

ESTCP Cost and Performance Report

(ER-0312)



Perchlorate Removal, Destruction and Field Monitoring Demonstration

March 2007



ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT

ESTCP Project: ER-0312

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ACRONYMS AND ABBREVIATIONS

A&E	architect and engineering firm
AF	acre feet
AFB	Air Force Base
AFCEE	Air Force Center of Environmental Excellence
AMCOM	Army Aviation and Missile Command
ARA	Applied Research Associates, Inc.
BPOU	Baldwin Park Operable Unit
BV	bed volume
ClO_4^-	perchlorate
CSTR	continuously stirred tank reactors
DAB	decyltrimethylammonium bromide
DHS	Department of Health Services
DoD	Department of Defense
DWEL	drinking water equivalent level
ELAP	Environmental Laboratory Accreditation Program
EPA	Environmental Protection Agency
ESTCP	Environmental Strategic Technology Certification Program
gpm	gallons per minute
HASP	Health and Safety Plan
HCl	hydrochloric acid
I&C	Instrumentation and Control
IPR	In-Progress Review
ISEP	ion separation
IX	Ion Exchange
LSI	Langelier Saturation Index
MCL	maximum concentration limit
Meq/L	milliequivalents per liter
MMR	Massachusetts Military Reserve
NASA	National Aeronautics and Space Administration
NFESC	Naval Facilities Engineering Service Center
NPDES	National Pollutant Discharge Elimination System

ACRONYMS AND ABBREVIATIONS (continued)

O&M	operation and maintenance
OIT	operator interface terminal
OSHA	Occupational Safety and Health Administration
P2	Pollution Prevention
PEO	Program Executive Office
pKa	ionization constant
PLC	programmable logic controller
PM	Program Manager
ppb	parts per billion
PPE	Personal Protective Equipment
psig	pounds per square inch, gauge
QA	Quality Assurance
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Project Plan
RfD	reference dose
RSA	Redstone Arsenal
SBA	strong base anion
SPE	solid phase extraction
SSC	Site Safety Coordinator
TCE	trichloroethylene
TDS	total dissolved solids
TPM	Technical Program Manager
VOC	volatile organic carbon
WBA	weak base anion

ACKNOWLEDGEMENTS

The success of this demonstration was due in part to the coordination and assistance of individuals from many organizations. Special appreciation is extended to Dr. Andrea Leeson, Mr. Scott Dockum, and Ms. Katie Conaway of the Program Office of the Environmental Security Technology Certification Program (ESTCP) for their guidance and support; Mr. Bryan Harre of the Naval Facilities Engineering Service Center (NFESC) for acting as the contracting officer representative; Ms. Terry de la Paz and Mr. Carl Wes Smith of the Redstone Arsenal Environmental Program Office for hosting and coordinating site access on Redstone Arsenal; Mr. Larry Galloway for his assistance in site preparation, coordination of peripheral equipment operation, and demobilization; and Mr. Brian Rhodes and Mr. Don Burton for coordinating disposal of treated groundwater. Special thanks is also extended to Mr. Charles Black, Mr. Sean Boyd, and Mr. Eric Rutherford of Mid-South Testing & Engineering for assisting with on-site support.

Technical material contained in this report has been approved for public release.

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1.0 EXECUTIVE SUMMARY

The Department of Defense (DoD) has used perchlorate (ClO_4^-) as an oxidizer in ordnance items and rocket motors for more than half a century. This very water soluble and environmentally persistent compound now contaminates drinking water for tens of millions of people in the United States. In 2002, the U.S. Environmental Protection Agency (EPA) released a provisional perchlorate Oral Reference Dose (RfD), which translated into a drinking water equivalent level of 1 part per billion (ppb). This drinking water equivalent level (DWEL) was recently increased to 24.5 ppb following the release of a report by the National Academy of Science.

As a result of EPA establishing a reference dose for perchlorate having a DWEL of 24.5 ppb, DoD issued a policy letter that establishes 24 ppb as the “level of concern for managing perchlorate.” The letter further states that, “Once established, DoD will comply with applicable state or federal promulgated standards whichever is more stringent.” The letter also provides guidance for perchlorate with respect to sampling and analysis, record keeping, environmental restoration, operational ranges, drinking water systems, and wastewater discharges. These guidance letters will impact many end users and stakeholders. Issues that these end users and stakeholders face using ion exchange technologies include a simple and effective regeneration process, disposal of concentrated regenerant streams, and cost.

The cost for DoD to achieve compliance with these drinking water limits has been estimated to be in the billions of dollars. It is important to reduce estimated costs by identifying, demonstrating, and transitioning more efficient and economical approaches to achieving compliance for perchlorate contamination. Applied Research Associates, Inc., (ARA) was selected by the Environmental Security Technology Certification Program (ESTCP) to evaluate and demonstrate a complete perchlorate ion exchange process for groundwater treatment. To validate the performance and economics of the proposed process compared to current perchlorate treatment processes, the following objectives were established:

- Demonstrate perchlorate removal in groundwater from >50 ppb to ≤ 5 ppb with a regenerable, perchlorate-selective ion exchange process.
- Demonstrate an efficient regeneration technique of the perchlorate-selective ion exchange resin. Regenerant volume should be $<0.1\%$ of treated groundwater stream.
- Demonstrate removal or destruction of perchlorate (≤ 5 ppb) in the regenerant stream enabling discharge or reuse of the regenerant stream.
- Demonstrate the performance of a perchlorate field monitor capable of online, real-time perchlorate analysis with a minimum detection limit of 1 ppb.

To achieve these objectives, a demonstration was conducted at Redstone Arsenal in Huntsville, Alabama, using groundwater as the medium. The demonstration was conducted for 15 weeks during which treatment rates of 12, 18, and 24 bed volumes per hour (1.5, 2.25, and 3.0 gallons per minute (gpm)/ft³ of resin, respectively) were evaluated. Well RS498, a 6-inch extraction well, was selected as the groundwater source for the demonstration. Anion concentrations of the well were as follows: 1,500 to 2,200 ppb perchlorate, 4 ppm nitrate, 3 ppm sulfate, and 4 ppm

chloride. Performance of the weak base anion (WBA) resin technology was assessed by collecting and analyzing groundwater samples before and after treatment (specifically, pretreated groundwater and column effluents). Five columns were regenerated to characterize regeneration efficiency. The spent regenerant solutions from these regenerations were used in perchlorate destruction evaluations.

The ion exchange process using WBA resin was successful in treating perchlorate-contaminated groundwater. Results of the demonstration at Redstone Arsenal confirmed that prior to breakthrough, perchlorate was removed from the contaminated groundwater to below the method detection limit (4 ppb) using EPA Method 314.0. Regeneration of WBA resin columns was effectively and efficiently accomplished creating a spent regenerant solution volume no more than 0.05% of the volume of water treated. For treatment of the spent regenerating solutions, two processes, biodegradation and a zero-discharge approach using SBA scavenger resin, were demonstrated. Both processes were effective in removing perchlorate to below the method detection limit.

Results from this 15-week pilot demonstration indicate that this ion exchange technology has the following advantages that mitigate these issues.

- Complete ion exchange and regeneration processes controlled by pH
- Regeneration that uses low-cost and relatively safe caustic solution
- Low volume of regenerant required for complete resin regeneration (50 times less than brine regenerant required for regenerating strong base anion [SBA] resins).

A cost comparison and analysis is included in this report. The net present value analysis resulted in a water treatment cost of \$90 to \$95 per acre-ft (AF). Therefore, the treatment cost for the WBA technology is less than 25% of current regenerable resin systems (Calgon Carbon Corporation's ISEP system) and less than 50% of the least expensive single-use resin systems.

2.0 TECHNOLOGY DESCRIPTION

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

Ion exchange using perchlorate-selective WBA resin is effective for treating perchlorate contamination in any surface water, groundwater, or drinking water application. The primary advantages of ion exchange using WBA resin are the ease and simplicity of regeneration, the small volume of spent regenerating solution produced, the resulting lower operation and maintenance (O&M) cost of regeneration, and the lower cost and ease of disposal of the spent regenerating solution. This ion exchange process takes advantage of the pH dependent nature of WBA resins. At low pH, functional groups on these resins have a positive charge (i.e., R-NH₃⁺) allowing for anion exchange. However, at high pH, the resin functional groups lose a proton and are uncharged (i.e., R-NH₂) allowing for regeneration.

2.2 PROCESS DESCRIPTION

The WBA ion exchange process was designed to use standard equipment for ion exchange vessels, pH control and carbon dioxide stripping, and data acquisition. The process was also designed for minimal pumping operations and to use level sensors, flow meters, and programmable logic control for operation. The installation and operation requirements depend on specific site characteristics. In most cases, the system should be installed inside a building to provide security and protection from the elements. Table 1 provides key design criteria for the demonstration at Redstone Arsenal.

Table 1. Design Criteria.

Criteria	Minimum	Maximum	Nominal Design
Column inside diameter (in)	2.049	2.049	2.049
Resin bed depth (in)	32	40	36
Resin volume (liters)	1.73	2.16	1.95
Flow rate (bed volumes [BV]/hr)	12	28	16
Flow rate (gal/hr)	6.2	14.4	8.2
Pressure drop (pounds per square inch, gauge [(psig)])	5.0	12.2	6.8
Operating pressure	10	30	20
Operating pH	3.0	5.0	4.0
Discharge pH	7.0	8.3	7.6
Sampling (days per week)	2	5	3
Labor (hours per week)	3	10	6

The ion exchange process using WBA resins consists of three unit operations: pretreatment, ion exchange, and posttreatment (Figure 1). Processes for regeneration of the WBA resin and treatment of the generated residuals were also evaluated. These operations are described below.

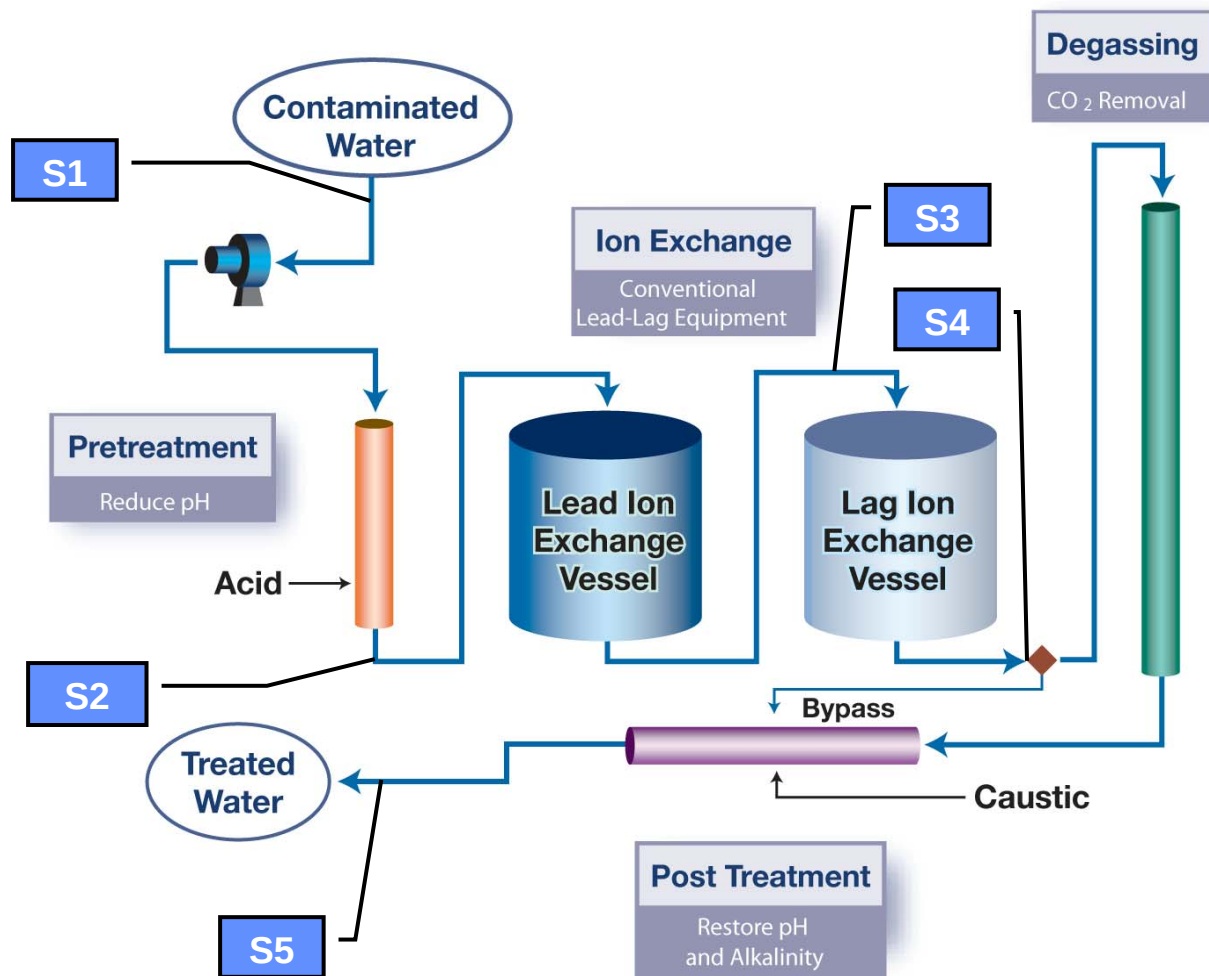


Figure 1. Demonstration Process and Sampling Locations.

2.2.1 Pretreatment and Ion Exchange

The function of pretreatment is to reduce the pH of the contaminated water to below the ionization constant (pKa) of the resin. Operational pH between 3 and 5 will prevent resin functional groups from being neutralized. The pH is controlled using a pH controller, an acid feed system, and a circulation pump and mixing vessel. At operational pH, any alkalinity present will be rapidly converted to carbonic acid in equilibrium with carbon dioxide. The system pressure is controlled at 10 - 20 psig to keep carbon dioxide in solution as dissolved carbon dioxide and carbonic acid. The amount of acid required for pretreatment depends on the alkalinity of the untreated water.

Ion exchange consists of two conventional ion exchange columns in series. The pretreated water passes through these columns in a lead-lag configuration. The ion exchange columns are also at operational pressure to prevent degassing of dissolved carbon dioxide in the resin bed.

2.2.2 Posttreatment

Following ion exchange, posttreatment is needed to restore pH and alkalinity of effluent before discharge. Posttreatment requirements are site-specific, depending on the desired alkalinity and pH of the treated effluent. Effluent alkalinity and pH requirements can be used to “dial in” posttreatment needs, including carbon dioxide stripping and neutralization using sodium hydroxide, soda ash, or calcite.

2.2.3 Regeneration

Regeneration of WBA resin is accomplished by increasing the pH to neutralize the functional groups. This can be accomplished by increasing the pH of two to three bed volumes (BV) of water and passing the solution over the resin. The target pH for the regeneration solutions was 12. Three different regeneration techniques were employed: single-pass, batch, and batch with “zero discharge” regeneration using a strong base anion scavenger resin (described in the Final Report). Anion analyses were conducted on each BV or batch of spent caustic regenerating solution and rinse water to determine regeneration effectiveness.

2.2.4 Residuals Treatment

Two processes were used for destroying/removing perchlorate from the regenerating solutions. Biodegradation was conducted using two continuously stirred tank reactors (CSTR) in series under anoxic conditions. A strong base anion resin was used to scavenge the concentrated spent regenerant solution as a super-loading approach. Results of residual studies can be found in Appendix A and Section 4.0 of the Final Report.

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

Prior to this demonstration, application of WBA resin ion exchange technology for perchlorate removal had been conducted only in laboratory-scale equipment as part of this project. The field monitor was derived from a similar monitor developed for explosives testing, but had been tested only in the laboratory under manual operation.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Three technologies are currently used commercially for remediating perchlorate contaminated groundwater: 1) biodegradation, 2) ion exchange using regenerable resins, and 3) ion exchange using nonregenerable or disposable resins. The WBA resin technology takes advantage of the performance, favorable public perception, and regulatory acceptance of ion exchange while minimizing the liabilities of current ion exchange systems. These liabilities include 1) the high cost of perchlorate-selective resins currently in use, 2) the large volume of residuals generated by regenerable systems, 3) the difficulty and high cost of treating residuals, and 4) resin replacement and incineration costs for nonregenerable systems.

Weak base, perchlorate-selective resins evaluated do not have the treatment capacity of strong base, perchlorate-selective resins. Even so, overall cost saving may be substantial since these resins can be economically regenerated. Pretreatment and posttreatment steps required for the WBA resin process do add process complexity compared to single-use ion exchange systems.

However, the complexity is not significantly greater than ISEP, the only commercial regenerable ion exchange perchlorate treatment technology currently in use. Pretreatment and posttreatment unit operations are very straightforward pH control processes. The WBA resin approach will likely be simpler and smaller than the ISEP process when the treatment and reuse of residuals is considered.

Water quality parameters including alkalinity, hardness, perchlorate concentration, sulfate concentration, and treated water alkalinity affect cost and performance. The amount of acid required to achieve operating pH is directly proportional to feed water alkalinity and therefore, pretreatment cost. Perchlorate concentration dictates the resin treatment capacity and regeneration frequency, which affects regeneration cost. In addition, perchlorate concentration and regeneration frequency impact the amount spent on regenerating solution and treatment cost. Hardness and desired alkalinity of treated water affect the caustic requirement for neutralization, which affects neutralization cost.

Sulfate concentration can also affect pretreatment cost. The most economical pretreatment approach is to use sulfuric acid. However, the use of sulfuric acid will increase the residual sulfate concentration. If feed alkalinity and sulfate concentrations are high, residual sulfate concentration could exceed the National Secondary Water Treatment guideline of 250 mg/L (the Secondary Water Treatment guideline for sulfate in California is 500 mg/L). In cases where the concentration of sulfate would exceed secondary treatment guidelines, it may be necessary to replace some or all of the sulfuric acid with the more expensive hydrochloric acid.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

Performance objectives identified for this technology included effectively removing perchlorate from contaminated groundwater; efficiently regenerating the WBA resin without loss of capacity; destroying perchlorate in the spent regenerant solution generated; and accomplishing perchlorate treatment and destruction at a cost lower than current treatment technologies. The primary methods used to assess performance were collecting and analyzing groundwater samples before and after treatment (specifically, pretreated groundwater and column effluents). Analytical results were also used to determine the treatment capacity of the WBA resin at the conditions tested. Operational data such as acid and caustic consumption were used to evaluate and confirm operating cost of this technology. Table 2 lists the performance objectives and metrics for this demonstration.

The qualitative and quantitative performance objectives identified in Table 2 for the ion exchange process using WBA resin were all met. The field monitor never operated remotely because of software and mechanical failures. As a result, the field monitor did not meet any of the quantitative performance objectives. Details describing the performance of the WBA resin ion exchange process and field monitor are summarized in the Final Report.

Table 2. Performance Objectives.

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met?
A. Ion Exchange			
Qualitative	1. System operability	Few or no process upsets	Yes
Quantitative	2. Meet perchlorate regulatory standards for potable water	≤ maximum concentration limit (MCL) (5 parts per billion [ppb])	Yes
	3. Low treatment cost	<\$100/acre-ft	Yes
	4. Ability to regenerate WBA resin base—change in treatment capacity	Capacity ±10%	Yes
	5. Efficiency of regeneration	<0.1 % vol residual	Yes
	6. Treatment of spent regenerating streams—removal of perchlorate	≤ MCL (5 ppb)	Yes
	7. Demonstrate WBA resin capacity	> 6100 BV	Yes
B. Field Monitor			
Quantitative	1. Near real-time perchlorate field monitoring capability	Analysis and reporting of all influent and effluent streams at least once per day	No
	2. Measurement accuracy	±20% of lab result	No
	3. Detection limit	1 ppb	No

3.2 SELECTING TEST SITES

The main criteria for site selection included 1) surface and/or groundwater perchlorate contamination levels that range from a few ppb to hundreds of ppb, 2) existing extraction wells and infrastructure providing access to the contaminated waters, and 3) site interest in hosting and supporting the demonstration. Based on these criteria, Redstone Arsenal, Massachusetts Military Reserve (MMR), and Hill Air Force Base (AFB), Utah, were considered. Of the three possibilities, Redstone Arsenal was selected for meeting these criteria with the added benefit of the site's proximity to Applied Research Associates, Inc.'s (ARA) Panama City, Florida office, which facilitated field support and operation and minimized costs associated with travel and transporting equipment and supplies.

3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

Redstone Arsenal, located in northern Alabama, was built in 1941 to produce conventional chemical ammunition for use in World War II. For more than 40 years, Redstone has been the heart of the Army's rocket and missile programs. Dr. Werner von Braun and his German rocket experts developed the first ballistic missile; this led to the establishment of the National Aeronautics and Space Administration's (NASA's) Marshall Space Flight Center in 1960. Today, Redstone is home to the U.S. Army Aviation and Missile Command (AMCOM), the Space and Missile Defense Command, numerous Program Executive Offices (PEO), and major components of the Defense Intelligence Agency and the Missile Defense Agency.

Site OU-10 at Redstone Arsenal has approximately 400 monitoring or extraction wells with perchlorate contamination ranging from very low ppb up to 10,000 ppb. Many of these wells also have volatile organic carbon (VOC) contamination, primarily trichloroethylene (TCE), which was considered prior to well selection. Redstone Arsenal assisted with site selection for the demonstration by providing ARA with perchlorate, TCE, and pump rate data for groundwater monitoring wells. Well selection guidelines included having the minimum TCE contamination possible while maintaining the capability to pump at a sufficient rate for the demonstration system (up to 12 gal per hour).

3.4 PHYSICAL SETUP AND OPERATION

The ion exchange pilot treatment system was fabricated at ARA's Panama City, Florida Research facility. The system was installed in an 8 by 20-ft enclosed trailer, and a series of functional tests were performed prior to field mobilization. The enclosed trailer was configured to provide breakered power, climate control, and protection from the elements while in the field.

A phone line was installed at the site on June 16, 2005, for accessing data using a web-based data acquisition system. On this same date, the well-pump and a disconnect box were installed to provide power for the demonstration trailer. The demonstration trailer was hauled to Redstone Arsenal on June 20, 2005. During this week, the system was prepared for the demonstration, and the field monitor was integrated. Arrangements were made for site access, and on-site consultants were trained to sample and monitor the system. The first test period of the demonstration was initiated on June 23, 2005.

The pilot demonstration system was operated in a continuous flow manner. The system, described in detail in Section 2.2, was designed with a data acquisition unit that was remotely accessed via the Internet. This allowed remote monitoring of key operating parameters, including pH, pressure, flow rate, and temperature of influent and column effluents. The demonstration, which was conducted in five test periods, ended on October 3, 2005. Demobilization was completed by October 7, 2005. The dates and duration of the five test periods are listed in Table 3.

Table 3. Duration of Each Test Period.

Task Name	Duration	Start	Finish	June					July					August					September				October		
				29	5	12	19	26	3	10	17	24	31	7	14	21	28	4	11	18	25	2	9	16	
Demonstration Schedule	121 days	Mon 6/6/05	Fri 10/7/05																						
Site arrival	0 days	Mon 6/6/05	Mon 6/6/05																						
Mobilization	3 days	Tue 6/21/05	Thu 6/23/05																						
Initiate GW Treatment	0 days	Thu 6/23/05	Thu 6/23/05																						
Test Period 1	27 days	Thu 6/23/05	Tue 7/19/05																						
Test Period 2	21 days	Tue 7/19/05	Mon 8/8/05																						
Test Period 3	20 days	Tue 8/9/05	Sun 8/28/05																						
Test Period 4	14 days	Thu 9/1/05	Wed 9/14/05																						
Test Period 5	13 days	Tue 9/20/05	Sun 10/2/05																						
Demobilization	5 days	Mon 10/3/05	Fri 10/7/05																						
Demonstration Complete	0 days	Fri 10/7/05	Fri 10/7/05																						

3.5 SAMPLING/MONITORING PROCEDURES

As part of the demonstration plan for this effort, a Quality Assurance Project Plan (QAPP) was developed and utilized to ensure that samples were collected and analyzed properly. This plan was developed based on Environmental Protection Agency (EPA) guidance and ARA's experience in operating ex situ groundwater treatment systems. The plan is included as Appendix B in the Final Report. The only exception to this plan was regarding perchlorate analysis using the online field monitor. Software and mechanical failures prevented remote operation of the online field monitor. As a result, the field monitor was never used to analyze groundwater and column effluent samples for perchlorate as originally planned. All perchlorate analyses were conducted using EPA Method 314.0.

Site visits were conducted at least 3 days per week to inspect the system, sample, record data, and prepare dilute acid and/or caustic solutions for the pretreatment and posttreatment units. Inspection and sampling typically required an hour per site visit. At the end of each test period, a sample set was collected and the flow was suspended to remove the spent lead column, transition the lag column to the lead column position, and replace the lag column with a freshly-regenerated column. Maintenance of the ion exchange system during this flow suspension also included replacing the in-line groundwater filter, cleaning and calibrating pH electrodes, and calibrating the digital flow meter. Following maintenance and any adjustments, the flow was initiated for the new test period. Spent columns from each test period were transported to ARA's laboratory in Panama City for regeneration.

There were five sample locations identified for the field demonstration system. These sampling points consisted of ball-valves that were plumbed in appropriate locations for representative

sampling. Each valve was clearly labeled to eliminate confusion and/or mislabeling of sample bottles. These locations are identified and described in Table 4.

Table 4. Sampling Locations.

	Sample ID	Valve Location
1	Pretreatment	Following pretreatment mix tank; before lead column
2	Lead column	Following lead column; before lag column
3	Lag column	Following lag column; before posttreatment tank
4	Posttreatment	Out of posttreatment tank; before discharge to holding tank
5	Groundwater	At well head

During the field demonstration, samples were collected from pretreatment and posttreatment units, and lead and lag column effluents at least three times per week by ARA personnel or technicians trained by ARA. Samples were analyzed for perchlorate, other inorganic anions, and basic water quality parameters at ARA's in-house laboratory using methods listed in Table 5. Samples taken at the end of each test period were split and shipped to Associated Laboratories in Orange, California, for an external confirmatory analysis for perchlorate as well as other general mineral and physical analyses. Table 5 lists sampling parameters and frequency during the ESTCP pilot demonstration.

Table 5. Sampling Summary for ESTCP Pilot Demonstration.

Parameter	Sample Point	Sample Frequency	Method	# Samples Collected*
Perchlorate	1,2,3,4	At least 3 times per week	EPA 314.0	184
Anions	1,2,3,4	At least 3 times per week	EPA 300.1	214
pH	1,2,3,4	Continuous	Online/field	---
General physical/mineral	4 and 5	Test period end	Various	10
VOC	4 and 5	Test period end	EPA 524.2	10

*These numbers do not include duplicates or quality assurance/quality control (QA/QC) samples collected and analyzed in accordance with the QAPP.

Operational data such as pH, flow, and pressure were collected and stored by a data acquisition system. These data along with acid and caustic tank levels were recorded in a log notebook by a technician on each sampling day. The technician would also call ARA personnel and provide the data while on site. This data was recorded in spreadsheets and reviewed to ensure that the system was operating as expected.

During regeneration tests, anion analyses (perchlorate, sulfate, nitrate, and chloride) were conducted on each bed volume of spent caustic regenerating solution using EPA Methods 314.0 and 300.1. The anion results were used to determine regeneration effectiveness and anion composition of the regeneration solution before perchlorate destruction tests were initiated.

Two processes for destroying perchlorate in spent regenerant solutions were evaluated—superloading a scavenger strong base anion resin and biodegradation. During superloading tests, sampling was conducted on each bed volume passed through the scavenger resin. During biodegradation tests, two bench-scale (2.5 liters) flow reactors were configured in series. The

pH, temperature, oxidative/reduction potential, and nutrient and caustic consumption were recorded daily for each reactor. Each reactor was sampled daily for perchlorate analysis using EPA Method 314.0. Other anion analyses (nitrate, sulfate, and chloride) were conducted at least twice per week using EPA Method 300.1. A sampling summary for regeneration and residual treatment tests is provided in Table 6.

Table 6. Sampling Summary for Regeneration and Residual Treatments.

Process	Parameter	Sample Frequency	Method	# Samples Collected
Regeneration	Perchlorate	Each BV	EPA 314.0	56
	Anions	Each BV	EPA 300.1	55
	pH	Each BV	SM 4500	36
Superloading	Perchlorate	Each BV	EPA 314.0	37
	Anions	Each BV	EPA 300.1	36
	pH	Each BV	SM 4500	0
Biodegradation	Perchlorate	Daily	EPA 314.0	95
	Anions	Weekly	EPA 300.1	69
	pH & ORP	Daily	Online	64

A complete sampling and analysis plan detailing analytical techniques, QA/QC requirements, and sampling procedures is included in the QAPP, attached as Appendix B of the Final Report and QA/QC results are provided in Section 4, Table 4-3 of the Final Report.

3.6 ANALYTICAL PROCEDURES

Samples were analyzed for perchlorate and anions, including nitrate, sulfate, and chloride using EPA Methods 314.0 and 300.1. The well and the post treated effluent were sampled at the end of each test period for these anions, TCE, and a series of general physical and mineral analyses. Table 7 lists the analytical procedures, and detailed descriptions of the analytical methods used during this demonstration are included with the QAPP, attached as Appendix B of the Final Report.

Table 7. Analytical Procedures Used During the Demonstration.

Parameter	Matrix	Lab	Method	Method Type
Perchlorate*	Aqueous	ARA	EPA 314.0	Ion chromatograph
Perchlorate*	Aqueous	ARA	Online monitor	Solid Phase Extraction (SPE)/colorimetric
Anions	Aqueous	ARA	EPA 300.1	Ion chromatograph
pH	Aqueous	ARA	SM 4500	Electrometric
**General physical/mineral scan	Aqueous	Environmental Laboratory Accreditation Program (ELAP)-certified	Various	Various
VOCs	Aqueous	ELAP-certified	EPA 8260	Gas chromatograph—mass spectrometer

*Notes: Critical compound for performance validation is ClO_4^- .

**General physical scan includes pH, color, turbidity, total alkalinity, total hardness, conductance, TDS, calcium, copper, iron, magnesium manganese, potassium, sodium, and zinc.

The critical parameter for this study was the analysis of anions—specifically, perchlorate—in groundwater. The perchlorate field monitor was designed to analyze daily perchlorate concentrations for the pretreated groundwater and ion exchange effluents using a method developed by ARA (described in the Appendix B of the Final Report). However, software and hardware failures described in Section 3.5.1 prevented remote operation of the monitor. Instead, daily samples of pretreated groundwater and column effluents were analyzed using EPA Methods 314.0 and 300.1 for perchlorate and anions (chloride, sulfate, and nitrate) during the first 2 weeks of the demonstration. After the first 2 weeks, samples were analyzed at least 3 days per week for perchlorate and anions. Additional analytical measurement, including pH, conductivity, solids, metals, color, turbidity, hardness, alkalinity, and VOCs were performed using the appropriate Standard/EPA method.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

The figures and tables in this section summarize data used to evaluate the performance of this demonstration involving ion exchange, regeneration, and perchlorate removal and destruction from spent regenerant solution. Performance criteria for assessing ion exchange included the ability to remove perchlorate in contaminated groundwater to below 4 ppb at flow rates equal to or greater than 12 BV per hour (1.5 gallons per minute [gpm]/ft³). Figure 2 shows perchlorate breakthrough data for lead columns when the flow rate was 12, 18, and 24 BV per hour (1.5, 2.25, and 3 gpm/ft³, respectively). Prior to breakthrough, the perchlorate concentration in the lead column effluent was less than 4 ppb at all flow rates. The perchlorate concentration in the lag column effluent was always below 4 ppb, even during breakthrough of the lead column.

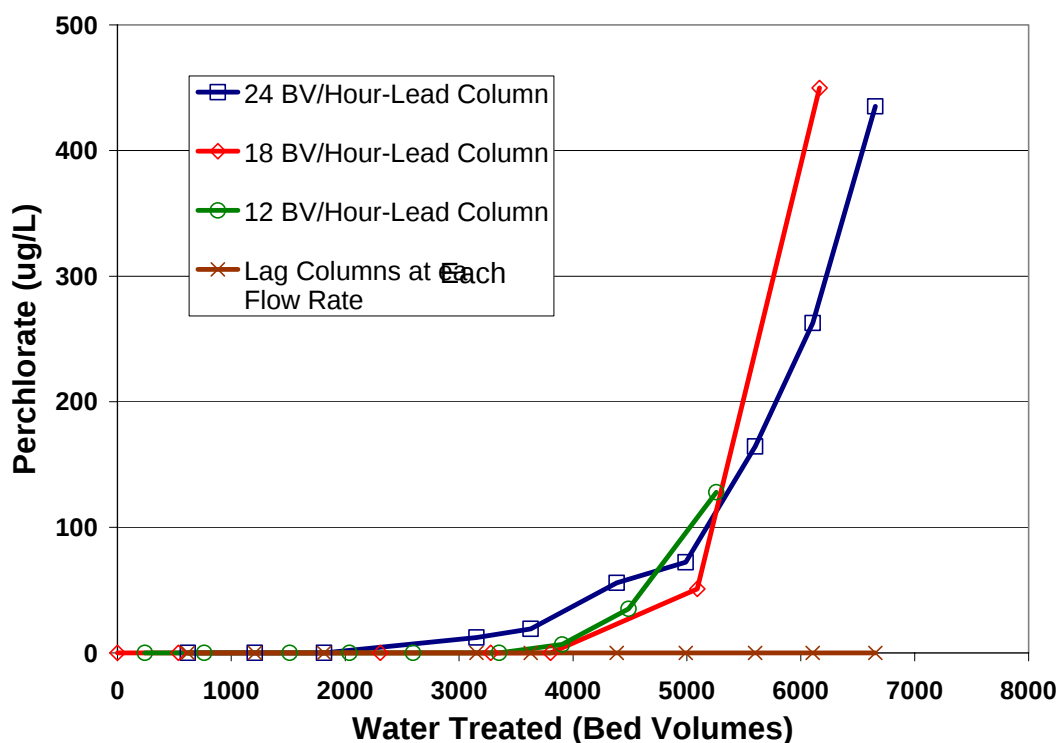


Figure 2. Perchlorate Breakthrough Curves.

The ability to efficiently and completely regenerate the resin while minimizing spent regenerant volume was also very important for assessing the performance of the demonstration. Five regenerations were conducted during which different regeneration processes were evaluated (i.e., flow direction, rate, and duration). Two approaches were evaluated for regenerating the spent ion exchange resin. These were single-pass regeneration and batch regeneration. The more conventional, single-pass approach (Figure 3) was used to regenerate the spent column from the first test period. The regeneration solution was prepared by adding caustic to three BV of water, which was passed over the resin at a flow rate of 2 BV per hour. The spent regenerant was collected for analysis and perchlorate destruction studies using the scavenger approach. For

complete regeneration using the single-pass approach, excess caustic was required (50%), and it was difficult to minimize the volume of spent regenerant.

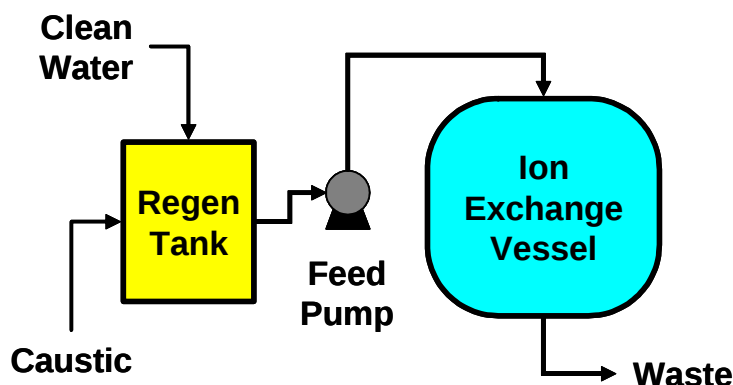


Figure 3. Single-Pass Regeneration.

A batch regeneration approach was also conducted (see Figure 4). A stoichiometric amount of caustic plus 10% excess was added to 3 BV of potable water to prepare the regenerating solution. This solution was circulated over the resin bed until the pH of the column effluent was greater than 12. The solution was drained from the column and collected for analysis and perchlorate destruction studies. The batch regeneration approach enabled complete regeneration while minimizing caustic consumption and spent regenerant volume. Batch regeneration was used for all remaining tests, and the spent regenerant solutions generated were collected for perchlorate destruction tests using biodegradation. Following regeneration, regardless of the approach, a rinse was conducted to adequately remove residual perchlorate from the regenerated resin bed. This was done to eliminate bleed at the start up of the next cycle. The rinse water was collected, analyzed, and used to dilute spent regenerant prior to the biodegradation study.

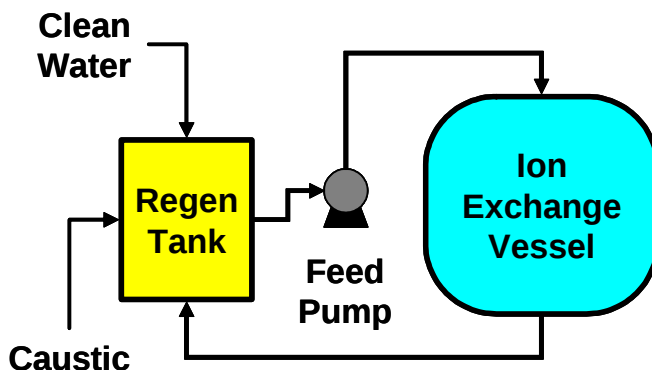


Figure 4. Batch Regeneration.

Table 8 summarizes regeneration results and parameters, including flow rate, duration and method. The volumes of spent regenerating solutions produced were equal to or less than 0.06% of the water treated. Two approaches were demonstrated to remove perchlorate in these solutions; a zero-discharge scavenger resin approach and biodegradation. Both approaches were

successful in removing perchlorate from the spent regenerant solution to below detection limits (<4 ppb).

Table 8. Regeneration Summary.

Regeneration #	Column ID	Calculated* Load (meq ClO ₄ ⁻)	Regenerant (meq ClO ₄ ⁻)	Recovery (%)	Spent Regeneration (% of treated water)	Flow Rate (BV/hr)	Duration (hr)	Regeneration Method
1	C1	177	177	100	0.04	2	1.5	Up flow, single-pass, fluidized bed with scavenging
2	C2	169	145	87	0.05	2	8	Down flow, batch, low flow rate
3	C4	136	140	104	0.06	28	2.5	Up flow, batch, high flow rate/short cycle
4	C1	228	191	84	0.05	22	2.5	Up flow, batch, high flow rate/short cycle
5	C2	266	255	96	0.05	30	20	Up flow, batch, high flow rate/long cycle

* Approximate value based on perchlorate concentrations in the untreated water, the treated water, and the total flow between samplings.

Two approaches were demonstrated for treating spent regenerant solutions. These included a zero-discharge approach using scavenger resin and biodegradation. The scavenger apparatus consisted of four 15-mm diameter columns in series packed with 90 cc of Purolite A-600, a strong base anion resin (see Figure 5). The spent regenerant from the first test period was passed over the columns loaded with Purolite A-600 at a flow rate of 10 BV per hour. Effluent from each of the four columns was collected every hour (every 10 BV) until completion. The results, plotted in Figure 6, show that perchlorate was completely removed from the spent regenerant by the first two scavenger columns.

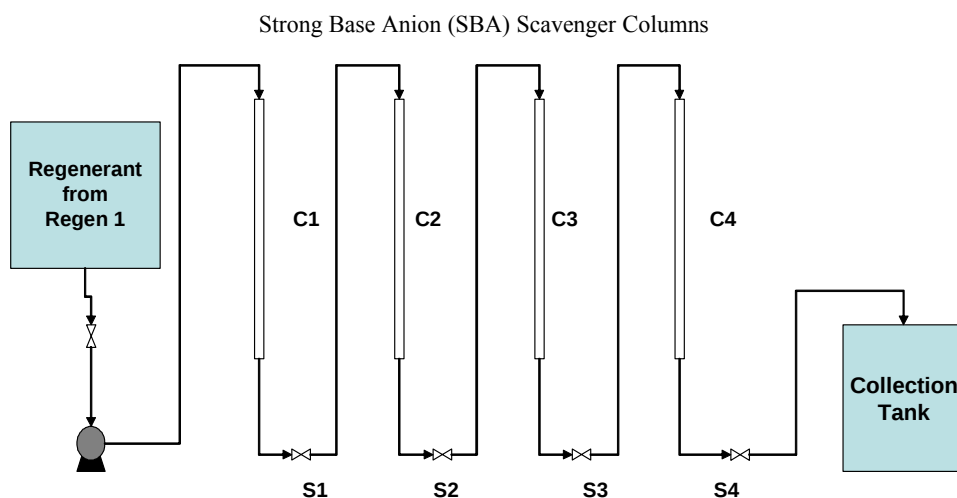


Figure 5. Scavenger Apparatus.

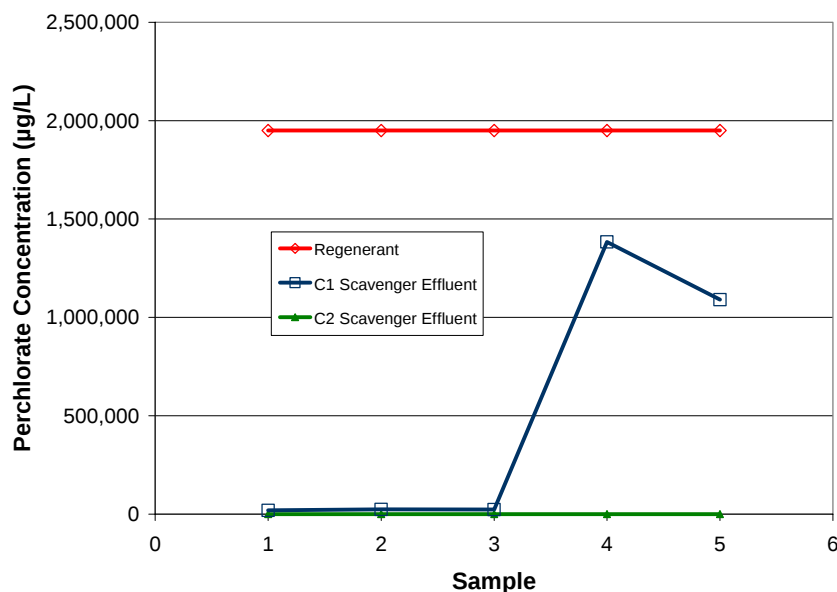


Figure 6. Superloading Results.

Biodegradation studies were also conducted to evaluate perchlorate destruction in spent regenerant. The apparatus consisted of two 2.5-liter, continuously stirred tank reactors (CSTR) in series. A carbon-based nutrient source (desugared molasses) was added to the first reactor, and the pH of both reactors was controlled. Spent regenerant solutions from test periods 2 through 5 were combined, diluted with spent rinse water to reduce the total dissolved solids (~1%), and neutralized prior to biodegradation. The average perchlorate concentration of the feed water during biodegradation testing was 600 mg/L. Biodegradation of the diluted spent regenerant was conducted over 33 days during which the perchlorate was reduced to below the method detection limit for this matrix using EPA Method 314.0. There was a 3-day period during which perchlorate was not reduced to below the detection limit in the second stage reactor. This was caused by insufficient nutrient (desugared molasses) addition. After adjusting the nutrient level, perchlorate was again reduced to below the detection limit.

4.2 PERFORMANCE CRITERIA

The effectiveness and success of this demonstration were measured against the primary and secondary performance objectives listed in Table 9. Assessment of criteria was based on comparing sampling results and/or operating data. Many of the primary performance criteria were based on comparing perchlorate concentrations of groundwater or pretreated groundwater to column effluents using EPA Method 314.0. For this reason, care was taken to ensure that sampling and analysis of these samples were compliant with the QAPP, attached as Appendix B in the Final Report. Quality control results for perchlorate analyses are summarized in Section 4.2 of the Final Report. Also, accurate and detailed data (i.e., pH, pressure, temperature, flow rate, etc.) and observations (maintenance activities and times) were logged into a laboratory notebook and/or electronic spreadsheets for analysis.

Table 9. Performance Criteria.

Performance Criteria	Description	Primary or Secondary
Contaminant reduction	Removal of perchlorate from groundwater via pump-and-treat ion exchange process to below the MCL	Primary
Resin regeneration	Effective and efficient regeneration of WBA resin enabling reuse	Primary
Process waste	• Small volume of spent regenerating solution (<0.1%) • Biodegradability of spent regenerating solution • Concentration of perchlorate in spent regenerating solution	Primary Primary Primary
WBA resin capacity	Groundwater treatment capacity	Primary
Treatment rate	Acceptable performance at 1.5 gpm/ft ³ of resin	Primary
Pretreatment pH	Effective operational pH	Secondary
Reliability	• Perchlorate leakage • pH control • CO₂ management • Resin useful life	Primary Secondary Secondary
Ease of use	• Degree of automation • Labor requirement • Skill level requirements	Secondary
Versatility	• Groundwater, drinking water, or wastewater • Wide range of perchlorate concentrations	Secondary
Maintenance	• Frequency • Complexity • Cost	Secondary
Scale-up constraints	• Representative bed depth • Representative flow rate • Pretreatment/posttreatment scale	Secondary
Field monitor operation	• Method detection limit (MDL) of 1 ppb • Precision $\pm$ 25 % • Dynamic range • Ease of use	Primary Secondary

Table 10 summarizes the expected performance, performance confirmation methods and the actual confirmation methods used to evaluate demonstration performance. The performance of the field monitor was not able to be assessed for field operation due to software failures. Details of these failures and laboratory assessments are provided in Section 3.1.B.1 of the Final Report and in the response for In-Progress Review (IPR) Action Item #1 submitted on November 1, 2005.¹

¹ White paper in response to Spring 2005 IPR Action Item #1 for Project CU-0312 submitted November 1, 2005.

Table 10. Expected Performance and Performance Confirmation Methods.

Performance Criteria	Expected Performance Metric (predemonstration)	Performance Confirmation Methods	Actual Performance (postdemonstration)
PRIMARY CRITERIA (Performance Objectives)			
Contaminant reduction	Remove ClO_4^- with IX process to ≤ 5 ppb	EPA Method 314.	Perchlorate concentration in the column effluent was below the criteria (5 ppb) in the lead columns until breakthrough. In the lag columns, perchlorate stayed below 4 ppb.
Resin regeneration	Effective regeneration of resin. +90% recovery of ClO_4^- loaded onto resin	Mass balance feed/effluent with data from EPA Method 314.	Mass balance calculations were conducted. The amount of perchlorate loaded on the columns was estimated based on the perchlorate concentration data for untreated water, the treated water, and the treatment flow duration. The amount of perchlorate in the spent regenerant was determined using ion chromatography. Table 8 is a summary of results and parameters for each regeneration cycle. The recovery of perchlorate from regenerated columns was greater than 90% for three regenerations. Recoveries for two regenerations were 87% and 84%. However, complete regeneration was achieved during each regeneration because there was no perchlorate bleed during the next treatment cycle for any of the regenerated columns.
Process waste	Generate $\leq 0.1\%$ spent regenerant volume of total volume treated	Collect and measure spent regenerant volume.	Spent regenerant solutions were collected, measured, and compared to the volume of water treated during the cycle. The volume of spent regenerant never exceeded 0.06% (see Table 8).
	Biodegradability of spent regenerating solution	Degrade ClO_4^- in solution process to ≤ 5 ppb with EPA Method 314.	Biodegradation of spent regenerant solution was conducted over 33 days. The perchlorate was reduced to below the detection limit for this matrix for all but 3 days of this period. The excursion was due to insufficient nutrient addition (desugared molasses). After adjusting the nutrient level, perchlorate was again reduced to below the detection limit.
	Concentration of ClO_4^- in regenerant solution	Remove ClO_4^- in regen solution to ≤ 5 ppb with EPA Method 314.	The scavenging process removed perchlorate below the detection limit using EPA Method 314.6.
Perchlorate capacity of resin	≥ 30 meq/L	Mass balance feed/effluent with online monitor and EPA Method 314.	The capacity of the lead column during each test period was calculated and normalized according to Section 3.1.A.4 in the Final Report. Each capacity calculated was greater than 30 milliequivalents per liter (meg/L) by at least a factor of two.

Table 10. Expected Performance and Performance Confirmation Methods (continued)

Performance Criteria	Expected Performance Metric (predemonstration)	Performance Confirmation Methods	Actual Performance (postdemonstration)
PRIMARY CRITERIA (Performance Objectives)			
Treatment rate	$\geq 1.5 \text{ gpm/ft}^3$	Flow rate monitor/totalizer.	The flow rates for the five periods were verified using a flow rate monitor that measured total flow and the duration of each test period. The average-actual flow rates during test periods 1 through 5 were 1.5, 1.6, 1.4, 2.5, and 3.4 gpm/ft ³ , respectively.
Reliability	Perchlorate leakage	Analysis at flow rates $>1.5 \text{ gpm/ft}^3$.	All columns were preconditioned by loading with perchlorate and regenerating before the demonstration. The lead and lag columns during the first test period had perchlorate bleed due to insufficient rinsing after regeneration. The regeneration procedure was modified to correct this leakage by increasing the rinse volume from 5 BV to 15 BV. No other leakage was observed after the modified regeneration procedure was in place, even at higher flow rates.
Field monitor operation	MDL $\leq 1 \text{ ppb}$	Statistical analysis of results of lowest standard.	Unable to determine due to software and mechanical failures
	Precision $\pm 25\%$	Statistical analysis of duplicates.	Unable to determine due to software and mechanical failures
SECONDARY CRITERIA (Performance Objectives)			
Pretreatment pH	Effective Operational pH	pH varied from 4.0 baseline, ClO_4^- removal measured.	Based on operational data recorded over the 15-week demonstration, the average pH was 3.92 with a standard deviation of 0.15.
Reliability	pH Control	Online pH monitor recorded with DAS.	Based on operational data recorded over the 15-week demonstration, the average pH was 3.92 with a standard deviation of 0.15.
	CO ₂ management	Influent/Effluent alkalinity measurement.	Neutralization and partial CO ₂ stripping was accomplished in a single vessel. Treated water had a residual bicarbonate alkalinity of greater than 50 mg/L.
	Resin useful life	ClO_4^- removal capacity measured after load/regen cycles.	Determined capacity of resin after each test period. Normalized and compared to all five test periods. The normalized results were within 9%. There was no indication of loss of performance over the duration of the demonstration.
Versatility	Groundwater, drinking water application, wide ClO_4^- treatment range	Remove ClO_4^- with IX process to $\leq 5 \text{ ppb}$ from feed of 1,000 ppb.	Reduced perchlorate concentration from $>2,200 \text{ ppb}$ to $<4 \text{ ppb}$. This demonstrated the capability to treat water containing a wide range of perchlorate concentrations ($<10 \text{ ppb}$ to $>2,000 \text{ ppb}$).

Table 10. Expected Performance and Performance Confirmation Methods (continued)

Performance Criteria	Expected Performance Metric (predemonstration)	Performance Confirmation Methods	Actual Performance (postdemonstration)
SECONDARY CRITERIA (Performance Objectives)			
Maintenance	Frequency, complexity	Experience and monitor from demonstration operation.	Maintenance activities were conducted at the end of each test period before initiation of the next test period. These activities included pH electrode calibration, flow meter calibration, and replacing the influent filter. Combined, these activities required less than 1.5 hours of effort from an individual. No additional maintenance was required.
Scale-up constraints	Representative bed depths, flow rates, pretreatment/posttreatment scale	System design with scale-up considerations, monitor from demonstration.	Resin bed depth for the pilot demonstration was equivalent to the resin bed depth in full-scale ion exchange vessels. Therefore, the performance demonstrated was representative of full-scale system performance with no scale-up constraints.

4.3 DATA ASSESSMENT

An assessment of performance data for ion exchange, regeneration, and perchlorate destruction in spent regenerant streams is provided in Section 4.1 of this report. Detailed performance results can also be found in Section 3.1 and Appendix A of the Final Report. Data provided in these sections indicate that performance claims for the ion exchange process demonstrated were met. However, performance claims of the field monitor could not be evaluated because it never achieved remote operation in the field.

The pilot demonstration system was operated in a continuous flow manner. After flow parameters were established, the only activities required were sampling and replenishing acid and caustic solutions for pretreatment and posttreatment operations. The system, described in detail in Section 2.1, was designed with a data acquisition unit that was remotely accessed via the Internet. This allowed remote monitoring of key operating data, including pH and temperature of the pretreatment system, column effluents, and posttreatment system; system pressure; and system flow rate.

Local technicians were trained over a 2 day period to monitor and sample the pilot system. Site visits were conducted at least 3 days per week to inspect the system, sample, record data in log books, and prepare dilute acid and/or caustic solutions and refill reservoirs for the pretreatment and posttreatment units. These inspections typically required an hour per visit. At the end of each test period, a sample set was collected, and the flow was suspended to remove the spent lead column, transition the lag column to the lead column position, and replace the lag column with a freshly regenerated column. Maintenance of the ion exchange system during this flow suspension also included replacing the in-line groundwater filter, cleaning and calibrating pH electrodes, and calibrating the digital flow meter. Following maintenance and any adjustments, the flow was initiated for the new test period. During site visits, handling of acids and caustics required that necessary safety precautions be taken. Training was conducted on the health and

safety plan, wearing appropriate safety equipment (i.e., glasses/goggles, spill-resistant coat, gloves, etc), properly handling and storing the chemicals, and knowing the location of key safety equipment (safety shower and eye wash, chemical spill kit, health and safety plan, emergency contact phone numbers, etc).

The performance metric for assessing system operability was the ability to operate as designed without process upsets or interrupted flow. During the demonstration, there was never a flow interruption due to a unit process upset. However, on two occasions the acid pump used in pretreatment lost prime. Fortunately, the situation was identified and corrected before the ion exchange resin was affected by treating neutral pH water. The pump was replaced, and pH of the influent was monitored frequently using the web-based data acquisition system.

4.4 TECHNOLOGY COMPARISON

Project performance results were compared as a low-cost alternative to existing pump-and-treat processes for perchlorate remediation. Therefore, this technology was compared to existing ion exchange technologies being used primarily to treat drinking water. These technologies include regenerable ion exchange processes that use salt as the regenerating agent such as the Calgon ISEP process and conventional lead-lag processes. A cost comparison is provided in Section 5.3, and key performance benefits compared to brine regenerable SBA resin are listed below:

- **Low O&M Cost.** \$70 to \$85 per AF compared to $\geq$ \$200 per AF for SBA processes
- **Low Effluent Volume.** Less than 0.02% of treated water for a drinking water application; 50 times more efficient than regenerating with brine
- **Inexpensive Zero-Discharge Process.** Use of SBA scavenger resin—allows for treated regenerating solution to be discharged to sewer
- **Standard Ion Exchange Equipment.** Fixed-bed, lead-lag configuration
- **Use of Typical Water Treatment Chemicals for Regeneration.** NaOH, H₂SO₄, and Na₂CO₃.

Issues associated with the use of WBA resin technology for perchlorate include:

- **Added Complexity.** Requires pretreatment and posttreatment operations as well as additional labor for operation and maintenance
- **Added Chemicals.** Must add acid and caustic to the product water, introducing potential safety issues associated with handling acid and caustic.
- **Higher Capital Investment.** Additional unit operations and footprint.

5.0 COST ASSESSMENT

5.1 COST REPORTING

5.1.1 Capital Cost

5.1.1.1 Application Scenarios

Cost data were developed for two different application scenarios: 1) full-scale remediation of groundwater with properties similar to the groundwater treated during the demonstration test at Redstone Arsenal and 2) full-scale groundwater treatment system for groundwater containing low concentrations of perchlorate (<100 ppb) – typical for most drinking water applications. The design and operation of the WBA resin treatment systems are similar for each scenario with the exception of the disposition of the spent regenerating solutions. For remediating high concentrations of perchlorate (scenario #1), biodegradation is the least expensive solution. For most drinking water applications (scenario #2), a scavenger resin is a less expensive and simpler process.

5.1.1.2 Basis

The design and operating bases for the two scenarios are summarized in Table 11. A treatment rate of 2,000 gpm was selected to permit direct comparison to single-use ion exchange systems that typically treat 1,000 or 2,000 gpm. Capital costs were derived from a budgetary cost estimate for a 400 gpm treatment system that was scaled to a 2,000 gpm system. Capital cost for the biodegradation system used in the remediation scenario is based on a similar-sized commercial treatment system. It is assumed that the treated water alkalinity could be reduced to less than 5 mg/L for remediation scenarios.

Table 11. Summary of Design and Operating Bases.

Parameter	Remediation	Drinking Water
Treatment rate, gpm	2,000	2,000
BV per hour	24	24
gpm/ft ³ of WBA resin	3	3
Groundwater composition		
Perchlorate mg/L	1.5	0.05
Bicarbonate Alkalinity, mg/L	150	150
Treated water composition		
Perchlorate, mg/L	<0.004	<0.004
Bicarbonate alkalinity, mg/L	N/A - 5	30
WBA resin treatment capacity, BV	6,500	15,500
Regeneration solution	Biodegrade and discharge to sewer	Scavenge perchlorate and reuse or discharge to sewer
Biodegradation treatment rate, gpm	2.0 (or 0.1% of feed)	N/A
Scavenger resin capacity, meq/L	N/A	800

5.1.1.3 Major Equipment

Table 12 provides a summary of major equipment for both treatment scenarios.

Table 12. Major Equipment.

Equipment Description	Remediation	Drinking Water	Approx. Unit/Package Cost
Tanks and Vessels			
Ion exchange vessels (2 trains) – 12-ft diameter	4	4	48,000
Regeneration and protonation tanks – 6,000 gal	2	2	3,000
Regeneration rinse feed tank – 2,500 gal	1	1	1,850
Acid and Caustic storage tanks – 6,000 gal	2	2	6,630
Pumps			
Regeneration and protonation – 400 gpm	2	2	21,250
Acid feed for protonation and pretreatment	2	2	1,950
Caustic feed for regeneration and posttreatment	2	2	2,700
Rinse/transfer	2	2	12,150
Instrumentation and Controls			
pH controllers	4	4	1,370
Level sensors/switches	4	4	1,500
Flow meters	3	3	2,500
Programmable logic controller and operator inter-face terminal (OIT) (pkg)	1	1	17,240
Other			
WBA resin (lead & lag +10% margin) per ft ³	1,466	1,466	500
Biodegradation system, CSTR – 2 gpm (pkg)	1	N/A	850,000
Ion exchange scavenger 15 ft ³ transportable	N/A	4	7,500
Stripping tower	N/A	1	95,000

5.1.2 Operating and Maintenance Cost

5.1.2.1 Primary O&M Cost Components

The primary O&M cost components are acid and caustic consumed in pretreatment, posttreatment, and regeneration operations. Sulfuric acid (H₂SO₄) is the least expensive and safest strong acid to use for pretreatment and for resin protonation after caustic regeneration. However, hydrochloric acid (HCl) may be used without major cost impact for treating low-alkalinity (<50 mg/L) groundwater, or for scenarios that result in infrequent regeneration (>5,000 BV treatment capacity). Sodium hydroxide (NaOH) is the least expensive and most efficient caustic to use for resin regeneration. In addition, high concentrations of sodium salts that result from the regeneration process will not cause precipitation or scaling problems, which could be the case if other caustic compounds were used for regeneration.

Sodium hydroxide was used in the cost evaluation for posttreatment neutralization, which is required to restore pH and residual alkalinity for drinking water applications. Other caustic compounds, such as soda ash (Na₂CO₃) or calcite (CaCO₃), may be used for posttreatment and may be less expensive and more efficient than sodium hydroxide for some applications. Use of soda ash and calcite for posttreatment depends on treated water hardness and alkalinity

requirements. Carbon dioxide stripping may not be required for low-alkalinity groundwater, or non-drinking-water applications.

The WBA resin ion exchange treatment process is designed to eliminate the need for additional pumping operations. The cost for pumping water to the system is common to any pump-and-treat system and, therefore, was not included in this cost analysis. The power requirement for an air blower for the stripping tower is minimal for two reasons: 1) stripping towers will be required only for certain high-alkalinity drinking water applications, and 2) CO₂ is very easy to strip from water and can be stripped in natural draft systems. Therefore, a low air volume or blower power is required. The power requirement for controls and for the small acid and caustic pumps used in this process will also be minimal. The power required for regeneration pumps will be significant; however, these pumps will operate intermittently with an anticipated duty cycle of less than 25%. The average electrical power consumption is estimated to be no more than the equivalent of 10 horsepower or 20 kw-hr/AF.

The cost of treating spent regenerating solution is included in the cost evaluation. For drinking water applications, this cost includes the cost for scavenger resin replacement and incineration. Scavenger resin vessels are small (15-30 ft³), transportable vessels that will be leased from and serviced by a third party. Spent regenerating solution from large treatment systems (>5,000 gpm), or from remediation of groundwater with high concentrations of perchlorate (>500 ppb), may be more economically treated using a CSTR anoxic biodegradation process.

A full-scale ion exchange process will be fully automated, being controlled by a programmable logic controller (PLC), and require little labor. However, some labor will be required for maintenance; collecting samples; monitoring the receipt of acid, caustic, and scavenger resin; monitoring and evaluating system performance; and monitoring resin regeneration (~once per month). Average labor requirement is estimated to be 10 hours per week.

Macroporus styrene divinylbenzene WBA resin can maintain performance for more than 5 years in industrial applications that require daily regenerations. Regeneration frequency for drinking water and remediation applications are predicted to be no more than 15 to 30 times per year based on pilot performance. Therefore, WBA resin life for groundwater treatment applications is predicted to be 7 years.

5.1.2.2 O&M Cost Basis

Table 13 provides a summary of the cost bases used for the major O&M costs. Chemical costs are based on quotes for bulk tank truck delivery to a southern California site. Scavenger resin cost includes disposal and servicing costs for Purolite A-530E or A-600-type resin. WBA resin cost is the current market price for commercially available Purolite D4170 resin. Biodegradation cost includes chemicals, nutrient, power, and maintenance cost (but not labor) for a small CSTR treatment system sized to treat the effluent from a 2,000 gpm ion exchange process.

Table 13. Material Cost Basis.

Description	Cost
Sulfuric acid, 96-98%	\$0.05/lb
Sodium hydroxide, 50%	\$0.15/lb
Scavenger resin service (replace, dispose, transport)	\$180/ft ³
Weak base anion resin	\$500/ft ³
Electricity	\$0.15/Kw-hr
Operator labor	\$60/hr
Biodegradation cost (ClO ₄ ⁻ dry basis)	\$2.00/Kg

Table 14 provides a summary of capital and O&M cost for 2,000 gpm remediation and drinking water treatment systems. The normalized cost basis is dollars per AF of water treated. This is the most appropriate basis for comparing high flow rate remediation and drinking water treatment systems. One AF is equal to 325,851 gal of water.

Purchased equipment cost in Table 14 was derived from the equipment unit and package costs and the quantities provided in Table 12. The other components of capital cost—installation, instrumentation and controls, piping, electrical services, site work, service facilities, engineering, construction expenses, and other indirect costs—were estimated as a percentage of the purchased equipment cost. This is an appropriate capital cost estimating procedure for order-of-magnitude estimates for new plants. Percentages were based on published factors (Plant Design and Economics for Chemical Engineers, Fifth Edition; Peters, Timmerhaus, & West) and factors used recently by an architect and engineering firm (A&E) that was consulted for a similar project. The percentages used also took into account the complexity and maturity of the unit operations involved. The biodegradation unit cost was based on a budgetary cost estimate provided by an A&E for a similar-size treatment system. The biodegradation unit cost includes all engineering, installation, and start-up costs.

Operating costs were derived from the cost bases provided in Table 13. Labor hours were based on 20 hr/wk for drinking water applications and 40 hr/wk for remediation applications due to the addition of a biodegradation treatment system. Additional operating cost for the biodegradation system was added to include the cost of nutrient, chemicals, and electricity.

Table 14. Cost Summary.

Cost Category	Cost Subcategory	Cost Basis (\$)	
		Remediation	Drinking Water
Capital Costs	Purchased equipment cost*	325,000	450,000
	Purchased equipment installation	162,500	225,000
	Instrumentation and controls	97,500	135,000
	Piping	113,750	157,500
	Electrical services	48,750	67,500
	Site work	65,000	90,000
	Service facilities	162,500	225,000
	Engineering	146,250	202,500
	Construction expenses	130,000	180,000
	Other indirect	48,750	67,500
	Biodegradation unit (installed)	850,000	N/A
	Subtotal:	2,150,000	1,800,000
	Start-up and testing	75,000	75,000
	Initial resin charge	733,000	740,500
	Total Capital Costs:	2,958,000	2,615,500
Operating Costs	Labor**	62,400	31,200
	Consumables**		
	Sulfuric acid	51,920	50,120
	Sodium hydroxide	28,790	59,760
	WBA resin replacement	104,760	104,760
	Scavenger resin replacement	N/A	17,200
	Biodegradation unit operation	11,770	N/A
	Electricity	9,720	9,720
	Total Operating Costs:	269,360	272,760
	Quantity treated AF	3,180	3,180
	Calculated unit O&M costs, \$/AF	\$84.70	\$85.77

* Based on Table 12

** Based on Table 13

5.1.3 Economy of Scale

There is significant economy of scale for multiple-train systems larger than 2,000 gpm. Regeneration and protonation tanks and pumps are underutilized in single-train (one 2,000-gpm IX system) or dual-train (two 1,000-gpm IX systems) treatment processes. Since regeneration and protonation can be accomplished in 2 days or less, the duty cycle for this equipment may be less than 10% for a single train or 20% for a dual train. Therefore, the regeneration equipment for a 2,000-gpm system could support the regeneration requirement for a 10,000-gpm treatment facility with little additional cost. A similar underutilization situation exists with the scavenger-resin treatment equipment. The equipment used for the 2,000 gpm scenario would be adequate for a 10,000-gpm treatment system.

The pretreatment and posttreatment operation would be performed in single pretreatment and posttreatment systems regardless of the scale of the treatment operation. Pretreatment and

posttreatment equipment costs would be scaled proportional to the treatment requirement, and the scaling exponent would be 0.5 or less.

The cost of the biodegradation system for remediation applications is not proportional to scale at the very small treatment volume required. The scaling exponent for the biodegradation system in the treatment range of 2 to 10 is less than 0.25. Therefore, a 10-gpm treatment system will cost less than 50% more than a 2-gpm treatment system.

The labor requirement for biodegradation is independent of scale for this application. Labor associated with the ion exchange process will increase modestly due to the additional regeneration events necessary for a multiple-train treatment system. Based on these economies of scale, the projected cost for a 10,000-gpm treatment system was developed and provided in Table 15. Operating costs are 10 to 20% lower for the 10,000-gpm system.

Table 15. Capital and Operating Costs for a 10,000-gpm Treatment System.

	Remediation	Drinking water
Capital cost	\$9.65 million	\$9.00 million
Normalized operating cost—per AF	\$69.54	\$78.46

5.2 COST ANALYSIS

5.2.1 Major Cost Drivers

5.2.1.1 Groundwater Alkalinity

The amount of acid required for groundwater pretreatment to attain the pH necessary for good performance is directly proportional to groundwater alkalinity. Acid cost is \$1.03/AF for every 10 mg/L of bicarbonate alkalinity in the groundwater, based on sulfuric acid at \$0.05 per pound, delivered. In high pH water (>8.3), carbonate and hydroxide also contribute to the acid requirement. In this situation, converting total alkalinity to bicarbonate alkalinity permits accurate pretreatment costs to be developed.

5.2.1.2 Perchlorate Concentration

Groundwater perchlorate concentration directly affects the cost of scavenger resin for drinking water applications and the cost of biodegradation for high-concentration, remediation applications. Since perchlorate is very concentrated in spent regenerating solution, more than 100 times more perchlorate can be exchanged onto a strong-base scavenger resin than is removed by the weak-base primary resin for drinking water applications where the groundwater is less than 100 ppb. Based on a loading ratio of 100:1 (SBA equivalents for spent regenerant water to WBA equivalents for groundwater), and resin replacement and disposal cost of \$180/ft³, the scavenger cost is \$1.08 AF for every 10 ppb of perchlorate removed from the groundwater.

For remediation applications (>1 ppm), perchlorate biodegradation O&M cost is approximately \$2 per kg of perchlorate biodegraded. Therefore, the cost for biodegrading spent regenerating

solution is \$2.47/AF of groundwater treated for every 1 ppm of perchlorate removed for the groundwater.

5.2.1.3 Treated Water Alkalinity

Posttreatment cost is directly proportional to the alkalinity required in the treated water. For drinking water applications, the treated water must possess properties that do not contribute to either scaling or corrosion in water distributions systems. Water alkalinity between 30 and 60 mg/L will generally satisfy this requirement. However, scaling indices, such as the Langelier Saturation Index (LSI) that are used to predict scaling and corrosion tendencies, are a function of pH, temperature, calcium hardness, total dissolved solids, and alkalinity. Therefore, specific posttreatment approaches are highly dependent on site-specific water quality. For instance, a very hard water or high total dissolved solids (TDS) water may not require a high residual alkalinity (<30 mg/L), and the converse may be true for soft water. Water quality will also affect treatment chemicals. Calcite (CaCO_3) is a very effective, low-cost approach to neutralize acid and increase alkalinity and hardness of low-hardness, low TDS groundwater. However, soda ash (Na_2CO_3) or caustic soda (NaOH) would be more appropriate treatment chemicals for high TDS, high alkalinity water. The conservative approach taken for this analysis uses caustic soda (\$0.15/lb delivered). Posttreatment cost is \$5.38/AF for every 10 ppm of residual bicarbonate required. Alternative treatment approaches (CaCO_3 , and Na_2CO_3) must be considered on a case-by-case basis and have the potential to reduce treatment cost. For a remediation application where water is re-injected into the contaminated aquifer, CO_2 removal by stripping and/or neutralization/alkalinity adjustment may not be required.

5.2.1.4 Resin Regeneration Cost

Regeneration cost is independent of groundwater perchlorate concentration below 100 ppb because the perchlorate isotherm for the resin tested is linear from 1 to 100 ppb. This means that within this linear range, the slope of the line or capacity of the resin is approximately the same. Regeneration costs are minimal for several reasons 1) low regeneration frequency (~4 weeks), 2) near stoichiometric amounts (5% excess) of caustic needed for regeneration, and 3) near stoichiometric amounts (~5% excess) of acid needed for protonation. Remediation of water with much higher perchlorate concentrations will result in more frequent regenerations, but this is not a linear relationship. For remediation of water at Redstone Arsenal (1.5-2.0 ppm perchlorate), the regeneration frequency was modeled to be every 11 days versus every 27 days for drinking water applications (50 ppb) at a treatment rate of 3 gpm/ft³.

5.2.1.5 WBA Resin Cost

Resin replacement cost is a major component of operating cost for several reasons. The best performing commercial resin produced by Purolite costs \$500/ft³. While this resin is commercially produced, production rates are relatively low at this time. Higher production rates may lead to reduced cost. Perchlorate treatment systems for drinking water require a “multi-barrier” or two-stage, lead-lag treatment configuration. This configuration, in effect, doubles the amount of resin necessary for a treatment process. Assuming that resin performance will diminish gradually over time, a 10% margin was included by increasing resin volume by 10%.

The annualized cost of resin replacement was based on a 7-year life for both drinking water and remediation applications.

Table 16 summarizes the major operating cost components (chemicals, resin, labor, and electricity) and shows each cost component as a percentage of the total. It is evident that resin replacement cost is the primary component of O&M cost followed by pretreatment and posttreatment cost for drinking water applications. Labor cost for the remediation scenario includes labor for operation of the biodegradation treatment system. Labor cost, as a percent of the total, will decrease with scale.

Table 16. Summary of Operating Cost Components.

Cost Element	Remediation		Drinking Water	
	\$/AF	%	\$/AF	%
Pretreatment acid	\$15.35	18.1%	\$15.35	17.9%
Posttreatment caustic	\$2.69	3.2%	\$16.13	18.8%
Regeneration caustic and acid	\$7.34	8.7%	\$3.07	3.6%
WBA resin replacement	\$32.94	38.9%	\$32.94	38.4%
Scavenger resin replacement	N/A	N/A	\$5.41	6.3%
Effluent biodegradation	\$3.70	4.4%	N/A	N/A
Labor	\$19.62	23.2%	\$9.81	11.4%
Electricity	\$3.06	3.6%	\$3.06	3.6%
Total:	\$84.70	100.0%	\$85.77	100.0%

5.2.2 Life-Cycle Analysis

A 20-year plant life and 6% interest rate were used to determine the net present value of the operating costs. The results of this analysis show that the water treatment cost for the WBA technology is only \$90 to \$95 per AF. It is important to note that operating cost of the WBA technology is much less than current technologies. The low operating cost is the primary factor contributing to the low treatment cost.

5.3 COST COMPARISON

Treatment costs in dollars per AF were evaluated for five different scenarios: 1) a WBA resin application for drinking water that uses a scavenger resin to treat spent regenerating solution, 2) a WBA resin application for remediation of groundwater that uses biodegradation to treat spent regenerating solution, 3) the SBA regenerable resin process (ISEP) using CalRes 2000 that is in operation at La Puente, California, 4) the single-use, SBA resin process using PWA2 resin that is in operation at the Lincoln Avenue Water Company site, Altadena, California, and 5) a proposed single-use, SBA resin process using CalRes 2100 or USF 9710 planned for Castaic Lake Water Agency, California. The cost analysis is summarized in Table 17.

Costs for the WBA scenarios are based on the data provided in Table 14. Costs for the other scenarios were provided in a table published by the California Department of Health Services (DHS) dated October 14, 2004, and based on NASA Action Memorandums dated August 24, 2004, and April 19, 2006. The actual costs provided in the DHS table for the ISEP process were \$2.8 million for capital and \$1.6 million for O&M. However, these costs did not include

Table 17. Cost Comparison Summary.

System	WBA Drinking Water	WBA Groundwater Remediation	SBA-ISEP La Puente	SBA Lincoln Avenue	SBA Castaic Lake
Capacity, gpm	2,000	2,000	2,500	2,000	2,400
Treatment Vol. AF/yr	3,182	3,182	3,978	3,182	3,818
Annual O&M cost	\$273,000	\$270,000	\$1,950,000	\$1,084,124	\$940,000
Capital cost	\$2,615,500	\$2,958,000	\$4,800,000	\$2,480,000	\$3,700,000
Interest rate	6%	6%	6%	6%	6%
Plant life	20	20	20	20	20
O&M present worth	\$3,131,288	\$3,096,879	\$22,366,346	\$12,434,817	\$10,781,726
Total present worth	\$5,746,788	\$6,054,879	\$27,166,346	\$14,914,817	\$14,481,726
Treatment Cost, \$/AF	90	95	341	234	190

treatment or disposal of the perchlorate-contaminated spent regeneration brine solution. ARA recently did an analyses under contract to the Baldwin Park Operable Unit (BPOU), controlling authority for La Puente, California for brine treatment. The least expensive approach, biodegradation, would add \$2 million in capital cost and \$350,000 in O&M cost. These costs were added to the values provided by DHS and the sum used in Table 17. The Lincoln Avenue system is leased. An approximate estimate of capital cost was derived by multiplying the lease cost (\$9,500/mo.) by the term (20 years) and adding known site improvement costs (\$200,000). The Castaic Lake system is proposed. No attempt was made to adjust the 2004 costs to 2006 values.

A 20-year plant life and 6% interest rate were used to determine the net present value of the operating costs. The results of this analysis clearly show that the water treatment cost for the WBA technology is less than 25% of current regenerable resin systems (ISEP) and less than 50% of the least expensive single-use resin systems. It is important to note that the treatment cost for the WBA technology is only slightly dependent on capital cost. This is due to the large difference in operating cost of the WBA technology compared to current technologies. For instance, a 50% increase in the estimated capital cost for a WBA drinking water system from \$2.616 million to \$3.923 million would only increase the treatment cost from \$90/AF to \$111/AF. This is still less than one third of the cost for current regenerable resin processes and less than half the cost for existing single-use resin processes.

6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

Key factors affecting cost were acid and caustic consumed in pretreatment, posttreatment, and regeneration operations. For pretreatment, alkalinity of the contaminated water directly impacts the volume of acid required. Sulfuric acid (H_2SO_4) is the least expensive strong acid to use for pretreatment and for resin protonation after caustic regeneration. However, hydrochloric acid (HCl) may be used without major cost impact for treating low-alkalinity (<50 mg/L) groundwater, or for scenarios that result in infrequent regeneration ($>5,000$ BV treatment capacity).

The amount of alkalinity required in the posttreated water (water for discharge) directly impacts the cost of posttreatment. Sodium hydroxide was used in the cost evaluation for posttreatment neutralization, which is required to restore pH and residual alkalinity for drinking water applications. Other caustic compounds, such as soda ash (Na_2CO_3) or calcite (CaCO_3), may be used for posttreatment and may be less expensive and more efficient than sodium hydroxide for some applications. Use of soda ash and calcite for posttreatment depends on treated water hardness and alkalinity requirements. Carbon dioxide stripping may not be required for low-alkalinity groundwater, or non-drinking water applications.

The concentration of perchlorate in the contaminated water will also impact the cost of this process. Higher concentrations will require more frequent regenerations. Sodium hydroxide (NaOH) is the least expensive and most efficient caustic to use for resin regeneration. In addition, high concentrations of sodium salts that result from the regeneration process will not cause precipitation or scaling problems, which could be the case if other caustic compounds were used for regeneration.

6.2 PERFORMANCE OBSERVATIONS

Demonstration performance with respect to acceptance criteria for the performance objectives and the secondary performance criteria identified in the demonstration plan are discussed in Sections 3.1, 4.1, and 4.2 of this report. The performance criteria identified for the ion exchange process objectives were met. However, to mitigate failure or contaminant breakthrough using this technology, two redundancy measures were identified: 1) redundancy of pH monitoring and control for the pretreatment operation will prevent neutralization and loss of capacity of the WBA resin if pH control was lost, and 2) configuring columns as lead and lag acts as a safety measure to prevent perchlorate leakage or breakthrough.

6.3 SCALE-UP

Ion exchange equipment availability can limit the treatment rate to 1,000 to 2,000 gpm; however, these systems can consist of multiple trains to overcome this limitation. There is significant economy of scale for multiple-train systems larger than 2,000 gpm. Regeneration equipment for a 2,000-gpm system could support the regeneration requirement for a 10,000-gpm treatment facility with little additional cost (see Section 5.1.3). A similar underutilization situation exists

with the scavenger-resin treatment equipment. The equipment used for the 2,000-gpm scenario would be adequate for a 10,000-gpm treatment system.

The pretreatment and posttreatment operation would be performed in single pretreatment and posttreatment systems regardless of the scale of the treatment operation. Pretreatment and posttreatment equipment costs would be scaled proportional to the treatment requirement and the scaling exponent would be 0.5 or less.

The cost of the biodegradation system for remediation applications is not proportional to scale at the very small treatment volume required. The scaling exponent for the biodegradation system in the treatment range of 2 to 10 is less than 0.25. Therefore, a 10-gpm treatment system will cost less than 50% more than a 2-gpm treatment system.

The labor requirement for biodegradation is independent of scale for this application. Labor associated with the ion exchange process will increase modestly due to the additional regeneration events necessary for a multiple-train treatment system. Based on these economies of scale, the projected cost for a 10,000-gpm treatment system was developed and provided in Table 15. Operating costs are 10 to 20% lower for the 10,000-gpm system.

6.4 OTHER SIGNIFICANT OBSERVATIONS

Water quality parameters including alkalinity, hardness, perchlorate concentration, sulfate concentration, and treated water alkalinity affect cost and performance. The amount of acid required to achieve operating pH is directly proportional to feed water alkalinity and, therefore, pretreatment cost. Perchlorate concentration dictates the resin treatment capacity and regeneration frequency which affects regeneration cost. In addition, perchlorate concentration and regeneration frequency impact the amount of spent regenerating solution and treatment cost. Hardness and desired alkalinity of treated water affect the caustic requirement for neutralization, which affects neutralization cost.

The most economical pretreatment approach is to use sulfuric acid. However, the use of sulfuric acid will increase the residual sulfate concentration. If feed alkalinity and sulfate concentrations are high, residual sulfate concentration could exceed the National Secondary Water Treatment guideline of 250 mg/L (the Secondary Water Treatment guideline for sulfate in California is 500 mg/L). In cases where the concentration of sulfate would exceed secondary treatment guidelines, it may be necessary to replace some or all of the sulfuric acid with the more expensive hydrochloric acid.

6.5 LESSONS LEARNED

The following list summarizes some of the key lessons learned for implementing WBA resin technology:

- Treating waters with low alkalinity would not require a CO₂ stripping step.

- The zero-discharge scavenger resin process is best suited for spent regenerant solutions generated from treating waters with lower perchlorate concentration (<100-500 ppb).
- Biodegradation is best suited for spent regenerant solution(s) generated from treating waters with higher perchlorate concentration (>100-500 ppb).
- Other contaminants such as nitrate, selenate, arsenate, and/or chromate may be treated concurrently under certain circumstances.

The primary problems with the perchlorate monitor demonstration were mechanical and control-related failures. The concept, approach, and chemistry of the method are valid and effective. Therefore, we should have teamed with an instrument manufacturer who could have provided off-the-shelf devices that would reliably execute the mechanical and control functions. This would have permitted the demonstration effort to focus on method performance issues (detection limits, matrix interference, etc.) instead of the mechanical performance and control issues that plagued the monitor portion of this project. The monitor portion of this effort would have required funding at a level two to three times the budgeted amount to resolve both the mechanical and control issues and define the chemical performance of the method.

6.6 END-USER ISSUES

Ms. Terry de la Paz and Mr. Carl Wes Smith of the Environmental Restoration Office of Redstone Arsenal were updated on progress and performance of the technology throughout the demonstration. They reported progress in their Tier 1 meetings, which included representatives from Redstone Arsenal, NASA, Alabama Department of Environmental Management, and EPA. ARA will present demonstration results at the next Tier 1 meeting (approximately mid-April 2006). One issue that Redstone Arsenal faces is the presence of co-contaminant TCE. TCE present in the wells did not adversely impact perchlorate treatment using WBA resin; however, treatment in conjunction with ion exchange will be needed to remove TCE from the contaminated water.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

On January 26, 2006, EPA adopted a reference dose (RfD) for perchlorate of 0.0007 mg/kg-day. This RfD equates to a Drinking Water Equivalent Level (DWEL) of 24.5 micrograms per liter (or 24.5 ppb). As a result of EPA establishing a reference dose for perchlorate, the DoD issued a policy letter that established 24 ppb as the “level of concern for managing perchlorate.” The letter further states that, “Once established, DoD will comply with applicable state or federal promulgated standards whichever is more stringent.” The letter also provides guidance for perchlorate with respect to sampling and analysis, record keeping, environmental restoration, operational ranges, drinking water systems, and wastewater discharges.

While attending the 2005 Partners Symposium, ARA met with a California DHS regional representative who expressed interest in this technology being demonstrated for drinking water applications. Treating drinking water using ion exchange has already been approved by the California DHS; however, a demonstration of the WBA resin ion exchange process will promote

the permitting of this technology. Since this meeting, ARA has met with Dr. Rick Sakaji of the California DHS and designed a strategy for permitting this technology.

A patent application was filed to protect this technology, jointly owned by ARA and Purolite, and efforts to commercialization of the process are underway. ARA and Purolite will market this technology to a wide range of clients. ARA has many contacts with DoD agencies addressing perchlorate concerns and DoD contractors. Purolite markets their products worldwide and provides over 70% of the resin currently being used to remove perchlorate from drinking water at approximately 20 different sites in the United States. Purolite and ARA have a very large incentive to commercialize and transfer this technology to DoD and the private sector.

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APPENDIX A

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