

N65928.AR.001121
NTC ORLANDO
5090.3a

FINAL REPORT OF FINDINGS FOR REMOVAL OF ARSENIC FROM GROUNDWATER AT
OPERABLE UNIT 3 (OU 3) NTC ORLANDO FL
1/2/2001
PRIMA ENVIRONMENTAL

**Final
REPORT OF FINDINGS**

**OU3 Treatability Study: Removal of Arsenic from Groundwater
NTC Orlando, FL**

N7457 – RFP 045 (DW)

Submitted to

Mr. S. Raju Dantuluri
TetraTech NUS, Inc.
800 Oakridge Turnpike, Suite A600
Oak Ridge, TN 37831

Submitted by

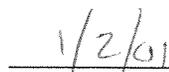
PRIMA Environmental
10265 Old Placerville Road, Suite 15
Sacramento, CA 95827-3042

January 2, 2001

Prepared by:


Cindy G. Schreier, Ph.D.
Principal, PRIMA Environmental

Date:





Recd on 1/5/01
MS.

January 2, 2001

Mr. Raju Dantuluri
Tetra Tech NUS
800 Oakridge Turnpike, Suite A600
Oak Ridge, TN 37831

**RE: Final Reports, Arsenic Retardation and Arsenic Removal, OU3 NTC
Orlando,FL**

Dear Raju:

Enclosed are three hardcopies of each of the final Reports of Findings "Arsenic Retardation at OU3" and "OU3 Treatability Study: Removal of Arsenic from Groundwater". I have also sent hardcopies to Denny Wilson in your procurement office.

Electronic versions of the reports (MS Word) as well as relevant data files (MS Excel) are also included. If you have any trouble opening these files, please let me know.

If you have any questions regarding the enclosed reports please do not hesitate to contact me. Thank you for the opportunity to be of service.

Sincerely,
PRIMA Environmental

Cindy G. Schreier, Ph.D.
Principal

EXECUTIVE SUMMARY

Three sorbents—surfactant-modified zeolite, iron-modified zeolite, and activated alumina—were evaluated for their ability to remove arsenic from groundwater at Operable Unit 3 at the former Naval Training Center in Orlando, Florida. Of these, only alumina removed arsenic to below the detection limit of 5 µg/L. The arsenic capacity of the alumina measured in the final column test was 2,520 µg As/g alumina. This may be an underestimate because capacity appears to be dependent upon residence time, which would be much greater in the field than in the laboratory. None of the sorbents removed the secondary chemicals of concern, MCPA or MCPP.

Based on the results of this study, PRIMA Environmental recommends that a field pilot test be conducted using alumina as the sorbent for arsenic. The primary goal of the pilot test should be to determine the capacity of the alumina in the presence of native organic matter and at a flowrate representative of field conditions.

TABLE OF CONTENTS

1.0 INTRODUCTION.....	1
2.0 MATERIALS AND METHODS	2
2.1 MATERIALS.....	2
2.1.1 Sorbents.....	2
2.1.2 Groundwater	2
2.2 METHODS	2
2.2.1 Preparation of Synthetic Groundwater.....	2
2.2.2 Batch tests	2
2.2.3 Preliminary Column Tests	3
2.2.4 Final Column Tests	4
2.2.5 Analytical Methods.....	4
2.2.5.1 Arsenic	4
2.2.5.2 Alkalinity	5
2.2.5.3 Chloride and Nitrate.....	5
2.2.5.4 Eh.....	5
2.2.5.5 MCPP and MCPA.....	5
2.2.5.6 pH.....	5
2.2.5.7 Sulfate	5
2.2.5.8 Iron and Aluminum.....	5
2.2.6 Data Analysis.....	5
2.2.6.1 Calculation of Bed Volumes through Column.....	5
2.2.6.2 Calculation of Arsenic Capacity	6
3.0 RESULTS AND DISCUSSION.....	7
3.1 BATCH TESTS.....	7
3.1.1 Arsenic Removal.....	7
3.1.2 Effect of Sorbents on Water Quality.....	7
3.1.2.1 Inorganic Parameters	7
3.1.2.2 Organic Parameters.....	7
3.2 PRELIMINARY COLUMN TESTS.....	9
3.3 FINAL COLUMN TESTS	9
3.3.1 Arsenic Removal.....	9
3.3.1.1 Arsenic Removal—FeZ	15
3.3.1.2 Arsenic Removal--Alumina	17
3.3.2 Effect of Sorbents on Water Quality.....	17
3.3.3 Observations Regarding Synthetic GW.....	18
4.0 CONCLUSIONS AND RECOMMENDATIONS.....	19

List of Tables

Table 1. Selected Physical Characteristics of Test Sorbents	2
Table 2. Preliminary Column Parameters*	4
Table 3. Final Column Parameters*	4
Table 4. Batch Test Results	8
Table 5. Arsenic Removal, Preliminary Columns*	9
Table 6. Preliminary Column Data	12
Table 7. Limited Analyte List, Final Columns	14
Table 8. Arsenic Removal, Final Columns*	15
Table 9. Arsenic Speciation for Influent and FeZ Effluent	15
Table 10. Extended Analyte List, Final Columns.....	16

List of Figures

Figure 1. Schematic Diagram of Preliminary and Final Columns.....	3
Figure 2. Total Arsenic Concentrations in Influent and Effluent Streams, Preliminary Columns.....	10
Figure 3. Arsenic Speciation, Preliminary Columns	11
Figure 4. Total Arsenic Concentrations in Influent and Effluent Streams, Final Column.....	13

1.0 INTRODUCTION

PRIMA Environmental performed treatability testing to evaluate the ability of three sorbent materials to remove arsenic from groundwater at Operable Unit 3 at the former Naval Training Center in Orlando, Florida. The materials tested were

- Iron-modified zeolite (FeZ)
- Surfactant-modified zeolite (SMZ), and
- Activated alumina (alumina)

The objectives of the study were to

- ♦ Determine whether the sorbents could remove arsenic
- ♦ Estimate the capacity of the sorbents
- ♦ Determine whether the sorbents could also remove secondary contaminants, the herbicides MCPP and MCPA.

Batch and column tests were conducted in order to accomplish these goals.

2.0 MATERIALS AND METHODS

2.1 Materials

2.1.1 Sorbents

Three sorbents were received from TetraTech NUS (TtNUS): Cabsorb ZK406SMZ (a surfactant-modified zeolite), Iron Saturated Zeolite--Chabazite Fe, and DD-2 Activated Alumina (Alcoa Industrial Chemicals). They were designated SMZ, FeZ and Alumina, respectively. Selected physical characteristics of these materials are given in Table 1. The sorbents were stored at room temperature (approximately 25°C).

Table 1. Selected Physical Characteristics of Test Sorbents

	SMZ	FeZ	Alumina
Color	Off-white	Orange/brown	white
Particle shape	Irregular, round	Irregular, round	Irregular, flat
Particle size	8-14 mesh	8 x 20 mesh	14 x 20 mesh
Porosity*	0.5072	0.7460	0.8142
Bulk Density	0.94 g/cm ³	0.57 g/cm ³	0.67 g/cm ³

*Measured by Sierra Testing Laboratories, El Dorado Hills, CA.

2.1.2 Groundwater

Site groundwater (GW) was received from TtNUS and stored at 5°C. Water was brought to room temperature prior to beginning a test. All containers were kept tightly capped in order to minimize diffusion of air/oxygen into the water.

2.2 Methods

2.2.1 Preparation of Synthetic Groundwater

Synthetic groundwater (syn-GW) was prepared in 30 gallon batches by sparging Type II laboratory water with nitrogen gas for approximately 24 hours to remove oxygen. Once dissolved oxygen was reduced to below 2.5 mg/L, sulfuric acid, hydrochloric acid, nitric acid, trisodium phosphate, calcium hydroxide, sodium bicarbonate, magnesium chloride, lime and in some cases, dry ice, were added to obtain water quality parameters similar to site groundwater. Syn-GW was spiked with sodium arsenite to obtain an initial arsenic concentration of 300-500 µg/L. For the final columns, syn-GW was also spiked with approximately 150-800 µg/L each of MCPP and MCPA, two herbicides characteristic of the site groundwater. A floating cover was placed over each batch of syn-GW to prevent formation of headspace and to minimize the diffusion of oxygen into the water.

2.2.2 Batch tests

For each sorbent, four replicates were prepared by adding 100 mL of site groundwater (GW) to 1 g of sorbent. The replicates were spiked with As(III) (sodium arsenite) to give

initial As(III) concentrations of 3.9 mg/L, 8.4 mg/L, 89 mg/L, and 445 mg/L. A replicate without added arsenic was prepared by adding 990 mL GW to 9.9 g sorbent; this replicate was the “as received” test and was not spiked. The headspace in the reaction bottles was purged with nitrogen gas to minimize intrusion of oxygen into the system. The bottles were then capped and placed on a reciprocal shaker. After 23 hours, pH, Eh, and temperature, were measured. A sub-sample was centrifuged and the aqueous phase analyzed for Total As. Total Fe, Sulfate, Nitrate, Chloride, MCPP and MCPA were analyzed in the “as received” replicates. A series of controls containing no sorbent, was also prepared.

Although the concentration of As(III) in site GW does not exceed 1 mg/L, higher As concentrations were used in this study in an effort to estimate the capacity of each sorbent. Such information would aid in comparing the materials and in estimating the breakthrough time for column tests.

2.2.3 Preliminary Column Tests

Based on the results of Section 2.2.2, two sorbents (FeZ and Alumina) were selected for further study. Preliminary column tests were run to determine the minimum contact time needed to achieve the desired degree of arsenic removal and to estimate the time required for breakthrough to occur. Breakthrough was defined as the time required for the effluent concentration of total arsenic to be $> 5 \mu\text{g/L}$. The columns were prepared as shown in Figure 1. Selected column parameters are given in Table 2. Pore volume, bed volume and residence time are defined as follows:

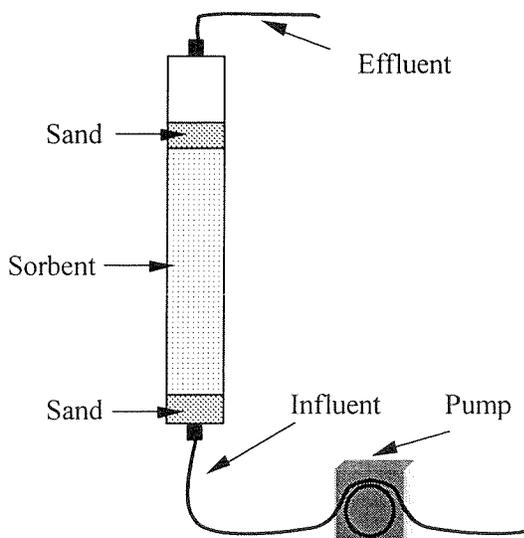


Figure 1. Schematic Diagram of Preliminary and Final Columns.

- *Pore volume*—volume of the void space of the sorbent as packed in the column; determined by measuring the volume of water needed to fill the pore space of a known mass of sorbent.
- *Bed volume*—bulk volume of the sorbent as packed in the column; determined from graduation markings (in mL) on the column.
- *Residence time*—the average time a given volume of water is in contact with the sorbent. Residence time is calculated by dividing the pore volume by the flowrate.

Syn-GW was used as the influent. Two batches of syn-GW (30 gallons each) were needed to complete the test. Both influent and effluent were sampled periodically and analyzed for Total As, As(III) and As(V).

Table 2. Preliminary Column Parameters*

	FeZ	Alumina
Column size	1 in. diam x 2.5 in.	1 in. diam. x 2 in.
Direction of flow	Upgradient	Upgradient
Mass of sorbent	20 g	20 g
Pore volume of sorbent	26 mL	24 mL
Bed volume of sorbent	~ 35 mL	~ 30 mL
Flowrate	2.7 mL/min first 5 days, 1.4 mL/min thereafter	2.4 mL/min first 5 days, 1.2 mL/min thereafter
Residence time	9.6 min (first 5 days) 18 min (after 5 days)	10 min (first 5 days) 20 min (after 5 days)

* See Section 2.2.3 for definitions of pore volume, bed volume and residence time.

2.2.4 Final Column Tests

The final column tests were similar to the preliminary column tests, but used different sized columns and amounts of sorbent (Table 3). In addition, the synthetic GW was spiked with MCPP and MCPA as well as As(III). Samples were collected periodically and analyzed for Total As, pH and Eh. Selected samples were also analyzed for MCPA, MCPP, chloride, nitrate, sulfate, alkalinity, iron and aluminum. Seven batches of syn-GW (at 30 gallons each) were required to complete the test. In most cases, columns were shut down for 8-48 hours between batches.

Table 3. Final Column Parameters*

	FeZ	Alumina
Column size	1.25 in. diam x 3.75 in.	1.25 in. diam. x 3.5 in.
Direction of flow	Upgradient	Upgradient
Mass of sorbent	50 g	50 g
Pore volume of sorbent	65 mL	60 mL
Bed volume of sorbent	~ 88 mL	~ 75 mL
Average Flowrate	4.8 mL/min	6.7 mL/min
Average Residence time	14 min	8.9 min

* See Section 2.2.3 for definitions of pore volume, bed volume and residence time.

2.2.5 Analytical Methods

2.2.5.1 Arsenic

Total arsenic concentration was measured via hydride generation atomic absorption spectrometry (HGAA). As(III) concentration was measured via HGAA, but without the

pre-reduction step. The concentration of As(V) is defined as the difference between the Total As and As(III) concentrations.

2.2.5.2 Alkalinity

Alkalinity was measured by titration by either Alpha Analytical, Sparks NV; CLS Labs, Rancho Cordova, CA; or Sequoia Analytical, Sacramento, CA.

2.2.5.3 Chloride and Nitrate

Chloride and nitrate were measured either with an ion selective electrode (PRIMA Environmental) or by ion chromatography (Alpha Analytical, Sparks NV; CLS Labs, Rancho Cordova, CA; or Sequoia Analytical, Sacramento, CA)

2.2.5.4 Eh

Eh was measured using a platinum electrode and filling solution appropriate for samples with ionic strength < 0.2 mole/L.

2.2.5.5 MCPP and MCPA

MCPP and MCPA were analyzed by Alpha Analytical (Sparks, NV) using EPA Method 8151.

2.2.5.6 pH

pH was measured using a pH electrode. During adjustment of pH of synthetic groundwater, pH was measured by placing the electrode directly in the tank. In all other cases, pH was measured by collecting a sub-sample.

2.2.5.7 Sulfate

Sulfate was measured turbidimetrically using a Hach DR2010 Spectrophotometer and test kit.

2.2.5.8 Iron and Aluminum

Total iron was measured either colorimetrically using Hach DR2010 Spectrophotometer and test kit, or by using EPA 200.7. Aluminum was measured using EPA 200.7.

2.2.6 Data Analysis

2.2.6.1 Calculation of Bed Volumes through Column

The number of bed volumes put through a column was calculated according to

$$\# \text{ Bed Volumes} = (\text{Flowrate} \times \text{Time}) / \text{Bed Volume}$$

“Bed volumes through column” is defined as the number of bed volumes put through over the course of the test. “Bed volumes at breakthrough” is defined as the number bed volumes put through when the concentration of Arsenic in the effluent first exceeds 5 µg/L. See Section 2.2.3 for definition of bed volume.

2.2.6.2 Calculation of Arsenic Capacity

For column tests, arsenic “test capacity” is defined as the amount of arsenic sorbed per mass of sorbent at the completion of the test. “Test capacity” does not indicate whether arsenic was completely removed, nor does it necessarily represent the maximum amount of arsenic that could be adsorbed. The arsenic test capacity was calculated according to:

$$\text{Capacity} = \frac{\sum_0^s \left\{ \left[\text{As}(\text{in}) - \left(\frac{1}{2} \right) (\text{As}(\text{out})_{s-1} + \text{As}(\text{out})_s) \right] \times \text{Flowrate} \times \Delta\text{Time} \right\}}{\text{Mass}} \quad \text{Eqn 1}$$

where

As(in) = concentration of As in influent

As(out)_{s-1} and As(out)_s = concentration of As in effluent at sample number *s* and *s-1*; this is the average effluent concentration between two sampling points

Flowrate = flowrate through the column

ΔTime = difference in time between samples *s* and *s-1*, and

mass = mass of sorbent

“Capacity at breakthrough” is defined as the amount of arsenic that was adsorbed before arsenic was detected at a concentration ≥ 5 µg/L in the effluent. It was estimated using Eqn. 1, with *s* = sample number at which As in effluent first exceeded 5 µg/L.

3.0 RESULTS AND DISCUSSION

3.1 Batch Tests

3.1.1 Arsenic Removal

The results of the batch tests are shown in Table 4. The SMZ sorbent did not remove arsenic from unamended site GW (0.35 mg/L test) or from site GW spiked with 89 or 445 mg/L arsenic. Some removal (21-46%) was achieved when intermediate concentrations of arsenic were used. FeZ removed 89% of the arsenic from unamended site GW, though this still resulted in an aqueous arsenic concentration of 0.039 mg/L. In contrast, alumina completely removed arsenic from unamended site groundwater and removed 57% of the arsenic in the 445 mg/L test, indicating a large capacity for arsenic.

Based on these results, FeZ and alumina were chosen for further testing (Sections 3.2 and 3.3).

3.1.2 Effect of Sorbents on Water Quality

3.1.2.1 Inorganic Parameters

The effect of the different sorbents on several water quality parameters of site GW are listed in Table 4. SMZ decreased the alkalinity from 60 mg/L to 8 mg/L, decreased sulfate from 48 mg/L to 32 mg/L and increased chloride from 11 mg/L to 40 mg/L. It had little effect on nitrate, pH or Eh. FeZ had no effect on alkalinity, chloride or nitrate, but increased the sulfate concentration to 135 mg/L. The pH of the system decreased from 5.82 to 4.44, while Eh increased, suggesting that the sorbent is somewhat oxidizing. Iron was also detected in the aqueous phase, though this may have been due to abrasion (the batch tests were mixed) rather than dissolution. Finally, alumina had little effect on alkalinity, chloride, or nitrate, but decreased sulfate to 13 mg/L. The pH increased to 6.90, and Eh decreased from 83 mV to 0.5 mV, indicating reducing conditions.

Although many differences were seen between the untreated and treated samples, it should be noted that these changes may be transitory in a flow through system such as a column reactor or permeable barrier. For example, changes may be due in part to the initial reaction between sorbent and water. Once a column has been flushed with a few pore volumes of water, the sorbent may have little influence on water quality.

3.1.2.2 Organic Parameters

The only organic parameters specifically tested for were MCPP and MCPA. Neither of these was detected above the 100 µg/L detection limit.

Site GW contains organic matter, however. The amount was not quantified, but was sufficiently high to impart an orange color to the water. Both SMZ and alumina removed the color. This may be important since long-term exposure to organic matter could affect arsenic sorption capacity. (Note that the color was not due to iron(II)—see Table 4.)

Table 4. Batch Test Results

Sorbent	Arsenic					pH	Eh mV	Temp, C	Alkalinity mg/L CaCO3	Total Fe, mg/L	Sulfate mg/L	Chloride mg/L	Nitrate mg/L	MCPD µg/L	MCPA µg/L
	Initial Aqueous*	Aqueous mg/L	Sorbed mg/kg	Aqueous %	Sorbed %										
SMZ	0.35 ppm	0.38	-3	110	-9	5.74	88	21	8	0	32	40	< 0.1	< 100	< 100
	3.9 ppm	2.1	181	54	46	5.97	92	21							
	8.4 ppm	6.6	176	79	21	6.02	92	21							
	89 ppm	89	35	100	0	7.01	61	21							
	445 ppm	440	535	99	1	8.81	-57	21							
Alumina	0.35 ppm	<0.002	35	0	100	6.90	0.5	21	74	0	13	11	0.1	< 100	< 100
	3.9 ppm	0.028	388	1	99	6.83	9	21							
	8.4 ppm	0.48	788	6	94	6.97	13	21							
	89 ppm	12	7,735	13	87	7.48	-3	21							
	445 ppm	190	25,535	43	57	8.99	-47	21							
FeZ	0.35 ppm	0.039	31	11	89	4.44	152	21	56	1.2	135	9.5	< 0.1	< 100	< 100
	3.9 ppm	0.77	314	20	80	4.49	160	21							
	8.4 ppm	3.6	476	43	57	4.53	169	21							
	89 ppm	75	1,435	84	16	5.21	135	21							
	445 ppm	370	7,535	83	17	7.04	79	21							
Control (no sorbent added)	0.35 ppm	0.4		114		5.82	83	21	60	0	48	11	< 100	< 100	< 100
	3.9 ppm	3.3		84		5.97	92	21							
	8.4 ppm	8		96		5.99	100	21							
	89 ppm	84		94		7.35	55	21							
	445 ppm	390		88		8.97	-63	21							
GW As Received, before batch test		0.35				5.85	97	17.8	62	0	49	10	< 100	< 100	< 100

* Total of Arsenic in GW + added arsenic (III); note that 0.35 ppm is groundwater as received

3.2 Preliminary Column Tests

The results of the preliminary column tests are shown in Figures 2 and 3 and in Tables 5 and 6. The results plotted in Figure 2 show that As was not completely removed by FeZ. Reducing the flowrate by a factor of two did not increase the degree of arsenic removal (Figure 2, Day 5). The lack of removal does not appear to be related to arsenic speciation because both As(III) and As(V) were detected in effluent from the FeZ column (Figure 3).

Table 5. Arsenic Removal, Preliminary Columns*

	FeZ	Alumina
Total Bed Volumes through column	2,060	2,930
Bed Volumes at breakthrough	n.a.**	2,930
Test Capacity, $\mu\text{g As/g sorbent}$	180	1,500
Capacity at Breakthrough, $\mu\text{g As/g sorbent}$	n.a.**	1,500
Breakthrough, days	n.a.**	~ 45

* See Section 2.2 for definitions and methods of calculation.

** not applicable—arsenic never completely removed

In contrast, complete removal of arsenic was achieved with alumina for approximately 43 days (2,770 bed volumes). Breakthrough (effluent concentration $>5 \mu\text{g As/L}$) occurred by 45 days (2,930 bed volumes). Although the effluent concentration was only $8.5 \mu\text{g/L}$, the test was stopped due to time constraints.

Based on these columns, the capacities of the sorbents for arsenic are $180 \mu\text{g As/g}$ for FeZ and $1,500 \mu\text{g As/g}$ for alumina.

3.3 Final Column Tests

3.3.1 Arsenic Removal

The concentrations of Total Arsenic in influent and effluent from the FeZ and alumina columns are depicted in Figure 4 and in Table 7. Arsenic was assumed to be constant in each batch of syn-GW and thus was typically analyzed only once per batch; the dotted lines were added to the influent data in Figure 4 to help visualize this. The capacities and bed volumes put through the columns are given in Table 8.

**Figure 2. Total Arsenic Concentrations in Influent and Effluent Streams
Preliminary Columns**

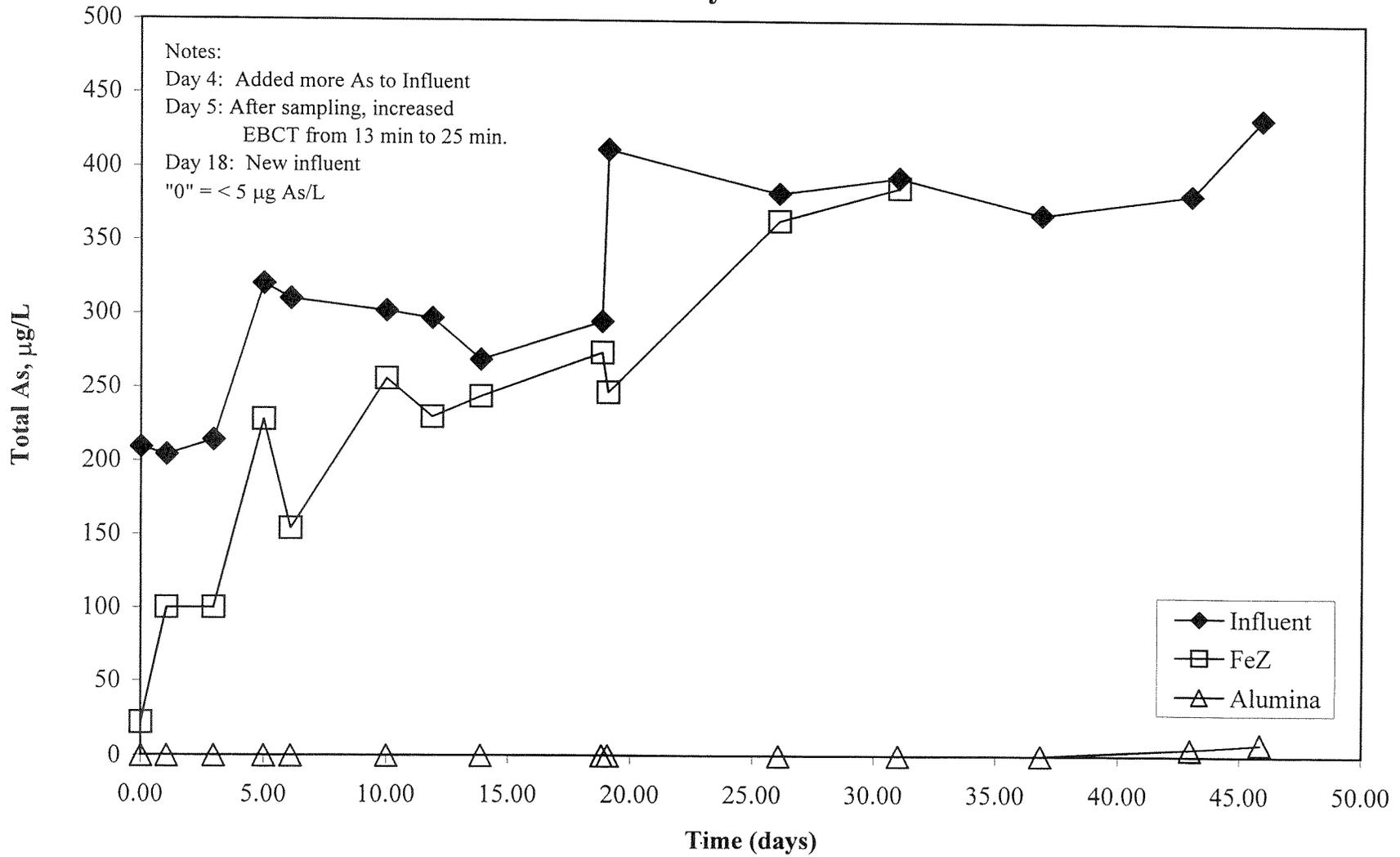


Figure 3. Arsenic Speciation, Preliminary Columns

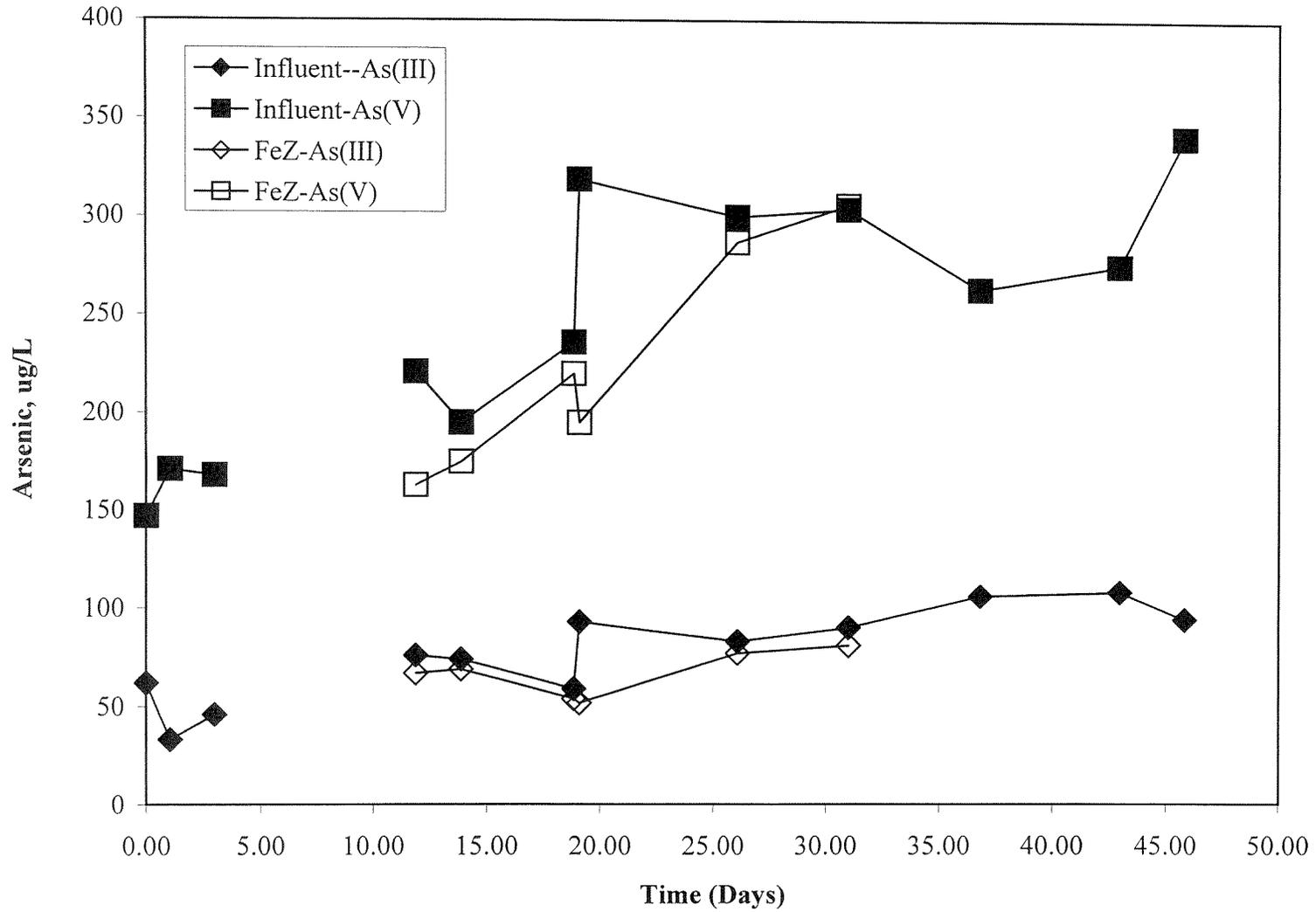


Table 6. Preliminary Column Data

Time Days)	Influent				FeZ			Alumina
	Total As µg/L	As(III) µg/L	As(V) µg/L	% As(III)	Total As µg/L	As(III) µg/L	As(V) µg/L	Total As µg/L
0.01	209	62	147	30	22			< 5
1.06	204	33	171	16	100			< 5
2.99	214	46	168	21	100			< 5
5.00	320				228			< 5
6.08	310				154			< 5
10.00	302				256			< 5
11.88	297	76	221	26	230	67	163	
13.88	269	74	195	28	244	69	175	<5
18.83	295	59	236	20	274	54	220	<5
19.08	412	93	319	23	247	52	195	<5
26.08	383	83	300	22	364	77	287	<5
31.00	394	90	304	23	387	81	306	<5
36.83	369	106	263	29				<5
42.96	383	108	275	28				4.8
45.83	435	94	341	22				8.5

Figure 4. Total Arsenic Concentrations in Influent and Effluent Streams, Final Columns

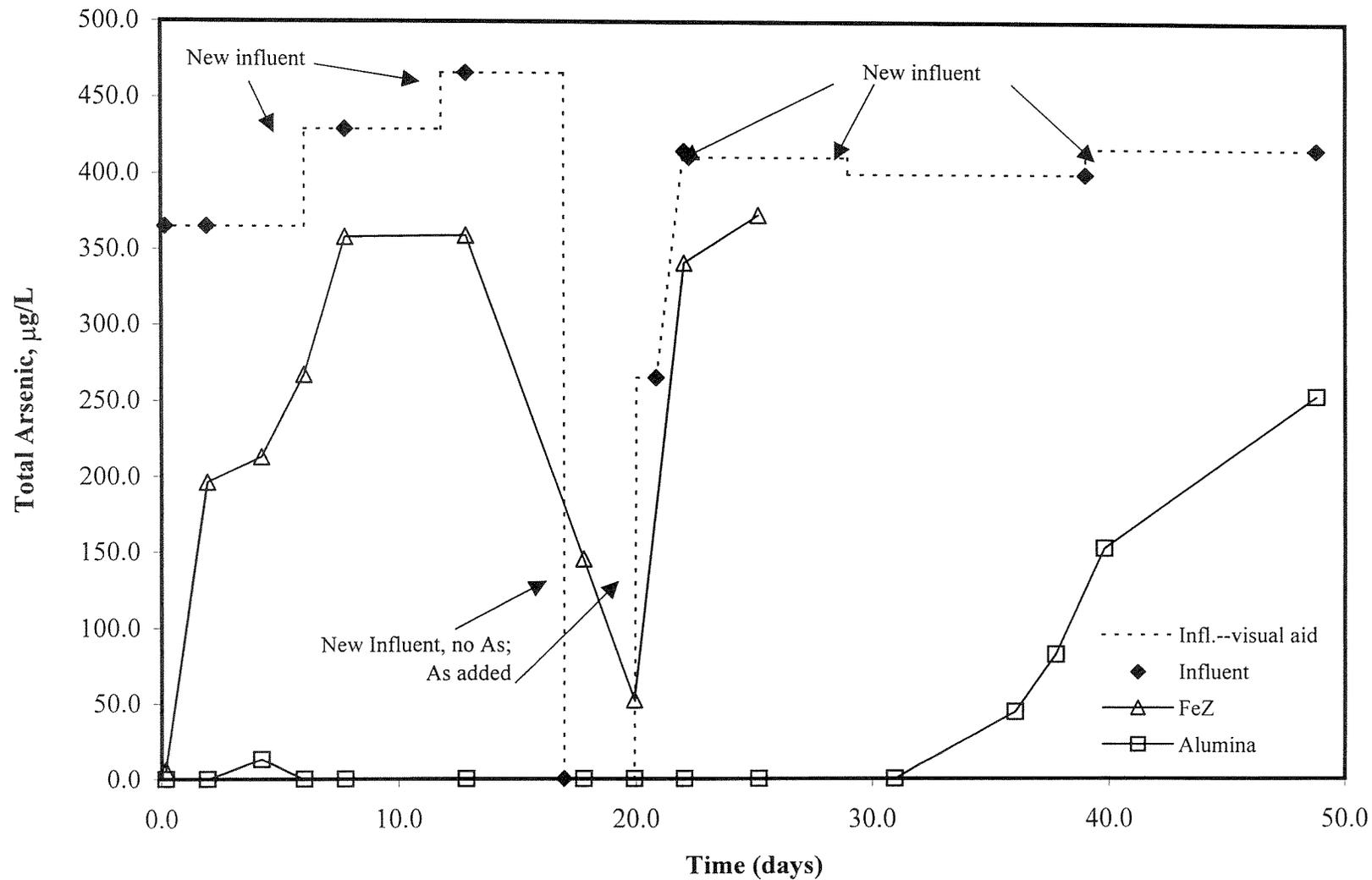


Table 7. Limited Analyte List

Influent Batch #	Day	Total As, µg/L			pH			Eh, mV			Temp. C [#]
		Influent	FeZ	Alumina	Influent	FeZ	Alumina	Influent	FeZ	Alumina	
1	0.2	365	5.9	< 5	6.96	4.43	8.23	84	234	78	25
1	1.9	--	196	--	--	6.71	--	--	68	--	25
1	4.2	--	213	13	--	6.02	6.28	--	159	94	25
1	6	--	267	< 5	--	7.55	6.28	--	134	111	25
2	7.7	429	358	< 5	5.87	6.31	6.21	73	160	134	25
3	12.8	466	359	--	5.51	5.99	--	122	192	--	25
4	17.7	< 5	145	< 5	5.59	5.75	5.72	209	251	247	21
4	19.9	< 5	52	< 5	5.75	5.67	5.64	240	251	244	18
4	20.8	265	--	--	7.21	--	--	176	--	--	21
4	22	415	341	< 5	7.21	7.09**	6.78**	168	164	165	21
5	22.3	411	--	--	5.67	--	--	172	--	--	21
5	25.2	--	373	--	--	6.31**	--	--	158	--	21
6	30.9	--	--	< 5	--	--	6.48	--	--	8	21
6	36	--	--	44	--	--	6.66	--	--	5	21
6	37.7	--	--	82	--	--	6.69	--	--	20	21
6	39	400	--	--	6.55	--	--	63	--	--	21
7	39.8	--	--	152	--	--	6.66	--	--	56	21
7	48.8	417	--	253	--	--	6.54	--	--	53	21

** pH drifted up 0.5-1 pH units before stabilizing at reported value

Room temperature

Table 8. Arsenic Removal, Final Columns*

	FeZ	Alumina
Total Bed Volumes through column	2,020	6,260
Bed volumes at breakthrough	< 16	3,980
Test Capacity, µg As/g sorbent	330	3,270
Capacity at Breakthrough, µg As/g sorbent	< 10	2,520
Breakthrough (>5 µg/L), days	< 0.2	~ 36

* See Section 2.2 for definitions and methods of calculation.

3.3.1.1 Arsenic Removal—FeZ

As with the preliminary columns, FeZ did not completely remove arsenic. Total Arsenic in the first effluent sample was 5.9 µg/L (0.2 days). However, the effluent concentration never reached the influent concentration. Speciation data (Tables 9 and 10) indicate that arsenic speciation was not responsible for the lack of removal since both As(III) and As(V) were present in FeZ effluent.

Table 9. Arsenic Speciation for Influent and FeZ Effluent

Infl. Batch #	Day	Influent				FeZ			
		As(III) µg/L	As(III) %	As(V) µg/L	As(V) %	As(III) µg/L	As(III) %	As(V) µg/L	As(V) %
1	0.2	290	79	75	21	--	--	--	--
1	1.9	--	--	--	--	45	23	151	77
2	7.7	94	22	335	88	75	21	283	79
3	12.8	317	68	149	32	79	22	280	78
4	17.8	< 5	--	< 5	--	30	21	115	79

Arsenic appears to easily desorb from FeZ. From Day 17 to Day 20, the concentration of arsenic in the influent was < 5 µg/L due to accidental omission of As during preparation of the syn-GW. During this time, arsenic was detected in the FeZ effluent. In contrast, the concentration of arsenic in effluent from the alumina column remained below the detection limit of 5 µg/L. (See Table 10). This implies that arsenic sorbed to alumina will remain sorbed when flushed with clean site GW.

The test capacity for total arsenic on FeZ was 330 µg As / g FeZ, though it must be emphasized that effluent As concentrations were approximately equal to influent concentrations throughout most of the test. This loading is approximately twice as great as seen in the preliminary columns. The reason is unclear, but may be related to the down time during preparation of syn-GW. Downtime (during which flow to the columns was turned off and water in the columns was allowed to stand undisturbed) could permit As sorbed on the surface of the particles to migrate into pores, thereby freeing up surface adsorption sites.

Table 10. Expanded Analyte List

Influent Batch #	Day	Influent	FeZ	Alumina	Influent	FeZ	Alumina	Influent	FeZ	Alumina
		Total As, µg/L			As(III), µg/L			As(V), µg/L		
1	0.2	365	--	--	290	--	--	75	--	--
1	1.9	--	196	< 5	--	45	--	--	151	--
2	7.7	429	358	< 5	94	75	--	335	283	--
3	12.8	466	359	< 5	317	79	--	149	280	--
4	17.8	< 5	145	< 5	< 5	30	--	< 5	115	--
6	39	400	--	--	--	--	--	--	--	--
7	48.8	417	--	253	89	--	49	328	--	204
Batch #	Day	pH			Eh, mV			Alkalinity, mg/L		
1	0.2	6.92**	--	--	84	234	78	110	--	--
1	1.9	--	6.71	--	--	68	--	--	83	130
2	7.7	5.87	6.31	6.21	73	160	134	52	49	56
3	12.8	5.51	5.99	6	122	192	169	10.7	16.4	12.9
4	17.8	5.59	5.75	5.72	209	251	247	59.6	57	62.5
6	39	6.55	--	--	63	--	--	26	--	--
7	48.8	--	--	6.54	--	--	53	--	--	14
Batch #	Day	Sulfate, mg/L			Nitrate as NO ₃ , mg/L			Chloride, mg/L		
1	0.2	45	--	--	27	--	--	10	--	--
1	1.9	--	46	36	--	26	27	--	10	10
2	7.7	47	48	45	28	31	29	11	11	11
3	12.8	45	45	41	67.7	70.4	66.9	13.3	12.2	12.8
4	17.8	46	45	50	35.4	36.8	35.6	12	11.4	11.4
6	39	--	--	--	30.8	--	--	12	--	--
7	48.8	54	--	39	--	--	28.6	--	--	11
Batch #	Day	Iron, mg/L			Aluminum, mg/L			MCPP, µg/L		
1	0.2	< 0.1	--	--	--	--	--	< 100	--	--
1	1.9	--	< 0.1	< 0.1	--	--	< 0.05	--	< 100	< 100
2	7.7	0.24	< 0.1	< 0.1	< 0.05	< 0.05	< 0.05	130	< 100	< 100
3	12.8	0.0227	0.0502	< 0.01	0.0635	--	< 0.05	120	< 100	100
4	17.8	0.0576	< 0.01	--	0.063	--	< 0.05	--	--	--
4	20	--	--	--	--	--	--	810	860	760
6	39	--	--	--	< 0.05	--	--	--	--	--
7	48.8	--	--	--	--	--	< 0.05	--	--	--
Batch #	Day	MCPA, µg/L								
1	0.2	100	--	--						
1	1.9	--	75*	110						
2	7.7	120	< 100	< 100						
3	12.8	140	120	< 100						
4	17.8	--	--	--						
4	20	560	620	610						
6	39	--	--	--						
7	48.8	--	--	--						

* Compound present, but quantitation uncertain
 ** pH drifted up 0.5-1 pH units before stabilizing at reported value

3.3.1.2 Arsenic Removal--Alumina

Alumina was extremely effective at removing arsenic (Figure 5, Tables 7 and 8). Arsenic was not detected above 5 µg/L in the effluent until 36 days. (The only exception is at Day 4.2, when, for reasons that are unclear, arsenic was 13 µg/L.) By 48.8 days, the effluent concentration was still only about 60% of the influent.

At breakthrough (> 5 µg As/L), the arsenic capacity for alumina was 2,520 µg As/g sorbent. This is 67% greater than the breakthrough capacity in the preliminary column. Possibly, the down time during preparation of syn-GW permitted As to migrate into pores of the particles, thereby freeing up surface adsorption sites. This hypothesis is supported by the observation that when flow to the column was stopped and water allowed to stand in the column undisturbed for 8 days, arsenic concentration in the effluent dropped from about 253 µg/L before stopping flow to 83 µg/L after resuming flow, even though the influent concentration had not changed (data not shown).

The “test As capacity” is approximately 30% greater than the breakthrough capacity. This indicates that arsenic can be removed even once the effluent concentration was greater than 5 µg/L. Whether this test capacity can be reached under field conditions can only be determined by a field pilot test.

Alumina does not appear to affect the speciation of arsenic, nor is arsenic readily desorbed from alumina by clean water. As seen in Table 9, both As(III) and As(V) are present in effluent from the alumina column. As(III) accounts for 19% of the total As in effluent and 21% of the Total As in influent. When the influent arsenic concentration was < 5 mg/L, no arsenic was detected in effluent from the alumina column. This is expected since alumina used for arsenic removal in water treatment is typically regenerated by flushing the alumina with 4% sodium hydroxide (Montgomery, J.M. *Water Treatment Principles and Design*, John Wiley & Sons: New York, 1985).

The effect of organic matter, which is present in site GW but not in synthetic GW, was not addressed in this study. Organic matter was not added to synthetic GW because it was not practical to identify the organic matter or to obtain representative material. The effect of organic matter on the arsenic capacity of alumina is unknown, but should be investigated in a field pilot test prior to full-scale implementation of this technology.

3.3.2 Effect of Sorbents on Water Quality

Neither FeZ nor alumina had a noticeable effect on alkalinity, chloride, nitrate, sulfate, MCPA or MCPP (Table 10). Aluminum was not detected in effluent from the alumina column, suggesting that alumina does not readily dissolve or abrade under simulated groundwater conditions. Similarly, iron was not detected in effluent from the FeZ column, except at 12.8 days. The reason is unclear, but indicates that iron is not easily removed from the zeolite.

The pH was not affected by the sorbents except for the first few bed volumes (Tables 7 and 9). In the case of FeZ, the pH of the effluent decreased from 6.96 to 4.43, while the pH of the alumina effluent rose to 8.23. It must be noted that measurement of pH was difficult in many cases because of drift. This was most common in samples with low Eh. In addition, although influent pH was adjusted to between 5.7 and 5.9 before a batch was placed on-line, subsequent pH measurements often yielded different values. The reason may be a combination of factors, including non-equilibrium in the influent when pH was first measured, as well as drift during measurement.

In general, Eh was also not affected by the sorbents (Tables 7 and 9). The only exception is the first few bed volumes of the FeZ column, in which Eh was appeared to be more positive (oxidizing) in the effluent than in the influent.

3.3.3 Observations Regarding Synthetic GW

Syn-GW rather than site GW was used in this study due to the difficulty of shipping and storing the necessary amount of water (~ 300 gallons) at PRIMA Environmental's facility. Although every effort was made to ensure consistency among batches of syn-GW, the influent data in Table 9 clearly show that preparation of a consistent synthetic groundwater was not straightforward. Despite this variability, PRIMA Environmental is confident that the syn-GW prepared was able to provide a reasonable understanding of how FeZ and alumina would behave under field conditions.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Batch and column tests demonstrated that alumina is an excellent sorbent for both Arsenic(III) and Arsenic(V) in synthetic groundwater. The arsenic capacity in the final column tests was 2,520 $\mu\text{g As/g alumina}$. This may be an underestimate because capacity appears to be dependent upon residence time, which would be much greater in the field than in the laboratory. Neither the surfactant-modified zeolite nor the iron modified zeolite removed arsenic to $< 5 \mu\text{g/L}$. None of the sorbents removed MCPA or MCPP.

Based on the results of this study, PRIMA Environmental recommends that a field pilot test be conducted using alumina as the sorbent for arsenic. The primary goal of the pilot test should be to determine the capacity of the alumina in the presence of organic matter and at a flowrate representative of field conditions. PRIMA Environmental also recommends that the potential for desorption of arsenic from the alumina by clean groundwater be considered—either through a literature review or through additional bench-scale testing—prior to full-scale implementation of this technology.