF/ANSI challenge waters

Substance	Influent challenge (mg/L)	Maximum effluent concentration (mg/L)	Method	Compounds
As (V)	0.050 ± 0.005	0.010	GFAA	$Na_2HAsO_4{\cdot}7H_2O$
As (V)	0.30 ± 0.03	0.010	GFAA	$Na_2HAsO_4{\cdot}7H_2O$

Table 4-3. Background compositions for the synthetic NSF/ANSI challenge waters

Cation	Cation Concentration		Anion	Anion Concentration	
	meq/L	mg/L		meq/L	mg/L
Na^+	3.197	73.5	HCO_3^-	3.00	183.0
Ca^{2+}	2.00	40.0	SO_4^{2-}	1.00	48.0
Mg^{2+}	1.00	12.0	Cl^-	2.00	71.0*
			NO_3^--N	0.143	2.0
			F^-	0.053	1.0
			PO_4^{3-}-P	0.0013	0.04
			SiO_3^{2-}	0.33	24.9
Total	6.237	126.2	Total	6.237	326.8

*According to prescribed challenge water, the chloride concentration is 71.0 mg/L.

However, HCl (1M) was used to adjust the pH of the synthetic water to pH 6.5, which results in higher chloride content (107 mg/L) used in our tests.

In each batch, 200 liters of synthetic water were prepared in a 55-gallon tank. The dissolution of chemicals followed the procedures below.

a) Dissolve 18.6g sodium silicate ($Na_2SiO_3{\cdot}9H_2O$) in tap water. Stir and transfer the solution to the test tank to achieve a test tank concentration of 93 mg/L $Na_2SiO_3{\cdot}9H_2O$.

b) Dissolve 50.0g sodium bicarbonate ($NaHCO_3$) in DI water. Stir and transfer the solution to the test tank to achieve a test tank concentration 250 mg/L $NaHCO_3$.

c) Adjust the pH of the test tank solution using hydrochloric acid (HCl) to 6.5 ± 0.25 for the low pH test.

d) Separately dissolve 25.6g magnesium sulfate ($MgSO_4{\cdot}7H_2O$), 2.4g sodium nitrate ($NaNO_3$),and 0.44g sodium fluoride (NaF) in tap water to achieve test tank concentrations of 128 mg/L, 12 mg/L, and 2.2 mg/L respectively.

e) Dissolve 0.036g sodium phosphate ($NaH_2PO_4{\cdot}H_2O$) in tap water. Stir and transfer the solution to the test tank to achieve a test tank concentration of 0.18 mg/L $NaH_2PO_4{\cdot}H_2O$.

f) Dissolve 22.2g calcium chloride ($CaCl_2$) in tap water. Stir and transfer the solution to the test tank to achieve a test tank concentration of 111 mg/L $CaCl_2$.

g) Adjust the pH of the test tank solution using hydrochloric acid (HCl) to 6.5 ± 0.25 for the low pH test.

h) Dissolve sodium arsenate ($Na_2HAsO_4{\cdot}7H_2O$) in DI water prior to addition to the test tank. For the lower level challenge, 0.0100g sodium arsenate ($Na_2HAsO_4{\cdot}7H_2O$) was added to achieve a test tank concentration of 50 µg/L sodium arsenate. For the higher level challenge, 0.0600g sodium arsenate ($Na_2HAsO_4{\cdot}7H_2O$) was added to achieve a test tank concentration of 300 µg/L sodium arsenate.

i) Adjust the pH of the test tank solution using hydrochloric acid (HCl) to 6.5 ±

0.1 for the final pH of the test tank.

The resultant solutions were then stirred for ~10 hours, and then, the pH and concentrations of all chemicals in the solutions were confirmed through laboratory analysis. No further mixing was performed thereafter and during the tests. All the challenge waters were used within 24 hours.

In addition, a simulated field groundwater was prepared based on the water quality data from the intended pilot test site of El Paso Water Utilities (EPWU). **Tables 4-4** gives the background compositions of the simulated groundwater. Both As(III) and As(V) were included in this water, each accounting for 50% of the total As of 30 µg/L (i.e. As(III) = As(V) = 15 µg/L).

Table 4-4. Background compositions for a simulated EPWU well water

Cation	Cation Concentration		Anion	Anion Concentration	
	meq/L	mg/L		meq/L	mg/L
Na^+	4.46	102.5	SO_4^{2-}	2.67	128.0
Ca^{2+}	1.47	29.3	Cl^-	2.73	52.0*
			F^-	0.05	1.0
			NO_3^--N	0.14	2.0
			PO_4^{3-}-P	0.001	0.04
			SiO_3^{2-}	0.33	24.9
Total	5.93	131.8	Total	5.93	203.0

In each batch, 200 liters of simulated groundwater were prepared in a 55-gallon tank. The dissolution of chemicals followed the procedures below.

a) Dissolve 18.6g sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) in tap water. Stir and transfer the solution to the test tank to achieve a test tank concentration of 93 mg/L $Na_2SiO_3 \cdot 9H_2O$.

b) Adjust the pH of the test tank solution using hydrochloric acid (HCl) to 8.3 ± 0.25 for the low pH test.

c) Separately dissolve 37.9g sodium sulfate (Na_2SO_4), 2.4g sodium nitrate ($NaNO_3$), and 0.44g sodium fluoride (NaF) in tap water to achieve test tank concentrations of 189mg/L, 12 mg/L, and 2.2 mg/L respectively.

d) Dissolve 0.036g sodium phosphate ($NaH_2PO_4 \cdot H_2O$) in tap water. Stir and transfer the solution to the test tank to achieve a test tank concentration of 0.18 mg/L $NaH_2PO_4 \cdot H_2O$.

e) Dissolve 11.9g calcium chloride ($CaCl_2$) in tap water. Stir and transfer the solution to the test tank to achieve a test tank concentration of 81 mg/L $CaCl_2$.

f) Adjust the pH of the test tank solution using hydrochloric acid (HCl) to 8.3 ± 0.25 for the low pH test.

g) Dissolve sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and sodium arsenite ($NaAsO_2$) in DI water prior to addition to the test tank. 0.063g sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) was added to achieve a test tank concentration of 15 μg/L as As(V). In the mean time, 0.0052g sodium arsenite ($NaAsO_2$) was added to achieve a test tank concentration of 15 μg/L as As(III).

h) Adjust the pH of the test tank solution using hydrochloric acid (HCl) to 8.3 ±

0.1 for the final pH of the test tank.

The resultant solution was stirred for ~10 hours, and the chemical compositions confirmed through laboratory analysis. The stable solution was then used within 24 hours.

4.1.2 Column runs for As removal

The key components of the test setup include an ion exchange column (2 x 0.33 ftxft, length (L) x inner diameter (D)), a peristaltic pump (Omega, USA), various containers, and a mechanical stirrer (Ryan Herco, USA). Precision woven polypropylene mesh (McMaster, USA) was placed at the inlet as well as the outlet of the column to support the resin bed or to prevent larger particles from entering into the column. In addition, a layer of glass wool was also placed on top of the resin bed to facilitate even distribution of the influent water. The column was operated in the downflow mode during the exhaustion runs.

For the higher-tier NSF challenge water (300 μg/L as As(V)), ~0.8 liter of XUS 3N-Cu was packed in the column, which gave a bed height of 10 cm, or an EBCT of 4.0 min and SLV of 0.15 m/hr. For the lower-tier NSF challenge water (50 μg/L as As(V)), ~1.6 liter of XUS 3N-Cu was packed in the column to give a bed height of 20 cm, which translated to an EBCT of 8.0 min and SLV of 0.15 m/hr. For each run, synthetic water was pumped through the fixed PLE bed at a flowrate of 200 mL/min. Influent water in each water tank (55-gallon) was prepared and replaced every 15 hours. Breakthrough curves of arsenic and other primary components chloride, bicarbonate, sulfate, and pH) were followed in each run until arsenic breakthrough (i.e. when As exceeded 10 μg/L) occurred.

4.1.3 Regeneration

Regeneration of an arsenate-saturated XUS 3N-Cu bed was carried out in the same fixed-bed configuration. Based on our prior bench-scale work on regeneration of arsenate-saturated DOW 3N-Cu (the resin similar to XUS 3N-Cu used here), more than 96% of sorbed arsenate was recovered using 4% (w/w) NaCl at pH 9.1 within 22 bed volumes of the regenerants (An et al., 2005). To preliminarily test the effectiveness, we used ~25 bed volumes of 6% (w/w) NaCl at pH 9.1 as the regenerant to treat the arsenate-saturated XUS 3N-Cu.

Before regeneration, an exhausted bed was rinsed using DI water for ~25-30 bed volumes with water in the headspace removed. Then the regenerant was pumped through the bed at an EBCT equal to that as in the respective service runs (i.e. 4 min for the higher tier water and 8.0 min for the lower tier water). After regeneration, the bed was briefly rinsed (10 BVs) using DI water and reused for another service run.

4.1.4 Oxidation of As(III) to As(V)

Since XUS 3N-Cu does not remove As(III) effectively, pre-oxidation is needed to convert As(III) to As(V) before the PLE treatment if elevated concentrations of As(III) are present. From an economic view point, it is desired to convert As(III) to As(V) by dissolved oxygen provided the reaction kinetics is acceptable. In a simple way, this may be achieved by storing the groundwater in a clear well for some extended times (under stirring if needed) and expose the water to air. To test the oxidation rate, conversion of As(III) to As(V) was monitored with the 200 liters of simulated field water (EPWU) in a 55-gallon water tank equipped with a flange-mount mixer (1/3 HP, operated at 1725 RPM) for a 7-day period. The range of DO during the oxidation process was 7.7-8.9 mg/L, and pH of the solution remained in the range of 7.9-8.5 during the experiments.

Chemical analysis

Water samples from the test runs were collected manually and analyzed immediately in our laboratory. Chemicals of analytical reagent grade or higher were used for all analytical purposes. Both arsenic species was analyzed using a Perkin Elmer Atomic Adsorption Spectrophotometer, which has a detection limit of 3µg/L as As. To separate As(III) and As(V), raw water samples were first treated with a known amount of the same PLE at a PLE-to-solution ratio of 1g-to-10mL for 2 hours, which was able to completely remove As(V) from the samples, while leaving intact As(III) species. Raw or treated groundwater samples were collected in 60-mL polypropylene bottles and preserved with 0.0005M of EDTA and 0.01M HAc. The addition of the reagents reduced the pH of the groundwater samples to ~3.5. All samples were analyzed within two days. The concentration of As(V) was determined from the difference between the total arsenic and As(III) remaining in the sample. Bicarbonate was analyzed with a UV-Persulfate TOC Analyzer (Phoenix 8000).

4.2 Results and Discussion

Arsenic breakthrough curves

Figure 4-1 shows the breakthrough histories of arsenate with the two tiers of NSF/ANSI 53 challenge waters during two separate columns run using XUS 3N-Cu. **Figure 4-1a** shows breakthrough histories of arsenate and other anions with the high-tier NSF challenge water (300 μg/L As(V)), whereas **Figure 4-1b** shows breakthrough histories of arsenate and other co-ions with the low-tier NSF challenge water (50 μg/L as As(V)). It suggests that the NSF/ANSI prescribed water, especially the high-tier challenge water, gives rather unfavorable conditions to XUS 3N-Cu. Based on our prior bench-scale studies, the PLE is highly resistant to sulfate competition, and its arsenic selectivity is discounted more severely by the presence of high concentrations of bicarbonate. However, this NSF/ANSI water prescribed an unusually high concentration of bicarbonate (~180 mg/L) but much lower sulfate content (~50 mg/L). As a result, the advantage of the PLE was not well utilized. Nonetheless, the resin was able to remove As to below 10 μg/L for more than 3000 bed volumes of the low tier influent water per service run.

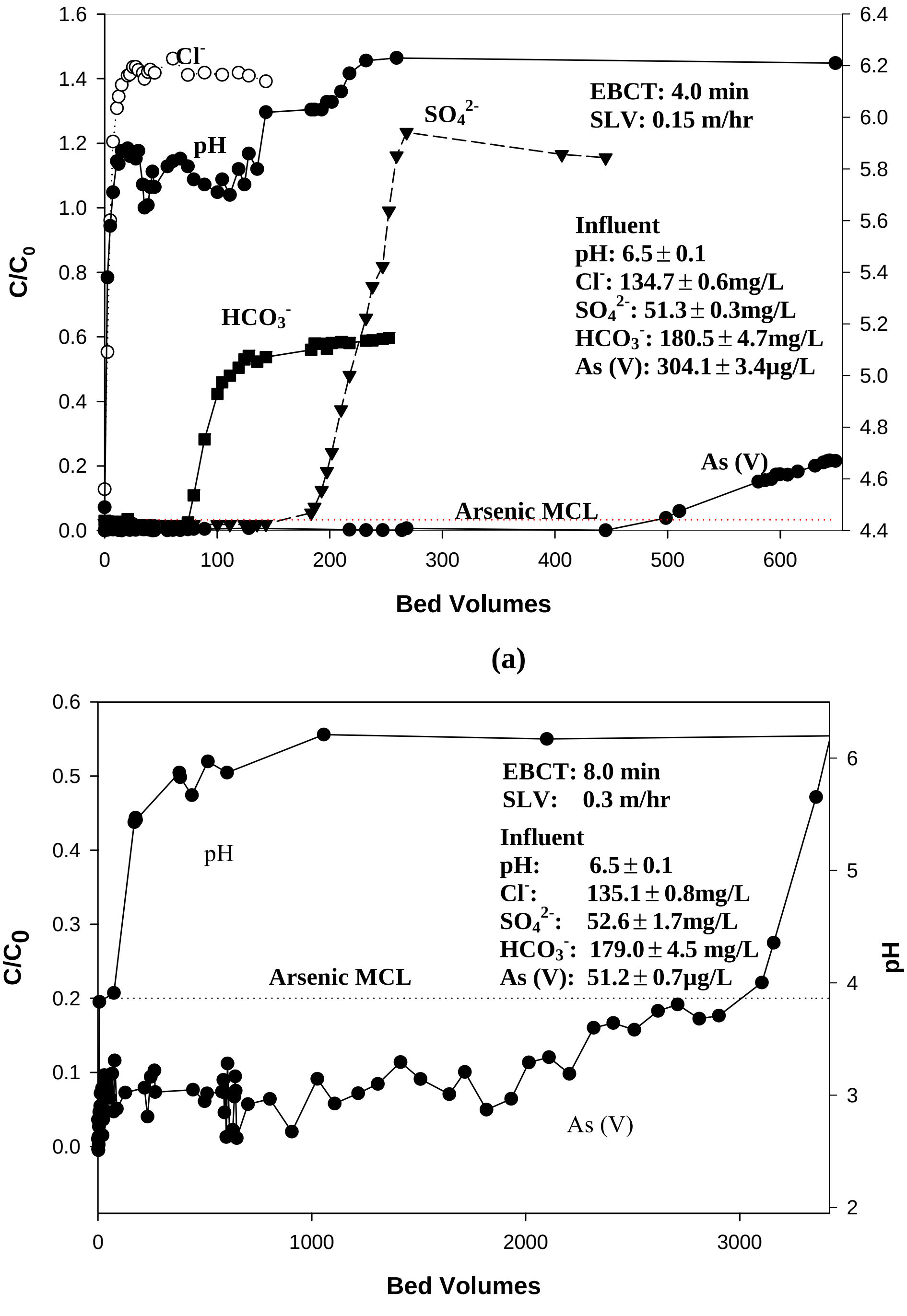


Figure 4-1. Breakthrough histories of arsenate and competing anions under the conditions of the NSF/ANSI 53 challenge waters (**a**. high tier arsenic, and **b**. low tier arsenic) during column runs using a polymeric ligand exchanger, XUS 3N-Cu, at pH 6.5

Figure 4-2 presents two breakthrough curves of As(V) under the high-tier NSF/ANSI 53 water conditions during two consecutive column runs and one breakthrough curve with the low-tier NSF water during a subsequent run with the same regenerated resin. The regeneration was carried out using ~15 BVs of 6% NaCl (pH=9.0; EBCT=30 min). For the high-tier water, breakthrough took place at ~500 BVs, and the two breakthrough curves nearly coincided. This observation indicates that the resin regeneration was rather complete. **Figure 4-2** also shows that when the influent As was lowered from 300 to 50 μg/L, the treatment capacity was nearly proportionally increased by a factor of 6, despite the two times shorter EBCT. It should be noted that compared to the water quality conditions studied by An et al. (2005), the NSF/ANSI water (especially the high tier water) presents rather unfavorable conditions to XUS 3N-Cu because of the presence of the unusually high concentration of bicarbonate (~180 mg/L). Based on our previous bench-scale tests, the PLE is highly resistant to sulfate competition, which offers an unprecedented advantage over commercial standard IX resins that favor sulfate over arsenate. However, the PLE's arsenic selectivity can be discounted more severely by the presence of high concentrations of bicarbonate. Therefore, the unique advantage of PLE can be best utilized when influent water is low in alkalinity and/or high in sulfate content. Apparently, this is not the case for this NSF/ANSI challenge water, which is high in bicarbonate (~180 mg/L) but low in sulfate (~50 mg/L). Nonetheless, the pilot-test results confirmed that the resin was able to remove As(V) to below 10μg/L for more than 3000 bed volumes of the low-tier influent water per service run. This treatment capacity is more than 5 times greater than standard IX resins.

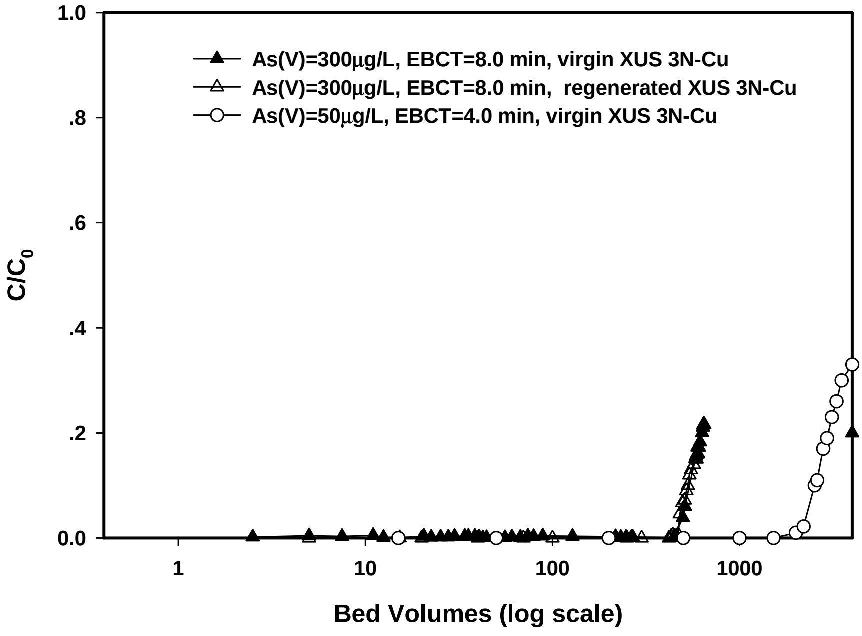


Figure 4-2. Breakthrough histories of arsenic(V) under the conditions of high- and low-tier NSF/ANSI 53 challenge waters during column runs (0.1-m column; pH=6.5) using virgin or regenerated XUS 3N-Cu (High-tier water: As(V) = 300µg/L; EBCT = 8.0 min Low-tier water: As(V) = 50µg/L; EBCT = 4.0 min).

Conversion of As(III) to As(V)

Figure 4-3 shows the change of trivalent arsenic concentration over time in the simulated field water under stirring. Evidently, the oxidation of As (III) by air is a rather slow process (half life > 7 days). Within two days, the conversion was <5% (from 14.5 to 13.8 µg/L). At Day 7, ~39% As(III) was transformed to As(V). Therefore, in case that high concentration of As(III) is present, extended exposure may be needed to fully convert As(III) to As(V) before the PLE treatment, or additional oxidizing units may be employed to speed up the conversion.

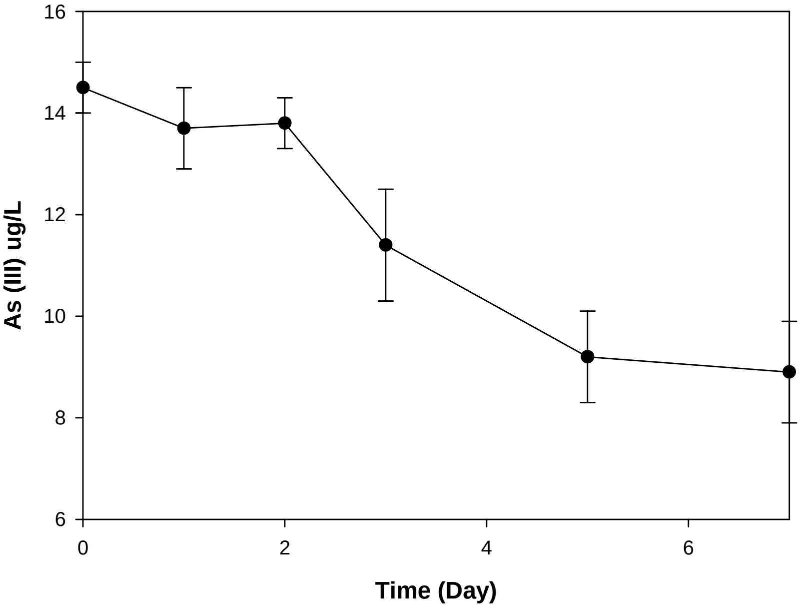


Figure 4-3. The concentration of As(III) remaining in simulated EPWU well water when the water was exposed to air and under stirring.

CHAPTER 5. PILOT SCALE FIELD TESTING OF THE PLE TECHNOLOGY-PART I

The primary objective in this stage of work was to carry out the pilot-scale field tests under various operating conditions at the site of El Paso Water Utilities (EPWU).

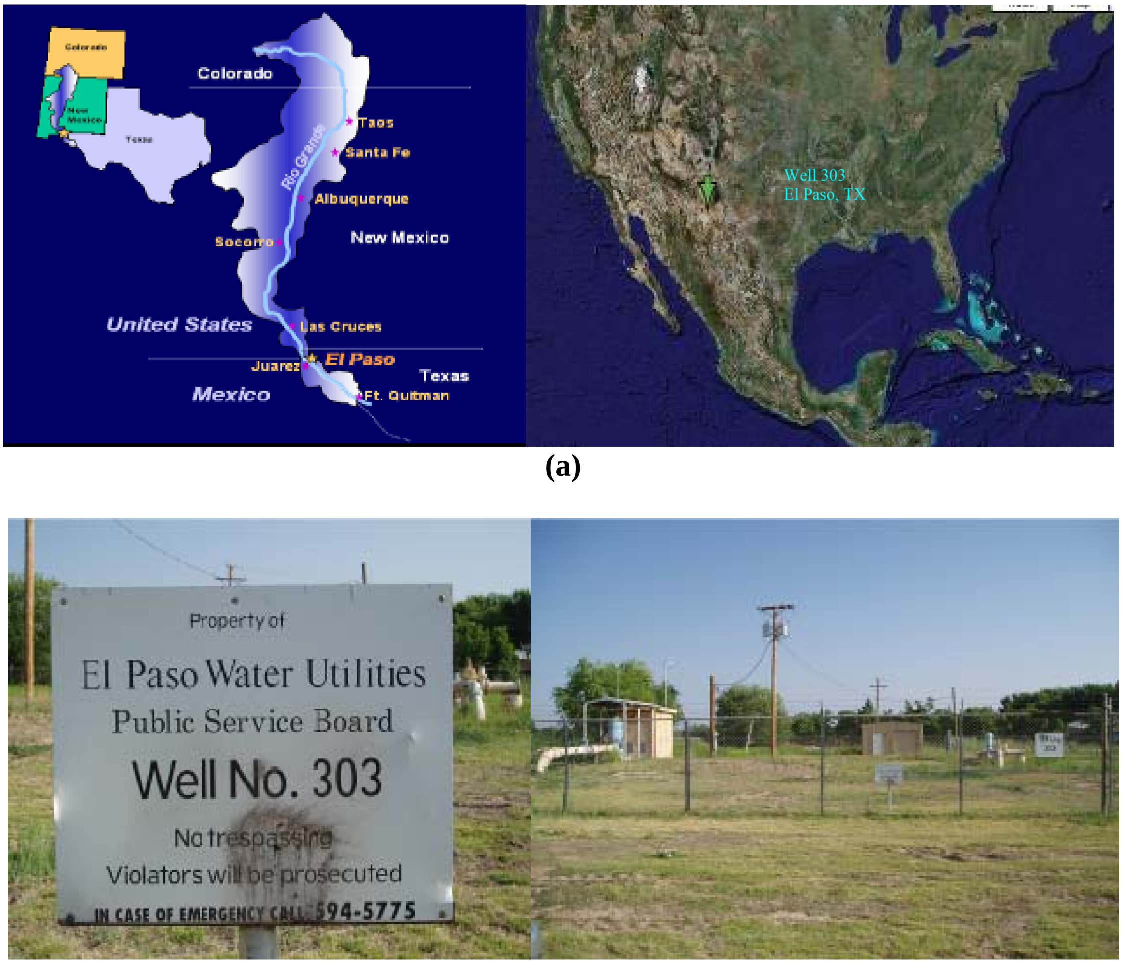
Major activities include: 1) Transportation, installation and test operation of the pilot-testing setup at the proposed field testing site; and 2) Carrying out two column runs under different bed heights and flowrates using the actual contaminated groundwater from Well 303 at the EPWU site. Detailed experimental procedures and main results are summarized as follows.

5.1 Methods and Procedures

5.1.1 Site Description

The pilot study was conducted at Well 303 in El Paso, TX which is capable of producing ~1,500 gallons per minute (gpm) of groundwater. Prior to beginning the pilot study, a wastewater storage tank was constructed, which has a dimension 12 x 9 x 3 ft, length (L) x width (W) x depth (H)) to temporarily store the effluent water from the ion exchange columns. A discharge permit was obtained with El Paso Water Utilities

(EPWU) and under the EPA 40 CFR part 403 for industrial discharge. Power supply (120 V, 20 amps) was also installed by the EPWU. A well pump was used to pump the groundwater out to the surface storage tanks, where water was exposed to air for 15 h before it was further pumped into the PLE columns. The pilot equipment was housed in a framed metal building. The building, a pump house, an electrical supply room, and the wastewater pond were secured within a 100-foot chain link fence. **Figures 5-1** positions the site location and a bird's-eye view for the pilot units.



(a)

(b)

Figure 5-1. Global position of the pilot-test site at El Paso Water Utilities **(a)** and an outlook of pilot testing site, Well 303 **(b)**.

Initial set-up of the testing facilities

As shown in **Figure 5-2**, water for the pilot test units was obtained from a well. EPWU installed a coupling and a valve so that water could be withdrawn for the pilot study. The pilot units utilized PVC Schedule 40 pipe and fittings for interconnections. The main pilot set-up were installed on a secured metal building (16x12x8 ftxftxft, length (L) x width (W) x Height (H)), which is located right behind the electricity supply room. A capacity of 1200 gallons of plastic water tank was used for the storage of tap water and was refilled as needed. Treated water and spent backwash water from ion exchange units were discharged to the wastewater pond via a manhole located on the east side of the metal building.

(a) **(b)**

Figure 5-2. Well pump with electricity supply room **(a)** and the metal building with a 1200-gallon water storage tank **(b)** at the pilot testing site, Well 303, EPWU.

As shown in **Figure 5-3,** two clear plastic swimming pools were used for raw water storage, each having a capacity of 1000 gallons. For the field tests, raw well water was first stored in the storage pools under gentle stirring before it is introduced into the PLE column. This practice may convert a fraction of the As(III) to As(V), and thus, favors the removal process. Raw water was then delivered via two variable-speed peristaltic pumps to the PLE columns.

(a) **(b)**

Figure 5-3. Raw water equalizing tanks (the swimming pools) **(a)** and the pilot test column set-up **(b)** at the pilot testing site, Well 303, EPWU.

5.1.2 Column runs for As removal

Two parallel column runs were carried out during this period, with the 8-in (large) column and the other with the 4-in (small) column. The column set-up was the same as in the previous lab design, and column breakthrough tests were conducted in the downflow mode. Prior to the tests, all PLE beds were briefly backwashed to remove any precipitates or suspended solids. Virgin XUS 3N of ~10% of the XUS 3N-Cu bed was placed in the small column (D = 4 inches) right after the primary 8-in PLE column to catch any Cu(II) possibly leaked during the operations. For the first round of the column test, the bed height for the large PLE column was fixed at 30 cm and the flowrate was set at 2.3L/min, which translates into an empty bed contact time (EBCT) of 4.0 min.

For comparison, a benchmark test was performed using the smaller column (D = 4 inches). In this case, the PLE bed height was fixed at 20 cm and flowrate was set at 400 mL/min, which corresponds to an EBCT of 4.0 min. In this case, PLE subjected to one regeneration (6% NaCl) was used. **Figure 5-4** displays setups of the two PLE columns used in the pilot tests.

In addition to the planned field experiments, one columne run was conducted in the field using oxidizing agents like hydrogen peroxides to speed up the conversion of As(III) to As(V). The treatment performance measured the arsenic removal capacity of XUS 3N-Cu under ambient conditions (pH = 8.3, room temperature: day time average 35 ^{o}C, night time average 21 ^{o}C, effluent water temperature = 22 – 33 ^{o}C). Additional column runs were carried out at an adjusted lower pH of 6.5 to determine the effect on arsenic removal capacity as a function of pH.

(a) **(b)**

Figure 5-4. The small column (D = 4 inches) set-up **(a)** and the primary column set-up **(b)** with the polymeric ligand exchanger, XUS 3N-Cu.

In this stage, regeneration test of the arsenate-saturated XUS 3N-Cu bed for the primary column was carried out in the same way as in the preliminary pilot-scale tests using NSF 53 challenge waters except that tap water was used for the regeneration in this case instead of DI water.

5.1.3 Schematic of the pilot test system

Figure 5-5 shows the schematic of the pilot test system, which was mounted on a 2x4 (mxm) wood board as a mobile and standalone treatment unit. The key components of this test setup include: 1) a primary ion exchange column (1.2x0.2 mxm, LxD), made from a 8-inch diameter PVC column; 2) a smaller (0.6x0.1, mxm, LxD), or the 4-inch diameter PVC column, which was placed right after the primary PLE column; 3) two service run pumps (Cole Parmer, Vernon Hills, Illinois, USA) and a pump for regeneration runs (Omega, Stamford, Connecticut, USA); and 4) a mechanical stirrer (Ryan Herco, Burbank, California, USA), various containers, and tubing. Precision woven polypropylene mesh (McMaster, Atlanta, GA, USA) was placed at the inlet as well as the outlet of the columns to support the resin bed. In addition, a layer of glass wool was also placed on top of the resin bed to facilitate even distribution of the influent water. Virgin XUS 3N of 10% of the primary PLE bed was placed in the 0.1-m column. This small column serves to trap any possible copper bleeding from the primary column over long runs, and thereby, quantify copper leakage as a function of time and water quality parameters. When the virgin XUS 3N is saturated by copper, a new XUS 3N-Cu is made, which can be used to supplement the capacity drop in the primary PLE column.

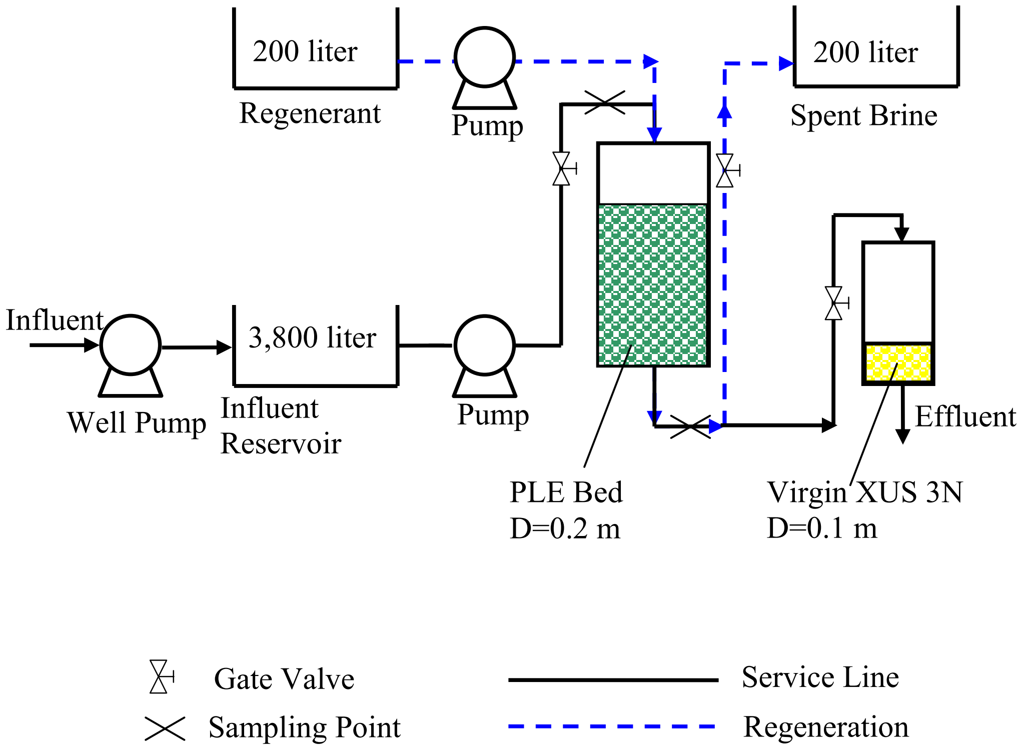


Figure 5-5. Schematic of the pilot-scale ion exchange system at Well 303, EPWU.

5.1.4 Water sampling

Both influent and effluent water samples were collected during the column runs and immediately (within a day) shipped back to Auburn for analysis. In most cases, sample analyses were conducted within one week. **Table 5-1** summarizes the key water quality parameters for the Capacity Verification Tests (CVT), which produces the operational and water quality data up through and beyond the defined arsenic breakthrough level (10 μg/L) for the PLE. Noted that the first sample was collected 10 minutes after startup, and subsequent samples were collected every two hours in the first two days. Besides the indicated field and laboratory parameters, flow rate was also monitored and calibrated twice daily during the testing period. Some modifications were made to this plan according to the actual operating conditions and practices.

Table 5-1. Water quality parameters and sampling frequency during the pilot tests

Parameter	Sampling frequency	Sampling location	Testing location
TDS	3 samples per day	Influent and Effluent	On-site in El Paso, TX
Temperature	Twice a day	Influent and Effluent	On-site in El Paso, TX
pH	Three times a day	Influent and Effluent	On-site in El Paso, TX
Arsenic	3 samples per day	Influent and Effluent	Auburn, AL
Bicarbonate	3 samples per day	Influent and Effluent	Auburn, AL
Chloride	3 samples per day	Influent and Effluent	Auburn, AL
Sulfate	3 samples per day	Influent and Effluent	Auburn, AL
Cu(II)	3 samples per day	Influent and Effluent	Auburn, AL

5.1.5 Sample preservation and on-site separation of As(III) and As(V)

Various methods for preserving As-laden field samples and for separating As(V) and As(III) species in water have been reported (Bednar, 2002, 2004; Gallagher et al. 2004; Samanta and Clifford, 2005, 2006; Kim et al. 2007). Generally, acids or combination of EDTA and acetic acid (HAc) has been used to preserve arsenite and arsenate species prior to analysis. Samanta et al. (2005) reported that the preserved water samples can maintain the same arsenic speciation in the laboratory for up to 85 days after collection with the EDTA-HAc method. Thus, the EDTA-HAc method was chosen to maintain the integrity of the samples before they were analyzed at Auburn. Raw water samples were collected in 60-mL polypropylene bottles with 0.0005 and 0.01M of EDTA and HAc, respectively. The reagents were mixed thoroughly by hand shaking. To separate As(III) and As(V) in the raw water samples, select water samples were first treated with a known amount of the PLE following the method we developed (See **Chapter 4**, page 36) immediately after sampling. The PLE was able to selectively remove completely As(V) from the samples, but is inert to As(III) species. Both preserved and treated waster samples were packed in a cooler and immediately shipped back to our environmental lab in Auburn, AL via UPS 2nd day shipping. The samples were then either analyzed immediately or kept in a refrigerator at 4 °C and analyzed within three days.

5.1.6 Chemical analysis

All of the chemicals were analyzed following the methods described in **Chapter 3** and **4**. For analysis of bicarbonate, we prepared new calibration solutions using sodium bicarbonate at pH 8.3 instead of using the commercial standard inorganic carbonate (IC) solutions. Our freshly prepared standards provided more accurate measurements for bicarbonate concentration in our water samples. Chemicals of analytical reagent grade or higher were used for all analytical purposes. All data were obtained by analyzing triplicate samples and are reported as mean ± standard deviation (SD).

5.2 Results and Discussion

Fixed bed testing of XUS 3N-Cu was studied at the pilot-scale for arsenic removal at

Well 303 of EPWU. This section provides the results of arsenic removal testing.

5.2.1 Pilot operations

The first round column runs (with the 8-inch column and the 4-inch column) last for 18 days, during which the flowrate was checked and corrected twice daily. The peristaltic pump tubing was switched or replaced every five days to maintain the constant flowrate, which appears to be a shorter life time than expected (The manufacturer recommended life time is ~400 hours). The average flowrate was 2.29 ± 0.09 L/min for the 8-inch column (EBCT= 4.2 min) and 368.0 ± 5 .0 mL/min for the 4-inch column (EBCT = 4.3 min). In both cases, the flowrate was fairly constant during the operations. **Figure 5-6** shows the flowrate histories for the two columns during the tests.

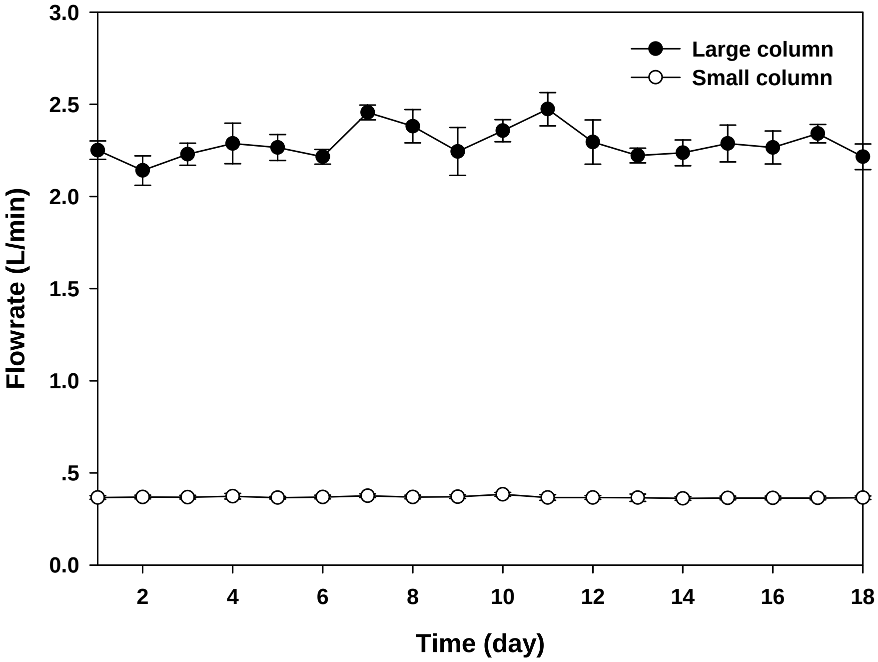


Figure 5-6. Flowrate histories for the two columns with polymeric ligand exchanger, XUS 3N-Cu during Part I pilot-test at Well 303, EPWU.

Change in pH of the influent and effluent

Both influent and effluent pH was monitored during operations, which provided important information on the water chemistry during the column runs. **Figure 5-6** shows the pH histories for the raw water (influent) and effluent for the two column runs. The pH value of the influent remained quite stable at an average of 8.30 ± 0.27 during the tests. However, based on long-term monitoring data provided from EPWU, the water pH of Well 303 fluctuated from 7.2 to 9.1 during the period of 1/27/1998-11/1/2004, suggesting that the pH in the groundwater aquifers is subject to seasonal changes. Thus, seasonal changes in the sources and fluxes of dissolved inorganic carbon (DIC) in groundwater need to be taken into account in the arsenic removal process. The effluent pH profiles for the columns showed an initial (<1200 BV) sharp drop followed by a gradual comeback. This pH drop can be attributed to a number of factors, including 1) direct uptake of OH^- ions by PLE, 2) removal of arsenate in the form of $HAsO_4^{2-}$ leading to release of H^+ ions, and 3) removal of alkalinity (bicarbonate and carbonate). In addition, the pH drop for the larger column was much more than that for the small column, which indicates that the fresh XUS 3N-Cu resin takes up more OH^- ions than the regenerated PLE.

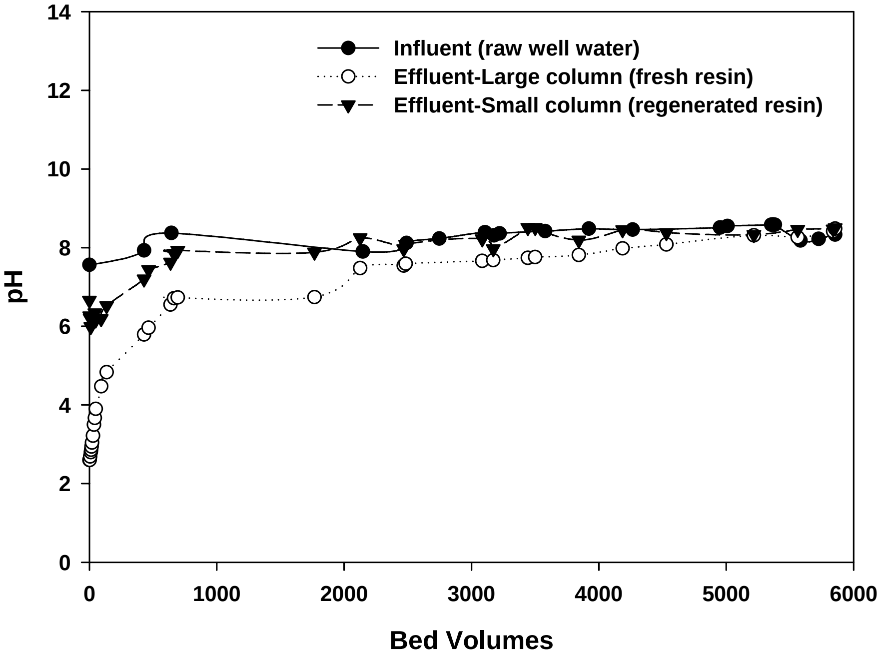


Figure 5-7. pH of influent/effluent during operations using polymeric ligand exchanger, XUS 3N-Cu in Part I pilot testing site, Well 303, EPWU

5.2.2 Removal of As(III) during the column runs

The EPWU influent water contains both As(III) and As(V). As the PLE is selective only to As(V), it is necessary to quantify the As(III) level in the influent during the column runs. To this end, As(V) from each sample was first completely removed by adding a known amount of PLE, and then the samples were analyzed for As(III). **Figure 5-7** shows the influent and effluent As(III) concentration histories during the column runs May-June, 2007. The influent level of As(III) was rather stable at 14.02 ± 2.12 µg/L. Although the PLE resin is known to be only selective to As(V), the As(III) concentration was also lowered upon the treatment. One mechanism for the removal can be that a fraction of As(III) was converted to As(V) in the column and subsequently taken up by the PLE. Our tests on raw water indicated that the half life of As(III) in the air is greater than 7 days, and less than 5% of As(III) was converted to As(V) in the first two days. Given the slow oxidation process, the rather appreciable removal of As(III) in **Figure 5-8** suggests that the copper-loaded PLE bed may be catalyzing the oxidative conversion of As(III) to As(V). The conversion of As(III) to As(V) was also evident from the fact that the actual amount of sorbed As(V) during the operations was greater than expected based on the influent concentrations.

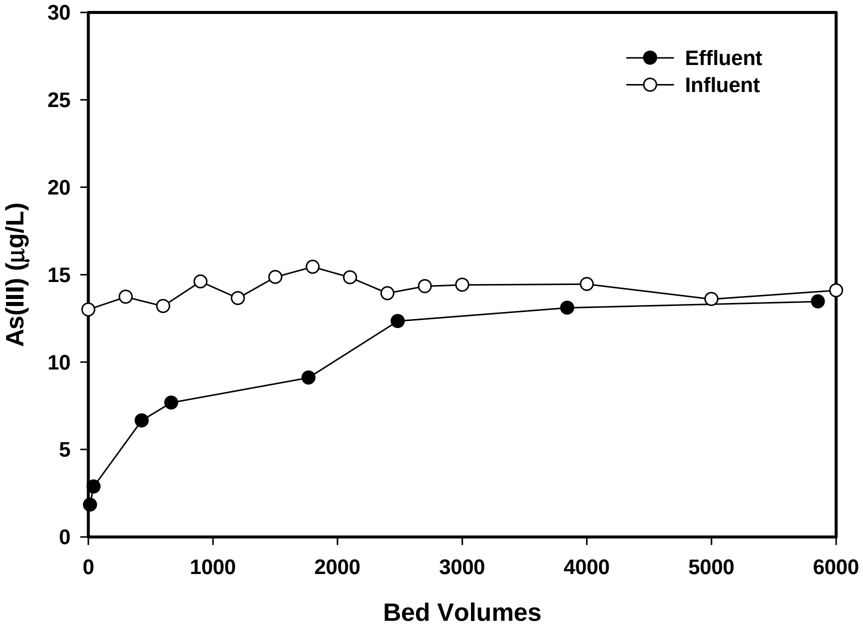


Figure 5-8. Influent or effluent arsenic(III) concentration histories during filed column runs (8-inch column; EBCT=4.2 min) using virgin XUS 3N-Cu at Well 303, EPWU.

In addition, arsenite can be removed in the form of anionic complexes. At neutral pH, As(III) exists predominantly as $As(OH)_3$ species, whereas HCO_3^- is the predominant carbonate species. Arsenious acid can complex with bicarbonate through H-bonding between the hydroxyl of the As(III) species and the carbonyl group of bicarbonate, to give the anionic complex, $As(OH)_3(HCO_3^-)_2$ (Han, 2007). Therefore, a fraction of As(III) can be taken up by the PLE through electrostatic interactions between the immobilized Cu^{2+} ions and the negatively charged complexes. Nonetheless, the PLE does not appear to be practically effective for removal of As(III) species. In fact, no significant As(III) was observed during batch isotherm experiments where the solution-to-resin ratio was much lower than that in the column configuration. Consequently, for groundwater containing high concentrations of As(III), pre-conversion of As(III) to As(V) would be needed to take advantage of the PLE's high selectivity for arsenate. Several technologies have been available for oxidation of As(III). For example, As(III) can be oxidized to As(V) by manganese oxides (Driehaus et al., 1995), H_2O_2 and Fenton's reagent (Pettine et al., 1999), photochemical oxidation (Yang et al., 1999), and microbiological oxidation (Hambsch et al., 1995).

5.2.3 Breakthrough histories of arsenic and other major anions

Figures 5-9 and **5-10** show the breakthrough histories of total arsenic and some major competing anions (sulfate, bicarbonate and chloride) during the column runs. Despite the presence of high fraction of As(III), the fresh and regenerated PLE beds treated more than 3500 BV and 3000 BV, respectively, of the contaminated water before the breakthrough of total arsenic occurred. This capacity value appears to be lower than that observed in our prior bench-scale experiments, where >6000 BV of water was treated. This reduced BV value is attributed to 1) the presence of high fraction of As(III), 2) the fairly high and unfavorable influent pH (8.3), 3) greater bicarbonate concentration and competition from other anions, and 4) the rather marked temperature fluctuation (22 – 33 ^{o}C). It can be expected that the treatment capacity can be greatly increased when As(III) is pre-converted to As(V). From **Figure 5-9,** it appeared that the conversion rate of As(III) to As(V) was pH-dependent, however, more experiments and data are needed to substantiate this judgment. The arsenate breakthrough history in **Figure 5-10** is very similar to that observed in our previous lab results using the low-tier NSF 53 challenge waters (see **Chapter 4**, page 38).

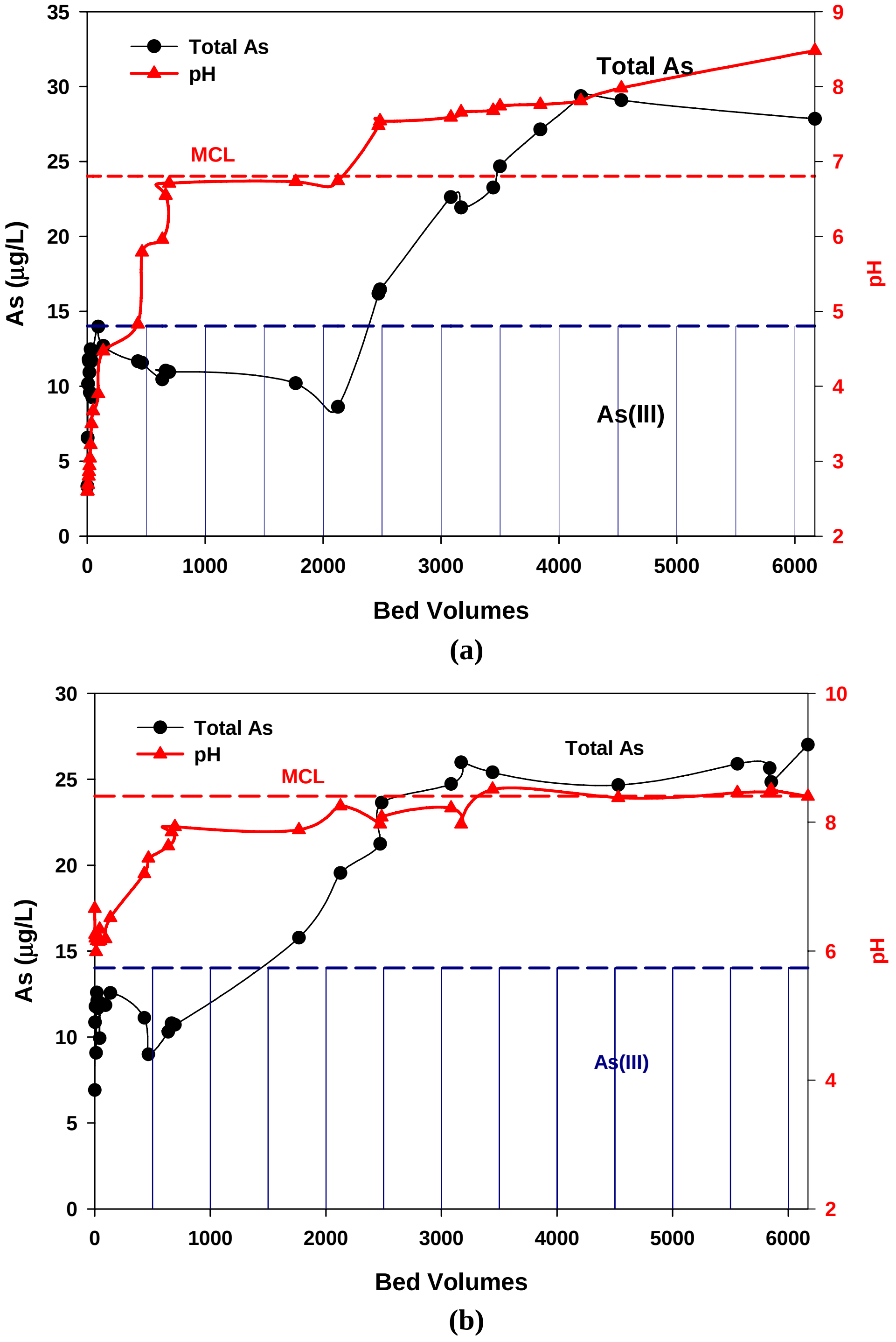


Figure 5-9. Breakthrough histories of arsenic during column runs (**a.** 8-in column, and **b.** 4-in column) using the polymeric ligand exchanger, XUS 3N-Cu at Well 303, EPWU.

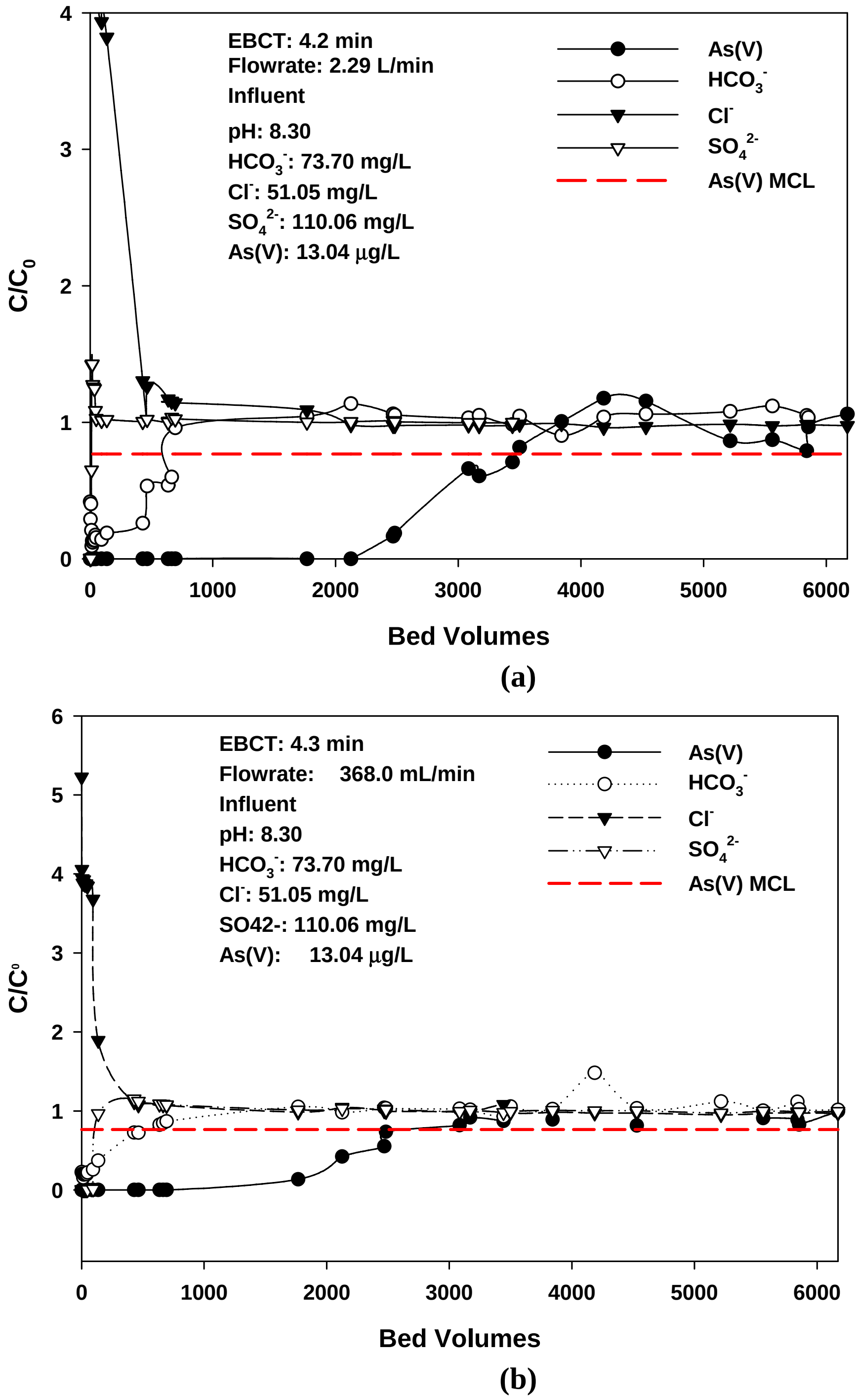


Figure 5-10. Breakthrough histories of As(V) and other competing anions during the column runs (**a.** 8-inch column, and **b.** 4-inch column) using XUS 3N-Cu for treating the groundwater from Well 303, EPWU.

CHAPTER 6. PILOT SCALE FIELD TESTING OF THE PLE TECHNOLOGY-PART II

The primary objective in this stage of work was to continue the pilot-scale field tests under various operating conditions at the site of El Paso Water Utilities (EPWU). These test runs, together with those in **Chapter 5** provide critical information to optimize this water treatment technology for the intended full scale implementation.

Major tasks include: 1) Carrying out multiple service column runs under various conditions (flowrate, pH levels, and with or without pre-oxidation) using regenerated PLE and actual groundwater influents from Well 303 of the test site; 2) Carrying out multiple regeneration runs to evaluate the effectiveness of the PLE regeneration process; and 3) Developing a standard curve for measuring the hydraulic head loss as a function of flow rate through the arsenic-laden PLE bed. Detailed experimental procedures and main results are summarized as follows.

6.1 Methods and Procedures

All reagents, apparatus and chemical analysis were prepared or performed using the same methods described in Report 4 except that hydrogen peroxide (35 wt. %, Acros) was used for testing the effect of pre-oxidation of As(III) on the arsenic removal. Chemicals of analytical reagent grade or higher were used for all analytical purposes. All data were obtained by analyzing triplicate samples and are reported as mean ± standard deviation (SD).

6.1.1 Column runs for As removal

Three column runs were carried out during this period, with the same configuration as the prior work (see **Chapter 5**). **Table 6-1** summarizes the timeline for the column runs during this test period. Prior to the beginning of the tests, resins subjected to one or two operation cycles (service + regeneration) were first backwashed using the tap water for all the PLE beds. All tests were carried out under ambient conditions (room temperature: day time average 34 ^{o}C, night time average 22 ^{o}C; water temperature: influent water=24-31 ^{o}C, effluent water =23-32 ^{o}C).

Table 6-1. Part II pilot-test timeline (period: 07/04/2007-08/10/2007) at Well 303, EPWU.

Item	Started: 07/04/2007																																		End: 08/10/2007			
Time (Day)	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
Run a	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
Run b	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░	░																				
Run c																			░	░	░	░	░															
Run d																								░	░	░	░	░	░	░	░	░	░	░	░	░	░	░

a. 8-inch column (Service run, EBCT=8.0 min, PLE subjected to one operation cycle, no pH adjusted)
b. 4-inch column (Service run, EBCT=3.9 min, PLE subjected to one operation cycle, pH adjusted to 6.5)
c. 4-inch column (Regeneration run, EBCT=30.0 min, Regenerant: 6% NaCl, pH=9.0)
d. 4-inch column (Service run, EBCT=4.0 min, PLE subjected to two operation cycles, H_2O_2 pre-treated influent water)

One column run was performed with the large PLE column (D=8 inches). In this case, the bed height was set at 30 cm and the flowrate was kept at 1.2 L/min, which translates into an empty bed contact time (EBCT) of 8.0 min. The large column run lasted 38 days and no pH adjustment for the influent water was performed.

Two more column runs were performed in sequence by using the smaller column (D=4 inches). For comparison with Part I column runs (see **Chapter 5**), the PLE bed height was set at 20 cm and flowrate was kept at 400 mL/min, which translates into an EBCT of 4.0 min. During the first 18 days' of operation, the pH of raw well water in the 200-L mixing tank was adjusted to 6.5 ± 0.1 by using dilute HCl and then stabilized for ~15 hours before transferred to 1000-L swimming pool as influent water.

6.1.2 Regeneration

Regeneration of an arsenate-saturated XUS 3N-Cu bed was carried out in the same way as described in the prior work (See **Chapter 5**, page 47). In all cases, we used ~30 bed volumes of 6% (w/w) NaCl at pH=9.0 as the regenerant to regenerate the arsenate-loaded XUS 3N-Cu bed.

6.1.3 Water sampling and preservation

In this period, water collection, lab analysis, and flowrate monitoring were performed in the same way as in prior work. The same procedure for field separation of As(III) and As(V) and EDTA-HAc preservation was followed (See **Chapter 4**, page 36). Note that sampling frequencies of influent/effluent for the 4-inch column run with pre-oxidation were slightly changed due to actual operations and fewer samples were collected in this case.

6.1.4 Hydraulic head Loss through the exhausted PLE Bed

To determine the head loss at the end of the service run as a function of the superficial liquid velocity (SLV), the same lab procedure was followed as in our prior work (See **Chapter 3**, page 26). In brief, head loss through the saturated PLE bed (subjected to one operation cycle) was tested in the small column (2ftx0.33ft, LxD) over a broad range of SLV (0.28-5.8 m/h).

6.2 Results and Discussion

6.2.1 Pilot operations

Influent flowrate

During column runs in this period, the flowrate was checked and corrected twice a day. The peristaltic pump tubing was switched or replaced every week to maintain the constant flowrate. The average flowrate was 1.20 ± 0.03 L/min for the 8-inch column (EBCT=8.0 min), 408.1 ± 14.6 mL/min for the 4-inch column (EBCT=3.9 min, pH adjusted to 6.5), and 396.2 ± 12.9 mL/min for 4-inch column (EBCT=4.0 min, H_2O_2 pre-treated). In all cases, the flowrate remained fairly stable throughout the operations. **Figure 6-1** shows the flowrate histories during the three column runs.

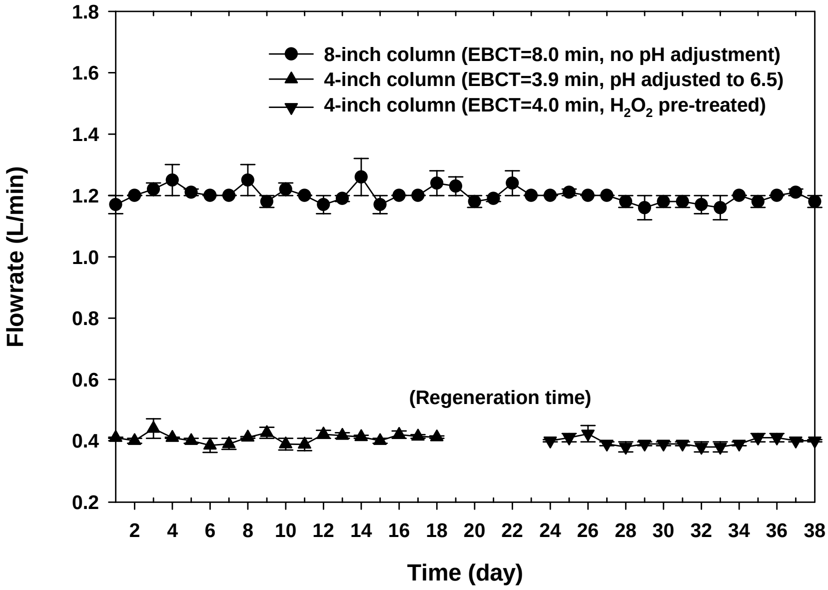


Figure 6-1. Flowrate histories for pilot testing (Part II) at Well 303, EPWU.

pH in the influent and effluent

Table 6-2 summarizes the raw water characteristics for Well 303 of EPWU over the duration of this study (May 2007–August 2007). The average raw water temperature varied slightly at around 27±1.6 ^{o}C during the summer. The tests were performed under ambient conditions (pH = 8.0-8.4; Room temperature: day time average 35 ^{o}C, night time average 21 ^{o}C). The pH value of the influent remained quite stable at an average of 8.3 during the tests although the long-term monitoring data showed that the pH can fluctuate seasonally from 7.2 to 9.1.

Table 6-2. Raw water quality data over duration of pilot-scale study.

Month (2007)	Temperature (^oC)	pH	Turbidity (NTU)	TDS (mg/L)	Iron (mg/L)	SiO_2 (mg/L)	As(Tot.) (μg/L)	As(III) (μg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)
May	26.5	8.3	0.31	337	0.30	19.9	27.1	14.0	51.1	110.1	73.7
June	28.0	8.4	0.27	341	0.27	26.0	27.1	14.0	51.1	110.1	73.7
July	27.7	8.3	0.30	340	0.08	25.4	29.7	15.9	57.0	115.7	71.1

Pressure drop, TDS and backwashing

Pressure drop across the PLE bed and levels of TDS in the influent water can affect the backwash frequencies and duration.

To compare the hydraulic pressure drops through fresh and arsenic-laden (after a service run) PLE beds, the hydraulic pressure drop per unit bed height was measured as a function of superficial liquid velocity (SLV) (gpm/ft^2). **Figure 6-2** shows the mean pressure drop as a function of SLV for the PLE beds. A second order polynomial function was used to fit the measure pressure drop data. There is no statistically significant difference between the data for fresh and arsenic-laden PLE (T=-0.082, p-value=0.9354; T test). According to the correlation equation between unit-bed height pressure drop (pressure drop/PLE bed height, psi/ft) and SLV (flowrate/cross-sectional area, gpm/ft^2), the calculated pressure drops caused by resins are in the range of 0.46-0.75 psi for 8-inch column (which corresponds to flowrate: 1.2L/min-2.4L/min) and 0.25-0.37 psi for 4-inch column (flowrate: 200mL/min-400mL/min), which was less than 1 psi under all conditions. Thus, head loss buildup was not the limiting factor during the operation runs. In each operation cycle, the PLE bed was only briefly backwashed with ~15 BV's of the local tap water before and after regeneration, respectively.

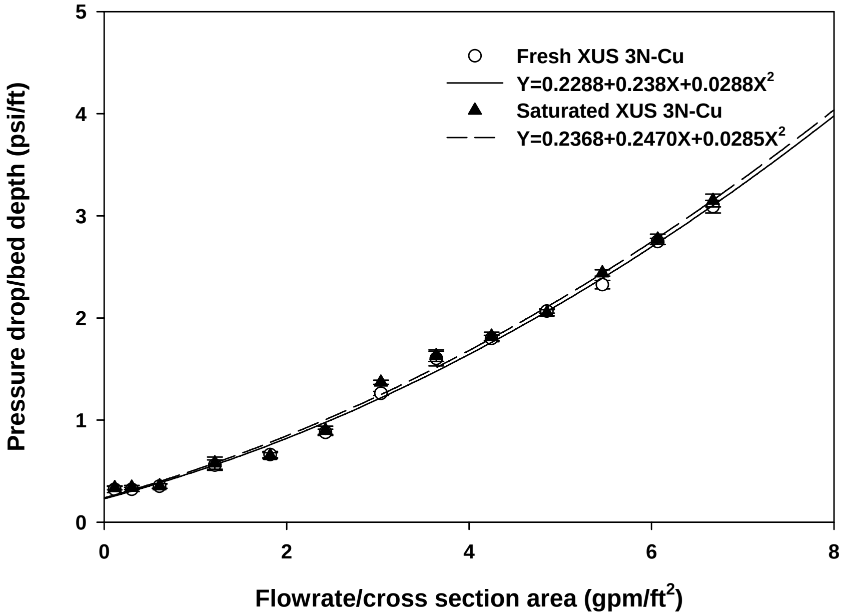


Figure 6-2. Hydraulic pressure drop per unit bed height as a function of SLV (gpm/ft^2).

Figure 6-3 shows the TDS profiles for the influent and effluent during four pilot tests. In all cases, TDS levels in the influent/effluent were in the range of 292-352 mg/L. Noted that there is no significant difference in TDS levels between pH adjusted (pH=6.5) and unadjusted (pH=8.3) influent water, suggesting that no appreciable turbidity will be formed in the PLE bed under the ambient groundwater conditions. It was postulated that elevated levels of iron and silica may result in rapid pressure buildup and lead to more frequent backwashing. This was not observed in these tests. This is possibly due to the low iron content (iron=0.30 mg/L, see Report 1) and relatively low level of silica ([SiO_3^{2-}] =24.90 mg/L, see **Chapter 4**, page 30) in the feed water. It should also be noted that each inlet line is equipped with a two-layer filter screen, which prevented larger objects from entering into the columns.

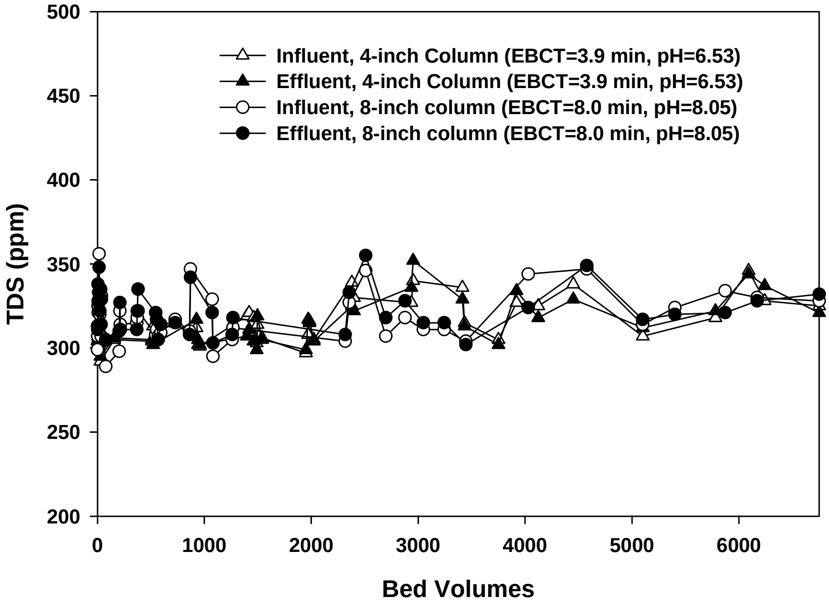
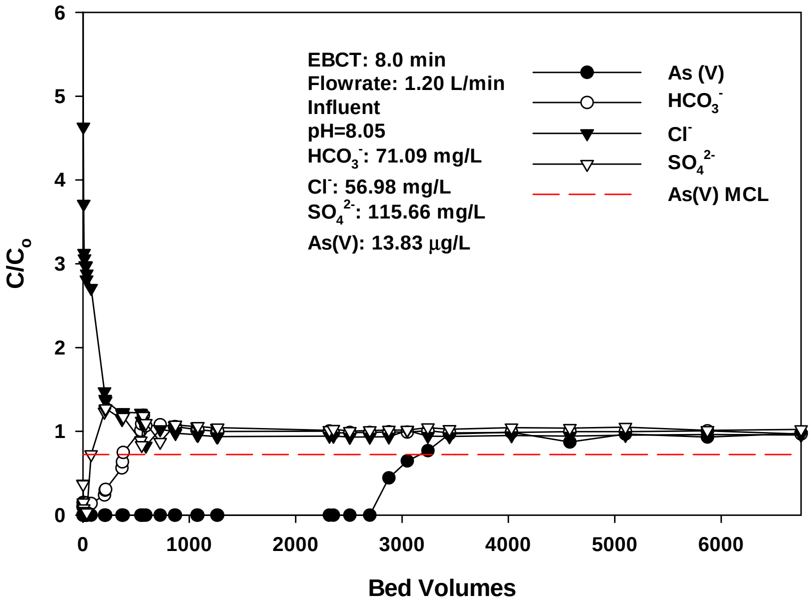


Figure 6-3. TDS profiles for influent/effluent during operations using the polymeric ligand exchanger, XUS 3N-Cu, during Part II pilot tests at Well 303, EPWU.

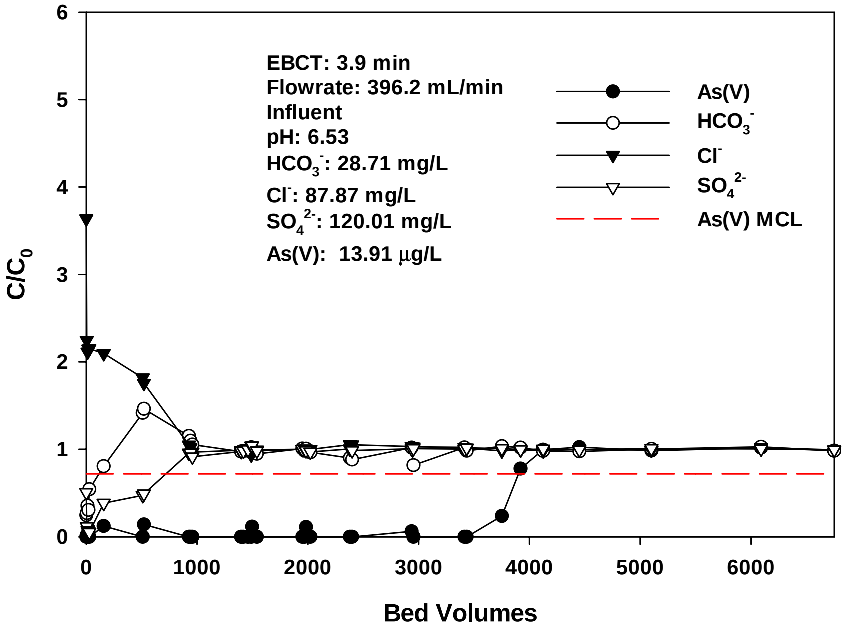
6.2.2 Breakthrough histories of arsenic and other major anions

EBCT effect on breakthrough histories

Figure 6-4 shows the breakthrough histories of As(V) and some major competing anions (sulfate, bicarbonate and chloride) during the column runs. Despite the presence of high fraction (~52%) of As(III) and high concentrations of competing anions, the regenerated PLE beds treated more than 3200 BV and 3900 BV of the groundwater, respectively.



(a)



(b)

Figure 6-4. Breakthrough histories of As(V) and other competing anions during Part II pilot testing (**a.** 8-inch column, and **b.** 4-inch column) at Well 303, EPWU.

Figure 6-5 compares the arsenic breakthrough curves with the 8-inch column but at an EBCT of 8.0 min and 4.2 min. Evidently, the breakthrough profile at 8 min was steeper although the overall breakthrough bed volumes was not increased as the EBCT was doubled, suggesting that mass transfer limitation in the EBCT range was not significant. The arsenic capacity for the 8-inch column (EBCT=8.0 min, pH=8.05, PLE subjected to one regeneration) was about 8% lower than that for the fresh virgin bed (EBCT=4.2 min, pH=8.30, virgin PLE). The capacity drop of the PLE bed can be attributed to the incomplete regeneration of the PLE bed.

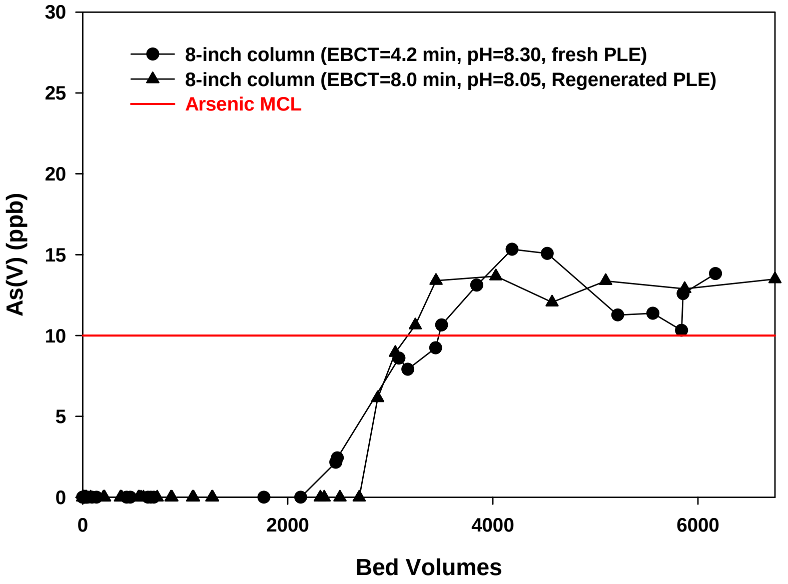


Figure 6-5. Breakthrough histories of As(V) under different EBCT using the polymeric ligand exchanger, XUS 3N-Cu, during pilot tests at Well 303, EPWU.

pH effects of breakthrough histories

OH^- ions can strongly interact with PLE, and solution pH can affect the speciation of arsenate. Therefore, pH is an important factor for the PLE process. The influent and effluent pH was monitored during the operations, which provided important information on the water chemistry during the column runs. **Figure 6-6** shows the pH histories for the raw water (influent) and for effluents using virgin and regenerated XUS 3N-Cu, respectively, during the field operations. The effluent pH profiles for the columns showed an initial sharp drop followed by a gradual recovery. This pH drop can be attributed to a number of factors, including 1) direct uptake of OH- ions by PLE, 2) removal of arsenate in the form of $HAsO_4^{2-}$ leading to release of H^+ ions, and 3) removal of alkalinity (bicarbonate and carbonate). In addition, the pH drop was much less significant for the regenerated resin than for the fresh resin. For practical application, the pH fluctuation can be equalized when the treated water is mixed in the clear wells.

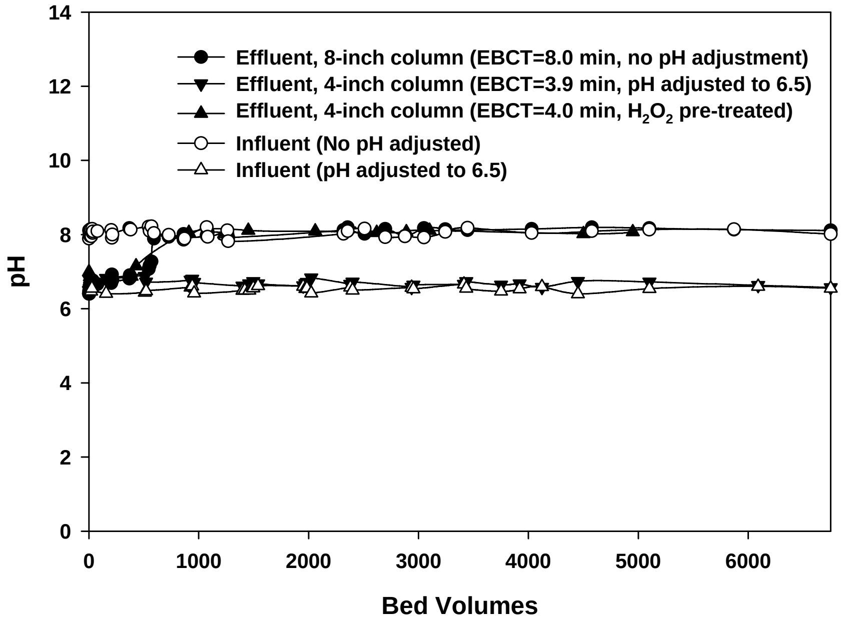


Figure 6-6. Water pH in influent/effluent during operations using the polymeric ligand exchanger, XUS 3N-Cu, during Part II pilot tests at Well 303, EPWU.

As pH for most groundwater falls in the range of 6.5-8.3 (Sawyer, 1978), slight pH reduction can be beneficial to overcome the competition from bicarbonate and hydroxyl anions, thereby increasing the arsenate sorption capacity. **Figure 6-7** shows pH effect on As(V) uptake during the field operations. A decrease in the influent water pH from 8.3 to 6.5 increased the treatment capacity by ~30%, confirming that slightly acidic pH is more favorable for arsenic removal by PLE (An et al. 2005).

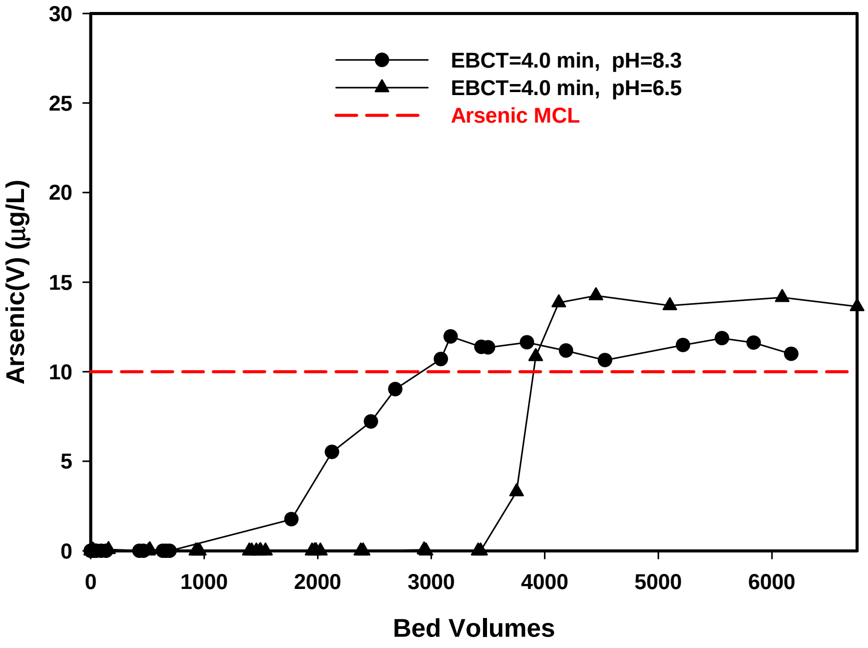


Figure 6-7. Effect of influent pH on breakthrough histories of As(V) during two field column runs (0.1-m column) using virgin XUS 3N-Cu at Well 303, EPWU.

Figures 6-8 and 6-9 show the breakthrough histories of chloride and bicarbonate, respectively, during the service runs with the 4-inch column. The chromatographic peaking of chloride occurred at ~500 BVs for the column runs at alkaline pH (>8.0), but occurred at ~1,000 BVs when the influent pH was 6.53. The longer peak tailing at the lower pH is also attributed to the greater concentration of chloride in the influent water (note that HCl was added to lower the influent pH, which resulted in a ~60% greater chloride concentration). The addition of HCl also caused a ~60% drop in bicarbonate in the influent water. In all cases, the highest chloride concentration did not exceed ~350 BV's, and thus, the relatively short-lasting peaking did not pose any appreciable water quality shocks in the effluent. Compared the prior results (4-inch column, EBCT=4.3 min at pH=8.3) in **Figure 6-9**, the disappearance of chromatographic peaking of bicarbonate at pH=6.5 occurred ~200 BV's earlier, at almost the same bed volumes with chloride, which indicated that sorption of bicarbonate at lower pH was less favored.

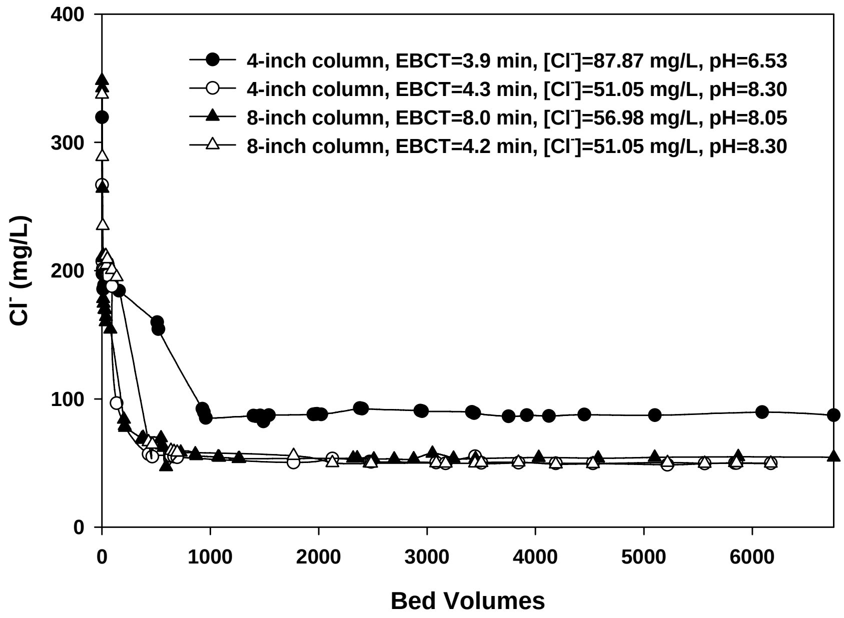


Figure 6-8. Breakthrough histories of chloride during operations using the polymeric ligand exchanger, XUS 3N-Cu, during Part II pilot tests at Well 303, EPWU.

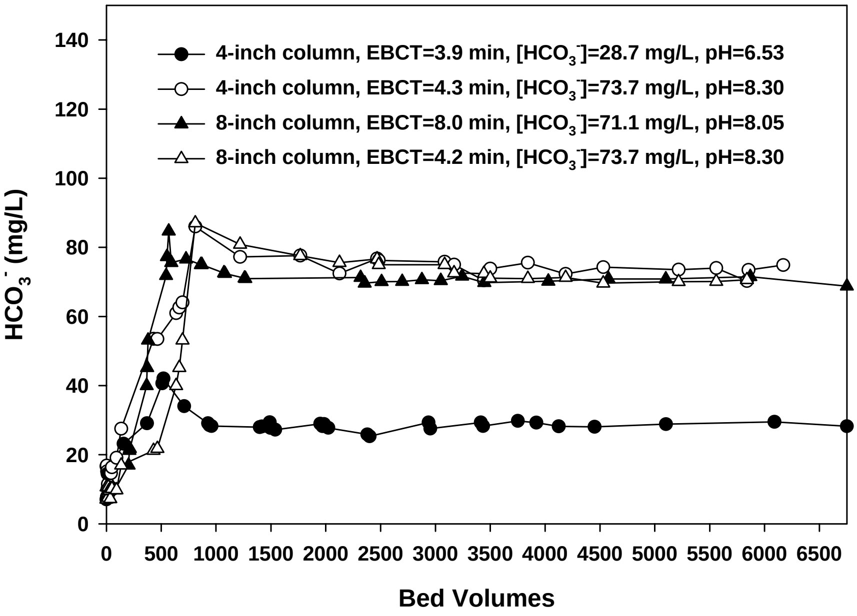


Figure 6-9. Breakthrough histories of bicarbonate during operations using the polymeric ligand exchanger, XUS 3N-Cu, during Part II pilot tests at Well 303, EPWU.

H_2O_2 pre-oxidation of As(III) to As(V)

In addition to the above-mentioned column tests, we also conducted one field test by using H_2O_2 pre-treated influent well water. The oxidation of As(III) in the presence of H_2O_2 was investigated by Yang et al.. At an initial As(III) concentration of 40mg/L and a molar ratio of As to H_2O_2 of 1 to 4, total oxidation occurred within 10 min. The oxidation rate was described by pseudo-first-order kinetics. Pettine et al. (1999) found that the oxidation of As(III) by H_2O_2 is a highly pH dependant reaction. They found that H_3AsO_3 was not oxidized in the presence of H_2O_2 but the dissociated species ($H_2AsO_3^-$ and $HAsO_3^{2-}$) existing at pH values above 9 are rapidly oxidized. **Figure 6-10** shows breakthrough histories of total arsenic and its competing anions during the field column run using H_2O_2 pre-treated influent well water. Our data for the influent water quality also showed the inconsistent conversion rate of As(III) to As(V) ranging from 17% to 65% under raw water condition (average pH=8.3). Insufficient mixing and oxidation time may lead to this variation of coverion rate. Contributing to the significant fraction of As(III) converted to As(V) from the pre-treatment, the breakthrough of As(V) occurred ~2,600 BVs in this case.

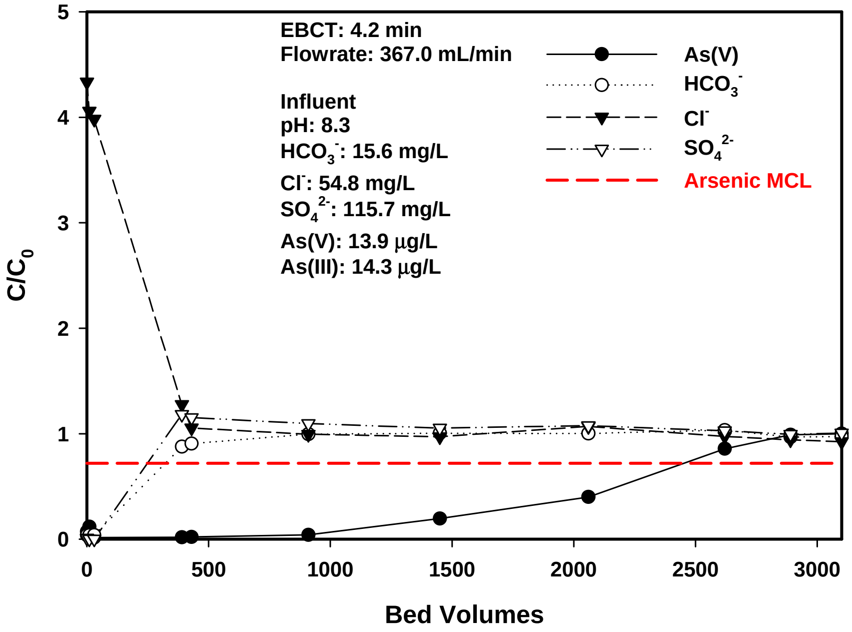


Figure 6-10 Breakthrough histories of arsenic(V) and its competing anions under H_2O_2 pre-treatment operations using the polymeric ligand exchanger, XUS 3N-Cu, during Part II pilot tests at Well 303, EPWU.

6.2.3 Regeneration and repeated use of PLE bed

Figure 6-11 shows the elution histories of arsenic during two regeneration runs of the arsenate-exhausted XUS 3N-Cu bed with 6% (w/w) NaCl at pH 9.0. In the second regeneration run, the same spent regenerant brine was reused with only pH adjusted back to 9.0 (no salt was added). It is noteworthy that most sorbed arsenate was recovered in less than 4 BVs of the regeneration, indicating a much less regenerant need than the 22 BVs of the same regenerant previously observed for DOW 3N-Cu (An et al. 2005). This much improved regeneration efficiency of XUS 3N-Cu over DOW 3N-Cu is attributed to the uniform size of XUS-3N-Cu, which leads to much improved sorption/desorption kinetics. The recovery of As(V) was 90% using the fresh brine (5 BVs), and it was lowered to 87% when the spent brine was reused. Also superimposed in **Figure 6-11** is the elution profile of bicarbonate during the regeneration run with fresh brine. While the elution peaking occurred almost at the same time as arsenate, a longer tailing was evident for bicarbonate, with 89% sorbed bicarbonate recovered within 10 BVs of the regeneration. The results indicate that the regenerant demand is actually controlled by bicarbonate rather than arsenate in the sorbent phase. Note that the bicarbonate recovery exceeded 100%, which can be due to the elevated dissolution of CO_2 into the regenerant at the alkaline pH (Stachowicz et al., 2007).

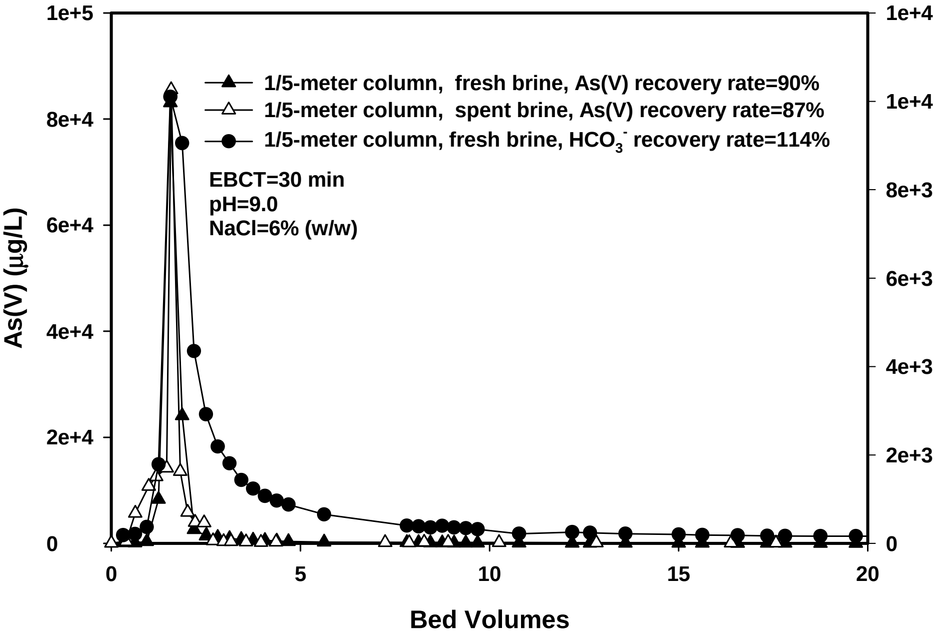


Figure 6-11. Elution histories of As(V) during regeneration of arsenate-saturated XUS 3N-Cu using fresh or spent brines (NaCl=6%, pH=9.0). Column diameter = 0.2 m.

Bench-scale studies indicated that the regeneration efficiency for DOW 3N-Cu can be increased by either increasing the concentration of sodium chloride or raising the brine pH level (An et al. 2005). **Figure 6-12** compares the regeneration profiles of an exhausted XUS 3N-Cu bed at NaCl concentrations of 6% (w/w) and 8% (w/w) or at two levels of regenerant pH. Prior to the regeneration runs, the PLE bed was exhausted with ~3200 bed volumes of the NSF 53 challenge water (50μg/L As(V), pH=8.5). Mass balance calculation revealed that the arsenate recovery was increased from 92% to 97% (within 8 BVs of regeneration) when the pH of the regenerant brine was increased from 9 to 10. The recovery was increased to 100% when the concentration of the regenerant brine was increased from 6% to 8% when the brine pH was held at 9.

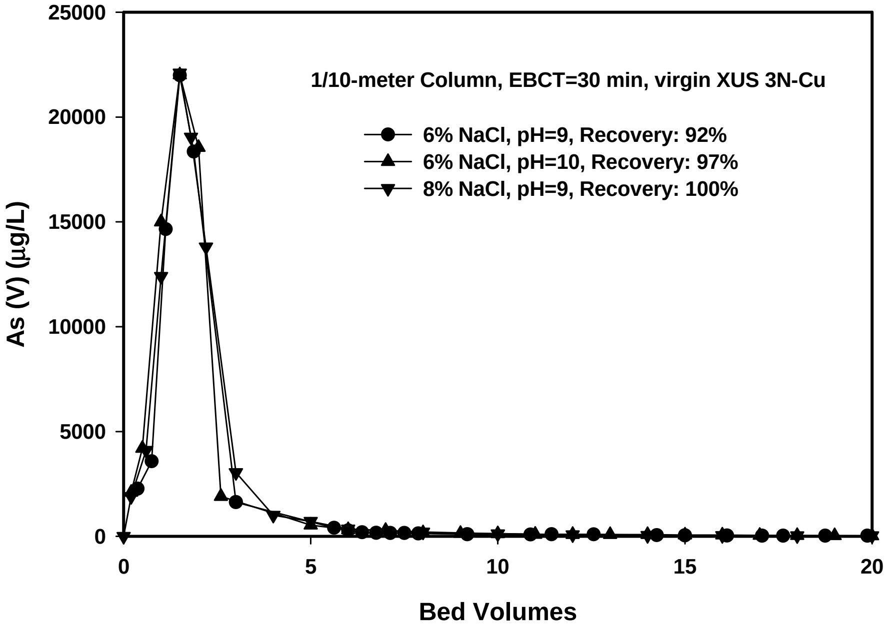


Figure 6-12. Arsenic elution histories during regeneration of an arsenate-exhausted XUS 3N-Cu bed using fresh brine under various conditions (pH=9, 10; NaCl=6%, 8%). Column diameter = 0.1 m.

To test the long-term process viability, the same XUS 3N-Cu bed was tested in eight cycles of operations (one cycle = service run + regeneration run) using 15 BVs of 8% NaCl as the regenerant (pH=9; EBCT=30 min). The same regenerant was repeatedly used with only pH adjustment during the runs. **Figure 6-13** shows the breakthrough histories of As(V) during eight consecutive cycles of service runs using the high-tier NSF 53 challenge water. The breakthrough curves nearly coincide and As(V) broke through at ~2,900 BVs in all cases. Mass balance measurements also indicated that almost 100% As(V) recovery was achieved during each regeneration during the operations.

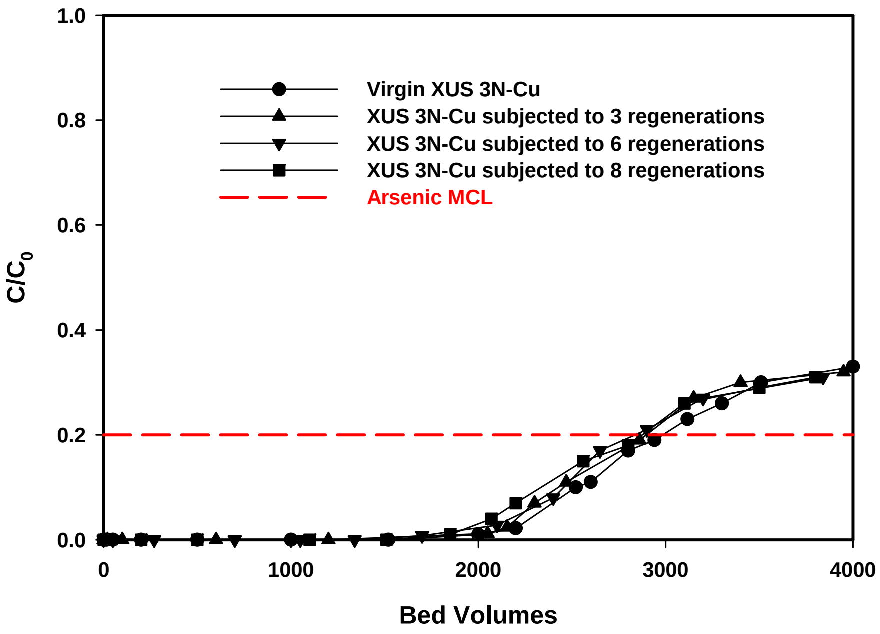


Figure 6-13. Breakthrough histories of arsenic(V) under conditions of the low-tier NSF/ANSI 53 challenge water during multiple consecutive cycles of runs using virgin or regenerated XUS 3N-Cu (Influent: As(V) = 50μg/L; EBCT = 4.1 min; pH = 8.5; Regenerant: NaCl = 8% (w/w); pH = 9.0; EBCT=30.0 min; BVs = 15). Column diameter = 0.1 m.

6.2.4 Copper leaking during column runs

In order to evaluate the possible copper leakage during the pilot testing column runs, total copper concentration in the effluent water was followed. In addition, a small column (4-inch) loaded with fresh XUS 3N was placed after the primary 8-inch PLE column to capture any copper leakage from the PLE. This copper capturing process is also a process of copper loading (i.e. preparation of a column of supplementary PLE). Mass balance calculation of copper eluted from the primary PLE column showed that the copper leakage per operation cycle (saturation and regeneration) was less than 0.077% of total the copper loaded in the resin (see **Figure 6-14**). The minimal copper leakage is in accord with the fact that the arsenate capacity of the PLE was essentially unchanged over multiple cycles of column runs shown in **Figure 6-13**. This is attributed to the strong metal-ligand interactions between Cu^{2+} and nitrogen donor atoms in the host polymer matrix (Zhao et al., 1998).

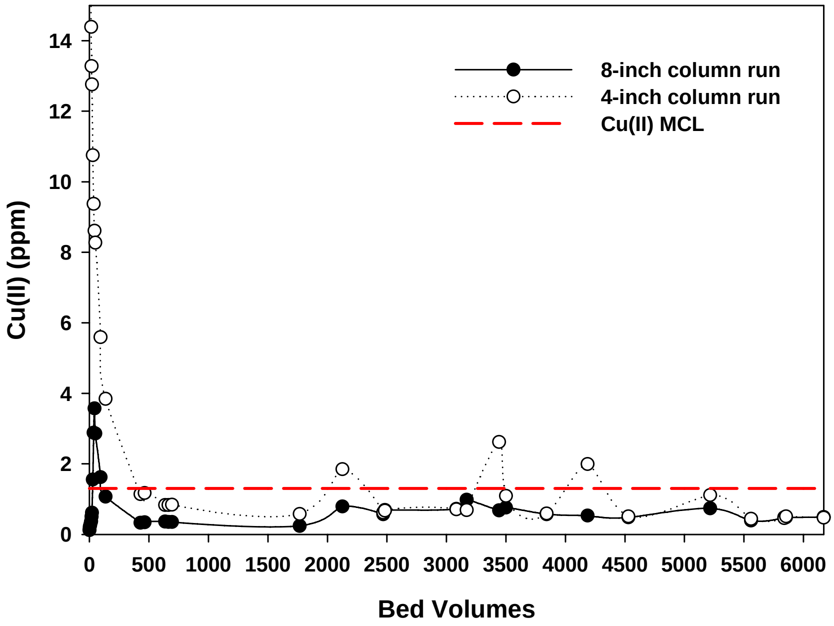


Figure 6-14.. Cu(II) leaking histories during operations using the polymeric ligand exchanger, XUS 3N-Cu, during pilot tests at Well 303, EPWU.

CHAPTER 7. STABILIZATION OF ARSENIC-LADEN PROCESS WASTE RESIDUAL

Although the same regeneration brine can be reused for multiple cycles of regeneration runs, it will eventually reach a limit where the regeneration efficiency becomes inhibitively low as arsenic level goes up. To minimize the quantity of process waste residual, we tested an engineered approach to treat the spent brine, with the hyposis that the teated brine can be reused, and the final As-laden sludge will leach less arsenic.

The primary objectives in this stage of work were to 1) confirm the effect of brine pH on the PLE's regeneration efficiency, and 2) determine the optimal conditions and processes for treating the exhausted arsenic-laden regenerant brine. The goal for the regenerant brine treatment was to minimize the volume of the arsenic-laden process waste residual and minimize the leachability of arsenic in the process waste residual.

Major tasks include: 1) Conducting a regeneration column run for an exhausted PLE bed using fresh brine at pH=10.0 and 6% of NaCl; 2) Carrying out multiple batch experiments to treat the spent brine using soluble $FeCl_3$ and comparing its performance with five types of commercially available iron nanoparticles, including zerovalent iron powder, iron oxides (hematite or α-Fe_2O_3 and maghemite or γ-Fe_2O_3) and magnetite (Fe_3O_4). Detailed experimental procedures and main results are summarized as follows.

7.1 Methods and Procedures

All reagents, apparatus and chemical analysis were prepared or performed following the same procedures described in previous chapters except for iron nanoparticles.

7.1.1 Iron or iron oxide nanoparticles

Four iron-based nanoparticles were tested for treating As-exhausted brine. These commercial iron-based nanoparticles and their suppliers are listed as follows:

a. Iron powder in hexane. Average particle size: 100nm (Toda Kogyo Corp., Japan)

b. Iron oxide (Alpha-Fe_2O_3) powder. Particle size 20-50nm (Nanostructured & Amorphous Materials Inc., Los Alamos, NM, USA)

c. Iron oxide (Gamma-Fe_2O_3) powder. Particle size: 20-50nm (Nanostructured & Amorphous Materials Inc., Los Alamos, NM, USA)

d. Magnetite (Fe_3O_4) powder. Average particle size: 20-30nm (Nanostructured & Amorphous Materials Inc., Los Alamos, NM, USA).

7.1.2 Effect of pH on regeneration of PLE

To test the effect of regenerant pH on the PLE's regeneration efficiency, regeneration of a PLE-exhausted bed was carried out using 6% of NaCl at pH 10 following the same approach as described in prior work (see **Chapter 4**, page 35), where regeneration was conducted at pH 9.0. Prior to the regeneration run, a PLE bed was exhausted in the 4-inch column with the NSF-53 challenging water (low tier, 50 ppb as As(V)) following the same procedures of the service runs as described in prior work (see

Chapter 4, page 34). Fresh XUS 3N-Cu was used in this case, and ~25 bed volumes of the regenerant brine were introduced into the PLE bed at an EBCT of 30 min.

More detailed investigation on the pH effect was further carried out in batch experiments. First, 1 g of virgin XUS 3N-Cu was equilibrated with 1 mg/L of As(V) solution mimicking the field water compositions for 15 hours at pH 7.0. Then, each 0.1g of the air dried As-laden PLE was added into plastic bottles containing 60-mL of fresh or spent regeneration brine at a final pH of 8.0, 9.0, 10.0, 11.0, and 12.0, respectively. The mixtures were then equilibrated on a gang mixer for ~2 hours at 200 rpm, and then allow standstill for ~1 hour, and supernatant was sampled and analyzed for arsenic using a Perkin-Elmer Graphite Furnace AA.

The maximum As capacity of XUS 3N-Cu was also determined by completely removing the immobilized Cu^{2+} (and thus arsenic sorbed thereon) by immerging 50 mL of ~6% (w/w) of an ammonia solution with 0.1 g of XUS 3N-Cu (under shaking) for ~2 hours. Arsenic in the solution was then analyzed using a Perkin-Elmer Graphite Furnace AA. The As Cu capacity for the PLE was determined to be 12.7± 0.5 mg/g resin, which is close to the value of maximum As capacity (15.3 mg/g) calculated based on the fitted Langmuir model of arsenic sorption isotherm on PLE (An et al., 2005).

The arsenic recovery rate of the As-laden PLE was calculated based on arsenic desorbed in the regenerant brine and the total arsenic sorbed on the PLE (12.7±0.5 mg/g resin).

7.1.3 Preparation of regenerant brine

The fresh regenerant brine contains 6% (w/w) of NaCl. After repeated uses, arsenic, bicarbonate and sulfate will accumulate, and eventually the spent brine needs to be treated to remove arsenic and to minimize the production of the process waste residual. To study the effectiveness of various options of the treatment of the spent brine, simulated spent regenerant brine (SRB) was prepared based on the major water quality data of EPWU and our analysis of the compositions present in the spent brine from the pilot test site. **Table 7-1** gives the background compositions of the simulated SRB. The fresh or simulated SRB was used for all the batch brine treatment experiments. To study the effect of pH on the brine treatment, the brine pH was adjusted using 1M NaOH or 1M HCL to 8, 9, 10, 11, and 12, respectively.

Table 7-1. Background compositions for spent regenerant brine

Cation	Cation Concentration		Anion	Anion Concentration	
	meq/L	mg/L		meq/L	mg/L
Na^+	1039.5	23909	SO_4^{2-}	12.5	600
			Cl^-	1014	36000
			HCO_3^-	5.0	305
			As(V)	8.0	300
Total	1039.5	23909	Total	1039.5	37205

For the batch experiments, 10-liter simulated SRB was prepared in a 15-liter bucket. The solution preparation followed the procedures below:

a) Dissolve 593g sodium chloride (NaCl) in 10-liter DI water in the bucket to achieve a final concentration of 59.3 g/L NaCl.

b) Separately dissolve 8.878g sodium sulfate (Na_2SO_4), 4.2g sodium bicarbonate ($NaHCO_3^-$), and 0.0125g sodium arsenate ($Na_2HAsO_4.7H_2O$) in the DI water and transfer into the bucket to obtain a final concentration of 600 mg/L as SO_4^{2-}, 305 mg/L as HCO_3^-, and 300 mg/L as As(V).

c) Adjust solution pH using sodium hydroxide (NaOH) to 9.0±0.1.

The resultant solution was stirred for ~8 hours, and then the chemical compositions were confirmed through laboratory analysis. The stable solution was then used within 24 hours.

7.1.4 Treatment of spent regenerant

A series of batch experiments were performed to determine the optimal conditions and processes for the treatment of the spent regenerant brine. The effectiveness of arsenic removal from the spent brine was tested in batch reactors by the addition of various concentrations of $FeCl_3$ and under various conditions (pH, temperature, aging time and ionic strength). The treatment effectiveness was compared to that when various iron-based nanoparticles were applied. In all cases, $FeCl_3$ and iron-based nanoparticles (iron powder, alpha-Fe_2O_3, gamma-Fe_2O_3, and Fe_3O_4) were added to 60-mL plastic vials at various Fe/As molar ratios under a given pH. The solutions were then placed on a gang mixer for ~2 hours operated at 200 rpm. Then, the mixtures were set standstill for 1 h to allow the particles to precipitate. The pH of the supernatant was then measured, and if needed, adjusted using 1M NaOH or 1M HCl. After pH adjustments, the mixtures were mixed again and allowed for precipitation for a range of 1 to 20 hours. Then, the supernatant was sampled in duplicate, centrifuged (centrifuged at 4000rpm for 10 minutes), filtered through a 0.45µm syringe filter, and then analyzed for arsenic using a Perkin-Elmer Graphite Furnace AA.

For all iron-based materials, the Fe/As molar ratio was set at 0, 2, 5, 10, 20, and 40, respectively to test the effects of the *Fe*-to-*As* molar ratio on the treatment effectiveness. **Table 7-2** summarizes the batch experiments.

Table 7-2. Dosage of various iron-based materials (as Fe-to-As molar ratio) for treatment of spent regenerant brine containing 4mM of As(V)

Iron compounds	Fe/As molar ratio					
	0	2	5	10	20	40
Fe^0 (g)	0	0.027	0.067	0.134	0.268	0.536
Alpha-Fe_2O_3 (g)	0	0.077	0.192	0.383	0.766	1.533
Gamma-Fe_2O_3 (g)	0	0.077	0.192	0.383	0.766	1.533
Fe_3O_4 (g)	0	0.111	0.278	0.556	1.111	2.222
$FeCl_3$ (g)	0	0.078	0.195	0.389	0.778	1.557

For screening purposes, two pH levels (pH=6.5 and 8.3) were chosen at this stage. In addition, the effects of pH on arsenic removal from the brine using $FeCl_3$ were studied in the pH range of 2-12 and at a fixed Fe/As molar ratio of 10. After 20 hours of equilibration, the final pH was recorded and the supernatants were sampled and analyzed for arsenic.

To test the aging (or treatment time) effect on arsenic removal and arsenic leachability from the resultant precipitates, the treatment contact time was varied at 1 hour, 5 hours, 10 hours, and 20 hours, and at an Fe/As molar ratio of 5 and 10. In addition, to evuluate the leachibility of the resultant sludge, two leaching tests were conducted for each sample, including Toxicity Characteristic Leaching Procedure (TCLP) (EPA Method 1311) and Waste Extraction Test (WET) (California Department of Health Services, SOP No. 910). General approach for preparing samples for such leaching tests is summarized as followss:

1) Fe/As molar ratio=10; settling time=10 hrs.
2) Final brine pH=7.5; mixtures are aged for 2 or 5 days.
3) Precipitates are placed in a hood and allowed to air dry.
4) Iron-precipitates reach a drying equilibrium after at least 14 days.
5) Leaching tests (TCLP or WET) are conducted after air drying period.

7.2 Results and Discussion

7.2.1 Regeneration of As-laden PLE

Bench-scale studies indicated that the arsenic recovery during regeneration of DOW 3N-Cu can be increased by either increasing the concentration of sodium chloride or raising the brine pH level (An et al. 2005). To demonstrate the effect, regeneration of an XUS 3N-Cu bed, which was exhausted with ~3200 bed volumes of the EPWU water, was carried out. **Figure 7-1** compares the arsenate elution profiles during regeneration of As-saturated XUS 3N-Cu using fresh NaCl (6%) at two levels of pH (9.0 and 10.0). Mass balance calculation revealed that the arsenate recovery was increased from 92% to 96% when the pH of the regenerant brine was increased from 9 to 10.

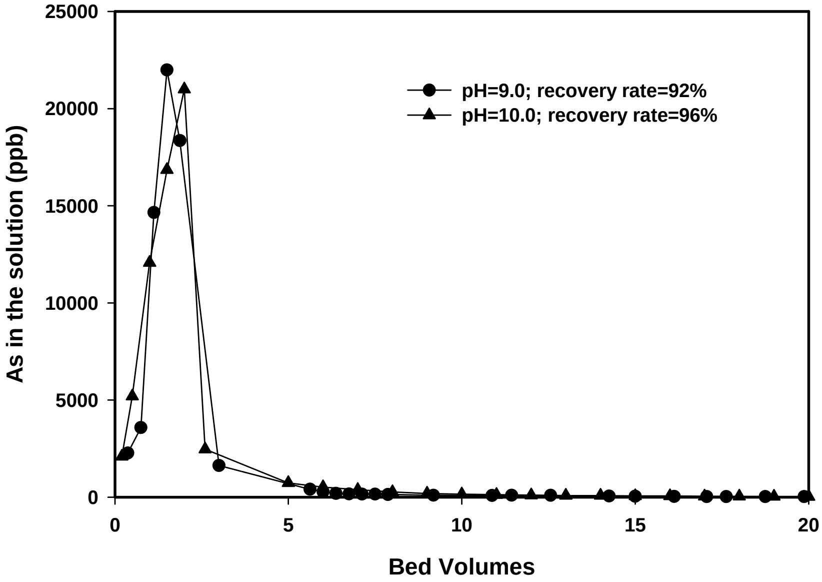


Figure 7-1. Arsenic elution histories during regeneration of an arsenate-exhausted XUS 3N-Cu bed using fresh brine (6% NaCl) at pH 9 and 10.

More detailed investigation into the effect of pH on the regeneration efficiency of As-laden XUS 3N-Cu was conducted in batch experiments. **Figure 7-2** compares the arsenate recovery when the PLE was treated with either fresh or spent 6% (w/w) NaCl at pH 8.0, 9.0, 10.0, 11.0 or 12.0, respectively. **Figure 7-2** also shows that the regeneration efficiency increased steadily as the brine pH was raised from 8 to 10 for both the fresh and spent regenerant brine. It was also evident that at pH >10, the regeneration efficiency of the spent brine was nearly the same as that of the fresh brine. The reaction stoichiometry for arsenate regeneration can be described by **Eq. (7-1)**:

$$R-Cu^{2+}(HAsO_4^{2-})+Cl^-+OH^- \rightarrow R-Cu^{2+}(Cl^-)(OH^-)+HAsO_4^{2-} \quad \textbf{(7-1)}$$

Evidently, the participation of OH$^-$ in the ligand exchange reaction at alkaline pH greatly enhanced the regeneration efficiency.

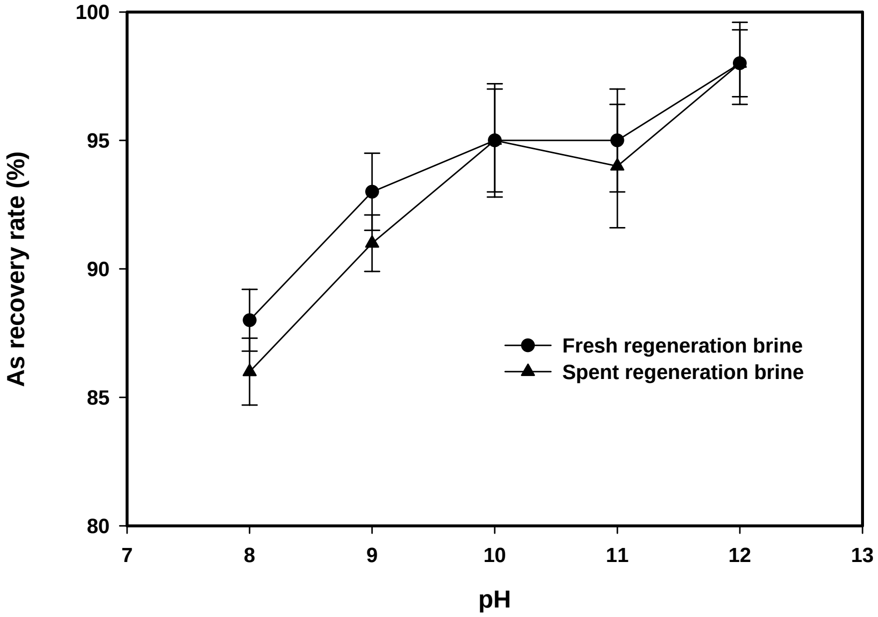


Figure 7-2. Arsenic recovery from spent XUS 3N-Cu using 6% fresh or spent NaCl as a function of final brine pH (The duplicate data are reported as in mean ± deviation).

7.2.2 Treatment of spent regenerant brine

After repeated reuses, the regeneration power of the spent brine will be exhausted. Thus, removal of arsenic from the brine is necessary to minimize the process waste production and to further reuse the spent brine.

As removal using $FeCl_3$ and various iron-based nanoparticles as a function of dosage

Figure 7-3 shows the percentage arsenic removal as a function of material dosage at a constant pH of 7.5. For ferric chloride, Cheng et al. (1994) observed the same trend in jar tests where $FeCl_3$ was added to treat a raw water containing an 17-20 µg/L of As(V). Note that the initial concentration of As(V) in our batch tests is four orders of magnitude greater (~300,000 µg/L). Despite the presence of 6% NaCl, $FeCl_3$ at an Fe/As molar ratio of 10 or higher was able to remove more than 98% of As(V) from the brine. Such an efficient removal of As(V) by Fe^{3+} is attributed to two concurrent mechanisms, direct precipitation of ferric arsenate and adsorption of arsenate to the ferric hydroxide precipitates followed co-precipitation. The sorbent nanoparticles (ZVI and iron oxides) were also able to remove arsenate from the brine especially when the dosage exceeded an Fe-As molar ratio of 20 although the removal was not as effective as $FeCl_3$. Apparently, the presence of high concentrations of NaCl in the brine inhibited the sorption or surface complexation, which is the sole mechanism for arsenic removal by these nanoscale sorbents (Manceau, 1995), of arsenate to the nanoparticles. This observation also reveals the important role of precipitation in the arsenic removal process. Among the four sorbents, the magnetite nanoparticles appeared least effective for arsenic removal. It should be pointed out, however, that both As(III) and As(V) can form inner sphere complexes on iron oxides. Thus, when As(III) species are present, these nanoscale sorbents may outperform ferric chloride.

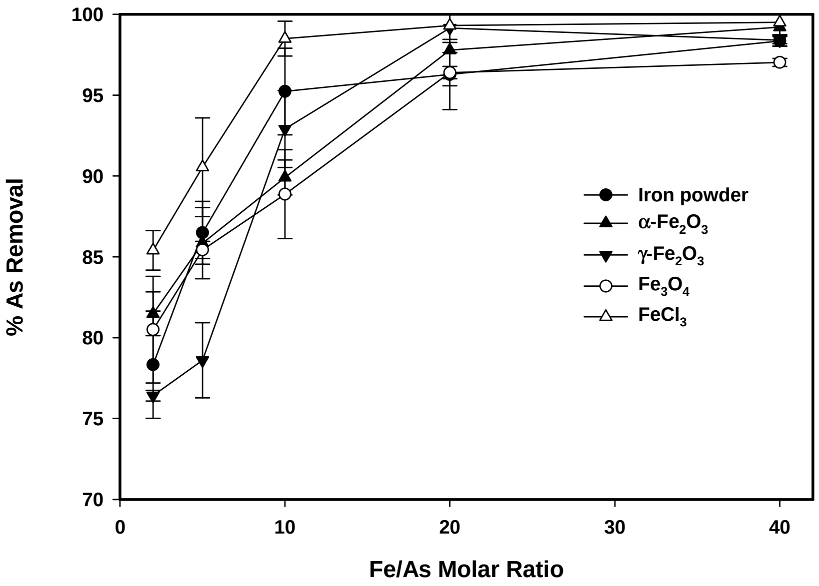


Figure 7-3. Percentage arsenic removal from a spent brine (6% NaCl, pH=9) as a function of material dosage (treating contact time=5 days, final pH=7.5; settling time=10 hours).

Arsenic removal as a function of pH

Literature studies indicated that the sorption behavior of arsenic is strongly influenced by solution pH and the oxidation state of arsenic (Ferguson, 1972; Smedley amd Kinniburgh, 2002; Islam et al., 2004). For ferric chloride, **Figure 7-4** compares the pH effect in the range of 2 to 12 at a fixed Fe/As molar ratio of 40 (settling time=10 hours) for the treatment of synthetic spent regenerant brine. Greater than 98% of arsenic removal was achieved within the pH range of 6.5 to 8, while As removal decreased substantially either at pH lower than 4 or higher than 12. This result suggests that there exists a fairly broad pH range for optimal As removal from the spent brine at the relatively high dosage of $FeCl_3$.

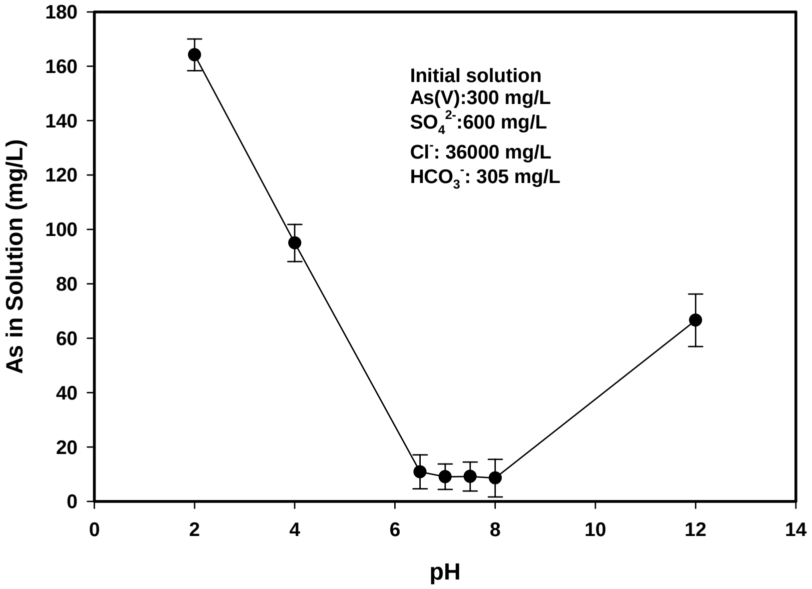


Figure 7-4. Effect of pH on arsenic removal from spent regeneration brine using ferric chloride (treating contact time=2 days, Fe/As=20, settling time=10 hours).

Figure 7-5 shows that arsenate adsorption to various iron oxide nanoparticles was 20%-42% greater at pH 6.5 than at pH 8.3. At pH 6.5, the surface has net positive charges that can attract anionic arsenate species in addition to Lewis acid-base interactions. In addition, **Table 7-3** gives pH_{ZPC} for iron-based nanoparticles based on literatures. At the higher pH, more surface charges are negative, which repels the $HAsO_4^{2-}$ anions in the solution. In addition, hydroxyl anions become more competitive for the sorption sites at elevated pH.

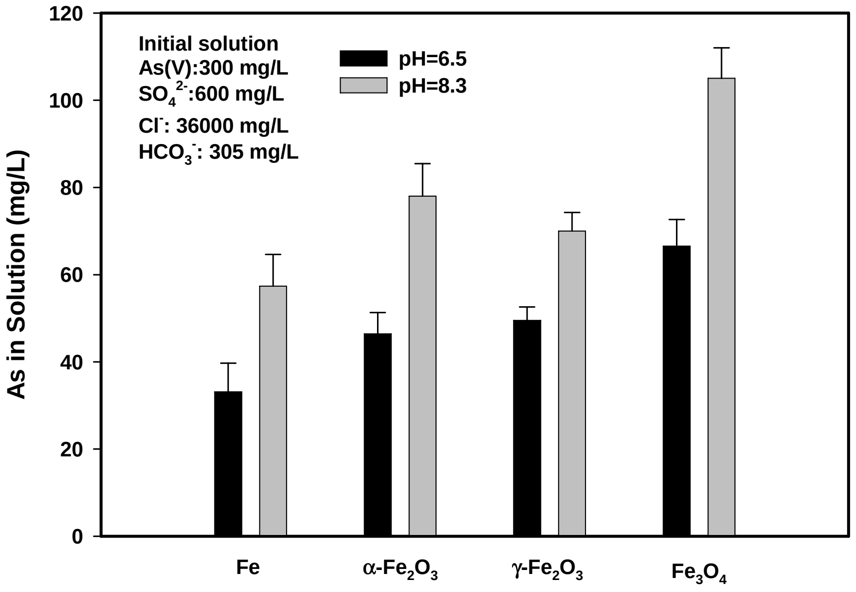


Figure 7-5. Effect of pH on arsenic removal for spent regeneration brine using various iron oxide nanoparticles (Fe/As=2, settling time=10 hours).

Table 7-3. Zero Point Charge (pH_{ZPC}) for iron-based nanoparticles

Iron-based nanoparticles	pH_{ZPC}	References
Fe^0	7.8	Kanel, et al., (2005)
Fe_2O_3	6.1-6.3	Westerhoff (2006)
Fe_3O_4	7.0	Plaza, et al., (2002); Kosmulski, et al., (2002)

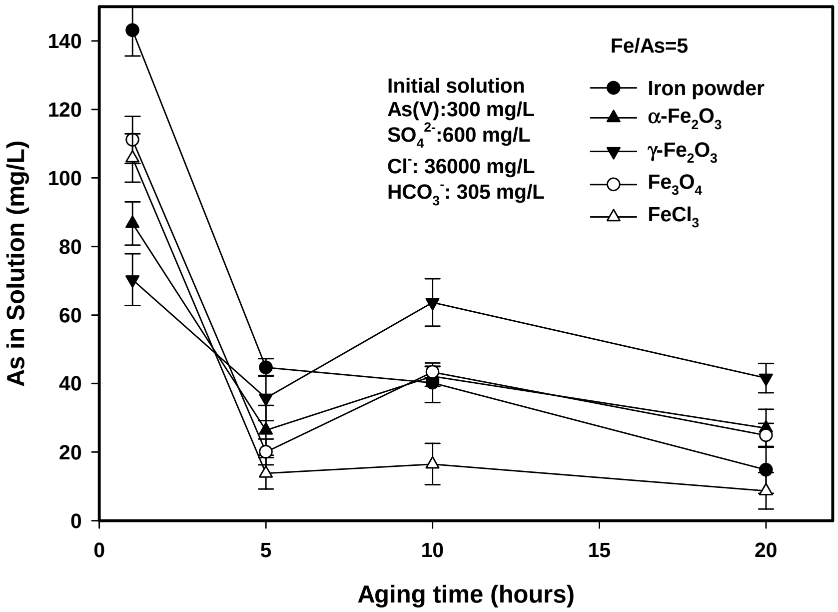
For all the cases, 1N NaOH and 1N HCl were used to adjust pH and final pH was recorded. **Table 7-4** shows pH changes during the batch tests. For all the nanoparticles, the pH change was less than 1 pH unit when no pH adjustment was carried out. In contrast, the addition of ferric chloride decreased the pH drastically to 2.17.

Table 7-4. Change in pH during brine treatment with various iron-based materials (Fe/As 20, 5-day treating contact time, and settling time 10 hours).

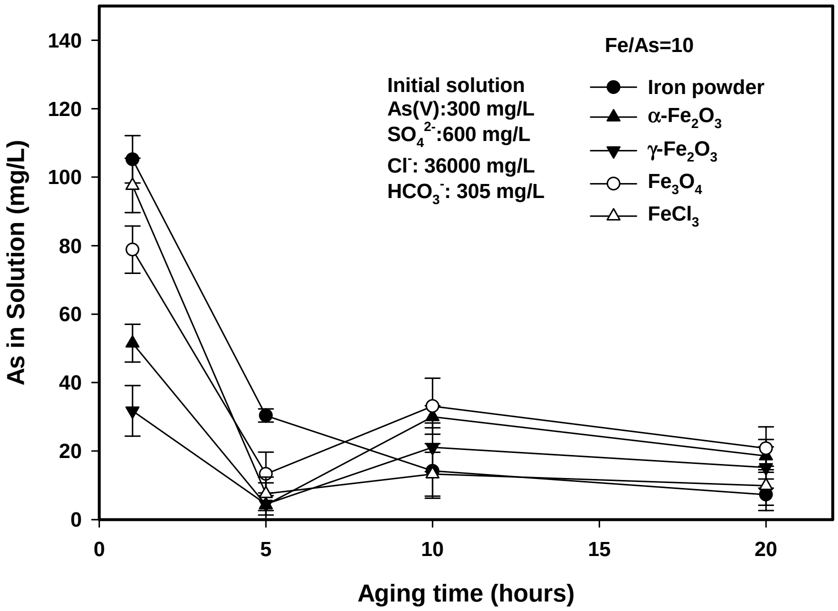
Iron compounds	Initial pH	pH after treatment (unadjusted)	Final pH (adjusted)
Fe	6.5	7.57	6.5
	8.3	8.20	8.3
Alpha-Fe_2O_3	6.5	7.10	6.5
	8.3	8.20	8.3
Gamma-Fe_2O_3	6.5	7.16	6.5
	8.3	8.22	8.3
Fe_3O_4	6.5	7.05	6.5
	8.3	8.40	8.3
$FeCl_3$	6.5	2.17	6.5
	8.3	2.17	8.3

Arsenic removal kinetics

Slow adsorption kinetics of arsenate to ferrihydrite has been reported to be due to a diffusion-controlled rate determining step (Fuller et al. 1993). Thus, treatment residence time could be a critical factor for the treatment process. **Figures 7-6(a)** and **(b)** show arsenic remaining in the solution phase as a function of settling time at a fixed Fe/As molar ration of 5 and 10, respectively (pH=7.5). The data indicated that the system for both cases reached a steady state after ~ 5 hours of settling.



(a)



(b)

Figure 7-6. Arsenic removal using various iron-based materials as a function of settling time at Fe/As molar ratio of 5 **(a)** and 10 **(b)** (pH=7.5 for all cases).

Leaching test

Previous experiments have indicated that pH 6-8 is the optimal range for As(V) removal from the brine solution (see **Figure 7.4** and **7.5**). Here, at final treatment pH of 7.5, the effect of leaching test was explored. For all the cases, the same resultant sludge was prepared based on the general approach prescripted earlier (see **Chapter 7**, page 88). **Table 7-5** shows the TCLP and WET testing results for the same resultant sludge using $FeCl_3$ and the four types of iron-based nanoparticles at aging period of 2-day and 5-day, respectively. The data indicate that $FeCl_3$ needs longer aging period than iron-based nanoparticles. Because each test can easily pass either TCLP or WET leaching tests after sufficient air drying period (~2 weeks), the resulted sludge would not be characterized as hazardous wastes.

Table 7-5. Leaching test results of resultant sludge using various iron-based compounds at two different aging periods (2-day and 5-day)

Materials	2-Day Aging Period		5-Day Aging Period	
	TCLP (mg/L)	WET (mg/L)	TCLP (mg/L)	WET (mg/L)
1. $FeCl_3$	1.8	3.3	0.61	0.97
2. Fe^0	0.66	0.85	0.65	0.86
3. α-Fe_2O_3	0.61	0.74	0.61	0.72
4. γ-Fe_2O_3	0.63	0.77	0.63	0.74
5. Fe_3O_4	0.71	0.83	0.69	0.82

CHAPTER 8. SCALE-UP ANALYSIS AND ECONOMICS

8.1 Introduction

In order to determine the cost effectiveness of the XUS 3N-Cu ion exchange technology, a full-scale arsenic treatment process design was conceived. The approach for implementation at a full-scale treatment facility was developed based on the findings of pilot- or field-scale testing. As with any new technology, capital and operating costs will ultimately determine the PLE feasibility. A basic cost estimate was prepared at three level of treatment capacity of 0.1, 1.0, and 10.0 mgd, where the As/sulfate aqueous phase concentration remained the same at 20-year design plan.

The Toxicity Characteristic Leaching Procedure (TCLP) is a currently accepted method for assessing arsenic residuals in all states except California, which employs a more stringent procedure, known as Waste Extraction Test (WET). The toxicity of the waste will also affect the disposal costs. Treatment residuals failing the TCLP or WET (both with a limit of 5 mg/L As) will be deemed a hazardous waste and may increase the disposal cost (Meng et al., 2001).

8.2 Methods

Parameters of the PLE resin such as total removal capacity, resin run length, frequency, regeneration efficiency and optimal working conditions properties were determined from our previous pilot-scale tests. The key parameters include: an empty bed contact time (EBCT) of 4.0 minutes, and a treatment capacity of 3,200 BVs of influent water per service run. The influent contaminant concentrations were: As = 30 μg/L, SO_4^{2-} = 110 mg/L, HCO_3^- = 72mg/L, and Cl^- = 54 mg/L. Nearly 100% recovery of the resin capacity can be achieved using ~10 BVs of 8% NaCl brine (40 g/L NaCl). The EBCT for the regeneration is 25 minutes. The expected shelf-life according to DOW Chemical for XUS resins is 8-10 years. Under these conditions a process design is conceived. Only As(V) is considered the target arsenic specie. The same brine is assumed to be reused 8 times before it is treated. Either $FeCl_3$ or Fe_2O_3 (alpha- or gamma-) additions of Fe/As 10 is used to pass the TCLP and WET.

Full-Scale Ion Exchange System Design

Considering a plant capacity of 0.1 MGD, a schematic of full-scale ion exchange system is shown in **Figure 8-1.**

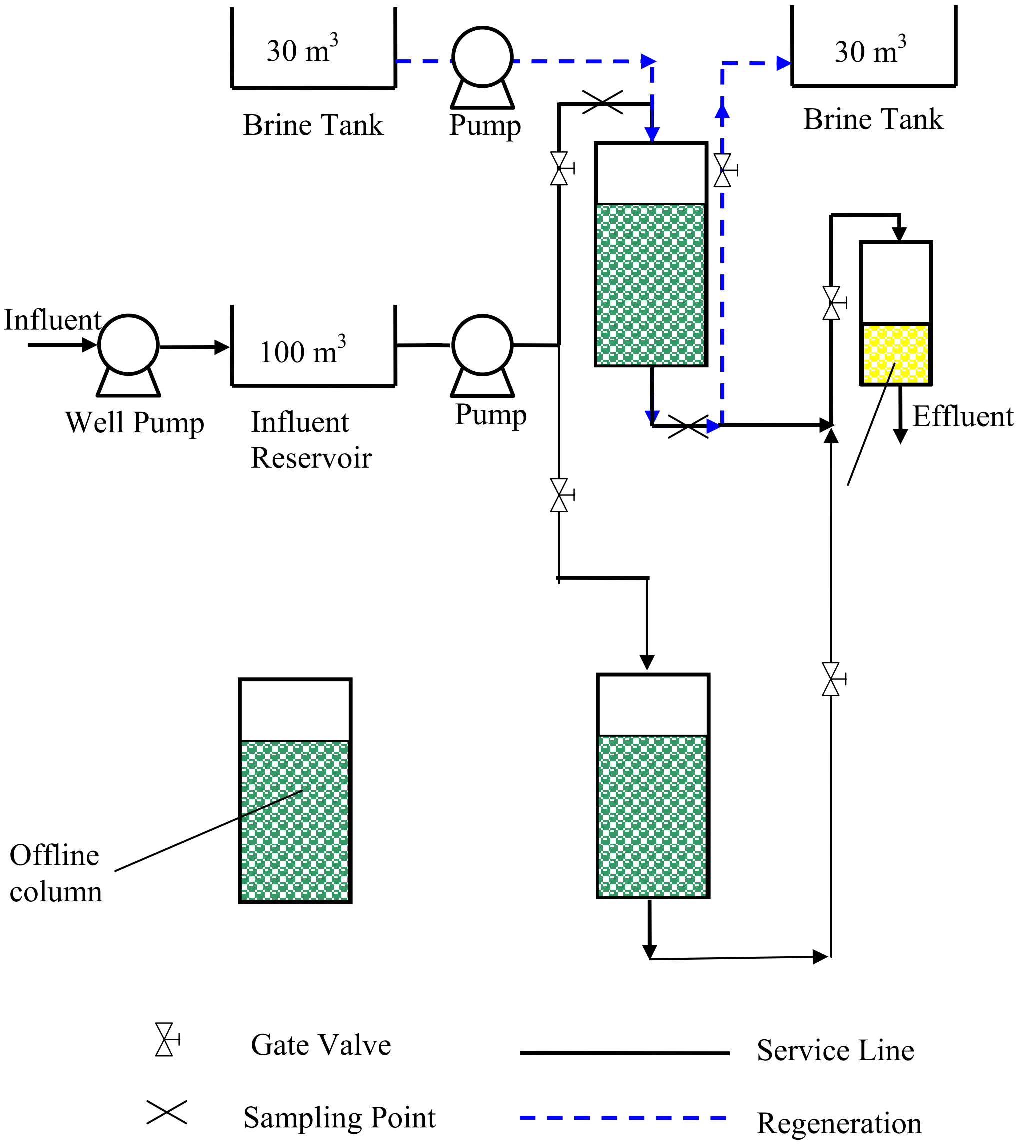


Figure 8-1. Schematic of an As-selective ion exchange system

The volume of resin required was determined using the design flowrate of 0.1mgd and EBCT of 4.0min. 20% of additional resin is considered to account for the capacity loss over a 20-year design. Once the volume of resin needed for a specific flow rate is determined, the column is determined based on the following design parameters (Clifford, 1999): column height must be double resin bed-height to account for 100% potential expansion of resin, diameter-to-height ratio must stay within the range 0.2:1-2:1. Process designs for all flow rates are based on a two-column system.

Based on the pilot-scale flow rate, the time per exhaustion cycle was calculated which allowed for the determination of the exhaustion cycles needed per year for a 20-year period. In addition, assuing that the regeneration brine can be reused 8 times before it is exhausted, the number of brine treatment cycles are also calculated for 20-year periods. The number of brine cycles needed per 20-year period allowed for the calculation of total brine volume required.

Using the total water volume treated, resin volume used, and brine volume used in a 20-year period; the amount of additives (NaOH, NaCl, and $FeCl_3$/Alpha-Fe_2O_3) are calculated. Pilot-scale tests provid the concentrations of additives necessary for optimal pH, salinity, and coagulant addition (for brine treatment).

Sludge production is determined based on pilot-scale tests, brine volume used and the number of brine treatment cycles calculated. The amount of sludge produced (g/L) was extrapolated for a 0.1, 1.0 and 10.0 MGD process with a 20-year design plan.

Cost Data

The cost estimates provided here consists of an estimate for planning purpose only.It is based on vendor-provided quotes under market conditions at the time of this report. The assumption of this cost analysis is based on adding ion exchange treatment at an existing water treatement plant, thus housing and buiding cost are not included. Column costs are calculated using the equation: $63.288*(\text{volume resin (gal)}^{0.679})$ (EPA, 2000b).

Resin costs are based on quotes from Dow Chemical (Midland, MI, USA) for XUS 3N resin. Costs for pumps, columns and mixers were based on quotes from McMaster (Atlanta, GA, USA). Labor hours were calculated using the following equation (EPA, 2000b): Labor (hrs) = #weeks * (3* #exhaustion cycles). #weeks and #exhaustion cycles are on a per 20-year period. In this case, $28/hr was used for labor costs (EPA, 2000b). All chemical additive costs are obtained from Fisher Scientific (Pittsburgh, PA, USA).

Cost calculation for design flow of 0.1mgd, 20-year plan

Influent contaminant concentrations:

As = 30 µg/L, SO_4^{2-} = 110 mg/L, HCO_3^- = 72mg/L, and Cl^- = 54 mg/L.

Assumptions:

EBCT=4.0 min, run length=3000 BVs, design flowrate=0.1mgd=262.9 L/min

1) Bed Volume (BV) = EBCT*Flowrate =1051.5 L=1.05 m^3
2) Resin Volume (V_{resin}) = BV*(1.2) =1.26 m^3 = 44.5 ft^3 = 332.9 gallon

   For 20-year design, (20 yr/ 8 yr) * V_{resin} = 3.15 m^3 = 111.2 ft^3 = 831.8 gallon
3) XUS 3N resin cost = 111.2 ft^3 * (\$217 / ft^3) = \$24130
4) Vessel Volume (V_{Tot}) = (1.5) * BV = 1.58 m^3

   For 2-column system, each column volume (V) = V_{Tot} /2 = 0.79 m^3 = 208.7 gallon
5) Bed Height (H) = 3 ft = 0.91 m (Note: 3ft < H < 6 ft)
6) Column Diameter (D) = 2* Sqrt (V/(pi*H)) = 1.06 m (Note: 0.2:1 < (H/D) < 2:1)
7) Column cost = 63.288 * (V)^0.679 = \$2378.4 (Note: V in gallon)

   For 2-column system, Total column cost = 3 * \$2378.4 = \$7135.2

8) Total volume of water treated per year = 36500000 gal =138168 m^3

\# of brine treatment cycles per year = 138168 m^3 / (3000 BV *(1.05 m^3/BV) * 8) = 6

For 20-year plan, Total # of brine treatment cycles = 120

9) Total volume of brine used = 120 * 10 BV * (1.05 m^3/BV) = 1260 m^3= 332857 gal

10) NaCl used = 1260 m^3 * (1000L/m^3) * (40 g/L) * (1kg /1000g) = 50400 kg

NaCl cost = 1.7 $/kg * 50400 kg = $85680

11) NaOH used = 1130 kg ;

NaOH cost = 6.51 $/kg * 1130 kg = $7356

12) Total As(V) treated per year =4.15 kg;

For 20-year plan, Total As(V) treated = 83 kg

13) $FeCl_3$ used =10* (162.21/74.92) * 83 kg = 1797 kg

$FeCl_3$ cost = 17.8 $/kg * 1797 kg = $31987

14) alpha-Fe_2O_3 used = 5* (159.69/74.92)* 83 kg = 885 kg

alpha-Fe_2O_3 cost = 31.2 $/kg * 885kg = $27612

15) Exhaustion cycles per year = 46; For 20-year plan, Total exhaustion cycles = 920

16) For 20-year plan, total labor hours = 48*20 + (3* 920) = 3720 hours

Total labor cost = 28$ * 3720 = $104160

Following the same procedures, cost estimation for 1.0mgd and 10.0mgd flowrate design at 20-year plan are calculated, respectively. And the costs per 1000 gallons treated are calculated.

8.3 Results and Discussions

Table 8-1 summarizes costs for 20-year plan. Costs are given for different flowrates in dollars per 1000 gallons treated. The cost estimation suggests that there is no significant cost difference using either $FeCl_3$ or iron oxide nanoparticles in this case. Frey et al. (1998) reported that handing and disposal of process wastes on average makes up average 23% of the total process costs. Our data indicates ~17% of total process cost is contributed to brine treatment, which is almost 26% cost reduction if compared with average ratio (23%) of brine treatment and disposal.

Table 8-1. Cost estimate summary for 20-year plan

Flowrate (mgd)	Influent As(V) (μg/L)	Cost per 1000 gal ($/ 1000 gal)	
		Use $FeCl_3$	Use alpha-Fe_2O_3
0.1	30	0.41	0.41
1.0	30	0.37	0.37
10	30	0.35	0.35

Table 8-2. Cost summary and annual requirement at 0.1mgd for 20-year plan

	Annual Requirement	20-year Design Period
Exhaustion Cycles	46	920
Volume of Resin (gallon/ft^3)	322.9 gal/ 44.5 ft^3	831.8 gal/ 111.2 ft^3
Brine Treatment Cycles	6	120
Volume Water Treated (gal)	36500000	730000000
Volume Brine Used (gal)	16643	332857
NaCl (kg)	2520	50400
NaOH (kg)	57	1130
Alpha-Fe_2O_3 (kg)	44	885
Labor (hours)*	186	3720

Table 8-3. Component summary for 0.1mgd design flowrate (20-year plan)

Component	Cost	Per unit	Reference	Total Costs	Annual Cost (20-year Plan)
Capital Costs					
XUS 3N	$217	ft^3	Dow Chemical	$24130	
XUS 3N-Cu	$239	ft^3	Add 10%	$26543	$1327
Columns	$2378	column	EPA, 2000	$7134	$357
Brine Treatment Tank	$14700		McMaster Inc.	$14700	$735
Brine Tank	$3800		McMaster Inc.	$7600	$380
Pumps	$4700		McMaster Inc.	$14100	$705
Pipes, valves	$2300	lum	McMaster Inc.	$2300	$115
				Subtotal	$3619
O & M Costs					
NaOH	$6.51	kg	Fisher Scientific Inc.	$7356	$368
NaCl	$1.7	kg	Fisher Scientific Inc.	$85680	$4284
Alpha-Fe_2O_3	$31.2	kg	Nanostructured & Amorphous Materials Inc.	$27612	$1381
$FeCl_3$	$17.8	kg	Fisher Scientific Inc.	$31987	$1599
Labor	$28	Hour	EPA, 2000	$104160	$5208

CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS

9.1. Conclusions

The newly implemented MCL rule for arsenic in drinking water is affecting thousands of water utilities such as EPWU. As new treatment technologies are emerging, arsenic-selective ion exchangers such as the PLE may provide the water utilities with a competitive alternative to comply with this challenging regulation. Major findings from this field study can be summarized as follows:

1). The copper-loaded PLE, XUS 3N-Cu, offered very high selectivity for arsenate over other competing anions that are omnipresent in natural groundwater. When arsenate is considered as the targeted arsenic species, XUS 3N-Cu can treat more than 3,000 bed volumes of the field water per operation cycle at an EBCT of ~4.0 min.

2). Arsenic breakthrough profile at EBCT 8 min was sharper than at EBCT 4 min. Yet, the overall breakthrough bed volumes were comparable. This observation suggests that the PLE process can be operated under hydrodynamic conditions similar to those with standard IX resins.

3). XUS 3N-Cu can be highly efficiently regenerated using 6-8% NaCl at pH ~9.0, and the same regenerant can be reused for multiple cycles of operations with only pH adjustment. Nearly 100% recovery of As(V) can be repeatedly achieved within 5 BVs of the 8% regenerant at pH 9.0. After 8 cycles of operation, the PLE bed offered the same arsenate removal capacity as the virgin bed, i.e. the PLE can be used in multiple cycles of operation without significant loss in capacity. The efficient regeneration of PLE using the same regenerant offers advantage over various iron-based media that are used on a disposable basis (i.e. dispose after one time use). Compared to standard anion IX resins, the regeneration frequency is much lower thanks to the 5 times greater arsenate removal capacity.

4). The PLE can effectively remove As(V) under typical groundwater conditions and in the pH range of 6.5-8.3, with the lower pH being more favorable.

5). The arsenic selectivity of PLE is best utilized for treating water of high sulfate and relatively low alkalinity. The NSF/ANSI challenge water conditions, especially the high-tier water, do not appear to favor the PLE's best performance. Given the diversity of various sorbent materials, the challenge water may not serve a universally fair basis for comparing performances of these materials.

6). The PLE was uniquely selective for arsenate. When As(III) is the most predominant arsenic species, pre-oxidation of As(III) to As(V) is likely needed although the PLE is able to remove a fraction of As(III).

7). Copper leakage was minimal and can be trapped during the operations using a small column of the template chelating resin, XUS 3N. No appreciable head-loss buildup was evident under the raw groundwater conditions.

8) Either ferric chloride or nanoscale particles of Fe_2O_3 (alpha or gamma form) can be used for stabilizing arsenic-laden residues at Fe/As molar ratio of 10 and optimal pH range of 6-8.

9.2. Recommendations

1) Arsenic species in most natural waters are in both As(III) and As(V) forms. Thus, cost-effective approach to convert As(III) to As(V) before using PLE for the treatment should be further developed.

2) Environmental risk assessment of iron nanoparticles used for stabilizing arsenic-laden residues is recommended before full-scale test.

3) Brine treatment process can be controlled to enhance both treatment and cost efficiency. Our findings potentially benefit utilities around the country that employ IX for As-removal and handle As-laden process waste residuals. It is recommended for utilities treating As-laden brines to include addition of iron oxide nanoparticles at Fe/As molar ratio of 10 as an effeicent and cost-effective method.

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APPENDIX

List of Acronyms or Nomenclatures

AL	Action Level
ANSI	American National Standards Institute
BV	Bed Volume
CVT	Capacity Verification Test
DIC	Dissolved Inorganic Carbon
DO	Dissolved Oxygen
DOW 3N	A chelating resin from DOW Chemical with the trade name DOWEX M4195
EBCT	Empty Bed Contact Time
EPWU	El Paso Water Utilities
FLAA(S)	Flame Atomic Absorption (Spectrophotometer)
GFAA(S)	Graphite Furnace Atomic Absorption (Spectrophotometer)
GPM	Gallons Per Minute
IC	Ion Chromatograph
IX	Ion Exchange
MCL	Maximum Contaminant Level
Min	Minute

mL	Milliliter
MRDL	Maximum Residual Disinfectant Level
NTU	Nephelometric Turbidity Unts
PLE	Polymeric Ligand Exchanger, i.e. copper-loaded DOW 3N or XUS 3N
PVC	Poly Vinyl Chloride
QA/QC	Quality Assurance/Quality Control
SC	Specific Conductance
SLV	Superficial Liquid Velocity
SRB	Spent Regeneration Brine
SS	Suspended Solid
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
XUS 3N	A chelating resin from DOW Chemical with the trade name XUS43578