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# Pilot Test of Arsenic Adsorptive Media Treatment Technologies at Socorro Springs, New Mexico

## Materials Characterization and Phase I Results

**Malcolm Siegel, Alicia Aragon, Hongting Zhao, Randy Everett, Malynda Aragon, Melody Nocon, Brian Dwyer, Justin Marbury, Carolyn Kirby, and Katharine North**

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## Abstract

The Arsenic Water Technology Partnership (AWTP) program is a multi-year program funded by a congressional appropriation through the Department of Energy to develop and test innovative technologies that have the potential to reduce the costs of arsenic removal from drinking water. As a member of the AWTP, Sandia National Laboratories carries out pilot tests of the most promising technologies selected by panels of independent experts. The Sandia pilot demonstration at the Socorro Springs site tested arsenic removal performance of five different adsorptive media under constant ambient flow conditions. The media studied included two granular ferric oxides (E33 and ARM 200), a titanium oxide (Metsorb), an ion exchange resin impregnated with iron oxide nanoparticles ($ArsenX^{np}$) and a zirconium oxide (Isolux). Well water at Socorro Springs has approximately 50 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). Pilot scale performance was defined as capacity (bed volumes until breakthrough at 10 ppb (10 μg/L) arsenic). The amount of arsenic sorbed by the media was studied using other methods to allow a more robust evaluation of their relative performance. These included two kinds of Rapid Small Scale Column Tests (RSSCT), batch sorption isotherm studies, and kinetic sorption studies. It was found that the E33 media outperformed all other media in all tests with the exception of one of the RSSCTs. This comparison of the results of the laboratory and pilot scale studies could be useful to communities that cannot afford to carry out comparative pilot tests of multiple media, especially if other information about backwash requirements and costs (capital and labor) are already available.

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Note: The appendices are available at the Sandia National Laboratories Arsenic Water Technology Partnership websites: http://www.sandia.gov/water/arsenic.htm and http://www.sandia.gov/water/pubs1.htm or from the lead author.

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# FOREWARD

The Arsenic Water Technology Partnership (AWTP) program is a multi-year program funded by a congressional appropriation through the Department of Energy to develop and test innovative technologies that have the potential to reduce the costs of arsenic removal from drinking water. The AWTP members include Sandia National Laboratories, the American Water Works Association (Awwa) Research Foundation and WERC (A Consortium for Environmental Education and Technology Development). The program is designed to move technologies from bench-scale tests to field demonstrations. The Awwa Research Foundation is managing bench-scale research programs, Sandia National Laboratories is conducting the pilot demonstration program, and WERC will evaluate the economic feasibility of the technologies investigated and conduct technology transfer activities.

The objective of the Sandia Arsenic Treatment Technology Demonstration (SATTD) project is the field demonstration testing of both commercial and innovative technologies. The scope for this work includes: (1) identification of sites for pilot demonstrations; (2) accelerated identification of candidate technologies through Vendor Forums, proof-of-principle laboratory and local pilot-scale studies, collaboration with the Awwa Research Foundation bench-scale research program and consultation with relevant advisory panels; and (3) pilot testing multiple technologies at several sites throughout the country (Siegel et al. 2005).

The primary deliverables of the SATTD project are engineering analyses of candidate technologies. The analyses will consider such questions as:

1. How effective is the technology at achieving and maintaining sub-MCL arsenic outflows?
2. How sensitive is performance to feed water solution chemistry?
3. What operational aspects are critical to performance?
4. What is the impact on other aspects of operation and maintenance (O&M) (e.g., sludge accumulation, fluoride levels, etc.)?

The Socorro Springs pilot test was conducted in several phases. Phase I involved tests of five adsorptive media under ambient groundwater pH conditions. Phase IIa involved short preliminary tests designed to evaluate the effects of pH change and flow interruption on the performance of the spent media. In Phase IIb, the performance of fresh media under ambient pH and lower pH was evaluated. This report describes the results of Phase I. Future reports will describe the results of Phase II.

A Pilot Test Specific Test Plan (PTSTP) (Siegel et al. 2006a) describes the test procedures that were planned for the study. The PTSTP is based on protocols developed by the NSF International Environmental Technology Verification (NSF-ETV) Program modified to reflect the experimental nature of the SATTD project and to take into account site-specific conditions. It was developed with the assistance of NSF International, Inc. Modifications to the original test plan are described in this report.

# EXECUTIVE SUMMARY

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 50 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 [10 μg/L] arsenic) of the adsorptive media in the same chlorinated water.

The commercially-available media that were evaluated in the test are listed below.

| Type | Manufacturer | Product |
|---|---|---|
| Granular Ferric Oxide | Adedge | E33 |
| Granular Ferric Oxide | Engelhard Corporation | ARM 200 |
| Granular Titanium Oxide | Hydroglobe | Metsorb |
| Nano Particle Zirconium Oxide | MEI | Isolux 302M |
| Iron Impregnated Resins | Purolite | $ArsenX^{np}$ |

The amount of arsenic sorbed by the media was studied using different methods to allow a more robust evaluation of their relative performance. For the flow experiments (pilot and rapid small-scale column tests [RSSCTs]), the number of bed volumes (BV) of water passing through the media columns until the regulatory limit (10 ppb [(10 μg/L]) was exceeded in the effluent was recorded. For both the batch tests and the flow experiments, the sorption capacity of the media (amount of arsenic adsorbed by the media) when the treated water was 10 ppb (10 μg/L) was also calculated or measured. For flow experiments, the capacities were calculated from mass balance; for batch tests, a sorption isotherm was fit to the data, and a capacity was calculated at 10 ppb (10 μg/L).

The absolute and relative sorption performances depended both on the media and the test methodology. In addition, the results are valid only for the particular water studied and only for the specific batches of media provided by the companies for this test. For the pilot tests, the values of BV and capacity at 10 ppb (10 μg/L) arsenic show a fairly consistent relationship among the adsorptive power of the media:

$$E33 > Isolux\ 302M \sim ArsenX^{np} > Metsorb > ARM\ 200.$$

The RSSCTs are scaled-down columns packed with smaller diameter adsorption media that receive higher hydraulic loading rates to significantly reduce the duration of experiments. Two kinds of RSSCTs were used: constant diffusivity (CD) and proportional diffusivity (PD). The relative performances of the media in the CD tests were consistent with the pilot tests results; however, the absolute capacities and the BV values did not agree well with the pilot. For the PD experiment, the order of relative capacities at 10 ppb (10 μg/L) differed from the BV order. The absolute BV values agreed with the pilot results to within a factor of 2; however, the order was

different. It should be noted that CD and PD data cannot be directly compared. They are two special cases, corresponding to upper and lower limits of performance. The best predictor will be different for different media; i.e., E33 is predicted best by PD, and ARM 200 is predicted best by CD.

Batch sorption studies were carried out to obtain isotherm parameters to estimate the capacity of the media at different influent concentrations. The batch studies provided upper limits to the arsenic adsorption capacity of the media; the calculated capacities at 10 ppb (10 μg/L) were between 2 times and 6 times those calculated from the pilot studies.

Arsenic sorption is controlled by a number of physical and chemical properties of the adsorptive media. In order to understand and predict the sorption of arsenic by the media used at the Socorro pilot site, some basic mineralogical, physical and surface chemical analyses (XRD, SEM/EDS, BET, attrition loss) were carried out. It was found that the surface area of the pristine material was not directly related to the performance; E33, the media with one of the lowest surface areas, had the best performance.

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$^{o}$C). The aging studies carried out over a three-month period showed that ARM 200 media partially recrystallized and was transformed to hematite. 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; surface areas may have changed. Additional analyses of the data including attrition loss and chemical changes to the media during the pilot tests are being carried out to better interpret the results.

Thus in summary, at target treatment effluent levels of 10 ppb (10 μg/L) arsenic, the E33 media outperforms all other media in all laboratory and field tests but the PD RSSCTs. The sorption capacity (mg As/g media) in the pilot tests for two of the media (E33 and Isolux 302M) could be predicted within about 70% by batch sorption tests. The PD RSSCTs were more accurate predictors of the pilot tests results for Metsorb and ArsenX$^{np}$ media (within 5%). The capacity of the ARM 200 measured in the pilot test could be predicted within 30% by the CD RSSCT but was grossly over predicted by the other tests. Laboratory tests (batch sorption and RSSCTs) are much less expensive to conduct than pilot tests and provide reasonable qualitative predictions of field scale performance. These results suggest that laboratory studies could be useful to communities that cannot afford to carry out comparative pilot tests of multiple media, especially if other information about backwash requirements and costs (capital and labor) are already available.

# ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| °F | degrees Fahrenheit |
| AA | activated alumina |
| AOP | Administrative Operating Procedure |
| ARCOC | Analytical Request Chain of Custody |
| Awwa | American Water Works Association |
| BET | Brunauer, Emmett and Teller |
| BTC | breakthrough curve |
| BV | bed volume |
| CA WET | California Waste Extraction Tests |
| CD | constant diffusivity |
| cm | centimeter |
| CVT | Capacity Verification Test |
| D | depth |
| DFPSDM | dispersed flow pore and surface diffusion model |
| DQO | data quality objectives |
| DWS | drinking water system |
| EBCT | empty bed contact time |
| EPA | U. S. Environmental Protection Agency |
| ETV | Environmental Technology Verification |
| g | gram |
| gpd | gallons per day |
| gpm | gallons per minute |
| H | height |
| HazMat | hazardous material |
| HDPE | high density polyethylene |
| HSDM | homogeneous surface diffusion model |
| ICP-MS | inductively coupled plasma mass spectrometry |
| L | liter |
| lb | pound |
| m | meter |
| MCL | maximum contaminant level |
| MDL | method detection limit |
| mg/L | milligram per liter |
| mL | milliliter |
| mm | millimeter |
| MSDS | Material Safety Data Sheets |
| N/A | not applicable |
| NA | not analyzed or available |
| ND | not detected |
| NELAP | National Environmental Laboratory Accreditation Program |
| NR | not reported |
| NSF | NSF International (formerly known as National Sanitation Foundation) |
| O&M | operation and maintenance |
| pCi/L | picoCuries per liter |

| | |
|---|---|
| PD | proportional diffusivity |
| ppb | parts per billion |
| ppm | parts per million |
| PTSTP | Pilot Test Specific Test Plan |
| QA/QC | quality assurance/quality control |
| QAPP | quality assurance project plan |
| RSSCT | rapid small-scale column test |
| SEM/EDS | Scanning Electron Microscope/Energy Dispersive Spectroscopy |
| SIVT | Systems Integrity Verification Test |
| SMO | (Sandia National Laboratory's) Sample Management Office |
| SMOCL | Sample Management Office Contract Lab(s) |
| SNL | Sandia National Laboratories |
| SOP | standard operating procedure |
| TCLP | toxicity characteristic leaching procedure |
| TOC | total organic carbon |
| W | width |
| WERC | A Consortium for Environmental Education and Technology Development |
| WQL | (Sandia National Laboratory's) Water Quality Laboratory |
| XRD | X-ray diffraction |
| ZPC | zero point of charge |
| μg/L | microgram per liter |

# 1.0 INTRODUCTION

## 1.1 Purpose

Sandia National Laboratories (SNL) is conducting pilot scale evaluations of the performance and cost of innovative drinking water treatment technologies aimed at meeting the new arsenic maximum contaminant level (MCL) of 10 µg/L (effective January 2006). The first pilot tests in the program are being conducted in New Mexico (Siegel et al. 2005). The New Mexico Environment Department identified over 90 public water systems that currently exceed the 10 µg/L MCL for arsenic. From this list, SNL considered ten communities for field scale pilot demonstrations. Socorro Springs in Socorro, New Mexico, was the first demonstration site to be selected. The first part of demonstration (Phase I) began in January 2005 and ended in July 2005. The information from the test will help the City of Socorro choose the best arsenic treatment technology for the Socorro Springs well. The pilot demonstration is a project of the Arsenic Water Technology Partnership program, a partnership between the American Water Works Association (Awwa) Research Foundation, SNL, and WERC (A Consortium for Environmental Education and Technology Development).

Pilot-scale testing provides a cost effective method to optimize a water treatment methodology prior to full-scale implementation in a community system. The final water treatment system can be modeled and tested using a pilot-scale demonstration that considers the long-term needs of the community. More specifically, a pilot-scale system is used to vary design process parameters (such as detention time, filtration rate, or mixing energy) and treatment materials (filter media, new chemicals, or chemical doses) to provide the information necessary for the full-scale design. This information or performance criteria include the following areas:

- Performance, as measured by arsenic removal
- Costs, including capital and Operation and Maintenance (O&M) costs
- O&M requirements, including personnel requirements, and level of operator training
- Waste residuals generation

Prior to and concurrent with the field test, a number of laboratory studies were carried out to characterize the physical and chemical properties of the media. The results of these studies, which are described in this report, aid in understanding and predicting the sorption of arsenic by the media.

## 1.2 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 shutoff valve. Below the shutoff valve, an eight-inch subsurface, carbon steel line delivers approximately 540 gpm water via gravity 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. 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$^{o}$F [32.2$^{o}$C]) and the chlorine pumps. Socorro personnel stated that the temperature inside the building remains at 50$^{o}$F (10$^{o}$C) or above year-round. During the summer in Phase II of the test, however, it was necessary to install an air conditioner to keep the temperature low enough to protect electronic gauges and meters in the pilot system.

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.

## 1.3 Water Quality

A "snapshot" of the Springs Site raw water quality is presented on Table 1-1. 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.

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 by fine-grained particles present in the groundwater or produced during oxidation of the groundwater.

**Table 1-1. Nominal Socorro Water Quality.**

| Parameter | Unchlorinated Feed Water | Chlorinated Feed Water |
|---|---|---|
| Conductivity (µS) | 356-360 | 356-360 |
| Temperature (degrees Celsius) | 30.1-30.5 | 30.1-30.5 |
| Free chlorine (mg/L as $Cl_2$) | ND | 0.5 – 0.8 |
| pH | 8.03-8.07 | 7.89-7.91 |
| Iron (ppb) | 43.3 | 38.2 |
| Total Arsenic (ppb) | 42.4 | 42.9 |
| *Speciated Arsenic* | | |
| Particulate (ppb) | ND | 1.9 |
| As(III) (ppb) | ND (0.53) | 2.1 |
| As(V) (ppb) | 42.4 | 40.9 |
| Titanium | ND (0.381) | ND (0.38) |
| Zirconium (ppb) | 0.22 | ND (0.22) |
| Alkalinity (ppm) | 123 | NA |
| Nitrate (ppm) | 0.48 | 0.4 |
| Calcium (ppm) | 17.5 | 17.4 |
| Magnesium (ppm) | 4.1 | 4.1 |
| Sodium (ppm) | 57.0 | 57.1 |
| Silica (ppm) | 25.0 | 24.9 |
| Aluminum (ppb) | 24.2 | 23.2 |
| Vanadium (ppb) | 11.4 | 11.3 |
| Gross Alpha/Beta (pCi/L) | NA | Alpha-6.50, Beta-3.52 |
| Chloride (ppm) | 11.5 | 12.1 |
| Fluoride (ppm) | 0.62 | 0.5 |
| Sulfate (ppm) | 28.7 | 28.4 |
| Total Organic Carbon (TOC) | NA | 0.5 |

ppm = parts per million; ppb = parts per billion
NA = not available; ND = not detected above method detection limit (MDL is given)

## 1.4 Participants in Test

### 1.4.1 *Manufacturers*

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 (Siegel et al. 2006b). An expert panel, chosen from broad spectrum of water treatment disciplines, evaluated the potential arsenic removal technologies being presented. Each technology was scored to a set of pre-selected criteria that are described at the Forum website: **http://www.sandia.gov/water/arsenic.htm**. The commercially available media that were evaluated in the test are listed below.

| Type | Manufacturer | Product |
|---|---|---|
| Granular Ferric Oxide | Adedge | E33 (AD33) |
| Granular Ferric Oxide | Engelhard Corporation | ARM 200 |
| Granular Titanium Oxide | Hydroglobe | Metsorb |
| Nano Particle Zirconium Oxide | MEI | Isolux 302M |
| Iron Impregnated Resins | Purolite | ArsenX$^{np}$ |

As the technology providers, MEI, Purolite, Engelhard Corporation, Hydroglobe, and Adedge were responsible for providing quality controlled media and information regarding suggested pilot system design and operational parameters. In addition, the technology providers were asked to provide technical assistance to SNL during operation and monitoring of their respective arsenic adsorptive filter media. Note that the media from Adedge is properly referred to as E33; earlier publications and graphs in this study referred to it as AD33; both names are used in this report.

### 1.4.2 *Field Testing Organization*

As the testing organization, SNL was responsible for conducting verification testing of the arsenic adsorption media filters. As part of the verification testing, SNL was responsible for:

- Defining the roles and responsibilities of appropriate verification testing participants;
- Providing needed logistical support, establishing a communications network, and scheduling and coordinating the activities of all verification testing participants;
- Verifying that the location selected as the test site had feed water quality consistent with the objectives of the verification testing;
- Managing, evaluating, interpreting and reporting on data generated by the verification testing;
- Preparing a pilot test specific test plan (PTSTP) for the verification testing;
- Overseeing testing activities, obtaining test samples and delivering those samples to the laboratory for analysis, tabulating and analyzing the testing data and preparing the final report;
- Properly disposing of spent media in accordance with classification based on the toxicity characteristic leaching procedure (TCLP) and California Waste Extraction Tests (CA WET); and
- Removing pilot equipment from the site and returning it to SNL at test completion.

### 1.4.3 *NSF International*

NSF International (NSF) is an independent, not-for-profit organization founded in 1944 for the purpose of developing standards and third-party conformity assessment services to government, manufacturers and consumers of products and systems related to public health, safety, and environmental quality.

NSF entered into an agreement on October 1, 2000, with the United States Environmental Protection Agency (EPA) to create a Drinking Water Systems (DWS) Center dedicated to technology verifications. NSF manages an Environmental Technology Verification (ETV) Program within the DWS Center for the purpose of providing independent performance evaluations of drinking water technologies. Evaluations are conducted using protocols developed with stakeholder involvement. Verified results of product evaluations presented in

reports from ETV tests should accelerate a technology's entrance into the commercial marketplace.

NSF International is providing support to SNL under a technical assistance contract. The following are specific NSF roles and responsibilities:

- Review of the PTSTP to insure compliance with the general requirements of the EPA/NSF ETV Protocol for Equipment Verification Testing for Arsenic Removal and specific requirements of EPA/NSF Equipment Verification Testing Plan for Adsorptive Media Processes for the Removal of Arsenic,
- Test site audit to confirm testing follows the PTSTP, and
- Final report review including technical, format and quality assurance/quality control (QA/QC).

### 1.4.4 *Sample Management Office Contract Laboratories*

Sandia National Laboratories teamed with the Sample Management Office (SMO) and used Sample Management Office Contract Laboratories (SMOCLs). SMO supports SNL with Analytical Request Chain of Custody (ARCOC), sample handling and shipping, technical and contractual coordination, data validation and management, etc. SMOCLs are National Environmental Laboratory Accreditation Program (NELAP) accredited and hold applicable certifications.

# 2.0 PILOT TEST

## 2.1 Objectives

The objectives of the Socorro Pilot Test include evaluations of:

1. the comparative treatment performance of five adsorptive media using chlorinated water from the Socorro Springs;
2. comparison of media performance to predictions based on vendor data and results of laboratory studies carried out at SNL (rapid small-scale column tests [RSSCT] and supporting experiments);
3. limited assessment of maintenance and operational requirements for all media;
4. the effect of contact time on the performance of one of the media;
5. the effects of pH adjustment on the performance of selected media; and
6. the corrosivity and scale-forming potential of treated water.

The design of the pilot system and intended standard operating procedures are described in detail in the Pilot Test Specific Test Plan (PTSTP) for the Socorro Springs Pilot (Siegel et al. 2006a). The pilot test is being conducted in two phases. In Phase I, Objectives 1 through 4 are evaluated. Phase II will include evaluation of all the above objectives (1-6). This report describes the results of Phase I and initial results of Phase II through August 1, 2005 (Phase IIa). An addendum to the PTSTP will be written to describe design and operation procedures during Phase II.

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, efforts will be directed at collection of some operational parameters. 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. Section 2.2.5 provides a summary of the basis for design of the pilot columns for all five media.

## 2.2 Pilot Test Design

### 2.2.1 *Arsenic Removal Using Adsorptive Media*

The treatment process for all five arsenic adsorption media filters involves 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 and chemical attachment of the adsorbate (arsenic) to the surface of the adsorbent media grains. The removal capacity and effectiveness of the arsenic removal media are dependent on a number of factors including the effective surface area, which is a function of the accessibility of the porosity of the media grains; the concentrations of ions competing for sorption sites; the concentration of arsenic in the feed water; the pH of the feed water; steric factors affecting the accessibility of the pore sites by arsenic ions; and the time available for arsenic ions to migrate to pore sites. This last property is related to the flow rate of the feed water that conveys the arsenic into the bed of adsorbent media. Adsorbent media contain large quantities of very small pores throughout the media grains.

As water passes down through a filter vessel containing fixed bed media, the arsenic concentration declines within the media until it is no longer detectable. As the upper portion of the media becomes saturated, the treatment region (mass transfer zone) progresses downward until all adsorptive capacity is used and complete arsenic breakthrough occurs. If the adsorbent media perform as expected, then no arsenic will be detected in the treated water for at least four to six months. (The lower limit of detection for arsenic using the Inductively Coupled-Mass Spectrometer at SNL's Water Quality Laboratory (WQL) is less than 2 µg/L.) Eventually, as the adsorbent capacity of an adsorbent medium is exhausted, 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.

### 2.2.2 *Test Media*

The Socorro pilot study tested five media:

- Four metal oxides and
- One ion exchange/metal oxide combination.

Table 2-1 presents the material properties of the arsenic adsorption media being tested. Additional information about the surface properties of the media is found in Section 3.1. Note that the media from Adedge is properly referred to as E33; earlier publications and graphs in this study referred to it as AD33; both names are used in this report, depending on when the results were first obtained.

**Table 2-1. Adsorptive Media Specifications.**

| Media | Isolux 302M | Metsorb | ARM 200 | ArsenX$^{np}$ | E33 |
|---|---|---|---|---|---|
| Chemical Constituents | Amorphous inorganic zirconium oxide, 60-95%<br><br>Balance water | Nano-crystalline titanium dioxide | Iron oxide/ hydroxide | Nanoparticle selective resin with iron oxide as the functional group | Iron oxide/ hydroxide |
| Physical properties | | | | | |
| Bulk density ($lb/ft^3$) | 56 | 50 | 30 - 45 | 49 - 52 | 30 |
| BET[a] Area ($m^2/g$) | 300 vendor; 499 SNL | 211 | 262 | 120 | 140 vendor; 147 SNL |
| Moisture | 5-40% by volume | N/A | N/A | N/A | N/A |
| Sieve sizes, US std. | N/A | 16 x 60 | 12 x 40 | 16 x 50 | 10 x 35 |
| Particle size | White Powder form,<br><br>< 5 μm | White granular beads,<br><br>1.18 x 0.25 mm | 1.40 x 0.425 mm | 1.18 x 0.3 mm | Amber colored granular,<br><br>0.5 x 2.0 mm |
| Approvals | | | | | |
| As of July 2005 | NSF Section 61 certified | NSF Section 61 certified | NSF Section 61 certified | NSF Section 61 certified | NSF Section 61 certified |

[a] Brunauer, Emmett and Teller

Predictions of Performance by Vendors

The data quality objectives (DQO) for this test plan are based in part on comparison of predicted and observed performance of the media. Vendors were asked to provide estimates of the media performance in the Socorro Springs waters based on their previous studies. However, these predictions were not defined on a scale that allowed comparison to each other (i.e., 10 ppb [10 µg/L] breakthrough or $C/C_o$ or were not obtained). The information that was obtained is summarized in Table 2-2.

**Table 2-2. Predictions of Media Performance.**

| Media/ Company | Anticipated Treatment Capacity | Anticipated Cost/ 1000 gallons |
|---|---|---|
| Isolux 302M media/ MEI | > 85,000 bed volumes | o Returnable cartridge model ~ $0.70<br>o Stationary RFC Model ~ $0.50 |
| ArsenX$^{np}$/ Purolite | > 60,000 bed volumes<br>(50% breakthrough) | ~ $0.25 to $0.35 |

Engelhard Corporation, Adedge, and Hydroglobe did not supply specific performance and cost information for Phase I of the pilot. It should be noted that after the test was completed, it was determined by the vendors that the ArsenX$^{np}$ and the ARM 200 batches used in the tests of their media were either defective due to problems in manufacturing procedures or had been supplanted by newer media.

Media Handling and Pretreatment Requirements

The vendors provided instructions for storage and handling requirements for their respective media. These are described in Tables 3-5 through 3-9 of the PTSTP (Siegel et al. 2006a) and were carried out for this pilot. 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.

### 2.2.3 *Equipment Characteristics*

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, and
    c. Pressure control and relief;
2. Carbon dioxide injection system (pH adjustment method), 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, which is the location of the pilot unit. 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 opaque 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 loosing 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 contains ten columns, each designed as independent 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, another three-way valve (service or backwash mode), sample tap, totalizing flow meter, check valve, and all associated piping. (Refer to Drawings SOC-01 and SOC-02 in Appendix A of the PTSTP [Siegel et al. 2006a].)

### 2.2.4 *Equipment Photograph and Flow Diagram*

A photograph of the Socorro Springs Pilot Skid unit and a flow diagram of the columns, valves and connections are shown in Figure 2-1 and 2-2, respectively.

**Figure 2-1. Socorro Springs Pilot Skid Unit.**

SOCORRO SPRINGS FLOW DIAGRAM

**LEGEND:**

- Manual Ball Valve
- Pressure Gauge
- Rotameter
- Totalizing Water Meter
- Sample Point
- Check Valve
- Pressure Reducing Valve
- Pressure Relief Valve
- 3-Way Valve

| 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 |

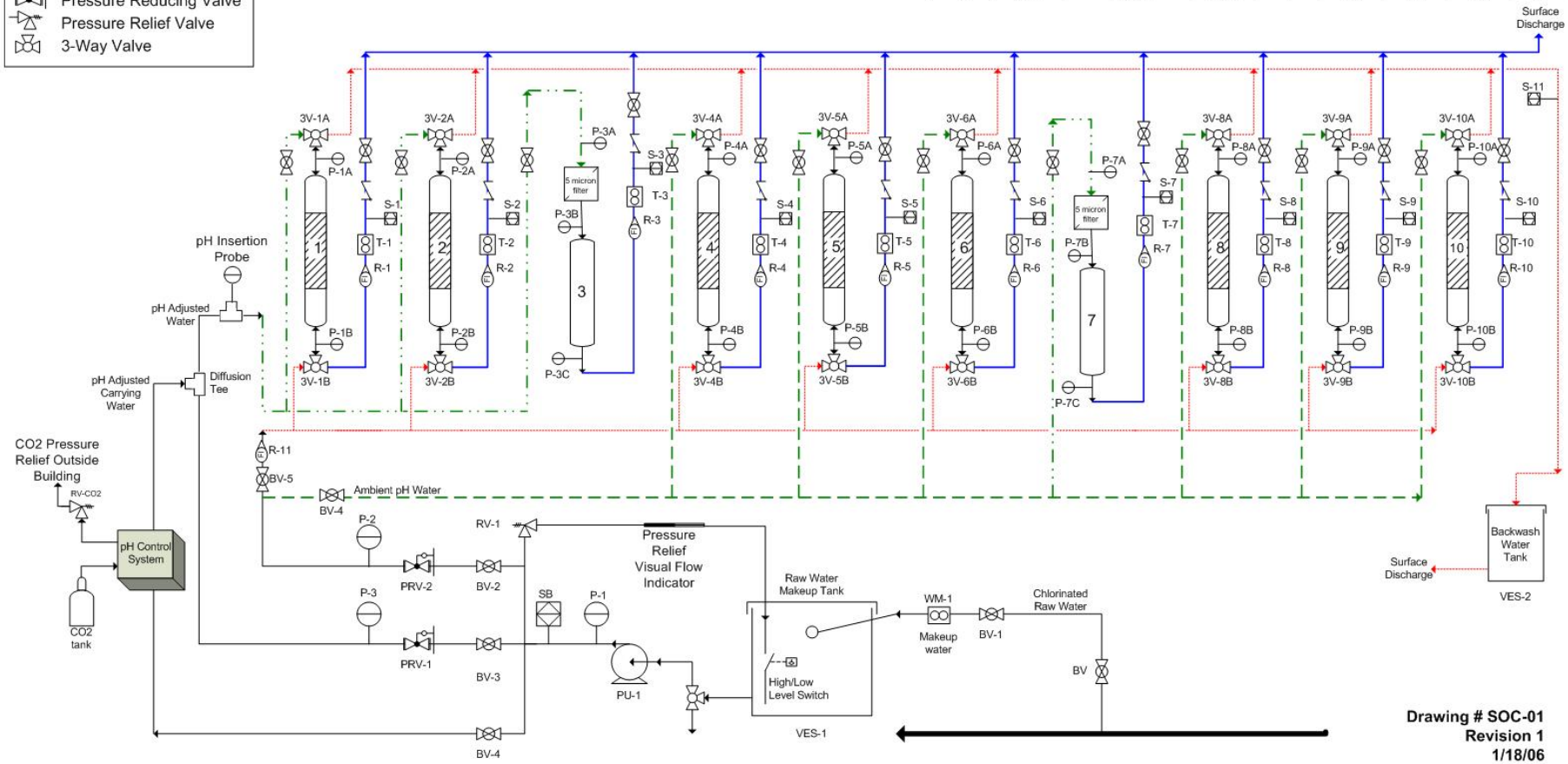



**Figure 2-2. Socorro Springs Pilot Flow Diagram**

## 2.2.5 *Design Criteria*

The ten arsenic adsorptive columns were designed based on information on particle size, desired hydraulic loading rate, and optimum empty bed contact times (EBCTs) supplied by the vendors (Siegel et al. 2006a). Columns 4-10 were used in Phase I and IIa of the test; all ten columns were used in Phase IIb. Table 2-3 presents a summary of the final design basis for the seven columns used in Phases I and IIa; this differs slightly, but not significantly from the original design basis. Initial design data for each media are found in Appendix B of the PTSTP (Siegel et al. 2006a). Design information for the Isolux 302M column is found in Appendix A of this report.

**Table 2-3. Summary of Final Design Basis.**

| **Vendor Media** | **MetSorb** | **E33** | | | **Isolux 302M** | **ARM 200** | **ArsenX$^{np}$** |
|---|---|---|---|---|---|---|---|
| Number of Pilot Scale Columns | **1** | **3** | | | **1** | **1** | **1** |
| Hydraulic Loading Rate (HLR), gpm/ft$^2$ | **8** | **6** | | | **1.2** | **6** | **8.2** |
| Column Number (Drawing SOC-01 [a]) | 6 | 8 | 9 | 10 | 7 | 4 | 5 |
| EBCT, minutes | 2 | 2 | 4 | 5 | 0.29 | 4 | 3 |
| Pre-filtration requirements | No | No | No | No | Yes (0.5μm) | No | No |
| Influent pH | 7.7 | 7.7 | 7.7 | 7.7 | 7.7 | 7.7 | 7.7 |
| Column Height, (Hc), inches | 39 | 39 | 60 | 60 | 10 | 60 | 60 |
| Column Diameter (D), inches | 3 | 3 | 3 | 3 | 2.47 OD [b] 1.5 ID | 3 | 3 |
| Media Depth (Hm), inches | 25.7 | 19.3 | 38.5 | 48.1 | 0.57 | 38.5 | 39.2 |
| Media Volume (V), liters | 2.97 | 2.23 | 4.50 | 5.57 | 0.45 | 4.46 | 4.74 |
| Water Flow rate (Q), gpm | 0.4 | 0.3 | 0.3 | 0.3 | 0.5 | 0.3 | 0.4 |
| Face Velocity (v), ft/min | 1.07 | 0.80 | | | 0.17 | 0.80 | 1.09 |
| Backwash Flow rate ($Q_{BW}$), gpm | 0.3 | 0.3 | | | N/A | 0.3 | 0.2 |

a Siegel et al. 2006a

b Isolux column is a patented radial flow column with adsorptive media contained in an annulus; see Appendix A..

## 2.3 Field Test Procedure

### 2.3.1 *Principles of Operation*

The unistrut skid frame is modular in construction and contains a single bank of ten columns for parallel operation in the down-flow mode. The filter bank itself does not require electricity to operate. Each of the ten-filter columns can be in the service, off-line, or backwash mode regardless of the other columns operational mode. Each filter column can operate either intermittently or continuously. All modes of operation are manually controlled using ball valves.

In the operational mode the flow rate of each column is controlled by that column's rotameter. When backwashing, only one column is backwashed at a time using a common manifold for all columns. Backwashing is manually initiated based on differential pressure across a column. A portion of the service water is diverted via a tee and ball valve to the backwash rotameter to control the backwash flow rate for the specific column designated for backwash. Backwash is in an up-flow mode. Prior to backwashing of a column, a minimum of two times the volume of the backwash manifold is purged.

To facilitate a volumetric balance of the Springs Site pilot system, a flow meter measures total flow (volume in gallons) from the Springs main line pipe to the pilot pumping system; each column has a rotameter and totalizing flow/secondary flow rate measurement, the treated water manifold has a flow meter, and the backwash system has a rotameter and shut-off valve.

Flow rates for each column are controlled with rotameters. The difference in feed water and treated water pressure readings (each column has a treated water gauge) provides loss of head across each filter.

Grab samples for on-site and laboratory analyses are collected from the feed water and treated water sample taps, located upstream and immediately downstream of the adsorption media filter columns. Samples from these taps are collected following the opening of their respective ball valves and a flush period of five seconds.

The arsenic adsorption media filters operated continuously during the integrity verification test and during the capacity test with the exception of the potential for an occasional backwash (as required by unacceptable head loss across a filter bed). This was compatible with the Springs Site constant operation. The MEI Isolux 302M and Purolite ArsenX$^{np}$ media are potentially regenerable; however, regeneration is not a part of this pilot project.

At the conclusion of the Adsorption Capacity Verification Testing, the media were removed from each column and returned to SNL for post-test characterization. The results of these tests will be described in a later report. TCLP and CA WET analyses were performed for each media prior to final disposal.

### 2.3.2 *Integrity Verification and Capacity Verification Tests*

The pilot test was divided into two stages: System Integrity Verification Testing and Adsorptive Capacity Verification Testing. The test began on January 26, 2005. The integrity and adsorptive capacity verification tests were initiated simultaneously. The integrity verification test ran for a 2-week (13 full days plus 8 hours) period. The adsorptive capacity verification test ran until July 26, 2005. At that time, approximately 10 ppb (10 µg/L) of arsenic was detected in the treated water or the full capacity of the column could be reasonably estimated for several of the columns.

During the System Integrity Verification Testing Phase (Task 2 of the PTSTP), water samples were taken daily. In this test, SNL evaluated the reliability of equipment operation under the environmental and hydraulic conditions at the Socorro Springs pilot site and determined whether performance objectives could be achieved for arsenic removal at the design operating parameters for the arsenic adsorption media system. The adsorption media filters were operated for integrity testing purposes within the operational range presented in the equipment design. The objectives of the integrity test were:

- Study the changes in physical properties of the media (compaction, release of fines) during the initial stage of the test;
- Study transient changes in the chemistry of the effluent during initial stages of the test;
- Establish equipment operational reliability under field conditions;
- Document feed water quality; and
- Collect operational and water quality data under field conditions that can be related to the operating time, throughput and water quality objectives.

The objectives of the Adsorptive Capacity Verification Testing were to produce quality operational and water quality data up through and beyond the defined breakthrough arsenic level (10 µg/L) for each sorptive media. During this test, water samples were taken twice a week. The test was designed to examine:

- The comparative treatment performance of five adsorptive media using chlorinated water at the ambient pH from the Socorro Springs by measuring the total number of bed volumes of raw water passed through the column until arsenic breakthrough (10 µg/L) or until an estimate of the breakthrough can be reasonably made;
- Comparison of media performance to predictions based on vendor data and results of laboratory studies carried out at SNL (RSSCT and supporting experiments);
- The effect of contact time on the performance (bed volumes [BV] until breakthrough) of the E33 granular ferric oxide media (Adedge);
- Required backwash water quantity and quality for each media over an extended time period;
- Required backwash and purge duration and frequency for each media over an extended time period; and
- Limited assessment of maintenance and operational requirements for all media over an extended time period.

As discussed below, the studies of backwash duration, frequency and water quality were not carried out because the pressure drops across the columns suggested that the backwash was not needed.

### 2.3.3 *Field Operation Procedures*

During each day of verification testing, arsenic adsorption media filter operating conditions were documented, including the rate of head-loss increase. The volumetric flow rate through an adsorptive media vessel was a critical parameter and was monitored and documented. Adsorptive media performance is affected by the EBCT, which varies directly with the volumetric flow rate through the vessel. Field operation and maintenance procedures are described in Appendix D to PTSTP (Siegel et al. 2006a).

The following information was recorded on-site on forms shown in Appendix D of the PTSTP:

- Date
- Column number
- Experimental run number
- Water type (feed, treated, waste type)
- Hours of operation
- Feed (service) and treated water flow rate
- Feed and treated water production
- Feed and treated water pressure
- Feed water temperature
- Feed and treated water turbidity
- Feed and treated water pH
- Feed and treated water free chlorine

The PTSTP Appendix D includes procedures for analysis of backwash requirements as follows:

- Occurrence of a backwash
- Backwash water flow rate (backwash manually initiated by field engineer)
- Backwash duration
- Backwash total volume

As discussed below, however, backwash of the columns during routine operation was not carried out.

Sample collection and management were in accordance with the SNL SMO Procedure for Sample Management and custody, AOP 95-16. SMO procedures incorporate methods specified for sample preservation and holding times. These requirements are presented in Table 2-4 for each water quality parameter.

**Table 2-4. Water Quality Sampling Protocol.**

| Parameter | Sample Bottle | Sample Volume | Sample Preservation | Sample Hold Time |
|---|---|---|---|---|
| On-site analyses [a] | 1 L HDPE | 1 L | None | N/A |
| Nitrate [b] | 250 mL HDPE | 250 mL | None, cool to 2-6°C | 48 hours |
| Metals [c] | 500 mL HDPE | 500 mL | Optima Nitric Acid, pH<2 | 6 months |
| Alkalinity, chloride, fluoride, sulfate [b] | 1 L HDPE | 1 L | None, cool to 2-6°C | 28 days; Alkalinity 14 days |
| Total Suspended Solids (TSS) [d] | 1 L HDPE | 1 L | None, cool to 2-6°C | 7 days |
| Arsenic Speciation [e] | 1 at 1L HDPE, 3 at 250 mL HDPE | 1 at 1L and 3 at 250 mL | None in the 1 L, Optima Nitric Acid in the 250 mL, pH<2 | 6 months |
| Total Organic Carbon (TOC) [d] | 250 mL amber glass | 250 mL | Ultrapure Sulfuric acid, pH<2, cool to 2-6°C | 28 days |
| Gross Alpha/Beta [d] | 1 L HDPE | 1 L | Optima Nitric Acid, pH<2 | 6 months |

a On-site analyses included conductivity, temperature, pH, free chlorine, apparent color, turbidity, and dissolved oxygen. Separation of As(III) from As(V) for speciation was done on site by aluminosilicate adsorbent cartridge.
b These analyses were carried out by the SMOCL and/or the WQL.
c Metals include arsenic, calcium, magnesium, sodium, aluminum, titanium, vanadium, zirconium, and silica.
d Analyses were carried out by the SMOCL.
e Separation of As(III) from As(V) for speciation was done on site by aluminosilicate adsorbent cartridge. See Appendix E of the PTSTP (Siegel 2006a) for details. The 1-L HDPE bottle was used to take the initial untreated sample; from this initial sample, the three 250-mL samples were made and sent for analysis.

Operational Data Collection During System Integrity Verification Testing

- Treated water flow rate was monitored at least once per day and adjusted, as needed, with the rotameter and diaphragm valve located on the treated water pipe. Flow rate was recorded and was set in accordance with the recommended rates shown for each media in Tables 3-11 through 3-15 of the PTSTP (Siegel et al. 2006a) and in Appendix B of this report.
- Feed water and treated water production were monitored at least once per day at the totalizer meters located on the feed water and treated water pipes.
- Feed water pressure was monitored at the pressure gauge located on the feed water pipe on the top of each media column.
- Treated water pressure was monitored at the pressure gauge located on the treated water pipe at the bottom of each column. This was performed at the same time as the feed water pressure measurement. The difference between these valves represents head loss through the media.

Operational Data Collection During Capacity Verification Testing

- Treated water flow rate was monitored once per day at the rotameter located on the treated water pipe.

- Feed and treated water production (flow rates) were monitored once per day at the totalizer meters located on the feed and treated water pipes.
- Feed water pressure was monitored once per day at the pressure gauge located on the feed water pipe to each column.
- Treated water pressure was monitored once per day at the pressure gauge located on the treated water pipe on each column.

Arsenic Sampling and Hold Samples

Samples for analysis of total arsenic were taken daily during the SIVT and twice a week (biweekly) during the CVT (Table 2-5). According to the original PTSTP, hold samples for laboratory arsenic were to be collected on a weekly basis during the CVT (staggered from standard samples) and held (approximately 2 weeks) pending the results of the first weekly arsenic sample. This was procedure was not followed due to limitations in laboratory capabilities at the start of the test. Instead, samples were taken twice each week and all samples were analyzed until breakthrough. The total arsenic sampling frequency and minimum frequency for arsenic speciation is presented in Table 2-6.

Water Quality Data Collection

In addition to arsenic, other water quality constituents were analyzed in the feed water, treated water and wastewater (see Table 2-5). The original intended sampling frequency is described in Tables 5-6, 5-7, and 5-8 of the PTSTP. This frequency was designed to provide sufficient water quality data to effectively characterize the breakthrough profile of arsenic and to develop a representative wastewater quality profile. However, during the actual test, the sampling frequency changed due to operational considerations, or it was observed that certain water quality parameters stabilized. Temperature, pH, turbidity, conductivity, and free chlorine were analyzed as originally planned on-site. Measurements of apparent color and dissolved oxygen were made initially but discontinued early in the test. Because initial measurements of gross alpha and beta activity showed negligible activities (Table 1-1), measurements of these parameters were made only a few times during the test.

**Table 2-5. Water Quality Sampling Schedule.**

| Parameter | Sampling Frequency (SIVT) [e] | Sampling Frequency (CVT) [f] | Test Streams | Method Used [d] | Comments |
|---|---|---|---|---|---|
| *On-Site Analyses* | | | | | |
| Conductivity | Daily | Biweekly | Feed/treated | HACH 8160B (Direct Measurement Mtd) | Equivalent to EPA 120.1, Std Mtd 2510B |
| Temperature | Daily | Biweekly | Feed/treated | Std Mtd 2550 B | Utilized digital thermometer on HACH conductivity meter |
| pH | Daily | Biweekly | Feed/treated | Std Mtd 4500-$H^+$ | |
| Free Chlorine | Daily | Biweekly | Treated | HACH 8021 (DPD) | Equivalent to Std Mtd 4500-Cl G |
| Turbidity | Daily | Biweekly | Feed/treated | Std Mtd 2130 B | |
| *Laboratory Analyses* | | | | | |
| Total Arsenic [a] | Weekly | Biweekly | Feed/treated | EPA 200.8 | |
| Speciated Arsenic [b] | Minimum 3X during test | Minimum 3X during test | Feed/treated | EPA 200.8 | |
| Iron | Daily | Weekly or Monthly | Feed/treated | EPA 200.8 | |
| Titanium [c] | Daily | Weekly or Monthly | Treated | EPA 200.8 | |
| Zirconium [c] | Daily | Weekly or Monthly | Treated | EPA 200.8 – SMOCL; AA Spec.– WQL | |
| Alkalinity | Daily | Weekly or Monthly | Feed/treated | Std Mtd 2320 B | |
| Total Suspended Solids | Daily | Weekly or Monthly | Treated | Std Mtd 2540 B | |
| Metals Na, Ca, Mg, Al, Mn, V | Weekly | Weekly or Monthly | Feed/treated | EPA 200.7 – SMOCL AA Spec. EPA 200.8 – WQL | V, Al, Mn by EPA 200.8; Other metals by AA Spec. at WQL |
| Silica | Weekly | Weekly or Monthly | Feed/treated | EPA 200.7 – SMOCL HACH 8185 – WQL | HACH method is the Silicomolybdate Method |
| Anions ($NO_3^-$, $SO_4^{2-}$, $Cl^-$, $F^-$) | Weekly | Weekly or Monthly | Feed/treated | EPA 300.0 | $NO_3^-$ by SMOCL only |
| Total Organic Carbon (TOC) | Weekly | Weekly or Monthly | Feed/treated | SW-46 9060 | SMOCL Only |

a Total Arsenic was measured by ICP-MS inductively coupled plasma mass spectrometry) in the WQL in lieu of on-site qualitative analysis. The SMOCL also analyzed for total arsenic.
b Separation of As(III) from As(V) for speciation was done by aluminosilicate adsorbent cartridge. See Appendix E of the PTSTP (Siegel et al., 2006a) for details.
c Ti analyses only for Hydroglobe Columns; Zr analyses only for MEI cartridges.
d Reference for the Standards Methods is APHA, 1998; reference for EPA Methods is US EPA, 2005.
e System Integrity Verification Test
f Capacity Verification Test

**Table 2-6. Arsenic Sampling Plan Laboratory Analyses – SMOCL and WQL. [a]**

| Test Period | Sample Sources | Sample Frequency | Sampling Period | No. of Days Samples Speciated |
|---|---|---|---|---|
| Integrity Verification | Feed, treated | Daily | 14 days | 3 |
| Adsorption Capacity Verification | Feed, treated | 2 times per week | Until total arsenic > 10 μg/L | At least 3 |

a Either WQL or SMOCL or both laboratories performed analyses for arsenic. Initially, SMOCL performed all analyses until WQL had completed all quality control checks and comparisons. WQL then analyzed all arsenic samples, and SMOCL performed a "split sample analysis" at least once per month for a quality check.

## 2.3.4 *Quality Assurance/Quality Control*

Quality Assurance Responsibilities

A number of individuals were responsible for monitoring equipment operating parameters and for sampling and analysis QA/QC throughout the verification testing. Primary responsibility for ensuring that both equipment operation and sampling and analysis activities complied with the QA/QC requirements of the PTSTP (Siegel et al. 2006a) rested with SNL. Changes to the original procedures described in the PTSTP were authorized by SNL staff.

Weekly QA/QC Verifications

- In-line rotameter (clean any foulant buildup as needed)
- In-line totalizer meters (clean any foulant buildup as needed and verify flow volume)
- Tubing (verify good condition of all tubing and connections and replace as necessary)

Beginning and End of Test Checks

All pressure gauges were checked for accuracy at the beginning of the test period using a calibration gauge.

Analytical Methods

The analytical methods utilized in this study for both on-site and laboratory analyses of water quality parameters are listed in the Table 2-5 above. Deviations from the original plan described in the PTSTP are described above.

Data Reduction, Validation, and Reporting

To maintain good data quality, specific procedures were followed during data reduction, validation, and reporting. Data Reduction refers to the process of converting the raw results from the equipment into concentration or other data in a form to be used in the comparison. The purpose of this step is to provide quality data that will be presented in a form that is useful for all stakeholders. These data were obtained from logbooks, instrument outputs, and computer outputs.

There were two types of data validation that needed to be addressed, field data and laboratory data. For the field data (including data collected from the WQL):

- The operator verified the correctness of data acquisition and reduction;
- SNL reviewed calculations and inspected laboratory logbooks and data sheets to verify accuracy of data recording and sampling; and
- Calibration and QC data were examined by the individual operators and the lead engineer.

Data Management and Analysis

The Sandia National Laboratories computer system was used as the repository of all operational and analytical data. The data consisted of results of analyses and measurements that were detailed in the Tasks section of the PTSTP. The data were entered into computer spreadsheets and submitted in electronic and hard copies.

## 2.4 History of Test (Phase I and IIa)

Phase I of the Socorro Springs Pilot test began on January 26, 2005 with the concurrent start of the Integrity Verification Test and the Capacity Verification Test. Phase I was completed on July 26, 2005; Phase IIa began on July 27, 2005. In this test, the pH of several columns was lowered to 6.8 by $CO_2$ gas injection into the influent water (pH adjustment test). On August 6, 2005, flow was stopped and then restarted on August 19 in several columns (flow interruption test). The additional capacity of the columns due to this flow interruption and the continued capacity extension associated with the pH drop was studied until November 9, 2005. For several of the columns and after completion of a test, pore water analyses were extracted or solid samples of the media were taken to study the profile of the mass transfer zone. The results of Phase IIa tests and the post-test characterization will be described in a separate report. Table 2-7 lists highlights of the test history; Appendix B contains a more detailed time line and can be found on project websites: http://www.sandia.gov/water/arsenic.htm and http://www.sandia.gov/water/pubs1.htm or from the lead author.

**Table 2-7. Timeline for Socorro Springs Pilot Test - Phase I and IIa.**

| Date | Event or Action |
|---|---|
| 10/15/04-11/30/04 | Gathered pH, turbidity and conductivity samples weekly |
| 11/30/04 | Installed columns |
| 12/7/04 | Loaded media into columns |
| 1/26/05 | Phase I (no pH adjustment) Two-Week Integrity Verification started<br>Samples taken daily on Columns 4-10, chlorinated & raw water<br>Capacity Verification Test started concurrently |
| 2/1/05 | NSF Visit to site: Inspection of Pilot equipment, training, and question and answer session |
| 2/9/05 | MEI Isolux cartridge has a ΔP of 38 psi – cartridge is depleted. |
| 7/18/05-7/22/05 | TOMCO pH Control ($CO_2$) System Installed |
| 7/26/2005 | Phase I completed |
| 7/27/05 | pH adjustment test (Phase IIa) began in Columns 4, 5, 6, and 9.<br>Ambient pH continued in Columns 8 and 10. |
| 7/28/05 | Column 6 (Hydroglobe Metsorb) has high Δ P, was isolated and taken offline. |
| 8/6/05 | Pump not working, pH adjustment test interrupted. |
| 8/19/05 | Flow interruption test began in Columns 4, 5, 8; daily arsenic samples taken |
| 8/21/2005 | Column 9 taken off line. |
| 8/30/2005 | Columns 6 and 9 a removed for mass transfer zone study |
| 10/5/2005 | Column 8 saturation reached; pH was lowered |
| 8/30/05-11/9/05 | Phase IIa (extended capacity test) continued in Columns 4, 5, 8 (adjusted pH) and Column 10 (ambient pH); daily arsenic samples taken. |

## 2.5 Pilot Test Results – Operations

### 2.5.1 *Media Preparation and Initial Backwashing*

During Phase I operations, five media were tested: AdEdge (E33), Engelhard (ARM 200), Hydroglobe (Metsorb), MEI (Isolux), and Purolite (ArsenX$^{np}$). Each media had a different bulk density, and each of the columns had specific design parameters as described in Table 2-3. All media except for the MEI Isolux were delivered dry or wet (ArsenX$^{np}$ only) and ready to load into SNL adsorption columns. The MEI Isolux product is very fine in texture and was provided as a cartridge, which was inserted into a housing for operation at the pilot.

The volume, weight, and height of each of the media loaded into adsorption columns (excludes MEI Isolux) were recorded at several points in time: initial, after transport to the Socorro Springs site, after backwashing (BW), after additional media was added, and at the start of the pilot. This information is summarized in Tables 2-8 and 2-9.

**Table 2-8. Summary of Socorro Springs Media Heights.**

| Column | Manufacturer/Media | Height of Media (inches) | | | |
|---|---|---|---|---|---|
| | | Design | Initial (dry) | After BW (wet) | Start of Pilot (1/26/05) |
| 4 | Engelhard/ARM 200 | 38.5 | 37.88 | 43.00 | 38.94 |
| 5 | Purolite/ArsenX$^{np}$ | 39.2 | 38.88 | 39.20 | 39.19 |
| 6 | Hydroglobe/Metsorb | 25.7 | 25.25 | 26.75 | 26.00 |
| 8 | AdEdge/E33 (2-min EBCT) | 19.3 | 19.13 | 23.25 | 19.30 |
| 9 | AdEdge/E33 (4-min EBCT) | 38.5 | 37.88 | 40.63 | 37.75 |
| 10 | AdEdge/E33 (5-min EBCT) | 48.1 | 47.63 | 47.63 | 48.00 |

**Table 2-9. Summary of Socorro Springs Media Weights.**

| Column | Manufacturer/Media | Weight Of Media (lb) | | |
|---|---|---|---|---|
| | | Initial | Added | Total |
| 4 | Engelhard/ARM 200 | 2410.6 | 194.9 | 2605.5 |
| 5 | Purolite/ArsenX$^{np}$ | 3515.5 | 279.9 | 3795.4 |
| 6 | Hydroglobe/Metsorb | 2315.4 | 157.7 | 2473.1 |
| 6 | *Re-loaded* | | | *2383.9* |
| 8 | AdEdge/E33 (2-min EBCT) | 1177.1 | 100.0 | 1277.1 |
| 9 | AdEdge/E33 (4-min EBCT) | 2352.5 | 167.9 | 2520.4 |
| 10 | AdEdge/E33 (5-min EBCT) | 2769.4 | 243.7 | 3013.1 |

All of the media experienced minor compaction (less than 2% difference from initial height) during transport to the site and required additional media to meet design height requirements. Most of the media swelled after water was added and the columns were backwashed. The most significant increase in height was observed in Columns 4 and 8 with a 14% and 22% increase, respectively. This is an important consideration as the additional height can cause difficulties in backwashing due to reduced freeboard space above the packed bed. The increased volume of media yields slightly higher EBCT than originally designed. This should improve performance of the media.

Columns 4 to 6 and 8 were backwashed in December 2004 for 15 to 30 minutes. The backwash flow rates varied from 0.2 to 0.6 gpm. The backwash process consisted of initiating upward flow at the lower flow rate (typically 0.2 to 0.3 gpm) and increasing the flow until the bed was completely fluidized. Backwashing was stopped when the water "ran clear", indicating the fine particles were removed. Fine particles can cause plugging and will lead to increased pressure drops and reduced flow. Columns 9 and 10 were backwashed in January 2005, along with a second backwash of Columns 6 and 8. Column 6 was reloaded and backwashed as well. The Isolux cartridge (#7) was not installed until the start of the pilot in January 2005. Note that some of the columns were backwashed in December but because the test was delayed, stood moist for a month; this may have affected performance.

Throughout operation of the Socorro Springs pilot, none of the adsorption columns experienced pressure drops above 2 psi and thus were never backwashed. Near the end of the pilot, Column 6 experienced a high pressure drop, which started to increase in late July. The column should have been backwashed at a pressure drop of 8-10 psi, but the backwash was never performed due to a miscommunication in the field. The column's pressure drop increased to 36 psi within 1 week and the column lost flow. Multiple backwashes did not help, and the column was taken offline.

It is somewhat unexpected to see no increase in pressure drop across each of the columns. As water passes through the columns, it is expected that a gradual increase in pressure drop would occur due to particles in the water and compaction of the media. The media compacted as much as 2 to 5 inches in some of the columns. One possible reason for this observation (no pressure drop increase) is the fact that the three-way valves could have leaked and therefore not shown the true pressure at the tops of the columns. Another possibility is that the pressure gauges could have been inaccurate and/or malfunctioning when in use.

The initial design for flow control of the columns was to adjust the flow upstream of the column, as shown in Figure 2-3. The initial design (upstream control) caused the entire pressure drop to be taken by the rotameter, which was used to control the flow rate. This caused a very low pressure (1 to 5 psi) to be supplied to the columns. This was noticed after several no-flow conditions found by the electronic flow meters. It was originally thought that the flow meters were malfunctioning. Once the flow control adjustment equipment was moved down stream of the columns, the incoming pressure increased, and no-flow conditions no longer occurred (a few of the flow meters still had problems measuring the cumulative flow).

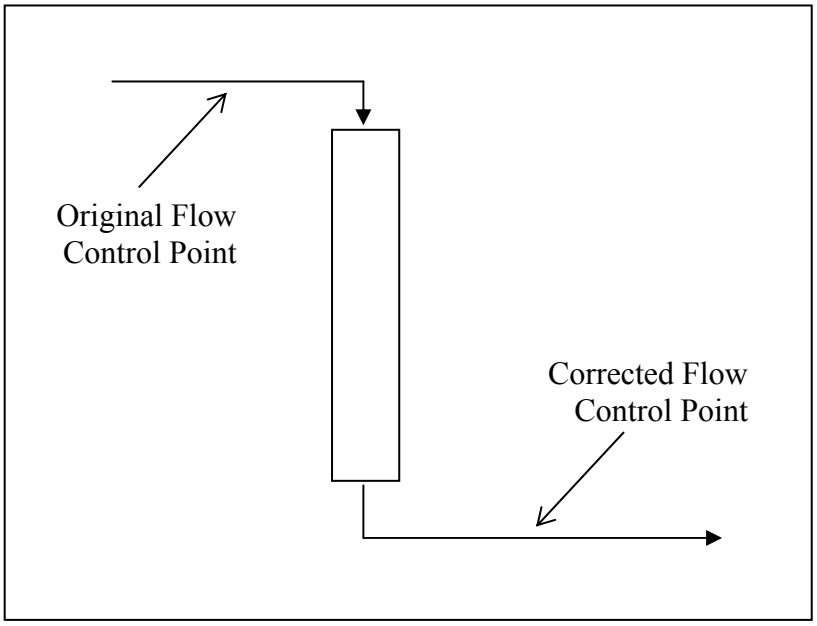



**Figure 2-3. Diagram of Flow Control.**

## 2.5.2 *Lessons Learned & Observations*

Many issues were observed and corrected during operation of the Socorro Pilot Phase I. These are summarized below.

Adsorptive Column Design

The initial location of the rotameters (which are used to control the column flow rate) is critical to proper control. The initial Socorro design was to have up-gradient flow control (rotameters were located upstream of the column). However, this location lead to the entire pressure drop occurring at the rotameter, with low or no pressure to the column itself. Moving the rotameters to the effluent side of the columns in February 2005 allowed for better flow control and a higher pressure to the columns.
*Recommendation*: Design for down-gradient flow control (rotameter located downstream of the column).

The initial location of the sampling ports was upstream of the rotameters, which caused high pressure water when sampling. Also, some solids came out of the sampling port, leading to higher turbidities and potentially higher arsenic levels (due to desorption of arsenic from solids).
*Recommendation*: The sampling port should be down-gradient of the rotameter (which takes the pressure drop – controlling flow out of sample port).

Ideally, it is best to maintain the design heights for each portion of the column – the support gravel, media, and freeboard for proper backwashing. Conflict may occur when there is a high EBCT and a low ceiling height (as was the case in Socorro), but whenever possible it is best not to sacrifice the support gravel height. Another possible solution is a hub or inlet assembly buried in the support media, but this would not be the preferred choice.

It is preferable in future designs to avoid the use of three-way valves (they are not positive enough in their shut off to ensure no leakage) and to use regular ball valves for positive shut off.

Backwashing

Backwashing adsorptive media prior to beginning the testing is necessary. It is important to keep track of the mass of media – the volume decrease (density increases) during packing, transport to site, and when encountering water. Care must be taken to keep track of the total mass added.

Backwash durations varied significantly from manufacturers suggested time. Our process was to backwash until the water showed signs of clearing – visually most fines were gone. Backwashing resulted in 6-8% loss of media, by volume. To ensure the pilot started with the design EBCT, the media beds were topped off to original design height.
*Recommendation*: Backwashing appears to break down the media. The intensity, frequency and duration are definite factors that need to be investigated further.

Column Packing

Loading the media into the columns, also known as packing the columns, can be done using two methods: dry or wet. Packing the columns dry is easier in that it is easy to handle the media and calculate the mass added. Packing the columns wet can cause some of the media to swell and form "clumps", which can potentially affect the flow and change the EBCT.
*Recommendation*: When starting the experiment, it is better to fill columns with water from the bottom and remove air at every point possible (drain port, air relief tap) as the water progresses upward. Vapor in the columns causes problems and should be avoided or removed before moving on.

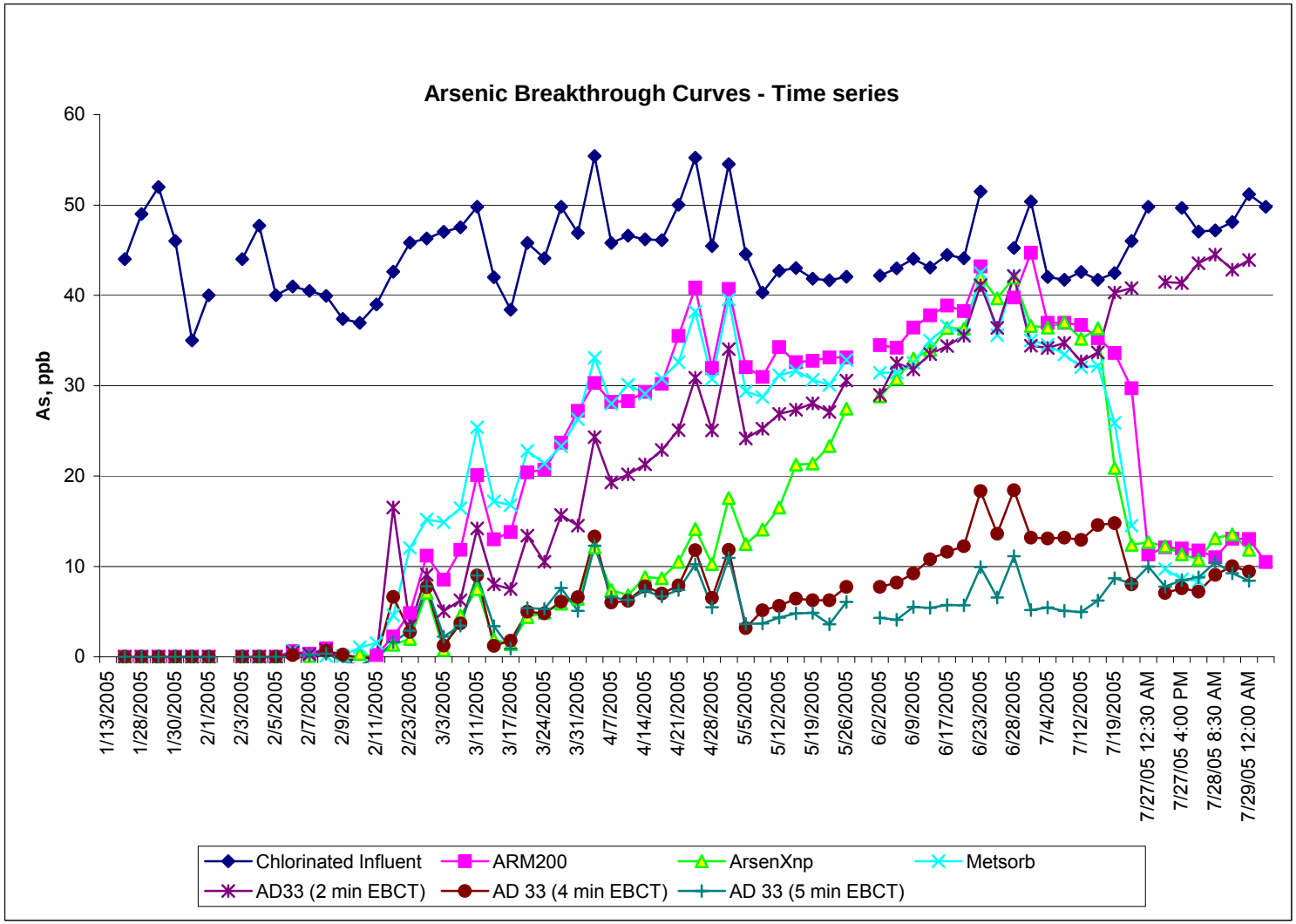
## 2.6 Pilot Test Results – Arsenic

Breakthrough curves for arsenic in the pilot test columns are shown in Figures 2-4, 2-5a and 2-5b. In Figure 2-4, the arsenic concentration in the chlorinated influent is compared to the arsenic concentrations in four of the media for each sampling event in Phase I and Phase IIb. Data for the fifth column (Isolux) from sampling events are presented separately in Appendix C (available at http://www.sandia.gov/water/pubs1.htm or from the lead author). Note that changes in the arsenic concentration of the influent are often correlated with changes in the effluent. In some cases, concentration spikes in the effluent bring the arsenic levels in the effluent above the MCL for short periods of time. Such behavior suggests that a series (lead-lag) configuration with two treatment vessels may be desirable for these adsorptive media. Note also the effect of the pH adjustment leading to sharp decreases in effluent arsenic concentrations on approximately July 26, 2005.

Figure 2-5a compares the arsenic concentrations at equivalent numbers of bed volumes of flow through the columns for five media run at the EBCT recommended by the vendor media through July 19, 2005, just before the pH adjustment. Figure 2-5b compares the breakthrough curves for

the 3 columns of E33 run at 2-min, 4-min and 5-min EBCTs. Appendix C contains plots of influent and effluent arsenic and vanadium concentrations for all of the columns individually

An interlaboratory study comparing arsenic concentrations in 227 check samples measured by WQL and GEL (General Engineering Laboratories, LLC; Charleston, SC 29407) was carried out. The maximum difference observed was 10.2 ppb (WQL-GEL); the minimum difference was -6.5 ppb (WQL-GEL); the average difference was 1.1 ± 3.4 ppb. Evaluation of the possible effect of this bias on the shape of the breakthrough curves suggested that the uncertainty in estimates of number of BVs required to reach breakthrough at 10 ppb in the column effluents was less than 15%. This is similar to the uncertainty in the method used to estimate the breakthrough point (visual examination of the curves). More details of the comparison are found in Appendix D to this report (available at http://www.sandia.gov/water/pubs1.htm or from the lead author.)




*Note nonlinear time-axis. Note: AD33 = E33.

**Figure 2-4. Arsenic Breakthrough and Influent Arsenic Concentrations for Adsorbent Media Columns at Socorro Springs.**

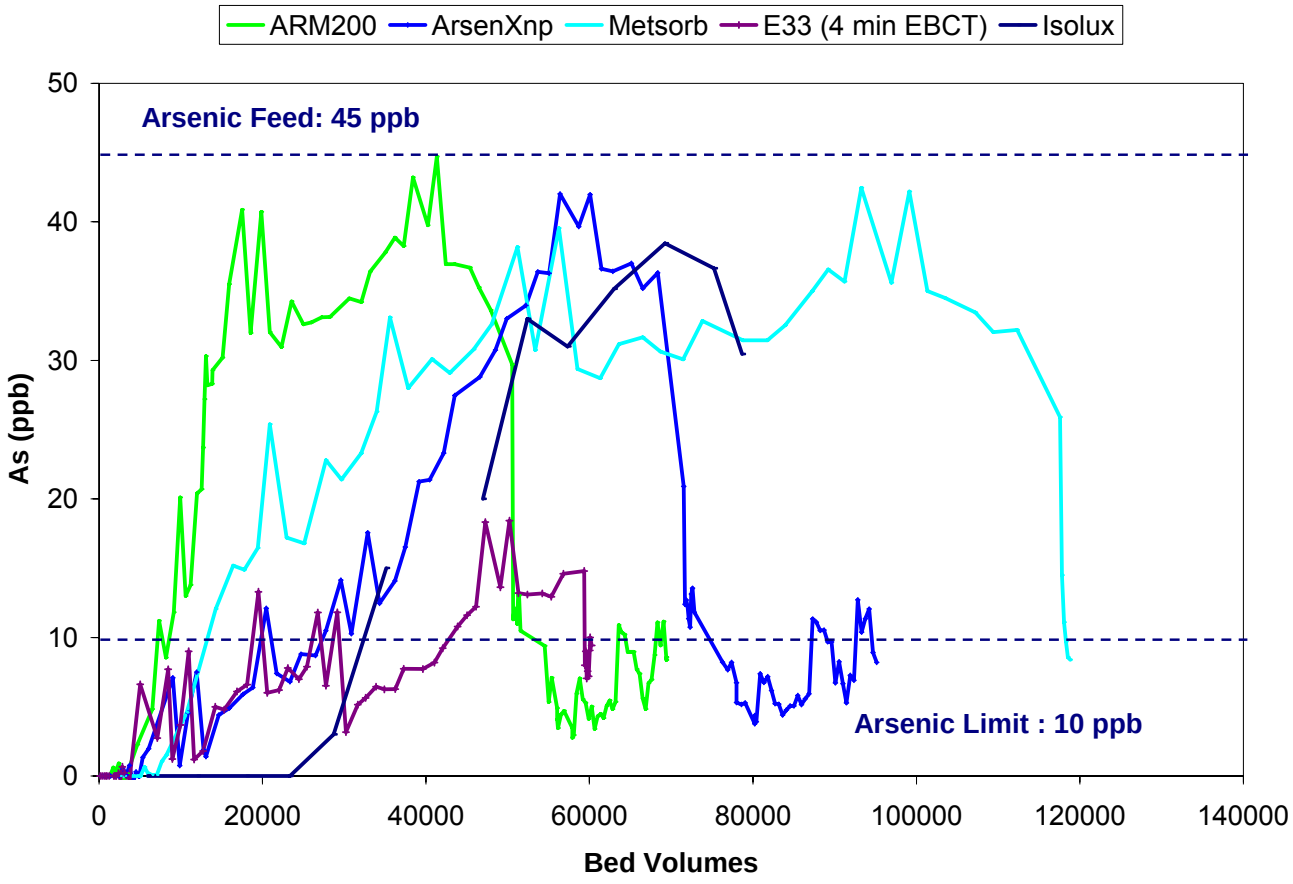



**Figure 2-5a. Arsenic Concentrations in Column Effluent as Function of Cumulative Bed Volumes Passed through Columns for Five Media Using EBCT Recommended by Vendor.**

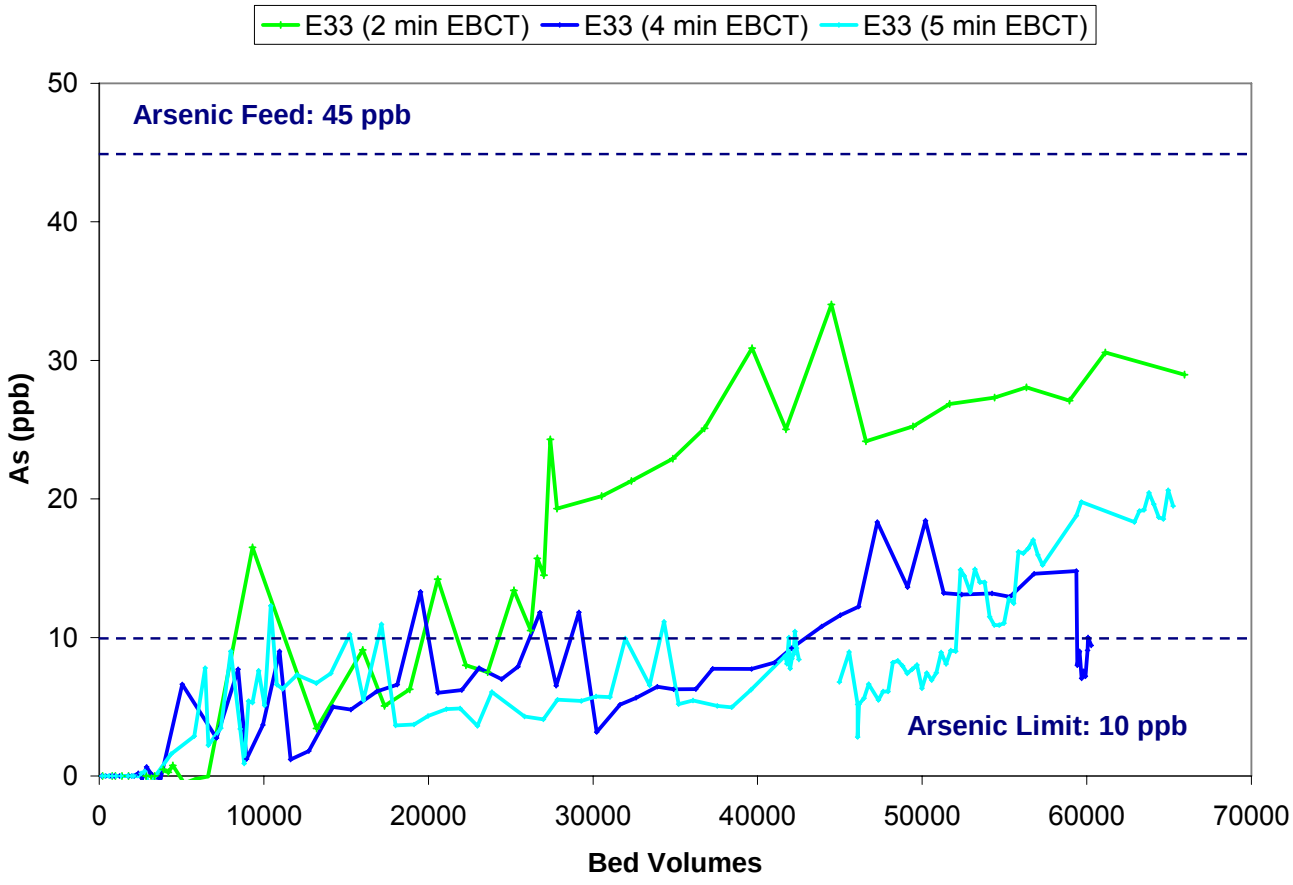



**Figure 2-5b. Arsenic Concentrations in Column Effluent as Function of Cumulative Bed Volumes Passed through Columns for E33 Media Using Three Different EBCTs.**

Figures 2-4 and 2-5 show that arsenic (as As(V)) was removed completely from the chlorinated water initially in all of the columns and that as the capacity of the media for arsenic was exhausted over the course of several months, arsenic concentrations in the effluent rose. Figure 2-4 shows that the influent arsenic concentration was variable over the course of test period, ranging from 35 ppb to 55 ppb. This variability may result from non-uniform mixing of water from the two sources of water that feed the Socorro Springs well site. Figure 2-4 also shows that these changes in the arsenic concentration in the influent were matched to similar changes in the effluents of all columns.

Table 2-10 compares the numbers of BVs of influent flow through the columns required to reach 10 ppb (10 μg/L) in the effluent or to reach a relative concentration $C/C_o = 0.8$ in the effluent (where $C_o$ is the influent arsenic concentration). These estimates of BVs were read directly from Figure 2-5a and may be subject to observation bias especially where the breakthrough curve (BTC) is uneven near the As = 10 ppb (10 μg/L) level.

**Table 2-10. Arsenic Breakthrough in Pilot Test Columns Run at EBCT Recommended by Vendors.**

| Parameter | ARM 200 | Metsorb | ArsenX$^{np}$ | Isolux 302M | E33 (4 min) |
|---|---|---|---|---|---|
| BV to 10 ppb (10 μg/L) | 8600 | 13000 | 27000 | 32000 | 43000 |
| Capacity at 10 ppb, mg/g | 0.60 | 0.70 | 1.38 | 1.67 | 3.56 |
| Capacity at 35K BV, mg/g | 1.17 | 1.39 | 1.75 | 1.67 | 3.01 |
| $C/C_o$ at 35K BV | 0.88 | 0.60 | 0.35 | 0.38 | 0.15 |
| BV at $C/C_o = 0.8$ | 33000 | 87000 | 53000 | 63000 | > 84000* |
| Capacity at $C/C_o = 0.8$ | 1.15 | 2.26 | 2.10 | 2.23 | > 4.03* |

* Based on assumption that performance with 4-min EBCT is at least as good as that with 2-min EBCT (see Table 2-11).

The concentration of arsenic (mg As/g media) in the adsorptive media (capacity) at 10 ppb (10 μg/L), 35000 BV and $C/C_o = 0.8$ are also shown in Table 2-10 and may be a more unbiased measure of sorption. These are calculated from the area of the plots in Figure 2-5a between the influent concentration curve and the effluent concentration (total mg arsenic) and the weight of the media. The values of BV and capacity at 10 ppb (10 μg/L) arsenic show a fairly consistent relationship among the adsorptive power of the media:

E33 >Isolux 302M ~ AsX$^{np}$> Metsorb > ARM 200

The numbers of BVs of influent flow required to reach a relative concentration $C/C_o = 0.8$ in the effluent is relevant to use of adsorptive media in a "lead-lag" treatment configuration. In this type of system, two treatment vessels are used in series. The media in the treatment vessel in the "lead" position would be used to near-exhaustion while the second vessel located downstream in the "lag" position would be used to remove residual arsenic, i.e., polish the water to below the 10 ppb MCL. The pilot test results show that at the higher effluent levels ($C/C_o = 0.8$), Metsorb has a higher capacity than Isolux 302M and ArsenX$^{np}$. Results for E33 are estimated from performance of the media with an EBCT of 2 minutes as discussed below.

Table 2-11 compares the BTCs and capacities for the E33 columns that had different media heights and therefore were run with different EBCTs. It can be seen that the number of BVs until the effluent reaches 10 ppb and the calculated arsenic adsorption capacity for 10 ppb increases with EBCT over the range studied. In the table, performance is compared to the results from the column run with a 2-min EBCT for several other parameters. The marginal changes in performance per minute change in EBCT are shown. The results show that the difference in performance between the smaller and mid-size columns is the most significant but suggest that increases in the EBCT may have limited benefit at longer times. This means that there may be little to be gained by increasing the EBCT appreciably above the recommendation of the vendor.

**Table 2-11. Comparison of Performance of E33 Columns with Different EBCTs.**

| Parameter | E33 | | |
|---|---|---|---|
| | Short 2 min | Med 4 min | Long 5 min |
| BV to 10 ppb (10 μg/L) | 24000 | 43000 | 52000 |
| BV relative to 2-min EBCT (%) | 100 | 179 | 217 |
| Marginal change BV /min EBCT | 0 | 9500 | 9000 |
| | | | |
| Capacity at 10 ppb, mg/g | 1.95 | 3.56 | 4.21 |
| Cap. relative to 2-min EBCT (%) | 100 | 183 | 215 |
| Marginal change (mg/g)/min EBCT | 0 | 0.81 | 0.64 |
| | | | |
| Capacity at 35K BV, mg/g | 2.59 | 3.01 | 2.92 |
| Cap. relative to 2-min EBCT (%) | 100 | 116 | 113 |
| Marginal change (mg/g)/min EBCT | 0 | 0.21 | -0.09 |
| $C/C_o$ at 35K BV | 0.50 | 0.15 | 0.12 |
| | | | |
| BV at $C/C_o$ = 0.8 | 84000 | NA | NA |
| Capacity at $C/C_o$ = 0.8 | 4.03 | NA | NA |

## 2.7 Other Solutes

The effect of the media on major solutes (Ca, Mg, Cl, Na, $SO_4$, pH, free chlorine and $SiO_2$) is described for each media in Appendix C. In general, the media did not remove appreciable amounts of Ca, Mg, Cl or Na. Sulfate was released by ARM 200 and ArsenX$^{np}$ for the first few thousand bed volumes. Free chlorine was removed to a limited extent by Isolux 302M during the first 60,000 BV. Free chlorine was absorbed completely by ArsenX$^{np}$ for the first 20,000 BV and then partially until 70,000 BV. This result is consistent with information from the vendor suggesting that exposure to free chlorine levels above 0.5 ppm will lead to degradation of the resin (F. Boodoo, The Purolite Company, personal communication, 7/12/2006). Calcium was

removed by Metsorb during the first 7000 BV. Fluoride was removed during the first 4000 to 5000 BV by E33 and ArsenX$^{np}$. Note: AD33 = E33 in these and all other figures.

Figure 2-6 and Figure 2-7 describe the effect of the media on pH and silica content of the effluent waters. The influent pH was about 7.9 and the $SiO_2$ concentration was about 25 ppm (see Table 1-1). It can be seen that the initial pH of effluent from the ArsenX$^{np}$ was acidic (pH = 4) but rose to ambient levels during the first 7000 bed volumes. The pH in the initial effluents from the other media was slightly depressed (several tenths of pH unit) but rose to ambient levels over the same flow volume. Figure 2-7 shows that all of the media absorb $SiO_2$ during the first 10,000 bed volumes but reach saturation with respect to silica uptake after that.

Data for vanadium sorption by the media are also found in Appendix C. Vanadium is present in the influent at trace levels like arsenic (13 ppb). It was removed to non-detect levels (< 0.5 ppb) by all the media.

## 2.8 Pilot Test Results – Extraction Tests (TCLP and CA WET)

All of the columns were returned to SNL for sampling of the solids. The columns were split in half by sawing through the columns and pulling a nylon cord through the media. Using a spatula, samples of media were taken in the center of one half of the column every three inches and at the edge of the column every three inches. About 20 2-g samples were taken from each core and digested in $HNO_3$ for analysis of arsenic, silica, fluoride and vanadium for studies of the mass transfer zones. The results of this analysis will be described in a later report.

A second set of samples comprised of sections from the top, bottom and middle of each core was taken, mixed, and then sent to an EPA certified laboratory for a TCLP test ( US EPA 1992) All of the spent arsenic media passed the TCLP with respect to the regulated metals: arsenic (<0.125 mg/L), cadmium (<0.125 mg/L), barium (<31 mg/L), chromium (<0.05 mg/L), lead (<0.125 mg/L), selenium (<0.25 mg/L), silver (<0.125 mg/L), and mercury (<0.3 μg/L). (Note: in many case, the metals concentrations in the leachates were below instrumental detection limits after dilutions required for the ICP-MS analysis; therefore, only upper concentration limits can be calculated.) The results for regulated and several non-regulated metals (Cu, Zn, Ni) are given in Appendix E. The results of the TCLP test mean that the solid residuals can be disposed in sanitary landfills in New Mexico. The spent media were also subjected to the leaching test and acid digestion test of the CA WET (California Waste Extraction Test; State of California, 2005.) With the exception of ARM 200, all of the media passed these tests as documented in Appendix E (available at the Sandia National Laboratories Arsenic Water Technology Partnership websites: http://www.sandia.gov/water/arsenic.htm and http://www.sandia.gov/water/pubs1.htm or from the lead author.) The results of the pre-production batch of the ARM 200 media may not reflect the performance of the commercially-available media.

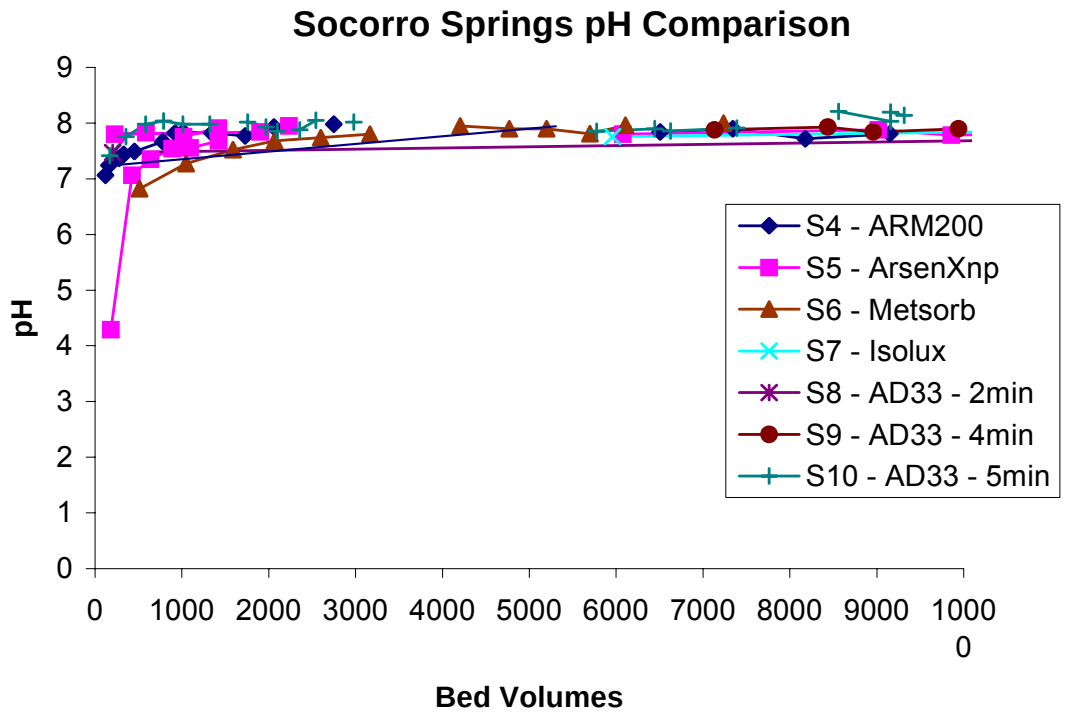



**Figure 2-6. Comparison of pH Levels in Effluent for First 10000 Bed Volumes for Different Media.**

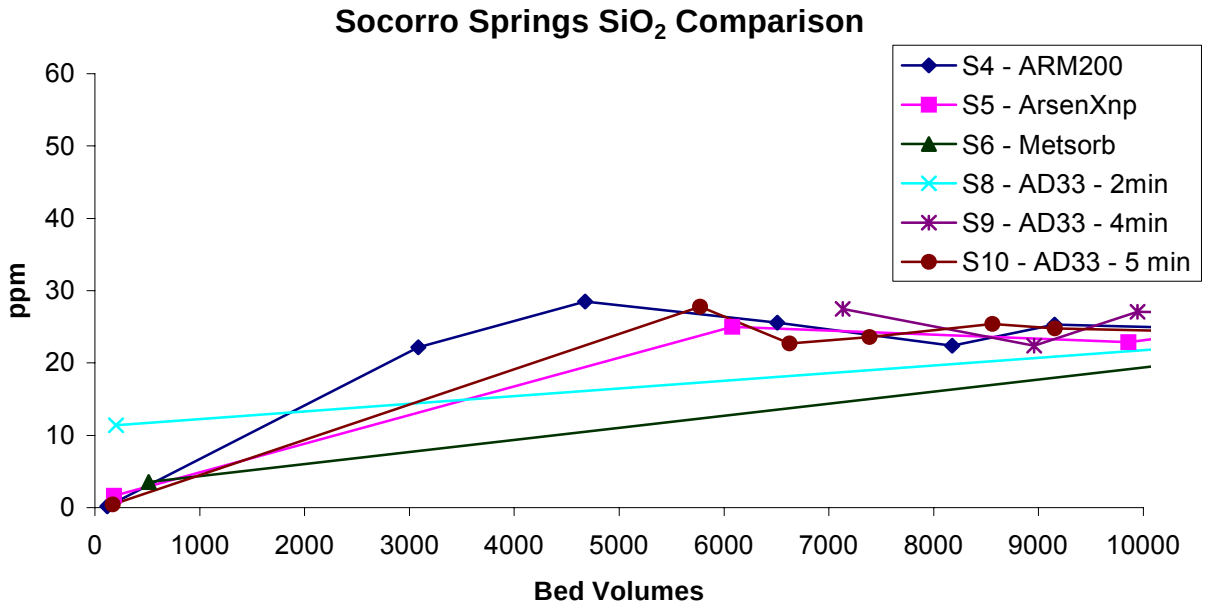



**Figure 2-7. Comparison of $SiO_2$ Levels in Effluent from Different Media Columns during First 10000 BVs.**

# 3.0 LABORATORY STUDIES

## 3.1 Media Characterization

Arsenic sorption is controlled by a number of physical and chemical properties of the adsorptive media. In order to understand and predict the sorption of arsenic by the media used at the Socorro pilot site, some basic mineralogical and surface chemical analyses were carried out. These included XRD (X-ray diffraction), SEM/EDS (Scanning Electron Microscope/Energy Dispersive Spectroscopy), and surface area analysis by the Brunauer, Emmett and Teller (BET) measurement technique.

### 3.1.1 *Materials and Methods*

Batches of adsorptive media (see Table 2-1) designed for use in full-scale treatment systems were supplied by these vendors or their local distributors:

- **Isolux 302M** (Isolux Technologies, Division of MEI)
- **Metsorb** (Hydroglobe)
- **ARM 200** (Engelhard Corporation)
- **ArsenX$^{np}$** (Purolite Company)
- **E33** (Adedge Technologies, Inc.)

XRD analyses were performed on a Bruker D8 Advance X-Ray Diffractometer using CuKa radiation, a step size of 0.05º and step time of 1 s, operated at 40 kV and 30 mA. The samples were ground to fine particles and dispersed using deionized water on a glass slide and dried at room temperature before analysis.

SEM/EDS data were collected on a JEOL JSM-6300V Scanning Microscope with energy dispersive capabilities operated at 20 kV. Powder samples were mounted directly on carbon conductive tabs and sputter-coated with gold (or carbon) before analysis.

BET surface area and pore size distribution were measured using QuantaChrome Autosorb-6B Analyzer (Quantachrome Corporation). The samples were degassed at 120ºC for ~12 hours (or 30ºC, ~24 hours for ArsenX$^{np}$). Surface areas were determined using the BET equation on 5-point $N_2$ gas adsorption isotherms, and the pore-size distributions were obtained from the desorption branches using the standard Barrett-Joyner-Halenda (BJH) method without further correction (Barrett et al. 1951).

The temperature of Socorro groundwater is around 90ºF (37$^{o}$C). A study was carried out to examine the possible effect of temperature on the media's crystallinity because potential alteration or "aging" may influence arsenic adsorption behavior. The samples were subjected to aging in deionized water at 20 or 37ºC for 9 to 11 weeks in a controlled temperature shaker table.

After the aging period, the samples were removed from the deionized water and treated as described above for XRD analysis.

### 3.1.2 *Results*

Table 3-1 summarizes the results of the SEM/EDS, BET and XRD studies. Isolux 302M has the highest BET surface area but the smallest average pore diameter. E33 and ArsenX$^{np}$ have the lowest BET surface areas and largest average pore diameters. Figures 3-1 and 3-2 compare the differential pore size and cumulative pore volume distributions of the different media. The pore size distribution curves show the range of pore sizes and the peaks indicate the dominant pore size. In the differential pore size distribution curve (Figure 3-1) the y-axis, Dv (logD), is the derivative pore volume divided by the derivative of the log value of pore diameter. The majority of the pore volumes of ARM 200 and E33 arise from pores with diameters of 400 to 700 Å (mode ~ 600 Å). Metsorb has a higher diameter dominant pore size range of ~ 500 to 800 Å (mode ~ 700Å). Narrow pores contribute to most of the total pore volume of Isolux 302M; the majority of the pores have a diameter ~ 50 A. Possible shrinkage of the resin during the degassing process as well as the presence of volatile compounds may contribute to the observed characteristics of ArsenX$^{np}$.

**Table 3-1. Summary of Analyses of Arsenic Adsorption Media.**

| Media | BET Surface Area ($m^2/g$) | Average Pore Diameter (Å) | Total Pore Volume (TPV) ($cm^3/g$) | Constituents (XRD) | Dominant Elements (EDS) |
|---|---|---|---|---|---|
| Isolux 302M | 499 | 23 | 0.29 | Amorphous zirconium oxide/hydroxide | Zr, O |
| Metsorb | 211 | 64 | 0.34 | Crystalline $TiO_2$ (*Anatase*) | Ti, O |
| ARM 200 | 262 | 99 | 0.65 | Amorphous Iron oxide/hydroxide (or very poorly crystalline *Hematite*) | Fe, O |
| ArsenX$^{np}$ | 120 | 174 | 0.05 | Amorphous iron oxide/hydroxide | Fe, O, C |
| E33 | 147 | 245 | 0.90 | Iron oxide/hydroxide (*Goethite*) | Fe, O |

Figures 3-3 through 3-7 show the XRD patterns of the five media. Three patterns are shown for each media: (1) the media as obtained from the vendor after grinding to the fine particle size for XRD analysis, (2) after 9 to 14 weeks aging at 20$^{o}$C, and (3) after 9 to 14 weeks aging at 37$^{o}$C in deionized water. It was found that, except ARM 200, all media showed no significant change in their XRD patterns upon aging; however for ARM 200, peaks of hematite showed up upon aging at 37ºC for 9 weeks. It is possible that this change in crystallinity could affect the sorption of arsenic at the Socorro pilot site. It has been reported (Dixit and Hering 2003; Ford 2002; Lin and Puls 2000; Martinez et al. 2001; Meng et al. 2001; O'Reilly et al. 2001; Sorensen et al. 2000a; Sorensen et al. 2000b) that the crystallinity/aging and phase transformation of materials (i.e., iron oxide) can play an important role in their adsorption/desorption behaviors as well as the fate of the adsorbed species in the spent sorbents.

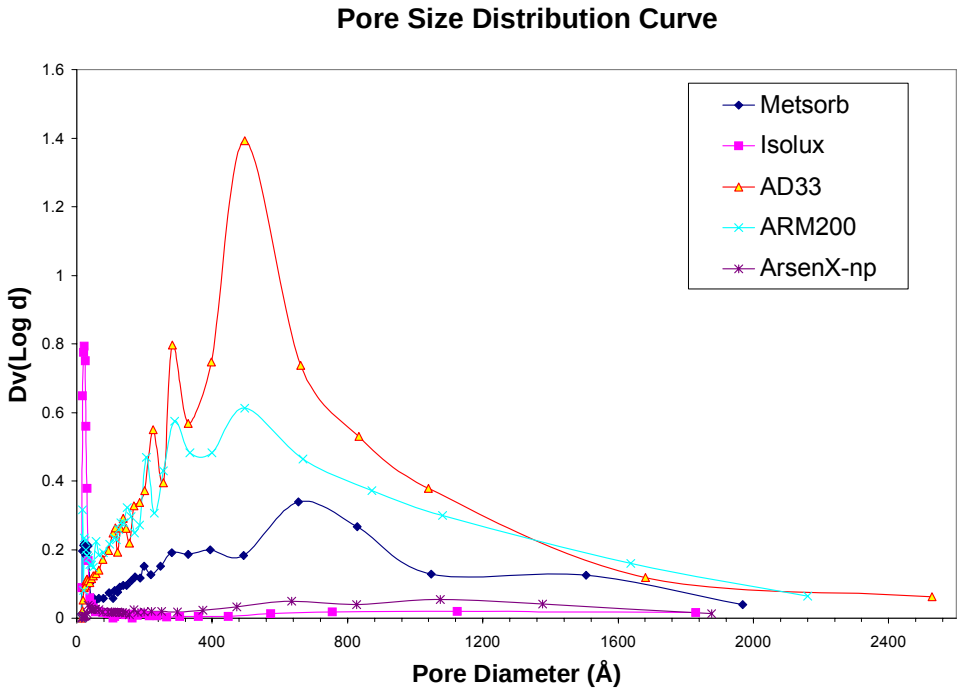



**Figure 3-1. Pore Size Distributions for Five Adsorbent Media.**

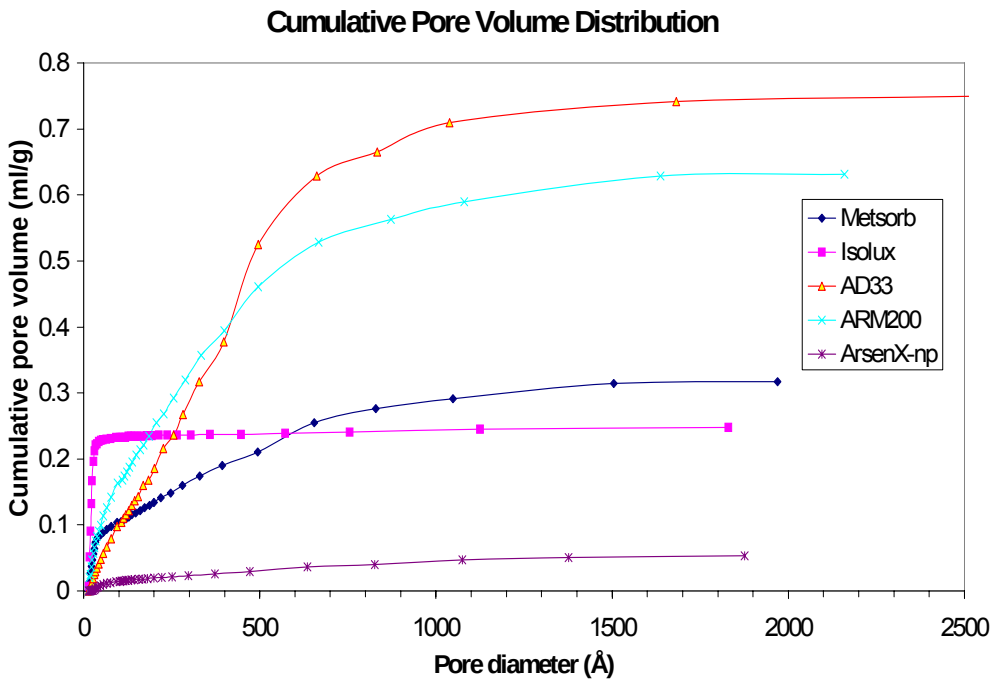



**Figure 3-2. Cumulative Pore Volume Distributions for Five Adsorbent Media.**

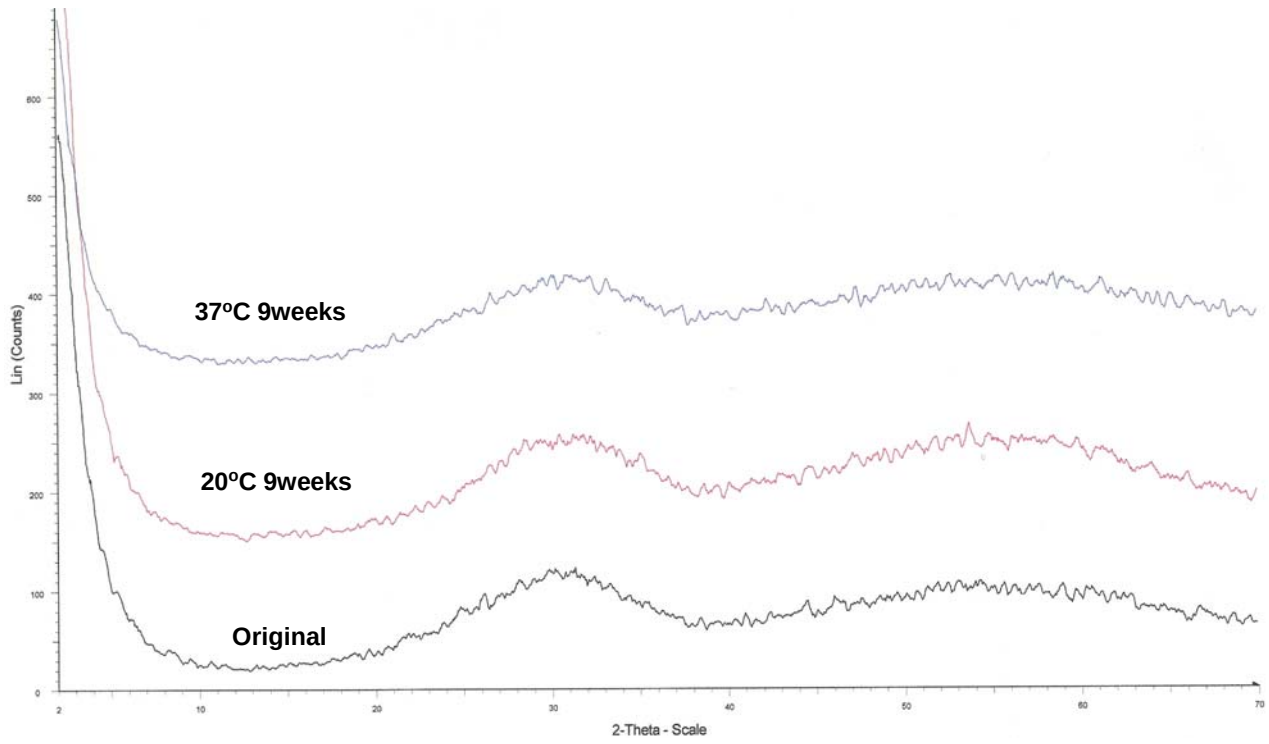



**Figure 3-3. XRD Patterns for Pristine and Aged Isolux 302M Media ($ZrO_2$).**

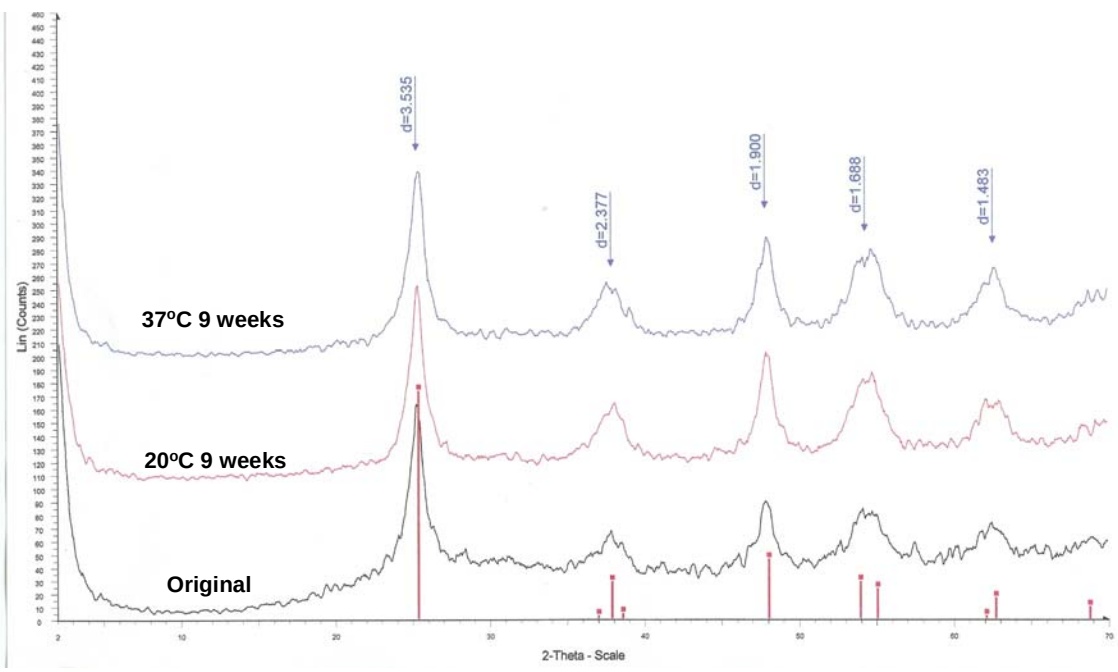



**Figure 3-4. XRD Patterns for Pristine and Aged Metsorb Media ($TiO_2$).**

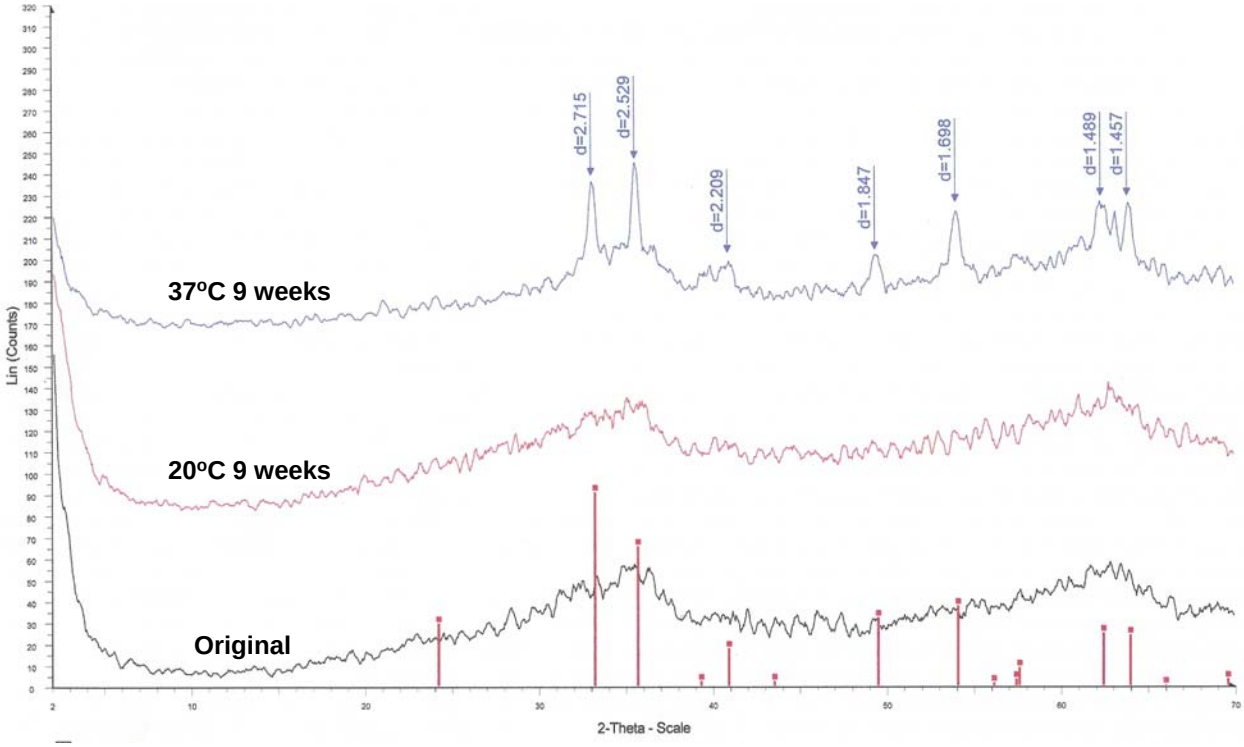



**Figure 3-5. XRD Patterns for Pristine and Aged ARM 200 Media (FeOOH and $Fe_2O_3$).**

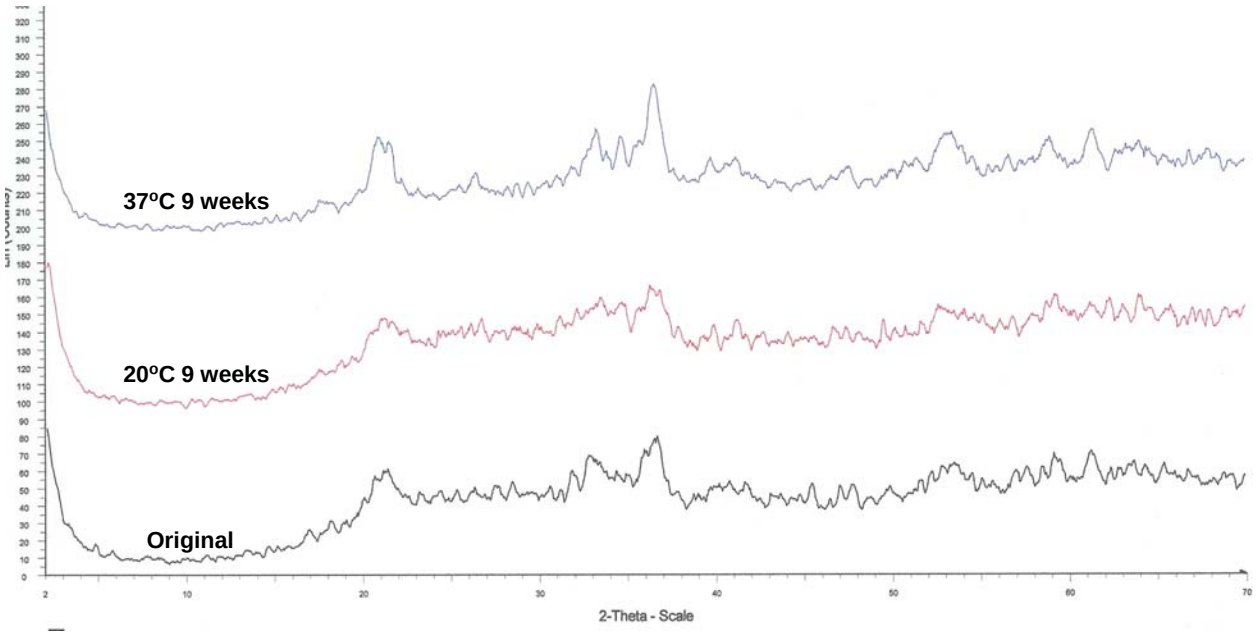



**Figure 3-6. XRD Patterns for Pristine and Aged ArsenX$^{np}$ Media (FeO – coated resin).**

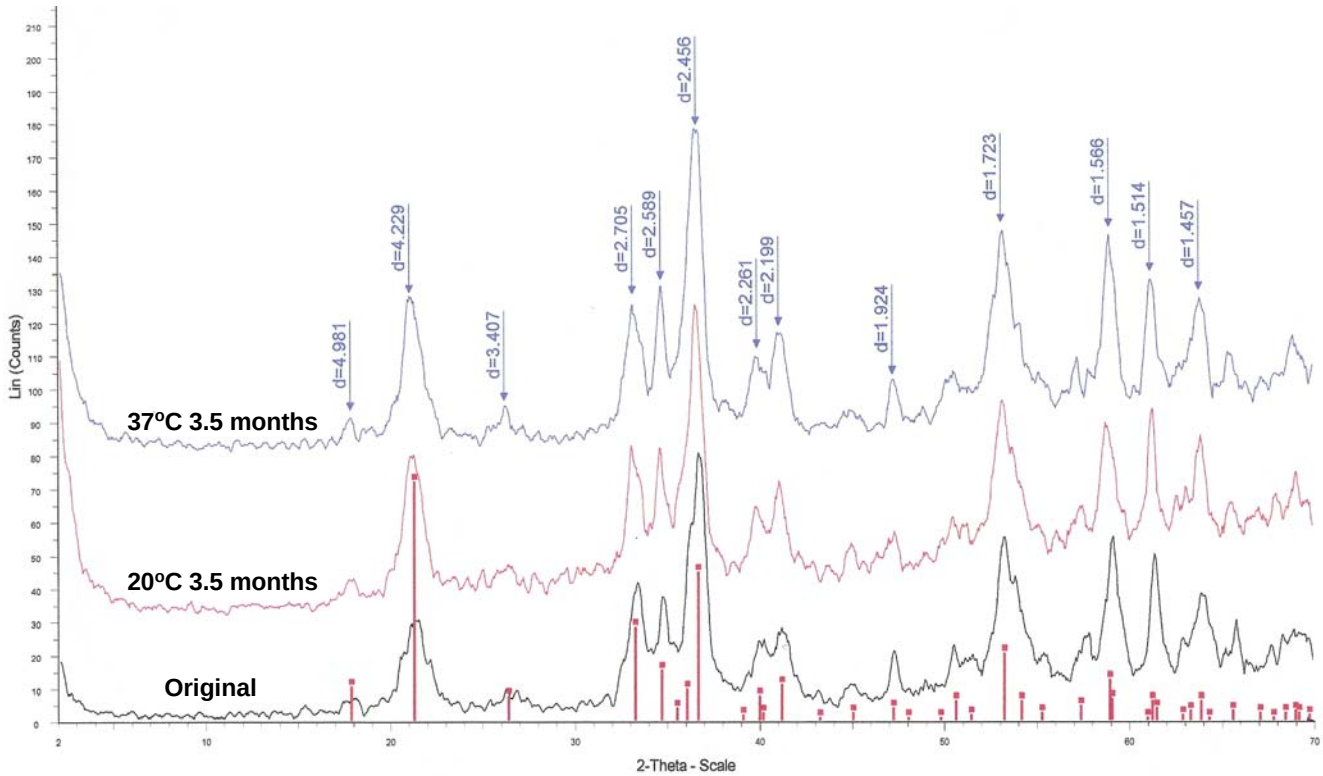



**Figure 3-7. XRD Patterns for Pristine and Aged E33 Media (FeOOH).**

Figures 3-8 through 3-12 show SEM photos of the pristine media. Note the angular nature of the E33, Metsorb and ARM 200 media; this may partially explain the large amount of fine particles produced from abrasion as described in Section 3.2. In contrast, the ArsenX$^{np}$ media is composed of smooth, spherical resin particles which do not produce many fines during abrasion. The SEM images also show that the Isolux 302M particles are much smaller than the other media grains. This property, together with the small average pore size shown in Figures 3-1 and 3-2, suggest that the high measured surface area may be dominated by external surface area. There were no observable differences when the pristine material was compared to the aged media after 9-11 weeks of exposure to the deionized water at 20$^{o}$C or 37$^{o}$C. The crystallinity, mineralogy, surface composition and morphology of samples of spent media after the pilot test will be compared to these baseline data in a later report.

**Isolux 302M**

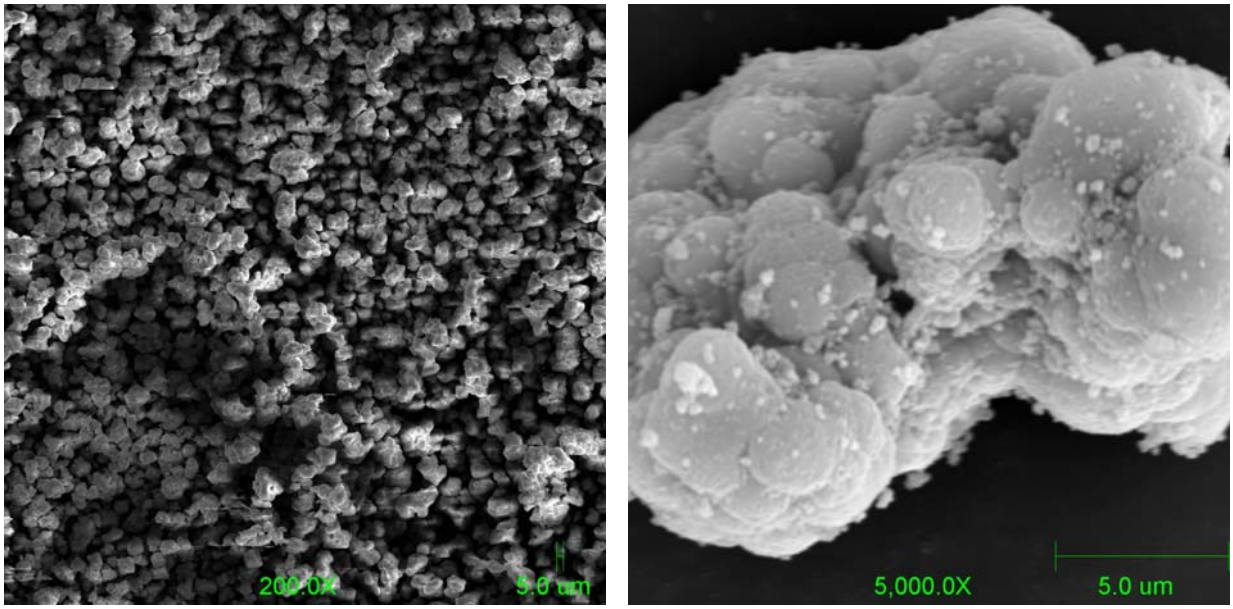



**Figure 3-8. SEM Photos of Isolux 302M Media (200x and 5000x magnification).**

**Metsorb**

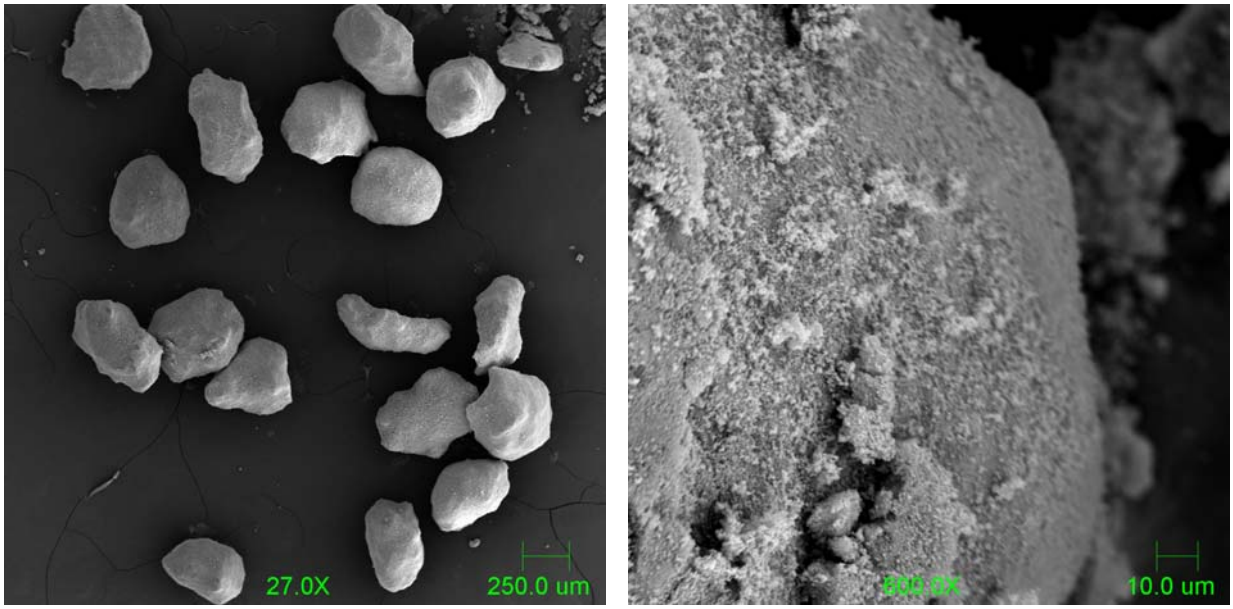



**Figure 3-9. SEM Photos of Metsorb Media (27x and 600x magnification).**

**ARM 200**

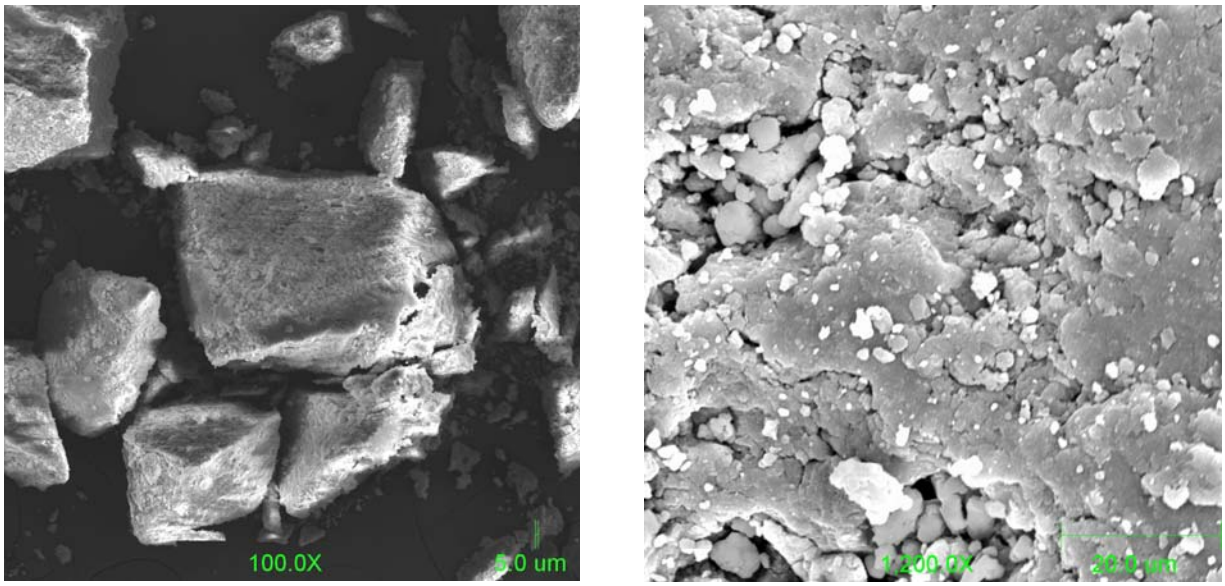



**Figure 3-10. SEM Photos of ARM 200 Media (100x and 1200x magnification).**

**ArsenX$^{np}$**

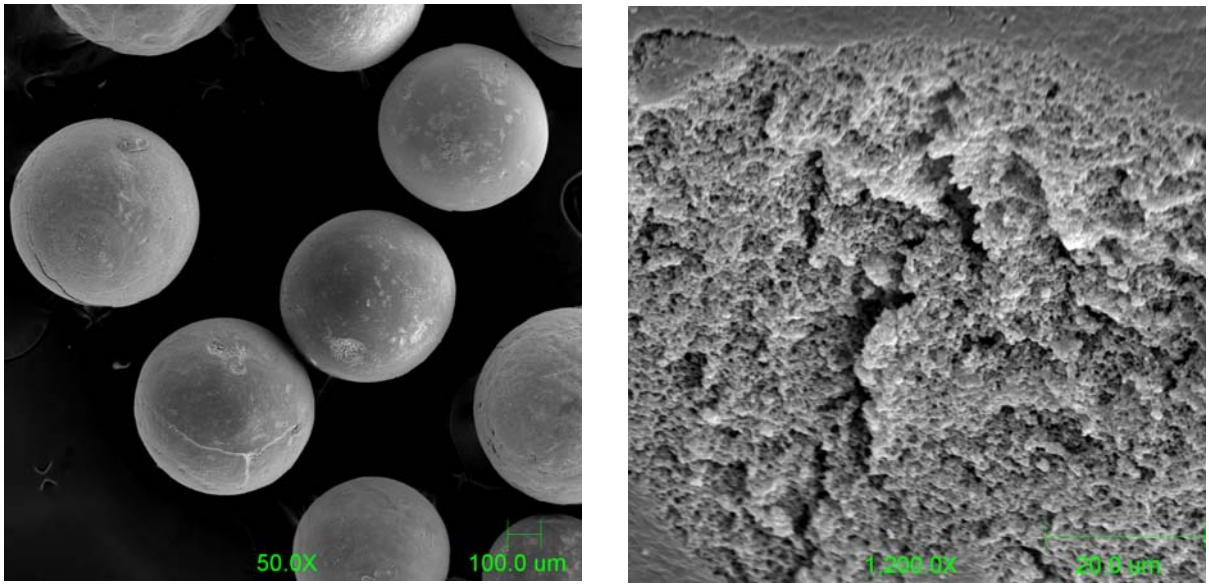



**Figure 3-11. SEM Photos of ArsenX$^{np}$ Media (50x and 1200x magnification).**

**E33**

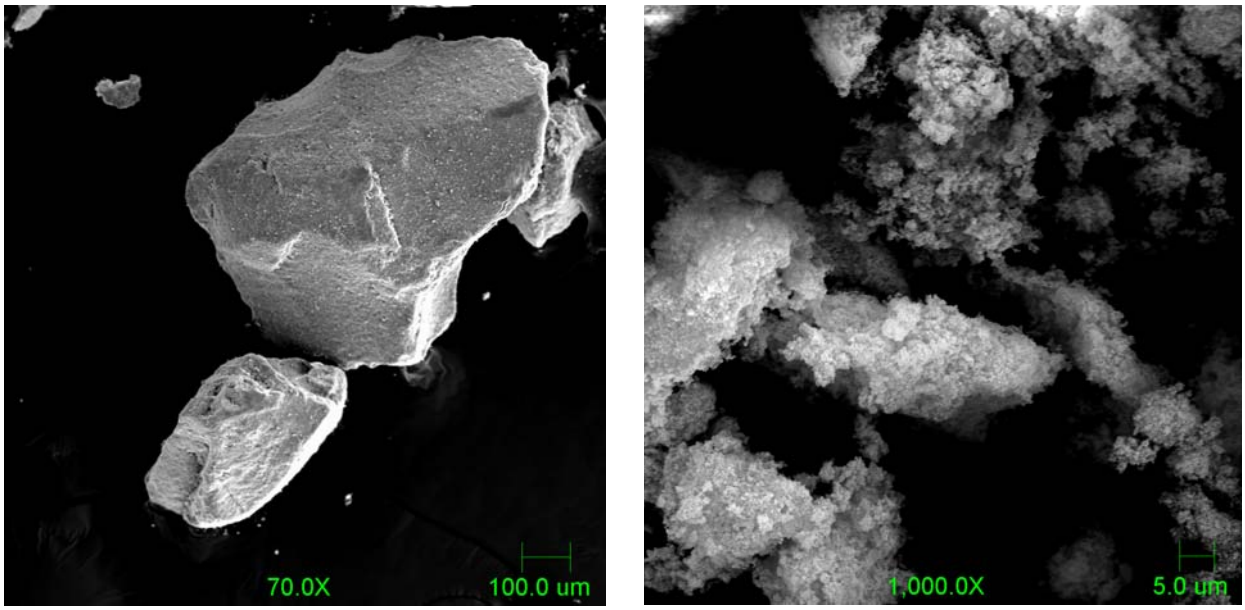



**Figure 3-12. SEM Photos of E33 Media (70x and 1000x magnification).**

## 3.2 Particle Size Analysis and Attrition Loss

### 3.2.1 *Purpose*

The particle size analysis was conducted to determine the attrition losses of media during shipping and with use in water systems. High attrition losses through production of fine particles will increase the amount of media needed because more media is lost during both system use and maintenance. The frequency of maintenance increases for media with high attrition losses because fine particles clog the adsorptive media bed, which builds up pressure in the system, and leads to more frequent backwashing. Increased backwash frequency in turn creates more fines, loss of media and further increases costs for the operation of a community water system. A more detailed description of the study is found in North (2006).

### 3.2.2 *Procedure*

Media samples were dried in an oven at 105°C overnight (over eight hours) in glass beakers and transferred to airtight Nalgene bottles after drying for storage in the hood. Immediately before beginning sieve analysis, approximately 200 grams of media was poured into a glass beaker inside the hood. The beaker was then placed on a balance located outside the hood, and minor adjustments were made to obtain 200 grams of media.

Nine sieves of sizes ranging from No. 10 (2.00 mm opening) to No. 400 (0.038 mm) were used in this analysis. The empty sieves and the pan were briefly oven-dried before analysis and, once they had sufficiently cooled, individually weighed on a balance, and then the weight was recorded on a data sheet.

The 200 grams of media was then poured into a stack of sieves, which were placed on a sieve shaker (W.S. Tyler Inc. Model RX-24, Combustion Engineering, Inc. Mentor, OH) within the hood. Paper towels were placed around the sieve shaker and wet down with deionized water from a squeeze bottle to minimize dust. For each media, sieve analysis was completed using two stacks of sieves. The first contained sieve numbers 10 (2.00 mm), 18 (1.00 mm), 40 (0.425 mm), 60 (0.250 mm), 80 (0.180 mm), and a pan. The second round of sieves contained numbers 100 (0.150 mm), 200 (0.075 mm), 325 (0.045 mm), 400 (0.038 mm), and the pan. After 15 minutes of shaking with the first stack, media remaining in the pan was transferred to the No. 100 sieve. The pan was placed below the No. 400 sieve, and the second stack was shaken also for 15 minutes.

After shaking was completed, the sieves were separated under the hood and transferred individually to the balance to be re-weighed. This weight was recorded on the data sheet. The contents of each sieve were then dumped into a trashcan placed next to the hood to contain the dust. The bottom of the trash was also lined with damp paper towels, and a squeeze bottle of deionized water was used to wash down excessive dust on the sides of the trash can. The base of the sieve was brushed with the sieve brush to remove particles stuck within the mesh. Sieves were then washed with Alconox soap and a sponge and placed in the oven at 105°C to dry completely before re-use.

Calculations for sieve analysis were completed using Excel spreadsheets for each media. Values for Sieve Mass (g) and Sieve Mass plus Mass of Dry Media (g) were used to calculate the Mass of Media Retained (g) and the Percentages Retained and Passing. The data was then plotted as Particle Diameter vs. Percent Finer, with Particle Diameter on a log scale. From this plot, it was possible to determine the values of $D_{10}$, $D_{30}$, and $D_{60}$, or the diameters corresponding to 10, 30, and 60 percent finer, respectively. Using these values, the Coefficient of Uniformity ($C_u$) and the Coefficient of Curvature ($C_c$) were calculated using these formulas:

$$C_u = \frac{D_{60}}{D_{10}} \qquad C_c = \frac{D_{30}^2}{D_{10} D_{60}} \qquad \text{(Eq. 3-1)}$$

### 3.2.3 *Results*

The results of the study are shown in Table 3-2. In addition to the media used in the Socorro Springs study, data from other media used in other pilot studies are presented in the table. Based on the data from analysis on each media, the percentage of media smaller than the smallest 'vendor declared' particle size was calculated. This resulting percentage is the attrition loss, and percentages ranged from 0.8 to 32.3 percent (see North 2006). For example, 13% of the E33 media was smaller than 35 mesh, whereas the vendor declared range of sizes was 10 x 35. Therefore a 13% attrition loss was determined for the E33.

**Table 3-2. Summary of Relevant Media Characteristics.**

| Media | Media Size (Vendor declared) | Percent Attrition | Cu | Cc |
|---|---|---|---|---|
| Purolite ArsenX$^{np}$ | 16 x 50 | 0.8 | 1.64 | 0.91 |
| Hydroglobe Metsorb | 16 x 60 | 0.8 | 1.97 | 0.87 |
| Kemiron CFH 10 | 18 x 35 | 3.1 | 1.57 | 0.93 |
| EaglePicher NXT-2 | 32 x 200 | 5.3 | 4.11 | 0.87 |
| ResinTech ASM 10 HP | 20 x 40 | 9.3 | 1.55 | 0.94 |
| Kemiron CFH 12 | 10 x 18 | 9.7 | 1.70 | 0.99 |
| Eaglehard ARM200 | 12 x 40 | 11.4 | 1.88 | 0.91 |
| Adedge E33 | 10 x 35 | 13.0 | 2.44 | 0.88 |
| DOW Adsorbsia | 10 x 60 | 16.3 | 1.91 | 0.89 |
| Kemiron CFH 24 | 5 x 10 | 29.8 | 1.43 | 1.43 |
| ADA Amended Silica | 10 x 40 | 32.2 | 2.00 | 0.93 |
| Virotec Bauxsol | < 35 | Inconclusive | 4.78 | 0.75 |
| MEI Isolux | <400 | Inconclusive | -- | -- |

Cu = Coefficient of uniformity; Cc = Coefficient of curvature

The vast majority of the media falls within the ranges declared by the vendors. For E33, some error resulted from the use of a No. 40 sieve instead of a No. 35 or No. 32 sieve (0.425 mm instead of 0.500-0.600 mm), which is the size specified by the vendor (Adedge).

The uniformity coefficient is the ratio, by weight, of the grain size that is 60 percent finer to the grain size that is 10 percent finer on the grain size distribution curve. This coefficient is an indication of how well sorted the media is. Well sorted material has greater uniformity.

A low uniformity coefficient means that particles are very similar in size and that media generally requires less backwashing and less potential loss in mass. A low uniformity coefficient is also desirable because fine-grained particles will be more likely to clog up the system, which would allow pressure build-up. High uniformity coefficient means that there is a wide range of particle sizes. For the attrition loss analysis, the uniformity should have a good spread between the sizes declared by the vendor.

Attrition losses for all sorption media types analyzed range from 0.8 percent to 32.2 percent; two media (Bauxsol, Isolux) had inconclusive results due to their very small particle sizes. Among the media used in the Socorro Pilot, ArsenX$^{np}$ had the lowest attrition loss (0.8%); E33 (listed as AD33) had the highest loss (13%). Media with lower attrition losses are preferable for use; however, this analysis cannot accurately predict the attrition of media being used in a water system. The addition of water, pressure, and backwashing may increase attrition losses above these values. Proper backwashing practices may minimize additional media loss due to attrition.

### 3.2.4 *Conclusion*

The attrition loss analysis provided information on the different commercially-available media for arsenic that can be used in decisions on the most appropriate sorption media to use for pilot projects and long-term community use. Attrition losses for all sorption media types successfully analyzed ranged from 0.8 percent to 32.2 percent. High attrition losses indicate that media may be less effective and more expensive, due to increases in the frequency of maintenance and purchase of additional media. Potential generation of fine particles which clog the treatment columns must also be considered in media selection; this may be related to the coefficient of uniformity, which indicates the range of particle sizes.

## 3.3 Adsorption Kinetics in Socorro Springs Water

### 3.3.1 *Objectives*

Batch kinetic sorption studies were carried out to determine an appropriate reaction time for establishing equilibrium conditions in the development of sorption isotherms. A second objective was to determine if sorption rates at room temperature (about 15 $C^o$) differed appreciably from those at the water temperature expected in the pilot test (about 40 $C^o$).

### 3.3.2 *Materials and Methods*

The tested media were ground and washed with deionized water to obtain 325 x 400 mesh, except for the $ArsenX^{np}$ resin, which was used as received. Adsorption kinetic studies were carried out using 0.2000 or 0.010 g samples (0.200 g for $ArsenX^{np}$) in 1000 mL arsenic-doped Socorro groundwater at 15 or 40ºC using a temperature-controllable water bath. The doped Socorro waters were prepared by mixing ten liters of the Socorro groundwater (nominal arsenic concentration of 44 μg/L) with 660 μL of a 1000 ppm arsenic stock solution to produce a solution with a nominal arsenic concentration of 110 μg/L. The water sample was put in a 1500 mL double-layered glass jar with the water from water batch flowing through the spacing between the layers. The temperature of the water was monitored to reach to 15ºC or 40ºC before adding the sorbents. Aliquots of the sample (~5 mL) were collected at around 2, 5, 15, 30, 60, 120, 240, 480, 600 and 1440, 1680 and 1920 minutes using a 10-mL syringe and filtered through GHP Acrodisc 0.2-μm syringe filter. The water samples were then assayed for arsenic concentration using inductively coupled plasma mass spectrometry (ICP-MS).

Adsorption kinetics are related to many factors such metal ion concentration, temperature, sorbent concentration, the nature of the solute, etc For many adsorption processes occurring on heterogeneous materials, it has been found that chemisorption is the rate-controlling step (Reddad et al. 2002; Ho and McKay 1998, 2000). Such processes can be described with a pseudo-second-order kinetic equation in which the reaction rate is dependent on the concentration of sorbed species and the equilibrium concentration of the sorbed species. The pseudo-second-order kinetic rate equation can be expressed as (Ho and McKay 1998, 2000; Reddad et al. 2002):

$$dQt \ / \ dt = k(Q_{eq} - Q_t)^2 \qquad \text{(Eq. 3-2)}$$

where $Q_{eq}$ (mmol As/g media) is the sorption capacity at equilibrium; $Q_t$ (mmol As/g media) is the solid-phase loading of arsenate at time *t*; and *t* is time (min). The k (g/mmol∗min) is the pseudo-second-order rate constant for the kinetic model. Considering the boundary conditions of $Q_t = 0$ (at $t = 0$) and $Q_t = Q_{eq}$ (at $t = t_{large}$), the following linear equation can be obtained:

$$t/Q_t = 1/v_o + t/Q_{eq} \qquad \text{(Eq. 3-3)}$$

$$v_o = k*Q_{eq}^2 \qquad \text{(Eq. 3-4)}$$

where $v_o$ (mmol/g∗min) is the initial adsorption rate. Therefore, by plotting *t* versus $t/Q_t$, the $v_o$ and $Q_{eq}$ values can be determined.

### 3.3.3 *Results*

Figures 3-13 through 3-17 in Section 3.3.4 show the kinetics of arsenic adsorption on the media tested in Socorro groundwater. The results suggest that arsenic adsorption in Socorro groundwater under the selected experimental conditions was a fast process. The results show that a 24-hour equilibration period (1440 minutes) should be sufficient to establish steady state or equilibrium for sorption experiments using similar particle sizes and initial arsenic concentrations. This information was used in designing the sorption isotherm experiments described in the next section.

The results were fitted using the pseudo-second-order kinetic model (Equation 3-3) to estimate the rate constants, initial sorption rates, and adsorption capacities for arsenate. Relevant parameters are summarized in Table 3-3. The high fitting coefficients ($R^2$ ~0.999) indicated that the adsorption of arsenic on the tested media could be well described using the pseudo-second-order kinetic model. This suggests that with the crushed particle sizes used in this study, the rate controlling step can be attributed to chemisorption rather than mass transfer. Additional studies using different particle sizes or arsenic concentrations could be conducted to test this hypothesis.

Figures 3-13 to 3-17 show that approximately 75% to 95% of the initial arsenic in solution (about 110 ppb) was removed by the end of the 24-hr equilibration period. The final arsenic concentration at equilibrium therefore ranged from about 6 ppb to 28 ppb. The measured equilibrium sorption capacities $Q_{eq}$ for different media are relevant to slightly different arsenic concentrations; therefore, differences among them are hard to interpret solely in terms of properties of the media.

Representative results of the model fitting with the experimental data are presented in Figures 3-18 through 3-27 in Section 3.3.5. The adsorption kinetic curves and the initial adsorption rate ($v_o$) indicate that the arsenic adsorption is faster at the higher solution temperature (i.e., 40ºC) compared to 15ºC. Both the rate constants (k) and the initial sorption rates are higher at the elevated temperature; however, the equilibrium sorption capacities were relatively insensitive to

temperature. Rate constants and initial adsorption rates decrease in the order: Metsorb > Isolux > ARM 200 > E33 >> ArsenX$^{np}$. The sorption rate for Isolux 302M is the most sensitive to temperature. E33 showed the highest equilibrium sorption capacity in the kinetic tests.

These differences are potentially attributable to differences in the physical and chemical properties of the media (i.e., composition, pore size, surface area, surface charge, arsenic affinity, etc.). The initial rate appears to be related to the mode of the pore size distribution curve rather than surface area of average pore diameter (Metsorb has highest mode (~ 700 Å) in the differential pore size distribution curve in Figure 3-1 but relatively lower values of the other parameters.) The much lower rate constants for ArsenX$^{np}$ might be attributable to its larger particle size and lower pore volume and surface area. These may be artifacts of the degradation of the media during the measurement process. These adsorption kinetic parameters could be informative in predicting arsenic removal performance of the media in different groundwater. Additional analysis of the results could yield initial estimates of intraparticle diffusion coefficients and enthalpies of sorption reactions; however, this is beyond the scope of the present report.

**Table 3-3. Kinetic Parameters for Arsenic Adsorption in Socorro Groundwater Using Pseudo-Second-Order Kinetic Model.**

| Media | Temperature (°C) | $R^2$ | k | $V_o$ (x10$^{-3}$) | $Q_{eq}$ mmol/g | $Q_{eq}$ mg/g |
|---|---|---|---|---|---|---|
| E33 | 40 | 0.999 | 6.08 | 2.43 | 0.020 | 1.50 |
| | 15 | 0.998 | 3.45 | 1.38 | 0.020 | 1.50 |
| | | | | | | |
| ARM 200 | 40 | 0.999 | 11.70 | 3.38 | 0.018 | 1.35 |
| | 15 | 0.999 | 5.40 | 1.95 | 0.019 | 1.42 |
| | | | | | | |
| Isolux 302M | 40 | 0.999 | 20.45 | 5.91 | 0.017 | 1.27 |
| | 15 | 0.999 | 1.85 | 0.60 | 0.018 | 1.35 |
| | | | | | | |
| MetSorb | 40 | 0.999 | 20.54 | 7.42 | 0.019 | 1.42 |
| | 15 | 0.999 | 5.30 | 1.91 | 0.019 | 1.42 |
| | | | | | | |
| ArsenX$^{np}$ | 40 | 0.992 | 1.03 | 0.201 | 0.014 | 1.05 |
| | 15 | 0.992 | 0.57 | 0.111 | 0.014 | 1.05 |

$R^2$= Model-fitting coefficient;
K = The pseudo-second-order rate constant for the kinetic model (g/mmol∗min);
$v_o$ = Initial adsorption rate (mmol/g∗min);
$Q_{eq}$ = The sorption capacity at equilibrium (mmol$_{As}$/g) or mg/g.

### 3.3.4 *Adsorption Kinetic Curves*

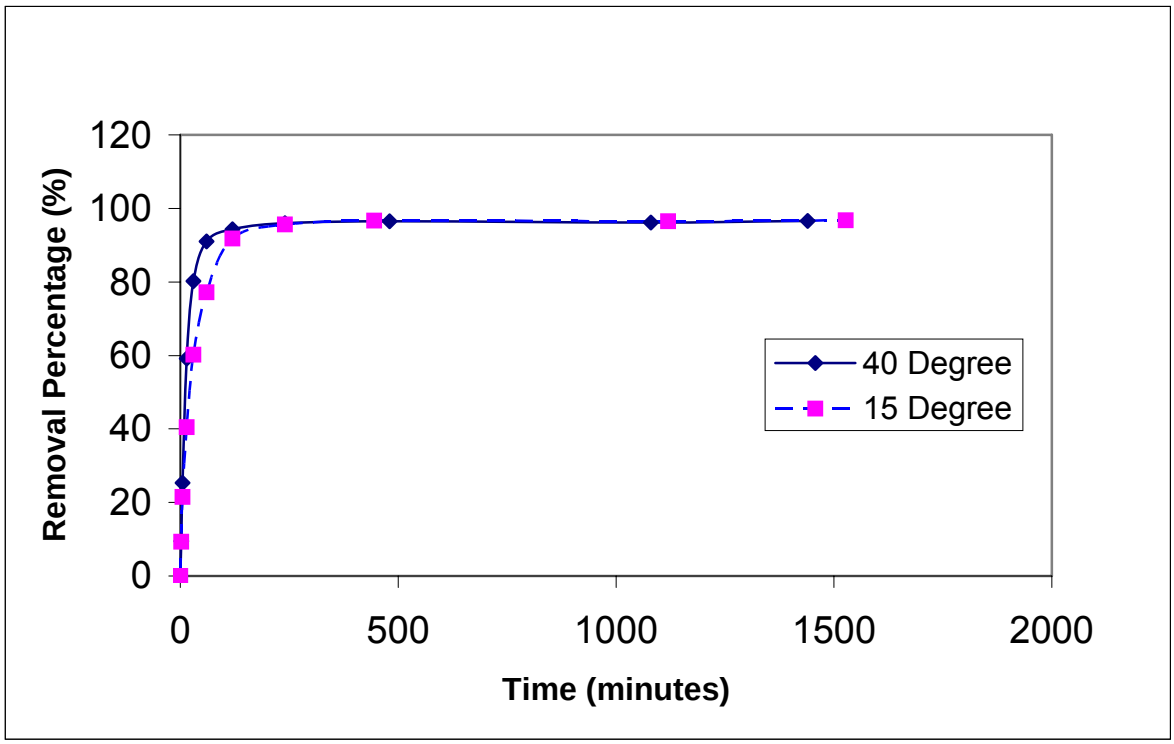



**Figure 3-13. Kinetics of As Removal by E33 at Two Temperatures.**

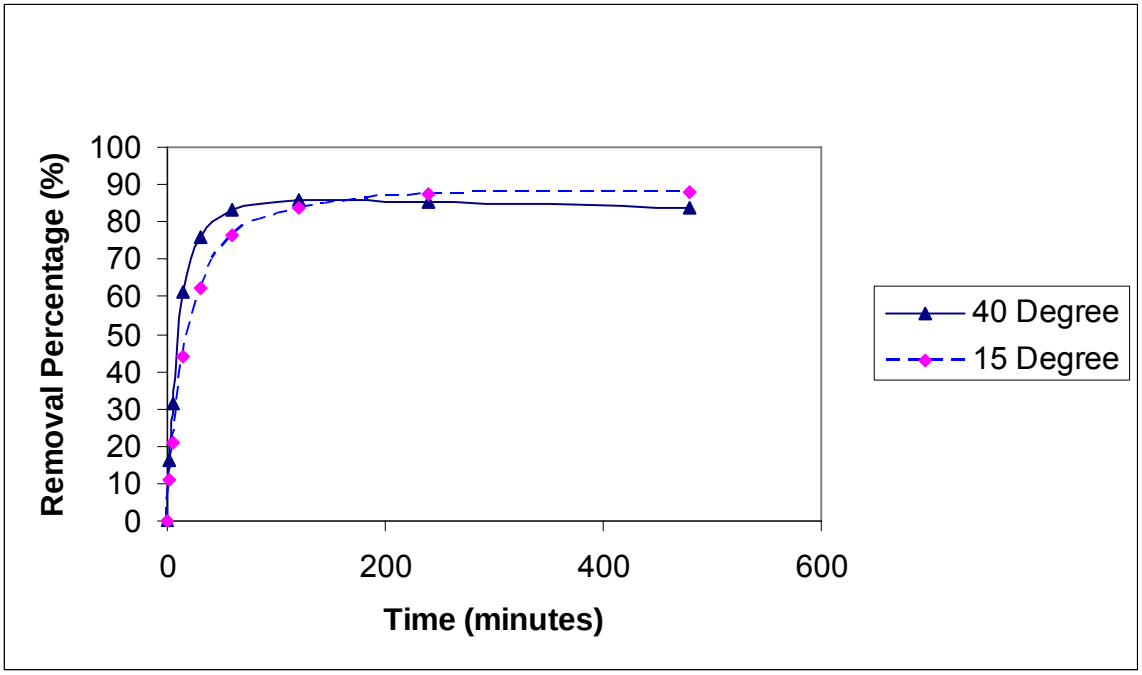



**Figure 3-14. Kinetics of As Removal by ARM 200 at Two Temperatures.**

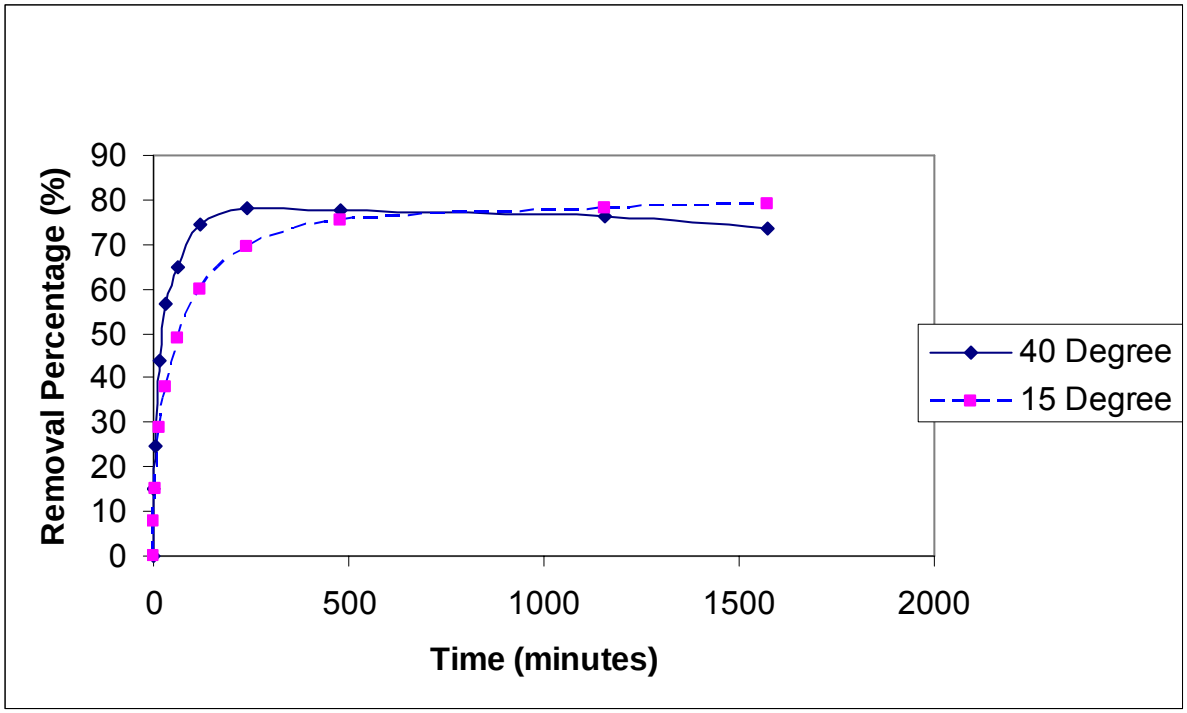



**Figure 3-15. Kinetics of As Removal by Isolux 302M at Two Temperatures.**

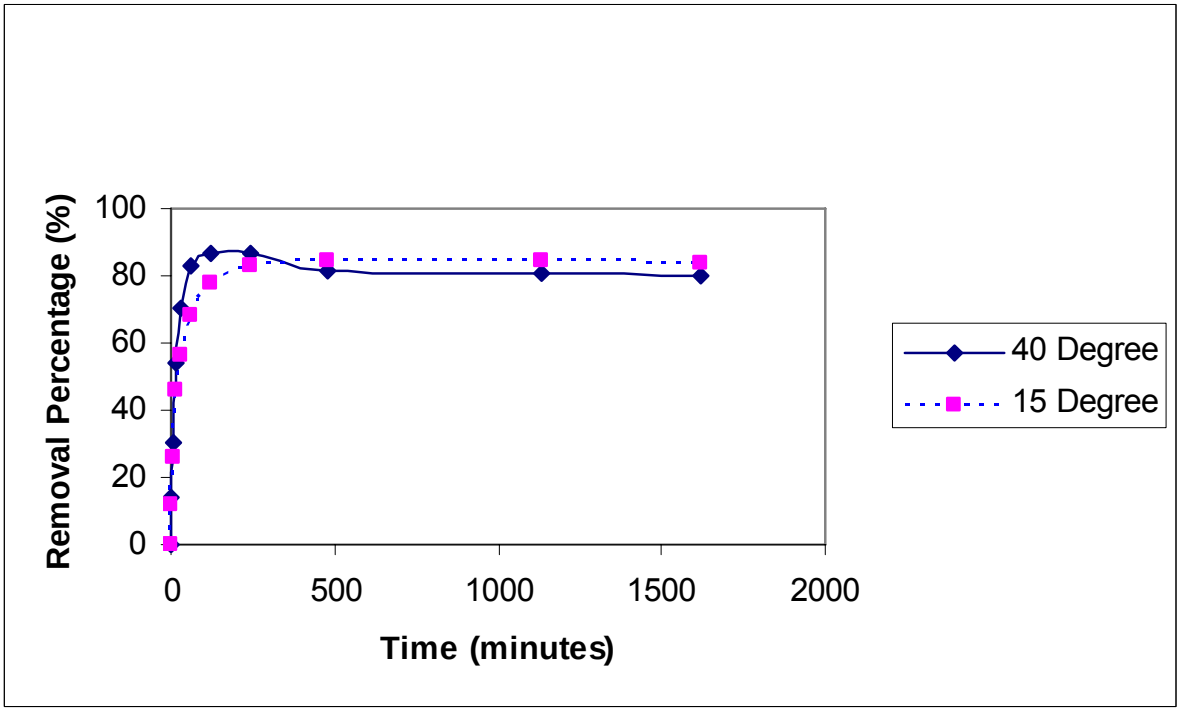



**Figure 3-16. Kinetics of As Removal by Metsorb at Two Temperatures.**

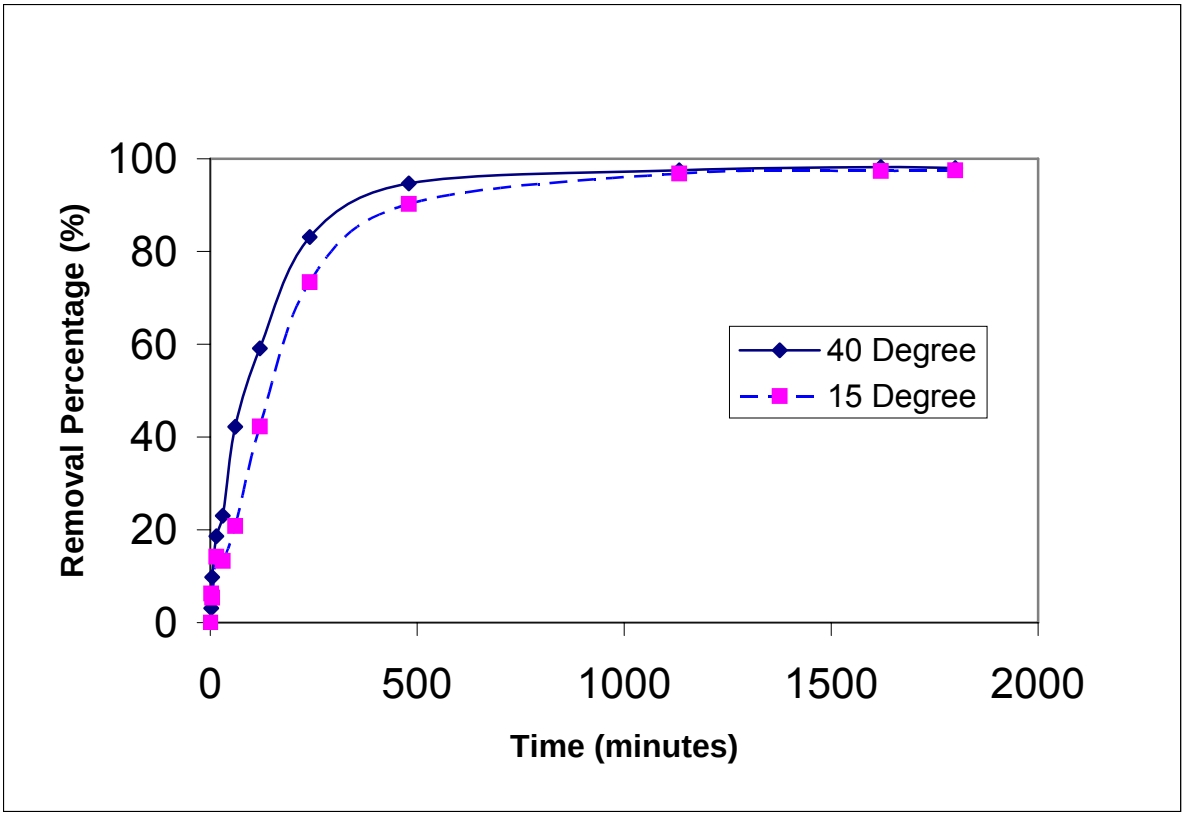



**Figure 3-17. Kinetics of As Removal by ArsenX$^{np}$ at Two Temperatures.**

### 3.3.5 *Illustrative Fitting by Using Pseudo-Second-Order Kinetic Model*

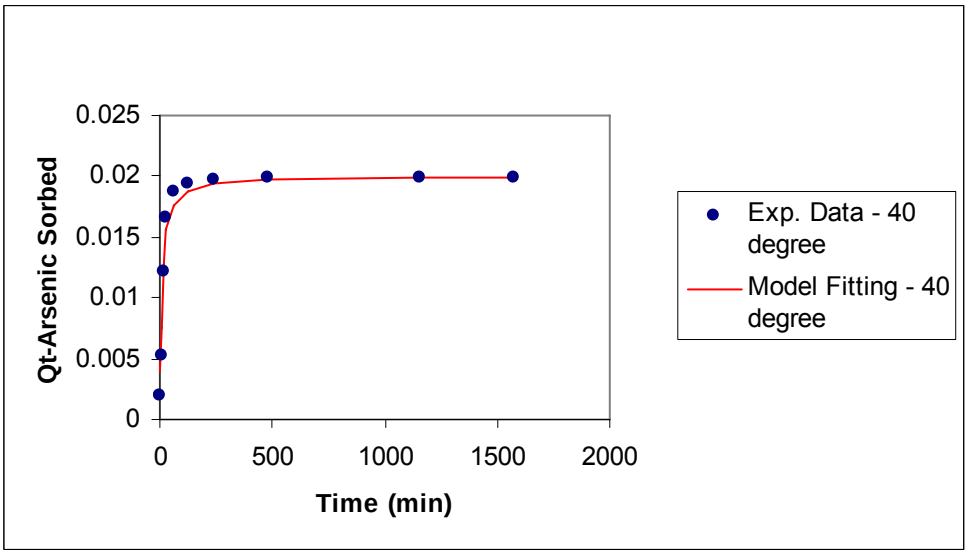



**Figure 3-18. Pseudo Second-Order Kinetic Model for As Sorption by E33 at 40°C.**

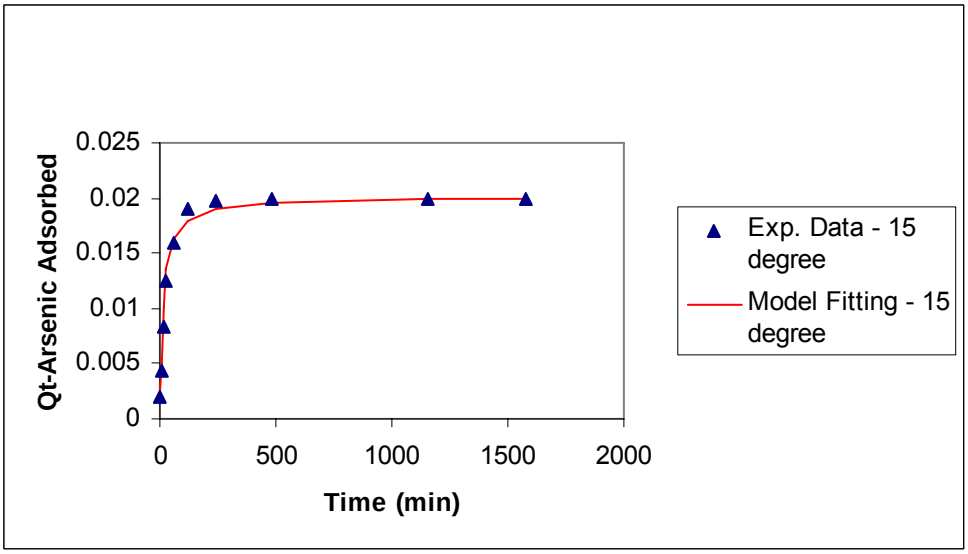



**Figure 3-19. Pseudo Second-Order Kinetic Model for As Sorption by E33 at 15°C.**

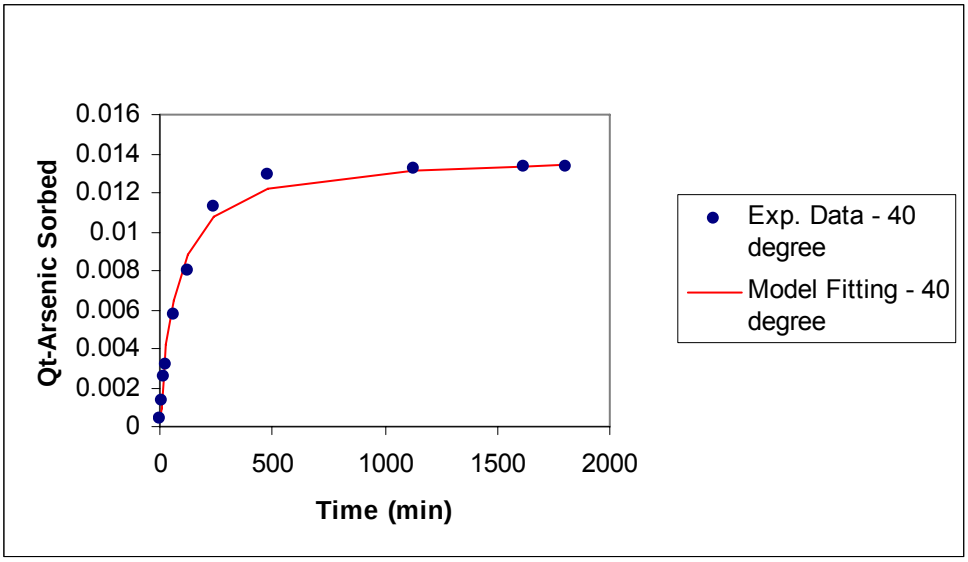



**Figure 3-20. Pseudo Second-Order Kinetic Model for As Sorption by ArsenX$^{np}$ at 40$^{o}$C.**

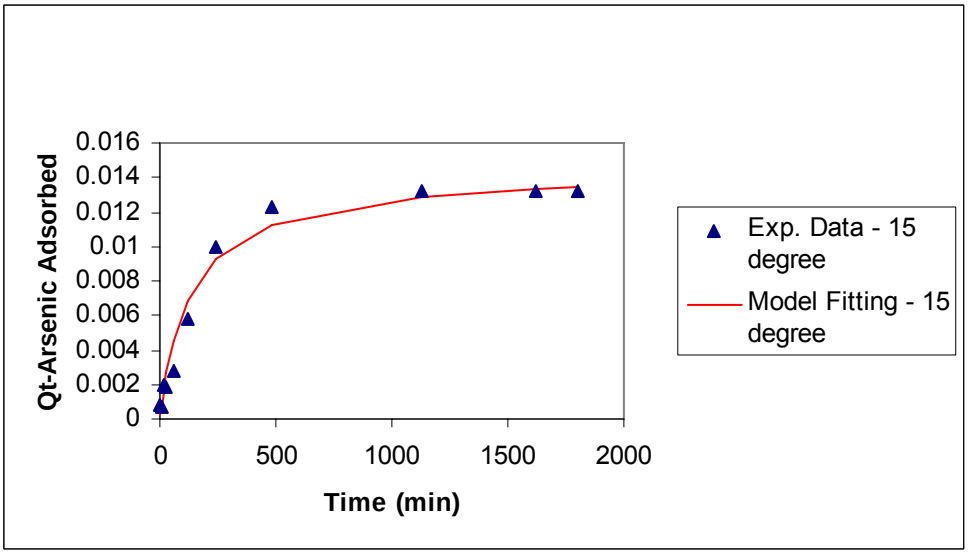



**Figure 3-21. Pseudo Second-Order Kinetic Model for As Sorption by ArsenX$^{np}$ at 15$^{o}$C.**

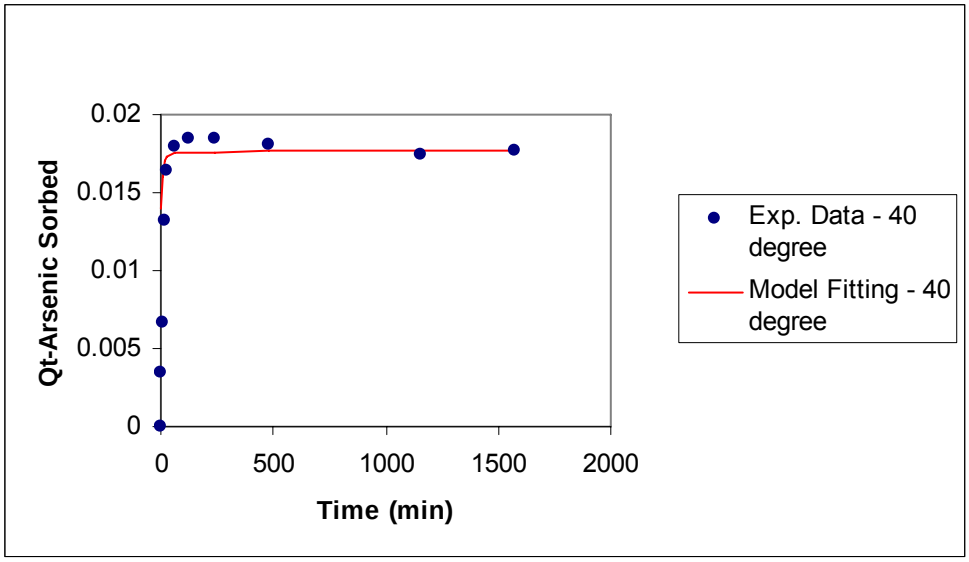



**Figure 3-22. Pseudo Second-Order Kinetic Model for As Sorption by ARM 200 at 40°C.**

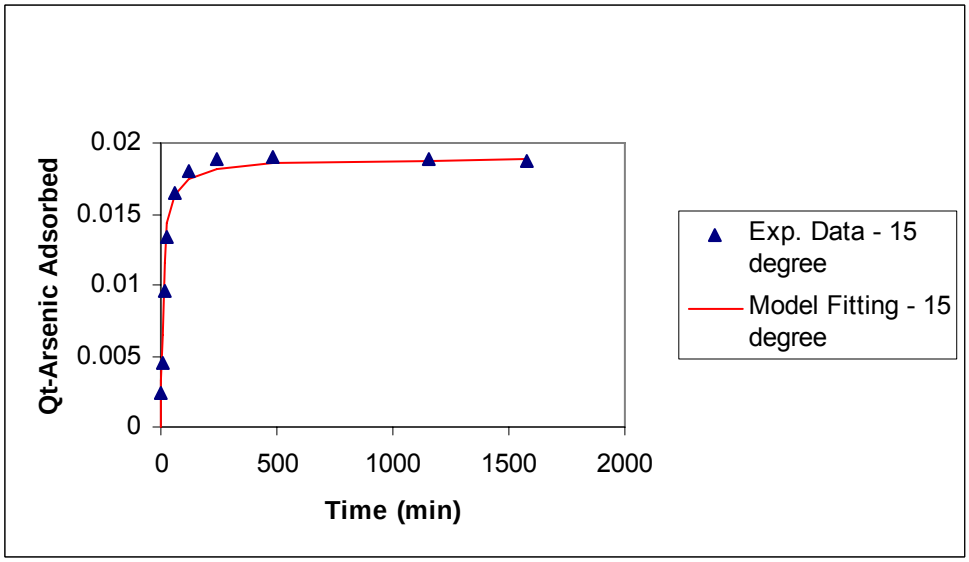



**Figure 3-23. Pseudo Second-Order Kinetic Model for As Sorption by ARM 200 at 15°C.**

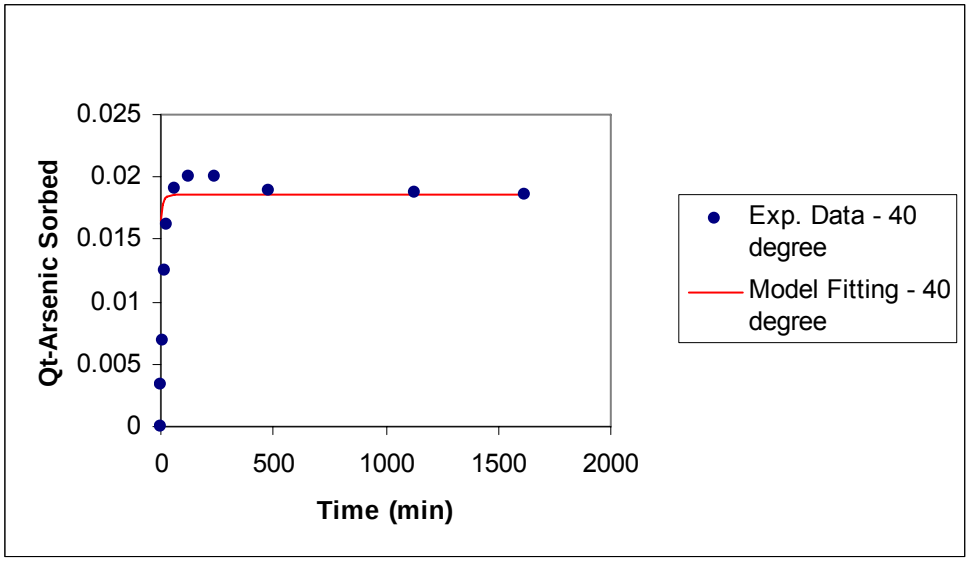



**Figure 3-24. Pseudo Second-Order Kinetic Model for As Sorption by Metsorb at 40°C.**

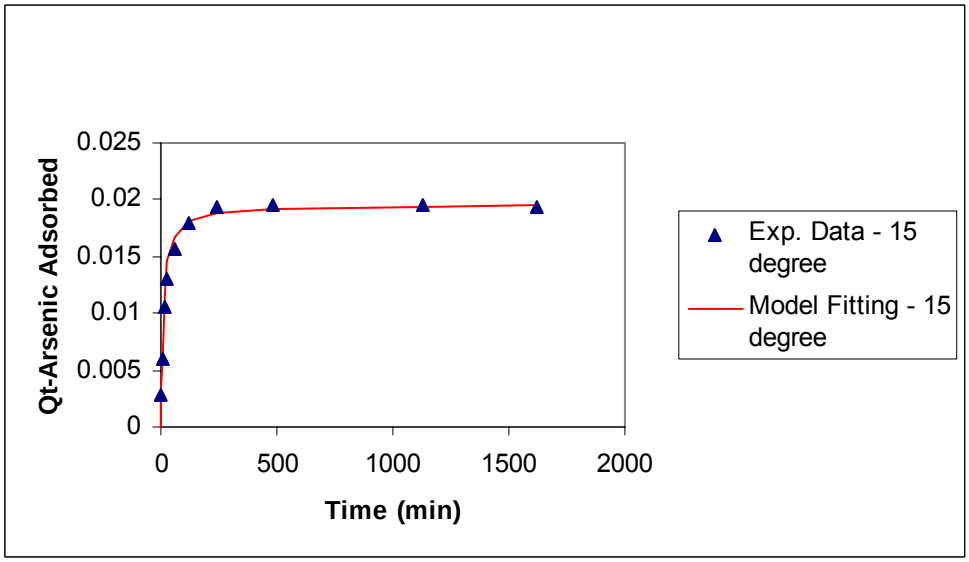



**Figure 3-25. Pseudo Second-Order Kinetic Model for As Sorption by Metsorb at 15°C.**

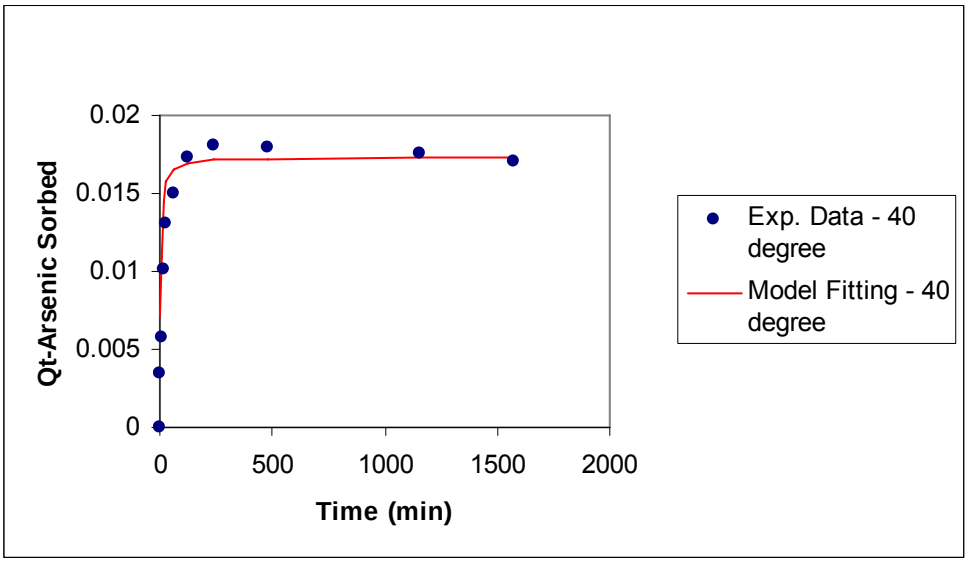



**Figure 3-26. Pseudo Second-Order Kinetic Model for As Sorption by Isolux 302M at 40°C.**

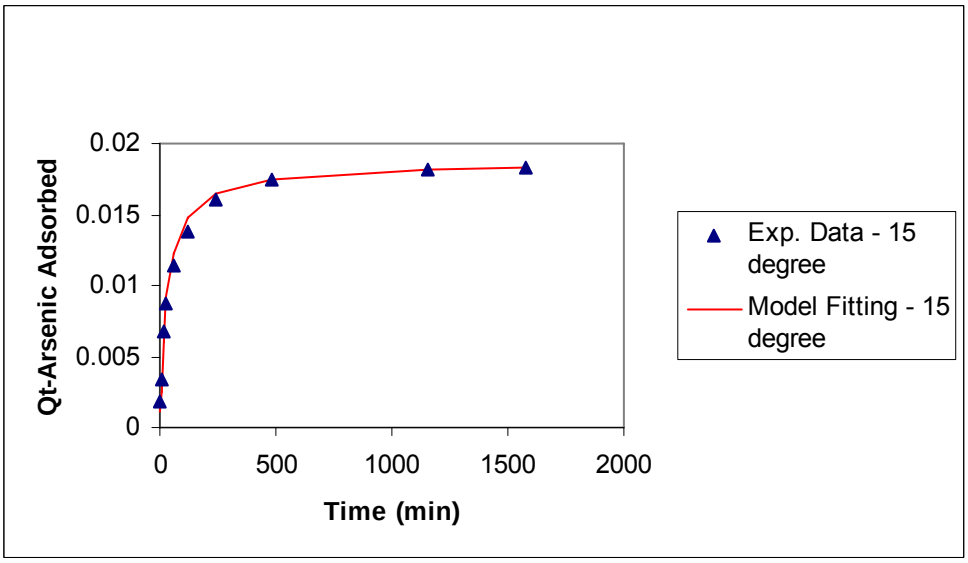



**Figure 3-27. Pseudo Second-Order Kinetic Model for As Sorption by Isolux 302M at 15°C.**

## 3.4 Isotherm Studies

Batch sorption studies were carried out to obtain isotherm parameters to estimate the capacity of the media at different influent concentrations. In general, the media were ground into smaller particles than were used in the pilot test in order to minimize the effects of mass transfer within the grains and thereby reduce the time required to reach steady state. The equilibration times were based on the kinetic studies described in the previous section.

### 3.4.1 *Media Preparation*

Raw metal oxide media was first ground with a mortar and pestle. After grinding, it was placed in a sieve shaker and thus, separated by its particle size. Sieve fractions were put into bottles and rinsed with distilled water. All of the wetted media, except for ArsenX$^{np}$ were dried at 105$^{o}$C overnight in an oven. After drying, samples were stored in bottles.

325 x 400 mesh particles were used for sorption experiments. Titrations with a strong base (1 N KOH) were performed to minimize potential pH drops during the equilibration due to acid residuals present on media surfaces from manufacturing. Five grams of each media sample were placed into a container and enough water was added to create slurry. Initial pH readings of the slurries were typically below pH = 7, and incremental doses of 0.3 mL of potassium hydroxide were added to solution to bring the slurries to a pH between 7 and 8 (bracketing the ambient pH of the utility water). Sufficient time (agitation overnight) was given to ensure a full surface reaction had occurred leading to a stable pH. If the pH dropped during this equilibration, the titration procedure was repeated.

The fully titrated slurries were placed in weighing trays and were air dried under a fume hood for a period of over two days. Each dry medium sample was placed into an individual storage container and was ready to use for sorption experiments.

### 3.4.2 *Sorption Experiments*

Ten one-liter stock solutions with initial arsenic concentrations ranging from ambient concentration (about 44 ppb [44 μg/L]) to 12 ppm (12 mg/L) were prepared from the sample utility water. The initial pH values of each of the ten one-liter stock solutions were recorded. Ten sample tubes containing initial concentration stock solutions were set aside for ICP-MS analysis.

For each media, a set of ten bottles was filled with approximately 50 mg of media and 40 mL of a specified initial concentration stock solution. Bottles were set for overnight agitation in a rotary agitator and were sampled approximately twenty-four hours after the beginning of agitation. (As described above, previous kinetic experiments on the media showed twenty-four hours to be a sufficient amount of time for equilibrium to occur).

The solution from each bottle was placed into a centrifuge for separation of the solids from the supernatant. The final pH in each bottle was recorded. The difference between the final and initial pH recordings was checked to ensure it was minimal. The supernatant was transferred into a sample tube via disposable syringe filters. The syringes and syringe filters were changed frequently to avoid cross-contamination of the samples. Final arsenic concentrations were measured by ICP-MS analysis.

### 3.4.3 *Data Analysis*

Data sets received from ICP-MS analysis consisted of initial and final arsenic concentrations from the sorption experiments. Final concentrations starting below 200 ppb were of interest for isotherm plots. $Q$, the amount of arsenic sorbed per mass of sorbent, was calculated from the following equation:

$$\frac{MassSorbed}{MassSorbent} = \frac{VolumeofSolution * (InitialAsConcentration - FinalAsConcentration)}{MediaMass} \quad \text{(Eq. 3-5)}$$

Isotherms were constructed with $Q$, the amount of arsenic sorbed (mg/kg), on the y axis and $C_{eq}$, equilibrium (final) arsenic concentrations (mg/L) on the x axis.

Three types of isotherms were plotted for each media. An equation for a linear isotherm was calculated from a linear regression of $Q$ and $C_{eq}$, with the following expression:

$$Q = k_d C_{eq} \quad \text{(Eq. 3-6)}$$

where $C_{eq}$ is proportional to $Q$ by a factor $k_d$ (L/kg).

An equation for a Freundlich isotherm was calculated from the linear regression of the logarithmic plot of $Q$ and $C_{eq}$, with the following expression:

$$Q = K_F C_{eq}^{nF} \quad \text{(Eq. 3-7)}$$

where the slope and the y-intercept of the logarithmic linear regression are equal to $n_F$ and $K_F$ (L/kg), respectively.

An equation for a Langmuir isotherm was calculated from the linear regression of the plot of $1/Q$ and $1/C_{eq}$, with the following expression:

$$Q = \frac{S_{\max} K_L C_{eq}}{1 + K_L C_{eq}} \quad \text{(Eq. 3-8)}$$

where the reciprocal of the y-intercept is equal to $S_{max}$ (mg/kg) and $\frac{1}{slope * S_{\max}}$ is equal to $K_L$ (L/mg).

These equations, with a chosen range of input $C_{eq}$ values, were plotted against the raw values of $C_{eq}$ and $Q$ to visually evaluate how accurately the isotherm equations fit the given data.

Table 3-4 summarizes the results of the isotherm experiments. The linear isotherm did not fit any of the isotherm data well ($R^2 < 0.66$) and were not considered any further. For two of the media, non-physical (negative) $S_{max}$ were obtained for the Langmuir plots and are noted as N/A in the table. Isotherm plots for all of the media are available in an Excel file from the first author. Note: In this table, sorption capacities are expressed in units of mg/kg to maintain consistency with units used in the experimental work; capacities are converted to units of mg/g when used in all other tables by multiplying by a factor of 0.001.)

**Table 3-4. Results of Isotherm Experiments.**

| **Isotherm** | **Freundlich $Q=K_FC^{nF}$** | | | | | **Langmuir $Q=(S_{max}K_LC)/(1+K_LC)$** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Media** | **$K_F$** | **$n_F$** | **$R^2$** | **$Q_{10ppb}$** | **$Q_{40ppb}$** | **$S_{max}$** | **$K_L$** | **$R^2$** | **$Q_{10\ ppb}$** | **$Q_{40\ ppb}$** |
| E33 | 21,000 | 0.31 | 0.997 | 4,970 | 7,670 | 10,000 | 300 | 0.960 | 7,500 | 9,230 |
| ARM 200 | 50,000 | 0.57 | 0.974 | 3,580 | 7,910 | 10,000 | 100 | 0.992 | 5,000 | 8,000 |
| ArsenX$^{np}$ | 57,000 | 0.55 | 0.925 | 4,630 | 9.860 | 14,000 | 70 | 0.983 | 5,770 | 10,320 |
| Isolux 302M | 92,700 | 0.77 | 0.881 | 2,670 | 7,770 | N/A | N/A | N/A | N/A | N/A |
| Metsorb | 75,800 | 0.90 | 0.937 | 1,180 | 4,130 | N/A | N/A | N/A | N/A | N/A |

N/A = not applicable
$S_{max}$ and Q=mg/kg; $Q_{10ppb}$ and $Q_{40ppb}$ refer to sorbed concentration at 10 ppb and 40 ppb As $C_e$ in solution, respectively, and were calculated from the isotherm equations.
$K_F$ = L/kg or ml/g; $K_L$ = L/mg.

## 3.5 RSSCT Studies

### 3.5.1 *Theory*

Laboratory studies to predict media performance of pilot-scale adsorption columns were conducted using rapid small-scale column tests (RSSCTs). RSSCTs are scaled-down columns packed with smaller diameter adsorption media that receive higher hydraulic loading rates to significantly reduce the duration of experiments. Results for RSSCTs can be obtained in a matter of days to a few weeks, whereas pilot tests can take a number of months to over a year.

This method uses scaling relationships that allow correlation of lab-scale column results operated at accelerated flow rates to full-scale column performance. The RSSCT concept is based upon a theoretical analysis of the adsorption processes that govern performance including solution and surface mass transport and adsorption kinetics. Mass transfer models have been used to determine dimensionless parameters that establish similitude between the small- and large-scale columns.

If perfect similitude is maintained, the RSSCTs will have breakthrough profiles that are identical to full-scale columns (Crittenden et al. 1987a). Two mass transfer models are most frequently used to model adsorption columns, the dispersed flow pore and surface diffusion model

(DFPSDM) and the homogeneous surface diffusion model (HSDM). The most general model, the DFPSDM, includes pore diffusion and surface diffusion, as well as axial dispersion. This model includes many of the known transport and kinetic phenomena that occur in fixed bed adsorbents; therefore, a dimensional analysis allows the development of scaling factors. The HSDM models surface diffusion while neglecting pore diffusion and axial dispersion. It has been shown that surface diffusion is much greater than pore diffusion for strongly adsorbed species (Hand et al. 1983); therefore, the contribution of pore diffusion to the adsorbate transport has been neglected.

Crittenden et al. (1987a, 1987b, 1991) developed scaling equations for both constant and non-constant diffusivities with respect to particle size. The scaling laws ensure that the RSSCT and the full-scale system will have identical breakthrough profiles. The basis for the RSSCT scaling laws is described below; variables are defined in Table 3-5; definitions of the terms are given in papers cited above.

**Table 3-5. Definition of Terms for RSSCT Scaling Equations**

| | |
|---|---|
| $D_s$ | Surface diffusion coefficient, $L^2/T$ |
| $EBCT$ | Empty bed contact time, $T$ |
| $k_f$ | Film transfer coefficient, $L/T$ |
| $LC$ | Subscript denoting large column |
| $R$ | Particle radius (geometric mean), $L$ |
| $Pe$ | Peclet number (dimensionless) |
| Re | Reynolds number (dimensionless) |
| $SC$ | Subscript denoting small column |
| $Sc$ | Schmidt number (dimensionless) |
| $x$ | Diffusivity factor (dimensionless) |
| $\varepsilon$ | Void fraction (dimensionless) |
| $\mu$ | Viscosity of the fluid, $M/LT$ |
| $v$ | Superficial velocity (hydraulic loading, Darcy velocity), $L/T$ |

By equating the modulus of surface diffusivity and assuming equal solute distribution parameters, a relationship between EBCTs for small- and large-scale columns is determined:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^2 \frac{D_{s,LC}}{D_{s,SC}} \qquad \text{(Eq. 3-9)}$$

The dependence of the surface diffusion coefficient on particle radius is defined by the diffusivity factor, x, as follows:

$$\frac{D_{s,SC}}{D_{s,LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^{x} \qquad \text{(Eq. 3-10)}$$

Combining these equations yields:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^{2-x} \qquad \text{(Eq. 3-11)}$$

A special case of non-constant diffusivity is a linear relationship between surface diffusivity and particle size (proportional diffusivity, PD). The diffusivity factor, x, becomes equal to one and the ratio of EBCTs becomes:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{R_{SC}}{R_{LC}} \qquad \text{(Eq. 3-12)}$$

A minimum value of $Re_{SC}$ is required to establish a minimum velocity that will not over exaggerate the effects of dispersion and external mass transfer. If the small and large columns maintain a constant ratio of their respective Reynolds numbers, the following relation is established:

$$\frac{\mathrm{Re}_{SC,\min}}{\mathrm{Re}_{LC}} = \frac{2v_{SC}R_{SC}/\mu\varepsilon}{2v_{LC}R_{LC}/\mu\varepsilon} \qquad \text{(Eq. 3-13)}$$

Canceling terms and rearranging gives the ratio of the hydraulic loading of the two columns:

$$\frac{v_{SC}}{v_{LC}} = \frac{R_{LC}}{R_{SC}}\frac{\mathrm{Re}_{SC,\min}}{\mathrm{Re}_{LC}} \qquad \text{(Eq. 3-14)}$$

Berrigan (1985) showed that dispersion was not important if the product of the Reynolds and Schmidt numbers was in the mechanical dispersion region; therefore, the ratio of hydraulic loadings could be calculated using:

$$\frac{v_{SC}}{v_{LC}} = \frac{R_{LC}}{R_{SC}}\frac{\mathrm{Re}_{SC,\min}\,Sc_{SC}}{\mathrm{Re}_{LC}\,Sc_{LC}} \qquad \text{(Eq. 3-15)}$$

A requirement for using this equation is that the small-scale column Peclet number ($Pe_{SC}$) must be greater than or equal to $Pe_{LC}$; otherwise, a reduction in the hydraulic loading may cause a significant amount of dispersion in the RSSCT.

If the surface diffusivity remains constant with respect to the particle radius (constant diffusivity, CD), then the diffusivity factor, x, is equal to zero and the ratio of EBCTs for small columns and large columns is:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^2 \qquad \text{(Eq. 3-16)}$$

The Stanton and Peclet numbers remain equal between the small scale and full-scale columns only if the surface diffusivity is independent of particle size. If Stanton numbers are identical between process sizes, then the liquid phase mass transfer coefficients can be related to particle radius by:

$$\frac{k_{f,SC}}{k_{f,LC}} = \frac{R_{LC}}{R_{SC}} \qquad \text{(Eq. 3-17)}$$

If this is the case, the hydraulic loading of the columns is inversely proportional to particle size (Crittenden et al. 1987a):

$$\frac{v_{SC}}{v_{LC}} = \frac{R_{LC}}{R_{SC}} \qquad \text{(Eq. 3-18)}$$

This relationship will provide equality between Reynolds numbers for both process sizes.

### 3.5.2 *Methods*

RSSCTs were scaled down from the pilot test scale and designed using both proportional diffusivity and constant diffusivity scaling equations. Design parameters for the pilot test scale and RSSCTs are shown in Table 3-6.

**Table 3-6. Comparison of Design Parameters for Pilot-Scale and Small-Scale Column Studies for Socorro, NM.**

| Parameter | Pilot Scale | RSSCT | Units |
|---|---|---|---|
| Column Diameter | 7.6<br>(3) | 1.0<br>(0.4) | cm<br>(in) |
| Particle Diameter | 0.25-2.0 | 0.15-0.18 | mm |
| EBCT | 2-5 | 0.05-0.9 | min |
| Bed Height | 50-130<br>(20-50) | 8-30<br>(3-12) | cm<br>(in) |
| Flow Rate | 1100-1900<br>(0.3-0.5) | 20-120<br>(0.005-0.03) | mL/min<br>(gpm) |
| Hydraulic Loading Rate | 24-32<br>(6-8) | 15-125<br>(3-32) | cm/min<br>(gpm/ft$^2$) |

Actual EBCTs for the PD test columns were as follows: E33 – 0.23 min, 0.38 min, 0.50 min; ARM 200 – 0.42 min; ArsenX$^{np}$ – 0.28 min; Metsorb – 0.39 min Actual EBCTs for the CD test columns were as follows: E33 – 0.007 min, 0.014 min, 0.017 min; ARM 200 – 0.019 min; Metsorb – 0.023 min.

### 3.5.3 *Results*

Breakthrough curves for the media studied are shown in Figure 3-28 and Figure 3-29. PD, CD and Pilot data are shown for comparison.

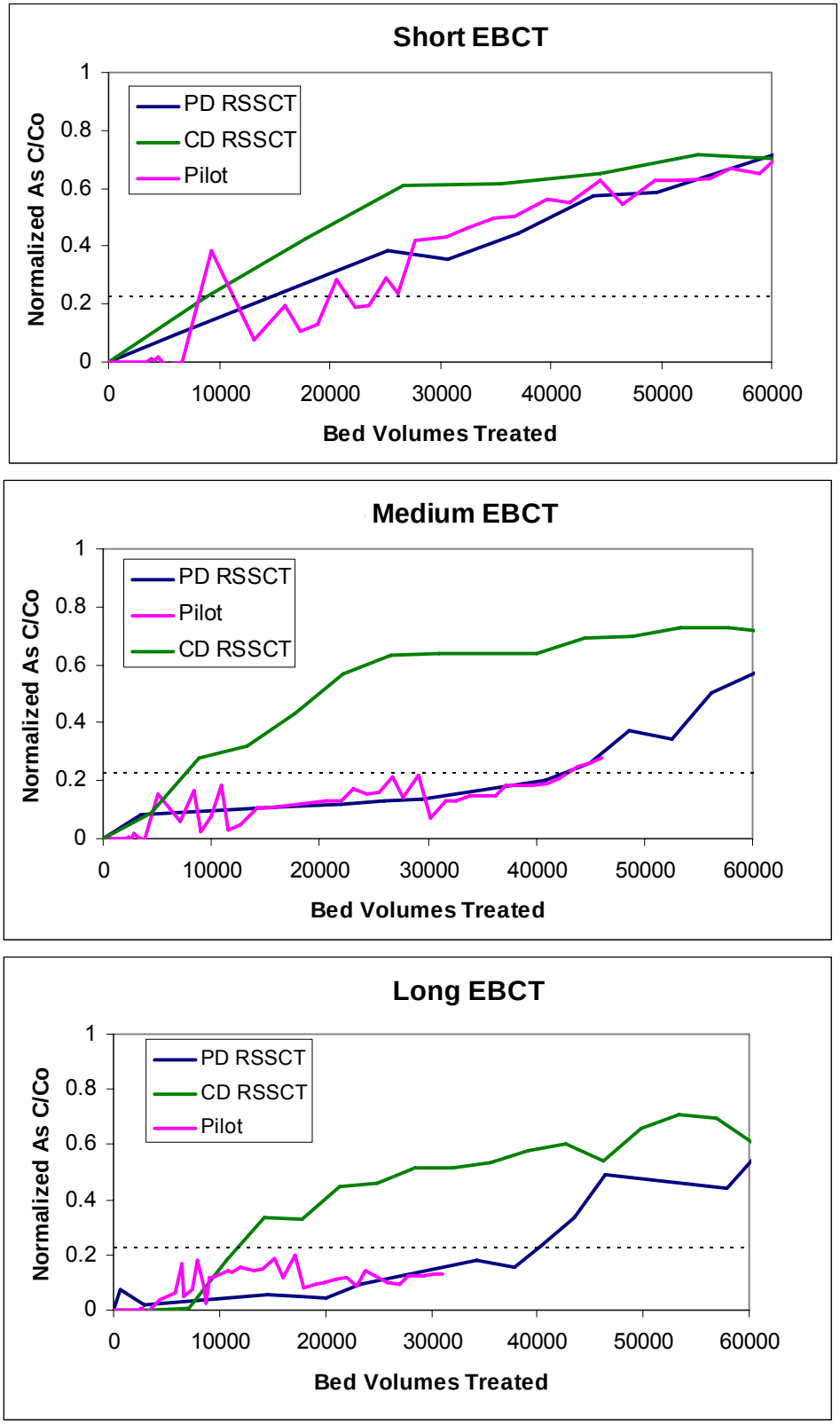



**Figure 3-28. Breakthrough Curves for Adedge (E33) Media for Three Different EBCTs.**

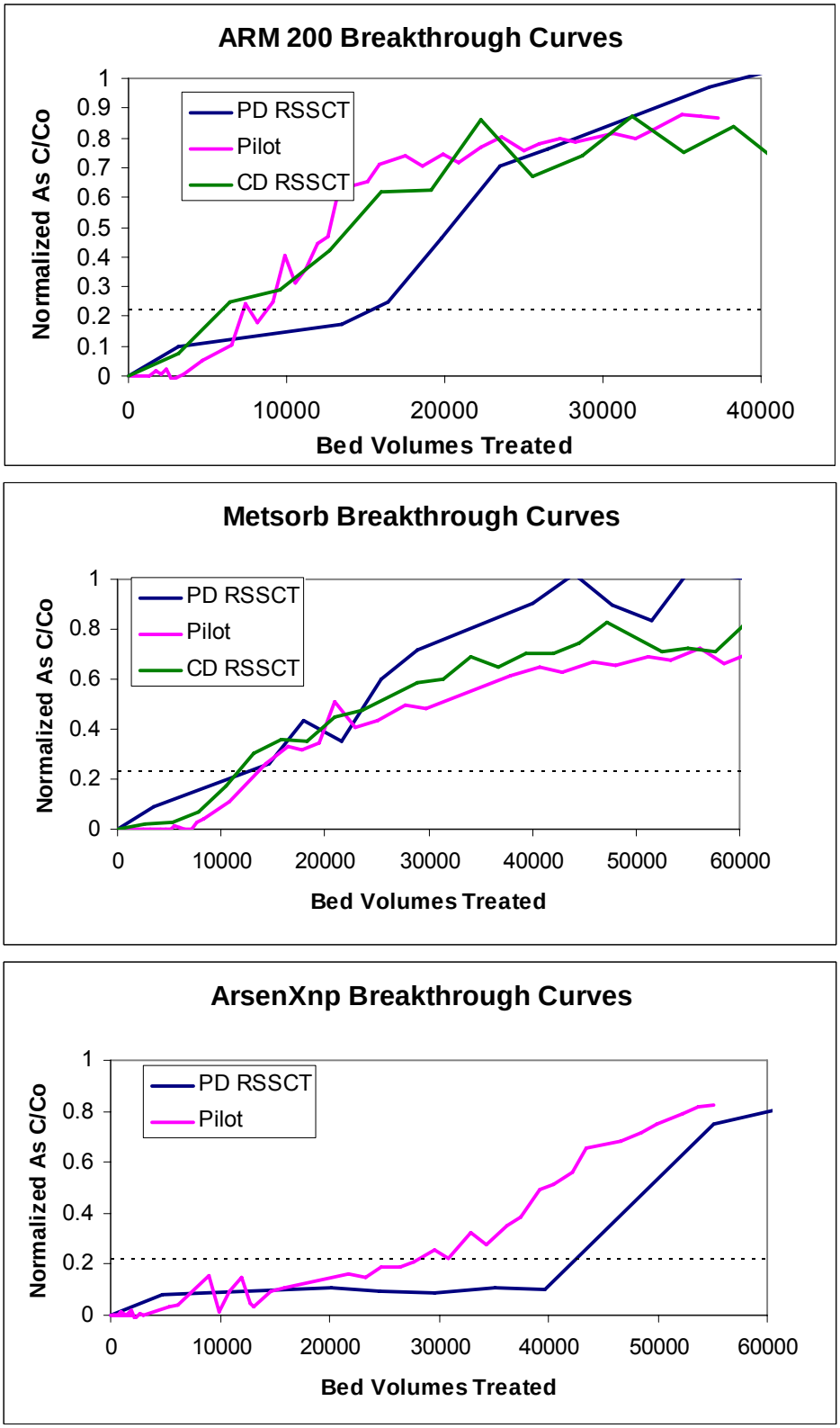



**Figure 3-29. Breakthrough Curves for ARM 200, Metsorb, and ArsenX$^{np}$ Media.**

### 3.5.4 *Discussion of RSSCT Results*

Table 3-7 summarizes the results of the RSSCT experiments shown in the above figures. In the table, the values of BV to 10 ppb (10 μg/L) are read from the BTC. The estimates of the concentration of arsenic (mg As/g media) in the adsorptive media (capacity) at 10 ppb (10 μg/L), 35,000 BV and $C/C_o = 0.8$ and $C_e = C_o$ (where the influent ($C_o$) and effluent ($C_e$) concentrations are equal) are also shown. The capacities are calculated from mass balance on arsenic data by integration of area above the BTC and below the influent arsenic concentration. These may be a more unbiased measure of sorption than the BV value as discussed below. The capacity at 10 ppb (10 μg/L) is calculated from raw data from BV = 0 to the point in the BTC where the arsenic concentration in the effluent ($C_e$) reached and stayed above 10 ppb (10 μg/L). The capacity at 35K BV is calculated from the raw data in a similar manner over the range from BV = 0 to where BV reached 35000. Lower limits for several of the parameters are listed in the table because the experiments were terminated before full or 80% capacity of the columns was reached.

It can be seen from inspection of Figures 3-28 and 3-29 and Table 3-7 that the number of BVs of influent, passing through the column until a target concentration is reached in the effluent, can be hard to estimate if the data are noisy. Thus, the number of BVs until breakthrough can be a very imprecise measure of the arsenic adsorption capacity of the media. This imprecision can also affect estimates of the capacity calculated from mass balance using the area above the BTCs. In particular, the uncertainty was very large in estimating the breakthrough and sorption capacity for the test of E33 with an EBCT of 0.23 min (corresponding to a 2-min EBCT in the pilot) leading to values for capacity that are not consistent with the results from the other E33 columns.

## Table 3-7. Results of RSSCT Experiments.

| | | E33 | | | ARM 200 | Metsorb |
|---|---|---|---|---|---|---|
| | | **0.007 [a] (2) [b]** | **0.0141 [a] (4) [b]** | **0.0171 [a] (5) [b]** | **0.0019 [a]** | **0.023 [a]** |
| CD RSSCT | BV to 10 ppb (10 μg/L) | 9000 | 7700 | 11700 | 6000 | 11500 |
| | Capacity at 10 ppb, mg/g | 1.25 | 0.72 | 1.18 | 0.42 | 0.66 |
| | Capacity at 35K BV, mg/g | 1.95 | 1.93 | 2.25 | 1.21 | 1.30 |
| | $C/C_o$ at 35K BV | 0.62 | 0.63 | 0.53 | 0.75 | 0.67 |
| | BV until $C_e = C_o$ | >370000 | >190000 | >150000 | >140000 | > 65000 |
| | Capacity at $C_e = C_o$, mg/g | > 9.60 | > 4.94 | > 4.63 | > 2.08 | > 1.72 |
| | BV at $C/C_o = 0.8$ | >370000 | 80000 | 97000 | 44000 | > 65000 |
| | Capacity at $C/C_o$ = 0.8, mg/g | > 9.6 | 3.06 | 3.83 | 1.35 | > 1.72 |

| | | E33 | | | ARM 200 | Metsorb | ArsenX$^{np}$ |
|---|---|---|---|---|---|---|---|
| | | **0.23 [a] 2 [b]** | **0.38 [a] 4 [b]** | **0.50 [a] 5 [b]** | **0.42 [a]** | **0.39 [a]** | **0.28 [a]** |
| PD RSSCT | BV to 10 ppb (10 μg/L) | 15400 | 43000 | 41000 | 16300 | 12800 | 43000 |
| | Capacity at 10 ppb, mg/g | 1.95 | 3.39 | 3.07 | 3.82 | 0.69 | 1.33 |
| | Capacity at 35K BV, mg/g | 2.66 | 3.11 | 2.89 | 5.45 | 1.24 | 0.94 |
| | $C/C_o$ at 35K BV | 0.42 | 0.17 | 0.17 | 0.93 | 0.82 | 0.11 |
| | BV until $C_e = C_o$ | 225000 | 180000 | 113000 | 39000 | 68000 | 76000 |
| | Capacity at $C_e = C_o$, mg/g | 5.08 | 5.61 | 5.02 | 5.46 | 1.31 | 1.38 |
| | BV at $C/C_o = 0.8$ | 94000 | 82000 | 83000 | 27000 | 40000 | 60000 |
| | Capacity at $C/C_o$ = 0.8, mg/g | 4.26 | 4.68 | 4.71 | 5.07 | 1.24 | 1.37 |

a EBCT (min) for RSSCT columns.
b EBCT(min) for equivalent E33 pilot scale column; EBCTs for ARM 200, Metsorb, and ArsenX$^{np}$ pilot columns were 4, 2 and 3 minutes, respectively.

# 4.0 DISCUSSION

## 4.1 Controls on Adsorption of Arsenic in Fixed Bed Media

One of the objectives of the study is to determine the most efficient way to predict the absolute and relative sorption capacities of different arsenic adsorptive media for community water systems.

To a first approximation, the effectiveness of fixed bed adsorptive media for arsenic removal depends on six factors:

1) chemical nature of the adsorbent affecting its ability to form electrostatic or specific chemical bonds with arsenic oxyanions;
2) pH of the solution;
3) redox speciation of As (i.e., As(III)/As(V) ratio);
4) concentration of aqueous species that will interfere with adsorption of arsenic by competing for adsorption sites or modifying adsorptive media surface charge, or physically blocking access of arsenic to the interior of the particles or grains of adsorptive media;
5) surface area and pore size distribution of the adsorptive media; and
6) hydraulic properties of the media during treatment.

This study addressed the first factor by examining the arsenic sorption capacity of five different metal oxyhyroxide media exhibiting a range of chemical compositions. The next three of the above factors are linked by chemical equilibria between the various aqueous species in the water entering treatment media. They are properties of the groundwater and because a single groundwater composition was used, they were not examined in this study. (Other pilot studies are being conducted in other groundwaters with different compositions so these effects will be evaluated at a later time in this program.)

The last two factors are affected primarily by physical mass transfer processes and media properties. The use of different media with contrasting physical properties in this work allowed some study of the influence of the properties on adsorption.

### 4.1.1 *Chemical Controls*

In this study, the adsorption of arsenic by media containing $\alpha$–FeOOH (E33, ArsenX$^{np}$?), $\alpha$–$Fe_2O_3$ (ARM 200?), $TiO_2$, and $ZrO_2$ (Isolux 302M) was compared. Table 4-1 lists the pH of the zero point of charge (ZPC) of several metal oxide sorbents commonly used as fixed bed adsorbents for arsenic. Above the pH of the ZPC, the surface has a net negative charge, and there will be an electrostatic repulsion between an anionic species and the surface. If sorption is to occur by a specific chemical bond, this repulsion must be overcome. At pHs typical of natural waters, arsenate is negatively charged; above a pH of about 9, arsenite also exists predominantly as an anionic species. Arsenate is more strongly sorbed and is more affected by pH over the pH

range 4 – 9 compared to arsenite; above pH of about 9, arsenite sorption is predicted to be relatively higher than that of arsenate. The pH of the chlorinated water used in the Socorro Springs pilot is about 8. Although the properties of the model metal oxides in the table may differ from the mixed oxyhydroxides that comprise the adsorptive media used in this study, some general sorption trends may be the same. Thus, the oxyanion arsenate is the dominant species in these studies and to be sorbed, must likely overcome a negative surface charge for $\alpha$–FeOOH (E33, ArsenX$^{np}$?), and $TiO_2$ (Metsorb), but perhaps not for $ZrO_2$ (Isolux 302M) or $\alpha$–$Fe_2O_3$ (ARM 200?).

**Table 4-1. pH of Zero Point of Charge ($pH_{ZPC}$) for Metal Oxyhydroxides Used in Arsenic Treatment.***

| oxide | $Al(OH)_3$ | $TiO_2$ | $\alpha$FeOOH | $\alpha Fe_2O_3$ | CuO | $La_2O_3$ | $ZrO_2$ |
|---|---|---|---|---|---|---|---|
| $pH_{ZPC}$ | 5-9.1 | 6.7 | 6.7 | 9.0 | 9.4 | 10.4 | 10-11 |

* from Yoon et al. 1979

## 4.1.2 *Physical Controls*

Figure 4-1 describes important physical processes involved in uptake of arsenic by adsorbent media. Note the concentration axes on the right side of the figure. The concentration of arsenic decreases from $c_b$ in the bulk solution, to $c_s$ at the fluid solid interface, to $c_p$ in the pores, as q, the concentration in the solid, increases. In dynamic systems, such as fixed bed treatment systems, the effectiveness of arsenic adsorption is dependent on the relative rates of several processes. These include: 1) kinetics of chemical surface complexation; 2) the kinetics of mass transfer of arsenic to the interior of the grains, and 3) the hydraulic loading rate (flow rates). The effectiveness of treatment will be highest when the arsenic species form specific chemical bonds quickly to reactive surfaces and the flow rate is low enough to allow arsenic species to migrate to fresh sorption sites in the grain interiors. High surface area and a uniform pore distribution with a mean pore size large enough to allow diffusion of the aqueous species lead to high sorption capacity.

In a flowing system, the balance between these rates is expressed by the shape of the mass transfer zone in which the concentration of the arsenic drops from its initially high value to a lower value corresponding to equilibrium sorption. In the current application to drinking water treatment, the adsorbent bed must be replaced or regenerated when the concentration of arsenic in the effluent exceeds the MCL (10 $\mu$g/L). Under favorable conditions where diffusion into the grain interior is rapid relative to hydraulic loading rate, the mass transfer zone will be relatively sharp, and a large fraction of the potential sorption capacity of the media will be utilized before replacement is warranted. Under unfavorable conditions, the mass transfer zone will be broad, the arsenic concentrations in the effluent will rise rapidly above the MCL, and most of the adsorbent bed will not adsorb arsenic before it needs to be replaced.

Different techniques (materials characterization, batch isotherm, batch kinetic, and RSSCT column) were used to examine these different chemical and physical effects in an attempt to determine which method would be most effective in predicting arsenic removal in the pilot scale tests.

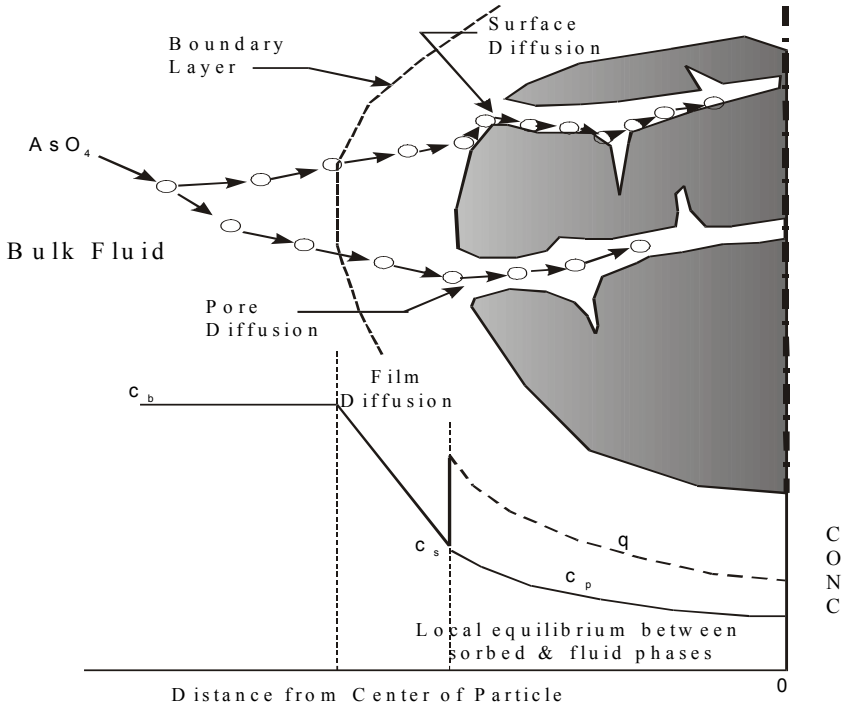



**Figure 4-1. Processes Controlling Transport of Arsenic from Bulk Solution to Interior of Granular Adsorbent Media (Crittenden 1987b).**

## 4.2 Comparison of Estimates of Media Performance Using Batch and Dynamic Tests

In this study, five methods were used to estimate the likely performance of adsorbent media in a full-scale treatment system at Socorro Springs: two batch sorption isotherms, two RSSCTs and pilot scale tests. Results from all five methods are summarized below and shown in Table 4-2. Examination of Figures 2-5a,b, Figure 3-28, Figure 3-29 and Table 4-2 suggests the following for the different media:

- E33 – the PD experiment is a better predictor than the CD experiment of media performance in the pilot test. The CD data under-predict the pilot performance.
- ARM 200 – the CD is better predictor of media performance in the pilot test.
- Metsorb – the CD curve better describes the shape of the pilot test curve; both designs predict breakthrough well.
- ArsenX$^{np}$ –the PD experiment does not seem to be a good predictor of the pilot test results. (Note: a CD experiment was unsuccessful.)

As was mentioned before, for the flow experiments (pilot and RSSCTs), the capacities are calculated from mass balance on arsenic data by integration of area above the BTC and below

the influent arsenic concentration; these may be a more unbiased measure of sorption than the BV value.

For the pilot test, the order of capacity at 10 ppb (10 μg/L) concentration in the effluent is:

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

For the CD experiment, the order of capacity at 10 ppb (10 μg/L) concentration in the effluent is:

E33 > Metsorb > ARM 200

For the PD experiment, the order of capacity at 10 ppb (10 μg/L) concentration in the effluent is:

ARM 200 >E33 >ArsenX$^{np}$ > Metsorb

For the Freundlich isotherm, the order of capacity at 10 ppb (10 μg/L) concentration in the solution is:

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

For the Langmuir isotherm, the order of capacity at 10 ppb (10 μg/L) concentration in the solution is:

E33 > ArsenX$^{np}$ > ARM 200

Thus, at 10 ppb (10 μg/L) arsenic in the solution, the E33 media outperforms all other media in all tests but the PD RSSCTs, where the capacity of ARM 200 is slightly higher than the E33. At higher effluent arsenic concentrations, E33 is the top performer in the pilot and the CD RSSCT but is outperformed by the other media in the other tests. It is important to note that the EBCTs recommended by the vendors were used in the pilot tests and that the relative performance of the media could change if different EBCTs are used. Note also that the capacities obtained in the isotherm tests are higher than those estimated from the dynamic tests. This is consistent with the expectation that the smaller particle sizes and longer contact times in the batch tests would lead to more effective mass transfer of arsenic into the interior of the adsorptive media grains.

**Table 4-2. Summary of Performance Data for Adsorbent Media Using Five Methods.**

| | | E33 | | | ARM 200 | Metsorb | Isolux 302M | ArsenX$^{np}$ |
|---|---|---|---|---|---|---|---|---|
| | | 2 min | 4 min | 5 min | | | | |
| Pilot | BV to 10 ppb (10 μg/L) | 24000 | 43000 | 52000 | 8600 | 13000 | 32000 | 27000 |
| | Capacity at 10 ppb, mg/g | 1.95 | 3.56 | 4.21 | 0.60 | 0.70 | 1.67 | 1.38 |
| | Capacity at $C/C_o$ = 0.8, mg/g | 4.03 | NA | NA | 1.15 | 2.26 | 2.23 | 2.10 |
| CD RSSCT | BV to 10 ppb (10 μg/L) | 9000 | 7700 | 11700 | 6000 | 11500 | No data | No data |
| | Capacity at 10 ppb, mg/g | 1.25 | 0.72 | 1.18 | 0.42 | 0.66 | | |
| | Capacity at $C/C_o$ = 0.8, mg/g | > 9.6 | 3.06 | 3.83 | 1.35 | > 1.72 | | |
| | Capacity at $C_e = C_o$, mg/g | > 9.6 | > 4.94 | > 4.63 | > 2.08 | > 1.72 | | |
| PD RSSCT | BV to 10 ppb (10 μg/L) | 15400 | 43000 | 41000 | 16300 | 12800 | No data | 43000 |
| | Capacity at 10 ppb, mg/g | 1.95 | 3.39 | 3.07 | 3.82 | 0.69 | | 1.33 |
| | Capacity at $C/C_o$ = 0.8, mg/g | 4.26 | 4.68 | 4.71 | 5.07 | 1.24 | | 1.37 |
| | Capacity at $C_e = C_o$, mg/g | 5.08 | 5.61 | 5.02 | 5.46 | 1.31 | | 1.38 |
| Freundlich isotherm | Capacity at 10 ppb, mg/g | 4.97 | | | 3.57 | 1.18 | 2.67 | 4.63 |
| | Capacity at 40 ppb, mg/g | 7.67 | | | 7.91 | 4.13 | 7.77 | 9.86 |
| Langmuir isotherm | Capacity at 10 ppb, mg/g | 7.50 | | | 5.0 | NA | NA | 5.77 |
| | Capacity at 40 ppb, mg/g | 9.23 | | | 8.0 | NA | NA | 10.32 |

# 5.0 SUMMARY AND CONCLUSIONS

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 50 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 [10 μg/L] arsenic) of the adsorptive media in chlorinated water from the site.

The commercially available media that were evaluated in the tests are listed below.

| Type | Manufacturer | Product |
|---|---|---|
| Granular Ferric Oxide | Adedge | E33 |
| Granular Ferric Oxide | Engelhard Corporation | ARM 200 |
| Granular Titanium Oxide | Hydroglobe | Metsorb |
| Nano Particle Zirconium Oxide | MEI | Isolux 302M |
| Iron Impregnated Resins | Purolite | ArsenX$^{np}$ |

Arsenic sorption is controlled by a number of physical and chemical properties of the adsorptive media. In addition to the pilot test at the well site, a variety of laboratory studies were carried out. These included:

1. Materials characterization using XRD, SEM and EDS
2. Batch Studies (2 sorption isotherm models and kinetic sorption studies)
3. Rapid Small Scale Column Testing (2 models)

In order to understand and predict the sorption of arsenic by the media used at the Socorro pilot site, some basic mineralogical, physical and surface chemical analyses (XRD , SEM/EDS, BET, attrition loss) were carried out. Correlations of these studies to the results fo the pilot scale tests showed that the surface area of the pristine material was not directly related to the performance: E33, the media with one of the lowest surface areas, had the best performance. Isolux 302M ($ZrO_2$) had the highest surface area (499 $m^2/g$), Metsorb ($TiO_2$) and ARM 200 (Fe-oxhyhydroxide) media had intermediate surface areas (211-262 $m^2/g$), and E33 (Fe-oxhyhydroxide) and ArsenX$^{np}$ (FeO-coated resin) had the lowest surface areas (120 – 147 $m^2/g$).

It was observed that the media differed in their physical response to the pilot test conditions. The water at Socorro Springs was warm (27$^o$C – 37$^o$C). The aging studies carried out over a 3-month period showed that ARM 200 media partially recrystallized and was transformed to hematite. This may be a cause of the relatively poor performance of this pre-production batch in the pilot and the differences in the results from the pilot when compared to the laboratory studies that 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

chemical changes to the media during the pilot tests should be carried out to better interpret the results.

The amount of arsenic sorption by the media was studied using different methods to allow a clearer comparison of the relative performance. For the flow experiments (pilot and RSSCTs), the number of BVs of water passing through the media columns until the regulatory limit (10 ppb [10 μg/L]) was exceeded in the effluent was recorded. For both the batch tests and the flow experiments, the sorption capacity of the media (amount of arsenic adsorbed by the media) when the treated water was 10 ppb (10 μg/L) was also calculated or measured. For flow experiments, the capacities were calculated from mass balance on arsenic data by integration of area above the BTC and below the influent arsenic concentration; these may be a more unbiased measure of sorption than the BV value. For batch tests, a sorption isotherm was fit to the data, and a capacity was calculated at 10 ppb (10 μg/L) or other values. Table 5-1 summarizes the sorption capacities calculated by the different methods to allow a clearer comparison of the relative performance with respect to the 10 μg/L MCL.

For the pilot tests using the EBCTs recommended by the vendors, the values of BV and capacity at 10 ppb (10 μg/L) arsenic show a fairly consistent relationship among the adsorptive power of the media:

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

At higher effluent levels ($C/C_o = 0.8$), Metsorb has a higher capacity than Isolux 302M and ArsenX$^{np}$ (see Table 3-7.

In general, in the batch sorption studies, the media were ground to a smaller particle size than that used in the pilot test in order to minimize the effects of mass transfer within the grains and thereby reduce the time required to reach steady state. The batch equilibration time of 24 hrs was based on kinetic studies. Freundlich isotherms could be fit to sorption data from all of the media; Langmuir fits were successful for only three of the media (E33, Metsorb and ArsenX$^{np}$). For the Freundlich isotherm, the order of calculated sorption capacity in equilibrium with a solution with 10 ppb arsenic was: E33 > ArsenX$^{np}$ > ARM 200 > Isolux 302M > Metsorb. Because the batch studies were designed to minimize kinetic and mass transfer rate effects, they provided upper limits to the arsenic adsorption capacity of the media. The calculated capacities in the Freundlich isotherms at 10 ppb (10 μg/L) were between 1.4 times (E33) and 6 times (ARM 200) those calculated from the pilot studies.

Rapid Small-Scale Column Tests are scaled-down columns packed with smaller diameter adsorption media that receive higher hydraulic loading rates to significantly reduce the duration of experiments. Results for RSSCTs can be obtained in a matter of days to a few weeks, whereas pilot tests can take a number of months to over a year. Two kinds of RSSCTs were used: constant diffusivity (CD) and proportional diffusivity (PD).

**Table 5-1. Comparison of Sorption Capacities (mg/g) of Adsorbent Media Using Five Methods.**

| | | E33 | | | ARM 200 | Metsorb | Isolux 302M | ArsenX$^{np}$ |
|---|---|---|---|---|---|---|---|---|
| | | 2 min | 4 min | 5 min | | | | |
| Pilot | Capacity at 10 ppb | 1.95 | 3.56 | 3.47 | 0.60 | 0.70 | 1.67 | 1.38 |
| CD | Capacity at 10 ppb | 1.25 | 0.72 | 1.18 | 0.42 | 0.66 | | |
| PD | Capacity at 10 ppb | 1.95 | 3.39 | 3.07 | 3.82 | 0.69 | No data | 1.33 |
| Freundlich isotherm | Capacity at 10 ppb | 4.97 | | | 3.57 | 1.18 | 2.67 | 4.63 |

The relative performances of the media in the CD tests were consistent with the pilot tests results: the order of capacity at 10 ppb (10 μg/L) concentration in the effluent is: E33 > Metsorb > ARM 200. However, neither the calculated sorption capacities (nor the BV values) agreed well with the pilot. For the PD experiment, the order of adsorption capacity at 10 ppb (10 μg/L) concentration in the effluent is: ARM 200 >E33 >ArsenX$^{np}$ > Metsorb; this order differed from the relative number of BVs to reach 10 ppb effluent concentration. The BV values from the PD experiments agreed with the pilot results to within a factor of 2; however, the relative order differed from that of the pilot.

In conclusion, this study had two main objectives: 1) to determine the relative performance of the different adsorptive media in pilot tests at Socorro Springs and 2) to determine if any of the laboratory tests provided accurate estimates of the pilot scale results. Pilot tests are an accepted method to estimate the performance of full-scale water treatment systems. At 10 ppb (10 μg/L) arsenic in the solution, the E33 media outperformed all other media in the pilot tests. Laboratory tests (batch sorption and RSSCTs) are much less expensive to conduct than pilot tests; thus, the insights gained from the second part of the study could be used to reduce the number of pilot-scale tests of multiple media. In this study, it was found that the sorption performances of the different media depended on the physical and chemical nature of the media and the test methodology. The relative performances of the media depended on the nature of the test.

The level of agreement between the sorption capacities measured by different tests was media-dependent (Table 5-2). The sorption capacity (mg As/g media) of three of the media (E33, Metsorb and Isolux 302M) as measured in the pilot tests could be predicted within about 70% by batch sorption tests. The PD RSSCTs were more accurate predictors of the pilot tests results for E33, Metsorb and ArsenX$^{np}$ media (within 5%). The capacity of the ARM 200 could be predicted within 30% by the CD RSSCT but was grossly over predicted by the other tests. These results are valid only for the particular water studied and only for the batches of media provided by the companies for this test. Laboratory tests (batch sorption and RSSCTs) are much less expensive to conduct than pilot tests and provide reasonable qualitative predictions of field scale performance. The results of this project suggest that laboratory studies could be useful to

communities that cannot afford to carry out comparative pilot tests of multiple media, especially if other information about backwash requirements and costs (capital and labor) are already available.

**Table 5-2. Estimated Sorption Capacities Relative* to Pilot Test Results.**

| Test | Media | | | | |
|---|---|---|---|---|---|
| | **E33 (4 min)** | **ARM 200** | **Metsorb** | **Isolux 302M** | **ArsenX$^{np}$** |
| RSSCT-CD | 0.20 | 0.70 | 0.94 | NA | NA |
| RSSCT-PD | 0.95 | 6.37 | 0.99 | NA | 0.96 |
| Freundlich | 1.40 | 5.95 | 1.69 | 1.60 | 3.36 |

* calculated as $[\text{capacity in As mg/g media}]_{test}/[\text{capacity in As mg/g media}]_{pilot}$

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