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Arsenic Pilot Plant Operation and Results-Socorro Springs, New Mexico-Phase 1

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Abstract

Sandia National Laboratories (SNL) is conducting pilot scale evaluations of the performance and cost of innovative water treatment technologies aimed at meeting the recently revised arsenic maximum contaminant level (MCL) for drinking water. The standard of 10 µg/L (10 ppb) is effective as of January 2006. The first pilot tests have been conducted in New Mexico where over 90 sites that exceed the new MCL have been identified by the New Mexico Environment Department. The pilot test described in this report was conducted in Socorro New Mexico between January 2005 and July 2005. The pilot demonstration is a project of the Arsenic Water Technology Partnership program, a partnership between the American Water Works Association Research Foundation (AwwaRF), SNL and WERC (A Consortium for Environmental Education and Technology Development).

The Sandia National Laboratories pilot demonstration at the Socorro Springs site obtained arsenic removal performance data for five different adsorptive media under constant ambient flow conditions. Well water at Socorro Springs has approximately 42 ppb arsenic in the oxidized (arsenate - As(V)) redox state with moderate amounts of silica, low concentrations of iron and manganese and a slightly alkaline pH (8). The study provides estimates of the capacity (bed volumes until breakthrough at 10 ppb arsenic) of adsorptive media in the same chlorinated water. Near the end of the test the feedwater pH was lowered to assess the affect on bed capacity and as a prelude to a controlled pH study (Socorro Springs Phase 2).

Acknowledgements

This project would not have been possible without the generous collaboration of the City of Socorro Water Utility Department. Special thanks to City of Socorro Water Utility Department and Frederick Partey from the New Mexico Institute of Mining and Technology. We acknowledge the invaluable help of Alicia Aragon, Emily Wright, Justin Marbury, Fotini Walton, Michelle Shedd, and Carolyn Kirby from Sandia National Laboratories.

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Acronyms and Abbreviations

AA	Atomic Absorption
APHA	American Public Health Association
AwwaRF	American Water Works Association Research Foundation
BET	Brunauer, Emmett and Teller
BV	bed volume
BW	backwash
CVT	capacity verification test
EBCT	empty bed contact time
gpm	gallons per minute
ICP-MS	inductively coupled plasma mass spectrometer
MCL	maximum contaminant level
MDWCA	Mutual Domestic Water Consumers Association
MGD	million gallons per day
mg/L	milligrams per liter
µg/L	micrograms per liter
NSF	National Sanitation Foundation
NTU	nephelometric turbidity units
O&M	operations and maintenance
ppb	parts per billion
POU	point-of-use
psi	pounds per square inch
PVC	polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
SIVT	systems integrity verification test
SMO	Sample Management Office
SMOCL	Sample Management Office Contract Laboratory
SNL	Sandia National Laboratories
TOC	total organic carbon
TCLP	Toxicity Characteristics Leaching Procedure
TDS	Total Dissolved Solids
TSS	Total Suspended Solids

USEPA	U.S. Environmental Protection Agency
WERC	A Consortium for Environmental Education and Technology Development
WQL	Water Quality Laboratory

1. Introduction

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 (AwwaRF 1999). The adsorption reaction mechanism of arsenic species onto solid metal (M) oxyhydroxide surfaces below pH 6.7 may be generically represented by the following chemical reaction (AwwaRF 1999, Edwards 1994, and Manning et al. 1998):

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

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

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).

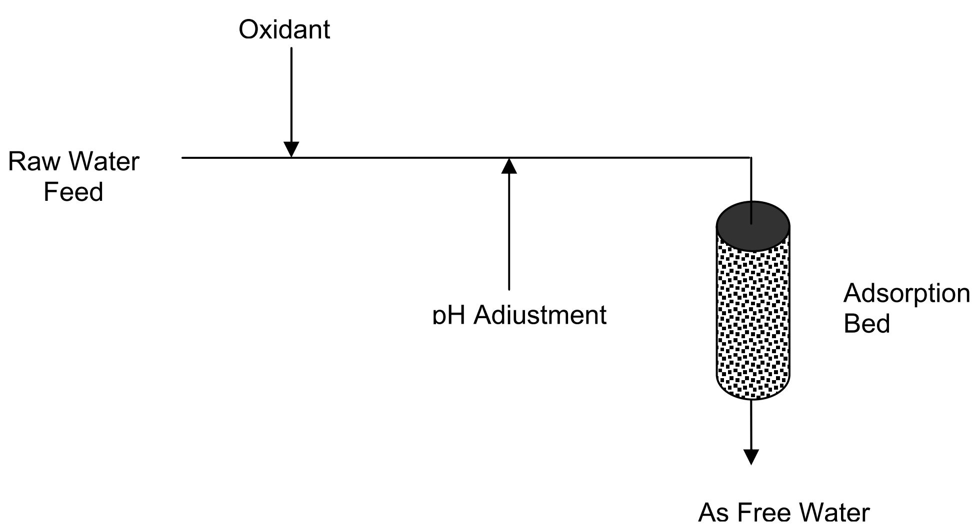

Figure 1-1. Diagram of the Sorption Process for Arsenic Removal

2. Objectives of the Socorro Springs Pilot Test

Sandia National Laboratories (SNL) is conducting pilot scale evaluations of the performance and cost of innovative water treatment technologies aimed at meeting the recently revised arsenic maximum contaminant level (MCL) for drinking water. The standard of 10 µg/L is effective as of January 2006. The first pilot tests have been conducted in New Mexico where over 90 sites that exceed the new MCL have been identified by the New Mexico Environment Department. The pilot test described in this report was conducted in Socorro New Mexico between January 2005 and July 2005. The pilot demonstration is a project of the Arsenic Water Technology Partnership program, a partnership between the American Water Works Association Research Foundation (AwwaRF), SNL and WERC (A Consortium for Environmental Education and Technology Development).

The pilot tests in Socorro consist of granular adsorption media packed in cylindrical columns Water flow is distributed from the top of the bed. Technologies were considered based primarily on the results of the 2003 and 2004 Vendor Forums held in October of each year at the New Mexico Environmental Health Conference. An expert panel, chosen from broad spectrum of water treatment disciplines, evaluated the potential arsenic removal technologies being presented. Results of these evaluations are described in the Forum website (http://www.sandia.gov/water/forums.htm) and summarized in Siegel, McConnell, Everett and Kirby, 2006. The commercial media for these tests are listed in Table 2-1.

Table 2-1 Commercial Designation of Media Used at Socorro Springs

Type	Manufacturer	Product
Granular Ferric Oxide	Adedge	E-33
Granular Ferric Oxide	Englehard Corporation	ARM 200
Granular Titanium Oxide	Hydroglobe	Metsorb
Nanoparticle Zirconium Oxide	MEI	Isolux 302M
Iron Impregnated Resin	Purolite	$ArsenX^{np}$

The objectives of the Socorro Pilot include evaluation of:

- The comparative treatment performance of five adsorptive media using chlorinated water from the Socorro Springs site;
- Comparison of media performance to predictions based on vendor data;
- Limited assessment of maintenance and operational requirements for all media;
- The effect of contact time on the performance of one of the media; and
- The effects of pH adjustment on the performance of selected media.

Prior to the pilot test, the media were characterized by laboratory studies including kinetics of adsorption, sorption isotherms, mineralogy, qualitative chemical analysis and electron microscopy. In addition, rapid small-scale column experiments were carried out to obtain scaling parameters for comparison of the results of bench-scale and pilot scale studies to full scale performance. These results are documented in Siegel et. al. 2007.

3. Description of Pilot Test

3.1 Site Description

The verification test site is the "Springs Site," located off Evergreen Road in Socorro, NM. The Springs Site has a permitted capacity of 550 gallons per minute (gpm). The sources of the supply are Socorro and Sedillo Springs located in the foothills west of the city of Socorro. Existing treatment consists of gas chlorination prior to storage in the Springs Site Water Tank. The two springs, Socorro and Sedillo, supplying continuous water to the Springs Site are composed of spring boxes located in the foothills approximately three-quarters of a mile to the southwest at an elevation approximately fifty feet above the Springs Site. Water from both springs is mixed slightly down gradient of the spring boxes, followed by a shut off valve. Below the shut off valve, an eight-inch subsurface, carbon steel line delivers via gravity the approximately 540 gpm, 90°F water to the chlorination building where the water is disinfected and oxidized using chlorine gas injection just prior to storage in the Springs Site Storage Tank. Overflow from the Springs Site Storage Tank flows via gravity to a second storage tank located approximately one mile to the east.

The pilot equipment is housed within a framed stucco building (shown in Figure 3-1). The building and power drop, the Springs water tank, and the treated water disposal infiltration gallery are secured within a seven-foot chain link fence. The building is heated by residual heat from the eight-inch water supply line (source water temperature is approximately 90°F) and the chlorine pumps. Socorro personnel stated that the inside building temperature remains at 50°F or above year-round.

During this pilot, a portion of the chlorinated Springs Site water was diverted to the arsenic adsorption media filters. The arsenic adsorption media filters are located inside the Springs Site chlorination building. The treated water and backwash wastewater from the arsenic adsorption media filters was discharged to an on-site subterranean infiltration gallery via a 2-inch polyethylene pipe. The total discharge was limited to 3 gpm or less; none of the treated water was returned to the drinking water distribution system. The discharge has been coordinated with the City of Socorro Water Utility Department. The City of Socorro water utility also assisted with on-site logistics and provided water, electricity, and site security.


Figure 3-1. Socorro Springs Pilot Plant Site

3.2 Pilot Plant Description

3.2.1 Pilot Test Design

The pilot-scale columns were designed based on full-scale design parameters to minimize scaling effects, thereby improving confidence in the results. It is understood that pilot-scale columns are sub-optimal for representation of full-scale maintenance and operational requirements; however, we have collected some operational parameters that will help define and characterize operational factors. These included the pressure drop across the media and the corresponding backwash requirements (frequency and volume), the adsorptive capacity of all media to breakthrough (defined as 10 µg/L or 10 ppb) and the adsorptive capacity to approximately 80% of the influent concentration for several of the media. Pilot-scale operational parameters for each media are based upon full-scale operating conditions as provided by the respective vendors. Table 3-1 provides a summary of the basis for design of the pilot columns for all five media.

3.2.2 Pilot Equipment

The Socorro pilot system is made up of the following modular components:

1. Raw water makeup system
   a. Polyethylene tank (also acts as chlorine contact tank);
   b. Pump;
   c. Pressure control and relief;
2. Carbon dioxide injection system (pH adjustment method[1]); and
3. Column skid

The raw water at Socorro Springs is chlorinated in the pipeline by the utility in a small building at the site (Figure 3-1). The chlorinated raw water is delivered to the pilot unit raw water makeup system using the normal pressure of the Socorro water system. The raw water makeup system contains an 80-gallon polyethylene tank supplying prime/suction water for the feed water pump. The storage tank has level controllers that maintain the water level in the tank and will shut off the supply pump to the pilot unit if the tank level drops too low to maintain feed water pump prime. The feed water pump is a vertical, non-self priming, multistage, in-line, centrifugal pump mounted on the tank foundation. The pump supplies feed water to the carbon dioxide system and the column skid at design pressures using pressure control valves and a pressure relief valve to avoid potential pump deadheading. The pump is protected against running dry or losing prime by a level float control in the makeup tank designed to shut off the pump at a low-level checkpoint. The pilot test skid (Figure 3-2) contains ten columns; each designed as separate arsenic adsorption media filters operating in parallel. Each column is modular in design consisting of the following components: rotameter, three-way valve (for service or backwash mode), up-gradient pressure gauge, column with adsorptive media, down-gradient pressure gauge, sample tap, totalizing flow meter, check valve, and all associated piping. (Refer to Drawings SOC-01 and SOC-02 in Appendix A-3). Columns were backwashed separately to avoid backwash water from different media mixing. The collection tank and backwash manifold were cleaned prior to backwash of a different media.

Appendix A-1 gives a chronological log of pilot plant operation. Various operating changes are chronicled as well as descriptions of repairs and adjustments.

[1] pH was kept at ambient (pH 8) during most of this test. A short adjustment (to pH 6.8) was made near the end of the test, but a full pH adjustment study is performed under Socorro phase 2.

Figure 3-2. Socorro Springs Pilot Skid Unit

Table 3-1 Summary of Design Basis

Vendor Media	Metsorb	E33			Isolux 302M	ARM 200	AresenX^{np}
Hydraulic Loading Rate gpm/ft^2	8	6			1.24	6	8.1
Column Number	6	8-10			7	4	5
Design EBCT, min	2	2	4	5	0.3	4	3
Pre-filtration required?	No	No	No	No	(5 µm)	No	No
Column Height, in	39	39	60	60	10" (cartridge)	60	60
Column Diameter, in	3	3			1 (ID)	3	3
Media Depth, in	25.7	19.3	38.5	48.1	N/A	38.5	39.2
Media Volume, Liters	2.97	2.23	4.46	5.57	0.116	4.46	4.74
Water Flow Rate, gpm	0.4	0.3			0.45	0.3	0.4
Backwash Flow, gpm	0.3	0.3			N/A	0.3	0.3

3.2.3 Adsorptive Treatment Process

The conceptual treatment process for all five arsenic adsorption media filters is based on passing arsenic-contaminated feed water through a fixed bed of media that has a strong affinity for arsenic. The arsenic is removed in fixed bed filtration via adsorption, the physical attachment of the adsorbate (arsenic) to the surface of the adsorbent media grains. The removal capacity and effectiveness of the arsenic removal media is dependent on a number of factors, of which surface area is of importance. The surface area is a function of the accessibility of the porosity of the media grains. Adsorbent media contains a large quantity of very small pores throughout the media grains. Other factors that determine the capacity and effectiveness of adsorbent media are accessibility of the sorption sites for arsenic ions, time available for arsenic ions to migrate to pore sites, competing ions for sorption sites, concentration of arsenic in the feed water, pH of the feed water, and flow characteristics of the feed water that conveys the arsenic into the bed of adsorbent media. The time available for arsenic sorption is directly proportional to the EBCT. The design basis (manufacturer's suggestions) for EBCT is shown in Table 3-1 and varies between 2 and 5 minutes. The Isolux media is inside a vendor-provided cartridge type bed that is designed for low EBCT operation

As water passes down through a filter vessel containing fixed bed media, the arsenic concentration declines until it is no longer detectable. As the upper portion of the media becomes saturated, the treatment region (mass transfer zone) progresses downward until a portion of the adsorptive capacity is used and arsenic breakthrough occurs (e.g. effluent arsenic is 10 ppb or greater). If the adsorbent media perform as expected, then no arsenic will be detected in the treated water for at least 4 to 6 months. (The lower limit of detection for arsenic using the Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at SNL's Water Quality Laboratory (WQL) is less than 2 µg/L). Eventually, as the adsorbent capacity of an adsorbent medium is decreased, detectable amounts of arsenic will appear in the treated water. The concentration of arsenic will gradually increase, and when the capacity of the medium is completely exhausted, the arsenic concentrations in the untreated and treated water will be the same.

3.3 Water Quality

A summary of the Springs Site average raw water quality is presented on Table 3-2. The water is generally of good quality except for arsenic, which exceeds the new MCL effective in January 2006. The water has moderate levels of silica, sulfate, and hardness and is near neutral in pH. The arsenic level is four to five times the January 2006 MCL of 10 µg/L (10 ppb).

Table 3-2 Socorro Springs Water Composition Before and After Chlorination

Parameter	Unchlorinated Feed Water	Chlorinated Feed Water
Conductivity (µS/cm)	NA[2]	340
Temperature (°C)	NA	30-35
pH	NA	7.9
Free Chlorine (ppm as Cl_2)	NA	0.7
Turbidity (NTU)	NA	0.1
Alkalinity (ppm)	124	130
Nitrate (ppm)	0.4	0.2
Iron (ppb)	50	50
Particulate As (ppb)	ND[3] (<0.5)	ND (<0.5)
As (III) (ppb)	ND (<0.5)	ND (<0.5)
As (V) (ppb)	42.3	43.3
Total Arsenic (ppb)	**42.3**	**43.3**
Titanium (ppb)	ND (<0.4)	ND (<0.4)
Zirconium (ppb)	ND (<0.2)	ND (<0.2)
Vanadium (ppb)	12.3	11.8
Aluminum (ppb)	<10	<10
Fluoride (ppm)	0.5	0.5
Chloride (ppm)	11.4	12.4
Sulfate (ppm)	28.6	29.3
Sodium (ppm)	52.1	52.8
Magnesium (ppm)	4.1	4.1
Calcium (ppm)	17.3	17.7
Silica (ppm)	24.4	24.5
TOC (ppm)	0.5	0.5

3.4 Media Description

The Socorro pilot study tested five media. These included four metal oxides and one ion exchange/metal oxide combination. The commercially-available media that were evaluated in the test are listed in Table 3-3.

[2] NA = Not Analyzed
[3] ND = Not Detected

Table 3-3 Adsorptive Media Specifications

Media	**Isolux 302M**	**Metsorb**	**ARM 200**	**ArsenX^{np}**	**E-33**
Manufacturer	MEI	Hydroglobe	Englehard	Purolite	Adedge
Chemical Constituents	Amorphous inorganic zirconium oxide 60-95%	Nano-crystalline titanium dioxide	Iron oxide / hydroxide	Nano-particle selective resin with iron oxide as the functional group	Iron oxide / hydroxide
Bulk density (lb/ft^3)	56	50	30-45	49-52	30
BET Surface Area (m^2/g)	300 vendor 499 SNL	210	260	120	140 vendor 150 SNL
Moisture	5-40% by volume	N/A	N/A	N/A	N/A
Sieve Sizes, US std.	N/A	-16+60	-12+40	-16+50	-10+35
Particle size	<5µm	1.18 x 0.25 mm	1.40 x 0.43 mm	1.18 x 0.3 mm	0.5 x 2.0 mm
NSF approval Status	Section 61 Certified	Section 61 Certified	Section 61 Certified	Section 61 Certified	Section 61 Certified

Purolite, Engelhard Corporation, Adedge, and Hydroglobe indicated that no pretreatment is required for their respective arsenic adsorption media; however, MEI utilizes a 5 µm, pleated pre-filter cartridge to minimize potential plugging of the media cartridge.

3.5 Sampling Plan

A detailed sampling plan was previously published as SAND 2006-1324 (Siegel et al, 2006a). During the test, some modifications were made to this plan in response to actual operating conditions and practices. The essential procedures for the actual operation of the Socorro Springs Pilot Plant are summarized in Table 3-4. There are two periods of sampling during the pilot study: the Systems Integrity Verification Test (SIVT) and the Capacity Verification Test (CVT). The SIVT is a 2-week period at the start of the pilot used to evaluate the reliability of equipment operation under the environmental and hydraulic conditions at the Socorro Springs pilot site and to determine whether performance objectives can be achieved for arsenic removal at the design operating parameters for the arsenic adsorption media system. The CVT period produces operational and water quality data up through and beyond the defined breakthrough arsenic level (10 µg/L) for each sorptive media.

Table 3-4 Water Quality Sampling Plan

Parameter	Sampling Frequency (IVT)	Sampling Frequency (CVT)	Method Used[4]	Comments
On-Site Analyses				
Conductivity	Daily	Bi-Weekly	HACH 8160B (Direct Measurement Method)	Equivalent to EPA 120.1, Standard Method 2510B
Temperature	Daily	Bi-Weekly	Standard Method 2550B	Utilized digital thermometer on HACH conductivity meter
pH	Daily	Bi-Weekly	Standard Method 4500-H^+	
Free Chlorine	Daily	Bi-Weekly	HACH 8021 (DPD)	Equivalent to Standard Method 4500-Cl G
Turbidity	Daily	Bi-Weekly	Standard Method 2130 B	
Laboratory Analyses				
Total Arsenic	Daily	Bi-Weekly	EPA 200.8	Total Arsenic measured within 48 hours of sampling by ICP-MS in the WQL in lieu of on-site qualitative analysis.
Speciated Arsenic	Weekly	Once	EPA 200.8	Separation of As(III) from As(V) done by aluminosilicate adsorbent cartridge. See Appendix E of the Siegel, et. al., 2006a (SAND2006-1324) for details.
Iron	Daily	Weekly	EPA 200.7 – SMOCL, AA Spectroscopy – WQL	
Titanium	Daily	Weekly	EPA 200.8	Analyses only for Hydroglobe columns
Zirconium	Daily	Weekly	EPA 200.8 – SMOCL AA Spectroscopy – WQL	Analyses only for MEI cartridges
Alkalinity	Daily	Weekly	Standard Method 2320 B	
Total Suspended Solids	Three times	Monthly	Standard Method 2540 B	SMOCL Only
Nitrate	Three times	Monthly	EPA 300.0	SMOCL Only
Metals	Daily	Weekly	EPA 200.7 – SMOCL AA Spectroscopy, EPA 200.8 – WQL	As, Ti, V, Al, Mn, Zr by EPA 200.8; Other metals by AA Spectroscopy at WQL
Silica	Daily	Weekly	EPA 200.7 – SMOCL HACH 8185 – WQL	HACH method is the Silicomolybdate Method
Anions	Daily	Weekly	EPA 300.0	
Total Organic Carbon	Three times	Monthly	SW-46 9060	SMOCL Only

[4] Reference for the Standard Methods is APHA, 1998; Reference for EPA methods is USEPA, 2005.

4. Test Results

4.1 Pilot Operations

The pilot plant columns shown in Figure 3-2 were installed and media loaded in December 2004. The media was backwashed right after installation, but the pilot was not started until January 2005. In addition, the original Metsorb was removed and replaced with fresh media and backwashed; it had formed an obstruction, which would not allow flow through the column. Each column was backwashed again prior to starting the pilot. The Isolux cartridge was not installed until the start of the pilot in January 2005.

After startup, electronic flow measurements were erratic due to malfunctioning digital flow meters. Until this problem was rectified, totalized flows were calculated from rotameter field readings and elapsed time of column operation. Another problem was caused by the original design of the columns, which had the flow control (via rotameters) upstream of the columns. This led to flow problems since the rotameters took the entire pressure drop, and hence no flow at times to the columns themselves. In February 2005, the flow control was moved to the effluent side of the columns.

None of the columns required backwashing throughout the duration of the pilot study since the pressure drop remained below 10 psi. This seemed unusual, as backwashing is typical in most filtration schemes. This may have been due to leaks in the three-way valves or possible inaccuracies in pressure gauge readings. At shutdown, several of the valves appeared to have been leaking (i.e. not providing proper inlet/outlet stream separation). Operational history is presented in Table A-1 of the appendix.

4.2 Water Chemistry Effects

Appendix A-2 presents the water chemistry measurements for the Socorro Phase 1 pilot plant runs. Most analytes were unaffected by the adsorption media as attested by the low standard deviations noted for both feed and product water. Two exceptions, however are silica and vanadium in product water samples which owe their higher standard deviations to the fact that both vanadium and silica are adsorbed very rapidly in the early stages of testing.

4.3 Adsorptive Media Performance

The effectiveness of an adsorptive bed is measured in the amount of water that it can treat to meet the 10 ppb arsenic standard. One means of reporting this is referred to as bed volumes (BV) of water passing through the media columns until the regulatory limit (10 ppb) was exceeded in the effluent. Bed volumes are a common thread between pilot scale and full scale operations. A utility would simply need to multiply the pilot BV for a specific media and water chemistry by the total volume of media required for a full scale system to obtain the amount of water that could be treated before exceeding the MCL. The arsenic sorption capacity of the media was also calculated from the mass balance. It is reported as milligrams of arsenic sorbed per gram of media at breakthrough (when the effluent reaches 10 ppb). For the pilot tests, the values of BV and capacity at breakthrough show a fairly consistent relationship.

Comparisons of the pilot tests to the laboratory studies can be found in Siegel et al. 2007. Many of the tests in the pilot were continued well after the 10 ppb breakthrough in order to look at complete exhaustion of the media bed. Figure 4-1 shows that as the tests continue, the product water essentially approaches the feed water arsenic concentration. It was decided near the end of the Phase 1 test to lower the pH of the feed water to examine the effect on the media. This effect is shown as a rather dramatic drop in the concentration of arsenic in the product of several of the media. The drop is most dramatic for the ARM 200, the ArsenX^{np} and the Metsorb media. The pH lowering was performed during July 2005 and is shown in Figure 4-1 and although performed on all columns on the same set of days, it appears at different bed volumes due to the experimental conditions. Lowering the pH allows more arsenic to be taken up by the media and forms the basis for a more controlled set of tests on the effects of pH adjustment. A subsequent report (Socorro Phase 2) will present the results of a side by side set of pilot plant tests using five different media. One set of columns will have the feed pH lowered (pH 6.8) and the other set will run at ambient (pH 8) conditions.

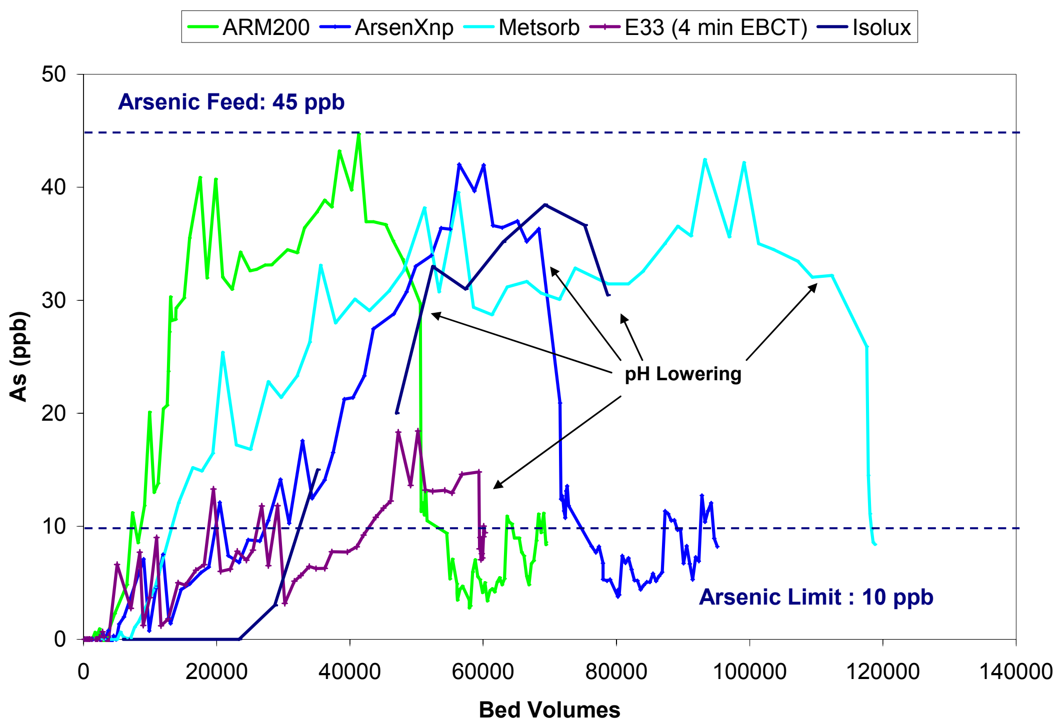

Figure 4-1. Socorro Springs Arsenic Breakthrough Curves

Figure 4-2 shows the effect of empty bed contact time on arsenic breakthrough for one media (E33). The relatively rapid feed rate corresponding to a 2 minute EBCT clearly has arsenic breakthrough at approximately 24,000 bed volumes, while the longer empty bed contact times extend the bed life to over 50,000 bed volumes. Most manufacturers suggest at least a 3 minute EBCT.

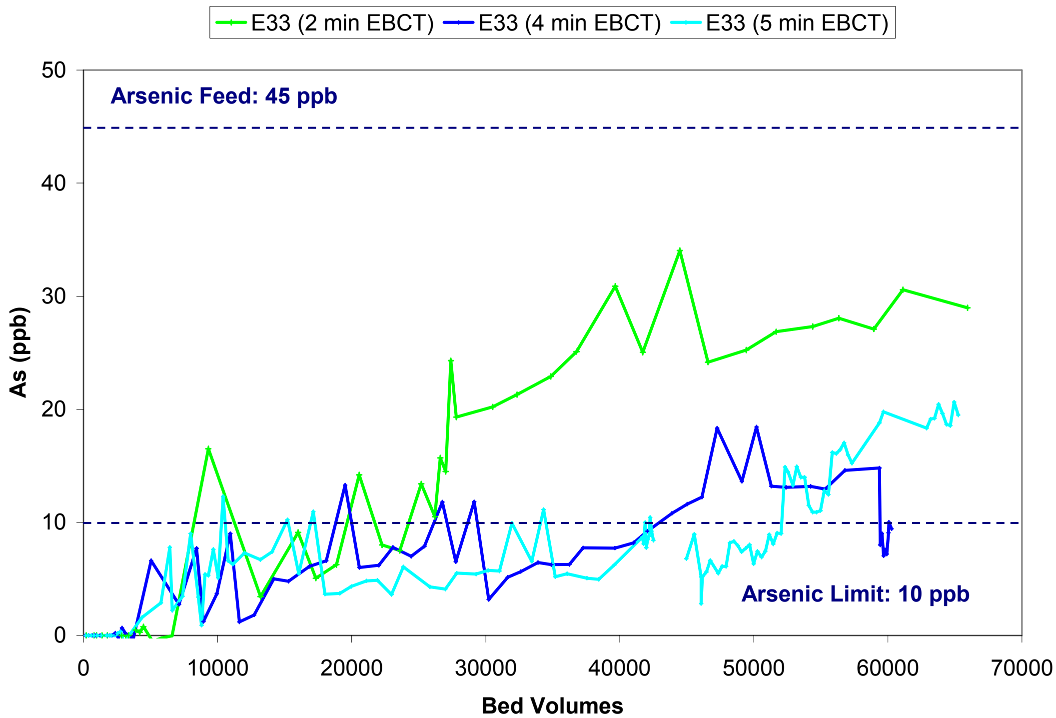

Figure 4-2 Empty Bed Contact Time Breakthrough Curves (E33)

4.4 Spent Media Characterization

The spent arsenic media passed the TCLP (US EPA 1992) 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). The media can be disposed of in a regular landfill.

Table 4-1 TCLP Analysis Results

Metal	Unit	RCRA Limits	Detection Limits	$ArsenX^{np}$	Metsorb	ARM200	E33 (2-min)	E33 (4-min)	E33 (5-min)
Arsenic	mg/L	5	0.125	0.146	ND	ND	ND	ND	ND
Barium	mg/L	100	0.075	1.73	30.6	6.14	1.18	0.696	1.7
Cadmium	mg/L	1	0.125	ND	ND	ND	ND	ND	ND
Chromium	mg/L	5	0.05	ND	ND	ND	ND	ND	ND
Copper	mg/L	N/A	0.5	0.319	0.198	0.69	0.428	ND	ND
Lead	mg/L	5	0.125	ND	ND	ND	ND	ND	ND
Mercury	µg/L	200	0.2	0.115	0.102	0.138	0.139	0.155	0.115
Nickel	mg/L	N/A	0.05	ND	ND	ND	ND	ND	ND
Selenium	mg/L	1	2.5	ND	ND	ND	ND	ND	ND
Silver	mg/L	5	0.125	ND	ND	ND	ND	ND	ND
Zinc	mg/L	N/A	0.25	0.117	0.102	0.239	0.197	ND	ND

5. Discussion and Conclusions

5.1 Media Effectiveness

For the pilot tests, the values of BV and capacity at 10 ppb (10 µg/L) arsenic show a fairly consistent relationship between the media:

E33 >Isolux 302M ~ ArsenX^{np}> Metsorb > ARM 200.

Rank ordering the performance of the media was done using the experimental empty bed contact times specified in Table 3-1. These EBCTs were the prescribed values from the media vendors. It is generally believed that a longer empty bed contact time will extend the life of the media, however, EBCTs longer than 5 minutes are not typically recommended by manufacturers.

The quantitative performance of the adsorptive media from pilot testing at the Socorro Springs pilot for arsenic removal have been tabulated in Tables 5-1 and 5-2. Row two of the tables lists number of bed volumes to breakthrough at 10 ppb, while row three of the tables show the bed volumes to 80% (C/C_0=0.8) of exhaustion. This value is important for cases where a facility may choose to have two adsorptive media vessels in series in what is commonly referred to as a "lead-lag" design. Row three through five of the tables present the capacity of the media for adsorbing arsenic and are reported as mg of arsenic sorbed per gram of media, (mg As/g media) normalized to 35,000 BV and the capacity at 80% exhaustion respectively.

Table 5-1 Breakthrough Bed Volumes and Media Capacity

Parameter	ARM200	Metsorb	ArsenX^{np}	Isolux
EBCT, min	4	2	3	0.3
BV to 10 ppb	8,600	13,000	27,000	32,000
BV at C/C_o = 0.8	33,000	87,000	53,000	63,000
Arsenic Loading at 10 ppb, mg/g	0.6	0.7	1.4	1.3
Arsenic Loading at 35,000 BV, mg/g	1.2	1.4	1.8	1.4
Arsenic Loading at C/C_o = 0.8, mg/g	1.1	2.2	2.1	2.0

Table 5-2 shows the effect of changing the empty bed contact time on the media capacity of Adedge E33. As expected, the longer EBCT extends the bed operation to over 50,000 BV, more than twice the capacity of the 2-minute EBCT column. Since the 4 minute and the 5 minute EBCT take longer to run, the BV at 80% exhaustion for these columns were conservatively estimated at > 63,000 BV. If the experiments were allowed to proceed to 80% exhaustion it is reasonable to expect that they would match or exceed the 79,000 BV value measured for the 2 min EBCT. Results in Table 5-2 show very good capacity at breakthrough for the E33 media (~4mg As /g media for 2-min EBCT).

Table 5-2 Breakthrough BV and Media Capacity at different EBCT

Parameter	E33		
	2 min	4 min	5 min
BV to 10 ppb	24,000	43,000	52,000
BV at C/C_o = 0.8	79,000	>63,000	>65,000
Capacity at 10 ppb, mg/g	1.9	3.6	4.2
Capacity at 35,000 BV, mg/g	2.5	3.0	2.9
Capacity at C/C_o = 0.8, mg/g	4.0	>5.0	>5.0

Table 5-3 shows a comparison of the bed volumes to breakthrough for the pilot tests along with extrapolated values of BV that are "normalized" for a 5-minute EBCT. "Normalization" was performed by dividing the "normalized- basis" EBCT by the pilot EBCT and multiplying this quotient by the pilot BVs. The actual values in Table 5-3 are valid only if there is a linear relationship between EBCT and capacity; this assumption has not been strictly supported by the results of this study.

Table 5-3 Media Comparison "normalized" for EBCT

Media	EBCT-pilot	BVs-pilot	BVs norm to 5 min EBCT
ARM200	4	8,600	10,750
Metsorb	2	13,000	32,500
ArsenXnp	3	27,000	45,000
E33-5min	5	52,000	52,000
E33-4min	4	43,000	53,750
E33-2min	2	24,000	60,000

It was found that the surface area of the pristine material may not be directly related to the performance; E33 the media with one of the lowest surface areas had the best performance (Siegel et al. 2007). It was also observed that the media differed in their physical response to the pilot test conditions. The water at Socorro Springs was warm (27 - 37°C). Aging studies carried out over a 3-month period showed that the ARM200 media partially recrystallized and was transformed to hematite (Siegel et al. 2007). Discussions with the vendor indicate that the ARM 200 was a preproduction batch. The vendor has sent a subsequent production batch that will be tested at the SNL Desert Sands pilot test. This may be a cause of the relatively poor performance of that media in the pilot and the differences in the results from the pilot when compared to the laboratory studies, which were carried out at room temperature. Different amounts of media were lost due to compaction and initial backwashing; and surface areas may have changed. Additional analyses of the data including attrition loss and chemical changes to the media during the pilot tests were carried out to better interpret the results as documented in North, 2005, and Siegel et al. 2007.

5.2 Water Treatment Cost Estimates

The total cost of Arsenic treatment consists of two parts: (1) Initial Capital Costs and (2) Annual Operations and Maintenance (O&M) Costs. Initial Capital Costs include the cost of a new or modified building, equipment costs for arsenic removal, and infrastructure improvements necessary for arsenic removal (e.g. pumps, piping, etc.). Annual O&M Costs include labor, electrical costs, media replacement costs, chemical pre-treatment and post-treatment (if applicable), and media disposal costs.

Arsenic treatment costs can have a wide range, due to the performance of the different kinds of media and the O&M costs associated with maintaining the system. In addition, each site will have its own specific water chemistry and site conditions which can contribute to unique costs.

At the Socorro Springs site, the average monthly water production is 18 million gallons per month. Economic calculations for this site are based on the following assumptions:

Design Basis:

- Bed Volumes are from the E33 performance in this pilot
- No backwash reclaim tank, nor solids capturing equipment are included
- No major infrastructure improvements are included
- Permitting, Engineering, and Installation cost estimates are included
- Cost comparison and price sensitivity is presented for general cases
- NOTE: pH adjustment will undoubtedly affect media capacity and treatment cost estimates, however a comparative discussion of pH adjustment will be reserved for the Socorro Phase 2 report.

Table 5-4 summarizes the input values used in the economic analysis using the pilot results. Results in Table 5-5 provide order of magnitude economic costs calculated by the ARCE model (US EPA, 2004) for each of the pilot designs (2, 4, and 5 minute EBCT). This table demonstrates that for this location the media costs heavily influence the total unit cost of water produced. The facility costs however, also influence the cost of water, but independently of media costs (baseline construction costs are the same).

Table 5-4 Capital and Annual O&M Costs for Arsenic Removal using Granular Media

Design Criteria	**E33-2min**	**E33-4min**	**E33-5min**
Vessel Flow Rate, gpm	353	353	353
Design Treatment Capacity, MGD	0.35	0.35	0.35
Configuration (series/parallel/unknown)	parallel	parallel	parallel
Unit Media Cost, $/cf	*$200.00*	*$200.00*	*$200.00*
Building, sf	200	288	338
Building Unit Cost, $/sf	$200	$200	$200
Annual Estimated Power Use, kWh/yr	38,084	38,084	38,084
Power Cost, $/kWh	0.10	0.10	0.10
Labor, Operations, hrs/yr	127.0	73.0	66.0
Unit Labor Cost, Operations, $/hr	$30	$30	$30
Labor, Management, hrs/yr	12	12	12
Labor, Management, $/hr	$80	$80	$80

Table 5-5 Capital and Annual O&M Costs for Arsenic Removal using Granular Media

Annual O&M Costs	**E33-2min**	**E33-4min**	**E33-5min**
Total Annual Media Costs, $/yr Based on Average Flow	$141,600	$79,296	$66,080
Annual Power Cost, $/yr	$3,808	$3,808	$3,808
Spent Media Production, Tons/yr	n/a	n/a	n/a
Total Estimated Labor Costs, $/yr	$4,770.0	$3,150.0	$2,940.0
Equipment Maintenance Costs, $/yr	$3,126.2	$6,252.4	$7,524.0
Capital Cost Summary			
Media & Equipment	$116,920	$233,838	$281,398
Building	$40,000	$57,600	$67,600
Construction & 20% Contingency	$48,143	$96,286	$115,870
Present Worth Analysis			
Net Interest Rate	4.0%	4.0%	4.0%
Period, Years	20	20	20
Total Annual O&M Costs, $/yr	$153,305	$92,507	$80,352
Present Worth of Annual O&M Costs, $	$2,083,460	$1,257,197	$1,092,016
Total Estimated Facility Cost	$205,063	$387,724	$464,867
Total Present Value of Facitlities, $	$2,288,523	$1,644,922	$1,556,883
Total Annual Amortized Cost (Capital + O&M)	$168,394	$121,036	$114,558
Total Unit Cost of Water Produced, $/1,000 gals	$1.32	$0.95	$0.90

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Appendix A-1 Socorro Phase 1 Arsenic Pilot Plant Log

Date	**Action**
10/15/04-11/30/04	Gathered pH, turbidity, conductivity samples weekly
11/30/04	Installed Columns
12/7/04	Loaded media into columns
12/9/04	Performed initial backwash of each column Noticed that each of the columns' media height was lower than design height
1/24/05	Added more media to each column – now at design height Backwashed each of the columns
1/26/05	Phase 1 (no pH adjustment) Two-Week Integrity Verification Starts Samples taken daily on columns 4-10, chlorinated & raw water
1/29/05	Totalizing water meters' displays aren't working – they are fixed several times by cleaning out, but continue to show zero total gallons
2/1/05	NSF Visit to site: Inspection of Pilot equipment, training, and question & answer session
2/4/05	Flow meters are moved from influent to effluent side of columns 4 & 5. Entire pressure drop was taken by the rotameters, which led to no or little pressure to the columns. This solved the problem.
2/9/05	MEI Isolux cartridge has a ΔP of 38 psi – cartridge is depleted.
2/14/05	Socorro Utilities personnel trained
3/11/05	Stopped sampling SA sample point (raw water); all Arsenic is present as As(V)
5/3/05	Software glitch on totalizing water meters is fixed, however problems continue with meters. High water temperature most likely caused their failure.
7/18/05-7/22/05	TOMCO pH Control (CO_2) System Installed Field Representative visited and verified settings, trained SNL personnel
7/26/05	Leak on pH adjustment water line to columns – fixed onsite Capacity Extension (pH lowering) Begins. Sample for analysis three times per day on 7/26, 27, 28
7/28/05	Column 6 (Hydroglobe Metsorb) has high ΔP, is backwashed several times but were unable to get column to flow. Column is isolated and taken offline.
8/6/05	Pump not working, capacity extension cancelled.
8/19/05	Pump purchased for Jemez pilot installed Flow Interruption study begins, daily arsenic samples taken
8/23/05	CO_2 system out of calibration (off by more than 0.4 pH units), once system is calibrated, no water flowing
8/24/05	Site visit determines that CO_2 had leaked into piping system, once bled off pump worked again
8/29/05	Leak on column 5. Column isolated until 8/30/05.
8/30/05-9/30/05	Flow interruption study continues, daily arsenic samples taken. Columns 6 and 8 are removed for mass transfer zone study

Appendix A-2 Water Chemistry Measurements

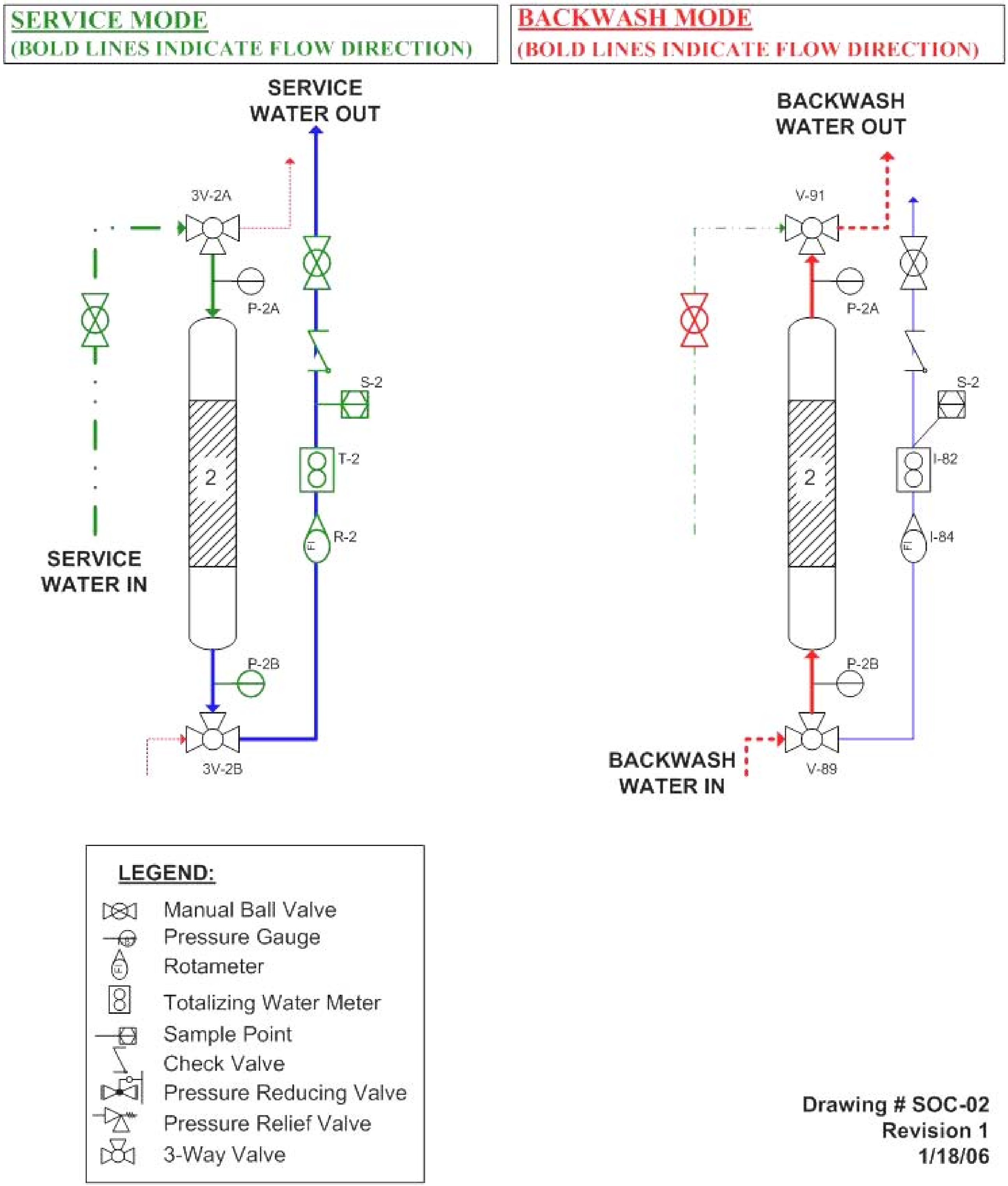
Appendix A-2 tables list relevant analyte concentrations for major ions as well as pH, TOC, conductivity, turbidity and free chlorine. We report the average (Avg), standard deviation (SD) and number of samples measured (N).

Column		pH	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Sulphate (mg/L)
SB	**Avg**	8.0	17.5	4.2	52.8	12.1	0.5	28.4
Chlorinated	**SD**	0.1	0.9	0.2	4.2	0.3	0.1	0.9
Feed	**N**	28	11	11	10	10	10	10
S4	**Avg**	7.8	16.8	4.1	52.7	12.2	0.5	28.8
ARM200	**SD**	0.2	1.9	0.2	4.0	0.4	0.1	1.7
	N	51	9	9	9	9	9	9
S5	**Avg**	7.8	17.5	4.3	52.3	12.2	0.4	28.6
ArsenXnp	**SD**	0.2	1.0	0.5	3.8	0.2	0.2	0.8
	N	51	10	10	10	10	9	9
S6	**Avg**	7.9	16.6	4.2	51.9	12.2	0.5	28.5
Metsorb	**SD**	0.2	3.2	0.3	3.5	0.3	0.1	1.0
	N	22	9	9	9	9	9	8
S7	**Avg**	8.0	17.7	4.2	52.6	12.6	0.5	29.8
Isolux	**SD**	0.1	0.1	0.0	3.0	0.3	0.0	0.8
	N	12	2	2	2	2	2	2
S8	**Avg**	7.9	17.6	4.2	52.5	12.2	0.5	28.5
AD33	**SD**	0.2	0.8	0.2	3.8	0.3	0.1	0.9
2-EBCT	**N**	50	10	10	10	10	10	10
S9	**Avg**	7.9	17.7	4.3	53.0	12.2	0.5	28.5
AD33	**SD**	0.1	0.7	0.2	4.8	0.4	0.1	0.9
4-EBCT	**N**	60	10	10	10	10	10	10
S10	**Avg**	7.9	17.6	4.2	52.6	12.2	0.5	28.5
AD33	**SD**	0.2	0.7	0.1	3.8	0.4	0.1	1.0
5-EBCT	**N**	62	10	10	10	10	10	10

Appendix A-2 Water Chemistry Measurements (cont)

Column		Vanadium (µg/L)	Nitrates (mg/L)	Silica (mg/L)	Cond. (µS/cm)	Free Cl_2 (mg/L as Cl_2)	Turbidity (NTU)	TOC (mg/L)
SB	**Avg**	11.8	0.4	24.5	346	0.7	0.1	0.5
Chlorinated	**SD**	1.5	0.0	1.1	5.2	0.1	0.0	0.2
Feed	**N**	15	7	12	25	13	25	9
S4	**Avg**	0.4	0.5	25.0	341	0.5	0.2	0.7
ARM200	**SD**	0.6	0.1	7.4	10	0.3	0.1	0.4
	N	14	7	11	25	25	13	9
S5	**Avg**	1.0	0.4	25.9	346	0.1	0.2	1.3
ArsenXnp	**SD**	3.0	0.0	9.8	14	0.1	0.1	1.1
	N	15	7	24	25	25	13	9
S6	**Avg**	1.2	0.4	27.2	342	0.5	0.3	0.9
Metsorb	**SD**	2.8	0.0	9.7	6.4	0.1	0.3	0.7
	N	10	7	10	23	23	11	9
S7	**Avg**	0.0	0.4	21.8	343	0.6	NA	0.5
Isolux	**SD**	0.0	0.0	4.7	4.0	0.3	NA	0.1
	N	2	2	2	12	12	0	2
S8	**Avg**	4.4	0.4	24.7	343	0.7	0.2	0.7
AD33	**SD**	3.9	0.0	3.4	4.9	0.1	0.0	0.3
2-EBCT	**N**	15	7	22	25	25	13	9
S9	**Avg**	1.1	0.4	25.2	343	0.7	0.1	0.6
AD33	**SD**	1.6	0.0	6.6	5.2	0.2	0.1	0.2
4-EBCT	**N**	16	7	22	25	25	13	8
S10	**Avg**	0.9	0.4	23.8	343	0.6	0.1	0.7
AD33	**SD**	1.5	0.0	5.5	5.0	0.2	0.1	0.4
5-EBCT	**N**	15	7	21	25	25	13	9

Appendix A-3 Pilot Flow Diagram

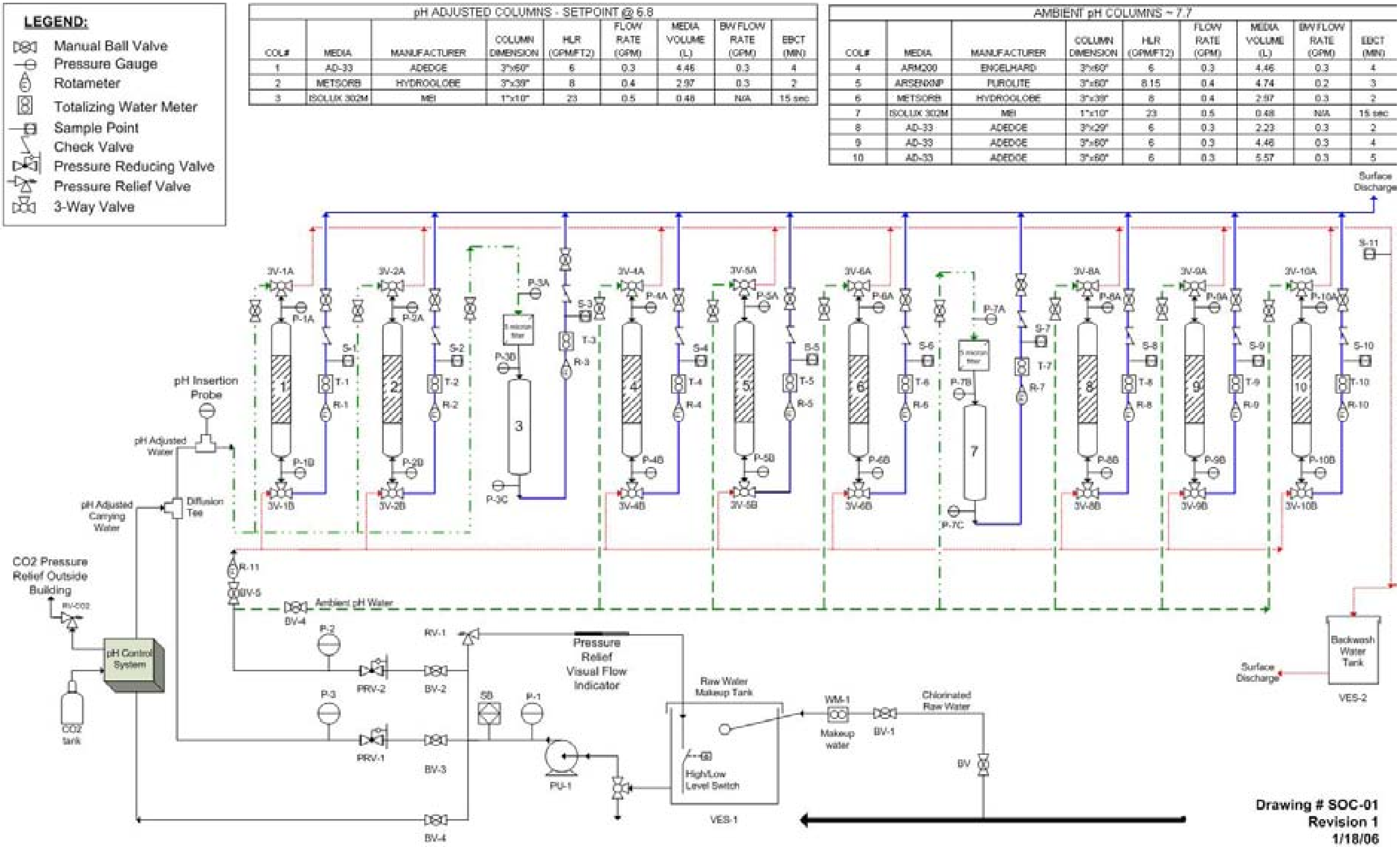


Appendix A-3 Pilot Flow Diagram (cont)

SOCORRO SPRINGS FLOW DIAGRAM

pH ADJUSTED COLUMNS - SETPOINT @ 6.8								
COL#	MEDIA	MANUFACTURER	COLUMN DIMENSION	HLR (GPM/FT2)	FLOW RATE (GPM)	MEDIA VOLUME (L)	BW FLOW RATE (GPM)	EBCT (MIN)
1	AD-33	ADEDGE	3"x60"	6	0.3	4.46	0.3	4
2	METSORB	HYDROGLOBE	3"x39"	8	0.4	2.97	0.3	2
3	ISOLUX 302M	MEI	1"x10"	23	0.5	0.48	N/A	15 sec

AMBIENT pH COLUMNS ~ 7.7								
COL#	MEDIA	MANUFACTURER	COLUMN DIMENSION	HLR (GPM/FT2)	FLOW RATE (GPM)	MEDIA VOLUME (L)	BW FLOW RATE (GPM)	EBCT (MIN)
4	ARM200	ENGELHARD	3"x60"	6	0.3	4.46	0.3	4
5	ARSENXNP	PUROLITE	3"x60"	8.15	0.4	4.74	0.2	3
6	METSORB	HYDROGLOBE	3"x39"	8	0.4	2.97	0.3	2
7	ISOLUX 302M	MEI	1"x10"	23	0.5	0.48	N/A	15 sec
8	AD-33	ADEDGE	3"x29"	6	0.3	2.23	0.3	2
9	AD-33	ADEDGE	3"x60"	6	0.3	4.46	0.3	4
10	AD-33	ADEDGE	3"x60"	6	0.3	5.57	0.3	5



Appendix A-4 Summary of Detailed Economic Calculations

INPUT DATA	E33-2min	E33-4min	E33-5min
Design Criteria	**Q=0.35 mgd**	**Q=0.35 mgd**	**Q=0.35 mgd**
Vessel Flow Rate (gpm)	353	353	353
Design Treatment Capacity. MGD	0.35	0.35	0.35
Configuration (series/parallel/unknown)	parallel	parallel	parallel
Number of Trains	1	2	2
Number of Vessels per Train	2	1	1
Bed Depth, ft	4.0	4.0	4.0
Vessel Diameter, ft	*4.0*	*6.0*	*7.0*
Total Facility Media Volume, cf	188.8	377.6	472.0
Media Bulk Density, PCF	*32*	*32*	*32*
Unit Media Cost, $/cf	*$200.00*	*$200.00*	*$200.00*
System Equipment Cost Summary			
Equipment Installation Cost, %	10%	10%	10%
Interior Piping Allowance,%	10%	10%	10%
I&C Allowance, %	3%	3%	3%
Electrical Allowance, %	2%	2%	2%
Yard Piping Allowance,%	10%	10%	10%
Building Facilities			
Building, sf	200	288	338
Building Unit Cost, $/sf	$200	$200	$200
Contractor & Engineering Cost Summary			
Engineering/Contractor Cost, %	30%	30%	30%
Permitting Cost, %	15%	15%	15%
Working Capital	$0	$0	$0
Start-up	$0	$0	$0
Contingency, %	25%	25%	25%
Annual O&M Costs			
Media Use Per Year, CF/Yr Based on Average Flow	708	396.5	330.4
Equipment Maintenance Costs, % of Capital Costs	5%	5%	5%
Annual Estimated Power Use, kWh/yr	38,084	38,084	38,084
Power Cost, $/kWh	0.10	0.10	0.10
Spent Media Production, Tons/yr	n/a	n/a	n/a
Labor, Operations, hrs/yr	127.0	73.0	66.0
Labor, Operations, hrs/yr	127.0	73.0	66.0
Unit Labor Cost, Operations, $/hr	$30	$30	$30
Labor, Management, hrs/yr	12	12	12
Labor, Management, $/hr	$80	$80	$80
Equipment Maintenance Costs, % of Capital Costs	5%	5%	5%

[1] E33 cost is typical average, per EPA Pilot Demonstrations (www.arsenictradeshow.org) and personal communications with AdEdge
[2] Bldg size calculated by allowing 3 additional feet on each side of vessel (see diagram below)
[3] Bldg cost based on average price in EPA Cost report #600r06083
[4] Power consumption is estimated in ARCE model, and is comprised of "System Pressure Loss" (29324.4 kWh/yr) and "Miscellaneous" power consumption (8760 kWh/yr)

Appendix A-4 Summary of Detailed Economic Calculations (cont)

OUTPUT DATA	E33-2min	E33-4min	E33-5min
Total GIM System Equipment Cost Summary	**Q=0.35 mgd**	**Q=0.35 mgd**	**Q=0.35 mgd**
Total Vessel Cost including Valves, $	$24,764	$49,527	$56,080
Subtotal System Costs, $ (System Direct Capital Cost)	$68,776	$137,552	$165,528
Building Facilities			
Building, sf	200	288	338
Building Unit Cost, $/sf	$200	$200	$200
Building Cost, $	$40,000	$57,600	$67,600
Contractor & Engineering Cost Summary			
Subtotal Estimated Facility Cost, $	$68,776	$137,552	$165,528
Engineering/Contractor Cost, $	$20,633	$41,266	$49,658
Permitting Cost, $	$10,316	$20,633	$24,829
Working Capital	$0	$0	$0
Start-up	$0	$0	$0
Contingency, $	$17,194	$34,388	$41,382
Total Indirect Cost, $	$48,143	$96,286	$115,870
Annual O&M Costs			
Total Annual Media Costs, $/yr Based on Average Flow	$141,600	$79,296	$66,080
Annual Power Cost, $/yr	$3,808	$3,808	$3,808
Spent Media Production, Tons/yr	n/a	n/a	n/a
Total Estimated Labor Costs, $/yr	$4,770.0	$3,150.0	$2,940.0
Equipment Maintenance Costs, $/yr	$3,126.2	$6,252.4	$7,524.0
Capital Cost Summary			
Media & Equipment	$116,920	$233,838	$281,398
Building	$40,000	$57,600	$67,600
Engineering/Contractor Cost, $	$20,633	$41,266	$49,658
Permitting Cost, $	$10,316	$20,633	$24,829
Working Capital	$0	$0	$0
Start-up	$0	$0	$0
Contingency, $	$17,194	$34,388	$41,382
Present Worth Analysis			
Net Interest Rate	4.0%	4.0%	4.0%
Period, Years	20	20	20
Total Annual O&M Costs, $/yr	$153,305	$92,507	$80,352
Present Worth of Annual O&M Costs, $	$2,083,460	$1,257,197	$1,092,016
Total Estimated Facility Cost	$205,063	$387,724	$464,867
Total Present Value of Facitlities, $	$2,288,523	$1,644,922	$1,556,883
Total Annual Amortized Cost (Capital + O&M)	$168,394	$121,036	$114,558
Total Unit Cost of Water Produced, $/1,000 gals	$1.32	$0.95	$0.90

Distribution:

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6	MS 0754	M. Aragon, 06316
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