

**FINAL REPORT—BERKELEY PIT
INNOVATIVE TECHNOLOGIES PROJECT,
PHASE III: HYDROMETRICS, INC.,
DEMONSTRATION OF SULFATE REMOVAL
USING THE WALHALLA™ PROCESS**

**MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 7**

Prepared by:

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Prepared for:

U.S. Environmental Protection Agency
Office of Research and Development
National Risk Management Research Laboratory
Cincinnati, Ohio 45268
IAG ID No. DW89938513-01-0

and

U.S. Department of Energy
Federal Energy Technology Center
Pittsburgh, Pennsylvania 15236
Contract No. DE-AC22-96EW96405

February 1999

REVIEWS AND APPROVALS:

Prepared by: _____
Project Manager

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Foreword

Industries are continuously developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. 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 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 the EPA to perform research to define, measure the impacts, and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of the EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis. This supports the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the U.S. Department of Energy (DOE) has responsibilities similar to the NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement (IAG) was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc., and Montana Tech of The University of Montana for the development of the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two federal organizations, and provides a vital communication link between the researcher and the user community.

The objectives of this demonstration were to test at the bench-scale, a method for remediating sulfate from Berkeley Pit water.

The information in this document has been funded wholly or in part by EPA under an IAG between EPA and DOE, IAG No. DW89938513-01-0.

Executive Summary

Hydrometrics, Inc., was contracted by Montana Tech of The University of Montana to test a process for removing sulfate in sufficient quantities from Berkeley Pit water to meet a prescribed discharge limit. Hydrometrics' objective was to determine whether a proprietary process, the Walhalla™ Process, could cost-effectively reduce sulfate concentrations from an initial concentration of approximately 8,000 mg/L to a final concentration of 500 mg/L, which is a nationwide discharge limit proposed by EPA. This project, along with several other bench-scale studies, was funded through the Berkeley Pit Innovative Technologies program. This final report includes the first and second bench-scale experimental results, a cost analysis, and recommendations for future testing.

In the Walhalla™ Process, a proprietary compound, SX-44, is added after conventional lime treatment to precipitate sulfate and any residual metals as the mineral ettringite. Ettringite, which is a hydrated calcium aluminum sulfate compound, is easily removed using a conventional clarifier. Final sulfate concentrations are dependent upon the SX-44 dosage and contact time.

Based on Hydrometrics' previous experience, significant sulfate removal occurs at a pH of 11.5 when the residence time is between 30 and 300 minutes, and the SX-44:sulfate weight ratio is between 1 and 1.5. Results from an initial screening experiment suggested these ranges would also be successful for removing sulfate from Berkeley Pit water.

In Experiment 1, mixing jars were used in batch (noncontinuous flow) testing to determine the effect of residence time and SX-44 dosage on Berkeley Pit water. Results from the screening experiment narrowed the residence times to 30, 105, and 180 minutes and SX-44:sulfate ratios to 0.8, 1.2, and 1.6. A full-factorial design was generated using the three levels for each factor to create nine process conditions. Experiment 1 showed the target sulfate concentration of 500 mg/L was easily met, with sulfate concentrations as low as 4 mg/L.

This designed experiment was repeated after results of the first experiment better determined a more localized range for each variable. Levels for residence time were changed to 60, 90, and 120 minutes; and the levels for SX-44:sulfate were changed to 0.8, 1.1, and 1.4. Experiment 2 was again successful in removing sulfate to below the target concentration of 500 mg/L.

A contour plot of the experimental data shows a residence time of 90 minutes and an SX-44:sulfate ratio of approximately 0.85 would reduce sulfate concentrations in Berkeley Pit water to the target concentration of 500 mg/L. These results were used to estimate costs for a full-scale sulfate-removal system at the Berkeley Pit following a lime treatment process. Estimated equipment and annual operating and maintenance costs for the system were \$1.2 million and \$3.9 million, respectively, with a net present value over 30 years (using a 5% discount rate of return and a 3% inflation rate) of \$89 million.

Because of the high operating and maintenance costs for the Walhalla™ Process, additional bench-scale and/or pilot-scale tests should be performed to determine the optimum residence time and SX-44 dosage that will produce the lowest net present value for a full-scale sulfate-removal system.

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1. Sulfate and Metals Removal

1.1 Project Objective

This project was one of several bench-scale studies funded as Berkeley Pit Innovative Technologies (BPIT) demonstration projects. The specific objective of Hydrometrics' project was to determine if the Walhalla™ Process could remove sulfate in sufficient quantities from Berkeley Pit water to meet a prescribed discharge limit.

Hydrometrics' experiments were focused on examining a potentially cost-effective, proprietary method for removing sulfate from Berkeley Pit water, since methods available for arsenic and metals removal are generally well

understood. Table 1-1 lists target levels for all constituents after treatment, since the Walhalla™ Process has been shown to also remove metals. However, sulfate was considered the only critical measurement.

The objective of this project was to reduce sulfate from an initial concentration of approximately 3,000 mg/L to a final concentration of approximately 500 mg/L using the Walhalla™ Process. The target concentration of 500 mg/L, which corresponds to a nationwide discharge limit of 500 mg/L proposed by EPA, was established by Montana Tech.

Table 1-1. Target Concentrations after Treatment

Parameter	Units	Method Detection	Critical	Target
		Limit	Measurement	Concentration
Cu	mg/L	0.01	No	0.01
Zn	mg/L	0.01	No	0.10
Cd	mg/L	0.001	No	0.05
Ni	mg/L	0.01	No	0.10
Fe	mg/L	0.03	No	0.30
Mn	mg/L	0.01	No	0.05
SO ₄	mg/L	1.0	Yes	500
pH	pH units	0.1	No	11.5

2. Process Technology

The Walhalla™ Process uses a proprietary compound, SX-44, to precipitate sulfate as the mineral formula ettringite $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}]$, which is then removed and handled using conventional sludge processing techniques. However, when the water being treated contains very high sulfate concentrations (greater than 2,000 mg/L) and/or significant concentrations of heavy metals, conditions often associated with acid-rock drainage, the process is usually preceded by lower-cost lime treatment to remove the excess sulfate (sulfate in concentrations greater than 2,000 mg/L) as gypsum and the metals as hydroxides. In Walhalla™ Process, sulfate concentrations below 100 mg/L are easily achievable, with the final concentration dependent upon the SX-44 dosage and contact time.

Recommended discharge limits for sulfate in the United States usually range from 250 to 2,000 mg/L, with a federal recommended maximum concentration of 250 mg/L in drinking water. In addition, excessive sulfate concentrations can cause scaling, corrosion, odor, and possible sulfuric acid evolution. The Walhalla™ Process has been used successfully to treat process waters associated with the electroplating, battery recycling, and power generation industries, and has been used successfully at the bench scale for treatment of mine drainage. For this work, the target sulfate concentration was 500 mg/L.

Figure 2-1 shows a simplified version of the Walhalla™ Process when the initial sulfate concentration is less than 8,000 mg/L but greater than 2,000 mg/L, and the water being treated contains significant metals concentrations. Figure 2-2 shows the simplest version of the process where only final sulfate removal is required. The process shown in Figure 2-1 was simulated in Hydrometrics' tests, except that Step 4 (pH reduction) was not performed. Reducing the pH of the water was not done as part of the demonstration because recarbonation

is well understood and was not considered a necessary part of these experiments.

The prerequisites for using the Walhalla™ Process are: 1) sodium and potassium concentrations below 1,000 mg/L, or sodium and potassium ionically balanced with chloride; 2) chemical oxygen demand (COD) below 250 mg/L; and 3) a pH control system with lime addition. Other than the lime addition system, Berkeley Pit water meets these criteria.

2.1 Step One—Initial Sulfate Precipitation

For water with a high metals content and sulfate level greater than 8,000 mg/L, hydrated lime is used to precipitate the sulfate in excess of 8000 mg/L as gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$). Since Berkeley Pit water has approximately 8,000 mg/L sulfate, Step 1 was not necessary. The sludge from this step would probably pass the Toxicity Characteristic Leaching Procedure (TCLP) and could be disposed in a Class II or Class III landfill. This would substantially reduce costs compared to combining this sludge with metals-bearing sludge from Step 2, which would require disposal in a Class I landfill.

2.2 Step Two—Metal Hydroxide Precipitation

Water containing excessive heavy metals concentrations, but with an initial sulfate concentration below 8,000 mg/L or which has already been treated with lime, is then adjusted to a pH between 10.5 to 11 with hydrated lime and mixed for a period of 40 to 60 minutes. This removes the metals as hydroxides and precipitates additional gypsum ($\text{SO}_4\cdot 2\text{H}_2\text{O}$) so that approximately 2,000 mg/L of sulfate remains in solution. With this step, laboratory tests may be necessary to determine the optimum pH for hydroxide precipitation since some metals will begin to go back into solution near pH 10.5.

Approximately 12–15 kg of gypsum and metals

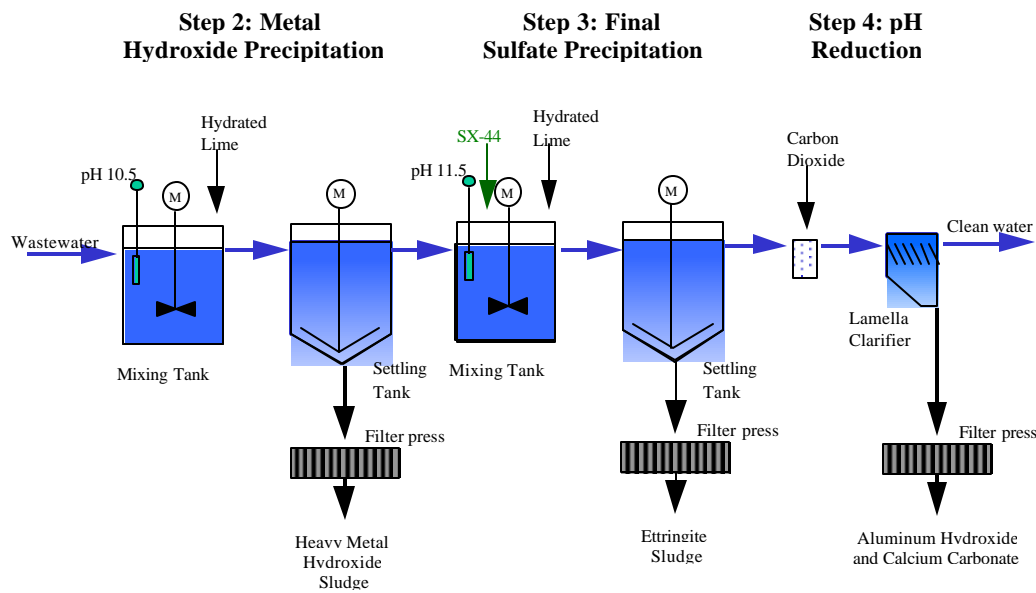
sludge are produced per cubic meter of Berkeley Pit water treated. Following dewatering, this sludge may require disposal in a Class I landfill if leachable metals concentrations exceed permissible limits for Class II or Class III landfills.

2.3 Step Three–Final Sulfate Precipitation

In this step, hydrated lime is added to increase the pH to approximately 11.5. Lime must be used (in place of other possible reagents such as caustic soda or soda ash) so enough calcium will be available for ettringite precipitation. Next, a proprietary chemical, SX-44, is added to precipitate additional sulfate. The typical dosage is 1.0 to 1.5 grams SX-44 per gram

sulfate. SX-44 combines with soluble gypsum to form solid ettringite. As ettringite forms, contaminants such as nitrate, chloride, fluoride, boron, and metals (if present in the water) are also incorporated into its structure. Insoluble gypsum will interfere with this reaction if not removed in a previous step.

This step requires 30 to 300 minutes, depending on the level of removal required, other contaminants in the water, and the amount of SX-44 added. Ettringite sludge is easily dewatered and may be reused in the process as seed sludge to reduce the quantity of coagulation aid required. Ettringite sludge can be disposed in a Class III landfill as it normally passes TCLP.



Note that three presses are shown to simplify diagram. Only two would be required with the goal of separating the hazardous and nonhazardous sludge.

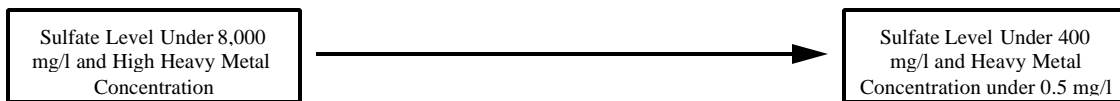
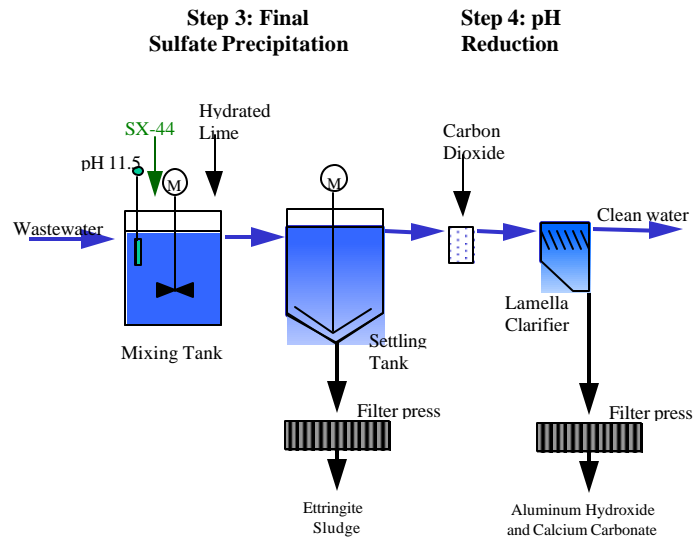


Figure 2-1. Two-step Walhalla™ Process with pH reduction.



Note that two presses are shown to simplify diagram. Only one would be required with the goal of separating the hazardous and nonhazardous sludge.

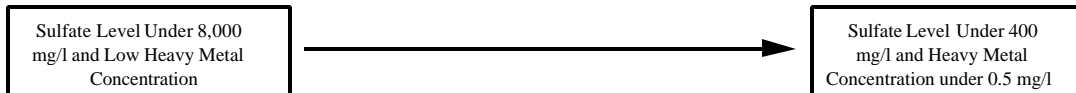


Figure 2-2. One-step Walhalla[™] Process with pH reduction.

3. Experimental Methodology

In the Walhalla™ Process, two main factors determine the amount of sulfate removed from process water: residence time and SX-44:sulfate weight ratio. Based on Hydrometrics' previous experience, significant sulfate removal occurs with residence times between 30 and 300 minutes and SX-44:sulfate ratios between 1 and 1.5. An initial screening experiment was performed at Hydrometrics' laboratory to determine whether these ranges would successfully remove sulfate from Berkeley Pit water. The screening experiment used two residence times, 30 and 60 minutes, and a SX-44:sulfate ratio of 1.6. Sulfate results were analyzed in the Hydrometrics laboratory using a Hach DR/2000 spectrophotometer. The results bracketed the target of 500 mg/L, as a 30-minute residence time produced a sulfate concentration of 725 mg/L, and a 60-minute residence time produced a sulfate concentration of 180 mg/L. This showed that these values for residence time and SX-44:sulfate ratio could meet the target concentration of 500 mg/L for Berkeley Pit water.

For the first experiment, an SX-44:sulfate ratio of 1.6 was chosen as a level to replicate the screening experiment, and additional ratios of 0.8 and 1.2 were chosen to determine how well sulfate could be removed using lower quantities of SX-44. A 30-minute residence time was chosen to replicate the screening experiment, along with longer residence times of 105 and 180 minutes. Table 3-1 shows the full-factorial design for Experiment 1.

This designed experiment was repeated

(Experiment 2) after results of the first experiment better determined the effective range of each variable. The residence times were 60, 90, and 120 minutes, and the SX-44:sulfate ratios were 0.8, 1.1, and 1.4. Table 3-2 shows the full-factorial design for Experiment 2.

Both experiments were batch tests (noncontinuous flow). Intermediate and final sulfate samples were taken in each experiment. Since metals were not the primary focus of the experiment, filtered samples for metals analysis were only collected with final sulfate samples.

Table 3-1. Experiment 1 Design

Condition	Residence Time (min.)	SX-44:Sulfate Ratio
1	30	0.8
2	30	1.2
3	30	1.6
4	105	0.8
5	105	1.2
6	105	1.6
7	180	0.8
8	180	1.2
9	180	1.6

Table 3-2. Experiment 2 Design

Condition	Residence Time (min.)	SX-44:Sulfate Ratio
1	60	0.8
2	60	1.1
3	60	1.4
4	90	0.8
5	90	1.1
6	90	1.4
7	120	0.8
8	120	1.1
9	120	1.4

4. Materials and Methods

Water from the Berkeley Pit (20 gallons) containing approximately 8,000 mg/L of sulfate was collected from a depth of 200 feet by Montana Tech personnel and shipped to Hydrometrics' laboratory. The Berkeley Pit water was used to conduct bench-scale experiments in Hydrometrics' laboratory in East Helena, Montana, from August through October 1998.

4.1 Experiment 1

4.1.1 Equipment Calibration

The pH meter was calibrated using JT Baker and Orion brand buffer solutions (Table 4-1).

4.1.2 Step 2–Metal Hydroxide Precipitation

Nine mixing jars were each filled with two liters of Berkeley Pit water at an initial pH of 2.51. The jars were then placed in the Phipps and Bird jar stirrer, mixing at 300 rpm. Approximately 75 ml of lime slurry (22% calcium hydroxide by weight) was added to increase the pH and maintain it at 10.5, which caused metals to precipitate. After one hour, 2.5 ppm of Percol 727 flocculant (Allied Colloids) was added to each jar and mixed at 50 rpm for 5 minutes, followed by a 10-minute settling time without mixing. One hundred milliliters of decant water from each jar was then filtered into sample bottles and sent to Energy Laboratories for sulfate analysis, while 1.2 liters of the remaining decant from each jar was filtered into clean mixing jars. This decant, with a pH of approximately 10, was measured for sulfate using a Hach DR/2000 spectrophotometer to determine the amount of SX-44 reagent to add to each jar of decant water.

4.1.3 Step 3–Final Sulfate Precipitation

The clean mixing jars, containing 1.2 liters of the decant water from Step 2, were placed in the Phipps and Bird jar stirrer, mixing at 300 rpm. Various quantities of SX-44 were added to each jar depending on the sulfate concentration

measured with the Hach DR/2000 spectrophotometer, and the SX-44:sulfate ratio assigned to each condition (Table 3-1). A small amount of lime was also added to increase the pH and maintain it at 11.5. Residence (mixing) times of 30, 105, or 180 minutes were used. After the appropriate residence time, between 1.0 and 2.0 ppm of Percol 727 flocculant was added, and the jar contents mixed at 50 rpm for 5 minutes, followed by a 10-minute settling time. The water from each jar then was filtered into two 100-mL sample bottles and sent to Energy Laboratories in Billings, Montana, for dissolved sulfate and metals analysis.

4.2 Experiment 2

The purpose of Experiment 2 was to better identify the optimum operating range for sulfate removal. Experiment 2 was essentially the same as Experiment 1 except that the operating range for residence time was narrowed from 30 to 180 minutes to 60 to 120 minutes, and the range for SX-44:sulfate ratio was decreased from 0.8 to 1.6 to 0.8 to 1.4. After Step 2, sulfate samples were sent to Energy Laboratories and analyzed before Step 3 began.

4.2.1 Equipment Calibration

The pH meter was calibrated using JT Baker and Orion brand buffer solutions (Table 4-2).

4.2.2 Step 2–Metal Hydroxide Precipitation

Nine mixing jars were filled with 2 liters of Berkeley Pit water having an initial pH of 2.16. Jars were then placed in the Phipps and Bird jar stirrer with a mixing speed of 300 rpm. Approximately 60 ml of lime slurry was added to each jar to increase the pH and maintain it at 11, which caused metals to precipitate. After one hour, 2.5 ppm of Percol 727 flocculant was added to each jar and mixed at 50 rpm for five minutes, followed by a 10-minute settling time. One hundred milliliters of decant water from each jar was filtered into sample bottles and sent to Energy Laboratories for sulfate analysis,

while 1.2 liters of the remaining decant from each jar was then filtered into clean mixing jars. To determine an accurate quantity of SX-44 to add to each jar, Step 3 was postponed until sulfate results were received from Energy Laboratories. Each jar of decant water, with a pH of approximately 11, was covered with Parafilm to prevent evaporation during the waiting period.

4.2.3 Step 3–Final Sulfate Precipitation

The jars, containing 1.2 liters of decant water from Step 2, were placed in the Phipps and Bird jar stirrer and mixed at 300 rpm. SX-44 quantities were added to each jar depending on the sulfate concentration determined by Energy Laboratories and the SX-44:sulfate ratio assigned to each condition (Table 3-2). Eight to ten milliliters of lime was added to each jar to increase the pH to 11.5. Residence times used were 60, 90, and 120 minutes. After the appropriate residence time, between 2.0 and 4.0 ppm of Percol 727 flocculant was added to each jar and mixed at 50 rpm for 5 minutes, followed by a 10-minute settling time. The water from each jar was filtered into 100-ml sample bottles, preserved with hydrochloric acid and sent to Energy Laboratories for sulfate analysis.

4.3 Treated Water

Treated water was sampled following filtration as described in Standard Operating Procedure 1 (Appendix A). Samples for dissolved metals analysis (100 ml) were preserved using high-purity nitric acid. Sulfate samples (also 100 ml) were not acidified. Samples were sent to Energy Laboratories for analysis.

4.4 Sample Containers and Tracking

Sterilized sample bottles were used to collect samples. After sampling, the containers were labeled with the following information:

- ownership of sample;
- date/time;
- preservative;
- sample identifying number; and
- remarks.

A bound laboratory notebook was kept with consecutively numbered pages. The information was recorded in indelible ink, and entries were initialed and dated. All corrections consisted of a single line-out deletion in indelible ink followed by the author’s initials and date. The laboratory notebook will be archived.

A standard chain-of-custody form accompanied the samples from the time they were obtained until they were delivered to the laboratory

Table 4-1. Calibration Results for the pH Meter

Buffer Solution	Buffer pH	Actual pH
JT Baker	7	7
JT Baker	4	3.98
Orion	7	7
Orion	4	4.01

Table 4-2. Calibration Results For The pH Meter

Buffer Solution	Buffer pH	Actual pH
JT Baker	7	7.02
JT Baker	4	4.00
Orion	7	7.03
Orion	4	4.00

5. Results and Discussion

5.1 Experiment 1

5.1.1 Sulfate Removal

The SX-44:sulfate ratios established for this experiment determined the quantity of SX-44 required to remove sulfate to the target of 500 mg/L. To accelerate the testing program, *approximate* sulfate concentrations were measured at Hydrometrics' laboratory using a Hach DR/2000 spectrophotometer, to determine the amounts of SX-44 to add to each condition during Experiment 1. The measured sulfate concentrations were 3,500 mg/L for jars 1 through 5 and 2,550 mg/L, 3,000 mg/L, 3,200 mg/L and 3,100 mg/L for jars 6 through 9, respectively. For a desired SX-44:sulfate weight ratio of 0.8, 2.88 g of SX-44 was added to 1.2 L of water in Condition 1 to attempt to reduce the sulfate concentration from 3,500 to 500 mg/L. The *actual* sulfate concentrations analyzed by Energy Laboratories were then used to calculate the *actual* SX-44:sulfate ratios (Table 5-1). For example, the lower initial sulfate concentrations of 2,250 mg/L measured by Energy Laboratories in Condition 1 means that the 2.88 g of SX-44 added actually created an SX-44:sulfate ratio of 1.2 (Table 5-1) versus the desired ratio of 0.8. Initial sulfate concentrations measured at Energy Laboratories were much lower than at Hydrometrics' laboratory and, therefore, increased all ratio values by 25% to 50%. The method used at Energy Laboratories, EPA method 300.1, is much more accurate; therefore, these values are regarded as the *true* sulfate concentrations.

Sulfate concentrations decreased significantly as SX-44:sulfate ratios increased, and residence times increased from 30 to 105 minutes (Table 5-1). The longest residence time (180 minutes) produced sulfate concentrations similar to the 105-minute residence time; this indicates that beyond 105 minutes, residence time has little or no effect on sulfate removal. Compared to the untreated sulfate concentration (8,730 mg/l), conditions 2 through 9 showed significant sulfate removal, ranging from 78.5% to 99.8%.

Conditions 3 through 9 all met the target concentration for sulfate, with four conditions less than 100 mg/l. Therefore, conditions 3 through 9 would be acceptable process conditions for sulfate removal; however, the most cost-effective condition still needs to be determined.

The experimental conditions and resulting sulfate concentrations were used to predict the SX-44:sulfate ratios and residence times required to achieve a given sulfate concentration. At a 120-minute residence time, for example, the predictions indicate a sulfate concentration of 500 mg/L at a ratio of 0.9. Increasing the residence time (to less than or equal to 135 minutes) or the ratio from this process condition should produce a sulfate concentration less than 500 mg/L. Alternately, at a residence time of 60 minutes, predicts a sulfate concentration of 500 mg/L at a ratio of 1.5. These points are the *optimistic* case because they are the lowest residence times and ratios that intersect the 500 mg/L sulfate concentration band. Alternately, choosing the midpoint of the 400 to 500 mg/L band would predict a slightly higher residence time and/or ratio.

A balance exists between lowering residence time (which translates into smaller treatment tanks and lower capital costs) and increasing SX-44 dosage (which translates into higher operating costs due to increased reagent cost). For the long-term treatment scenario envisioned for the Berkeley Pit, it appears that capital costs could be justifiably increased if it translated into significantly lower operating costs. Therefore, based on the results from Experiment 1, it appears that an optimum treatment condition would be a residence time of 120 minutes and an SX-44:sulfate weight ratio of approximately 0.9.

5.1.2 Metals Removal

Since the primary focus of this experiment was sulfate removal, residence times and SX-44:sulfate ratios were chosen solely for sulfate removal and not metals removal. Because

samples for metals analysis were not taken after Step 2, it is uncertain whether SX-44 addition and/or increased residence time at high pH (Step 3) increased metals removal beyond what would be expected with standard metal hydroxide precipitation (Step 2).

Nonetheless, all metals analyzed showed significant removal compared to their untreated levels, ranging from 99.6% to 100% (Table 5-2). Cadmium, manganese, nickel, and zinc met the target concentrations at all experimental conditions. One result for iron (0.31 mg/L) exceeded the target concentration of 0.30 mg/L. Where copper was detected, results ranged from 0.01 to 0.05 mg/L compared to the target concentration of 0.01 mg/L. None of the metals analysis indicated any trends related to the SX-44:sulfate ratios and residence times.

Based upon Hydrometrics' knowledge of the Walhalla™ Process and experience with metal hydroxide precipitation, these metals concentrations are lower than what would normally be expected at pH 11.5. Dissolved metals were probably removed to some degree along with sulfate during ettringite precipitation.

5.2 Experiment 2

Initially, Experiment 2 yielded unrepresentative and highly variable sulfate results. After discussions with Energy Laboratories, it was determined the samples were precipitating over time, thereby, altering the sulfate results. A *second* Experiment 2 (10/14/98) was repeated for sulfate analysis only, with samples preserved with hydrochloric acid. Dissolved metals results from the *first* Experiment 2 (9/10/98) are considered to be reliable and accurate and, therefore, are used in the metals removal discussions.

5.2.1 Sulfate Removal

After Experiment 1, it was determined the target sulfate concentration of 500 mg/L could easily be met. Based on these results and the contour plot generated from Experiment 1 data, SX-

44:sulfate ratios were modified from 1.0 to 2.1 to 0.8 to 1.4 to determine a more localized range of sulfate results. It was hoped these results would aid in determining a cost-effective sulfate removal process design.

To obtain a more accurate quantity of SX-44 needed for each condition, Energy Laboratories performed the sulfate analysis prior to Step 3 of Experiment 2. Since Energy Laboratories determined the intermediate sulfate concentrations, the SX-44:sulfate weight ratios did not need to be adjusted to account for *approximate* versus *actual* sulfate concentrations as in Experiment 1.

Residence times were also adjusted for Experiment 2 based on results obtained in Experiment 1. As mentioned in Section 5.1, sulfate results did not change from 105-minute to 180-minute residence times. Therefore, 90- and 120-minute residence times were chosen to determine whether sulfate removal efficiency would vary between the shorter times. For the 30-minute residence time in Experiment 1, sulfate results exceeded the target concentration at all but the highest SX-44:sulfate ratio condition (Table 5-1). It would probably not be cost-effective to use the highest SX-44:sulfate ratio needed to reach target concentrations at a 30-minute residence time. Therefore, to keep the SX-44:sulfate ratio lower, the lowest residence time was increased to 60 minutes for Experiment 2.

As in Experiment 1, sulfate concentrations decreased significantly as SX-44:sulfate ratios increased for all conditions (Table 5-3). Sulfate concentrations also decreased as residence time increased from 60 to 90 minutes. However, there was no direct correlation between residence time and sulfate removal in this experiment, at least at long residence times. The longest residence time (120 minutes) produced sulfate concentrations at two conditions that were greater than those at all 90-minute residence time conditions (Table 5-3). Again, this indicated the reaction was essentially finished at 90 minutes. Furthermore, the highest sulfate concentration for the 90-minute residence

time (431 mg/L) was lower than the lowest sulfate concentration for the 60-minute residence time (591 mg/L). Discussions with Energy Laboratories concerning Conditions 4 through 6 (90-minute residence time) sulfate results and the higher-than-expected sulfate result from Condition 7 (120-minute residence time) confirmed there were no issues with laboratory procedures; it is unknown why the data deviated from what was expected. With the exception of Conditions 4 through 7, the other sulfate results appeared to follow the same trends as in Experiment 1. As expected, Experiment 1 sulfate results were comparatively better than those in Experiment 2 due to the higher quantities of SX-44 added in Experiment 1. Therefore, only four conditions were less than the target concentration of 500 mg/L in Experiment 2 compared to seven conditions in Experiment 1. Compared to the untreated sulfate concentration (8,730 mg/L), all conditions showed sulfate removal ranging from 86% to 99%.

The experimental conditions and sulfate removal results from this experiment were used to predict the SX-44:sulfate ratios and residence times to obtain a sulfate concentration of 500 mg/L. For a 120-minute residence time, the plot predicts a sulfate concentration of 500 mg/L can be met at a ratio of 1.2. Alternately, with a residence time of 90 minutes, the plot predicts a sulfate concentration of 500 mg/L at a ratio of 0.85. Compared to the contour plot from Experiment 1, this plot predicts more cost-effective results at 90-minute residence times but poorer results beyond 115 minutes. Ultimately, a shorter residence time and a higher SX-44 dosage will decrease capital costs and increase operating costs, while a longer residence time and a smaller SX-44 dosage will increase capital costs and decrease operating costs. For long-term treatment of Berkeley Pit water, increased capital costs could probably be justified as a trade-off for lower operating costs. Therefore, based on the results from Experiment 2, it appears optimum treatment conditions would be a residence time of 90 minutes and an SX-44:sulfate weight ratio of 0.85.

5.2.2 Metals Removal

All metals analyzed in Experiment 2 were less than their respective detection limits (Table 5-4), with the exception of two zinc concentrations that were still less than the target concentration. Therefore, all metals met the target concentrations and had approximately 100% removal. The different residence times and SX-44:sulfate ratios in this experiment produced similar metals concentrations. To cost-effectively meet the metals limits, experiments could be performed using shorter residence times and lower SX-44:sulfate ratios. However, since sulfate (the primary focus of these experiments) did not meet the target concentration at shorter residence times and dosages, it is probably not cost-effective to optimize metals removal. Again, dissolved metals were probably removed to some degree along with sulfate during ettringite precipitation.

5.2.3 Data Quality

Samples for this project were collected according to guidelines outlined in the project specific Quality Assurance Project Plan. Data for critical and noncritical analyses was generated by Montana Tech of the University of Montana (Montana Tech) Analytical Laboratory with oversight by the Montana Tech Associate Project Manager.

Confirmatory analysis of critical samples was performed by ACZ Laboratories. As part of the analytical report, ACZ provided quality

assurance/quality control (QA/QC) summaries. (QA/QC summaries are available upon request from Montana Tech.) The data was validated according to the *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* by the Montana Tech Associate Project Manager. All data contained in this report has been appropriately flagged.

Table 5-1. Sulfate Removal—Experiment 1

	Residence Time (min.)	STEP 2	STEP 3	Sulfate Conc. (mg/L) ¹	SX-44:Sulfate Ratio	Sulfate Conc. (mg/L) ¹	Percent Removal ²	Target Concentration (mg/L) ¹
		Approximate (Hydrometrics) Sulfate Conc. (mg/L) ¹	Actual (Energy Labs) SX-44:Sulfate Ratio					
Raw	--	10,500	--	8730	--	--	--	~ 8000
D.I.	--	--	--	<1	--	--	--	--
Rinsate	--	--	--	<1	--	--	--	--
Condition 1	30	~3500	0.8	2250	1.2	1830	55.15	2000/500
Condition 2	30	~3500	1.2	2630	1.6	720	78.5	2000/500
Condition 3	30	~3500	1.6	2630	2.1	230	91.96	2000/500
Condition 4	105	~3500	0.8	2510	1.1	354	87.64	2000/500
Condition 5	105	~3500	1.2	2580	1.6	15	99.42	2000/500
Condition 6	105	2550	1.6	2090	2.0	4	99.80	2000/500
Condition 7	180	3000	0.8	2310	1.0	395	85.39	2000/500
Condition 8	180	3200	1.2	2650	1.4	56	97.93	2000/500
Condition 9	180	3100	1.6	2360	2.1	9	99.62	2000/500

1) Dissolved concentration.

2) Removal based SO₄ concentration following lime addition.

Table 5-2. Metals Removal—Experiment 1

	Residence Time (min.)	Ratio	Residence Time Ratio		Approximate (Hydrometrics) SX-44:Sulfate				Actual (Energy Labs) SX-44:Sulfate			Dissolved Concentrations (mg/L)		Percent Removal	
			Cd	Cu	Fe	Mn	Ni	Zn	Cd	Cu	Fe	Mn	Ni	Zn	
Raw	--	--	--	2.16	193	972	231	1.2	603	--	--	--	--	--	--
D.I.	--	--	--	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	--	--	--	--	--	--
Rinsate	--	--	--	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	--	--	--	--	--	--
Condition 1	30	0.8	1.2	<0.001	0.02	0.11	<0.01	<0.01	<0.01	99.98	99.99	99.99	100	99.58	100
2	30	1.2	1.6	<0.001	0.02	0.06	<0.01	<0.01	<0.01	99.98	99.99	99.99	100	99.58	100
3	30	1.6	2.1	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	99.98	100	100	100	99.58	100
4	105	0.8	1.1	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	99.98	100	100	100	99.58	100
5	105	1.2	1.6	<0.001	0.02	<0.03	<0.01	<0.01	<0.01	99.98	99.99	100	100	99.58	100
6	105	1.6	2.0	<0.001	0.05	0.31	0.02	<0.01	<0.01	99.98	99.97	99.97	99.99	99.58	100
7	180	0.8	1.0	<0.001	0.02	<0.03	<0.01	<0.01	<0.01	99.98	99.99	100	100	99.58	100
8	180	1.2	1.4	<0.001	0.01	0.09	<0.01	<0.01	0.04	99.98	99.99	99.99	100	99.58	99.99
9	180	1.6	2.1	<0.001	0.02	0.07	<0.01	<0.01	<0.01	99.98	99.99	99.99	100	99.58	100
Target Concentrations (mg/L)				0.05	0.01	0.30	0.05	0.10	0.10						

Table 5-3. Sulfate Removal—Experiment 2

	Residence Time (min.)	STEP 2 Actual (Energy Labs)		STEP 3 Sulfate Conc. (mg/L) ¹	Percent Removal ²	Target Concentration (mg/L) ¹
		Sulfate Conc. (mg/L) ¹	SX-44:Sulfate Ratio			
Raw ³	--	8730	--	--	--	~ 8000
D.I.	--	4	--	--	--	--
Rinsate	--	<1	--	--	--	--
Condition 1	60	2840	0.8	1150	86.83	2000/500
Condition 2	60	2820	1.1	879	89.93	2000/500
Condition 3	60	2800	1.4	591	93.23	2000/500
Condition 4	90	2800	0.8	431	95.06	2000/500
Condition 5	90	2710	1.1	406	98.93	2000/500
Condition 6	90	2680	1.4	93	95.35	2000/500
Condition 7	120	2980	0.8	1220	86.03	2000/500
Condition 8	120	3380	1.1	648	92.58	2000/500
Condition 9	120	3320	1.4	78	99.11	2000/500

1) Dissolved concentration.

2) Removal based on initial concentration of 8730 mg/L.

3) Raw concentration assumed from previous Experiment 1 on August 13, 1998.

Table 5-4. Metals Removal—Experiment 2

	Residence Time (min.)	Approximate (Hydrometrics) SX-44:Sulfate Ratio	Actual ¹ (Energy Labs) SX-44:Sulfate Ratio	Dissolved Concentrations (mg/L)						Percent Removal					
				Cd	Cu	Fe	Mn	Ni	Zn	Cd	Cu	Fe	Mn	Ni	Zn
Raw ¹	--	--	--	2.16	193	972	231	1.2	603	--	--	--	--	--	--
D.I.	--	--	--	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	--	--	--	--	--	--
Rinsate	--	--	--	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	--	--	--	--	--	--
Run 1	60	0.8	1.2	<0.001	<0.01	<0.03	<0.01	<0.01	0.02	100	100	100	100	100	100
2	60	1.1	1.4	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	100	100	100	100	100	100
3	60	1.4	2.0	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	100	100	100	100	100	100
4	90	0.8	1.0	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	100	100	100	100	100	100
5	90	1.1	1.4	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	100	100	100	100	100	100
6	90	1.4	2.1	<0.001	<0.01	<0.03	<0.01	<0.01	0.02	100	100	100	100	100	100
7	120	0.8	1.2	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	100	100	100	100	100	100
8	120	1.1	1.4	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	100	100	100	100	100	100
9	120	1.4	1.9	<0.001	<0.01	<0.03	<0.01	<0.01	<0.01	100	100	100	100	100	100

Target Concentrations (mg/L)

0.05 0.01 0.30 0.05 0.10 0.10

1) Results for metals obtained from the *first* Experiment 2.

6. Cost Analysis

6.1 Sulfate-Removal System Costs

To estimate costs for a full-scale sulfate-removal system at the Berkeley Pit, the most cost-effective condition (derived from bench-scale testing) is a 90-minute residence time and an SX-44:sulfate weight ratio of 0.85 to meet a target concentration of 500 mg/L. It was assumed lime treatment for metals removal would already be in place at the site; therefore, lime treatment costs were not included in either the capital or operating and maintenance (O&M) costs. All cost estimates are budgetary (i.e., plus or minus 30%) and based on a 2,100 gpm discharge rate.

6.1.1 Capital Costs

Capital costs were solely based on equipment costs and do not include design, construction, installation, permitting, or contingencies. The equipment cost for the Walhalla™ Process at 2100 gpm is estimated to be \$1.2 million (Table 6-1). This is assumed to be a polishing step following a lime precipitation process.

6.1.2 Operating and Maintenance Costs

Bench tests showed 2,000 mg/L or more of sulfate could successfully be removed after lime treatment to reach a target concentration of 500 mg/L. The approximate materials cost of SX-44 for removing 2,000 mg/L of sulfate (from an initial concentration of 2,500 mg/L to a final concentration of 500 mg/L) would be \$2.83 per 1,000 gallons of water treated (Table 6-2). This is an annual cost of over \$3 million for reagent alone. Other operating costs would include electricity, spare parts, polymer, carbon dioxide, and operating and maintenance labor. Sludge treatment, handling, and disposal costs are not

included. The operating cost breakdown and assumptions are shown in Table 6-2. It was assumed that one person for operation and maintenance would be required 7 days a week, 24 hours per day.

6.1.3 Net Present Value

The net present value (NPV) of the capital cost and the current O&M costs over 30 years, at a 5% discount rate of return and a 3% inflation rate, is approximately \$89 million (Table 6-3). However, SX-44 reagent in large volumes could possibly be purchased at a discounted rate that would considerably lower the O&M costs. For example, the normal cost for SX-44 is approximately \$0.20 per pound. Purchasing large volumes of SX-44 could potentially lower the cost to \$0.15 per pound, which would produce an annual cost of about \$2.3 million (a savings of \$800,000 per year). The NPV with the lower reagent cost would be \$72 million, a \$17 million savings (19%) over 30 years.

Pilot-scale testing would be required for Hydrometrics to determine more accurate cost estimates. With operating costs quite high due to high reagent costs, a pilot-scale test could potentially determine that a longer residence time (which translates into higher capital costs) and lower dosages of SX-44 (which translates into lower annual operating costs) could also meet the sulfate target concentration. Since the capital equipment cost (approximately \$1.2 million) is a very low percentage of the 30-year NPV (\$89 million), this investigation could definitely lower the projected NPV, even at a slightly higher capital cost.

Table 6-1. Estimated Capital Costs

Equipment	Description	Cost
SX-44 Silo	10,000 ft ³ total, screw feeder	\$367,500
Walhalla™ Tank	90-min. R.T., 200,000 gallon	\$110,000
Tank Mixer		\$36,800
Walhalla™ Clarifier	0.34 gpm/ft ² , 90-foot diameter	\$569,600
Polymer Makedown System		\$73,500
Polymer Metering Pump		\$7,350
CO ₂ Addition System	reduce effluent pH to 8	\$18,400
TOTAL		\$1,183,000

Table 6-2. Estimated Annual Operating Costs

Parameter	Cost	Assumptions
Electricity	\$43,750	\$0.035/kWh
Parts and Materials	\$29,600	Approx. 2.5% of equipment cost
SX-44 Powder	\$3,128,700	\$2.83/1,000 gal for 2,000 ppm sulfate removal (reagent cost=\$0.20/lb.)
Polymer	\$87,500	5 ppm dosage, \$1.15/lb
Carbon Dioxide	\$131,250	Lower pH from 10.5 or 11.5 to approx. 8
Operating Labor	\$219,000	24 hr/day, \$25/hr
Maintenance Labor	\$262,800	24 hr/day, \$30/hr
TOTAL	\$3,902,600	

Table 6-3. Net Present Value Calculations

Inflation Discount	3%	NPV	30 yrs
	5%		\$88,756,503
	Yrs.	Capital and O&M	Nominal Capital and O&M
	0	1998	\$5,085,805
	1	1999	\$3,902,598
	2	2000	\$3,902,598
	3	2001	\$3,902,598
	4	2002	\$3,902,598
	5	2003	\$3,902,598
	6	2004	\$3,902,598
	7	2005	\$3,902,598
	8	2006	\$3,902,598
	9	2007	\$3,902,598
	10	2008	\$3,902,598
	11	2009	\$3,902,598
	12	2010	\$3,902,598
	13	2011	\$3,902,598
	14	2012	\$3,902,598
	15	2013	\$3,902,598
	16	2014	\$3,902,598
	17	2015	\$3,902,598
	18	2016	\$3,902,598
	19	2017	\$3,902,598
	20	2018	\$3,902,598
	21	2019	\$3,902,598
	22	2020	\$3,902,598
	23	2021	\$3,902,598
	24	2022	\$3,902,598
	25	2023	\$3,902,598
	26	2024	\$3,902,598
	27	2025	\$3,902,598
	28	2026	\$3,902,598
	29	2027	\$3,902,598
	30	2028	\$3,902,598

7. Conclusions

Typical sulfate concentrations in Berkeley Pit water are between 8,000 and 10,000 mg/L. The Walhalla™ Process met the sulfate concentration target of 500 mg/L at several process conditions, with results as low as 4 mg/L. Although metals removal was not the primary focus of the project, both experiments performed had successful metals removal of nearly 100% at all conditions.

While residence time is an important factor to consider for a potential full-scale treatment system, SX-44 reagent quantities drive the overall cost of the system. Equipment and annual O&M costs for the most cost-effective condition based on bench-scale tests (90-minute residence time and a SX-44:sulfate weight ratio

of 0.85), were approximately \$1.2 million and \$3.9 million, respectively. Since the operating costs are substantial (mainly SX-44 reagent costs), any opportunity to lower the operating costs would justify increased capital costs. It would be beneficial to determine a residence time, in larger-scale tests, that requires the lowest possible SX-44 dosage to achieve a target concentration of 500 mg/L. Contour plots for Experiments 1 and 2 predicted slightly different results for the optimum residence time to achieve the lowest dosage requirement. Therefore, additional bench-scale and/or pilot-scale tests should be performed to determine the optimum residence time and SX-44 dosage that will produce the lowest net present value for a full-scale sulfate-removal system.

APPENDIX A

Standard Operating Procedure 1

Sample Collection of Initial Water, Filtrate, Effluent, and Eluted Samples for Analysis of Dissolved Metal Concentrations Using the Inductively Coupled Plasma Spectrometer (ICP).

Procedure:

1. Gently swirl the vessel containing the sample.
2. Using a peristaltic pump with a 0.45 mm filter, collect 250 ml of the sample.
3. Add concentrated high purity nitric acid for dissolved metal samples to a final concentration of 2%.

Sample Collection of Initial Water, Filtrate, Effluent, and Eluted Samples for Analysis of Sulfate Concentrations Using the ICP.

Procedure:

1. Gently swirl the vessel containing the sample.
2. Using a peristaltic pump with a 0.45 mm filter, collect 250 ml of the sample.