

# **Selenium Treatment/Removal Alternatives Demonstration Project**

## **Mine Waste Technology Program Activity III, Project 20**

by

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Butte, Montana 59702

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## **Notice**

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## Foreword

The mining and mineral processing industries are developing and modifying technologies that will enable these industries to operate more efficiently. If improperly dealt with, the waste generated by these industries can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by the Congress of the United States with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct EPA to perform research to define and measure the impacts and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis to support the policies, programs, and regulations of EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The National Energy Technology Laboratory (NETL) of the U.S. Department of Energy (DOE) has responsibilities similar to NRMRL in that NETL is one of several DOE centers responsible for planning, implementing, and managing research and development programs. This document is a product of the research conducted by these two Federal organizations.

This document is the final report for EPA's Mine Waste Technology Program (MWTP) Activity III, Project 20, Selenium Treatment/Removal Alternatives. MWTP is a program developed through an Interagency Agreement between EPA and DOE. MSE Technology Applications, Inc., manages MWTP and is responsible for the field demonstration and reporting activities. The information generated under this program provides a vital communication link between the researcher and the user community.

One of the objectives of MWTP is to identify the types of mining wastes impacting the nation and the technical issues that need to be addressed. Other objectives of the program are: 1) address these technical issues through application of treatment technologies; 2) determine the candidate technologies that will be tested and evaluated; and 3) determine the candidate sites where these evaluations will take place.

E. Timothy Oppelt, Director  
National Risk Management Research Laboratory

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Roger Wilmoth from NRMRL served as EPA's MWTP Program Manager, and Melvin Shupe from DOE served as DOE's Technical Program Officer. Mary Ann Harrington-Baker served as MSE's Program Manager, Helen Joyce served as MSE's Project Manager, and Jon Cherry served as the Project Manager for KUCC. KUCC was a major contributor to the project through in-kind services including: permitting, laboratory analysis, influent tank rental, transfer of water from Garfield Wetlands-Kessler Springs to the MSE Demonstration Site, site-specific safety training, warehouse services, and miscellaneous supplies and chemicals. Dr. Larry Twidwell from Montana Tech of the University of Montana was the technology provider of the catalyzed cementation process and also served as technical consultant for the chemical processes demonstrated. Dr. D. J. Adams and Tim Pickett of Applied Biosciences served as technology providers for the biological selenium reduction technology and the enzymatic selenium reduction technology. The organization and execution of this project was a collaborative effort between the participants mentioned above. Without these contributions, this project could not have been completed.

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## Acronyms

AA	atomic absorption
AB	Applied Biosciences Corporation
BASBR	baffled anaerobic solids bed reactors
BDAT	best demonstrated available technology
BSeR™	biological selenium reduction
EPA	U.S. Environmental Protection Agency
ICP	inductively coupled plasma
KEL	Kennecott Environmental Laboratory
KUCC	Kennecott Utah Copper Corporation
MCL	maximum contaminant level
MSE	MSE Technology Applications, Inc.
MWTP	Mine Waste Technology Program
ORP	oxidation-reduction potential
std dev	standard deviation
TCLP	toxicity characteristic leaching procedure
TNPV	total net present value

## Executive Summary

This document is the final report for the U.S. Environmental Protection Agency's (EPA) Mine Waste Technology Program (MWTP) Activity III Project 20—Selenium Treatment/Removal Alternatives Demonstration Project. MWTP is a program developed through an Interagency Agreement (IAG) between EPA and the U.S. Department of Energy. MSE Technology Applications, Inc. (MSE) manages MWTP and owns/operates the MSE Testing Facility in Butte, Montana. MSE proposed and was granted funding for the Selenium Treatment/Removal Demonstration Project during the April 1999 IAG Management Committee Meeting.

Selenium contamination originates from many sources including mining operations, mineral processing, abandoned mine sites, petroleum processing, and agricultural run-off. Kennecott Utah Copper Corporation's (KUCC) Garfield Wetlands-Kessler Springs site has a well characterized selenium contaminated artesian flow and was selected as the site for demonstrating various selenium treatment technologies. The contamination is of a low-level, high-volume nature that makes most treatment options expensive.

The objective of the Selenium Treatment/Removal Alternatives Demonstration Project was to test and evaluate technologies capable of removing selenium from Garfield Wetlands-Kessler Springs water to below 50 micrograms per liter ( $\mu\text{g/L}$ ), the National Primary Drinking Water Regulation Maximum Contaminant Level for selenium established by EPA. Several technologies with the potential to treat this water were presented in MWTP, Activity I, Volume VII, *Issues Identification and Technology Prioritization Report—Selenium*.

Three technologies were selected for field demonstration during this project:

- EPA's Best Demonstrated Available Technology (BDAT)—ferrihydrite precipitation with concurrent adsorption of selenium

onto the ferrihydrite surface (ferrihydrite adsorption) optimized by MSE;

- a catalyzed cementation process developed by Dr. Larry Twidwell of Montana Tech of the University of Montana with assistance from MSE; and
- a biological selenium reduction (BSeR™) process developed by Applied Biosciences Corporation (AB) of Salt Lake City, Utah.

Because ferrihydrite adsorption is considered EPA's BDAT for selenium removal from solution, it was considered the baseline technology and was used as a basis for comparison with the innovative selenium removal processes. All work was performed under an EPA-approved Quality Assurance Project Plan.

All three of the processes were able to achieve the target level for selenium in effluent samples under optimized conditions. Table ES-1 summarizes the results from the field demonstration for each technology and also includes results from additional testing of the catalyzed cementation process that occurred at MSE's testing facility following the field demonstration.

The BSeR™ process performed most consistently during the demonstration. During the 187 days of evaluation, all but four effluent samples from the BSeR™ process were below 10  $\mu\text{g/L}$ , and greater than 70% of the effluent samples were below detection (2  $\mu\text{g/L}$ ).

A secondary objective of the project was to perform an economic analysis for scale-up of the processes to treat 300 gallons per minute (gpm) flow at the Kessler Springs site. The retrofit of a vacant water treatment plant/associated equipment at the Kessler Springs site was used as the basis for the capital costs.

Table ES-2 is a summary of the outputs of the economic analysis for the selected technologies treating groundwater with 2 mg/L selenium operating at

300 gpm. The figures are the total net present value for each process that was demonstrated in the field. The figures used represent an order of magnitude cost estimate. The BSeR™ process was the most economically attractive technology demonstrated during this project.

A fourth technology—enzymatic selenium reduction—was demonstrated on a bench scale by AB. Enzymatic systems have the following advantages over live microbial systems: 1) the potential for greatly increasing kinetics; 2) nutrients are not required; and 3) the effects of toxic process solutions can be eliminated. Methods to economically prepare stable enzyme preparations and enzyme preparations from different microorganisms were investigated. Several immobilization polymers were evaluated to increase operational longevity. Calcium alginate performed the best in regards to ease of handling, toxicity, cost, and performance. Problems with stability or possibly the loss of an electron donor system were problematic throughout the testing. The stability or electron donor systems of the preparations tested was not sufficiently reproducible to warrant pilot-scale tests during this project.

These and other selenium treatment technologies were also reviewed under a Comprehensive Environmental Response, Compensation, and Liability Act feasibility study at the KUCC site. The BSeR™ process technology has been identified by KUCC as the preferred treatment for Garfield Wetlands-Kessler Springs water if KUCC is unable to recycle the selenium-bearing water into the existing process water circuit. Currently, KUCC is recycling 100% of the Garfield Wetlands-Kessler Springs flow back into various operations as make-up water. If the process water circuit is shut down, the BSeR™ process technology has been identified as the technology capable of treating the Garfield Wetlands-Kessler Springs water.



**Table ES-1.** Demonstration results summary.

<b>Ferrihydrite Adsorption Results</b>		
Treatment Condition	Mean Selenium Effluent Concentration ±Standard Deviation (n = sample size)	Minimum Selenium Concentration
Low iron (~1400 mg/L iron)	304 µg/L ±69 (n = 27)	115 µg/L
Medium iron (~3000 mg/L iron)	201 µg/L ±103 (n = 13)	42 µg/L (at midpoint of process)
High iron (~4800 mg/L iron)	90 µg/L ±28 (n = 5)	35 µg/L (at midpoint of process)
Ferrous/ferric (~1200 mg/L ferrous/1200 mg/L ferric iron)	563 µg/L ±280 (n = 5)	409 µg/L
Recycle Sludge (~2340 to 13,290 mg/L iron)	387 µg/L ±58 (n = 12)	77 µg/L
<b>Catalyzed Cementation Results</b>		
Treatment Condition	Mean Selenium Effluent Concentration (µg/L) ±Standard Deviation (n = sample size)	Minimum Selenium Effluent Concentration (µg/L)
Catalyzed Cementation	834 µg/L ±204 (n = 42)	193 µg/L
Catalyzed Cementation with Increased Oxidation/Decreased pH in the reactor tank	35 µg/L (n = 2)	26 µg/L
Additional Testing of Catalyzed Cementation at MSE	3 µg/L <sup>1</sup> ±4.4 (n = 5)	<1 µg/L
<b>BSeR™ Process Results</b>		
Residence Time	Mean Selenium Effluent Concentration (µg/L) <sup>2</sup> ± Standard Deviation (n - sample size)	Minimum Selenium Effluent Concentration (µg/L)
12 hrs (Series 1)	8.8 µg/L ±10.2 (n = 17)	< 2 µg/L
11 hr (Series 2)	4.9 µg/L ±4.9 (n = 16)	< 2 µg/L
8 hr (Series 3)	< 2 µg/L ±2.6 (n = 12)	< 2 µg/L
5.5 hr (Series 2)	< 2 µg/L ±2.1 (n = 26)	< 2 µg/L

<sup>1</sup> Nondetects were substituted with 50% of detection limit (0.5 µg/L).

<sup>2</sup> Nondetects were substituted with 50% of detection limit (1 µg/L).

**Table ES-2.** Comparative economic analysis of demonstrated technologies.

Cost	Ferrihydrite Adsorption	Catalyzed Cementation	BSeR™ Process
Capital	\$1,026,835 (includes system design, demolition, building modifications, equipment purchase and installation, construction, system start-up, commissioning, and project closeout)	\$1,083,285 (includes additional research and development work, system design, demolition, building modifications, equipment purchase and installation, construction, system start-up, commissioning, and project closeout)	\$603,999 (includes biofim support material, inoculum, system design, building modifications, equipment purchase and installation, construction, commissioning, and project closeout)
Annual Operating and Maintenance Cost	\$2,084,559 (includes reagent costs, manpower, maintenance, and power for equipment use)	\$1,165,358 (includes reagent costs, manpower, maintenance, and power for equipment use)	\$135,029 (includes nutrient costs, manpower, maintenance, and power for equipment use)
Net Present Value of Annual Operating and Maintenance Costs	\$16,992,127	\$9,499,323	\$1,100,682
Total Net Present Value	\$18,017,962	\$10,582,608	\$1,704,681
Net Present Value of \$/1,000 gallons treated	\$13.90	\$8.17	\$1.32

# 1. Introduction

## 1.1 Project Overview

This Final Report was prepared specifically for the Mine Waste Technology Program (MWTP), Activity III, Project 20—Selenium Treatment/Removal Alternatives Demonstration Project, which addresses the U.S. Environmental Protection Agency's (EPA) technical issue of *Mobile Toxic Constituents—Water*.

The Selenium Treatment/Removal Alternatives Demonstration Project consisted of demonstrating one standard process and three innovative processes for selenium removal from Garfield Wetlands-Kessler Springs Water at Kennecott Utah Copper Corporation (KUCC) in Magna, Utah.

## 1.2 Project Purpose

The purpose of the Selenium Treatment/Removal Alternatives Demonstration Project was to test and evaluate technologies capable of removing selenium from Garfield Wetlands-Kessler Springs water to below 50 µg/L, the National Primary Drinking Water Regulation maximum contaminant level (MCL) for selenium. Garfield Wetlands-Kessler Springs water has a selenium concentration of approximately 2,000 µg/L. Several technologies with the potential to treat this water were presented in MWTP, Activity I, Volume VII, *Issues Identification and Technology Prioritization Report—Selenium* (Ref. 1).

Three technologies were selected for field demonstration during Phase 1 of this project:

- EPA's Best Demonstrated Available Technology (BDAT) (Ref. 2)—ferrihydrite precipitation with concurrent adsorption of selenium onto the ferrihydrite surface (ferrihydrite adsorption) optimized by MSE Technology Applications, Inc. (MSE);
- a catalyzed cementation process developed by Dr. Larry Twidwell of Montana Tech of the University of Montana with assistance from MSE; and
- biological selenium reduction (BSeR™) process developed by Applied Biosciences (AB) of Salt Lake City, Utah.

Because ferrihydrite adsorption is considered EPA's BDAT for selenium removal from solution, it was considered the baseline technology and was used as a basis for comparison with the innovative selenium removal processes.

The demonstrations of the ferrihydrite and catalyzed cementation technologies were conducted at KUCC during October and November 1999. These two technologies were demonstrated in the MWTP demonstration trailer that was constructed as part of MWTP Activity III, Project 9—Arsenic Removal Demonstration Project. The BSeR™ process was designed by AB and constructed with assistance from KUCC. The BSeR™ process demonstration was conducted from October 1999 through April 2000.

Phase 2 of this project included additional testing of the catalyzed cementation process under optimized conditions identified during the field demonstration and bench-scale testing of an enzymatic selenium reduction process developed by AB. The additional testing of the catalyzed cementation process was conducted at MSE's testing facility in Butte, Montana, during March and April 2000. The bench-scale testing of the enzymatic selenium reduction technology was conducted at AB's testing facility in Utah from March 2000 through January 2001.

## 1.3 Scope of the Problem

Selenium is a problem in many wastewaters and is a common water contaminant throughout the world. Selenium contamination represents a major environmental problem in at least nine western U.S. states. This contamination originates from many sources including mining operations, mineral processing operations, abandoned mine sites, petroleum processing, agricultural runoff and natural groundwater. For mining waste, the principal sources of selenium contamination are copper- and uranium-bearing ores and sulfur deposits. Selenium is commonly found in mining wastewaters in concentrations ranging from 3 to >12,000 µg/L (Ref. 1). The National Primary Drinking Water Standard MCL is 50 µg/L for selenium. The National Fresh Water Quality Standard is 5 µg/L for selenium. The U.S. Fish and Wildlife Service has recommended that the national fresh water quality standard be lowered to 2 µg/L to protect fish, waterfowl, and endangered aquatic species. Questioning of this standard has arisen because some laboratory and field studies indicate that water borne selenium concentrations as low as 2.0 µg/L may bio-accumulate in aquatic food chains to toxic levels.

## 1.4 Site Description

KUCC's Garfield Wetlands-Kessler Springs site has a well defined selenium contaminated artesian flow with the following characteristics:

- groundwater containing selenate ranging from <50 to 10,000 µg/L;
- artesian flows 250–500 gpm, with selenium concentrations from 200 to 2,000 µg/L; and
- varying site water quality with some naturally occurring total dissolved solids concentrations greater than 5,000 mg/L.

Selenium, the primary contaminant of concern at this site, is present as selenate in the site's groundwater. Groundwater formerly surfaced from two main sources within the site into a large wetlands area on the boundary of the Great Salt Lake. Selenium contaminated artesian flow is currently captured and routed into KUCC's process water circuit. The contamination is of a low-level, high-volume nature that makes most treatment options expensive.

KUCC co-chairs a technical review committee with EPA, State organizations, and public groups to evaluate remediation/treatment strategies to substantially lower the release of selenium into the Garfield Wetlands and the Great Salt Lake. The Garfield Wetlands site is well characterized with site water and solids chemistry data available. A Garfield Wetlands site assessment indicated that natural selenium reduction is occurring at limited locations in the wetlands. Additionally, laboratory treatability testing of site waters indicated that these waters were at least somewhat difficult to treat, even though they appear by chemical analysis to only contain selenium as the major contaminant. A chemical profile of the Garfield Wetlands-Kessler Springs water is presented in Table 1-1.

This site provided an excellent opportunity to test the selected selenium removal technologies under MWTP. The BSeR™ process was constructed near Garfield Wetlands-Kessler Springs. The portion of the water emanating from the springs was fed directly to the biological process. The MWTP demonstration trailer was located near a vacant water treatment facility at KUCC approximately 2 miles from the Garfield Wetlands-Kessler Springs site. A photograph of the MWTP demonstration trailer and associated equipment at the demonstration site is shown in Figure 1-1. Feed water for the catalyzed cementation and the ferrihydrite precipitation processes was transported from Garfield Wetlands-Kessler Springs by a water truck and placed in a large bulk storage tank at that location.

**Table 1-1.** Composition of Garfield Wetlands-Kessler Springs Water

Analyte	Units	Sampled 5/5/99
Conductivity	µmho/cm	2,720
pH	standard units	7.08
Temperature	°C	13
Alkalinity	mg/L as CaCO <sub>3</sub>	315
Hardness	mg/L as CaCO <sub>3</sub>	601
Total Dissolved Solids	mg/L	1,520
Total Suspended Solids	mg/L	<3
Calcium	mg/L	145
Chloride	mg/L	496
Potassium	mg/L	11.6
Magnesium	mg/L	58
Sodium	mg/L	380
Sulfate	mg/L	294
Silver	µg/L	<1
Aluminum	µg/L	<5
Arsenic	µg/L	140
Barium	µg/L	34
Cadmium	µg/L	<1
Chromium	µg/L	<10
Copper	µg/L	29
Iron	µg/L	<300
Manganese	µg/L	<10
Molybdenum	µg/L	100
Nickel	µg/L	<40
Lead	µg/L	<5
Selenium	µg/L	1,950
Selenate	µg/L	1,870
Selenite	µg/L	49
Zinc	µg/L	<10

All field testing of these processes was conducted by MSE and AB with assistance from KUCC personnel as necessary. All sampling and field work was performed according to procedures outlined in the project specific quality assurance project plan and existing standard operating procedures.

All chemical analyses for collected samples were conducted at the Kennecott Environmental Laboratory (KEL) located at KUCC. KEL is certified by the State of Utah and audited annually by EPA. Confirmatory analyses were performed on 10% of samples at the HKM Analytical Laboratory located in Butte, Montana. A comparison of the KEL analyses and the HKM confirmatory analyses is presented in Appendix A—Summary of Quality Assurance Activities.

## 1.5 Technology Descriptions

The following technologies were demonstrated during Phase 1 of this project:

- BDAT—ferrihydrite adsorption of selenium;
- catalyzed cementation of selenium; and
- BSeR™ process.

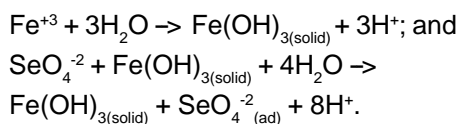
A brief description of each technology is provided in the following sections. During Phase 2 of the project, an enzymatic selenium reduction technology was evaluated, and additional data was collected for the catalyzed cementation technology.

### 1.5.1 Ferrihydrite Adsorption of Selenium

Ferrihydrite precipitation with concurrent adsorption of selenium onto the ferrihydrite surface (ferrihydrite adsorption) is EPA's BDAT for treating selenium-bearing waters. For adsorption of selenium using ferrihydrite to occur, the ferric ion (Fe<sup>+3</sup>) must be present in the water. Selenate (Se<sup>+6</sup>) is most effectively

removed from the water at pH levels below 4.

The chemical reactions for ferrihydrite precipitation of selenium are:



The selenium-iron solid product must be separated from the treated water before the process of selenium removal is complete. During the demonstration, solid-liquid separation was accomplished using a settler and filter press.

The selenium process water was delivered to the test site by a small tank truck and then transferred to a bulk storage tank. From the storage tank, the process water was pumped to the ferrihydrite adsorption process and the catalyzed cementation process. This arrangement provided the capability for operating both systems simultaneously.

Detailed in Figure 1-2 is the mechanical configuration of the ferrihydrite precipitation process system as tested during the pilot scale demonstration at a flow rate of approximately 5 gpm. Starting from the bulk storage tank, Garfield Wetlands-Kessler Springs water was introduced to the front end of the system. A digital programmable peristaltic metering pump controlled the flow rate of the process water through the treatment system. Following the pump, a turbine flow meter recorded the flow rate and the total volume of water processed.

The ferric chloride reagent was introduced next just in front of a static mixer. The static mixer ensured a homogeneous mix, thus, reducing reaction time.

From the static mixer, the process water was fed directly into an 80-gallon tank where a lime slurry was injected to increase the pH of the process water. A pH probe and controller monitored and adjusted the pH to an operator-selected set point. Additionally, the oxidation-reduction potential (ORP) of this tank was monitored and recorded. The overflow from the pH adjustment tank was collected in the transfer tank. A flocculent

was added to the second 80-gallon tank to assist with solid separation in the 1,000-gallon thickener. A level transmitter and level controller regulated the process water level in the transfer tank by adjusting the pumping rate of the transfer pump. At a flow rate of 5 gpm, the residence time of the thickener was about 200 minutes. This was adequate time for the solids to settle in the cone of the thickener tank.

The treated process water was removed from the top of the thickener and gravity fed to an 80-gallon batch transfer tank. To bring the pH of the water to neutral, a small amount of lime slurry was added to the transfer tank prior to final filtering and discharge. A pH probe and controller regulated the proper amount of lime slurry injected. The discharge pump operation was controlled by a level switch system that forced the water through a three-stage bag filter system. The filter system was a precaution against carryover of thickener solids in the event of an upset in the system.

Solids that accumulated in the bottom of the thickener were periodically removed by a diaphragm pump. This sludge slurry was then dewatered using a filter press. The liquid separated from the solids was returned to the thickener. The filter cake solids were removed from the filter press and prepared for analysis or disposal by placing them in appropriate containers. A photograph of the ferrihydrite adsorption process inside the MWTP demonstration trailer is presented in Figure 1-3.

### **1.5.2 Catalyzed Cementation of Selenium**

Catalyzed cementation is a process that was developed to remove arsenic and other heavy metals such as thallium and selenium from water. The term catalyzed cementation describes the process's ability to remove heavy metals from solution by cementation on the surface of the iron particles. It was anticipated that the catalyzed cementation process would have the ability to treat and remove selenium from solution regardless of its valence state (+6 or +4). To optimize the cementation process, proprietary catalysts are added to the process

to increase the selenium removal efficiency.

Detailed in Figure 1-4 is the configuration of the catalyzed cementation process system as tested during the pilot-scale demonstration. Starting from the bulk storage tank, Garfield Wetlands-Kessler Springs water was introduced to the front end of the system at approximately 1 gpm. A digital programmable peristaltic metering pump controlled the flow rate of the process water to the treatment system. Following the pump, a turbine flow meter was used to record the flow rate and the total volume of water processed. The catalyst reagent was introduced next, just in front of the first static mixer. The static mixer ensured a homogeneous mix and reduced the reaction time. Next, sulfuric acid was injected to lower the pH of the process water to the desired level. A second static mixer was used to speed-up the pH adjustment before the process water entered the elemental iron reactor. This reactor was a specialized tank designed to fluidize the iron particles. Additionally, pH and ORP were both closely monitored and recorded within this reactor. Iron particles that carried over were trapped in a small, cone-bottom tank and pumped back to the reactor for reuse.

Under gravity flow, the process water from the top of the small, cone-bottom tank was routed to a second 80-gallon reactor. Here, the pH of the water was raised with a lime slurry and an oxidizer was added to complete the required reaction. Flocculent was also added to this reactor to assist with solid separation. A level transmitter and level controller regulated the process water level in the reactor tank by adjusting the pumping rate of the transfer pump. At a flow rate of 1 gpm, the residence time of the thickener was about 15 hr. This was adequate time for the solids to settle in the cone of the thickener tank.

The treated process water was removed from the top of the thickener and gravity fed to an 80-gallon batch transfer tank. The operation of the discharge pump was controlled by a level switch system that forced the water through a three-stage bag filter system. The filter system was a precaution against carryover of thick-

ener solids in the event of an upset in the system.

Solids that accumulated in the bottom of the thickener were periodically removed by a diaphragm pump. This sludge slurry was then processed by a filter press. The sludge liquid separated from the solids was returned to the thickener. The filter cake solids removed from the filter press were prepared for analysis or disposal by placing them in appropriate containers. A photograph of the catalyzed cementation process in the MWTP demonstration trailer is shown in Figure 1-5. In addition to the ferrihydrite adsorption and catalyzed cementation processes, the BSeR™ process was also demonstrated.

### **1.5.3 Biological Reduction of Selenium**

To accomplish biological selenium reduction, researchers at AB of Salt Lake City, Utah, have developed the BSeR™ process using anaerobic solids bed reactors (BASBR). Selenium (selenate and selenite) was reduced to elemental selenium by specially developed biofilms containing specific proprietary microorganisms. This process produces a precipitate of elemental selenium. With the aid of backflushing, 97% of the selenium reduced in the system can be removed from the bioreactors. This process was designed by AB and constructed with assistance from KUCC.

The BSeR™ process was demonstrated using a defined mixture of *Pseudomonas* and other microbes for removing selenium from Garfield Wetlands-Kessler Springs water. A block flow diagram of the BSeR™ process is shown in Figure 1-6. A photograph of the BSeR™ process at the Garfield Wetlands-Kessler Springs site is shown in Figure 1-7.

Garfield Wetlands-Kessler Springs water was pumped to the BSeR™ process at a flow rate of approximately 1 gpm using a solar pump. A flow meter/totalizer recorded the actual flow rate and the total volume of water processed by the BSeR™ process. The Garfield Wet-

lands-Kessler Springs water then entered a series of 500-gallon bioreactors containing carbon/biosolids/biofilm combination or carbon/biofilm, depending on the test series. Nutrients were supplied to the reactors at three locations in the process. When the water had flowed through the appropriate number of bioreactors, it was filtered by a slow sand filter before discharge.

Testing done previous to the pilot-scale demonstration produced the patent pending BSeR™ process that is demonstrated to reduce selenate and selenite in mining process solutions, petroleum wastewaters, and agricultural run-off using both single microbes and site-specific selenium-reducing bacteria. Initial batch and continuous bioreactor tests demonstrated selenium removal up to 97% in wastewaters containing up to 33.1 mg/L selenium in 4 to 6 hr with high-density microbial and microbial cocktail biofilms. In additional laboratory tests using a semi-fluidized bed reactor, live microbial and microbial cocktail biofilms have demonstrated selenium reduction rates of approximately 40 mg/L per 6 hr (Refs. 3 through 6).

The BSeR™ process implementation/configuration approach was to characterize and optimize naturally occurring microbial and like proprietary laboratory strains for each site-specific application. Using known, tested microbial strains and enhanced biofilm establishment techniques prevented the nonintentional incorporation of pathogens, undesirable indigenous nonselenium reducing microbes, and helped to ensure optimum selenium removal rates.

### **1.5.4 Enzymatic Reduction of Selenium**

AB has isolated an optimized mixture of naturally occurring bacterial enzymes from heterotrophic bacteria previously isolated from selenium contaminated mining waters and soils. The bacterial enzymes reduce selenate and selenite in mining wastewaters to elemental selenium. Advantages of these cell-free systems over live bacterial systems in-

clude: (1) the potential for greatly increasing kinetics; (2) nutrients are not required; and (3) the effects of toxic process solutions can be eliminated. Bench-scale testing was performed to evaluate the enzymatic selenium reduction process and to make a decision whether to scale-up the process to pilot-scale for field demonstration. The enzymatic selenium reduction process was not recommended for scale-up due to the instability of the enzyme system matrix; therefore, a process flow diagram is not included for this technology.

## **1.6 Project Objectives**

The primary objective of the field demonstration project was to assess the effectiveness of the processes being tested for removing selenium from Garfield Wetlands-Kessler Springs Water. More specifically, the objective that was defined for the project was to reduce the concentration of dissolved selenium in the effluent waters to a level under the National Primary Drinking Water Regulation MCL for selenium (50 µg/L) established by the EPA.

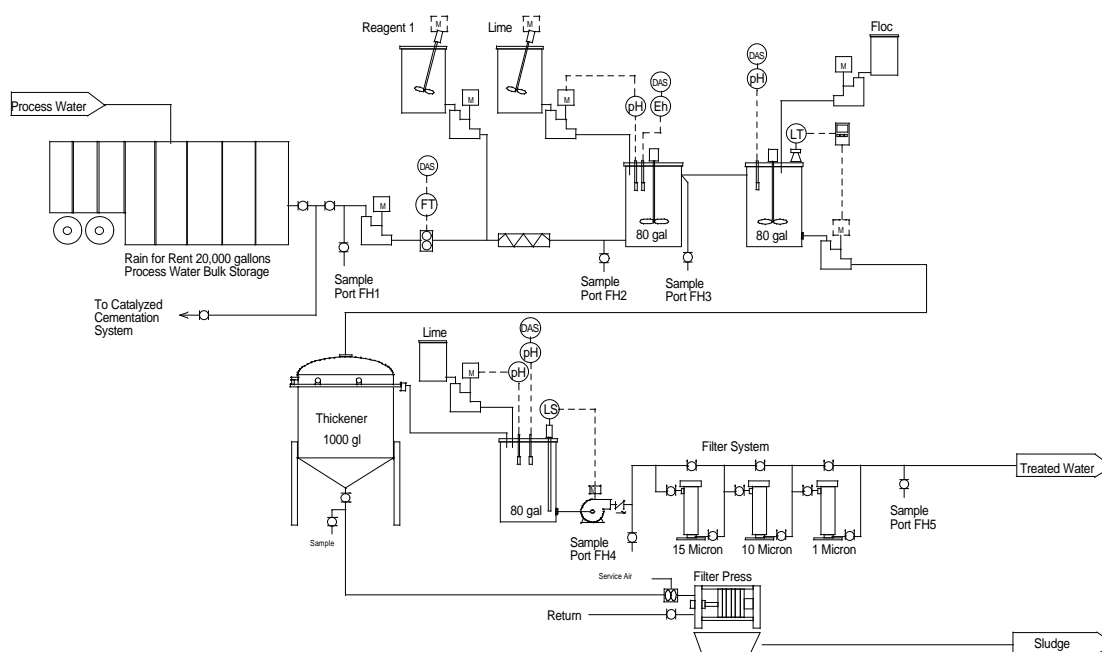
A secondary objective for the products from the catalyzed cementation and ferrihydrite precipitation processes was to render them environmentally stable by demonstrating that selenium results will be below the Maximum Concentration for Toxicity Characteristic using toxicity characteristic leaching procedure (TCLP) of 1.0 mg/L.

For AB's BSeR™ process, the product was expected to be marketable, and the secondary objective was to determine the purity and marketability of the product, and the impact the product had on process economics.

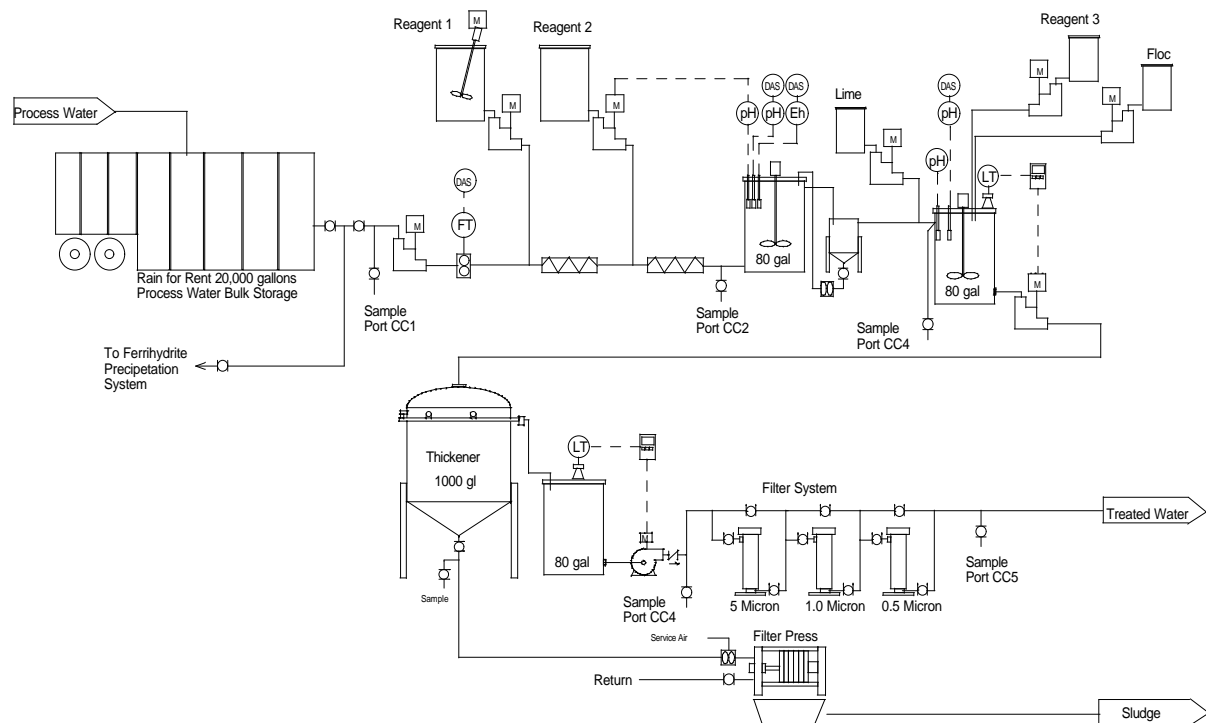
Another secondary objective was to perform an economic analysis for the scale-up of the processes tested to treat 300 gpm flow at the Garfield Wetlands-Kessler Springs site. The economic analysis for this project is presented in Section 3 of this report and represents an order of magnitude cost estimate.



**Figure 1-1. MWTP demonstration trailer at the field site.**



**Figure 1-2. Ferrihydrite precipitation process flow diagram.**

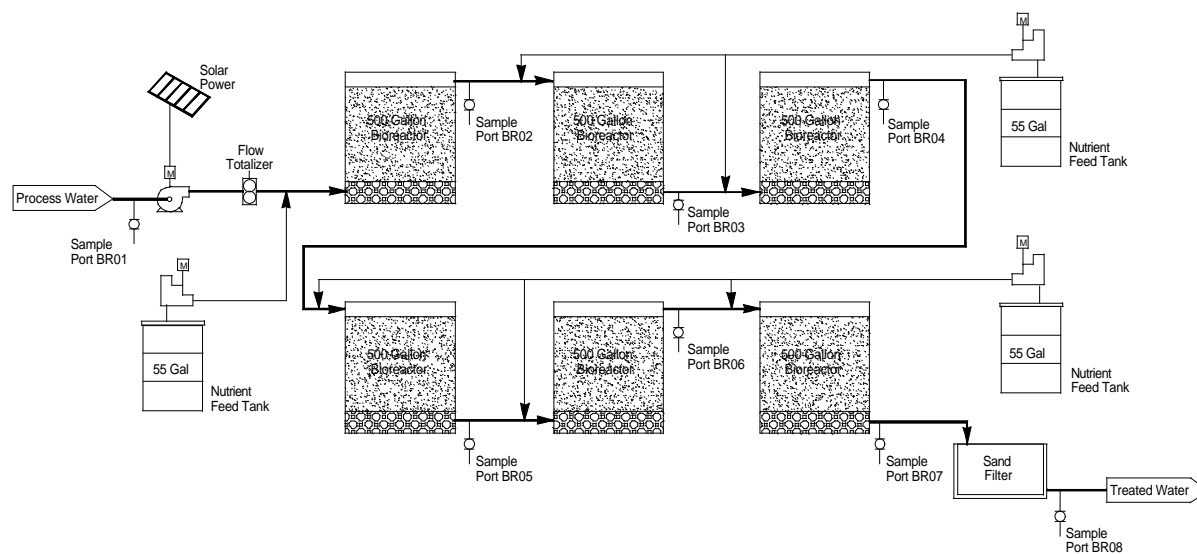


**Figure 1-4. Catalyzed cementation process flow diagram.**





**Figure 1-5. Catalyzed cementation process in MWTP demonstration trailer.**



**Figure 1-6. BSeR™ process flow diagram.**





**Figure 1-7. Field-scale BSeR™ process reactor.**

## 2. Demonstration Description and Results

The following sections provide a description of the pilot-scale demonstration and any additional work for each technology as well as a brief discussion of the demonstration results. Field and laboratory data associated with each pilot-scale and bench-scale technology demonstration are contained in Appendix B. The sampling and analysis schedules for each pilot-scale technology demonstration are contained in Appendix C.

The achievement of the primary project objective for each process was determined by analyzing effluent samples for dissolved selenium concentration. Appropriate statistical tests were performed to determine the effectiveness of each process for selenium removal. Procedures outlined in *Guidance for Data Quality Assessment* (Ref. 6) were used to determine whether the data from each process was statistically below the action level of 50 µg/L dissolved selenium. During the demonstration of the ferrihydrite precipitation and catalyzed cementation processes, several different testing conditions were necessary before the processes removed selenium below the action level. Eventually, all three processes did remove selenium to below the action level of 50 µg/L; however, the ferrihydrite adsorption and the catalyzed cementation processes did not remove selenium to below 50 µg/L on a consistent basis. To determine if the primary project objective had been met, a Wilcoxon Signed Rank Test was performed on the effluent data set for

each process. The Wilcoxon Signed Rank Test was selected because each of the distributions were non-normal. Data QUEST software was used to test for normality. Filibens statistic ( $n > 50$ ) was used for the BSeR™ process and the ferrihydrite adsorption process, while the Shapiro-Wilks test ( $n < 50$ ) was used for the catalyzed cementation process. Non-normality was detected for all three distributions at a 5% significance level. The null hypothesis for the Wilcoxon Signed Rank Test was  $H_0$ : mean  $\geq 50$  ppb, and the alternative hypothesis was  $H_a$ : mean  $< 50$  ppb. The calculated sum of the Ranks for each process was compared to the critical value ( $w$ ) at  $\alpha = 0.05$ . Because the number of samples was greater than 20, a large sample approximation to the Wilcoxon Signed Rank Test was performed by calculating the  $z$  statistic for each process and comparing it to the critical value of  $z_{1-\alpha}$ . The results of the inferential analysis for all three processes are presented in Table 2-1. The BSeR™ process was the only technology that could reject the null hypothesis at a 5% significance level; thus, the effluent data from the BSeR™ process effluent suggests that the alternative hypothesis is more likely. The only process that was shown to statistically reduce selenium below the action level of 50 µg/L was the BSeR™ process. In fact, all of the effluent data from all BSeR™ process tests were less than 50 µg/L with the exception of some samples collected during start-up phases as the biofilm was maturing.

### 2.1 Ferrihydrite Adsorption Demonstration and Results

The ferrihydrite precipitation process was optimized by MSE for the demonstration. During the demonstration, several different tests were run to obtain the lowest possible concentration of selenium in the effluent water.

The effluent samples from the ferrihydrite precipitation processes were characterized to determine how effectively each treatment condition removed selenium from the Garfield Wetlands-Kessler Springs water. The solid products from the ferrihydrite precipitation process were analyzed for TCLP constituents as well as total constituents of interest.

Ferrihydrite precipitation is considered EPA's BDAT for selenium removal. Several tests were performed to determine the iron concentration necessary to remove selenium to below the target level of 50 µg/L. The various tests included:

- low iron condition (~1400 mg/L iron);
- medium iron condition (~3000 mg/L iron);
- high iron condition (~4800 mg/L iron);
- ferrous/ferric condition (~1200 mg/L ferrous/1200 mg/L ferric); and
- sludge recycle conditions (~2340 to 13290 mg/L iron).

**Table 2-1.** Summary of Results for Wilcoxon Signed Rank Test

Process	R calculated	$w_{\alpha}$ critical	z calculated	$z_{1-\alpha,0.05}$ critical	Result
Ferrihydrite Adsorption	0	1,211	-6.846	1.645	*
Catalyzed Cementation	3	636	-21.85	1.645	*
BSeR™ Process	2,256	1,565	5.603	1.645	Reject the null hypothesis at a 5% significance level because $z$ calculated $> z$ critical.

\* There is not enough evidence to reject the null hypothesis at a 5% significance level because  $z$  calculated  $< z$  critical.

A graph of the results from the various test conditions is presented in Figure 2-1. The influent data represents Garfield Wetlands-Kessler Springs water, FH3 results were from midpoint in the system, and the effluent data are the discharge from the process. FH3 data are included because several times during the testing, results from midpoint in the process were less than the results at the effluent location. This may have been due to iron suppression of the selenium signal during inductively coupled plasma mass spectrometer analysis of the samples. The only conditions that removed selenium below 50 µg/L were the medium and high iron conditions, and this was only on a limited number of samples at the midpoint (FH3) of the process. Table 2-2 summarizes the results for each treatment condition.

2.1.1 Low Iron Test Results

The ferrihydrite demonstration was initiated in the MWTP demonstration trailer. The average pH during the low iron testing period was 3.9. The initial target iron concentration in the first 80-gallon tank in the process was approximately 1,400 mg/L iron (Fe/Se ratio, 900:1). Garfield Wetlands-Kessler Springs water was fed to the system at approximately 5 gpm. The mean selenium effluent concentration during the low iron tests was 303 µg/L [standard deviation (std dev), 69.4], well above the target of 50 µg/L. The minimum effluent selenium concentration during the low iron period was 115 µg/L.

2.1.2 Medium Iron Test Results

Because selenium removal was not at target levels, the target iron concentration was increased to 3,000 mg/L iron

(Fe/Se ratio, 2000:1). The average pH values recorded during this testing period was 4.1. The mean selenium effluent concentration during the medium iron concentration tests was 201 µg/L (std dev 103). The minimum effluent concentration achieved during this testing period was 42 µg/L selenium. Lower selenium results were achieved in the effluent samples with an increase in iron concentration from the low iron tests to the medium iron tests, so the iron concentration was further increased during the high iron concentration tests.

2.1.3 High Iron Test Results

The high iron test was initiated with iron concentrations of 4,800 mg/L (Fe/Se ratio, 3200:1). The mean selenium effluent concentration for this testing period was 90 µg/L (std dev 28), and the average pH value was 3.8. The minimum selenium effluent concentration achieved was 35 µg/L. Because reagent consumption (ferric chloride) was excessive during this period, high iron testing was suspended, and the system was set up to run a mixture of ferrous/ferric iron.

2.1.4 Ferrous/Ferric Test Results

To determine if the presence of ferrous iron in the system would positively impact selenium removal, a treatment condition using both ferrous and ferric iron was established. The amount of ferrous iron was increased in the system using ferrous sulfate. For this testing period, ferrous iron was approximately 1,200 mg/L, and ferric iron was approximately 1,200 mg/L. This process modification was not successful. The mean effluent selenium concentration during this test period was 563 µg/L (std dev 280). Once

these high selenium results were received from the laboratory, testing of this configuration was suspended.

2.1.5 Sludge Recycle Tests

The sludge generated from previous process tests was recycled during this test period. The iron used to attain the medium and high iron concentration conditions was in excess stoichiometrically so the sludge was recycled to take advantage of additional, available adsorption sites. To attain the desired iron concentration while minimizing reagent consumption, the sludge was recycled to the initial 80-gallon tank in the process. The mean selenium effluent concentration during this testing period was 387 µg/L (std dev 58). The minimum concentration of selenium in the effluent achieved during this testing period was 77 µg/L.

2.1.6 TCLP Results

To determine if the secondary objective had been achieved, filter cakes produced by the ferrihydrite adsorption process were subjected to TCLP analysis. The results are summarized in Table 2-3. While both filter cake samples failed TCLP for selenium (i.e., >1 mg/L), the total metal results presented in the last column of the table should be at least 20 times greater than the TCLP results but are instead less than detection. Therefore, TCLP results are questionable for the ferrihydrite adsorption process because the TCLP results for selenium do not correlate with the total selenium values. In the presence of excess iron, selenium is very difficult to detect in small concentrations.

Approximately 19,090 gallons of Garfield Wetlands-Kessler Springs water were processed during the ferrihydrite precipitation portion of the demonstration. The processed water was routed into KUCC's process water circuit and any wastes generated from the project were placed in KUCC's on site Comprehensive Environmental Response, Compensation, and Liability Act repository. Three days after the ferrihydrite tests were initiated, the catalyzed cementation process testing was initiated.

Table 2-2. Summary Results for Ferrihydrite Adsorption Tests

Treatment Condition	Mean Se Effluent Concentration ±Standard Deviation (n = sample size)	Minimum Selenium Concentration
Low iron	304 µg/L +69 (n = 27)	115 µg/L
Medium iron	201 µg/L +103 (n = 13)	42 µg/L (at midpoint of process)
High iron	90 µg/L +28 (n = 5)	35 µg/L (at midpoint of process)
Ferrous/ferric	563 µg/L +280 (n = 5)	409 µg/L
Recycle Sludge	387 µg/L +58 (n = 12)	77 µg/L

**Table 2-3.** TCLP/Total Selenium Results for Ferrihydrite Adsorption Filtercake Samples

Sample Description	Col. Date	AG-TCLP 0.1 mg/L	AS-TCLP 0.1 mg/L	BA-TCLP 0.1 mg/L	CD-TCLP 0.01 mg/L	CR-TCLP 0.1 mg/L	HG-TCLP 0.001 mg/L	PB-TCLP 0.1 mg/L	SE-TCLP 0.1 mg/L	SE-Total 0.5 mg/kg
FH Filtercake-221	10/31/1999	0.1	<0.1	0.1	<0.1	<0.1	0.001	<0.1	1.6	<0.5
FH Filtercake-225	11/18/1999	<0.1	<0.1	0.1	0.01	<0.1	<0.001	<0.1	1.1	<0.5

## 2.2 Catalyzed Cementation Process Demonstration

MSE tested several physical/chemical selenium removal technologies on a bench-scale to determine which technology would be tested on a pilot scale. Catalyzed cementation was the best selenium removal technology to emerge as a result of the bench-scale testing. Previous tests performed by Dr. Twidwell along with thermodynamic data strongly indicated that catalyzed cementation would be effective. Bench-scale results indicated that this process could remove selenium to below 50 µg/L. Scale-up to the pilot-scale did not immediately yield the same results.

Garfield Wetlands-Kessler Springs water was fed to the catalyzed cementation process at approximately 1 gpm. Chemistry conditions that were successful on a bench-scale were duplicated to maximize selenium removal. Despite attaining the proper conditions, selenium removal was not very successful for the majority of the tests. During the first 16 days of the test, the mean effluent selenium concentration was 834 µg/L (std dev 204). The minimum selenium concentration attained in the effluent water was 193 µg/L.

Near the end of the testing period, the pH in the cementation reactor was reduced to 3 and an increased oxidation condition was generated following the cementation step in an effort to improve the results. The mean effluent selenium concentration during this testing period was 35 µg/L, and the minimum effluent selenium concentration was 26 µg/L. These results were more promising than the initial portion of the testing, and the testing would have been continued; however, results were not received from the laboratory until the operation of the catalyzed cementation process had been

suspended. A summary of results from the field testing and additional testing of the catalyzed cementation process are summarized in Table 2-4. A graph of the influent and effluent selenium concentrations for the catalyzed cementation process is presented in Figure 2-2. Influent values represent the selenium concentration in Garfield Wetlands-Kessler Springs water, CC3 values represent midpoint of the process, and effluent values represent the discharge stream from the process. Approximately 10,000 gallons of Garfield Wetlands-Kessler Springs water were processed during the catalyzed cementation portion of the demonstration.

Additional testing to duplicate these optimum conditions for selenium removal was performed at MSE's testing facility. Preliminary results indicated that the process consistently removed selenium to below 40 µg/L, the inductively coupled plasma (ICP) detection limit at the HKM Laboratory. All samples below 100 µg/L were reanalyzed by furnace atomic absorption spectroscopy (AA) (detection limit 1 µg/L) to better quantify the selenium removal. The AA analysis yielded sample concentrations rang-

ing from <1 to 28 µg/L with a mean effluent concentration of 3 µg/L.

A process similar to catalyzed cementation is currently being investigated by Dr. Twidwell at Montana Tech of the University of Montana as part of MWTP, Activity IV, Project 19—*Removing Oxyanions of Arsenic and Selenium from Mine Waste Waters Using Galvanically Enhanced Cementation Technology*. The results of the research thus far have been very promising. If this modified cementation technology proves to be effective, it should be considered for pilot-scale testing.

Investigations utilizing agitated iron slurries and columns packed with iron have been performed by Eric Dahlgren (MSc graduate student at Montana Tech of the University of Montana and Dr. Twidwell (thesis advisor). These studies have demonstrated and optimized the cementation process applied to selenium removal from synthetic and actual plant process waters. Their results (Ref. 7) show that detection limit concentrations of selenium (<1 ppb) can be obtained utilizing the iron cementation technology.

**Table 2-4.** Summary of Results for the Catalyzed Cementation Process Demonstration

Treatment Condition	Mean Selenium Concentration (µg/L)±standard deviation (n = sample size)	Minimum Effluent Selenium Concentration (µg/L)
Catalyzed Cementation	834 µg/L ±204 (n = 42)	193 µg/L
Catalyzed Cementation with Increased Oxidation/Decreased pH in the Reactor Tank	35 µg/L (n = 2)	26 µg/L
Additional Testing of Catalyzed Cementation Under Optimized Conditions	3 µg/L <sup>1</sup> ±4.4 (n = 5)	<1 µg/L

<sup>1</sup> Nondetects were substituted with 50% of the detection limit (0.5 µg/L) to determine the mean selenium concentration.

**Table 2-5.** TCLP Results for Catalyzed Cementation Filtercake Samples

Sample Description	Col. Date	AG-TCLP 0.1 mg/L	AS-TCLP 0.1 mg/L	BA-TCLP 0.1 mg/L	CD-TCLP 0.01 mg/L	CR-TCLP 0.1 mg/L	HG-TCLP 0.001 mg/L	PB-TCLP 0.1 mg/L	SE-TCLP 0.1 mg/L
CC Filtercake-221	11/06/1999	<0.1	<0.1	0.1	<0.1	<0.1	0.001	<0.1	0.3
CC Filtercake-225	11/15/1999	<0.1	<0.1	0.1	0.02	<0.1	0.002	<0.1	<0.1

### 2.2.1 TCLP Results

To determine if the secondary objective was achieved, filter cake produced by the catalyzed cementation process was subjected to TCLP analysis. The results are summarized in Table 2-5. Both filter cake samples were below the TCLP threshold value for selenium of 1 mg/L. These results indicate that the catalyzed cementation process produced an environmentally stable precipitate, and therefore achieved the secondary project objective. In addition to the catalyzed cementation and ferrihydrite adsorption technologies, the BSeR™ process was also demonstrated.

## 2.3 Biological Selenium Reduction Process Demonstration

The BSeR™ process was demonstrated at the Garfield Wetlands-Kessler Springs site with a feed flow rate of approximately 1 gpm. Tests with residence times of approximately 12, 11, 8, and 5.5 hr (per reactor) were conducted. The BSeR™ process was demonstrated longer than the other processes to determine the reliability/longevity of the system. The BSeR™ process treatment unit was designed and built by AB with assistance from KUCC. Selenium values for all effluent samples were maintained below the 50 µg/L target for the entire test period. The pH in the individual reactor effluents ranged from 6.3 to 7.5, and the final discharge had an average pH of 7.26 over the entire pilot test period; anaerobic conditions were maintained in the reactors. Three different reactor series were operated in the field, treating a combined total of over 100,000 gallons of Garfield Wetlands-Kessler Springs water:

- Series 1 used 5 reactors in series (carbon/biosolids/biofilm) with a sixth reactor for inoculum and mixing nutrients to feed the reactors;
- Series 2 used 3 anaerobic reactors (carbon/biofilm) in series; and
- Series 3 used 3 anaerobic reactors (carbon/biofilm) in series.

Series 2 and 3 allowed for side-by-side comparison of two identical systems. Laboratory-scale reactors, started in advance of the field demonstration project, were used to help predict and optimize the BSeR™ process field reactors. Laboratory testing results are in Appendix D. An agricultural grade molasses was used as a base for a proprietary nutrient supplement that was mixed with the reactor feed waters to maintain the biofilm and provide energy for selenium reduction. A summary of the results from the BSeR™ process field testing is presented in Table 2-6. The mean selenium concentrations in the effluent for each residence time test were well below the 50 µg/L target concentration. Over 70% of the samples collected during the approximately 6 months of operation were below detection.

### 2.3.1 Series 1—Carbon/Biofilm and Biosolids Biofilm Reactors

The initial test configuration utilized both carbon/biofilm and biosolids/biofilm reactors in series. This test series was at a fixed retention time of 12-hr per reactor. After approximately 1 month of continuous operation, the reactors were decommissioned, and the matrix material was disposed. The five-reactor BSeR™ process system was terminated when the entire system was inadvertently heated to over 55 °C. The system was cleaned up, replumbed for operation as two, three-reactor systems; filled with new activated carbon; and reinoculated. Based on an evaluation of the biosolids matrix material, a decision was made to remove this matrix from future testing. The mean effluent concentration during this test series was 8.8 µg/L, and minimum effluent concentration was <2 µg/L. Figure 2-3 shows the results of these tests. The selenium removal was very good within the initial reactors; therefore, a decision was made that fewer reactors (three rather than five) could be used during subsequent test series.

**Table 2-6.** Summary of Results from BSeR™ Process Field Tests

Residence Time	BSeR™ Process Results	
	Mean Selenium Concentration (µg/L) <sup>1</sup> ± standard deviation (n = sample size)	Minimum Effluent Selenium Concentration (µg/L)
12 hr (Series 1)	8.8 µg/L ±10.2 (n = 17)	<2 µg/L
11 hr (Series 2)	4.9 µg/L ±4.9 (n = 16)	<2 µg/L
8 hr (Series 3)	<2 µg/L ±2.6 (n = 12)	<2 µg/L
5.5 hr (Series 2)	<2 µg/L ±2.1 (n = 26)	<2 µg/L

<sup>1</sup> Nondetects were substituted with 50% of detection limit (1 µg/L) to determine the mean selenium concentrations.

### 2.3.2 Series 2 and 3 Carbon/Biofilm Reactors

Two new series of reactors (three carbon/biofilm reactors each) were reconfigured for operation at the site. This new configuration allowed for side-by-side performance comparisons of two identical systems. In three different runs, systems were operated at retention times of 11, 8, and 5.5 hr (per reactor). Selenium removal, as a function of reactor retention time, is shown in Figure 2-4 combining data from the three reactor retention times (11, 8, and 5.5 hr). The average reactor temperature was about the same as the influent spring water ~16 °C and the pH of the influent and effluent waters ranged from ~7.0 to 7.7 with a general slight lowering of pH through the reactor systems. The heterotrophic facultative anaerobic nature of the selected microbial biofilm allowed effective selenium removal to below MCL levels at ORP values ranging from >200 to <-50 millivolts.

Biofilms capable of reducing both selenate and selenite produced an elemental selenium precipitate that was readily evident in the reactors and connecting tubes after ~48 hr of operation (see Figure 2-5). All but four effluent samples were below 10 µg/L, and greater than 70% of the effluent samples were below detection.

An ICP metals scan was performed on the system effluents to determine the removal efficiencies of other metals present in the Garfield Wetlands-Kessler Springs water. The BSeR™ process system also effectively removed trace levels of arsenic and copper from the system. Arsenic in the Garfield Wetlands-Kessler Springs water was removed from 70 µg/L to below detection, and copper was removed from 26 µg/L to below detection.

Laboratory tests demonstrated that agitation and/or back flushing freed much of the biologically reduced selenium from the biofilm support materials (granular carbon) and that filtration through a filter press would remove approximately 97% of the selenium. The collected elemental selenium/microbial product has a potential market niche as an animal feed supplement. Marketability analysis conducted in collaboration with an international feed supplement distributor indicates that the elemental selenium from the BSeR™ process can be used in various feed supplements. According to the distributor, the microbial biomass associated with the BSeR™ process will contribute an additional value.

### 2.4 Enzymatic Selenium Reduction Bench-scale Evaluation

Applied Biosciences has isolated an optimized mixture of naturally occurring bacterial enzymes from heterotrophic bacteria previously isolated from selenium contaminated waters and soils. The bacterial enzymes, which reduce selenate and selenite to elemental selenium were used to develop the enzymatic selenium reduction process. The enzymatic selenium reduction process was demonstrated at bench-scale by AB. The testing included the following tasks:

- test enzyme extracts from microbes with best demonstrated selenium reduction capabilities;
- optimize selenium enzyme extraction/purification protocols;
- examine immobilization/encapsulation formulations to increase the stability and extend the functional longevity of the enzyme preparations;
- evaluate the immobilized/encapsulated enzyme preparations for du-

rability and enzyme function (kinetics and stability); and

- determine initial bench-scale process operational parameters and any pretreatment recommendations.

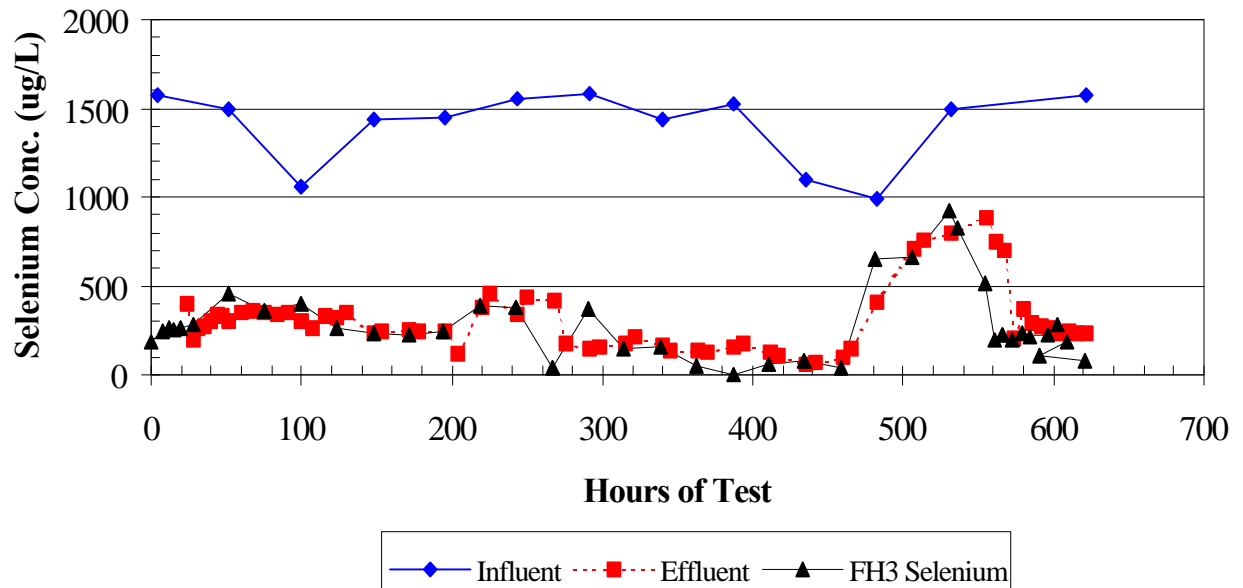
Top performing microbial cultures previously isolated from selenium containing mining wastes and soils were used as the source material for enzyme preparations. The prepared extracts were evaluated and screened over a 2-month period and compared to live cell preparations and appropriate controls. While the enzyme preparations initially exceeded the activity of the live cell preparations, a loss of stability was observed in the enzyme preparations that was not observed in the live cell preparations.

Due to the instability of the enzyme systems tested, the technology was not recommended for pilot-scale testing. The following conclusions were drawn based on the enzymatic selenium reduction bench-scale testing.

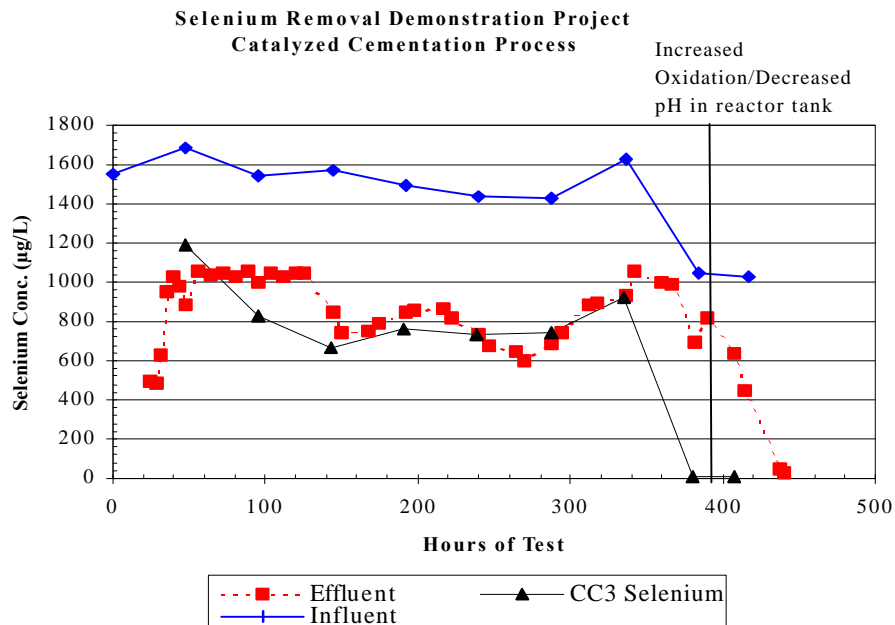
- Microorganisms are an alternative source for inorganic contaminant reducing enzymes.
- Selenium reduction in the presence of cyanide is possible using select enzyme preparations.
- Calcium alginate outperformed other encapsulation polymers in regards to ease of handling, toxicity, cost, and performance. AB's report summarizing the enzymatic bench-scale testing is contained in Appendix E.

Further research is recommended to further develop the electron donor system and enhance the operational longevity of the enzymatic selenium reduction technology. This research and development work is necessary to complete prototype development for this technology.

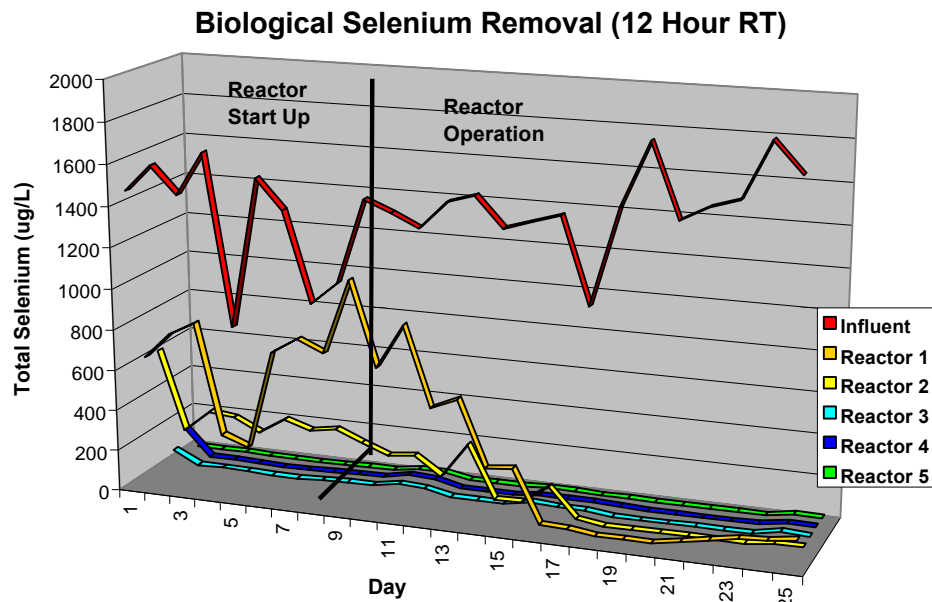
### Selenium Removal Demonstration Project Ferrihydrite Adsorption Process



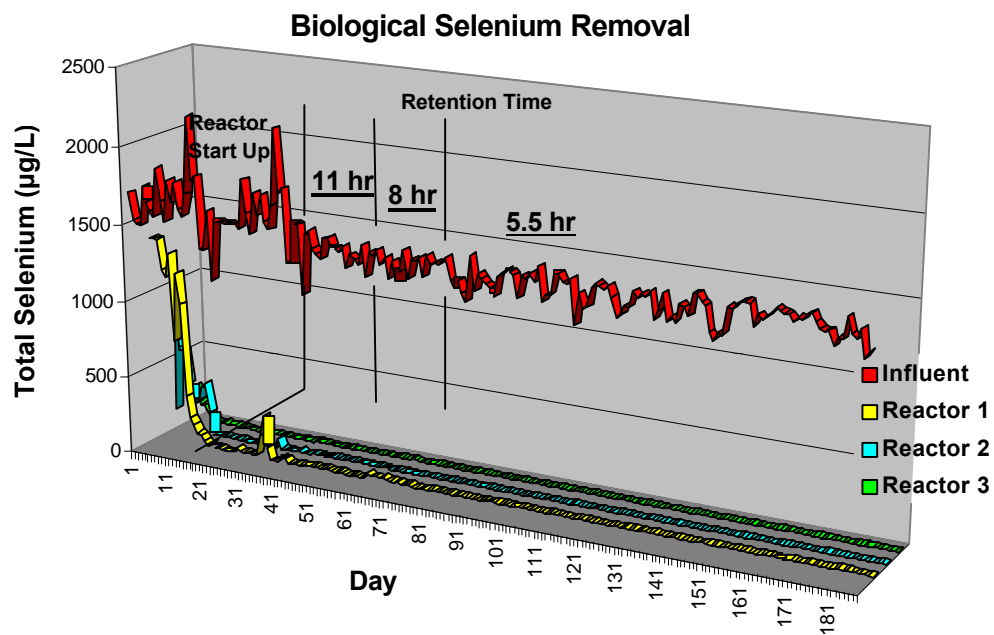
**Figure 2-1. Summary of results from ferrihydrite adsorption tests.**



**Figure 2-2. Summary of results for field catalyzed cementation process tests.**

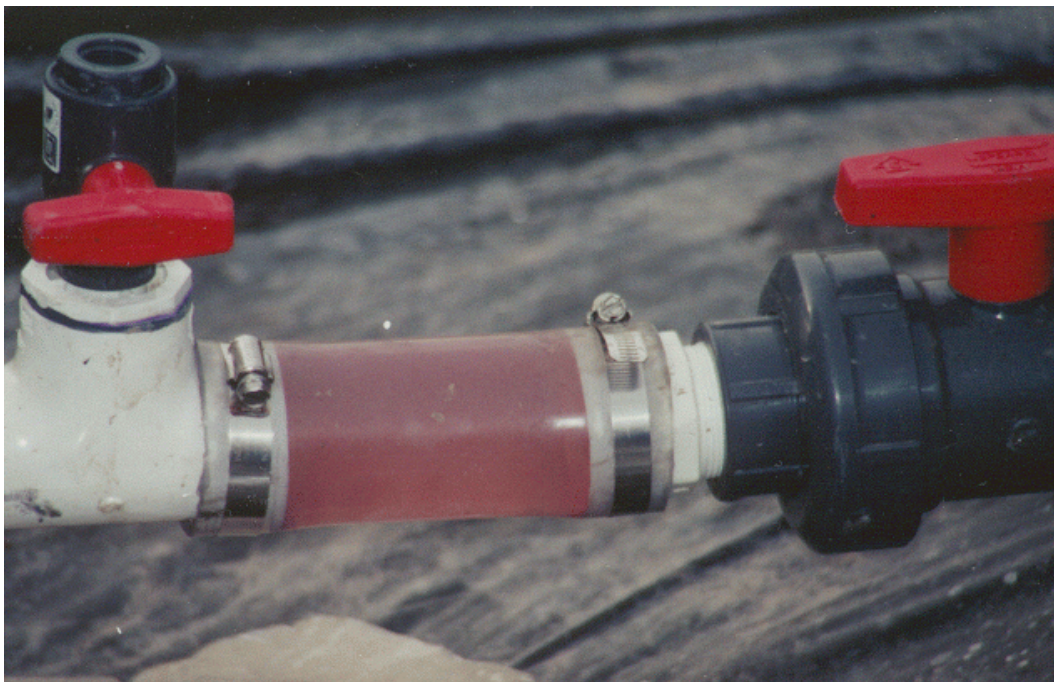


**Figure 2-3. Series 1 Pilot-scale BSeR™ process operation at a 12-hr retention time per reactor.**



**Figure 2-4. BSeR™ process pilot-scale reactor summary graph.**





**Figure 2-5. A red, amorphous, selenium precipitate observed in process piping after 8 hr of operation.**

### 3. Economic Analysis

A secondary objective of this study was to perform an economic analysis of the processes demonstrated. The costs presented are an order of magnitude cost estimate based on each of the treatment flow sheets. Definitions and cost estimation factors are taken primarily from similar work performed under MWTP. Itemized equipment lists were used where available.

Major cost items have been included. Capital costs include minor equipment, instrumentation, process piping, auxiliary engineering, and plant size factors for the ferrihydrite adsorption and catalyzed cementation processes. Capital costs provided by AB for the BSeR™ process included only biofilm support materials and \$40,000 to perform retrofits to the existing water treatment plant.

The following assumptions were made for completing the cost estimates:

- the processes would be installed at KUCC utilizing an existing water treatment facility;
- regulatory permits are in place;

- the Garfield Wetlands-Kessler Springs flow rate is 300 gpm, containing 2 mg/L selenium; and
- depreciation, leases, salvage and taxes were not considered.

A scale-up of each process to treat the entire 300 gpm of Garfield Wetlands-Kessler Springs flow was used as the basis of the economic analysis. Retrofit of equipment located at the existing water treatment facility was used as the basis for the scale-up. Because the field testing of the BSeR™ process and the catalyzed cementation process were only performed at 1 gpm, scaling up of these processes may not be as accurate as scaling up the ferrihydrite adsorption process that was demonstrated at 5 gpm.

#### 3.1 Ferrihydrite Adsorption of Selenium

The cost estimates presented for the scale-up of the ferrihydrite adsorption system are conceptual in nature and would be adjusted when an actual system design was implemented. Initial indications are that the reagent consumption

of this technology when effective (high iron condition) makes it cost prohibitive. The reagent consumption of this technology alone is estimated to be \$15.17/1,000 gallons treated when reagents are purchased in bulk. The estimates are based on information contained in the *Chemical Market Reporter* (Ref. 8). The majority of this cost was due to the high cost of the ferric chloride reagent, which accounts for \$14.31/1,000 gallons treated of the reagent costs. In a full-scale system, these costs would probably be lower if sludge generated was recycled to the reaction tank, thus, minimizing the fresh reagent usage.

Table 3-1 summarizes the capital costs and construction times necessary to retrofit the existing KUCC Waste Water Treatment Plant for ferrihydrite adsorption of selenium (high iron condition). The costs are associated with a system designed to handle a 300-gpm peak flow rate. Due to the difference in flow rate capability between the existing system and that of the scaled-up systems, most pumps and piping will require replacement.

**Table 3-1.** Capital Costs/Construction Schedule for Ferrihydrite Adsorption System Scale-Up

Task	Construction Time	Materials	Labor	Travel Nonlabor	Total
MSE System Design	11.3 weeks		\$145,450	\$11,538	\$156,988
MSE Subcontract Construction Oversight	8 weeks		\$51,530	\$21,568	\$73,274
MSE System Startup, Commissioning, and Project Closeout	5 weeks		\$44,190	\$10,266	\$54,375
Demolition, Building Modifications, Equipment Purchase, and Installation by Subcontract	12 weeks	\$612,107	\$36,079		\$648,850
Total	27.3 weeks				\$933,487
Schedule/Cost Contingency @ 10%	2.7 weeks				\$93,348
<b>TOTAL</b>	<b>30 weeks</b>				<b>\$1,026,835</b>

The cost of a filter press (approximately \$89,000) was also included in this estimate and may not be necessary depending on how the wastestreams from the system would be handled at KUCC. If a filter press was not necessary, the associated savings including shipping, filter press stand, sludge handling equipment, labor for installation, and design labor would be estimated at \$113,000.

## 3.2 Catalyzed Cementation of Selenium

The cost estimates presented for the scale-up of the catalyzed cementation system are conceptual in nature and would be adjusted when an actual system design was implemented. Initial indications are that the reagent consumption of this technology is still high, although approximately half of the reagent costs for the ferrihydrite adsorption system. The reagent consumption of this technology is estimated to be \$8.11/1,000 gallons treated. The majority of this cost is due to the cost of the oxidizing reagent, which accounts for \$5.81/1,000 gallons treated of the reagent costs. One way to reduce this cost would be to substitute the reagent used with a more cost effective alternative.

Table 3-2 summarizes the capital costs and construction times necessary to retrofit the existing KUCC Waste Water Treatment Plant. The costs are associated with a system designed to handle a 300-gpm peak flow rate. Due to the

difference in flow rate capability between the existing system and that of the scaled-up systems, most pumps and piping will require replacement.

The cost of a filter press (approximately \$89,000) was included in this estimate and may not be necessary depending on how the wastestreams from the system would be handled at KUCC. If a filter press was not necessary, the associated savings including shipping, filter press stand, sludge handling equipment, labor for installation, and design labor would be estimated at \$113,000.

Also included in this cost estimate is approximately \$75,000 in the system design task to perform additional research and development work on this process. Additional work is necessary to optimize reactor design, optimize elemental iron selection, optimize the conditions to maximize selenium removal, and optimize reagent additions.

The work of Dahlgren (Ref. 7) has shown that if a reactor is constructed so that very little air infiltration occurs, then the second-stage oxidation of the ferrous iron to ferric iron (with the subsequent ferric hydroxide, ferrihydrite, precipitation) is unnecessary. This is because the cementation process is very effective at removing selenium (<5 ppb) at pH 7–8. When the system is operated at pH 7–8, very little ferrous iron is produced (i.e., only a few ppm of iron dissolves). The ferrihydrite precipitation second stage of the present process is the most cost intensive step in the en-

tire treatment sequence. Therefore, the cost of the catalyzed cementation technology will likely be a cost competitive bioprocess or less than \$1.32 per 1,000 gallons (Ref. 9).

## 3.3 Biological Selenium Reduction (BSeR™) Process

Nutrient costs can be a primary contributor to the long-term operating cost of any biological process. Biotreatability results indicated that efficient short-term selenium reduction could be obtained with several media types; however, long-term selenium removal is dependent on a balanced nutrient mixture formulated to match process, microbial, and site water characteristics. The BSeR™ process has worked effectively in all waters tested with an inexpensive molasses-based nutrient. Nutrient costs can be reduced through careful microorganism selection and managed bioreactor microbial density. As determined in laboratory and pilot-scale tests, operating costs for the BSeR™ process are estimated to be less than \$0.50/1,000 gallons of treated water when nutrients are purchased in bulk quantities.

### 3.3.1 Nutrient Costs

Nutrient costs for reactor operation at the selected flow rates are shown in Table 3-3. Nutrient costs ranged from \$0.51/1,000 gallons at a reactor retention time of 11 hr to \$0.58/1,000 gallons with a reactor retention time of 5.5 hr and averaged \$0.54/1,000 gallons.

**Table 3-2.** Capital Costs/Construction Schedule for Catalyzed Cementation System Scale-Up

Task	Construction Time	Materials	Labor	Travel Nonlabor	Total
MSE System Design	13.5 weeks	\$74,580	\$156,670	\$11,487	\$242,737
MSE Subcontract Construction Oversight	7 weeks		\$44,730	\$18,952	\$63,683
MSE System Startup, Commissioning, and Project Closeout	5 weeks		\$44,190	\$10,266	\$54,456
Demolition, Building Modifications, Equipment Purchase and Installation by Subcontract	12 weeks	\$588,342	\$35,587		\$623,929
Total	26.5 weeks				<b>\$984,805</b>
Schedule/Cost Contingency @ 10%	2.7 weeks				\$98,480
<b>TOTAL</b>	<b>29.2 weeks</b>				<b>\$1,083,285</b>

**Table 3-3.** Nutrient Usage and Cost Per 1,000 Gallons as a Function of Retention Time

Retention Time	Flow (gal/min)	Time (days)	Water Treated (L)	Nutrient (g)	Nutrient Use (g/L)	Nutrient (g/1000 gal)	Nutrient (\$/ton)	Nutrient (\$/1000 gal)
11	0.3	14	22982.4	11,000	0.48	1818.8	250	0.51
8	0.4	14	30643.2	15,000	0.49	1860.1	250	0.52
5.5	0.6	7	22982.4	12,500	0.54	2066.8	250	0.58

### 3.3.2 BSeR™ Process Biofilm Support Cost

In a pump-and-treat bioreactor system, it is advantageous to use an optimized support material for biofilm establishment. The BSeR™ process allows for establishing high-density biofilms that result in faster kinetics. The results of this and previous tests, including full-scale bioprocess implementation, continue to validate the use of carbon as a bioreactor support material for the BSeR™ process. Laboratory and field-tests have proven the durability of carbon as a stable biofilm support for long-term BSeR™ process operation. In fact, testing indicates that the biofilm support materials should have a life expectancy of 15+ years. Pilot tests completed at the Garfield Wetlands-Kessler Springs site indicate that the current selenium levels (2.0 mg/L) can be reduced to near or below detection with a retention time of <5.5 hr.

The BSeR™ process normally uses granular carbon as a biofilm support to establish specific biofilms that will endure long-term exposure to contaminated waters containing indigenous

nonselenium reducing microorganisms.

This testing allowed additional comparisons and evaluations of other biofilm support materials. Granular carbon (8 x 30, I#900), evaluated in the laboratory along with the granular carbon from the field reactors, in bulk at a cost of \$0.48 per delivered pound, is the best biofilm support material tested to date for the BSeR™ process.

### 3.3.3 BSeR™ Process Capital Costs

Capital costs for the BSeR™ process are dependent on a great variety of factors including tank construction materials, use of available on-site tanks, pump and piping material specifications, and biofilm support materials. These factors all vary and can be adjusted to accommodate various site requirements of reactor materials, varying selenium contamination levels, and short or extended operating times. For example, the flow rates and projected extended operation times at the KUCC Garfield Wetlands-Kessler Springs site dictate a requirement for a durable biofilm support and shorter retention times; this was accommodated by using a biofilm support of granular carbon.

The cost of producing a bulk inoculum is estimated at \$0.75/1,000 gallons (cost dependent on BSeR™ process reactor size) and should only be required at start up. Two, 850,000-gallon clarifiers at the KUCC site would be used for this process. Granular carbon (8 x 30, I#900) costs \$0.48 per delivered pound. Conservatively, an estimated 360,000 lb of carbon support material is required for a 300 gpm BSeR™ process system at a cost of \$172,800. Laboratory and field tests suggest that the carbon can be used for a minimum of 25 reactor back flushing cycles for selenium removal and recovery, or an estimated 15 years at the Garfield Wetlands-Kessler Springs site.

Table 3-4 summarizes the capital costs estimated by MSE for the BSeR™ process system scale-up.

### 3.3.4 Comparative Economic Analysis

The three technologies demonstrated in the field were economically evaluated for a system operating at 300 gpm for 10 years @ 3.9% interest, 300 days per

**Table 3-4.** Capital Costs for BSeR™ Process System Scale-Up

Task	Construction	Materials	Labor	Total
AB System Design	4 weeks		\$53,807	\$53,807
AB Project Management	20 weeks		\$9,699	\$9,699
AB System Startup, Commissioning, and Project Closeout	5 weeks		\$113,875	\$113,875
Demolition, Building Modifications, Equipment Purchase and Installation by Subcontract	11 weeks	\$342,270	\$24,000	\$366,270
Total	20 weeks			\$549,090
Schedule/Cost Contingency @ 10%	2 weeks			\$54,909
TOTAL	22 weeks			\$603,999

year, to treat ground water containing 2 ppm selenium. The technologies were compared using the total net present value (TNPV) for each. The TNPV was determined by the following relationship:

$$\text{TNPV} = (\text{Capital Cost} + \text{NPV} \& \text{ MCost})$$

Where:

- TNPV is the total net present value;
- Capital Cost is the estimated capital cost to install each technolog

in the KUCC Wastewater Treatment Plant; and

- NPV & MCost is the net present value of the estimated annual operating and maintenance costs.

The NPV function in Excel was used to calculate the NPV Operating Cost for each technology. A summary of the economic analysis of the three technologies is presented in Table 3-5.

Among the three technologies, the BSeR™ process technology dominates both technical and economical perfor-

mance. Catalyzed cementation was the next most cost effective treatment. The baseline technology, ferrihydrite adsorption, was the least attractive alternative from an economic standpoint. The operating and maintenance costs for the ferrihydrite adsorption and catalyzed cementation technology are much higher than the BSeR™ process due to high reagent usage. Optimization of reagent usage coupled with reagent substitution with lower cost reagents would make ferrihydrite adsorption and catalyzed cementation more economically attractive.

**Table 3-5.** Comparative Economic Analysis of Demonstrated Technologies

Cost	Ferrihydrite Adsorption	Catalyzed Cementation	BSeR™ Process
Capital	\$1,026,835 (includes system design, demolition, building modifications, equipment purchase and installation construction, system start-up, commissioning, and project closeout)	\$1,083,285 (includes additional research and development work system design, demolition, building modifications, equipment purchase and installation, construction, system start-up, comissioning, and	\$603,999(includes biofilm support material, inoculum, system design, building modifications, equipment purchase and installation, construction, comissioning, and project closeout)
Annual Operating and Maintenance Cost	\$2,084,559 (includes reagent costs, manpower, maintenance, and power for equipment use)	\$1,165,358 (includes reagent costs, manpower, maintenance, and power for equipment use)	\$135,029 (includes nutrient costs, manpower, maintenance, and power for equipment use)
Net Present Value of Annual Operating and Maintenance Costs	\$16,992,127	\$9,499,323	\$1,100,682
Total Net Present Value	\$18,017,962	\$10,582,608	\$1,704,681
Net Present Value of \$/1000 gallons treated	\$13.90	\$8.17	\$1.32

## 4. Conclusions/Recommendations

Of the three technologies demonstrated, the BSeR™ process produced the most consistent results. A site-specific optimization is an essential component of any selenium removal process implementation, including the BSeR™ process. This optimization allowed the BSeR™ process to achieve economical removal efficiencies using realistic retention times while minimizing operating costs. Optimization of the BSeR™ process for the KUCC site produced a microbial cocktail that was later confirmed to efficiently remove selenium to near or below detection from Garfield Wetlands-Kessler Springs water using an inexpensive molasses-based nutrient blend and 5.5-hr retention times. The optimized microbial cocktail consisted of site-endemic and other naturally occurring, nonpathogenic microbes, including *Pseudomonas stutzeri* and *RC-large*. The BSeR™ process consistently removed selenium to below the target concentration (50 µg/L) and the majority of the time to below the detection limit of 2 µg/L.

The ferrihydrite adsorption process can also be optimized to achieve the desired level of selenium removal; however, reagent usage is excessive and cost prohibitive. Although this technology is considered the BDAT by EPA, it would not be feasible to utilize this technology to treat Garfield Wetlands-Kessler Springs water on a large scale. Another remaining question about this technology is the stability of the filter cake produced during this demonstration. Filter-cake samples did not pass TCLP for selenium but results were questionable because total metal analyses on the same samples did not correlate with the TCLP results.

The catalyzed cementation technology has also produced promising, albeit, erratic results. Additional testing of this process is necessary to provide more information about this innovative selenium removal technology. Further testing and optimization such as performing a solubility product or kinetic study to determine the optimum parameters for selenium and iron would make selenium removal using catalyzed cementation even more consistent and cost effective. The cementation reactor design may hold the key to the successful implementation of this technology. It is known that cementation of selenium can be accomplished in simple columns and stir tanks (Ref. 10). However, long residence times are required to achieve selenium removal to acceptable levels (Ref. 11). The recent work of Dahlgren (Ref. 7) and the continuation work by Dr. Twidwell (Ref. 9) has shown that iron packed columns are very effective for selenium removal (<1 ppb at pH 7) and require only a relatively short residence time (30 minutes). Current research indicates that novel agitation methods may provide the key to efficient selenium removal from solution. Testing of a system with a unique reactor design to accomplish the correct agitation method is necessary to further develop the catalyzed cementation technology.

The enzymatic selenium reduction technology was tested on a bench-scale during this project. The technology was not demonstrated in the field due to the instability of the enzyme reactor matrix. Plant enzyme preparations are commercially available; however, these plant-based preparations are much too expensive for water treatment applications. The use of microbial enzyme preparations

are expected to eventually reduce these costs. More research is necessary to gain a better understanding of what is occurring in the immobilization of the enzymes and the linking of electron donors within the various immobilization techniques. If the enzyme matrix can be demonstrated to be stable for 6 to 9 months, the process may be an economical treatment alternative. At the current operational longevity of 3 weeks to several months, the treatment costs become prohibitive. It is recommended that additional research be performed on the enzymatic selenium reduction technology because enzyme systems have the potential to outperform live microbial systems in many ways. Enzymatic technologies are still in the prototype development stage but have the potential to revolutionize drinking water and wastewater treatment.

In addition to further testing of the catalyzed cementation technology and enzymatic selenium reduction technology, other newly developed selenium treatment/removal technologies that may be ready for small-scale demonstration have been identified during this project. It is important to demonstrate these new technologies, in addition to the technologies tested during this project, to determine which technologies are effective at treating Garfield Wetlands-Kessler Springs water and also other waters with differing selenium concentrations and more complicated matrices. Further testing of these additional technologies could identify promising/economical technologies that could address the environmental problem of selenium contamination faced by the mining/mineral processing industries as well as the agricultural sector and the petroleum industry.

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