EPA/600/R-08/097
June 2008

Mine Waste Technology Program

Passive Treatment
For Reducing Metal Loading

By:

Diane Jordan
MSE Technology Applications, Inc.
Mike Mansfield Advanced Technology Center
Butte, Montana 59702

Under Contract No. DE-AC09-96EW96405
Through EPA IAG No. DW89-92197401-0

Norma Lewis, EPA Project Manager
Systems Analysis Branch
National Risk Management Research Laboratory
Cincinnati, Ohio 45268

This study was conducted in cooperation with
U.S. Department of Energy
Environmental Management Consolidated Business Center
Cincinnati, Ohio 45202

National Risk Management Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Disclaimer

This publication is a report of work conducted under the Mine Waste Technology Program that was funded by the Environmental Protection Agency and managed by the Department of Energy under the authority of an Interagency Agreement.

Because the Mine Waste Technology Program participated in EPA’s Quality Assurance Program, the project plans, laboratory sampling and analyses, and final report of all projects were reviewed to ensure adherence to the data quality objectives. The views expressed in this document are solely those of the performing organization. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party’s use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments, and groundwater; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This project was conducted under the Mine Waste Technology Program. It was funded by the EPA and administered by the U.S. Department of Energy (DOE) in cooperation with various offices and laboratories of the DOE and its contractors. It is made available at www.epa.gov/minewastetechnology by EPA's Office of Research and Development to assist the user community and to link potential users with the researchers.

Sally Gutierrez, Director
National Risk Management Research Laboratory

Abstract

This report summarizes the results of Mine Waste Technology Program (MWTP) Activity III, Project 48, *Passive Treatment Technology Evaluation for Reducing Metal Loading*, funded by the U.S. Environmental Protection Agency (EPA) and jointly administered by EPA and the U.S. Department of Energy. MSE Technology Applications, Inc. performed the technology demonstration.

The overall project objective was to evaluate passive treatment media for a given water chemistry that could provide information to identify potential treatment systems to reduce the dissolved metals loading contribution from Canyon Creek by 50%.

A 50/50 blend of groundwater retrieved from Canyon Creek sampling site wells CC1508 and MW-CCTW01S was used in column and batch testing. The data from batch testing was used to determine parameters for the column testing. Initial tests determined the equilibrium loading of each passive media. The three media with the highest heavy metals loading were used to determine passive treatment bed design characteristics (mass transfer zone, breakthrough curves, precipitation issues, etc.) during the column study.

In EPA Region 10, as well as other EPA regions, research has been initiated to implement and evaluate a variety of reactive media for water treatment at a number of sites. It should be noted that information from this study is not directly transferable to other sites because water chemistry is site-specific and performance of media will therefore vary from site to site.

Contents

Page

Figures

Tables

Acronyms and Abbreviations

Cd	cadmium
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
GFH	granular ferric hydroxide
Mn	manganese
MSE	MSE Technology Applications, Inc.
MWTP	Mine Waste Technology Program
NRMRL	National Risk Management Research Laboratory
ORP	oxidation-reduction potential
Pb	lead
QA	quality assurance
SC	specific conductivity
SRB	sulfate-reducing bacteria
SU	standard unit
Zn	zinc

Acknowledgments

This document was prepared by MSE Technology Applications, Inc. (MSE) for the U.S. Environmental Protection Agency's (EPA) Mine Waste Technology Program (MWTP) and the U.S. Department of Energy's (DOE) Environmental Management Consolidated Business Center. Ms. Diana Bless is EPA's MWTP Project Officer, while Mr. Gene Ashby is DOE's Technical Program Officer. Ms. Helen Joyce is MSE's MWTP Program Manager. Ms. Norma Lewis is the EPA Project Manager, Ms. Lauren Drees is the EPA Quality Assurance Officer, and Ms. Diane Jordan is the MSE Project Manager. The project would not have been as successful without the assistance of the following individuals:

Bill Adams, EPA Region 10
Gary Hickman, CH2M HILL
Rebecca Maco, CH2M HILL
Basin Environmental Improvement Project Commission
Gary Wyss, MSE Technology Applications, Inc.
Martin Foote, MSE Technology Applications, Inc.
MSE Laboratory

Executive Summary

Mine Waste Technology Program (MWTP), Activity III, Project 48, *Passive Treatment Technology Evaluation for Reducing Metal Loading*, was funded by the U.S. Environmental Protection Agency (EPA) and jointly administered by EPA and the U.S. Department of Energy (DOE). MSE Technology Applications, Inc. performed the technology demonstration. This project evaluated passive treatment systems to reduce the metals loading from Canyon Creek in Burke, Idaho.

Various passive treatment systems have been emplaced in the Coeur d'Alene Basin. Those systems consist primarily of both open wetland systems and closed contained systems represented by the following:

- EPA's MWTP Nevada Stewart Permeable Reactive Barrier Demonstration Project – A passive, Apatite II™ (a fishbone apatite) system was used to treat approximately 20 gallons per minute at the Nevada Stewart Mine reducing zinc, cadmium, manganese, lead, and iron to instrument detection limits through certain cells.
- Idaho Department of Environmental Quality's Success Mine Seep Treatment – This system demonstrated the effectiveness of Apatite II™ to reduce the total metals loading, mainly zinc, cadmium, and lead, by 75% at the system outflow and, to date, the system has met its objective.
- Bureau of Land Management's Sydney Adit Drainage Treatment – This project consists of several field pilot water studies including: 1) a bioreactor, 2) a reactive medium system, and 3) biochelators to reduce the metals loading to receiving waters.
- EPA Region 10 – This treatability study was performed by CH2M HILL, as EPA Region 10's Remedial Action Contractor, on active and passive processes to investigate sulfate-reducing bacteria (SRB) and lime high-density sludge processes for treatment of these waters.

These systems were able to reduce the metals loading in the waters treated; however, in some cases it was reported that short-circuiting and clogging restricted the systems ability to function efficiently. Additionally, the designs that were implemented limited the ability of the systems to handle fluctuating seasonal flows.

The purpose of this project was to evaluate passive treatment media to reduce the metals loading contribution from Canyon Creek by 50%. This goal was established under the Bunker Hill Mining and Metallurgical Complex Operable Unit 3 Record of Decision in September 2002.

It should be noted that information from this study is not directly transferable to other sites because water chemistry is site-specific and performance of media will therefore vary from site to site.

Of the seven media tested, three were determined to be applicable for treating Canyon Creek groundwater: granular ferric hydroxide (GFH), Bauxsol™, and Apatite II™. Of these three media, Apatite II™ showed a higher capacity to remove zinc (the primary element of concern) from this water when compared to GFH and Bauxsol™.

1. Introduction

1.1 Project Description

Mine Waste Technology Program (MWTP), Activity III, Project 48, *Passive Treatment Technology Evaluation for Reducing Metal Loading*, was funded by the U.S. Environmental Protection Agency (EPA) and jointly administered by the EPA and the U.S. Department of Energy (DOE) through an Interagency Agreement. EPA contracted MSE Technology Applications, Inc. (MSE) through the MWTP to evaluate passive treatment media.

The overall project objective was to evaluate passive treatment media to reduce the metals loading contribution from Canyon Creek. This goal was established under the Bunker Hill Mining and Metallurgical Complex Operable Unit 3 Record of Decision in September 2002.

1.2 Background

Historical mining practices and the naturally occurring geochemistry can result in the heavy metal contamination of soil, sediment, surface water, and groundwater in drainages. One method of mitigating these sources of contamination is through the implementation of passive treatment systems intercepting flow emanating from the source. A passive treatment system is one that requires minimal maintenance. Passive treatment systems, using a variety of media (i.e., phosphate-based material such as fishbone apatite, sawdust based organic mix using anaerobic bacteria, synthetic polymer adsorbents, and zero valent iron) have been proposed and, in some cases, have been applied. Selection of an appropriate media to treat a given water chemistry at a specific site is sometimes very difficult. Most passive treatment systems that have been installed have been successful at reducing dissolved metal loadings from contaminated waters. However, in general, passive treatment systems have been problematic due to reduced permeability over time caused by reactive media clogging with precipitates and foreign debris.

Various passive treatment systems have been emplaced in the Coeur d'Alene Basin. Those systems consist primarily of both open wetland systems and closed contained systems including:

- EPA's MWTP Nevada Stewart Permeable Reactive Barrier Demonstration Project – A passive, Apatite II™ (a fishbone apatite) system was used to treat approximately 20 gallons per minute at the Nevada Stewart Mine reducing zinc (Zn), cadmium (Cd), manganese (Mn), lead (Pb), and iron to low dissolved concentrations.
- Idaho Department of Environmental Quality's Success Mine Seep Treatment – This system demonstrated the effectiveness of Apatite II™ to reduce the total metals loading, mainly Zn, Cd, and Pb, by 75% at the system effluent.
- Bureau of Land Management's Sydney Adit Drainage Treatment – This project consists of several field pilot water studies including: 1) a bioreactor, 2) a reactive medium system, and 3) biochelators to reduce the metals loading to receiving waters.
- EPA Region 10 – This treatability study was performed by CH2M HILL, as EPA Region 10's Remedial Action Contractor, on active and passive processes to investigate sulfate-reducing bacteria (SRB) and lime high-density sludge processes for treatment of Canyon Creek waters.

All systems listed above were able to reduce the metals loading in the waters treated; however, in some cases it was reported that short-circuiting and clogging restricted the ability of these systems to function efficiently. Additionally, the designs that were implemented limited the ability of the systems to handle fluctuating seasonal flows.

1.3 Site Description

Laboratory testing of the passive treatment media for removal of heavy metals from Canyon Creek groundwater was performed at the MSE Testing Facility in Butte, Montana.

1.4 Project Objectives

The project objective was to evaluate passive treatment media for a given water chemistry that would provide information to identify additional treatment options. These treatment options would be applicable for reducing the metals loading contribution from Canyon Creek.

1.5 Experimental Overview

A 50/50 blend of groundwater was retrieved from a sampling site well CC1508 and MW-CCTW01S for use in the column and batch testing. The data from batch testing was used to determine parameters for bench-scale studies. These tests are designed to characterize the ability of the media to act as a passive treatment system for the removal of heavy metals from groundwater. Initial tests centered on determining the equilibrium loading of the passive media. The top five media with the highest heavy metals loading were used for additional studies designed to determine passive treatment bed design characteristics (mass transfer zone, breakthrough curves, precipitation issues, etc.).

1.5.1 Batch Testing

To characterize and quickly evaluate various passive treatment medium, equilibrium isotherms were developed for each media. An initial sample of the groundwater was analyzed for total suspended solids, total recoverable metals, and dissolved metals. pH and oxidation-reduction potential (ORP) measurements were conducted initially and at the end of each test.

For each media an isotherm was constructed by varying the mass of media for a fixed volume of groundwater added. To insure equilibrium was achieved, equilibrium rate studies were carried out on each of the media. The equilibrium capacity studies were run at five masses for each while keeping the groundwater volume constant at 500 milliliters (mL). An Erlenmeyer flask with constant agitation during the reaction period was used as shown in Figure 1-1. The media was added in the amounts of 1 gram (g), 2 g, 5 g, 10 g, and 50 g. Samples were taken at the expiration of equilibrium time as determined in the rate studies. The samples were filtered through a 0.45-micron filter to determine the final equilibrium dissolved concentrations of Cd, Pb, and Zn.

The amount of metal adsorbed from solution divided by the mass of media added to the flask was plotted against the final equilibrium concentration found in solution are shown in Figures 3-2 to 3-8. This plot was used to determine adsorption characteristics of each media and determine if the media was suitable for passive treatment of Canyon Creek groundwater.

1.5.2 Column Testing

Three media, Apatite II™, Bauxsol™ and GFH, were selected from the equilibrium loading tests and further tested in a column configuration. The specific column design was determined based upon loading data provided from equilibrium testing. The limits of the design were to size the columns such that breakthrough would be observed after passing a maximum of 15 liters through the bed. Based upon the loading observed in the batch testing, an appropriate volume of passive media was loaded into the column. Denstone, a ceramic bed support media, was used at the bottom and top of each column to act as a flow dispersion media. The columns were approximately 1-inch inside diameter by 24 inches long with packings varying from 50 to 250 mL of passive media. The column configuration is shown in Figure 1-2. The object of the column studies was to characterize the breakthrough curves associated with Zn, Cd, and Pb for each of the three passive media.

Groundwater obtained from Canyon Creek was introduced to the bottom of the columns and samples were taken at the outflow until breakthrough was complete or the test was discontinued due to time/budgetary constraints. Samples were analyzed for Zn, Pb, and Cd until breakthrough was achieved. Breakthrough was determined with the first appearance of Zn in the effluent.

The pressure drop across the bed was monitored daily using a manometer to determine if any precipitates or other bed fouling phenomena occurring. This information was used to determine the best media for the Canyon Creek groundwater chemistry.

Figure 1-1. Batch testing.

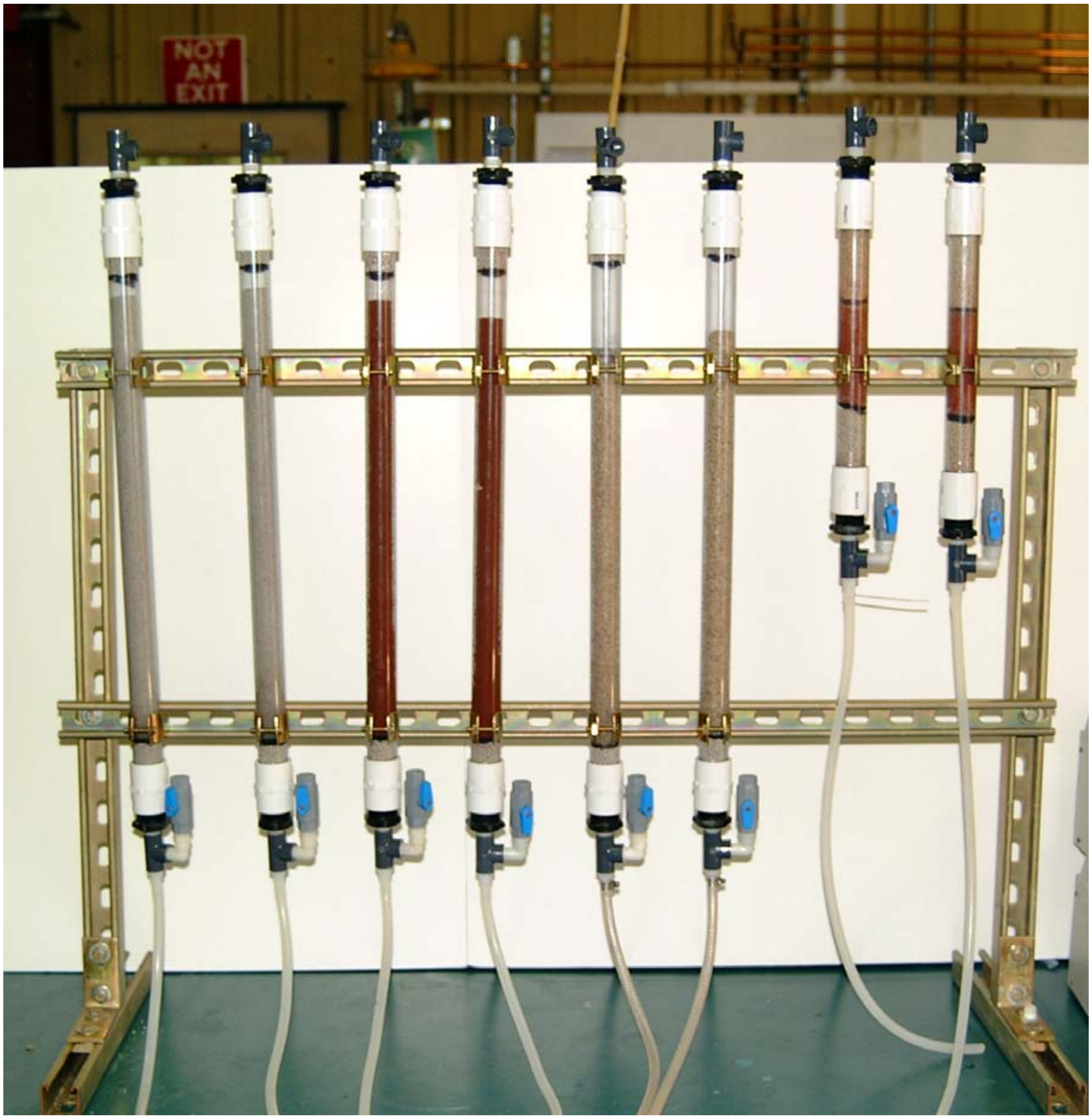

Figure 1-2. Laboratory columns with media.

2. Quality Assurance

A summary of the quality assurance (QA) activities associated with MWTP Activity III, Project 48, *Passive Treatment for Reducing Metal Loading* can be found in Appendix A.

3. Results

3.1 Bench-Scale Testing

The first test that was conducted on the groundwater collected near Canyon Creek was the development of a titration curve. This curve is illustrated in Figure 3-1 and shows that an inflection occurs near a pH of 9.0, which is most likely related to the hydrolysis of the dissolved Zn in the water.

3.1.1 Batch Testing – Rate of Removal

Samples of the water in contact with a specific media were taken at specific times during the test, filtered, and analyzed for dissolved Zn to determine the concentration that remained from the initial 41,500 micrograms per liter (μg/L). As such, this test determined the rate of removal of Zn from the water by the specific media.

The results of the rate test showed that the media could be classified into two groups. The first group included those media that rapidly increased the pH of the groundwater to levels greater than 10.0 and maintained that level. This group of media consisted of partially charred dolomite; Bauxsol™; partially calcined limestone; a 50:50 mixture of limestone and calcium oxide; a 50:50 mixture of limestone and magnesium oxide; and sodium hydrosulfide. The rate test results for the first group of media are contained in Table 3-1.

As is denoted in Table 3-1, all of the media in the first group removed greater than 96% of the dissolved Zn from the groundwater within one hour of contact and increased the pH of the groundwater to levels greater than 10 within the first two hours of the test. pH values for the groundwater were not taken after one hour of contact time. However, fundamental knowledge of the chemical processes that occur with these highly alkaline media can be relied upon to state that in all likelihood the increase in pH occurred within the first few minutes of contacting the water with each media. . An inflection point was defined in the pH titration curve for the Canyon Creek water near a pH value of 9.0, which is shown in Figure 3-1. It is probable that the primary method of Zn removal from the Canyon Creek groundwater for this first group of media was due to hydrolysis of Zn and the precipitation of Zn hydroxide solids formed by that process. In the case of sodium hydrosulfide, it is probable that a significant portion of the Zn was removed from solution by the formation of Zn sulfide. The Zn removal results produced by the first group of media generally tended to increase with time of contact. All of the media in the first group removed greater than 99% of the dissolved Zn from the groundwater within eight hours of contact, which was the time to reach equilibrium determined in the rate test.

It is possible that this increased removal of dissolved Zn was due to a number of secondary processes, which included increased precipitation of Zn hydroxides over time; adsorption onto the surfaces of the fine-grained portions of the media that did not dissolve during the test; co-precipitation from the water with other elements; adsorption onto the surface of previously precipitated Zn hydroxides; and adsorption onto the surface of other metallic hydroxides formed during the test. It is not possible with the limited amount of data developed during the rate test to determine which, if any, of these secondary processes contributed in a significant manner to the removal of Zn from the water.

The second group of media included those that did not significantly increase the pH of the groundwater. This group of media consisted of Apatite II™, ferrihydrite coated sand, GFH, aluminum-iron coated sand, Juniper bark, and manganese oxide coated sand. The test results for the second group of media are contained in Table 3-2.

As shown in Table 3-2, the Apatite II™ media removed significantly more of the Zn from the water than any of the other media of the second group. Apatite II™ removed more than 98% of the dissolved Zn from the groundwater in the first hour of contact. During the second hour of the test, additional Zn was removed to the minimum concentration of 71.1 μg/L, which translates to 99% removal. At completion of the 8-hour test, the final concentration of Zn was 228 μg/L. Overall, Apatite II™ performed very effectively during the batch tests and showed the fastest rate of removal of the second group of media.

The remaining five media in the second group removed between 12% and 47% of the dissolved Zn from the groundwater within the first hour of contact. These five media continued to remove dissolved Zn from the groundwater through the remaining period of the 8-hour test. The final removal percentages for these media varied between 76.5% for GFH and 18.5% for the aluminum–iron coated sand. None of the media in the second group raised the pH to a level where significant hydrolysis of Zn would occur. As such, the method of removal for these media was probably some form of adsorption or ion exchange. Again, it is not possible, due to the limited amount of data developed during the rate test, to determine the specific process or processes by which Zn was removed from the groundwater by these media.

Evidence has been cited to show that all of the media contained in Group 1 removed large quantities of Zn from the Canyon Creek water by a process that was probably hydrolysis followed by precipitation. By definition, this sequence of processes is found in active not passive processes. As such, the media that were tested as Group 1 were eliminated from further testing with the exception of the Bauxsol™ medium. All other media in Group 1 do not exhibit passive tendencies, as they would require frequent media replacement and/or post-treatment pH adjustment for discharge. The Bauxsol™ media is designed to combine both hydrolysis processes and adsorptive processes. In an attempt to determine the adsorptive capabilities of the media, Bauxsol™ was included, along with all the media from Group 2, in the next test sequence.

3.1.2 Batch Testing – Equilibrium Capacity

The second type of treatability testing conducted on the groundwater collected near Canyon Creek was a batch test in which an attempt was made to measure the equilibrium capacity of each medium to remove the specific metals from the water. As previously described, the test involved contacting varying quantities of media with a fixed quantity of water for a period of time necessary for the system to come to equilibrium. The contact time varied as determined in the rate test. Samples of the water were then taken and analyzed for the various metals of concern. Once the data was collected, calculations were made that determined the amount of each metal that was sorbed per unit mass of each media. The equilibrium concentration of each metal remaining in the water, the mass of sorbent used for each test run, and the calculated quantity of metal sorbed per unit mass of media are shown in Table 3-3. From the data shown in Table 3-3, Zn isotherm curves were developed using the Freundlich isotherm for each of the seven media. Zinc concentration data was used for this calculation as it is the heavy metal of concern in the Canyon Creek water. In the development of these curves, the quantity of metal sorbed per unit mass of media was plotted versus the equilibrium concentration of Zn remaining in the water. These Zn isotherm plots are shown in Figures 3-2 through 3-8.

The isotherms shown in the aforementioned figures can be separated into three categories. The first category contains those isotherms that exhibit a concave upward shape. The isotherms for iron-aluminum coated sand and juniper bark are contained in this category. Materials that exhibit this form of isotherm have low metal loading capacities at low equilibrium concentrations of Zn in solution and are therefore not considered favorable for the removal of Zn from the Canyon Creek water.

The second group of isotherms displayed a downward concave graph. Media with this type of loading response have a high loading capacity at lower solution equilibrium concentrations. These media possess characteristics that are more favorable for removal of Zn from solution. The Apatite II™ and ferrihydrite-coated sand plots are characteristic of this type of isotherm.

The final isotherm category exhibits shapes that are complex in that the isotherm shows multiple inflections denoting that the chemical processes forming the isotherm are not dominated by sorption or ion exchange. The two media with isotherms that fall into this category are GFH and Bauxsol™.

3.1.3 Column Test – Equilibrium Capacity

The third treatability test conducted using the groundwater collected near Canyon Creek, was a test using two sets of continuously flowing columns. Each of the sets of columns contained a control column and columns filled with the three media Bauxsol™, Apatite II™, and GFH. One set of columns was operated at a flow rate of 2 mL/min and the second set of columns was operated at a flow rate of 5 mL/min. Samples of the effluent from each column were taken periodically throughout the test period and analyzed for Zn, Cd and Pb. A number of chemical parameter readings including ORP, pH, and specific conductivity (SC) were also taken throughout the test period. The data generated from the columns with a flow rate of 2 mL/min is contained in Table 3-4 while the data generated from the columns with a flow rate of 5 mL/min is contained in Table 3-5. It should be noted that the feed water to the columns contained a Zn concentration of approximately 41,600 μg/L, a Cd concentration of 245 μg /L, and a Pb concentration of 187 μg /L. Graphical representations of the column results for Zn are presented in Figures 3-9 through 3-12.

As can be seen from the data presented in the aforementioned tables and figures, each of the columns acted differently depending upon the contained media and the flow rate of the feed solution. The control columns that were filled with silica sand were not able to remove significant amounts of Zn from the influent solution at flow rates of 2 or 5 mL/min. The column receiving feed solution at 2 mL/min was able to remove a small quantity of the Zn from the influent solution while the column receiving feed solution at 5 mL/min was not able to remove an appreciable amount of Zn from the solution. Neither of these columns was able to remove an appreciable amount of Cd from the feed solution.

However, both of the columns were able to remove a feasible amount of Pb from the feed solution during the initial portion of the test. Breakthrough of Pb occurred in the 5-mL/min column between 1 and 33 bed volumes, while breakthrough of Pb occurred in the 2-mL/min column between 35 and 70 bed volumes. Breakthrough is defined as the first appearance of contaminant of concern in the effluent. A slower flow rate and the corresponding increased residence time of the feed solution in the column allowed the sand grains (and the associated impurities) in the 2-mL/min column to sorb the Pb from solution more effectively than at the faster 5-mL/min flow rate. The sand filled columns did not produce a significant effect or trend on any of the chemical parameters (pH, ORP, or SC) measured during the test period. Although not shown in Tables 3-4 or 3-5, the difference in the pressure between the inlet and outlet of the columns was also measured periodically throughout the test period. Both of the sand filled columns showed no increase in head loss or differential pressure during the testing.

Visual observations of all the columns were also made throughout the test period. The sand filled columns did not change appreciably during the period of the test.

Both of the columns filled with GFH were able to remove significant quantities of Zn from the feed solution at flow rates of 2 and 5 mL/min. Breakthrough of Zn occurred in the 2-mL/min column between 99 and 110 bed volumes and in the 5-mL/min column between 86 and 114 bed volumes. As shown in Figure 3-10, the column that was flowing at a rate of 2 mL/min removed more Zn than did the 5-mL/min column. Like the previously discussed sand columns, this result is a function of the residence time of the solution in the column. Both of the GFH filled columns required time in contact with the feed water to remove 90% of the dissolved Zn, which translates to a concentration of approximately 400 μg /L.

With regards to Cd, the GFH filled column that flowed at 2 mL/min did not exhibit a concentration breakthrough during the test period. The GFH filled column flowing at a rate of 5 mL/min showed a potential concentration breakthrough beginning between 114 and 141 bed volumes. Bed volume is the sum of the pore volume plus the volume of the sorbent. Both of the GFH filled columns were able to remove the dissolved Pb in the feed water to low levels throughout the testing period. No concentration breakthrough was observed from either column for Pb. Both of the GFH filled columns lowered the pH of the effluent solution when compared to the influent solution after approximately 80 bed volumes had past through the columns. Prior to this portion of the test, the pH of the effluent solution was close to that of the influent solution. The ORP of the effluent solution from both of the GFH filled columns was erratic throughout the test period with no discernable trend. No major changes in the SC of the effluent solution were observed. Both of the GFH filled columns maintained similar differences in pressure between the inlets and outlets of each column throughout the test period. The information garnered through visual observation of the GFH filled columns did not change appreciably during the period of the test.

The two Apatite II™ filled columns functioned very differently with respect to the removal of dissolved Zn from the feed solution depending on the flow rate of the feed solution. The Apatite II™ filled column that flowed at 2 mL/min was able to remove dissolved Zn to levels below the analytical detection limit throughout the period of the test. However, this process was not due solely to sorption of the Zn. As can be seen from the data in Table 3-4, after approximately 30 bed volumes the ORP of the effluent solution dropped significantly. The reduced environment in this column facilitated the growth of SRB. The presence of SRB was denoted by the odors of hydrogen sulfide and other biological materials emanating from the column during the latter portions of the test. It should be noted that Apatite II™ is a biologically formed material that contains significant amounts of oils and other secondary compounds. Apatite II™ has been known to develop growths of SRB in other similar tests under low-flow conditions (McCloskey, 2003). One of the byproducts of the SRB is soluble hydrogen sulfide that can react strongly with metals such as Zn to form insoluble Zn sulfide solids. It is speculated that the secondary process contributed to the removal of Zn, as well as Cd and Pb, from the influent solution. The Apatite II™ filled column that had a flow rate of 5 mL/min did not develop large quantities of SRB during the test. The ORP of the effluent from the 5-mL/min column did not drop appreciably throughout the test and no hydrogen sulfide odor was observed. It is probable that the increased flow rate was able to deliver enough dissolved oxygen to the column to prevent a major drop in ORP and a significant development of SRB.

The dissolved Zn concentration in the effluent from the 5-mL/min column showed a breakthrough at approximately 140 bed volumes. No major changes in the pH of the effluent solution from both of the Apatite II™ filled columns occurred during the test period. The SC of the column with a flow rate of 5 mL/min did not change in a noteworthy manner during the test period. However, the SC of the column with a flow rate of 2 mL/min trended to higher values after approximately 40 bed volumes had passed through the column. This increase was probably due to the presence of soluble byproducts from the activities of SRB. The pressure difference between the influent and effluent portions of both Apatite II™ filled columns decreased throughout the period of the test. It was observed that Apatite II™ tends to swell when it is first wetted which probably contributed to the increase in the pressure difference initially, but once the swelling stopped the pressure difference stabilized. No discernable changes to the Apatite II™ filled columns were visually observable during the period of the test.

A breakthrough in the dissolved Zn concentration of the effluent solution was denoted from both of the Bauxsol™ filled columns during the test. That breakthrough occurred from the 2-mL/min flow rate column after approximately 65 bed volumes of solution had passed through the column, while the breakthrough from the 5-mL/min column occurred after approximately 40 bed volumes of solution had passed through the column. The dissolved concentrations of Cd and Pb broke through from both of the Bauxsol™ filled columns at approximately the same point in the test, as was the case for the dissolved Zn concentration. The pH and the ORP of the effluent solution from both of the Bauxsol™ filled columns also showed marked changes in value at approximately the same point during the test that the previously mentioned breakthroughs occurred. The pH of both columns decreased and the ORP increased at the point of breakthrough. This data supports the conclusions determined about the removal method of metals from water by Bauxsol™. In that, elevated values of pH led to hydrolysis followed by precipitation of solid materials. In addition, visual observation of the Bauxsol™ filled columns denoted a grey-white gelatinous solid forming in the column on the surface of the red-colored Bauxsol™ during the test. Lastly, the difference in pressure within the column between the influent and effluent portions of both Bauxsol™ filled columns increased dramatically throughout the period of the test. This increase in pressure differential was probably due to the precipitation and deposition of fine-grained, solid materials formed during the test process.

Subsequent to the completion of the column tests, a calculation was made in an attempt to determine the total quantity of Zn that was removed by each column up to breakthrough of the dissolved Zn concentration. The results of that loading calculation are shown in Table 3-6.

The calculation does not take into consideration the fact that dissolved Zn concentration in the effluent from the Apatite II™ column with a flow rate of 2 mL/min did not breakthrough. In addition, the dissolved Zn concentration breakthrough for the two sand filled columns was not identified, as the effluent from these two columns was always at or near the influent concentration. Nevertheless, the calculation does yield some interesting information. The columns with the slower flow rate yielded larger capacities for all of the tested medias. The material in the columns filled with Apatite II™ had considerably higher capacities than the other media, even at the faster rate of flow. The materials filling the GFH columns and the Bauxsol™ columns had relatively similar capacities for the removal of Zn.

One of the parameters that the test attempted to discern was the sorptive capacity of Bauxsol™ beyond the Zn removal capabilities of that media by hydrolysis. Using the same type of calculation detailed in Table 3-6, it can be shown that the Bauxsol™ media was able to remove 5,844 µg per g of media at a flow rate of 5 mL/min from approximately 84 bed volumes of feed water and that the 2-mL/min column was able to remove approximately 3,547 µg per g of media from approximately 56 bed volumes of feed water. This calculation was only performed between breakthrough of the dissolved Zn concentration and a total volume of approximately 120 bed volumes. Breakthrough of Zn occurred sooner in the 5-mL/min flow rate column with a lower number of bed volumes when compared to the 2-mL/min flow rate column.

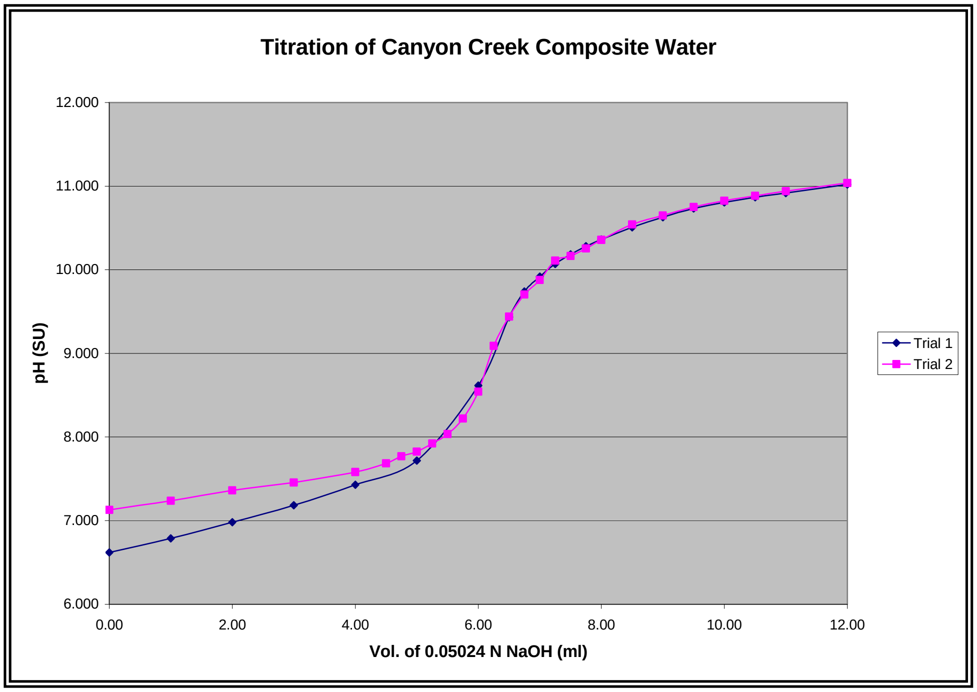

Figure 3-1. Titration curve for Canyon Creek groundwater.

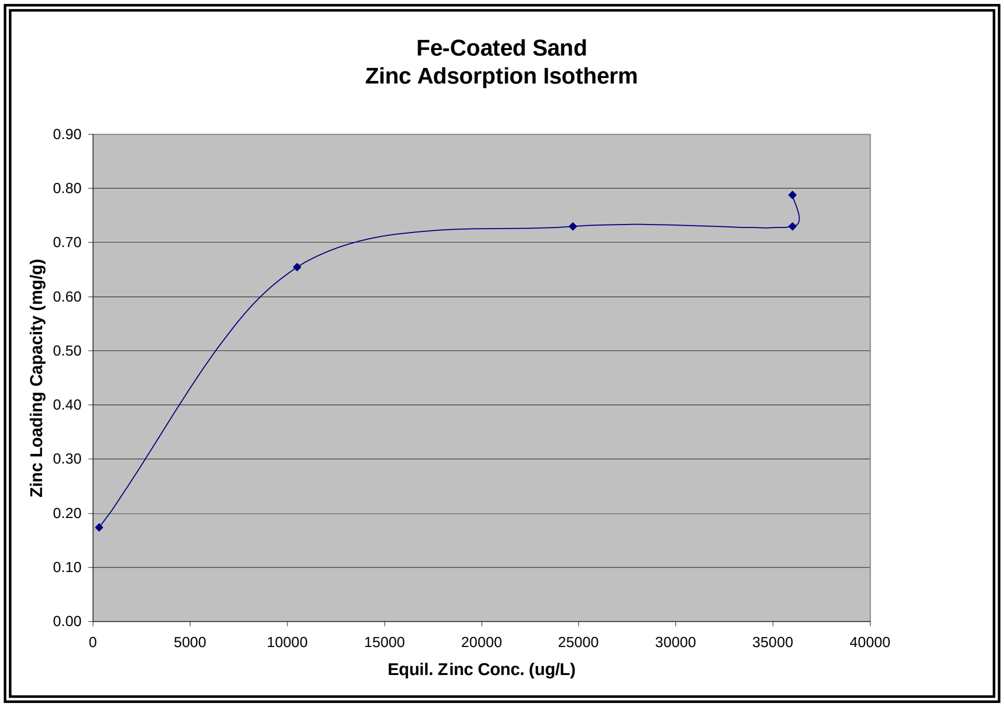

Figure 3-2. Iron coated sand isotherm.

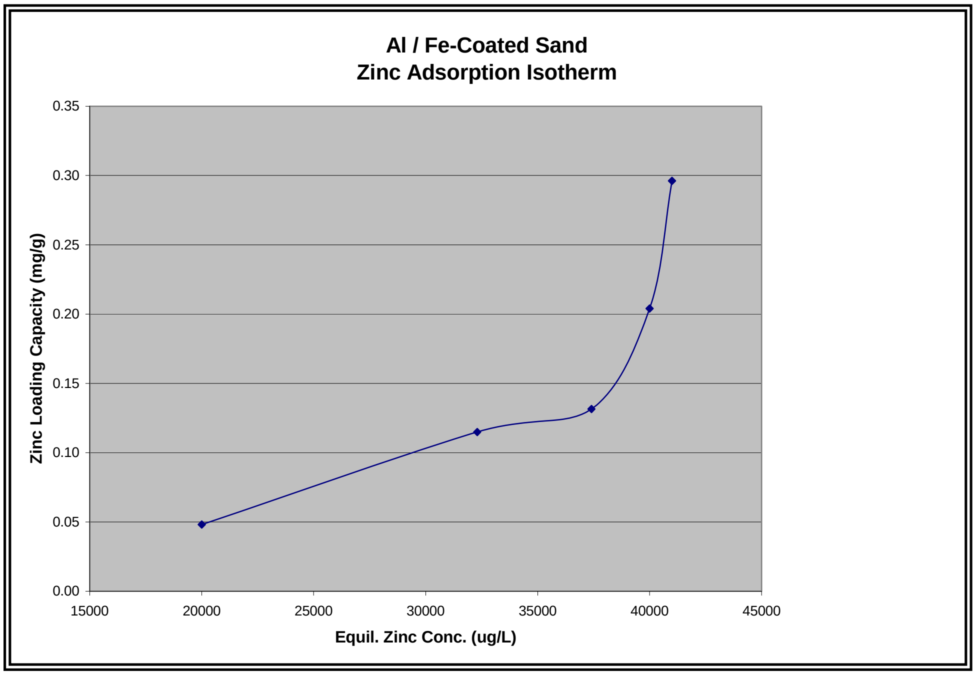

Figure 3-3. Iron-aluminum coated sand.

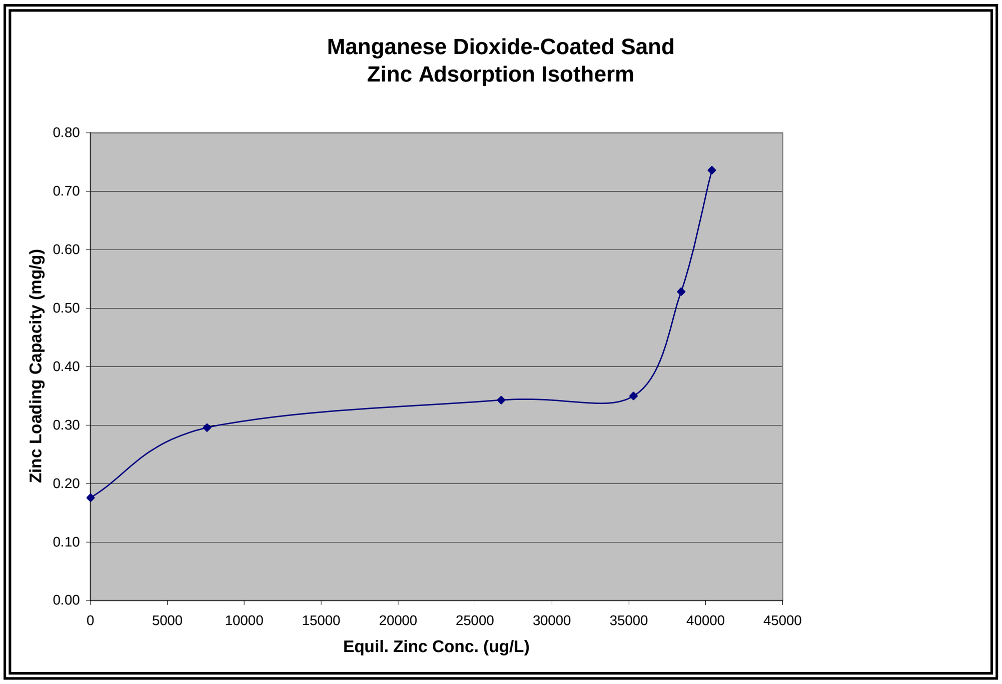

Figure 3-4. Manganese dioxide isotherm.

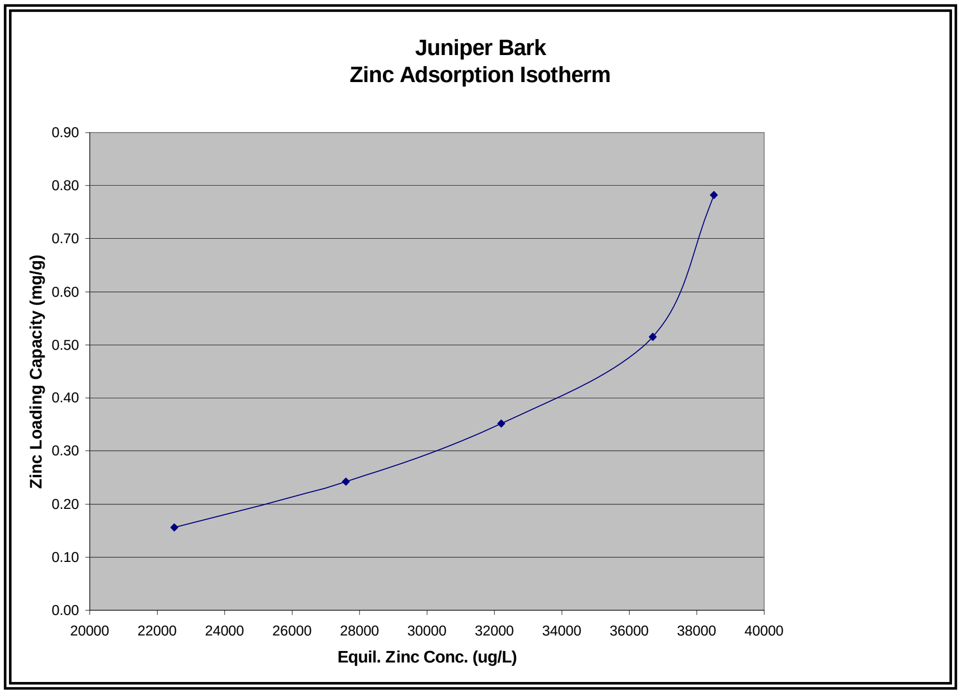

Figure 3-5. Juniper bark isotherm.

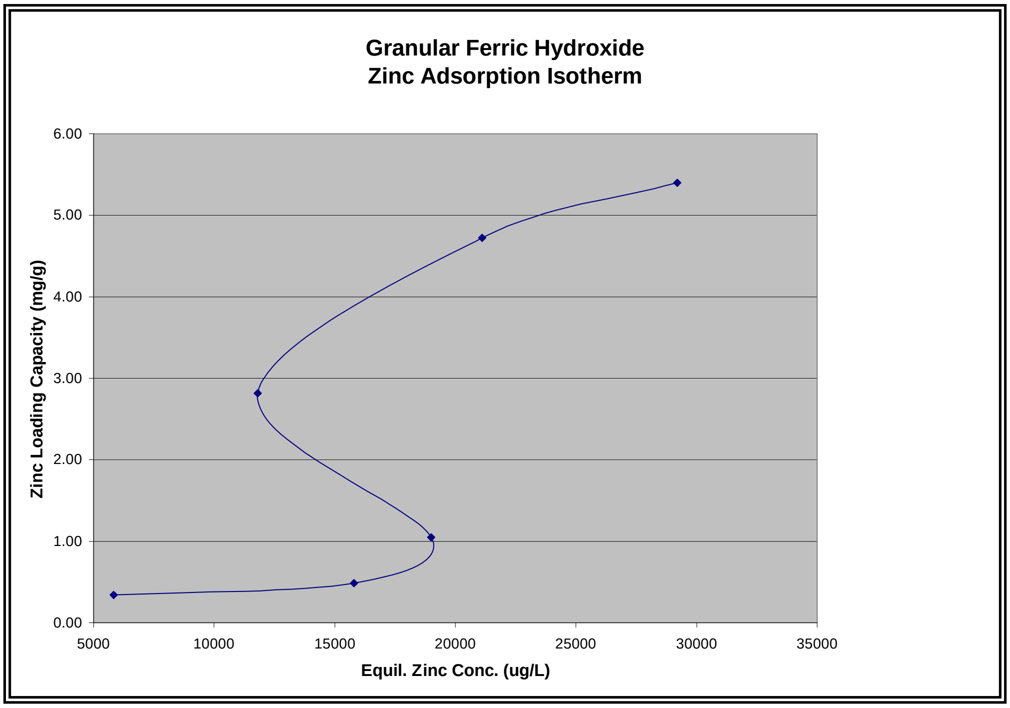

Figure 3-6. Granular ferric hydroxide isotherm.

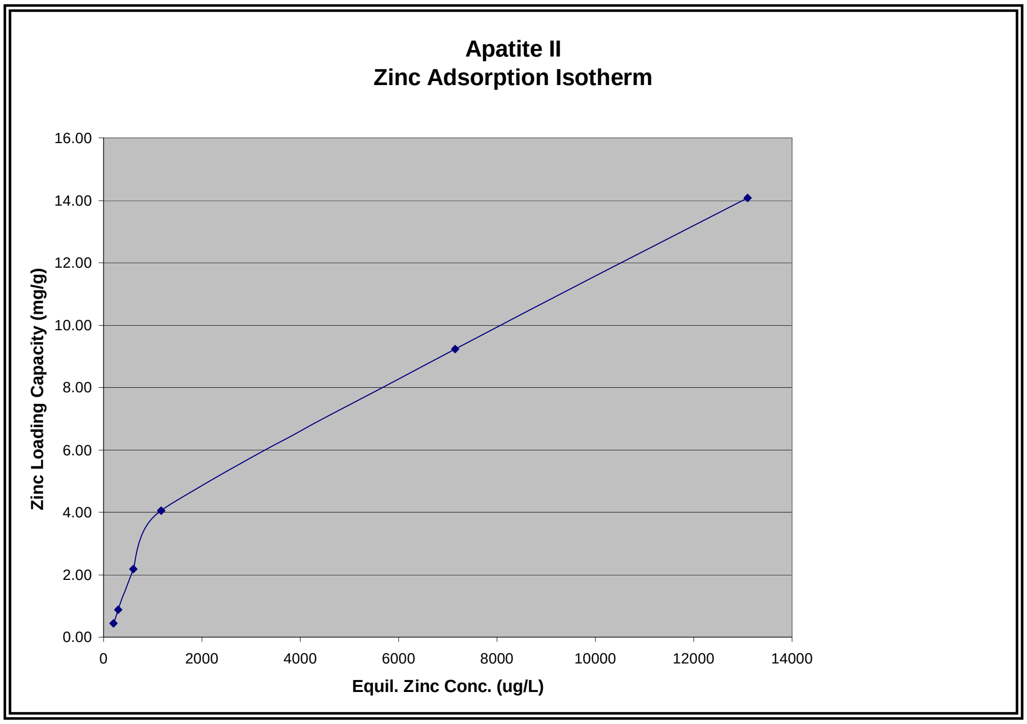

Figure 3-7. Apatite II™ isotherm.

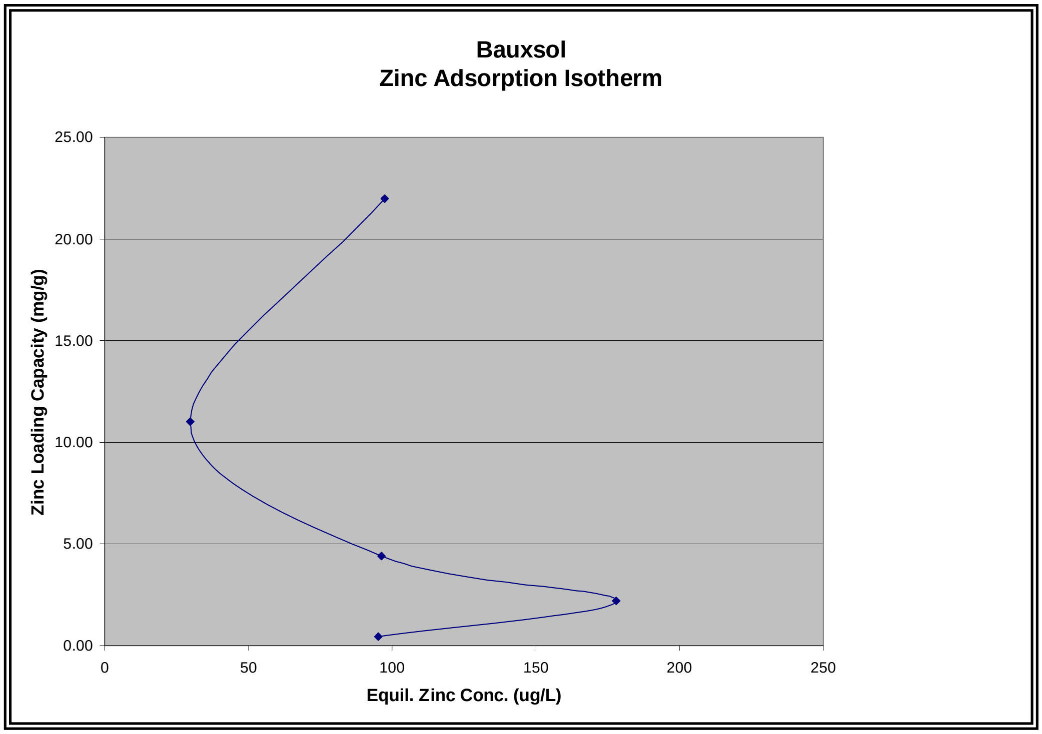

Figure 3-8. Bauxsol™ isotherm.

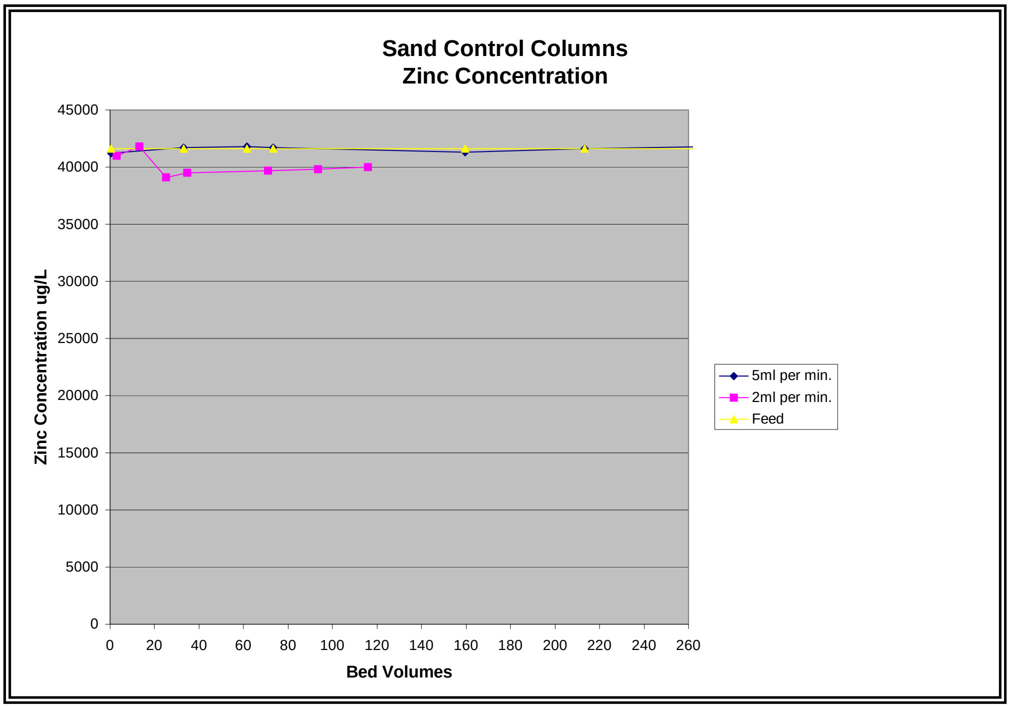

Figure 3-9. Control columns – Zn concentration vs. bed volumes.

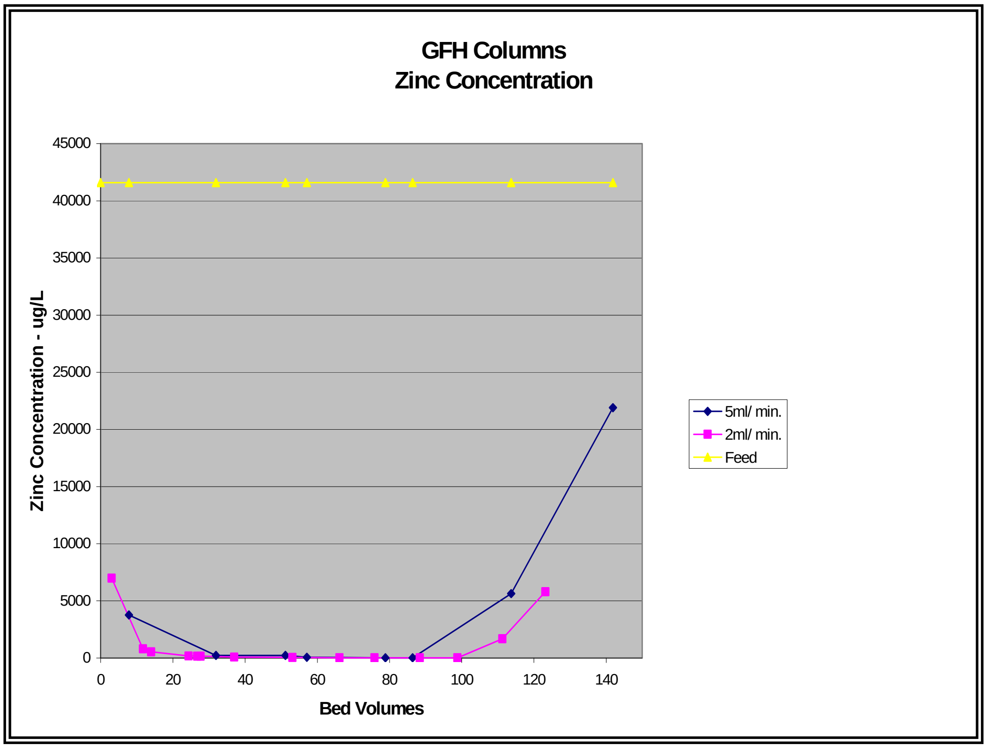

Figure 3-10. GFH columns – Zn concentration vs. bed volumes.

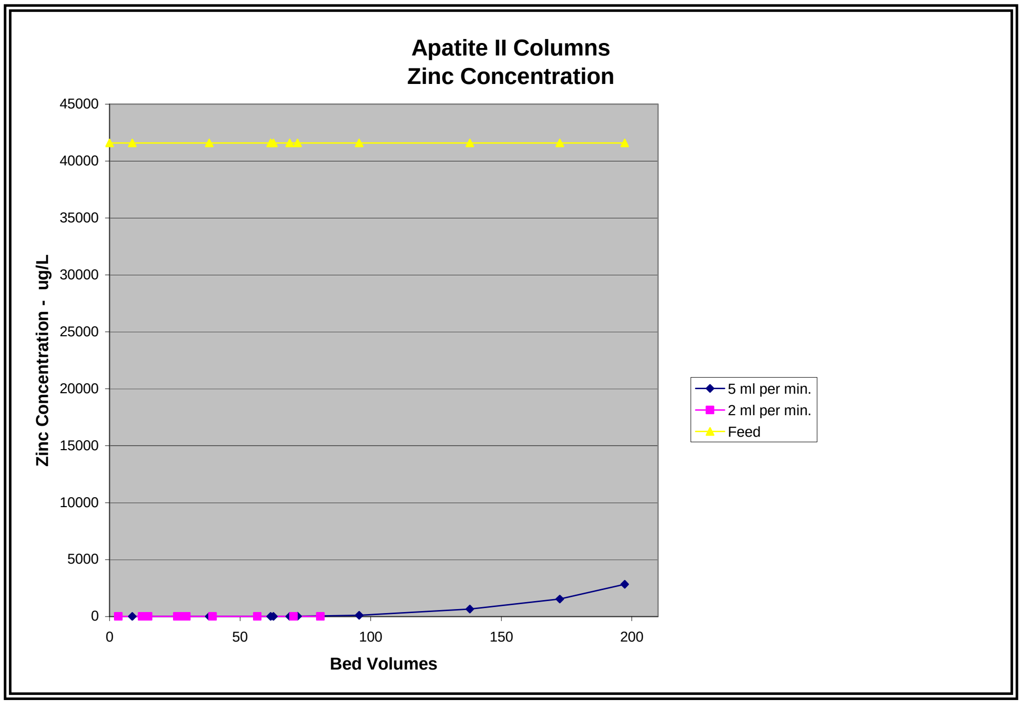

Figure 3-11. Apatite II™ columns – Zn concentration vs. bed volumes.

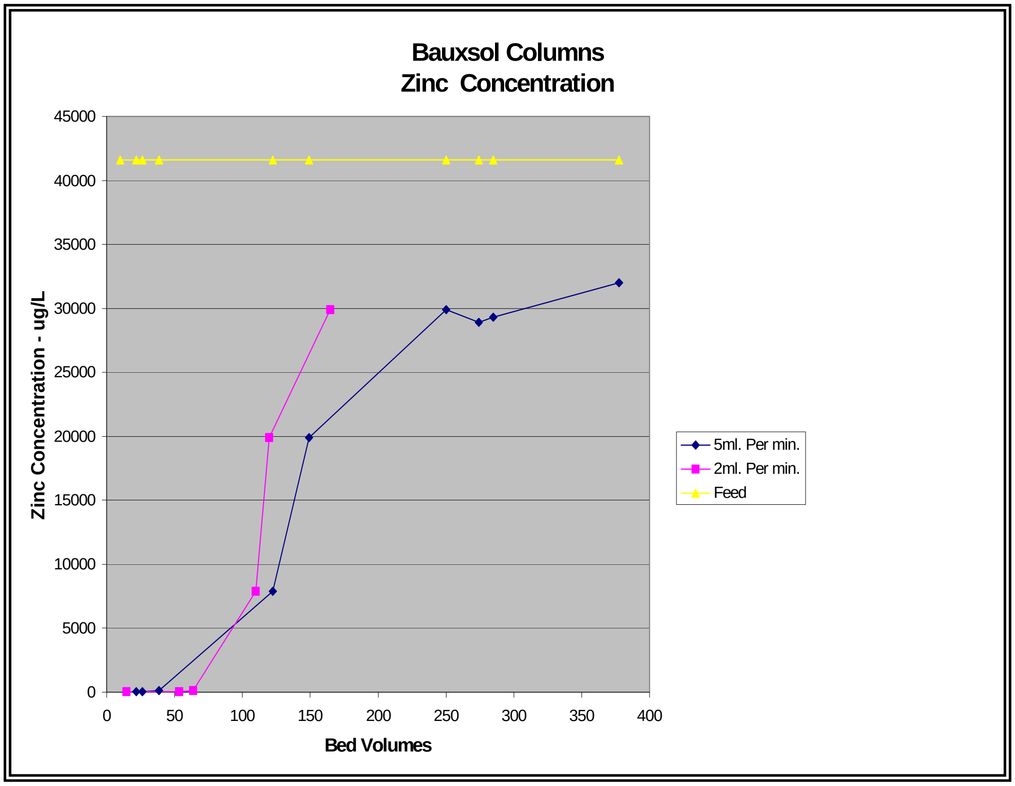

Figure 3-12. Bauxsol™ columns – Zn concentration vs. bed volumes.

Table 3-1. Rate Test Results – Reagent Group 1

Reagent Name	Initial Zn Conc. µg/L	Zn Conc. @ 1 Hr.	Zn Conc. & pH @ 2 Hr.	Zn Conc. & pH @ 4 Hr.	Zn Conc. & pH @ 8 Hr.
Partially charred dolomite	41,500	221 µg/L	37.7 µg/L – 12.5	7.34 µg/L – 12.1	7.34 µg/L – 12.2
Bauxsol™	41,500	68.8 µg/L	44.8 µg/L – 11.4	17.2 µg/L – 11.3	24 µg/L – 11.3
Partially calcined limestone	41,500	239 µg/L	226 µg/L – 12.5	193 µg/L – 12.5	160 µg/L – 12.3
50:50 mixture of limestone and calcium oxide	41,500	1,290 µg/L	885 µg/L – 12.6	469 µg/L – 12.6	352 µg/L – 12.3
50:50 mixture of limestone and magnesium oxide	41,500	39.8 µg/L	22 µg/L – 11.6	48.7 µg/L – 11.1	61.6 µg/L – 11.3
Sodium hydrosulfide	41,500	102 µg/L	413 µg/L L – 10.6	44.4 µg/L – 10.4	13.6 µg/L – 10.3

Table 3-2. Rate Test Results – Reagent Group 2

Reagent Name	Initial Zn Conc. µg/L	Zn Conc. @ 1 Hr.	Zn Conc. & pH @ 2 Hr.	Zn Conc. & pH @ 4 Hr.	Zn Conc. & pH @ 8 Hr.
Apatite II™	41,500	561 µg/L	71.1 µg/L – 6.9	262 µg/L – 6.7	228 µg/L – 7.0
Ferrihydrite coated sand	41,500	30,500 µg/L	27,800 µg/L – 6.4	25,900 µg/L – 6.2	23,000 µg/L – 6.2
GFH	41,500	22,000 µg/L	18,500 µg/L – 5.7	12,500 µg/L – 5.5	9,740 µg/L – 5.8
Aluminum-iron coated sand	41,500	36,700 µg/L	34,300 µg/L – 6.3	36,200 µg/L – 6.1	33,800 µg/L – 6.0
Juniper bark	41,500	32,000 µg/L	34,700 µg/L – 3.6	30,300 µg/L – 3.4	28,800 µg/L – 3.6
Manganese dioxide coated sand	41,500	28,100 µg/L	27,300 µg/L – 5.7	24,600 µg/L – 5.3	23,400 µg/L – 5.9

Table 3-3. Equilibrium Capacity Test Results

Reagent Name	Initial Zn Concentration – μg/L	Equilibrium Zn Concentration – μg/L	Equilibrium Cd Concentration – μg/L	Sorbent Mass – g	Loading – μg Zn Sorbed per g of Sorbent	Loading – μg Cd Sorbed per g of Sorbent
Apatite II™	44,080	13,100	35.94	1.1	14.08	99.65
	44,080	7,150	18.36	2	9.23	59.20
	44,080	1,170	2.77	5.3	4.05	23.81
	44,080	606	1.27	10	2.17	12.69
	44,080	293	0.65	25	0.88	5.09
	44,080	201	0.50	50.2	0.44	2.54
Ferrihydrite coated sand	44,080	36,000	162.04	1.19	0.79	15.65
	44,080	36,000	151.85	2.05	0.73	10.08
	44,080	24,700	76.03	5.31	0.73	6.75
	44,080	10,500	24.00	10.26	0.65	4.51
	44,080	326	1.03	50.45	0.17	1.01
GFH	40,000	29,200	148.00	1	5.40	42.68
	40,000	21,100	104.00	2	4.73	33.40
	40,000	11,800	53.20	5	2.82	14.74
	40,000	19,000	77.90	10	1.05	6.96
	40,000	15,800	50.20	25	0.48	3.45
	40,000	5,840	17.50	50	0.34	1.94
	40,000	6,160	18.20	50	0.34	–
Aluminum-iron coated sand	44,080	41,000	225.95	1.04	0.30	2.81
	44,080	40,000	214.03	2	0.20	2.06
	44,080	37,400	212.34	5.08	0.13	0.84
	44,080	32,300	202.25	10.25	0.11	0.52
	44,080	20,000	141.04	50.03	0.05	0.23
Juniper bark	44,080	38,500	223.41	1.07	0.78	4.45
	44,080	36,700	212.27	2.15	0.51	2.99
	44,080	32,200	182.31	5.07	0.35	2.16
	44,080	27,600	80.23	10.22	0.24	2.57
	44,080	22,500	124.19	20.74	0.16	0.95
Manganese dioxide coated sand	44,080	40,400	242.00	1	0.74	2.63
	44,080	38,400	226.59	2.15	0.53	2.66
	44,080	35,300	209.20	5.02	0.35	1.83
	44.080	26,700	164.02	10.14	0.34	1.80
	44,080	7,580	84.32	24.67	0.30	1.39
	44,080	16.4	9.87	50.12	0.18	0.98
Bauxsol™	44,080	97.4	6.96	1	21.99	124.1
	44,080	29.8	0.14	2	11.01	63.76
	44,080	96.2	0.08	5	4.40	25.51
	44,080	178	0.08	10	2.20	12.75
	44,080	95.1	0.16	50	0.44	2.55

Table 3-4. Column Test Results – Flow Rate – 2 mL/min

Reagent Name	**Bed Volumes**	**pH (SU)**	**ORP (mv)**	**SC (µS/cm)**	**Dissolved Zn – µg**	**Dissolved Cd – µg**	**Dissolved Pb – µg**
Control – Sand	3.0	7.11	154	335	41,000	241	0.16
	13.0	6.19	194.4	339	41,800	238	0.19
	25.3	6.14	173	339	39,100	241	0.39
	34.8	6.18	152.3	336	39,500	246	0.37
	71.1	6.56	95.8	339	39,700	249	106
	93.4	6.53	141.7	339	39,800	242	125
	115.9	6.55	168	339	40,000	242	145
Apatite II™	3.4	7.38	114.8	865	15.4	0.03	0.17
	12.5	6.79	133.6	371	15.4	0.03	0.12
	14.8	6.85	74.3	366	15.4	0.03	0.13
	25.9	6.72	126.6	365	15.4	0.03	0.11
	28.5	6.85	131.5	371	15.4	0.03	0.11
	29.4	–	–	–	15.4	0.03	0.10
	39.5	6.78	112.6	372	15.4	0.03	0.10
	56.6	6.68	94.4	386	15.4	0.03	0.12
	70.5	6.62	25.8	397	15.4	0.03	0.21
	80.7	6.57	76.7	408	15.4	0.03	0.15
	94.2	6.58	-1.0	469	15.4	0.03	0.15
	107.7	6.61	-.3	501	15.4	0.03	0.19
	120.8	6.59	-71.1	550	15.4	0.03	0.19
	133.7	6.60	-71.5	579	15.4	0.03	0.17
GFH	3.0	7.51	148.6	294	6,990	2.28	0.04
	11.7	4.79	204.9	244	802	3.30	0.06
	14.0	5.80	251.4	240	542	2.73	0.07
	24.4	5.23	176.1	240	185	1.19	0.07
	26.8	5.90	199.2	239	162	1.03	0.10
	27.7	–	–	–	169	1.02	0.10
	37.0	5.09	168.8	236	84.1	0.53	0.08
	53.1	5.95	163.6	238	41.6	0.25	0.05
	66.2	6.13	106.4	241	19.2	0.15	0.05
	75.9	5.16	142.9	234	15.4	0.06	0.04
	88.4	7.14	73.9	228	15.4	0.03	0.03
	98.8	7.21	111.8	218	15.4	0.03	0.04
	111.3	7.10	100.4	235	1,680	0.05	0.05
	123.2	6.89	150.3	251	5,800	0.09	0.06
Bauxsol™	14.4	11.22	7.4	917	241	0.03	0.16
	53.5	9.48	78.1	383	83.4	0.86	0.14
	63.8	8.77	47.7	370	126	1.89	0.18
	109.8	6.68	169.7	353	11,300	92.40	3.88
	119.8	6.71	150.5	352	9,990	87.40	3.63
	164.7	6.68	134.2	350	13,800	104.00	9.68

Table 3-5. Column Test Results – Flow Rate – 5 mL/min

Reagent Name	Bed Volumes	pH (SU)	ORP (mv)	SC (µS/cm)	Dissolved Zn - µg	Dissolved Cd - µg	Dissolved Pb - µg
Control - Sand	0.4	7.62	14.2	297	41,200	242	0.16
	33.1	6.80	249	338	41,700	246	12.6
	61.6	6.56	194.5	340	41,800	243	111
	73.3	6.40	141.2	338	41,700	243	96.3
	159.5	6.41	130.4	338	41,300	247	166
	213.3	6.58	163.5	340	41,600	242	164
	268.7	6.56	152.9	341	41,800	243	171
Apatite II™	8.7	7.13	145.6	417	15.4	0.03	0.12
	38.2	6.79	165.6	360	15.4	0.03	0.18
	61.7	–	–	–	15.4	0.19	0.24
	62.8	6.68	103.3	360	15.4	0.09	0.15
	69.0	6.70	118.2	360	20.5	0.03	0.11
	72.0	6.73	94.8	361	25	0.03	0.12
	95.6	6.82	82.8	365	110	0.17	0.13
	137.9	6.69	107.8	371	656	0.09	0.16
	172.4	6.72	101.9	376	1,530	0.36	0.14
	197.2	6.62	101.3	363	2,830	0.78	0.15
GFH	7.8	6.91	178.9	250	3,760	14	0.09
	31.9	6.33	209.3	236	229	1.2	0.08
	51.1	5.20	152.1	238	234	1.2	0.07
	57.1	5.60	173.3	236	57.2	0.37	0.12
	78.9	6.53	92.3	228	15.4	0.07	0.03
	86.4	7.49	91.5	229	19.2	0.06	0.04
	113.7	6.82	112.3	244	5,640	0.22	0.04
	141.9	6.63	128.0	297	21,900	5.68	0.03
Bauxsol™	21.8	10.51	-28.3	522	25.8	0.05	0.52
	26.1	9.79	27.6	414	23.6	0.03	0.53
	38.7	7.52	137.8	363	137	33.2	0.50
	122.3	6.62	152.4	347	7,870	89.4	7.49
	149.2	6.55	191.7	343	19,900	144	31.5
	250.2	6.30	142.2	343	29,900	190	77.0
	274.1	6.32	154.9	343	28,900	189	67.5
	285	6.54	135.7	345	29,300	191	72.0
	377.6	6.37	130.9	340	32,000	204	94.5

Table 3-6. Column Loading Capacities – by Reagent

Reagent Name	Total Column Effluent mL	Total Zinc Removed µg	Mass of Media in Column g	Media Removal Capacity µg/g
Sand – 2 mL/min	28,727	54,161	425	127.4
Sand – 5 mL/min	65,703	14,315	425	33.7
Apatite II™ – 2 mL/min	28,399	1,186,640	40	29,666
Apatite II™ – 5 mL/min	19,070	796,374	40	19,909
GFH – 2 mL/min	24,483	1,014,967	250	4,060
GFH – 5 mL/min	19,540	806,864	250	3,227
Bauxsol™ – 2 mL/min	3,285	136,900	25	5,476
Bauxsol™ – 5 mL/min	1,990	83,059	25	3,322

4. Conclusions

Of the seven media tested, the majority were not appropriate for treating Canyon Creek groundwater in a passive manner. Only three media, GFH, Bauxsol™, and Apatite II™, were considered feasible for testing within columns. Of those three media, Apatite II™ has a much higher capacity to remove Zn (the primary element of concern) from this water when compared to the other two media.

A number of operational parameters associated with the use of Apatite II™ exist that would have to be addressed to use the media for the commercial treatment of this water. These parameters include, but are not limited to the tendency of the media to become anaerobic and foster the development of SRB, the tendency of the media to swell when it is hydrated, and the known problems (i.e., high effluent biochemical oxygen demand and nutrients, hydrogen sulfide, odors, dissolved Mn, iron, and potentially arsenic) that occur with plugging when the media is used without being diluted with an inert material such as sand (McCloskey, 2003).

It should also be noted that the use of SRB represents another reasonable method of treating metal-laden waters of this type.

5. References

Benjamin, M. M. and Sletten, R.S., Metals Treatment at Superfund Sites by Adsorptive Filtration, U.S. E.P.A., Office of Research and Development, 1993.

The Dow Chemical Company, *DOWEX Ion Exchange Resins and Adsorbents*, May, 1997.

McCloskey, L., Final Report – Nevada Stewart Permeable Reactive Barrier Project, U.S. E.P.A. Mine Waste Technology Program, 2003.

Millard, S.P., Environmental Stats for S-Plus Software Program, 2002.

Pourbaix, M., *Atlas Of Electrochemical Equilibria In Aqueous Solutions,* National Association of Corrosion Engineers, 1974

U.S. Environmental Protection Agency, *Guidance for Data Quality Assessment*, EPA QA/G-9.

U.S. Environmental Protection Agency, *USEPA Contract Laboratory Program National Functional Guidelines for Inorganics Data Review,* Document OSWER 9240.1-45, EPA 540-R-04-004, October 2004.

Appendix A

Summary of Quality Assurance Activities

Summary of Quality Assurance Activities

Mine Waste Technology Program
Activity III, Project 48

BACKGROUND

The following is a summary of the quality assurance (QA) activities associated with MWTP Activity III, Project 48, *Passive Treatment for Reducing Metal Loading*. Analytical samples and field data were collected according to the schedule outlined in the approved project-specific QA test plan. All field and laboratory data available has been evaluated to determine the usability of the data. Data from both critical and noncritical analyses were evaluated. Critical analyses are analyses that must be performed to determine if project objectives were achieved, while noncritical analyses provide additional information about process control, as well as information that is of interest to project participants. The critical parameters, dissolved Cd, Pb, and Zn, were analyzed to support the project objective of evaluating passive treatment media that may have potential to reduce metals loading contribution from Canyon Creek by 50%.

INTERNAL TECHNICAL SYSTEMS AUDIT

An internal technical systems audit of the equilibrium capacity studies and laboratory column studies was performed by Mindy McCarthy, the MSE MWTP QA Manager, on February 7 and continued through April 23, 2007. There were no findings, five observations, and one additional technical comment identified during the audit.

On February 7 and 8, a segment of the equilibrium capacity studies was observed to evaluate the documentation associated with sampling and testing studies (i.e., field logbook, test sheets, and sampling documentation), and to evaluate adherence of the test and sampling procedures to the QA test plan in order to verify data quality. On April 23, a segment of the laboratory column studies was observed and evaluated for the same criteria as the equilibrium capacity studies portion of the audit. The observations resulting from the audit included improving field logbook documentation, noting deviations from the QA test plan in the final report, and adding valuable technical descriptions to the final report. To improve field logbook documentation, the field/sampling personnel were to ensure that the field personnel performing the daily study activities initialed each day’s logbook entry. The appropriate amendments were made and implemented to correct the observation.

Three observations pertained to deviations from the QA test plan. The first observation concerned a deviation regarding the number of passive media that were tested during the equilibrium capacity studies. The QA test plan indicated that 12 passive media would be tested at five different mass loadings during the equilibrium capacity study. Based on results from the equilibrium rate study, the passive media used during the equilibrium capacity testing was reduced to seven. Another observation noted a deviation concerning the number of passive media tested during the laboratory column studies. The QA test plan indicated that four passive media would be further tested in a column configuration. However, only three passive media were selected for the column studies, based on results of the equilibrium capacity studies. Another observation was that GFH might not have been properly characterized, based on its Freundlich plot. However, additional runs were performed after the original equilibrium capacity study testing and the mass loadings were re-plotted to properly characterize the media. There was no variation from the output of the GFH data that was reanalyzed from the original plot. The last observation was to include valuable technical descriptions in the final report to further clarify the study procedures.

Am additional technical comment was made because a statement in the sampling procedures in Section 5.1 of the QA test plan was not applicable. It was noted in the test plan that collected samples shall leave no headspace in the container to minimize air entrainment because the entrained air could react with species in the samples and affect analytical results. For the analyses presented in the plan, this provision was not applicable, so entrained air would not affect the outcome of the analytical results. This was necessary to mention because the samples taken during the studies did have headspace in the sampling containers. Upon observation, the samples were collected in the appropriate manner.

DATA EVALUATION

Data that was generated throughout the project was validated. The purpose of data validation is to determine the usability of data generated during a project. Data validation consists of two separate evaluations: an analytical evaluation and a program evaluation. The analytical evaluation focuses on laboratory data validation, field logbook evaluation, and field data evaluation, while the program evaluation concentrates on chain-of custody procedures, sampling and data completeness, and field quality control (QC) samples.

ANALYTICAL EVALUATION

An analytical evaluation of all data was performed to determine the usability of the data that was generated by MSE Laboratory for the project.

Laboratory Data Validation

Laboratory data validation was performed using *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (USEPA, 2004) as a guide. The data quality indicator objectives for critical measurements were outlined in the QA test plan and were compatible with project objectives and the methods of determination being used. The data quality indicator objectives were method detection limits (MDLs), accuracy, precision, and completeness. Control limits for each of these objectives are summarized in Table A-1. In addition to the data quality indicators listed in Table A-1, internal QC checks, including calibration, calibration verification checks, calibration blanks, matrix spike duplicates, interference checks, method blanks and laboratory control samples were used to identify outlier data and to determine the usability of the data for each analysis.

The validation of laboratory data determined that all analyses were performed within specified holding times, calibration procedures were correctly performed, and laboratory blanks contained no significant contamination. Check standards, duplicate sample analysis, and spike sample analysis were performed at the proper frequencies and were within the specified control limits. In some instances, sample concentrations were greater than four times the spike concentrations, and the recovery limits were not applicable. Serial dilutions were within acceptable limits, indicating that there were no matrix effects.

Measurements that fall outside of the control limits specified in the QA test plan or method requirements, or for other reasons were judged to be outlier, are normally flagged appropriately to indicate that the data was judged to be estimated or unusable; however, there were no data from this project requiring flags.

Field Logbook Evaluation

Field data validation began with an examination of the project logbook and project logsheets that were generated for this project. The general logbook contained logs of the daily study activities as well as the instrument calibrations for field measurements. Project log sheets were used to document study information for the passive media equilibrium rate studies data, the equilibrium capacity studies data, and the laboratory column studies data. Details for sample collection including sample dates and times, sample identification, sampling personnel, and field measurements were documented on these log sheets. Information recorded on the passive equilibrium rate studies log sheets included the particle size, pH and temperature measurements, and media mass and test water volume. The information that was recorded on the log sheets for the batch testing included the pH, temperature, ORP, and specific conductance (SC) measurements, as well as the adsorbent masses and test water volumes. Information recorded on the column testing log sheets included the effluent flow, effluent volume, pressure differential, pH, SC, and ORP measurements and the sample identification of samples taken.

Field Data Evaluation

Field data validation was performed to determine the usability of the data that was generated during field activities. The usability was determined by verifying that correct calibration procedures on field instruments were followed. All of the field measurements were classified as noncritical.

pH

Measurement of pH was manually performed by MSE personnel using the hand-held YSI multimeter. The pH meters had automatic temperature compensation and were capable of measuring pH to ± 0.1 pH units. The meter was calibrated daily prior to analysis using fresh 4, 7, and 10 buffer solutions.

The QA test plan requirements for pH measurements, both the required frequency and the required sample measurements, were realized.

Oxidation-Reduction Potential

Oxidation-reduction potential was measured using the YSI multimeter with a silver/silver chloride reference electrode to determine the ORP of samples. The electrode calibration was verified at the beginning of every sampling event using a solution of known ORP. The measured standard ORP measurements were documented, and the ORP values were within ± 20% of the known solution value.

The QA test plan requirements for ORP measurements, both the required frequency and the required sample measurements, were realized.

PROGRAM EVALUATION

The program evaluations included an examination of data generated during the project to determine that all field QC checks were performed and within acceptable tolerances. Program data deemed inconsistent or incomplete and not meeting the QC objectives outlined in the QA test plan would be viewed as program outliers and flagged appropriately to indicate the usability of the data; however, there were no data flagged.

Chain-of-Custody Procedures

Information provided on the chain-of-custody was accurate and complete, and any discrepancies noted by MSE Laboratory were communicated with the project manager and resolved through laboratory corrective action procedures.

Sampling and Data Completeness

All samples that were supposed to be collected were collected and were analyzed for the required analyses as outlined in the QA test plan.

Field QC Samples

In addition to internal laboratory checks, field QC samples were collected to determine overall project performance. All field QC samples were collected at the proper frequency for tests specified in the QA test plan. None of the field blanks collected for the project showed significant contamination. Field duplicates showed very good agreement to the original sample. No samples required qualification due to field QC sample results.

QA SUMMARY

The project personnel conducted QA/QC activities for this project in accordance with the procedures outlined in the QA test plan. All critical activities were documented in the field logbook and on the project log sheets, field instrumentation was properly calibrated, samples were properly collected, and field QC samples were appropriately taken. Based on the quality assurance activities of MWTP, Activity III, Project 48, the data generated was of sufficient quality to evaluate project objectives.

Table A-1. Data quality indicator objectives for precision, accuracy, MDL, and completeness.

Parameter	Matrix	Unit	MDL[a]	Precision[b]	Accuracy[c]	Completeness[d]
Dissolved Cd	Aqueous	µg/L	1	≤20%	75-125%	90%
Dissolved Pb	Aqueous	µg/L	1	≤20%	75-125%	90%
Dissolved Zn	Aqueous	µg/L	10	≤20%	75-125%	90%

[a] MDLs are based on what is achievable by the methods, and what is necessary to achieve project objectives and account for anticipated dilutions to eliminate matrix interferences. MDLs will be adjusted as necessary when dilutions of concentrated samples are required.

[b] Relative percent difference of analytical sample duplicates.

[c] Percent recovery of matrix spike, unless otherwise indicated.

[d] Based on number of valid measurements, compared to the total number of samples.