MWTP-107

FINAL REPORT—BERKELEY PIT INNOVATIVE TECHNOLOGIES PROJECT, PHASE II: INTERNATIONAL HYDRONICS DEMONSTRATION

MINE WASTE TECHNOLOGY PROGRAM ACTIVITY IV, PROJECT 7

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Prepared for:

U.S. Environmental Protection Agency 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 June 1998

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June 1998

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Foreword

Today, industries are 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 characterize environmental problems, develop effective solutions, and measure their impact.

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 (WETO) operating contractor, MSE Technology Applications, Inc. (MSE), and Montana Tech of The University of Montana (Montana Tech) 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 objective of this demonstration was to remediate Berkeley Pit water to the extent that it could be safely used for agricultural applications, to demonstrate the suitability of the technology in allowing continuous on-line treatment that could be scaled up to match present inflows into the Berkeley Pit, and to evaluate the possible recovery of the economic minerals in the compacted precipitate.

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

Executive Summary

The primary reason for this demonstration was the remediation of Berkeley Pit water to the extent that it could be safely used for agricultural application or discharged into local streams. Other goals were to demonstrate the suitability of the technology to a continuous on-line treatment that could be scaled up to match present inflows into the Berkeley Pit, to evaluate the possible recovery of the economic minerals in the compacted precipitate, and to determine the amount of zeolites produced per volume of Berkeley Pit water.

All of the target heavy metal cations, with the exception of manganese (Mn), were effectively removed from solution down to anticipated levels during the primary (pH 8+) precipitations. A series of seven precipitations done off-site performed identically to those described herein (with the exception of temperature) in 0.5 to 2.0-liter (L) batches had average residual Mn in the filtrate of 2.47 parts per million (ppm). It is presumed that during the demonstration at Montana Tech of the University of Montana (Montana Tech), the lower temperatures during the precipitation chemistry may have affected reaction rates, resulting in Mn levels being somewhat higher than anticipated.

The amorphous zeolites were produced in the manner and quantity anticipated. Based on the weight of silica added, the resultant products have silica content of 57.6 wt % to 66.6 wt %. This is slightly higher than the predicted 50+ % due to a lower iron (Fe) concentration (700-800 ppm) in the Pit water than the 1,000 ppm on which the mole/ratio addition was predicated. No attempt was made to alter the silica additions based on the lower Fe content; therefore, the mole/ratio of silica to metal oxides is slightly higher than the 3-4 of practice.

The copper (Cu) recovery circuit proceeded as expected, with the exception of higher than anticipated Fe levels in the filtrates from the pH 4+ precipitations. This resulted in higher than normal levels of Fe in the Cu concentrates. The Mn levels in the concentrates were acceptably low. The zinc (Zn) level found on the resin, which is an iminodiacetate chelating resin of the macroreticular type, is acceptable. The pH of the 4+ precipitation needs to be more carefully controlled. As it approaches 5, more Cu begins to be lost. Some trade-off of Fe removal (less than 1 ppm) and Cu recovery (5%-7% loss) needs to be made. Since levels of 2-ppm Fe in the resulting filtrate of low pH precipitations has been achieved, it is expected that temperature and reaction kinetics may have affected results achieved here.

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1. Introduction

The process described herein was conceived and developed by International Hydronics Corporation (IHC) and is intended for Mine Waste Technology Program (MWTP)/Berkeley Pit Innovative Technologies (BPIT) information only and is otherwise proprietary to IHC. The activities carried out at Montana Tech of the University of Montana (Montana Tech) were a demonstration of IHC's Zeolite Production Technology. The technology was used to remediate water from the Berkeley Pit, located in Butte, Montana.

The Berkeley Pit, an inactive open-pit copper mine located in Butte, Montana, has been filling with water since the early 1980s. To date, over 27 billion gallons of water are contained within the Pit, creating a lake over 800 feet deep. According to the latest modeling efforts, the gradient of the ground water flow will reverse directions by the year 2021, thus allowing the contaminated water to disperse out of the Berkeley Pit. At that time, the water will require treatment to prevent any further contamination of adjacent aquifers.

The BPIT Project is managed by Montana Tech through a subcontract with MSE Technology Applications, Inc. (MSE), which implements the MWTP. The purpose of the BPIT Project is to provide a test bed for innovative and/or high risk technologies for remediating Berkeley Pit water. The Project is focused on bench-scale testing of remediation technologies to help assist in defining alternative remediation strategies for the U.S. Environmental Protection Agency's (EPA) future cleanup objectives for the Berkeley Pit waters.

The demonstration on the Montana Tech campus followed a Quality Assurance Project Plan (QAPP) prepared by Montana Tech and IHC and approved by the EPA's National Risk Management Research Laboratory (NRMRL).

2. Process Description

Remediation of Berkeley Pit water is conducted in two major lines: 1) a heavy metals recovery circuit, whereby metals are removed on a total or selective basis, and 2) a sulfate (SO_4) removal/desalination circuit that involves the production of insoluble calcium sulfate ($CaSO_4$) and conversion of resultant sodium hydroxide (NaOH) to sodium carbonate (Na_2CO_3) for recycle within the treatment circuits (Fig. 2-1).

All of the heavy metals in the Berkeley Pit water are essentially removed from solution by the addition of soluble silica in the form of 40° or 41° Baume sodium silicate solution. Baume is a means of expressing solution concentration and is used for sodium silicate solution strengths. For example, the sodium silicate designated as 41° has a specific gravity of 1.38 g/cc and a mole ratio of 3.22 SiO₂:Na₂O. Sodium silicate is represented by the formula Na₂O@SiO₂. The solution concentration referred to has a ratio of 3.22 SiO₂:Na₂O. The hydrated sodium oxide neutralizes some acidity and the silica undergoes some polymerization at low pH, conducive to the formation of metal silicate complexes. The pH is then raised to a nominal level of 8.0 with NaOH, and the resulting gel is filtered. All of the five major heavy metal cations copper (Cu), iron (Fe), manganese (Mn), aluminum (Al), and zinc (Zn) are removed by being contained in this gel. Trace level metals are also removed.

The resultant zeolite gel is filtered a second time, washed, and further processed to produce the desired form, either amorphous or crystalline. The production of a specific physical or morphological form, such as pellets or controlled pore size, requires auxiliary equipment not specified here.

During actual full-scale operation, the sodium silicate solution can be produced on site from recovered Na₂CO₃ and sand procured from a local

source. Heat from the kiln could be used in the various aging/drying steps, and carbon dioxide (CO_2) from combustion could be used to generate Na₂CO₃ in the desalination circuit.

Copper is recovered by splitting the zeolite precipitation process into two stages and recovering the Cu through a combination of ion exchange (IX) and electrolytic deposition. Iron is oxidated and removed in the first precipitation to below 1 part per million (ppm) with some Al, depending on the final pH, which should be 4-4.5. The filtrate from this stage is fed to the IX circuit which effectively removes Cu while ignoring the other cations, even at high flow rates. This requires operation of the columns to exhaustion. The IX units are regenerated, resulting in a highly concentrated Cu sulfate solution that is then passed through an electrolysis cell using Cu cathodes and lead anodes resulting in a barren electrolyte solution and cathodic Cu. The barren electrolyte is returned for reuse in the IX resin regeneration cycle (Fig. 2-2). The effluent from the IX unit is sent to the second zeolite precipitation process conducted at the prescribed pH of 8 or slightly above. The process is the same as the first step; metals removed are Zn, (Mn), cadmium (Cd), and magnesium (Mg).

The effluent from the zeolite circuit enters the desalination circuit where residual calcium (Ca), Mg, and SO₄ are removed. Some Ca and Mg are removed in the zeolite precipitation by attachment to exchange positions on the zeolite. The effluent water from the zeolite circuit precipitates gypsum crystals in a spiractor, a large conical vessel with tangential inlet. For gypsum precipitation, the lime solution is introduced at high velocity to promote and maintain the required spiraling motion. This keeps the film surface clean, promoting rapid crystal growth.



Figure 2-1. Flow diagram of split (2 stage) precipitation circuit.



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Figure 2-2. Flow diagram of ion exchange regeneration cycle.

The crystals are hydraulically classified; grown crystals are removed from the lower section of the cone, separated by filtration, washed, and dried for subsequent usage. The SO_4 is reduced to 1,500 ppm in this stage.

Iron concentration in the Cu concentrate may adversely affect the electrolytic recovery or quality of the Cu. It is essential to remove all of the ferrous Fe in the initial (pH 4+) precipitation. For this reason, a preoxidation step may be necessary to reduce the Fe to as low a level as possible during the initial precipitation. Alternatively, a pre-ion exchange or guard column may be employed to pick up ferrous Fe escaping the precipitation. Neither of these alternatives, if necessary, would result in significant engineering or operating cost considerations.

The filter cakes produced from the precipitated gels are dried at elevated temperatures, typically 100° C to 200° C, then decrepitated with a small volume of water and redried. The resultant products are zeolites believed to be amorphous and noncrystalline in nature. Prior work has indicated an IX capacity of approximately 1 milliequivalent per gram (meq/gm). The zeolites have been shown to remove strontium from the solution from a concentration of 10 ppm to below 0.100 ppm, under equilibrium condition.

Following metals recovery, the resultant solution is approximately 1% sodium sulfate at a pH of 7-8. This solution may be subjected to concentration via membrane or evaporative means. It is proposed that SO_4 be removed through the addition of hydrated calcium oxide in the form of a thin slurry. The resultant slowly forming CaSO₄ precipitate is fed to a spiractor where formation of crystalline CaSO₄ is induced. Following this stage, excess Ca associated with 1,500-ppm soluble CaSO₄ is removed to levels of approximately 10 ppm through the stoichiometric addition of Na₂CO₃. This results is approximately 1% NaOH containing approximately 1,000-ppm SO_4 .

The NaOH produced in the above manner is carbonated using combustion gas or reaction gas from the sodium silicate kiln, resulting in some recycle of CO_2 and the production of a 1% solution of Na_2CO_3 . This may be concentrated by either membrane or evaporative means for use in the on-site production of sodium silicate.

The removal of Ca^{++} associated with soluble $CaSO_4$ is accomplished by adding soda to precipitate calcium carbonate ($CaCO_3$) in the second spiractor, and precipitate is treated as in the $CaSO_4$ step.

At this point, the process water essentially has a $CaSO_3$ concentration of 14-35 ppm and a SO_4 concentration of 1,500 ppm. Sodium is present at high levels (3,700 ppm) from the addition of caustic soda, Na_2CO_3 , and sodium silicate during the preceding treatment steps. Iron, Mn, Al, Zn, and Cu have been reduced to below 1 ppm. The trace metals that may be present, such as arsenic (As) and Cd, have been reduced to below potable levels.

The high sodium solution is carbonated using combustion gas from the SiO₂ kiln and concentrated by a brine concentration process such as reverse osmosis (RO), similar to large-scale desalination plants. This will produce a concentrate of Na₂CO₃ containing residual sodium sulfate. A portion is used in the soda softening stage of the desalination circuit. The remainder will require further evaporation/crystallization for use in the production of sodium silicate. The permeate is potable quality water consisting of 500-ppm total dissolved solids (TDS) or less and constituting 85%-90% of the final water volume.

The Na₂CO₃ concentration step requires further evaluation. Desalination/brine concentration must

be performed at this stage of the treatment process either by RO, evaporative, or some similar desalination process. Membranes capable of operating at elevated pH need to be evaluated for RO process consideration. Concentrate from any desalination process would likely be spray dried for ultimate processing. No waste products of any consideration are generated from any of the elements of this process.

2.1 Statement of Project Objectives

The BPIT demonstration demonstrated that the IHC technology will operate at levels required to produce output waters from the process in accordance with the limits set forth in Table 2.1. Also, the process will generate enough zeolite product for further testing and characterization (approximately 2 pounds).

2.2 Experimental Design

Water from the Berkeley Pit was collected and transported to the BPIT laboratory by the Montana Bureau of Mines and Geology. The water was collected from a depth of 200 feet and stored in a refrigerator at 4E C to help deter changes in the chemical composition of the water.

The basic elements of the process are itemized here, exclusive of analytical verification and exit report generation. The experimental design for treating the collected Berkeley Pit water was as given below.

Contaminant	Current Concentration (ppm)	Post Zeolite Precipitation (ppm)
Al	260	<1.00
As	0.8	<0.8
Cd	2.14	<1.00
Cu	172	<1.00
Fe	1,068	<1.00
Mn	185	1-2
${ m SO}_4$	7,600	7,600
Zn	550	<1.00
pH	2.85 *	. 8

Table 2-1. Table of Elements, Concentrations, and Target Concentrations

*pH is in standard units

Table 2-2. Experimental Design for Treating Collected Berkeley Pit Water

Zeolite Circuit

Single-stage (total) precipitation including filter cake aging and decrepitation	2×5 gallons				
Two-stage precipitation including filter cake aging and decrepitation	1×5 gallons				
Desalination Circ	cuit				
Calcium Sulfate/Lime Softening Demonstration	Simple precipitation if required				
Copper Recovery Option					
IX copper removal and concentration	Concurrent with 2-stage precipitation				

including regeneration cycle

3. Demonstration Details

The demonstration on site at Montana Tech included only the zeolite circuit and the metals recovery circuit (Fig. 3-1). The Pit water was treated in 5-gallon batches to demonstrate the various precipitation steps and the Cu recovery option. Procedures followed the practice employed in process development with the exceptions that large quantities of Pit water were not available during process development, and the temperature of the Pit water provided for demonstration was 3° C to 4° C vs. developmental work conducted at 22° C to 25° C.

3.1 Zeolite Production

The procedure for all precipitations employed initiation of mixing and obtaining stable pH readings. The prescribed batch dose of sodium silicate solution was added during continuous mixing and a reaction time of 30 minutes was allowed to transpire, at which time the pH was measured and recorded. Adjustment to pH 8.0 to 8.5 was then accomplished by the addition of 3-molar (M) NaOH and a reaction time of 30 minutes was allowed to ensue, during which slight additions of caustic were necessary to maintain the required pH. Caustic soda additions were recorded. At the end of the second reaction, the gel was vacuum filtered. This was done serially through a Whitman #541 filter to remove the cake followed by a "polishing" filtration to remove colloidal solids that may have broken through or escaped the initial filtration. A Whitman #42 filter was used for the second filtration. Samples for analysis were filtered through 0.45 Fm filters.

The resultant filter cake was dried in trays at approximately 100° C for 24 hours. During this time it loses over 90% of its weight in the form of water of hydration or entrained moisture. After cooling, the cake was decrepitated through the addition of small volumes of water, and rinsed with two washings of distilled water to remove salts. Normally, at industrial scale, the cake would be rinsed with block water at the time of filtration; however, this was not practical here. Certain cakes that will be identified later were dried at higher temperatures to determine if temperature had an effect on the resultant morphological properties. During decrepitation, the material gases out and fracturing occurs. After filter cake drying, the resultant material exists under some stress and contains small amounts of entrained gas in the form of air or CO_2 .

De-crepitation with water causes fracturing, releasing this small amount of trapped gas. The decrepitated amorphous zeolites are redried at 100° C. Decrepitation and rinse waters had near neutral pH.

Table 3-1 summarizes the precipitations performed, with corresponding data. The Pit water supplied for this work had been stored for one year and was provided at a temperature of 3° C to 4° C.

3.2 Copper Recovery

The Cu recovery option was accomplished by first performing a precipitation at approximately pH 4.5. Silicate was added in the prescribed manner at the same mole/ratio as in the macro (pH 8) precipitation, and the reaction times, pH adjustments, and filtrations were performed in an identical manner. Instead of an amorphous zeolite containing all five of the principal heavy metal cations, the resulting material will be Fe- and Albearing zeolite. The majority of Cu, Mn, and Zn remain in solution at this pH.

The resulting filtrate was passed through the IX column at approximately 0.25 bed volumes per minute (BV/min).



Figure 3-1. Flow diagram of equipment used in Berkeley Pit demo.

The effluent from the first column passes through a second column to catch Cu leakage prior to and during exhaustion. The first column is driven to exhaustion until the Cu concentration of the feed is equal to the Cu concentration of the effluent. This is done to ensure competing cations have been driven off the resin and is evidenced by significant Cu being picked up on the secondary column. Even so, some Zn is retained even after the Cu capacity has been saturated. The reason for this is not well determined, although it may be due to the exchange of Zn on strong acid sites or some exchange on limited carboxylic groups, in which case the Cu in the chelated positions on the resin does not completely exclude Zn because Cu is greater in diameter (roughly 3x that of Cu). In any event, the presence of Zn in the Cu concentrate is of no concern since it can be selectively separated during electrolysis.

The presence of Fe in the pH 4.5 filtrate (feed to IX) is undesirable due to potentially adverse effects on the electrowinning process. For this reason, pH needs to be tightly controlled during this phase. It needs to be high enough to oxidize and remove all the ferrous Fe, yet not proceed so high such that Cu, the next cation to precipitate, is lost. This precipitation step may require preoxidation, or special considerations during IX, as previously mentioned.

During regeneration, the secondary or breakthrough IX bed, already containing Cu, would be put into service and a third, regenerated column would serve as the secondary bed. Thus, in practice, three beds or columns would be used in an alternating fashion.

A total of 7.5 gallons of Pit water in two batches of 5 and 2.5 gallons were prepared for purposes of Cu recovery. Six gallons from the 7.5 gallon batch of Pit water were fed to the IX system in increments of 2.25, 2.25, and 1.5 gallons. After each feed, the primary column was exhausted and therefore regenerated, resulting in three Cu concentrate extracts. The secondary column was also regenerated each time and regenerants combined into one sample for purposes of determining total Cu recovery. This solution would have inordinately high levels of Zn and Mn due to not driving the resin to exhaustion or Cu saturation. In the absence of Cu, the resin will weakly retain other cations in preferential order.

Table 3.2 summarizes the analytical data obtained on the precipitation filtrates and IX circuit solutions.

Sample ID	pHi**	pHf	SiO2 Added (grams)	3M NaOH Added (cc)	Berkeley Pit Water Used	Zeolite Produced (grams)
Zeolite#1	2.8	8.62	132	250	5 gal.	229
Zeolite#2	2.1	8.77	132	300	5 gal.	225
Zeolite#3A	2.5	4.52	67	100		101
Zeolite#3B*	2.55	9.00	54	130	4.5 gal.	81
Zeolite#4	2.7	9.1	66	170	2.5 gal.	107 ***
Zeolite#5	2.77	4.73	34	50	2.5 gal.	51 ***

 Table 3.1.
 Zeolite Production

* Precipitation 3B is the ion-exchange effluent from precipitation 3A filtrate feed to IX. The pH during ion exchange drops from 4 to approximately 2.5 due to release of H^+ ions from some cation exchange (Zn) on carboxylic groups or strong acid sites on the resin.

** Initial pH measurements (pHi) were made at 3-7° C.

*** These filter cakes were cured at approximately 200° C, all others were at 100° C.

Sample ID	Al ppm	As ppm	Cd ppm	Cu ppm	Fe ppm	Mn ppm	Zn ppm	рН
IH 1-1	< 0.3	< 0.4	0.03	< 0.1	< 0.1	26.1	0.9	6.2
IH 1-2	< 0.3	<0.4	0.04	< 0.1	< 0.1	24.8	0.7	6.3
IH 1-3	< 0.3	<0.4	0.05	< 0.1	< 0.1	50.9	0.9	6.4
IH BP-1	285	<2	2.34	180	798	221	594	2.6
IH 2-1	< 0.3	<0.4	0.03	< 0.1	0.1	11.8	0.2	6.6
IH 2-2	< 0.3	<0.4	< 0.03	< 0.1	0.1	22.7	0.3	6.6
IH 2-3	< 0.3	<0.4	< 0.03	< 0.1	0.1	11.6	0.2	6.4
IH BP-2	278	<0.8	2.18	180	764	211	581	2.6
IH 3-1	58.4	<0.8	1.71	162	248	194	567	4.0
IH 3-2	54.4	<0.8	1.63	0.2	245	185	514	2.7
IH 3-3*	< 0.03	< 0.04	0.008	0.02	0.03	7.31	0.15	7.3
IH BP-3	296	<1	2.44	200	940	229	593	2.9
IH R-1**	81	N/A	4.0	9960	287	20	713	N/A
IH R-2**	76	N/A	4.4	11600	358	27	905	N/A
IH R-3**	69	N/A	4.3	10200	598	15	894	N/A
IH R-4***				1790				
IH 4	< 0.03		0.02	0.04	0.03	5.22	0.19	
IH 5A	44.2		2.14	155	257	186	610	

Table 3.2. Analytical Results

* Sample IH 3-2 is the ion-exchange effluent derived from IX feed of IH 3-1 and which was precipitated to produce the filtrate IH

** R-1 and R-2 are Cu concentrates, each derived from feed of 2.25 gallons of filtrates of 3A and 5A (IH-3-1 and IH-5) and producing, during regeneration, the indicated volumes. R-3 was derived from a feed of 1.5 gallons.

***R-4 was produced from compositing the regenerants of the secondary bed during the 3 runs.

4. Summary and Conclusions

4.1 Summary

All of the target heavy metal cations, with the exception of Mn, were effectively removed from solution down to anticipated levels during the primary (pH 8+) precipitations (#1,#2, and 4). Past work has achieved levels of Mn down to below 1 ppm. A series of seven precipitations performed identically (with the exception of temperature) in 0.5- to 2.0-L batches had average residual Mn in the filtrate of 2.47 ppm. The lowest concentration obtained was approximately 5.0 ppm, close to the target level of 2-3 ppm. It is shown from precipitations #1, 2, and 4 that as the reaction pH is taken incrementally higher, the resultant filtrate Mn concentration drops. It is presumed that during this demonstration, the lower temperatures during the precipitation chemistry may have affected reaction rates, resulting in Mn levels somewhat higher than anticipated. Temperature of the water during demonstration was 4° C; temperature used during process development was 20° C to 22° C.

The amorphous zeolites were produced in the manner and quantity anticipated. Based on the weight of silica added as shown in Table 4.1, the resultant products have a silica content of 57.6 wt % to 66.6 wt %. This is slightly higher than the predicted 50+ % due to lower Fe concentration (700-800 ppm) in the Pit water than the 1,000 ppm on which the mole/ratio addition was predicated. No attempt was made to alter the silica additions based on the lower Fe content; therefore, the mole/ratio of silica to metal oxides is slightly higher than the 3-4 of practice. The silica concentration was not adjusted because the silica solutions were made up prior to the demonstration based on the Fe content in the water used for process development.

The Cu recovery circuit proceeded as expected, with the exception of higher than anticipated Fe

levels in the filtrates from the pH 4+ precipitations (3A and 5A). This resulted in higher than normal levels of Fe in the Cu concentrates. What concentration of Fe can be tolerated in the electrowinning process is not known. The Mn levels in the concentrates were acceptably low. Zn picked up on the resin from the phenomena discussed previously is acceptable. It appears from these results and past practice that Cu will begin to be removed at lower pH levels than normal, probably from coprecipitation with Fe and/or the presence of polymerized silica. The pH of the 4+ precipitation needs to be more carefully controlled. As it approaches 5, more Cu begins to be lost. Some trade-off of Fe removal (less than 1 ppm) and Cu recovery (5%-7% loss) needs to be made. Since levels of 2-ppm Fe in the resulting filtrate of low pH precipitations has been achieved, it is expected that temperature and reaction kinetics may have affected results achieved here.

4.2 Third Party Review

The removal of heavy metals is readily accomplished using soluble silica and sodium hydroxide and is achieved at pH levels below that of using lime or caustic soda alone. The end products have useful properties such as IX media or adsorbents for other applications. The products are fairly resistant to mildly acidic conditions, losing from 0.012% Fe to 2.9% Mn of their heavy metal constituents at a pH of approximately 4.0. Little is known of the morphological characteristics of the materials produced. It is expected that crystalline structure may be promoted by slight adjustment of the reaction chemistry, such as increasing the mole/ratio of silica, or by experimental adjustment of curing temperature or rate. Crystalline structure may diminish friability and increase acid resistance; however, some desirable characteristics such as porosity or IX capacity may be adversely affected.

It is known that, of the heavy metals involved here, Fe and Al are more readily incorporated into a silica complex than divalent cations such as Cu or Zn. The zeolite produced at the pH 4 precipitation appears to be less friable than those produced at the higher pH. Therefore, it may prove to be superior in certain respects. Should this be the case, the low pH precipitation should receive more focus, particularly since it allows for the recovery of higher grade Cu.

More attention should be devoted to the recovery of Zn since it is the predominant cation after Fe and is present at more than three times the level of Cu and has a favorable market price. After Cu recovery, Zn needs to be separated only from Mn and could conceivably be quantitatively recovered. This would entail increased capital costs and operating costs if IX is employed.

The only significant concern from a performance basis on the work conducted during this demonstration was the poor Fe removal in the pH 4 precipitations. Whether this was a result of reaction kinetics from the low temperature or poor pH control, it can be overcome by incorporation of a preoxidation step, more closely controlled pH adjustment, or increased reaction time. The pH of the final filtrate in this step should be above 4.3.

4.3 Economic Considerations

Substantial consideration has been given to the economic feasibility in treating Berkeley Pit

water at the designated rate of 2,100 gallons per minute (gpm). The significant chemical feed costs are for on-site production of sodium silicate used in the zeolite circuit, and calcium oxide in the SO_4 removal stage. NaOH for pH control is recovered from the resulting 1% NaOH stream after CaSO₄ precipitation. The bulk of this stream is converted to Na₂CO₃ for silica fusion.

Concentration of the Na_2CO_3 stream is proposed to be accomplished by evaporation/condensation and crystallization rather than membrane technology.

Power costs above pumping, mixing, and filtration are associated with cake drying and silicate production. The power for both of these are accounted for under silicate unit production costs in the form of natural gas to operate the kiln.

The equipment for conducting almost all of these unit processes is common and readily available—pumping; dosing; mixing; vacuum or plate and frame filtration; tankage; conveying; etc. None of these activities requires extraordinary or excessively high capital cost equipment, nor are the operating labor costs associated with them excessive.

Installation labor costs have not been evaluated.

Table 4.1 suggests realistic capital equipment, chemical feed, and power operating costs, and are based on an operating rate of 2,100 gpm, 24-hr day.

Table 4.1. Economics

Chemical Feed Cos	ts:	
	Sodium Silicate-40° Be @ \$0.02/lb @ 0.21 lb/gal	\$12,700.00
	Calcium Oxide @ \$95.00/ton, FOB Works	\$5,500.00
	Total/Day	\$18,200.00
Capital Equipment	Costs:	
	Resin	\$1.35 MM
	Zeolite Precipitation Line	\$3.0 MM
	Filtration	\$4.0 MM
	Sulfate Precipitation and Filtration	\$2.0 MM
	Carbonate Concentration/Crystallization 2-MM gal units x 2, installed	\$25.0 MM
	Engineering	\$1.8 MM
	Installation and Site Work	\$3.4 MM
	Total	\$80.55 MM
Labor and Power O	perating Costs: Yearly based on 365 days	
	Labor: 15 men/shift x 3 shifts x \$25,000.00/yr. x 1.25	\$1.41 MM
	Power: 2,000 installed HP=1,500 Kw @ \$0.07/KwHR	\$0.92 MM
	Resin Replacement - 2%/yr	\$0.03 MM
	Total	\$2.36 MM
Anticipated Market	s: 24-hr. Day Basis	
-	Zeolite: 300,000 lb/day @ \$0.04/lb	\$12,000.00
	Electrolytic Copper: 180 ppm x 90% R @ 0.78/lb	\$3,529.00

Zeolite: 300,000 lb/day @ \$0.04/lb	\$12,000.00
Electrolytic Copper: 180 ppm x 90% R @ 0.78/lb	\$3,529.00
Total/Day	\$15,529.00
Total/Year	\$5,668,085.00

Assume no market for gypsum and 80% recovery of zinc @ \$0.058/lb	
Zinc @ 550 ppm @ # 80 % Rec. @ \$0.058/lb	\$8,000.00
Zeolite	. \$12,000.00
Copper	\$3,529.00
Total/day	. \$23,529.00
Total/Yr	8,588,085.00