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Performance Evaluation of ALCAN-AASF50-Ferric Coated Activated Alumina and Granular Ferric Hydroxide (GFH) for Arsenic Removal in the Presence of Competitive Ions in an Active Well: Kirtland Field Trial–Initial Studies

Nadim R. Khandaker, James Krumhansl, Linnah Neidel, and Malcolm Siegel

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Nadim R. Khandaker, James Krumhansl, Linnah Neidel, and Malcolm Siegel

Geochemistry Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0754

Abstract

This report documents a field trial program carried out at Well #15 located at Kirtland Air Force Base, Albuquerque, New Mexico, to evaluate the performance of two relatively new arsenic removal media, ALCAN-AASF50 (ferric coated activated alumina) and granular ferric hydroxide (US Filter-GFH). The field trial program showed that both media were able to remove arsenate and meet the new total arsenic maximum contaminant level (MCL) in drinking water of 10 μg/L.

The arsenate removal capacity was defined at a breakthrough effluent concentration of 5 μg/L arsenic (50% of the arsenic MCL of 10 μg/L). At an influent pH of 8.1 ±0.4, the arsenate removal capacity of AASF50 was 33.5 mg As(V)/L of dry media (29.9 μg As(V)/g of media on a dry basis). At an influent pH of 7.2 ±0.3, the arsenate removal capacity of GFH was 155 mg As(V)/L of wet media (286 μg As(V)/g of media on a dry basis). Silicate, fluoride, and bicarbonate ions are removed by ALCAN AASF50. Chloride, nitrate, and sulfate ions were not removed by AASF50. The GFH media also removed silicate and bicarbonate ions; however, it did not remove fluoride, chloride, nitrate, and sulfate ions. Differences in the media performance partly reflect the variations in the feed-water pH between the 2 tests. Both the exhausted AASF50 and GFH media passed the Toxicity Characteristic Leaching Procedure (TCLP) test with respect to arsenic and therefore could be disposed as nonhazardous waste.

Acknowledgements

This project would not have been possible without the generous collaboration of the Kirtland Air Force Base, Environmental Management Flight Group. Thanks also go to David Howard for helping in sampling and analyzing the water samples for arsenic. Alicia Aragon provided useful review comments and additions to the final version. Finally, this report is dedicated to Greg Garland, University of New Mexico, who built the Kirtland Field Trial setup. Shortly after building the test setup, Greg passed away.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Executive Summary

By 2006, public utilities in the United States will have to meet the new drinking water standard of 10 µg/L for arsenic. This will affect rural communities, particularly in the southwest United States, that rely on arsenic contaminated groundwater as their source of drinking water. Small rural water systems have limited treatment infrastructures, and additional efforts to remove arsenic will substantially increase the cost of treated water. There is a need to find effective and economical arsenic removal systems for the affected communities.

A field trial program was carried out to evaluate the performance of relatively new arsenic removal media at Well # 15, Kirtland Air Force Base, Albuquerque, New Mexico. Well # 15 historically has water with arsenic concentration greater than 10 µg/L. The media tested were ALCAN-AASF50 (ferric coated activated alumina) and granular ferric hydroxide (US Filter-GFH). The objective of the study was to evaluate the performance of the two media under the influences of existing pH and competitive ions present in water from an active well. Prior to contact with the media, the source water was modified by the addition of an oxidizing agent (hypochlorite) to convert arsenite (oxidation state III) to arsenate (oxidation state V).

The field trial program showed that both media were able to remove arsenate and meet the new total arsenic maximum contaminant level (MCL) of 10 µg/L in drinking water. The arsenate removal capacity was defined at a breakthrough effluent concentration of 5 µg/L arsenic (50% of the arsenic MCL of 10 µg/L). At an influent pH of 8.1 ±0.4, the arsenate removal capacity of AASF50 was 33.5 mg As(V)/L of dry media (29.9 µg As(V)/g of media on a dry basis). At an influent pH of 7.2 ±0.3, the arsenate removal capacity of GFH was 155 mg As(V)/L of wet media (286 µg As(V)/g of media on a dry basis). In general, previous tests by others show that decreasing the pH of the influent water increases the sorption capacity of arsenic removal media; hence, the lower operating pH may have contributed to the much higher performance of the GFH media than AASF50.

Silicate, fluoride, and bicarbonate ions were removed by ALCAN AASF50; chloride, nitrate, and sulfate ions were not removed the media. The GFH media also removed silicate and bicarbonate ions but did not remove fluoride, chloride, nitrate, and sulfate ions.

The GFH media contains a substantial amount of fine granules that over time contribute towards decreasing bed porosity, thereby decreasing the operational flow rate. In the operation of GFH columns, it is recommended that the media bed be periodically fluidized to wash out fines. At operating pH greater than 7.0, the structural integrity of the AASF50 media was good, as indicated by the constant flow rate observed for the duration of the test. Both the exhausted AASF50 and GFH media passed the Toxicity Characteristic Leaching Procedure (TCLP) test with respect to arsenic and therefore can be disposed as nonhazardous waste.

This work should be considered an initial scoping study to develop methods for testing adsorbent media for the Arsenic Water Technology Partnership Pilot Demonstration program. Due to logistical constraints on time, it was not possible to investigate the effects of lowering the operational pH to the range of 6.5 to 6.8 in terms of sorption capacity, removal efficiency, and stability. Future work should include simultaneous operation of the same media in separate columns under varying pH conditions. This study was limited to the adsorption of As(V) because the feed water was pre-chlorinated. Groundwater contaminated with arsenic may contain As(III) species, and therefore, pre-oxidation of As(III) to As(V) is required unless the media performance is evaluated for the removal of As(III). Finally, in this report the media performance evaluation was not correlated in terms of media cost based on volume and weight of dry media. A dollar value based on the cost of the media and the life of the media along with operational cost was not done and should be included in the scope of more extensive future evaluation projects.

Table of Contents

Page

Figures

Tables

Acronyms

ARC	arsenic removal capacity
AA	activated alumina
ASAP	Accelerated Surface Area and Porosimetry System
AWWA	American Water Works Association
BET	Brunauer, Emmett and Teller
EBCT	empty bed contact time
EDS	energy-dispersive spectra
EPA	Environmental Protection Agency
GFH	granular ferric oxyhydroxide
MCL	maximum contaminant level
NTU	nephelometer turbidity unit
RSSCT	rapid small scale column tests
SNL	Sandia National Laboratories
SEM	scanning electron microscope
S	siemen
TCLP	toxicity characteristic leaching procedure
USA	United States of America

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1. Introduction

Epidemiological studies carried out over the past three decades have established the link between adverse health effects and the presence of arsenic in drinking water (Cebrian et al. 1983, Chen and Wang 1990, and Brown and Chen 1994). The health effects of ingested inorganic arsenic include skin and internal cancers and non cancer-related effects on skin, vascular and gastrointestinal systems (US EPA 1998).

Aquifers in Bengal basin encompassing parts of West Bengal, India, and in Bangladesh, Taiwan, northern China, Hungary, Mexico, Chile, Argentina and many parts of the United States of America (USA) have arsenic at concentrations in excess of regulatory limits. By 2006 public utilities in the USA will have to meet the drinking water standard of 10 µg/L arsenic. This will affect numerous rural communities, particularly in the southwest USA that rely on arsenic contaminated groundwater as their source of drinking water. Small rural water systems have limited treatment capabilities (typically only chlorination); therefore, additional efforts to remove arsenic will substantially increase the cost of treated water (Bitner et al. 2001). Clearly there is an urgent need to find cost effective arsenic removal systems or to enhance the performance of existing systems in order to limit the financial burden on the affected communities. This is more a concern in areas such as Bangladesh, a country where over 70 million people are consuming arsenic contaminated water (Rawls 2002).

1.1 Fundamentals of Arsenic Removal by Adsorption

Adsorption is a mass transfer process in which a substance is transferred from the liquid phase to the surface of a solid where it becomes bound by chemical or physical forces. In the case of oxyanions such as arsenate and arsenite, adsorption occurs on the oxide water interface by forming a complex with surface sites that may be positively charged, such as a protonated surface hydroxyl group. In other instances, the reaction may involve a ligand exchange mechanism in which the surface hydroxyl group is displaced by the adsorbing ion (American Water Works Association {AWWA} Research Foundation 1999). The adsorption reaction mechanism of arsenic species onto solid metal oxyhydroxide surfaces below pH 6.7 may be generically represented by the following chemical reaction (AWWA Research Foundation 1999, Edwards 1994, and Manning et al. 1998):

$$\equiv\overline{S\text{-}OH} + H^+ + H_2AsO_4^- \rightarrow \equiv\overline{S\text{-}H_2AsO_4} + H_2O \text{ (arsenate sorption)}$$

$$\equiv\overline{S\text{-}OH} + H_3AsO_3 \rightarrow \equiv\overline{S\text{-}H_2AsO_3} + H_2O \text{ (arsenite sorption)}$$

Ion exchange is a special case of adsorption where ionic species in aqueous solution are removed by exchange with ions of a similar charge (not limited to protons) that are attached to a synthetic resin or mineral surface.

Adsorption processes commonly used in water treatment are adsorption onto activated alumina, ion exchange, and iron oxyhydroxides (Banerjee et al. 1999, Torrens 1999). Figure 1-1 summarizes the typical treatment setup for the sorption process for arsenic removal. The efficiency of each media depends on operating conditions such as pH, the presence of interfering ions, speciation of arsenic, system dependent parameters (e.g., empty bed contact time, surface loading rates, bed-porosity, etc.), and the use of oxidizing agent(s) in the pre-treatment train. In general, As(V) is easier to remove from water, since it is anionic above a pH of 2.2 and is attracted to positively charged metal hydroxide surfaces. As(III) is uncharged in most natural waters below pH 9.2 and has no charge affinity to surfaces. The charge neutrality makes it difficult to remove As(III) from natural waters (Edwards 1994).

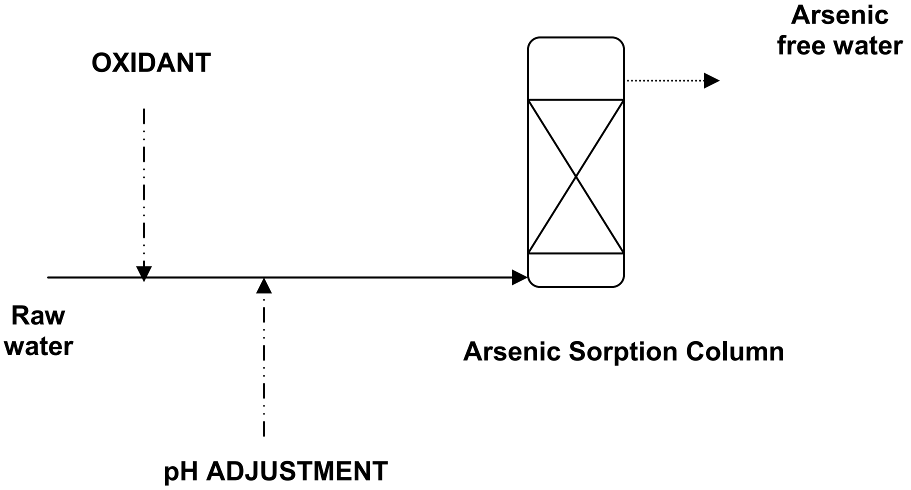

Figure 1-1. Schematic Diagram of the Sorption Process for Arsenic Removal.

1.2 Objectives of the Kirtland Field Trial

The field trial program was carried out to evaluate the performance of two widely used arsenic removal media, ALCAN-AASF50 (ferric coated activated alumina) and granular ferric hydroxide (GFH). These studies were designed to obtain operational experience in carrying out pilot tests similar to those envisioned for the proposed Arsenic Water Technology Partnership program. The well where the field program was carried out (Well #15) is located at Kirtland Air Force Base, Albuquerque, New Mexico, and historically has water with arsenic concentration greater than 10 μg/L. The two adsorption media were evaluated using the Well #15 water under the influences of existing pH and competitive ions. Prior to treatment in the fixed bed, the source water was modified by the addition of an oxidizing agent to convert arsenite (oxidation state III) to arsenate (oxidation state V). The tests provide a baseline for future tests in which the pH could be adjusted to obtain optimal media performance or for tests carried out without pre-oxidation. Finally, these tests also provide a baseline for comparisons with the performance of a proprietary Sandia National Laboratories (SNL) media (Brady et al. 2004) under similar conditions.

2.0 Materials and Methods

2.1 Reagents

All chemicals (reagent grade) and supplies were obtained from Fisher Scientific, Pittsburgh, Pennsylvania, USA, unless otherwise stated elsewhere in the paper.

2.2 Pre-oxidation of Well Water

To ensure that the arsenic in the well water was in the pentavalent form prior to entering the media columns, the arsenic feed water was treated with 5.0% commercial sodium hypochlorite solution to a level of approximately 1.0 mg/L of residual chlorine in a holding tank.

2.3 Analyses

All liquid samples collected were stored in high-density polyethylene bottles at 4°C in a refrigerator prior to analysis.

Analyses of arsenic and other trace metals were done on a Perkin Elmer SCIEX ELAN 6100 Inductively Coupled Plasma mass spectrometer. Typically, five replicates of the same sample were injected, and the average value reported. The method detection limit was calculated for arsenic as 1.0 µg/L. The accuracy of measurement for arsenic was taken as ±1.0 µg/L.

Analysis of pH was done according to Standards Method 4500-H^+ (Electrometric Method) using a Corning Pinnacle 530 pH meter, calibrated using pH 4.0, 7.0, and 10.0 standard pH solutions. Alkalinity was measured by the titration method, Standard Method 2320B (APHA 1998).

Temperature and conductivity was measured with a HACH SENS ion dual conductivity and temperature probe/meter. Turbidity was measured using HACH method 8237 with a HACH DR/2010 spectrophotometer. Silicate and residual chlorine were measured with a HACH DR/2010 spectrophotometer and utilized HACH methods 8185 and 8021, respectively (HACH 1996).

Measurement of sulfate, nitrate, chloride, fluoride, and phosphate ions were done using a Dionex DX-320 ion chromatograph with an AG17 guard column and an AS17 separator column with a 25-µL sample loop.

Scanning electron micrographs of the sorption media before and after the tests were taken with a JEOL JSM-6300V scanning electron microscope equipped with an energy-dispersive X-ray emission analyzer.

Surface area (Brunauer, Emmett and Teller (BET) method using nitrogen gas) of the sorption media was determined using a Micrometrics ASAP (Accelerated Surface Area and Porosimetry System) 2000. The samples were degassed at 90°C prior to analysis and analyzed using the multi-point method (5 points used).

Toxicity Characteristic Leaching Procedure (TCLP) tests were conducted for As, Ba, Cd, Cr, Pb, Se, Ag, and Hg on the arsenic-laden spent media from the column tests, according to the Environmental Protection Agency (EPA) Method 1311 (U.S. EPA 1992). (The TCLP involves placing the spent media in an acetate buffer at pH 5 for 18 hours and is designed to simulate leaching that would occur in an ordinary sanitary landfill). The TCLP limits for the leachates are as follows: As = 5 mg/L; Ba = 100 mg/L; Cd = 1.0 mg/L; Cr = 5.0 mg/L; Pb = 5.0 mg/L; Se = 1.0 mg/L; Ag = 5.0 mg/L; Hg = 0.2 mg/L. The TCLP tests were carried out at an EPA certified laboratory (Assaigai Analytical Laboratories Inc., 7300 Jefferson NE, Albuquerque, NM 87109).

Dry and wet densities (wet density was measured only for GFH) of the sorption media were measured by dividing the weight of the media by its volume. The weight of the media was measured using a Mettler AE 163 precision mass balance (to four decimal places), and the volume of the media was measured using a graduated cylinder with 0.5 mL markings.

The x-ray powder diffraction patterns were measured for the virgin and spent GFH media using a Bruker D8 Advance Diffractometer, in Bragg-Brentano geometry with Ni-filtered CuK-alpha radiation.

2.4 Experimental Program

The process diagram of the field trial setup is shown in Figure 2-1. A picture of the operational field trial setup is shown in Figure 2-2. Source groundwater for the test was obtained downstream from a pump station by tapping a 10-inch diameter distribution line. This source water next entered a 55-gallon high-density polyethylene tank (supplied by Fisher Scientific) via a flow control valve. The feed tank served both as a chlorine contact chamber and a pressure surge tank. The feed tank was equipped with an automated level control system, which also controlled the operation of both the sodium hypochlorite pump (Model QG20 supplied by Fluid Metering Inc., 29 Orchard Street, Oyster Bay, New York 11771) and the main 1/8 horse power centrifugal pump (Model 6305-500, supplied by Ryan Herco, 5511 Midway Park Place, NE, Albuquerque, New Mexico 87109) feeding the media columns. (During the later part of the test, the oxidant was added manually.) The water from the feed-tank passed through individual flow totalizers (cumulative flow meter recorder) before entering the bottom of each individual media column. Each media column was 4.0 inches in diameter by 3.0 feet in height and made of ¼-inch high-density polyethylene. Each media column was divided into two sections. The bottom six inches of the column contained graded gravel, which served as a containment base for the media and as a uniform water flow distributor. On top of the gravel bed lay the arsenic sorption media bed of uniform size composition. The water flowed up through each packed column at the flow rate of approximately 1.0 L/min at an empty bed contact time (EBCT) of 5.0 minutes. At the EBCT of 5.0 min, the bed behaved as a packed column. Alcan Chemicals, Brockville, Ontario, Canada, supplied the ALCAN AASF50 media. US-Filter (Courtesy of CH_2MHill), Colorado Springs, Colorado, supplied the GFH media. (A SNL proprietary media was also evaluated; results of this test can be found in Brady et al. 2004.)

Both influent and effluent samples (250 mL) were collected for laboratory analyses of arsenic, nitrate, sulfate, phosphate, fluoride, silicate, and alkalinity on a daily basis. The more common operational control parameters, such as flow rate, totalized flow, and the more common water quality parameters (pH, temperature, conductivity, turbidity, residual chlorine) for both influent and effluent samples were also measured on a daily basis. The composition of the influent water for both media is described in Table 2-1.

The field setup was operated until breakthrough, defined by an effluent water arsenic concentration of 5.0 µg/L. After breakthrough, each individual column was emptied, and samples of the saturated media were sent for scanning electron microscope (SEM) analysis and TCLP test.

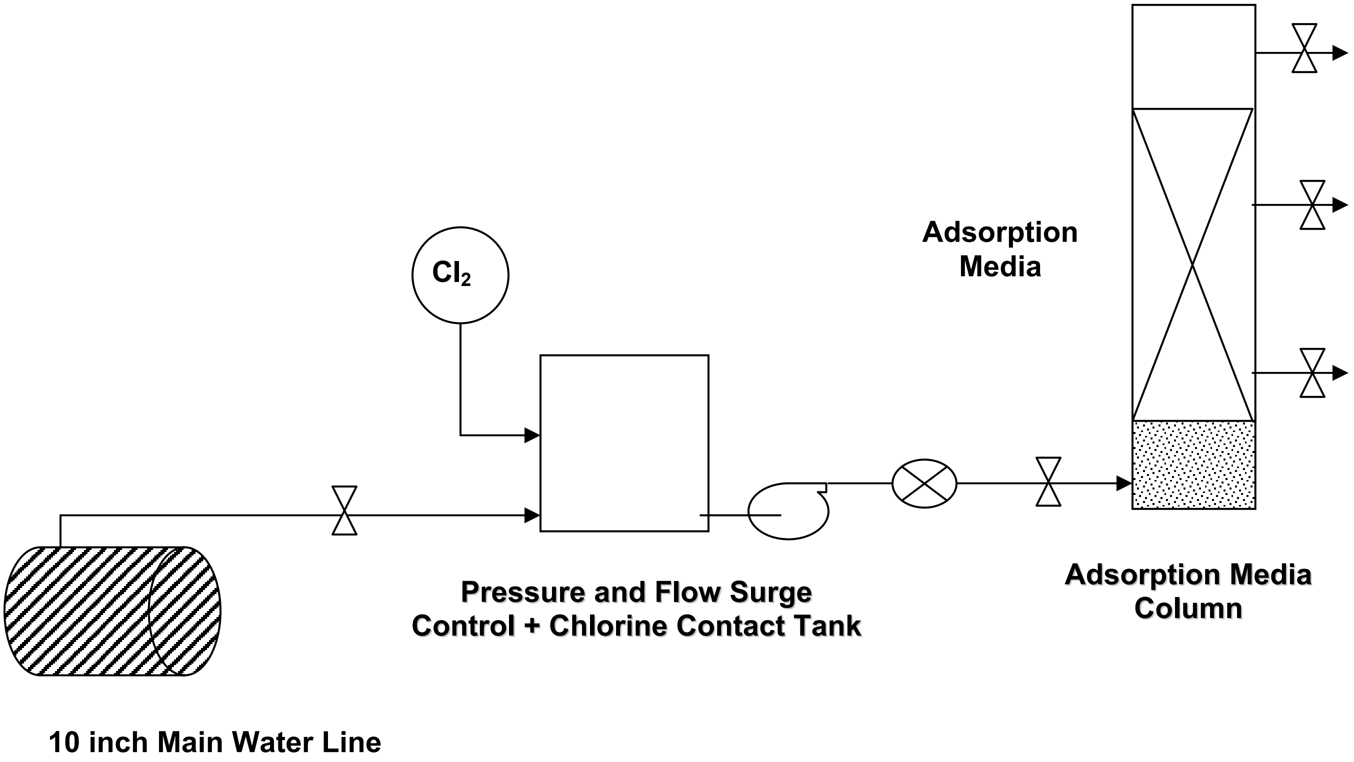

Figure 2-1. Process Flow Diagram of Field Trial Setup for Evaluation of Arsenic Sorption Media.

Figure 2-2. Picture of Field Trial Setup at Well 15, Kirtland Air Force Base.

Table 2-1. Influent Water Composition During Field Test

Analyte/value	**As**	**pH**	**Cl^-**	**F^-**	**NO_3^-**	**SO_4^{2-}**	**SiO_2**	**HCO_3^-**
units	**μg/L**		**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**
AASF50 Test Period 5/29/02 – 8/16/02								
average	13.07	8.10	46.02	0.50	0.23	29.63	44.49	85.67
Std dev	1.13	0.47	11.04	0.04	0.14	1.52	5.59	7.49
min	11.42	7.20	38.58	0.43	0.04	26.93	36.20	73.40
max	16.80	8.90	62.10	0.56	0.77	32.08	51.50	97.40
GFH Test Period 10/11/02 – 12/23/02*								
average	16.72	7.36	51.97	0.51	0.12	29.37	47.28	92.98
Std dev.	2.51	0.33	6.46	0.07	0.09	1.89	4.37	9.32
min	12.36	6.54	36.23	0.34	0.00	26.53	39.40	67.00
max	22.06	8.18	64.77	0.63	0.27	33.28	53.10	101.20

*Flow was interrupted in GFH test from 12/23/02 to 3/24/03 and was resumed from 3/24/03 until 4/8/03; only data for As are available the second period: average= 26.37 μg/L; std dev = 3.22 μg/L; min = 22.53 μg/L; max = 30.62 μg/L.

2.5 Operation of Field Test

Five liters of 28x48 mesh AASF50 were loaded in the column. The details regarding the physical characteristics of the AASF50 media along with the details of the process operating conditions are listed in the next section (see Table 3-1). The AASF50 column was operated in an upflow mode at an operational flow rate of 1.0 L/min, corresponding to an EBCT of 5.0 minutes. The duration of the test program for ALCAN-AASF50 was from May 29, 2002 to August 16, 2002.

Five liters of the wet GFH media (note that the manufacturer ships GFH in a wet basis) was loaded in the field test column. The details regarding the physical characteristics of the GFH media along with the details of the process operating conditions are listed in the next section (see Table 3-1). The test duration for the GFH media was from October 11, 2002 to April 8, 2003. The operation of the GFH column was halted for 91 days, from December 23, 2002 to March 24, 2003. Testing was suspended because Well 15 was out of operation due to unscheduled maintenance and water was not available for the Kirtland field trial system during this time. The GFH column was operated in an upflow mode at an operational flow rate of 1.0 L/min, corresponding to an EBCT of 5.0 minutes.

3. Results: Ferric Coated Activated Alumina (AASF50)

The flow rate profile through the duration of the test is given in Figure 3-1. The breakthrough profile of arsenic is shown in Figure 3-2. The breakthrough profile indicates that at the influent flow rate of 1.0 L/min of water, influent average pH of 8.1±0.4 (Figure 3-3), and average influent arsenic concentration of 12.9 ±0.9 µg/L, breakthrough (defined at 5 µg/L As) occurred after treatment of 2597 bed volumes of water. This corresponds to approximately 12,986 L of water treated. For a 5.0 µg/L effluent breakthrough arsenic concentration, the arsenic removal capacity of ALCAN-AASF50 was determined by mass balance (Equation 3-1 and 3-2) to be 33.5 mg As(V)/L of dry media or 29.9 µg As(V)/g of media on a dry basis using the values of media volume, dry density, and average influent arsenic concentration in Table 3-1.

$$\text{ARC-by volume of media} = (V_{tw} \times C_{in})/(V_{media}) \qquad (3\text{-}1)$$

$$\text{ARC-by weight} = (V_{tw} \times C_{in})/(W_{media}) \qquad (3\text{-}2)$$

where:

ARC-by volume of media = arsenic removal capacity by volume of media, mg of arsenic/liter of media;

ARC-by weight of media = arsenic removal capacity by volume of media, µg of arsenic/gram of media;

V_{tw} = total volume of water treated at the breakthrough concentration of 5.0 µg/L (50% of 10 µg/L arsenic MCL), liters;

C_{in} = average influent total arsenic concentration, µg/L;

V_{media} = volume of media, liters; and

W_{media} = weight of media loaded, grams.

The pH and conductivity profile for both the influent and treated water are shown in Figure 3-3 and Figure 3-4, respectively. The average pH of the influent and treated water were 8.1 ±0.4 and 7.7 ±0.6, respectively; the average conductivity values of the influent and treated water were 421 ±30 and 437 ±47 µS/cm, respectively. The turbidities of both the influent and treated water were below detection, indicating that both the influent and treated water were not turbid and well below the turbidity maximum contaminant level (MCL) of 1 normal turbidity unit (NTU).

The breakthrough profiles of the other anions of concern, silica, alkalinity (carbonate and bicarbonate ions), fluoride, chloride, nitrate and sulfate, are shown in Figure 3-5 through 3-10. Note that at the pH value of 8.1 ±0.4, silica, bicarbonate (alkalinity), and fluoride were removed along with the arsenate (see Figures 3-5, 3-6, and 3-7). However, chloride and nitrate were not removed, as shown in Figures 3-8 and 3-9, where effluent concentrations are seen to be similar to the influent concentrations. The concentration of sulfate is higher in the effluent than in the influent (see Figure 3-10); this suggests that sulfate ions were being released by the media.

Note that after 500 to 1500 bed volumes of water were treated, the bed was saturated with respect to the sorption of silica, bicarbonate, and fluoride ions, and yet arsenic still was adsorbed until 5860 bed volumes of water had passed through the column.

The SEM analysis of the virgin AASF50 and the exhausted media grains after the completion of the column tests did not show any change in the structural morphology of the media. This indicates that the media integrity was maintained and that the bed characteristics did not change, an observation further substantiated by the stable water flow rate observed throughout the test (see Figure 3-1). Energy Dispersive Spectrometry (EDS) analyses of the virgin and exhausted AASF50 media showed the presence of silica, aluminum and iron in the saturated media. In contrast, the virgin media did not show the presence of silica. It should be noted that no internal standards were used in the EDS analysis, and the observation regarding the presence of silica and other metals was qualitative at best. This to some degree substantiates what was seen in the breakthrough profile for silica from the column test, which showed that the media was removing silica (see Figure 3-5).

The spent arsenic media passed the TCLP test with respect to arsenic (<0.1 μg/L), barium (<1.6 mg/L), cadmium (<0.02 mg/L), chromate (<0.02 mg/L), lead (<0.05 mg/L), selenium (<0.17 mg/L), silver (<0.04 mg/L), and mercury (<0.0002 mg/L).

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Table 3-1. Table of Process Parameters and Media Properties for the Two Media Under Evaluation-Field Trial Kirtland.

Parameter	Unit	ALCAN-AASF50	GFH
1. Process-Parameters			
Empty Bed Contact Time	min	5.0	5.0
Volume of media loaded	liters	5.0	5.0
Water flow rate	liters/min	1.0	1.0
Size of media	mesh	28x48	Not sieved-wet media
Bed porosity		0.3-0.4 (approximate)	Changed over time
Bed height	inches	21	19
Date of operation		5/29/02 – 8/16/02	10/11/02 – 12/23/02 3/24/03 – 4/8/03
2. Media Properties			
Density-wet	g/cm^3	Not calculated	0.98
Density-dry	g/cm^3	1.12	0.53
Arsenic sorption capacity-volume	mg/L of media	33.5	155
Arsenic sorption capacity-dry weight	μg/g of media	29.9	286
Volume of water treated until breakthrough	liters	12,986	40,404
BET surface area	m^2/g	139.8	186.4
3. Influent Water Quality			
pH		8.1 ±0.4	7.2 ±0.3
Temperature	^{o}C	24-26	24-26
Average arsenic concentration	μg/L	12.9 ±0.9	19.21 ±4.1

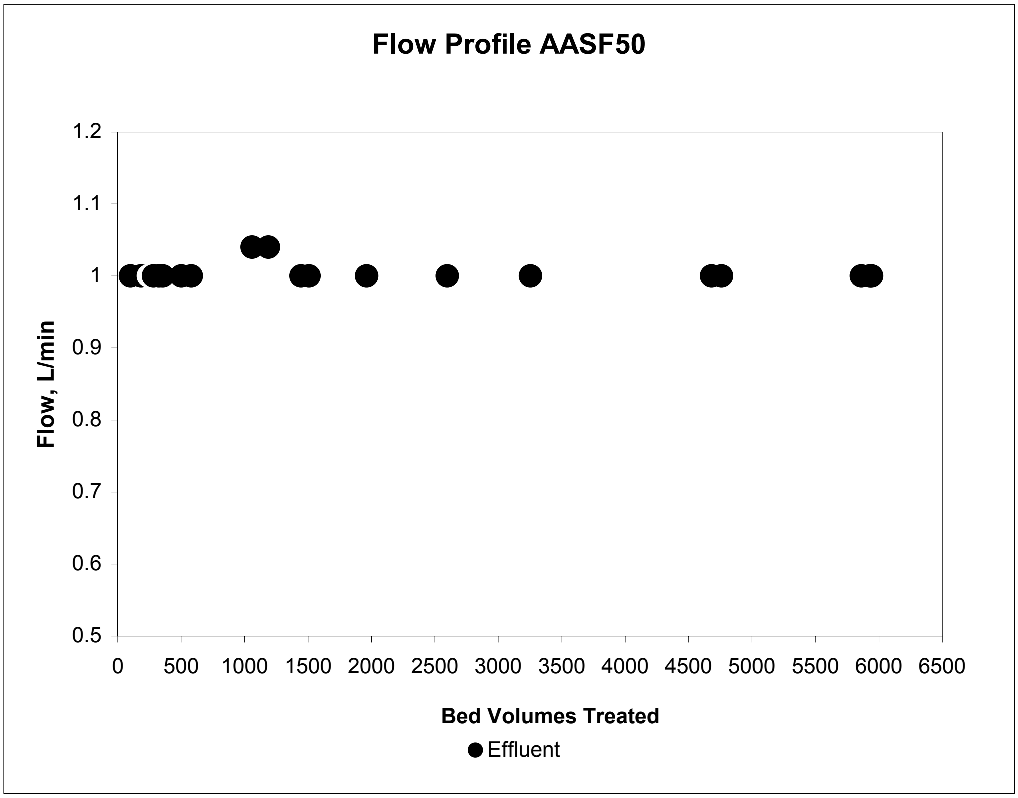

Figure 3-1. Water Flow Rate Profile of ALCAN-AASF50 Packed Column.

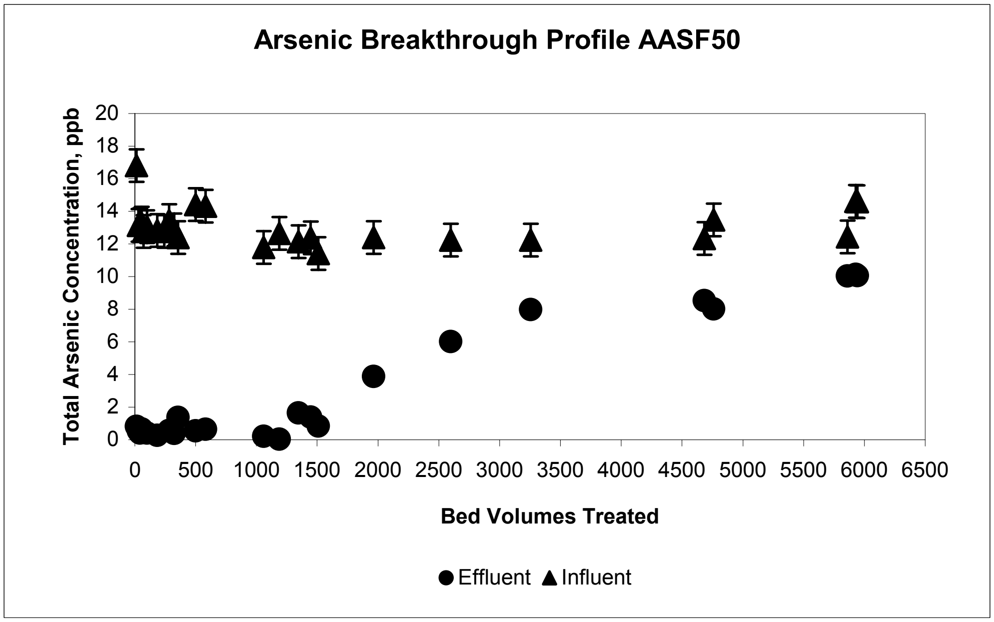

Figure 3-2. As(V) Breakthrough Profile of ALCAN-AASF50 Packed Column.

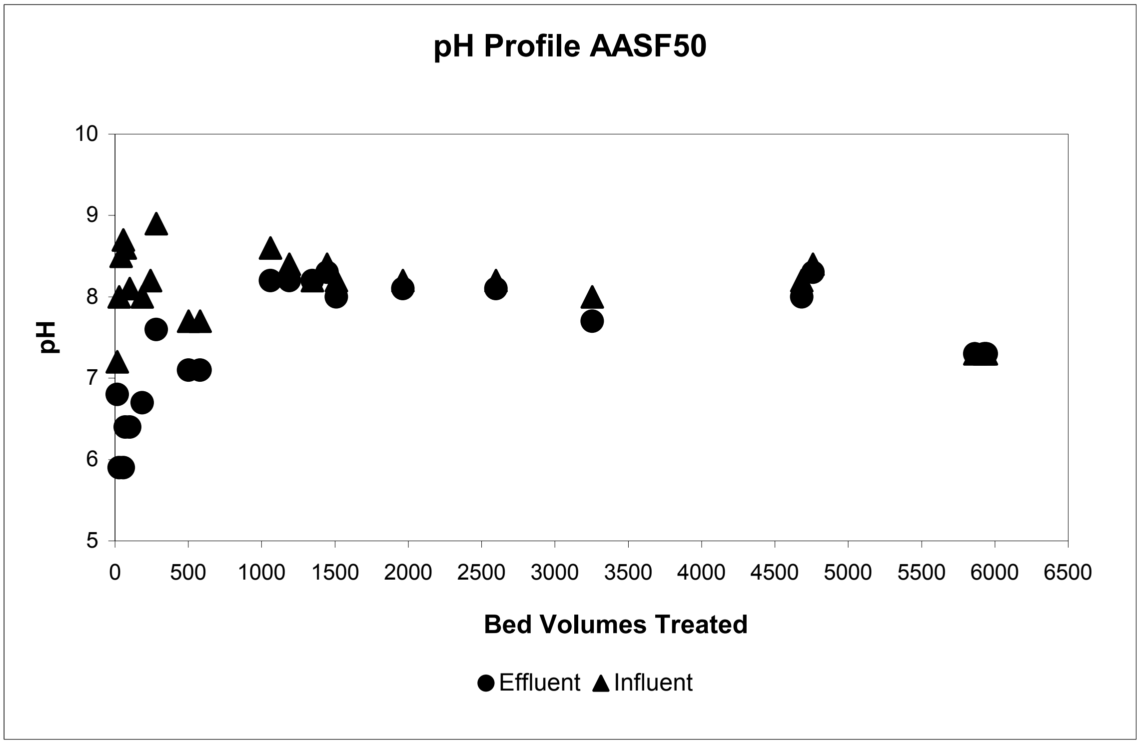

Figure 3-3. pH Profile of ALCAN-AASF50 Packed Column.

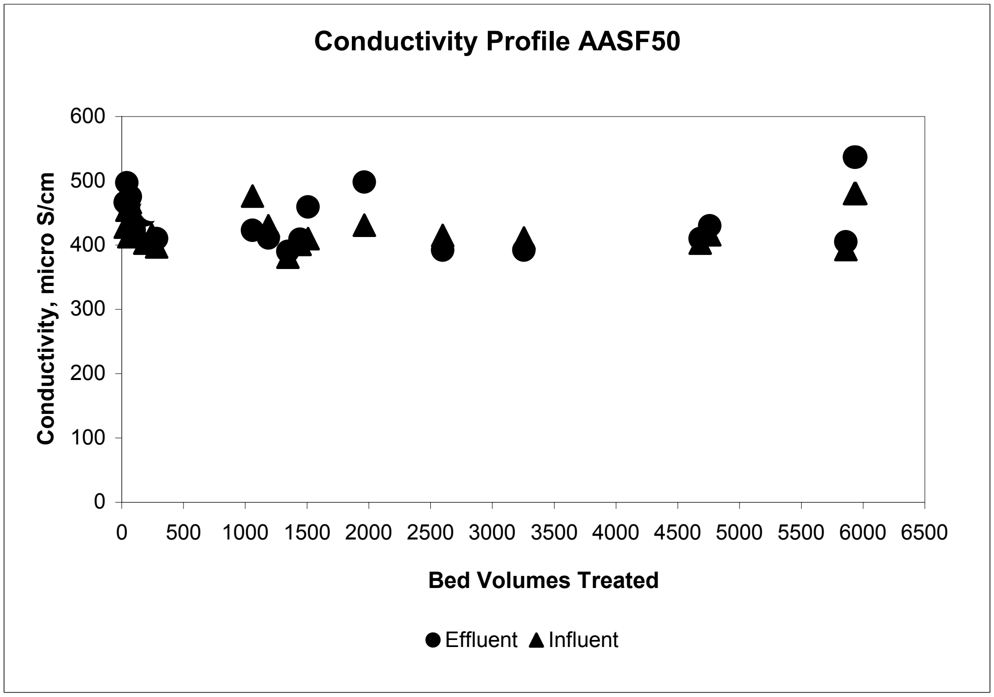

Figure 3-4. Conductivity Profile of ALCAN-AASF50 Packed Column.

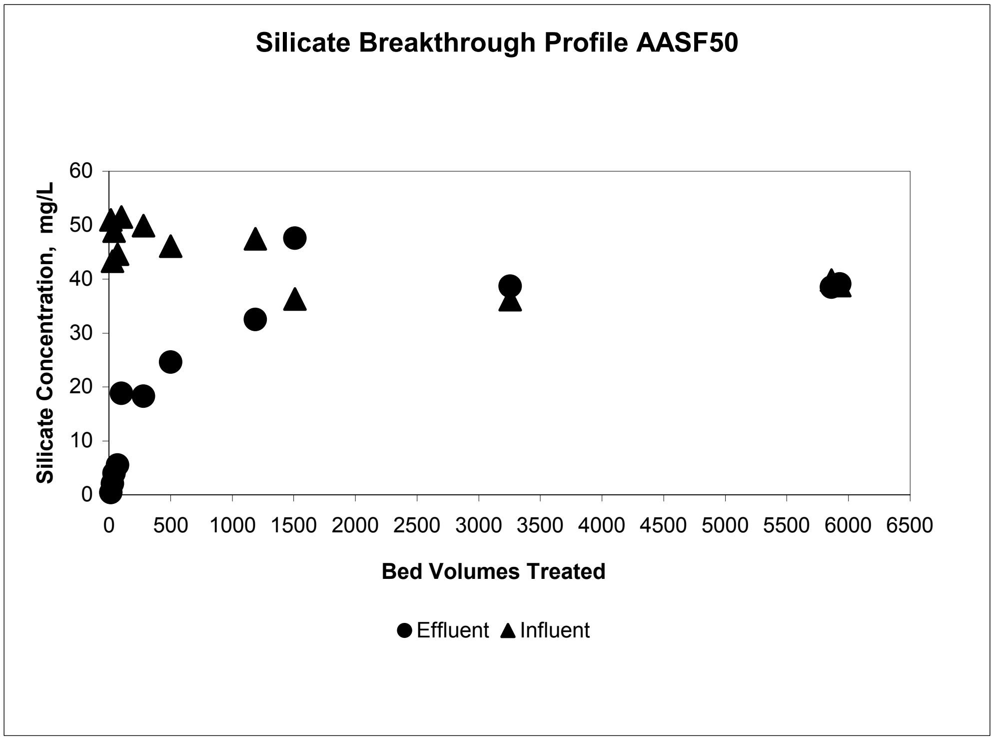

Figure 3-5. Silicates Breakthrough Profile of ALCAN-AASF50 Packed Column.

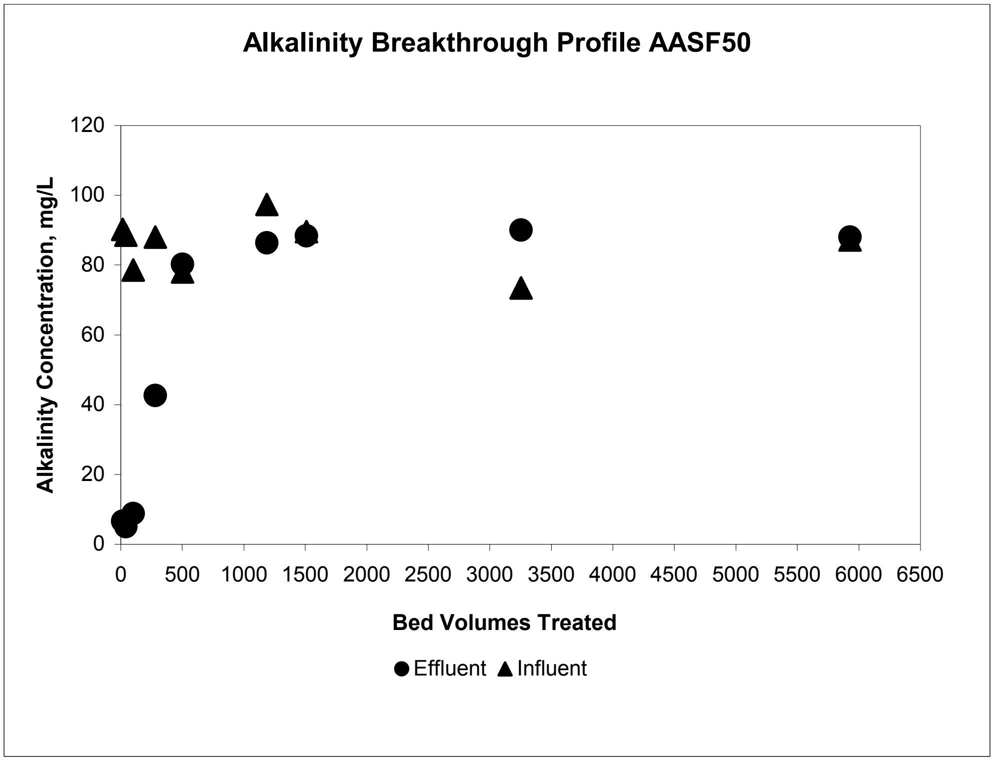

Figure 3-6. Alkalinity Breakthrough Profile of ALCAN-AASF50 Packed Column.

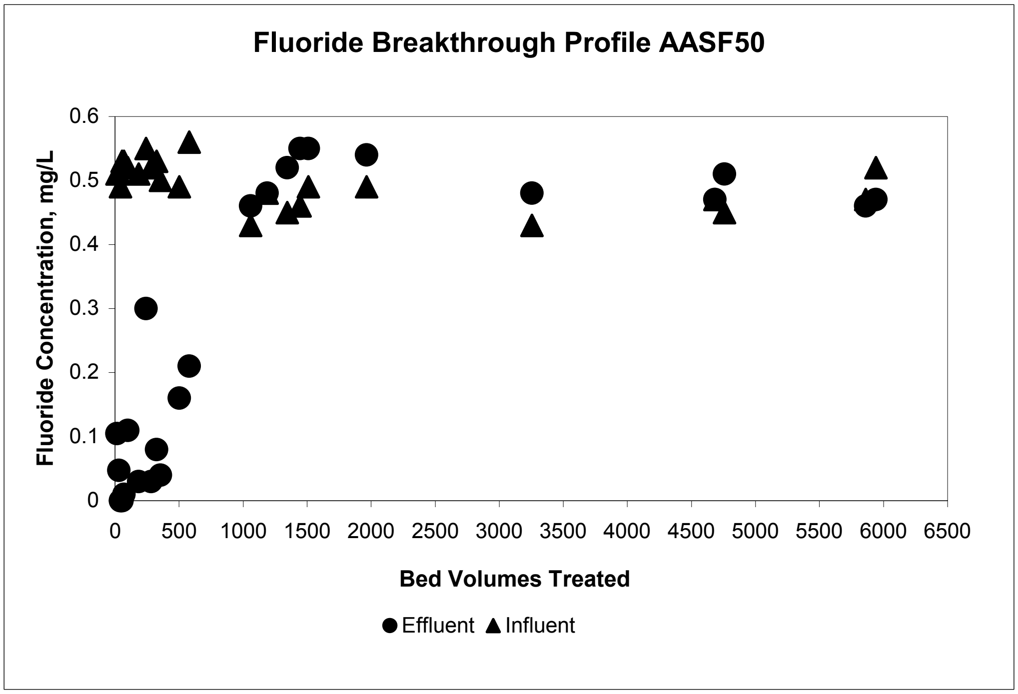

Figure 3-7. Fluoride Breakthrough Profile of ALCAN-AASF50 Packed Column.

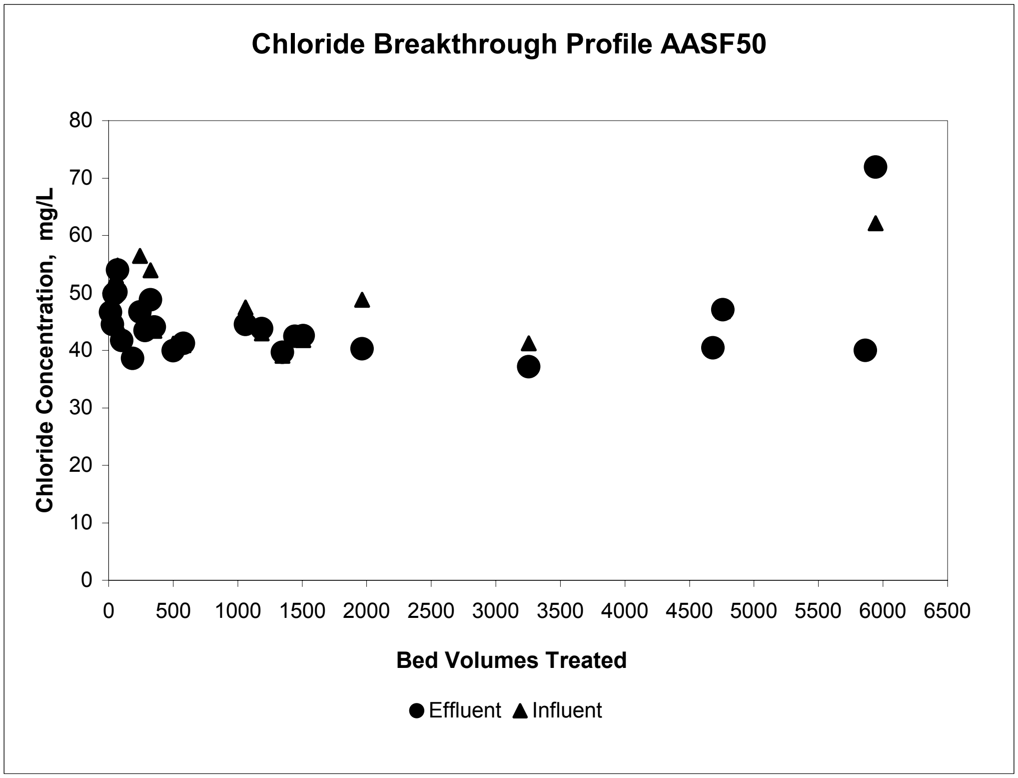

Figure 3-8. Chloride Breakthrough Profile of ALCAN-AASF50 Packed Column.

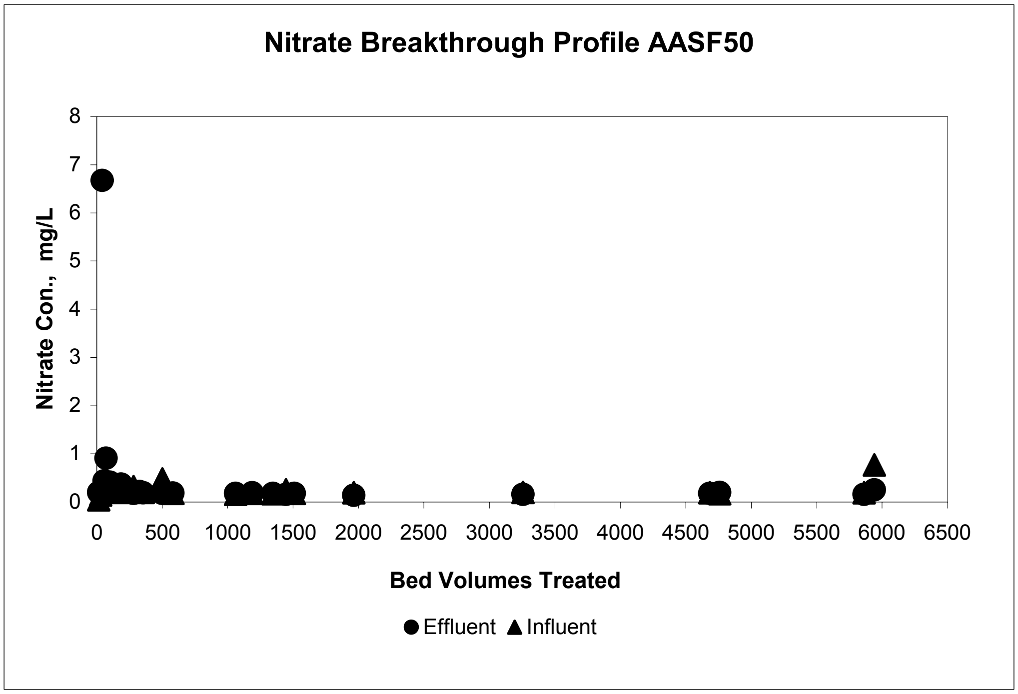

Figure 3-9. Nitrate Breakthrough Profile of ALCAN-AASF50 Packed Column.

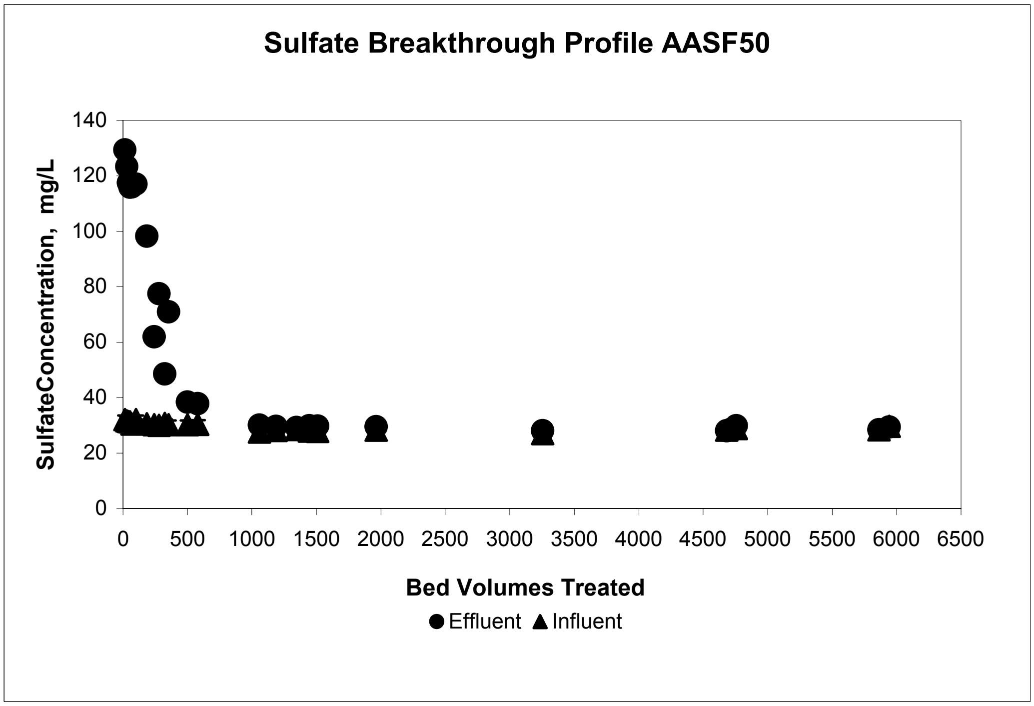

Figure 3-10. Sulfate Breakthrough Profile of ALCAN-AASF50 Packed Column.

4. Results: Granular Ferric Hydroxide (GFH)

The flow rate profile through the duration of the test is given in Figure 4-1. The starting EBCT of 5.0 minutes increased to an EBCT of ~10 minutes. The decrease in flow rate (increase in EBCT) was due to the decrease in bed permeability, either from the physical breakdown of the granular GFH media or mineralogical phase transformation of the GFH in the column. The SEM analysis of the virgin GFH media grains and exhausted media grains after the completion of the column tests did not show change in the structural morphology of the media. X-ray diffraction analysis of the virgin and exhausted media was unable to discern any morphological changes due to the amorphous nature of the media.

The breakthrough profile of arsenic is shown in Figure 4-2. The breakthrough profile indicates that, at the influent average pH of 7.2 ±0.3 (Figure 4-3) and average influent arsenic concentration of 19.21 ±4.1 µg/L, breakthrough occurred after treatment of 8080 bed volumes of water. This corresponds to roughly 40,404 L of water treated. By simple mass balance (see Equations 3-1 and 3-2), the arsenic removal capacity of GFH to a 5.0 µg/L effluent arsenic concentration was determined to be 155 mg of As(V)/L of dry media or 286 µg of As(V)/g of media on a dry basis, using the average influent arsenic concentration, and volume and densities of the media listed in Table 3-1.

As noted previously, during the field trial with the GFH media, the operation of the GFH column was halted for 91 days, from December 23, 2003 to March 24, 2003 (8548 bed volumes of operation). The effect of the prolonged interruption of operation was an initial decrease in effluent arsenic concentration upon restarting. The period of decreased effluent arsenic concentration lasted only for approximately 10 bed volumes of water treated. At 8462 bed volume, before flow interruption, the effluent concentration was 5.85 µg/L; at 8548 bed volumes, sampling soon after resumption of flow, effluent concentration was 4.23 µg/L. At 8557 bed volumes, the effluent concentration was 6.75 µg/L, after which the effluent concentration of arsenic started to rise at the same rate seen before the flow interruption (see Figure 4-2). Upon resumption of flow after the 91-day interruption, the influent arsenic concentration was higher. The range of influent arsenic concentration before the interruption in operation was 12.0 to 22.0 µg/L, whereas after resumption of operation, the influent arsenic concentration ranged between 24 and 31 µg/L.

The pH and conductivity profile for both the influent and treated water are shown in Figure 4-3 and Figure 4-4, respectively. The pH averages of the influent and treated waters were 7.2 ±0.3 and 7.1 ±0.3, respectively; the conductivities of the influent and treated waters were 473 ±78 and 499 ±95, µS/cm respectively. The turbidity of both the influent and treated water were below detection, indicating that both the influent and treated water were not turbid and the turbidity was well within the EPA-specified value of 1.0 NTU. Although the influent conductivity was relatively steady, the effluent conductivity profile shows periods of elevated conductivity. This may indicate possible washout of salts from the GFH media in the column.

The breakthrough profiles of the other anions of concern, silica, alkalinity (carbonate and bicarbonate ions), fluoride, chloride, nitrate and sulfate, are shown in Figures 4-5 through 4-10. At the influent water pH value of 7.2 ±0.3, the GFH media absorbed silica and bicarbonate alkalinity along with the arsenate (see Figures 4-5 and 4-6). However, fluoride, chloride, nitrate, and sulfate were not removed, as shown in Figures 4-7 through 4-10. At approximately 2000 bed volumes of water treated, the bed was saturated with respect to the sorption of silica and bicarbonate, whereas arsenic was adsorbed until the defined breakthrough point of 5.0 μg/L when 8080 bed volumes of water had been treated.

The spent GFH media passed the TCLP test with respect to arsenic (<0.1 mg/L), barium (5.2 mg/L), cadmium (<0.02 mg/L), chromate (<0.02 mg/L), lead (<0.05 mg/L), selenium (<0.05 mg/L), silver (<0.04 mg/L), and mercury (<0.0002 mg/L).

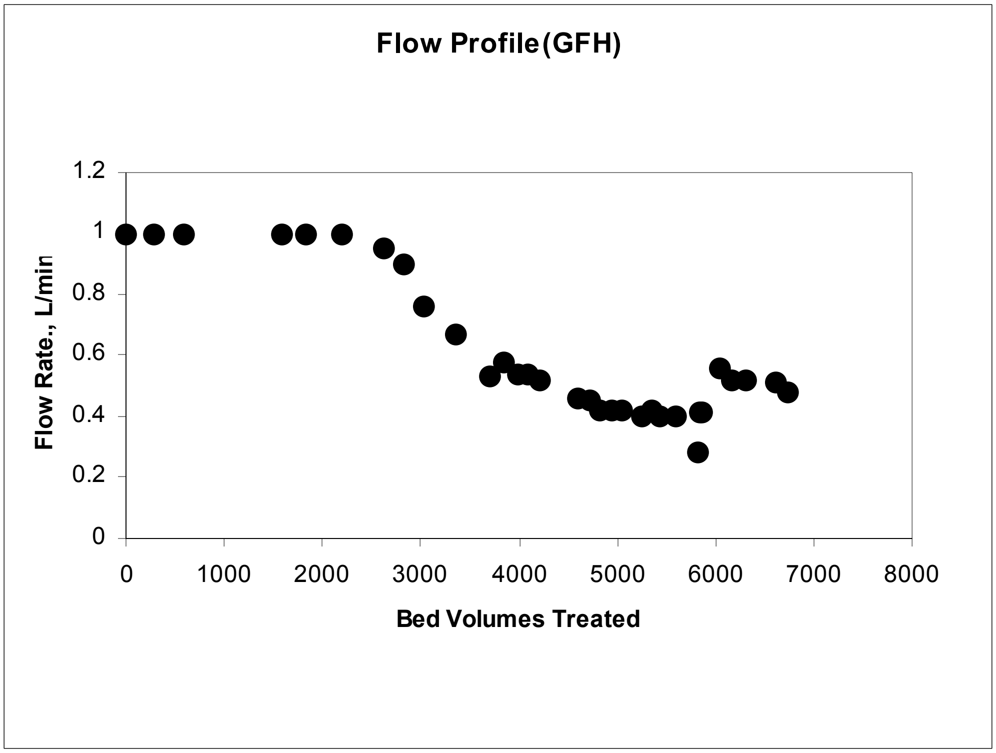

Figure 4-1. Water Flow Rate Profile of Granular Ferric Hydroxide (GFH) Packed Column.

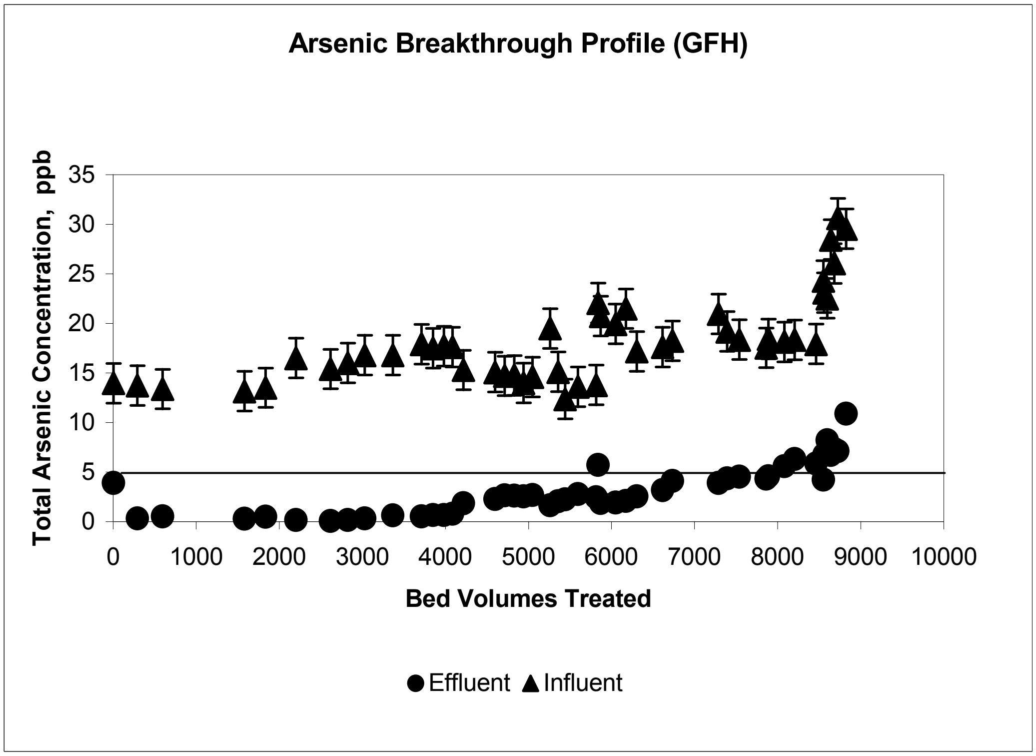

Figure 4-2. As(V) Breakthrough Profile of Granular Ferric Hydroxide (GFH) Packed Column.

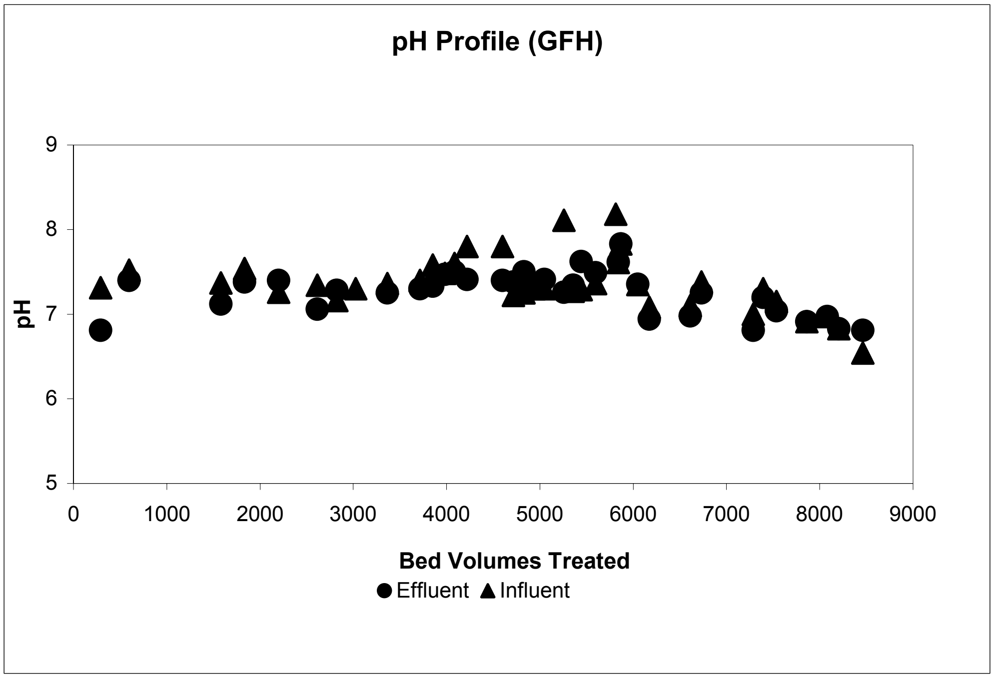

Figure 4-3. pH Profile of Granular Ferric Hydroxide (GFH) Packed Column.

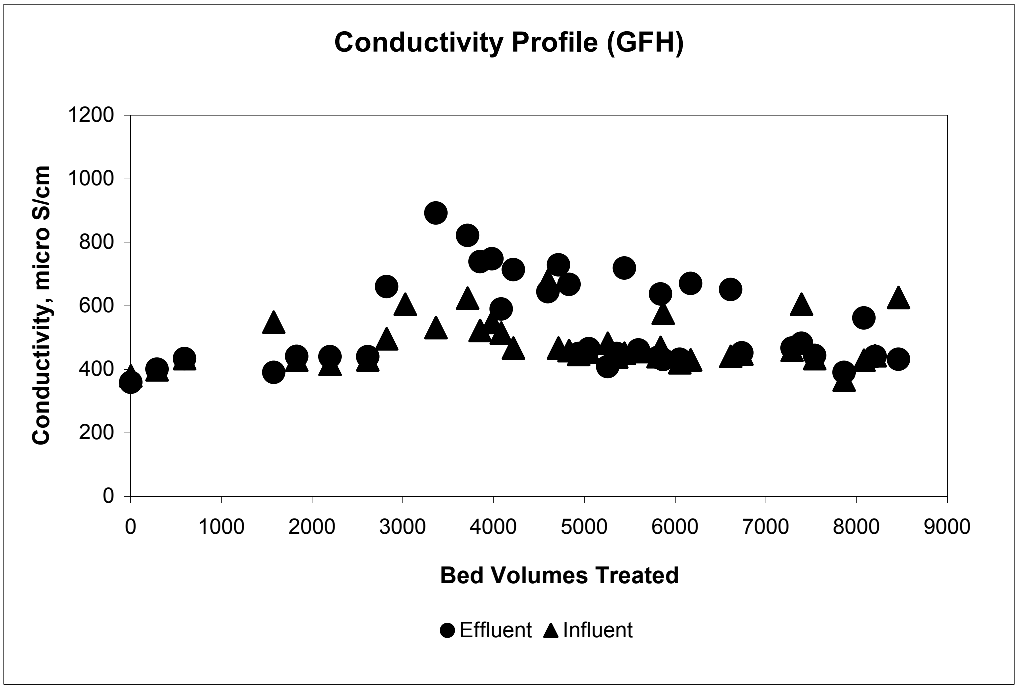

Figure 4-4. Conductivity Profile of Granular Ferric Hydroxide (GFH) Packed Column.

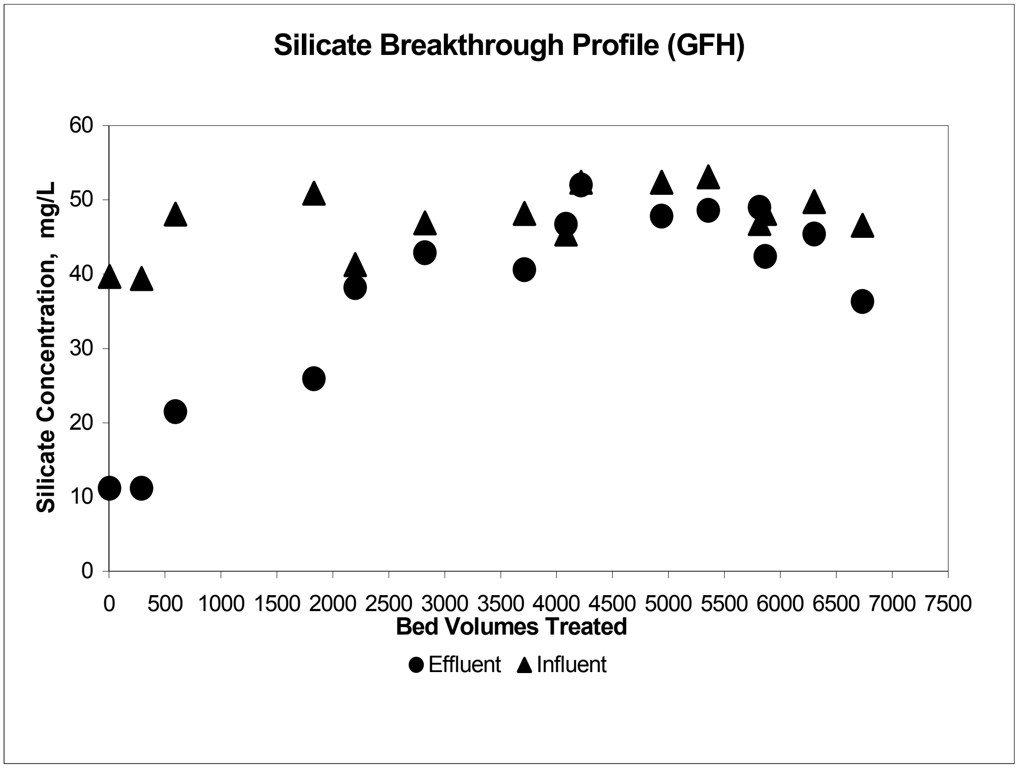

Figure 4-5. Silicates Breakthrough Profile of Granular Ferric Hydroxide (GFH) Packed Column.

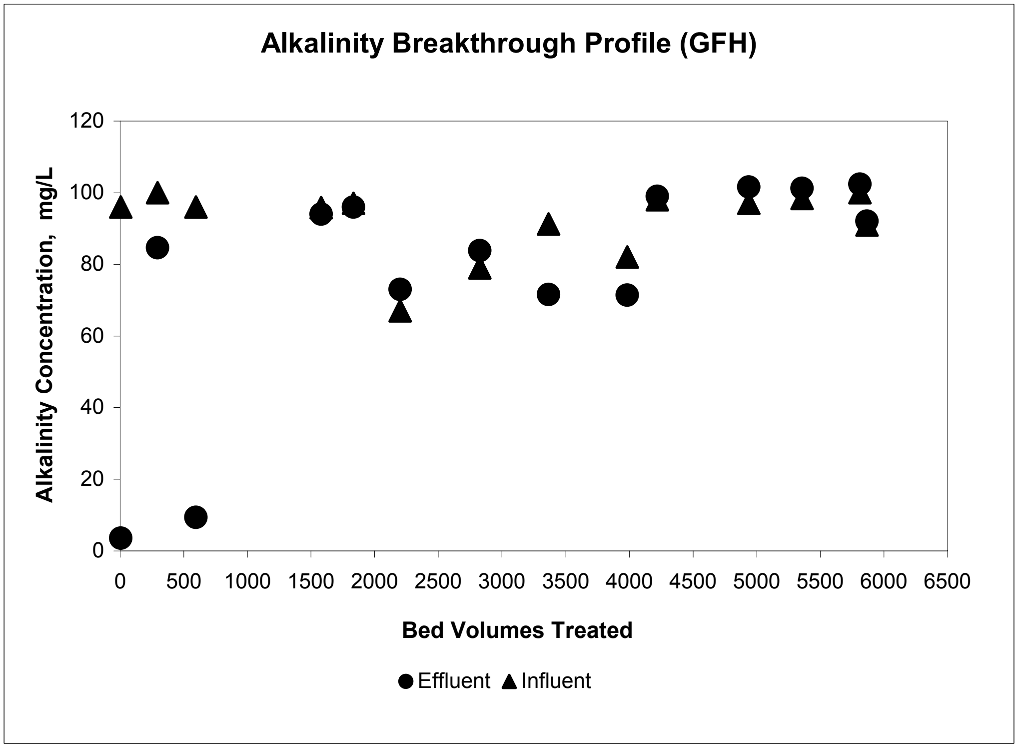

Figure 4-6. Alkalinity Breakthrough Profile of Granular Ferric Hydroxide (GFH) Packed Column.

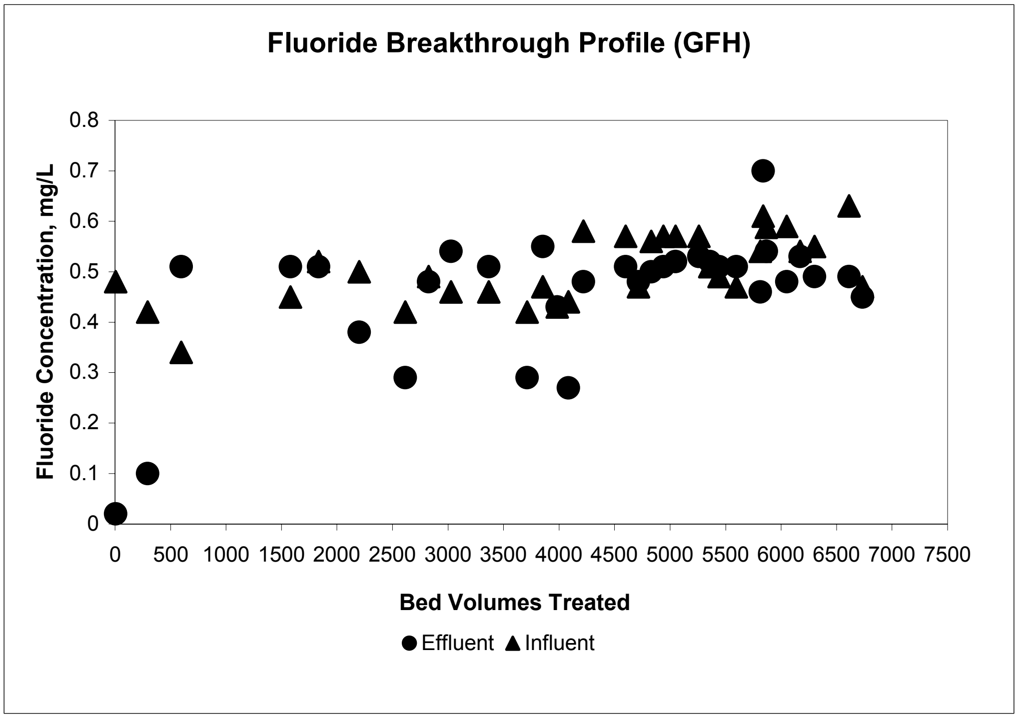

Figure 4-7. Fluoride Breakthrough Profile of Granular Ferric Hydroxide (GFH) Packed Column.

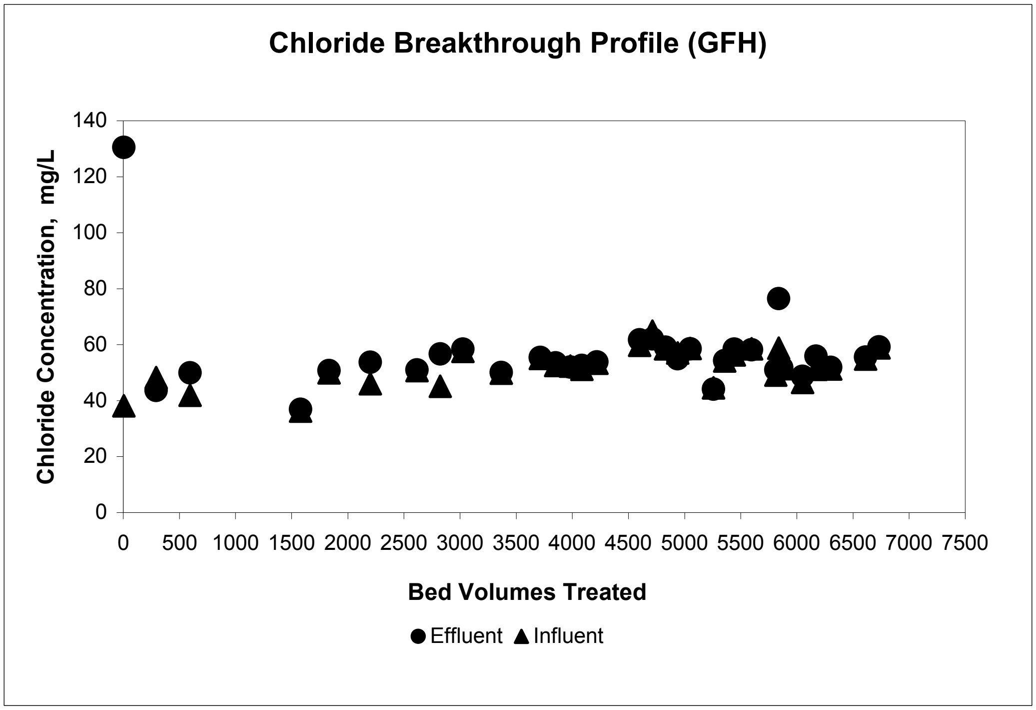

Figure 4-8. Chloride Breakthrough Profile of Granular Ferric Hydroxide (GFH) Packed Column.

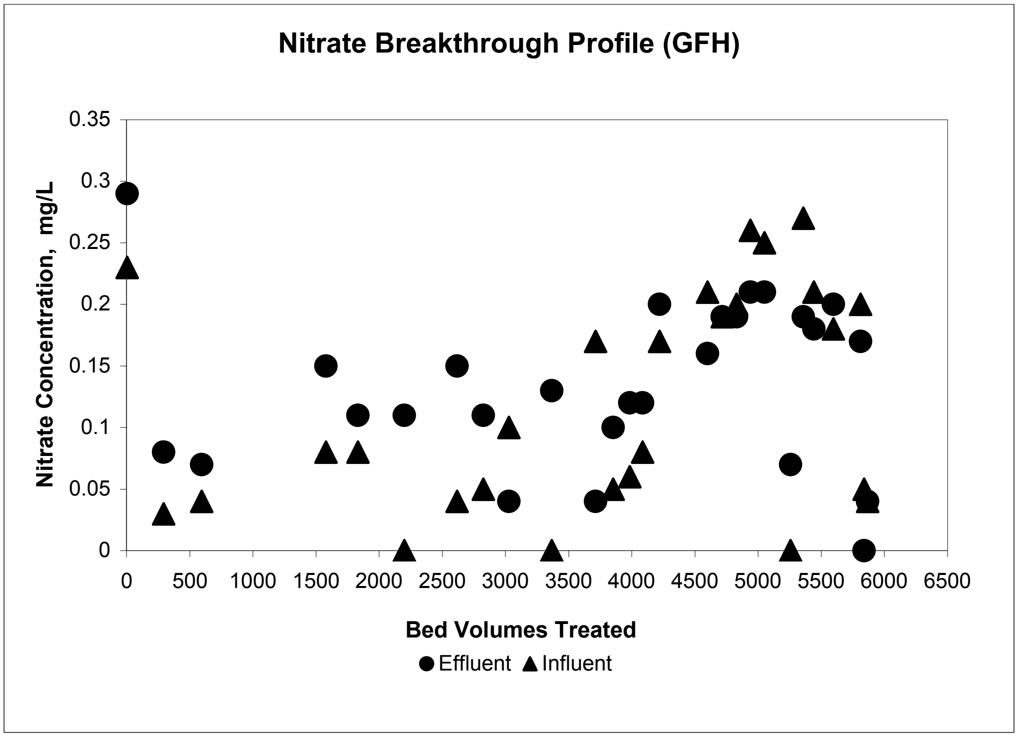

Figure 4-9. Nitrate Breakthrough Profile of Granular Ferric Hydroxide (GFH) Packed Column.

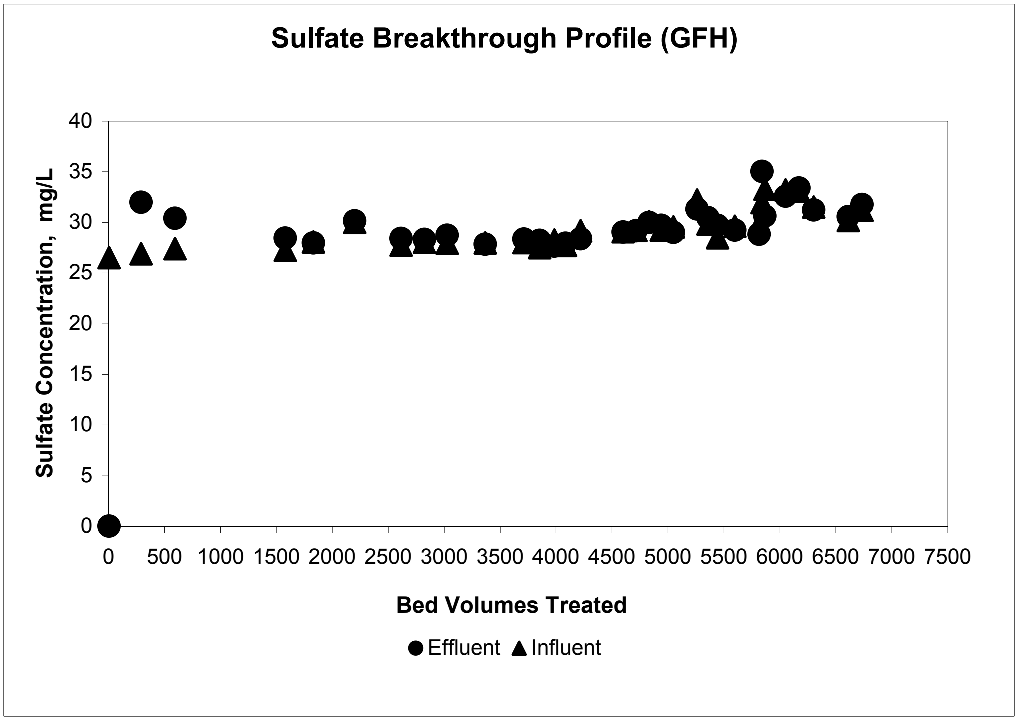

Figure 4-10. Sulfate Breakthrough Profile of Granular Ferric Hydroxide (GFH) Packed Column.

5. Discussion

These field trials were carried out to evaluate the performance of two arsenic removal media under the influences of existing pH and competitive ions using actual well water. The two arsenic removal media, ALCAN-AASF50 (ferric coated activated alumina) and GFH (granular ferric hydroxide), are widely used in water treatment and these results provide a performance baseline for future tests.

Capacity of media for arsenic removal

The results of the test program showed that both AASF50 and GFH were able to remove arsenate and meet the 10 µg/L MCL for total arsenic. At the EBCT of 5.0 minutes, influent average pH of 8.1 ±0.4 and average influent arsenic concentration of 12.9 ±0.9 µg/L, the arsenic removal capacity, corresponding to a 5.0 µg/L effluent arsenic concentration was 33.5 mg of As(V)/L of dry media or 29.9 µg of As(V)/g of media. With the same EBCT but at a lower pH (7.2 ±0.3) and higher influent arsenic concentration (19.21 ±4.1 µg/L), the arsenic removal capacity of the GFH was 155 mg of As(V)/L of wet media or 286 µg of As(V)/g of media on a dry basis.

The measured arsenic removal capacity performance of GFH media was significantly larger than that of ALCAN-AASF50. The capacity of GFH was 4.5 times greater than AASF50 per volume of media basis. The significance of this difference, however, is hard to assess. The well water pH during the evaluation of AASF50 was 8.1 ±0.4; whereas, during the period of evaluation of GFH media, the pH of the well water was 7.2 ±0.3. It has been observed by others that the sorption capacities of activated alumina and ferric oxyhydroxide media increase as the pH of the influent water is decreased (Rosenblum and Clifford 1984; Meng et al. 2000). Thus, the lower operating pH during the GFH test may have contributed to the much higher performance compared to that of the AASF50.

Competition of arsenic with other anions for sorption sites

The breakthrough profiles of other anions showed that both media removed silica and alkalinity, along with arsenic but not sulfate, nitrate, and chloride. During the period when the media bed was saturated with respect to the sorption of silica and bicarbonate, arsenic continued to be adsorbed by both media. AASF50 also removed trace amounts of fluoride present in the water but sulfate was washed out of the media. This is in contrast to the effect that sulfate has on the arsenic sorption behavior of some ion exchange resins. In such systems, arsenic is released when the media reaches sorption saturation with respect to sulfate.

The observation that both media removed silica is of considerable significance. Exhaustion of media capacity for silica occurred at about 1500 – 3000 bed volumes in both media (Figures 3.5 and 4.5). At the untreated well water pH range of 7.2 to 8.1 and silicate concentrations of 40 mg/L (<2500 times higher than arsenic concentration in the raw well water), negatively charged monovalent silica species $H_3SiO_4^-$ exist and can compete for sites on the metal hydroxide surface with arsenate (Langmuir 1997). Clifford and Lin (1991) further suggest that porous metal hydroxide media column capacity can be reduced by fouling due to the presence of colloidal silica. Whether such ‘poisoning’ affected the arsenic sorption capacity of these media is unknown.

Because of the high measured alkalinity of the untreated well water (<90 mg/L) and the pH range (7.0–8.1), carbonate equilibria favor the presence of charged HCO_3^- and CO_3^{2-} species (Stumm 1992). It is quite conceivable that the carbonate and bicarbonate ions could compete for sites with arsenic on the metal hydroxide media, however, both media have limited capacity for carbonate species as confirmed by the bicarbonate breakthrough patterns. The sorption capacities of both media were exhausted within 500 bed volumes (Figures 3.6 and 4.6) for both media, whereas arsenic sorption capacity for neither media was exhausted by the end of the test (>5900 BV for AASF50 and >8800 BV for GFH).

Stability of media

A relatively uniform flow rate was observed through the duration of the test with AASF50, suggesting that the bed permeability of the AASF50 media held constant. This differed from the performance of the GFH column where the operational EBCT increased from 5.0 minutes to an EBCT of ~10 minutes. The decrease in flow rate (increase in EBCT) was likely due to the decrease in bed permeability, either due to the breakdown of the granular GFH media or actual phase transformation of the GFH in the column. Although not preformed in this study, in actual operation of GFH columns, it would be advisable to periodically fluidize the bed to wash out fines, which contribute to the decrease in bed permeability.

Effect of flow interruption on performance

In many community water systems, water is pumped from groundwater wells for only a few hours each day. Interruption of flow through adsorptive media columns may increase their adsorptive capacity and may be beneficial to performance (J. Chwirka, CH2MHill, 2004 personal communication). During the field trial with the GFH media, the operation of the column was halted for 91 days, from December 23, 2002 to March 24, 2003. The effect of the prolonged interruption of the operation was a small (about 20%) decrease in effluent arsenic concentration upon restarting. This decrease lasted for approximately 10 bed volumes after which the effluent concentration of arsenic started to rise at the same rate seen before interruption of column operation. The reason for the dip in the effluent arsenic concentration profile after the flow interuption was not investigated in this field trial but is an important phenomenon that should be included in the scope of future investigations.

Suggestions for Future Tests

Because of its proximity to offices of SNL staff involved in the Arsenic Water Technology partnership program, the Kirtland Air Force Base Well #15 Pilot site provides a good opportunity to obtain experience in carrying out field tests, to develop new methods for pilot demonstrations, and to test equipment and process designs. The studies described in this report provide good baseline data for AASF50 and GFH media. Future studies should examine the effects of pH adjustment on performance of these and other media, evaluate the potential role of rapid-small scale column tests (RSSCT) in pilot design and determine the effect of EBCT on arsenic sorption capacity.

Due to budget constraints, the effect of lowering the operational pH in the range of 6.5 to 6.8 in terms of sorption capacity, removal efficiency, and stability of the media was not investigated. The scope of future work should include simultaneous operation of the same media in separate columns under varying pH conditions. Furthermore, this study was limited to the adsorption of

As(V), by pre-chlorinating the feed water. Groundwater contaminated with arsenic may contain As(III) species. In future studies the media performance can be evaluated for the removal of As(III).

Finally, in this report, the media performance evaluation was not correlated in terms of media cost. A treatment cost based on the cost of media, life of media, and operational cost was not calculated and should be included in the scope of future, more extensive evaluation projects.

6. Conclusions

The following conclusions can be drawn from the field trial program carried out to evaluate the performance of the arsenic removal media, ALCAN-AASF50 (ferric coated activated alumina) and granular ferric hydroxide (GFH) at Well #15 Kirtland Air Force Base, Albuquerque, New Mexico:

ALCAN-AASF50

- ALCAN-AASF50 media can remove arsenate at the influent pH of 8.1±0.4 to below the new total arsenic standard of 10 mg/L.
- At the influent pH of 8.1 ±0.4, the arsenate removal capacity of AASF50 was 33.5 mg of As(V)/L of dry media or 29.9 µg of As(V)/g of media on a dry basis at 5.0 µg/L effluent arsenic concentration (50% of arsenic MCL of 10 µg/L).
- Silicates, fluoride, and bicarbonate ions were also removed along with arsenic. Chloride, nitrate, and sulfate ions were not removed by AASF50.
- Arsenic removal still occurs even after media saturation for silica, nitrates, and fluoride.
- The exhausted media passed the TCLP test with respect to arsenic and other regulated metals.

GFH

- GFH media can remove arsenate at the influent pH of 7.2 ±0.3 to below the new total arsenic standard of 10 µg/L.
- At the influent pH of 7.2 ±0.3, the arsenate removal capacity of GFH was 155 mg of As(V)/L of wet media or 286 µg of As(V)/g of media on a dry basis at 5.0 µg/L effluent arsenic concentration (50% of arsenic MCL of 10 µg/L).
- Silica and bicarbonate ions were also removed along with arsenic. Fluoride, chloride, nitrate, and sulfate ions were not removed by GFH.
- Arsenic removal still occurs even after media saturation for silicates and alkalinity.
- The GFH media contains substantial amounts of fine granules that over time contribute to decreasing bed porosity, thereby decreasing the operational flow rate.

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