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Advances in biotreatment of acid mine drainage and biorecovery of metals: 1. Metal precipitation for recovery and recycle *

Henry H. Tabak[1]*, Richard Scharp[1], John Burckle[1], Fred K. Kawahara[1] & Rakesh Govind[2]
[1]*U.S. Environmental Protection Agency, ORD, NRMRL, Cincinnati, OH 45268, USA;* [2]*University of Cincinnati, Department of Chemical Engineering, Cincinnati, OH 45221, USA (*author for correspondence: e-mail: tabak.henry@epa.gov)*

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Abstract

Acid mine drainage (AMD), an acidic metal-bearing wastewater, poses a severe pollution problem attributed to post mining activities. The metals usually encountered in AMD and considered of concern for risk assessment are arsenic, cadmium, iron, lead, manganese, zinc, copper and sulfate. The pollution generated by abandoned mining activities in the area of Butte, Montana has resulted in the designation of the Silver Bow Creek–Butte Area as the largest Superfund (National Priorities List) site in the U.S. This paper reports the results of bench-scale studies conducted to develop a resource recovery based remediation process for the clean up of the Berkeley Pit. The process utilizes selective, sequential precipitation (SSP) of metals as hydroxides and sulfides, such as copper, zinc, aluminum, iron and manganese, from the Berkeley Pit AMD for their removal from the water in a form suitable for additional processing into marketable precipitates and pigments. The metal biorecovery and recycle process is based on complete separation of the biological sulfate reduction step and the metal precipitation step. Hydrogen sulfide produced in the SRB bioreactor systems is used in the precipitation step to form insoluble metal sulfides. The average metal recoveries using the SSP process were as follows: aluminum (as hydroxide) 99.8%, cadmium (as sulfide) 99.7%, cobalt (as sulfide) 99.1% copper (as sulfide) 99.8%, ferrous iron (sulfide) 97.1%, manganese (as sulfide) 87.4%, nickel (as sulfide) 47.8%, and zinc (as sulfide) 100%. The average precipitate purity for metals, copper sulfide, ferric hydroxide, zinc sulfide, aluminum hydroxide and manganese sulfide were: 92.4, 81.5, 97.8, 95.6 , 92.1 and 75.0%, respectively. The final produced water contained only calcium and magnesium and both sulfate and sulfide concentrations were below usable water limits. Water quality of this agriculturally usable water met the EPA's gold standard criterion.

Introduction and background

Acid mine drainage (AMD) from abandoned mines and from acid mine water pits is a major environmental issue in the United States and other countries wherever mining has been practiced on a large scale. AMD causes billions of dollars of damage to natural vegetation, silvaculture, rivers, watersheds, natural habitats and aquatic life with acid water flow rate from a few gallons per minute to several thousand gallons per minute during the spring season in the U.S. One of the largest locations of acid mine water in U.S is the Berkeley Pit located in Butte, Montana. The Pit contains over 25 billion gallons of acid mine water and encompasses 1.06 square miles. The accumulation of water into the Pit is approximately 3 million gallons a day, resulting in a rise of about 10 feet every nine months. Based on this data, it is estimated that the water will overflow sometimes between 2005 and 2015. This drainage typically contains dissolved solids of high concentrations and more than 3 g/l sulfate. Low

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pH and presence of heavy metals makes AMD treatment a major concern because of possible deleterious effects of the effluent on the environment.

The conventional AMD treatment is to use a base (either lime or sodium hydroxide) to elevate the pH and precipitate the metals from solution. Bhattacharya et al. (1981) studied arsenic and heavy metal removal from non-ferrous smelters by controlled precipitation with sodium sulfide and lime and used lower solubilities of metal sulfides to improve metal waste treatment. The pioneering work in the area of heavy metals by Bhattacharya et al. (1979, 1981) has shown that sulfide was significantly superior to lime or sodium hydroxide achieving 98% and better removals of cadmium, copper, iron, mercury, selenium and zinc in AMD. The treatments using lime present some serious limitations of application and effectiveness. They usually result in production of a mixture of unstable metal hydroxides which also lead to a greater disposal expense.

In recent years, the use of sulfate reducing bacteria (SRB) to reduce sulfate and precipitate metals in AMD has been proposed as an alternative to hydroxide precipitation. Maree & Strydom (1987) reported on biological sulfate removal from industrial effluents in an upflow packed bed reactor. They were able to remove heavy metals and sulfate ions using SRB with molasses as the feed material. After 90 days, they achieved an average sulfate removal of 89% and reduced the metal concentration of calcium, chromium, cadmium, lead, manganese, nickel, zinc and iron by more than 50% with a pH range from 5.0 initially to 8.1 for the effluent. Maree et al. (1987) in another study used SRB in a sludge blanket reactor for removal of heavy metal cyanide complexes and to treat sulfate from gold mine effluents. Dvorak et al. (1992) used the SRB to treat contaminated acidic water and for removal of metals. Spent mushroom compost consisting of manure, hay, straw, corn cobs and wood chips conditioned with gypsum and limestone, provided nutrients for SRB. Their results showed that iron, nickel and cadmium were removed as monosulfides, whereas aluminum and manganese were retained as hydroxide and carbonate respectively. DuPreez et al. (1982) reported on biological removal of sulfate from industrial effluents using producer gas as energy source.

Other research on the treatment of metal contaminated acid mine water using SRB has been reported in the literature that includes the studies on: comparative bioenergetics of sulfate reduction (Liu & Peck 1981): optimization of sulfur production in biological sulfide removing reactor and kinetic parameters of mixed culture oxidizing sulfide and sulfur with oxygen (Buisman et al. 1989, 1991); microbial sulfate reduction in acidic strip mine lakes (Gyure et al. 1990) and acid mine treatment (Dispande et al. 1991). Studies were published on the removal of nickel from mine waters using bacterial sulfate reduction (Hammock et al. 1993); on bench-scale treatment of acid mine water by SRB (Christensen et al. 1996); on biological sulfate reduction using gas-lift reactors fed with hydrogen and carbon dioxide or using synthetic gas (Van Houten et al. 1994, 1996); on biological process for sulfate and metals abatement (Herrera et al. 1997); and on biological sulfate removal and meal recovery from metallurgical operations (De Vegt et al. 1997, 1998).

Recently studies have been reported on: anaerobic treatment of sulfate-rich wastewaters (Hulshoff Pol et al. 1998); prevention of acid mine drainage by SRB by addition of organic substrates to mine waste piles (Kim et al. 1999); production of hydrogen sulfide by SRB in a two-column gas liquid reactor for the purification of metal containing effluents (Battaglia-Brunet 2000); biological treatment of sulfate rich wastewaters (Lens et al. 2000) and treatment by SRB of Chessy acid mine drainage and metal recovery (Foucher et al. 2001)

A major problem associated with the use of SRB for precipitating metal sulfides in the same reactor systems where SRB mediated sulfate reduction activity occurs is metal toxicity to active SRB cultures, as illustrated by the studies of Poulson et al. (1997), Chen et al. (2000) and Utgikar et al. (2000, 2001, 2002, 2003). The other problem associated with the use of SRB biomass in the metal precipitation reactors is that the precipitated metals are lost with the wasted microbiota, although the metals can be recovered from metal sulfide-containing sludge. Govind et al. (1997) proposed a two-stage process in which the metal precipitation step was separated from the SRB bioreactor system The separation of metal precipitation step from the biological sulfate reduction step is illustrated in Figure 1. In this process hydrogen sulfide produced by the SRB in the bioreactor system was used in the precipitation step to form insoluble metal sulfides. In this study, the developed and tested precipitation process was designed to use biogenic hydrogen sulfide gas generated from the wastewater; hence the precipitation process is referred to as a biorecovery process. The data were compared with the predicted values generated from the thermodynamic equilibrium program and kinetic parameters for growth of SRB at different temperatures and pH values were reported. The water treated was a synthetic mixture of similar composition to the Berkeley Pit water. Not only were the metals able to be removed from the biomass, but they were also removed efficiently. While most AMD treatments focus on total removal and land filling of heavy metals, Allen et al. (1999) in their studies on metal recovery and reuse from AMD, demonstrated a process that separates the metals (copper, zinc, iron, manganese and aluminum) thus allowing for metal recovery and reuse. This separation is accomplished by varying the pH of solution and precipitating the metals with hydrogen sulfide gas. EPA reports by Govind et al. (1999) on 'Confirmation of Dynamic Separation Efficiencies and Metal Precipitate Purity' and by Govind et al. (2001) on 'Berkeley Pit Metals Recovery/Precipitation Process' discussed the preliminary studies on both the four stage batch type and the 6 stage continuous metal precipitation, sequential separation and biorecovery process.

Objective

The main objective of this study was to use sulfide and hydroxide precipitation to separate metals from acid mine drainage to achieve high recoveries and metal precipitate purities, while producing a water suitable for discharge to the environment. The specific objectives of this research can be outlined as follows: (1) to develop a two stage process consisting of separate and parallel SRB bioreactor system for sulfate reducing activity in AMD and production of biogenic hydrogen sulfide to be used in the metal precipitation and biorecovery system, (2) to implement the initial four stage batch-type metal precipitation process scheme and experimentally determine the biorecovery and purity of the four metal precipitates, (3) to design a precipitator-clarifier system, based on calculated settling velocities of the various metal precipitates, (4) to operate a continuous flow process consisting of six metal precipitator-settler units; to separate copper (as copper sulfide), zinc (as zinc sulfide), iron (separate precipitates of ferric hydroxide and ferrous sulfide), aluminum (as aluminum hydroxide) and manganese (as manganese sulfide), (5) to determine optimum conditions (i.e., pH, temperature, etc.) for each precipitator-settler unit which maximize the metal precipitate purity and biorecovery, (6) to experimentally determine the biorecovery and purity of each metal precipitate and (7) to produce a usable water (to be used in agriculture for irrigation) that meets the Gold Standard. The acid mine water used in this study was the acidic metal-containing water from the Berkeley Pit, Butte, Montana, USA. Table 1 shows the average metal composition of acid mine drainage (pH = 2.2) from the Berkeley Pit. Metals that could potentially be marketed in sulfide form to the smelters, such as copper, zinc and manganese are present in appreciable concentrations as dissolved sulfates.

Table 1. Dissolved metal concentrations in Berkeley Pit mine water

Compound	Concentration (mg/L)
Al^{3+}	293
Cu^{2+}	223
Mn^{2+}	223
Fe^{2+}	514
Zn^{2+}	630
Cd^{2+}	1.38
Ni^{2+}	2.14
As^{3+}	0.512
Co^{2+}	1.23
SO_4^{2-}	2,400
Cl^{-}	16
Na^{1+}	213

Materials and methods

Metal concentrations

The concentration of metals including Fe^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Mn^{2+}, As^{2+}, Cd^{2+} & Co^{2+}, Pb^{2+}, Ni^{2+} in the acid mine water was analyzed using an ICAP 61E Plasma Emission Spectrometer (Thermo Jarrell Ash Corporation) using EPA Method 6010. The reference for this method is: http://www.epa.gov/epaoswer/hazwaste/test/6_series.htm. Liquid samples were filtered through a 0.22 μm membrane filter (Cole Parmer Company) to remove solids and diluted with 2% nitric acid solution to avoid precipitation of metals due to changes in pH. Dried precipitate samples were redissolved in concentrated nitric acid solution, and then diluted for analysis.

Development of a two stage process separating SRB bioreactor activity from metal precipitation units

A two stage process was developed and thoroughly tested in which metal precipitation using biogenic hydrogen sulfide was completely separated from the

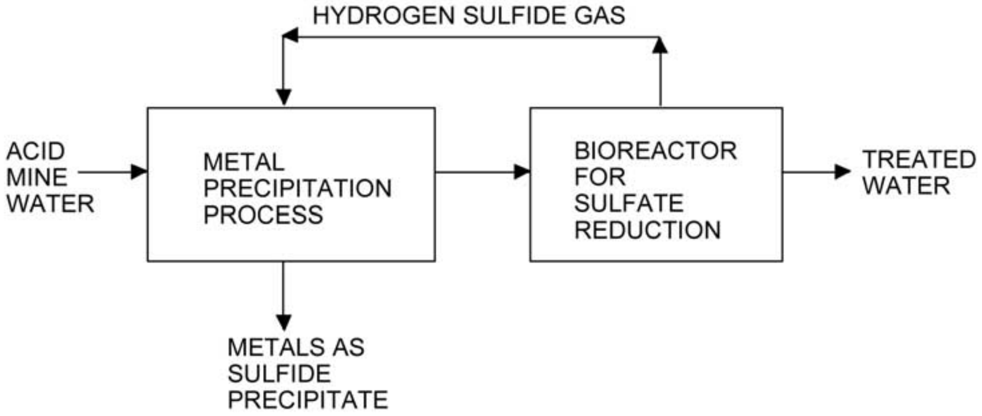

Figure 1. Schematic of the sequential treatment system wherein the metal precipitation step is separated from the biological surface reduction step.

SRB bioreactor system for AMD treatment and for sulfate reduction. The hydrogen sulfide, produced by the SRB dissimilatory sulfate reduction activity in the bioreactor system, was used in the precipitation step to form insoluble metal sulfides. The uniqueness of the two stage process is that it allows an integration of the SRB bioreactor and metal precipitation systems as two separate processes running in parallel in which the biogenic hydrogen sulfide, generated by SRB sulfate reduction activity in bioreactor systems, is used in the formation of metal sulfide precipitates in the acidic wastewater in the metal precipitation and recovery units. The SRB bioreactors used in our studies for production of hydrogen sulfide from sulfate reduction activity were either the conventional SRB bioreactors or the newly developed SRB hollow fiber membrane bioreactors. The SRB bioreactor systems for production of hydrogen sulfide were used as parallel processes with both the four stage batch type and six stage continuous type metal biorecovery process units. The recovery of metals in the metal precipitation units is considered as a biorecovery system since the metal sulfides are generated by the activity of biogenic hydrogen sulfide with the metals in the acidic wastewater.

Four stage batch type metal precipitation process

The developed four stage metal precipitation process is shown in Figure 2. Each precipitator unit is equipped with pH probes, feed lines for pH adjustment using hydroxide, and biogenic hydrogen sulfide or synthetic H_2S/CO_2 gas feed lines, where needed for metal sulfide precipitation. The baffles in the settling tanks reduce turbulence and enhance precipitate settling.

The precipitation process consists of four separate precipitator-settler units. The units are of glass type cylindrical U shaped design. The dimensions of the precipitator-settler unit are 18 inches (45.72 cm) in height with a diameter varying between 1 to 4 inches (2.54 to 9.16 cm). Argon gas is used to blanket the feed tank to prevent oxidation of the ferrous sulfate present in the acid mine water. The biogenic hydrogen sulfide from the SRB bioreactor units or a synthetic gas mixture (50 mole % hydrogen sulfide and 50 mole% carbon dioxide) was bubbled into the precipitator using a fine sparger. The Berkeley Pit acid mine water is pumped through a filter from 55 gallon plastic lined drums to the four stage system. The water flows into the top of a 250 ml aspirator bottle that acts as a holding tank and helps to maintain uniform flow. Each unit is equipped with a combination pH pump and controller (Cole-Parmer E56025-00) to maintain a proper pH. A Dwyer RMA-11 flow meter measures gas flows into each reactor and a Dwyer MMA-23 measures liquid reactor feed flow rate. The holding tanks for all reactors, except the aluminum hydroxide reactor, are 250 ml aspirator bottles (Corning 1220-250). The particulate filters are 10 m filters (Upchurch Scientific, A-31A). The base used is potassium hydroxide instead of sodium hydroxide because high conversions of sodium produce interference in ICP analysis of the metals. Solids are occasionally drained from the reactor to prevent excessive buildup. The acid mine water flow enters on the left-hand side and flows out on the right-hand side

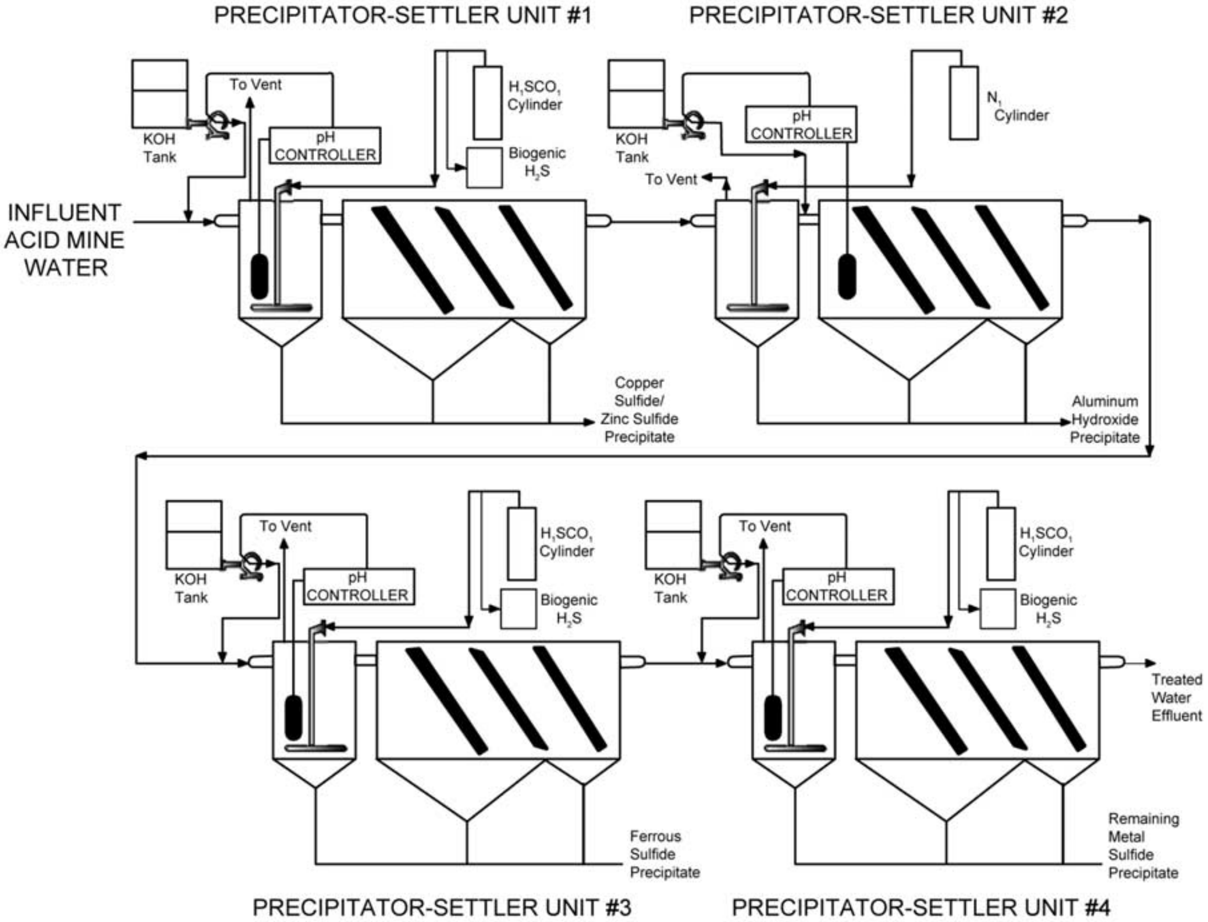

Figure 2. Schematic of the four step precipitation process studied for recovery of metals from acid mine drainage.

The water gravity flows through a flow meter and into the first reactor The first precipitator-settler unit, in which copper and zinc are co-precipitated for operational convenience, is operated at pH of 3.0. Liquid gravity flows from the bottom of the copper/zinc reactor and into the second reactor where aluminum hydroxide is precipitated.

The effluent from the first unit is sparged with nitrogen gas through a stripping column (28 inches (71.12 cm) in height and 3.5 inches (8.89 cm) in diameter) to remove any dissolved hydrogen sulfide and pumped into the second, aluminum precipitator-settler unit. The nitrogen gas flow rate to the stripper varied between 7 to 8 l/min. Hydrogen sulfide has to be removed before attempting to recover aluminum as aluminum hydroxide. The flow of nitrogen gas into the stripper is measured using Dwyer MMA-8 flow meter If the dissolved hydrogen sulfide is not removed, ferrous sulfide would co-precipitate with aluminum hydroxide. The pH in the second precipitator-settler unit is adjusted to a pH range of 4.0 and 5.0, by addition of 12N potassium hydroxide solution.

The effluent water from the second precipitator-settler unit is pumped into the third ferrous sulfide precipitator-settler unit, in which the pH is maintained at a pH of 5.0 by continuous and automatic addition of potassium hydroxide solution. A mixture of 50% hydrogen sulfide and 50% carbon dioxide gas is sparged into this third precipitator-settler unit, to precipitate ferrous sulfide from the acid mine water.

The liquid from the third precipitator-settler unit is pumped into the fourth and last precipitator-settler unit, where the 50% hydrogen sulfide and 50% carbon dioxide gas mixture is sparged at pH above 8.0 to precipitate the remaining metals as sulfide precipitates. The effluent from the fourth precipitator-settler is adjusted to neutral pH and disposed of properly.

Defining recovery and purity

Recovery is a measure of how well the precipitator-settler is able to precipitate the desired metal(s). Mathematically, recovery is defined as follows:

$$R = \frac{F_i x_i + B x_B - B y_o - F_i y_o}{F_i x_i + B x_B} \times 100\%, \qquad (1)$$

where F_i = liquid stream into the reactor (ml/min or ml), x_i = composition of metal 'i' in liquid stream into the reactor (ppm), B = base stream into the reactor (ml/min or ml), x_B = composition of metal 'i' in base stream into the reactor (ppm), y_o = composition of metal 'i' in liquid stream leaving the reactor (ppm).

Purity is the amount of desired metal precipitated from a reactor divided by the sum of all metals precipitated.

$$P = \frac{F_i(x_i - x_o) + B(x_B - x_o)}{\sum_{\text{all metals}} F_i(x_i - x_o) + B(x_B - x_o)} \times 100\%. \qquad (2)$$

Metal removal is computed as the difference between initial metal concentration in the feed and the metal concentration in the effluent leaving the system per each precipitator unit. It is then normalized by dividing by the initial concentration.

$$\text{Removal} = \frac{(x_i)_{\text{first stage}} - (x_o)_{\text{last stage}}}{(x_i)_{\text{first stage}}} \times 100\%. \qquad (3)$$

Studies on six stage continuous metal precipitation process

Studies were conducted to develop a six stage continuous metal precipitation process and to optimize the operating conditions for the sequential precipitation process. A six-stage precipitation process, shown in Figure 3, was assembled and operated at the bench-scale level for separating pure metal precipitates from the Berkeley Pit acid mine water. The process was operated at 15 ml/min flow rate and gravity overflow was used to transfer liquid exiting one stage to the inlet of the subsequent stage. The optimum operating conditions set for the six stage continuous metal precipitation process are summarized in Table 8. As in the batch type 4 stage metal precipitation system , either a biogenic hydrogen sulfide produced in the SRB bioreactors for AMD treatment and sulfate reduction or a synthetic hydrogen sulfide from cylinders containing a mixture of hydrogen sulfide and carbon dioxide were used in the 6 stage continuous type sequential metal separation systems.

The continuous process was operated for several months and liquid samples were taken from the effluent of the process as well as the precipitate samples and periodically analyzed for metal concentrations. Liquid influent and effluent samples were withdrawn on a weekly basis and process recoveries were calculated for each metal. Precipitate samples were also withdrawn on a weekly basis and % purity of each metal was obtained for each of the six metal precipitates. The process was only operating for a five hour time period every day. During the five hour period of operation each day, the process was operating continuously.

Results and discussion

Four stage batch type metal precipitation process

Table 2 shows the feed rates and base addition rates to each reactor in the treatment process. Because the pH controlled the added base in pulses, the average flow rate was calculated by measuring how much liquid had been used in an hour and estimating a flow rate on milliliters per minute. Table 3 shows the results of metal recoveries for the four stage precipitation-settling process. The results show that the first reactor was able to remove over 99% of the copper and zinc as a combined precipitate. After obtaining only a 90% recovery during the first set of experiments, the pH set-point for the pH controller was increased and aluminum recovery rose to 94%. Iron and manganese were both recovered at 99% and 95%, respectively, in most of the experiments. Thus, each step in the process was successful in removing the desired metal.

To determine whether or not each step was able to remove only the desired metal, the purity of the resulting precipitate was measured. The combined copper and zinc purity in the first precipitator was consistently over 95% purity for each metal. The aluminum hydroxide was typically over 90% pure. The third precipitator product, iron sulfide, was not consistently pure. The product obtained during the earlier portion of the tests indicate achievement of purities above 90%. The data collected during the later period was consistently around 60% purity mainly due to co-precipitation of manganese.

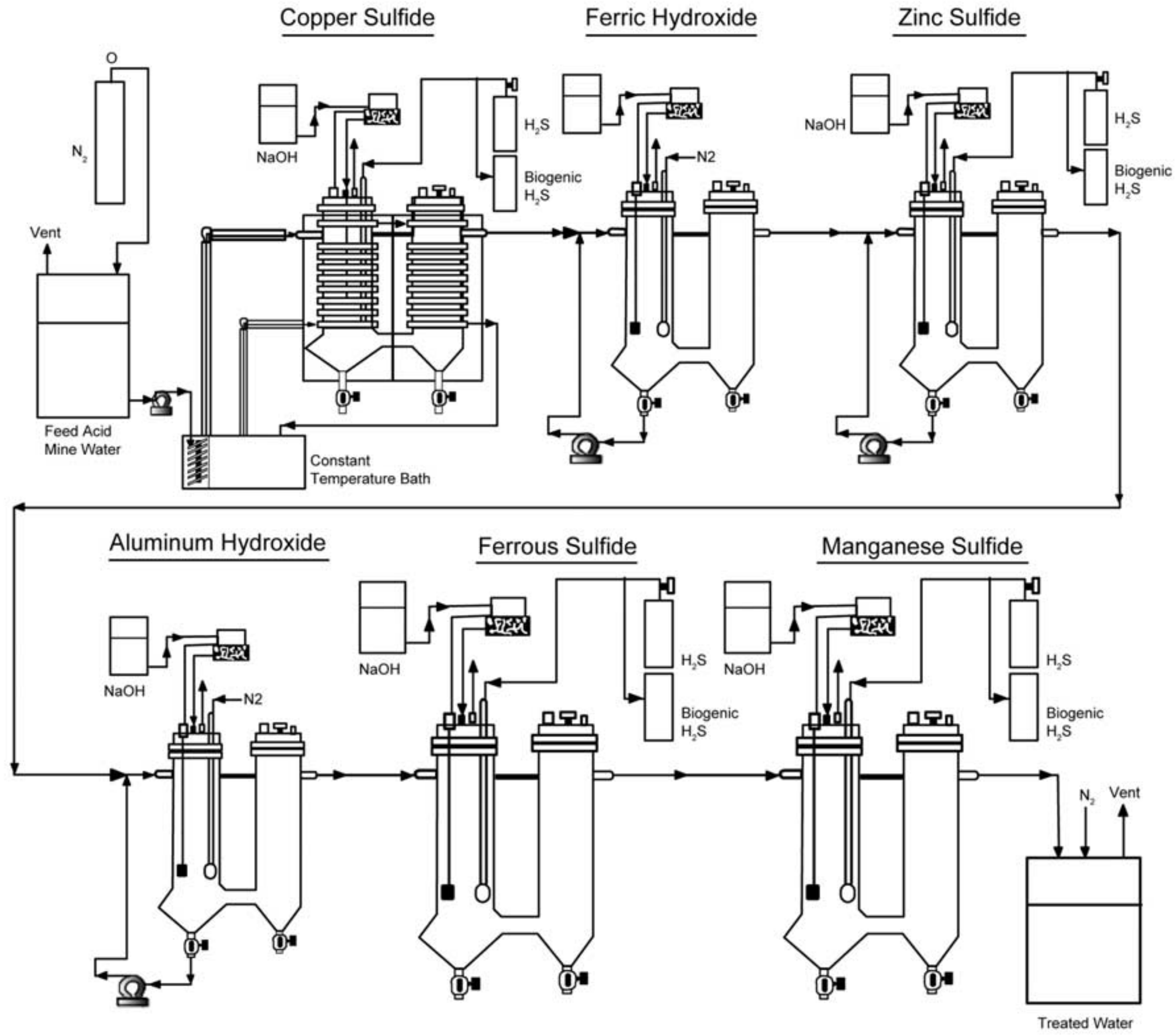

Figure 3. Schematic of the continuous precipitation-settling process.

Table 4 illustrates purity of each metal in each of the precipitator units. Calculated values are based on mass balance analysis and measured values are based on precipitate analysis. The poor results for iron and manganese in initial experimental runs are attributed to inadequate pH control and the presence of oxygen in the iron and manganese units. Subsequent better control of pH and oxygen contamination produced higher purity of the iron and manganese metals. Table 5 shows the overall metal removal efficiencies calculated from mass balance analysis for the entire process Because metal removal indicates the entire process's ability to remove metals, this value measures the overall treatment capability. Thus, the process is able to remove 95% or more of aluminum, cobalt, copper, iron, manganese, nickel and zinc. The process removed some of the calcium, chromium, and magnesium. Sodium and potassium were not removed from Berkeley Pit water. The percentage removals for magnesium varied from 9–49% and that for calcium were in the range of 16–53%. Chromium concentrations in the feed acid mine drainage were about 0.11 ppm and since the overall removal of chromium was based on the exit concentration being below the detection limit of the analytical instrument, chromium removals were calculated using the instrument detection limit.

The high degree of metal removal from the wastewater is confirmed by the analytical measurement results for the metal concentration in the treated wastewater effluent of the bench-scale system, as

Table 2. Reactor feed rates and base addition rates (ml/min) for the Berkeley Pit treatment process

Experiment number	Precipitator – settler #1		Precipitator – settler #2		Precipitator – settler #3		Precipitator – settler #4	
	Feed	Base	Feed	Base	Feed	Base	Feed	Base
1	85	1.6	80	2.1	80	1.4		
2	85	2.4	70	2.9	70	1.4		
3	90	2.5			90	1.5		
4	200	3.9	120	2.0	70	1.1		
5	200	2.5	150	1.5	90	1.5	70	0.9
6	100	0.9	100	0.9	105	2.6	80	0.7
7	100	2.4	80	1.4	70	1.1		
8	180	3.2	80	1.2	90	1.3	90	0.9
9	140	2.6	60	3.2				
10	200	2.6						
11	180	2.1						
12	200	3.1	180	2.9	140	3.2	120	2.1
13	200	3.2	180	2.9	130	3.9	110	1.7
14	200	3.3	160	2.7	150	3.3	130	2.3
15	200	2.1	180	3.0	130	3.3	100	1.5
16	200	2.7	180	2.8	140	5.9	120	1.8
17	180	2.4	160	2.6	100	2.8	100	1.3
18	210	2.8	180	3.1	160	4.0	110	1.8
19	200	2.8	150	2.1	120	3.6	80	1.2
20	200	2.9	190	3.0	150	3.4	120	1.8
21	200	2.6	160	2.7	130	2.9	90	1.4

shown in Table 6. In all cases, the measured concentrations of all metal species assayed in the effluent was below the detection limit with the exception of manganese and calcium. Assays for sodium, potassium and sulfate were also performed but are not reported in this paper.

Six stage continuous metal precipitation process data

Using the operating conditions illustrated in Table 8 for the operation of the six stage metal precipitation process, data were generated for the recovery and purity of metals for each of the four weeks of operation This sequential separation-precipitation process was allowed to continue for a period of six months but data are only reported for 4 weeks of operation in this paper. Table 9 shows the metal recoveries obtained during the six stage continuous process operation for each metal calculated from the weekly samples. The recoveries of each metal in the process were very high, since by the time the pH of the acid mine water had been increased to an exit value of 8.0, most of the metals had precipitated as either metal sulfides or metal hydroxides. Based on the recovery values of metals from the 6 stage units beyond the 4 week period, it can be concluded that there was no significant increase in the recoveries of the metals after a period of four weeks of operation.

Samples of precipitates taken weekly from each precipitator-settler unit were also analyzed for % purity of each metal and Tables 10 and 11 give the results of analysis on % purity during the first and the fourth week of operation of the continuous process. From the results presented it is clear that the continuous process is capable of producing precipitation of metals of high purity. The resultant water produced in the 6 stage continuous metal precipitation-biorecovery process was shown to contain metals and salts in concentration levels below the detection limits, judged to be usable for agricultural irrigation purpose and evaluated to meet the Gold Standard.

Table 3. Metal recoveries (%) for each metal for the four stage precipitation process operating on Berkeley Pit acid mine drainage

Experiment number	Precipitator – settler #1			Precipitator – settler #2		Precipitator – settler #3		Precipitator – settler #4	
	pH	Cu	Zn	pH	Al	pH	Fe	pH	Mn
1	2.21	100.0	99.9	4.85	97.0	6.28	100.0		
2	2.24	100.0	100.0	4.88	96.8	6.28	100.0		
3	2.21	100.0	99.9			6.15	97.6		
4	2.38	100.0	100.0	4.60	82.1	5.74	100.0		
5	2.24	100.0	100.0	4.78	86.7	6.42	100.0	9.83	100.0
6	2.22	100.0	100.0	4.84	88.8	12.84*	100.0	9.52	100.0
7	2.21	100.0	100.0	4.83	95.2	12.91*	100.0		
8	2.17	100.0	100.0	5.09	89.9	6.05	100.0	9.52	100.0
9				4.26	84.6				
10	2.27	100.0	99.9						
11	2.18	99.9	99.9						
12	2.56	100.0	99.9	5.23	92.0	6.19	100.0	10.34	100
13	2.76	100.0	99.9	5.31	96.1	6.33	99.6	10.27	99.0
14	2.71	100.0	99.5	5.39	96.1	6.18	99.8	9.93	95.1
15	2.15	100.0	99.8	5.46	97.1	6.29	99.9	9.94	99.1
16	2.45	100.0	99.8	5.13	92.9	6.58	99.6	9.39	96.3
17	2.35	99.9	99.9	5.48	97.1	6.36	99.8	9.42	100.0
18	2.37	99.9	99.9	5.94	99.2	6.33	100.0	10.16	99.0
19	2.41	100.0	99.8	4.65	77.1	6.45	100.0	9.17	99.3
20	2.50	99.8	99.7	5.13	92.8	6.09	99.7	10.48	100.0
21	2.29	99.9	99.9	5.68	98.5	6.22	99.6	9.74	89.2

* Denotes abnormal point.

Economics of the sequential separation and precipitation process for metals from acid mine water

An engineering cost analysis of the process was performed to provide an idea of the potential economic impact benefit of the process if developed and implemented on a larger scale basis. The estimated cost savings and economic value for converting the Berkeley Pit clean-up to a profitable metal biorecovery operation is shown in Table 7. The potential economic impact/benefit is illustrated by providing differences between three processes, namely: (1) Montana State EPA record of decision for a two stage lime precipitation process; (2) Selective Sequential Precipitation process for copper and zinc only; and (3) Selective Sequential Precipitation process for copper, zinc, aluminum, iron (ferric and ferrous metals) and manganese. The potential economic benefit from the above three processes is provided in terms of capital cost (million of dollars); cash flow per year (millions of dollars per year); cash savings per year (million of dollars per year) and the payout time (years). The potential economic impact/benefit analysis indicates that the cost recovery from sale of high purity metal precipitates from the Berkeley Pit acid mine water offsets very favorably the treatment costs. In addition, the ability to selectively precipitate and purify ferrous sulfide as a product of the six stage SSP process makes this precipitation system useful in our current studies to produce valuable products such as the pigments, goethite and magnetite from ferrous sulfide.

Conclusions

A two stage process was developed separating the SRB bioreactor activity for AMD treatment via sulfate reduction and production of biogenic hydrogen sulfide from the four stage and six stage metal sequential separation and birecovery units. The recovery of metals in the four and six stage SSP units is thus considered a biorecovery process due to the use of the biogenic hydrogen sulfide produced in the SRB bioreactor sys-

Table 4. Precipitate purity (%) for each precipitator unit; calculated values are based on mass balance analysis and measured values are based on precipitate analysis

Experiment number	Copper/zinc sulfide			Aluminum hydroxide		Ferrous sulfide		Manganese sulfide
	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
1		98.2		97.0	93.9	92.0		
2		99.5		96.8		79.7		
3		99.7		94.2	92.4			
4	96.8	95.8	66.1*	82.1		93.9		
5	99.2	97.1	68.2*	86.7	54.4	66.7	33.1	28.8
6	98.3	98.0		88.8	78.3*	34.3*	51.0	65.6
7		98.6 *		95.2		35.2*		
8		98.2	96.8	89.9	94.9	92.4	35.3	50.9
9	97.4			84.6				
10	99.2	99.8						
11		79.6						
12	98.6	98.1	94.3	92.0		55.5		7.2
13		81.7		96.1		67.5		10.1
14	98.7	99.7	93.2	96.1	66.8	59.6	14.0	9.2
15		99.7		97.1		57.4		8.1
16	98.9	99.5	95.2	92.9	58.4	61.9	8.0	12.0
17		77.2		97.1		57.4		34.3
18	98.7	99.7	89.1	99.2	63.3	58.1	9.2	8.9
19		99.8		77.1		61.6		33.7
20		99.2		92.8		70.5		7.5
21	99.0	86.9	85.1	98.5	59.3	63.6	13.7	5.6

* Denotes abnormal value.

Table 5. Metal removals calculated using mass balance analysis for the precipitation process for the Berkeley Pit acid mine water

Expt. No.	Al	Ca	Cd	Co	Cr*	Cu	Fe	Mg	Mn	Ni	Zn
5	100%	46%	100%	100%	80%	100%	100%	50%	100%	100%	100%
6	100%	16%	100%	100%	58%	100%	100%	19%	100%	100%	100%
8	100%	20%	100%	100%	71%	100%	100%	32%	100%	100%	100%
12	99%	53%	100%	100%	80%	100%	100%	36%	100%	100%	100%
13	99%	57%	99%	97%	55%	100%	100%	32%	100%	97%	100%
14	99%	47%	100%	100%	95%	100%	100%	20%	99%	91%	100%
15	99%	53%	100%	100%	75%	100%	100%	20%	100%	100%	100%
16	99%	41%	100%	100%	72%	100%	100%	20%	99%	90%	100%
17	99%	29%	100%	100%	35%	100%	100%	12%	100%	100%	100%
18	99%	53%	100%	100%	98%	100%	100%	19%	100%	88%	100%
19	99%	19%	100%	100%	36%	100%	100%	9%	100%	91%	100%
20	99%	50%	100%	100%	66%	100%	100%	49%	100%	91%	100%
21	99%	35%	100%	100%	41%	100%	100%	18%	98%	89%	100%

* Based on instrument detection limit.

Table 6. Analysis of effluent water from the last precipitator-settler unit (as measured by ICAP)

Compound	Concentration (mg/L)
Al^{3+}	0.50
Ca^{2+}	291.9
Cr^{3+}	BDL
Cu^{2+}	BDL
Mn^{2+}	0.40
Fe^{2+}	0.10
Zn^{2+}	BDL
Cd^{2+}	BDL
Ni^{2+}	BDL
As^{3+}	Not measured
Co^{2+}	BDL
SO_4^{2-}	24.0
NO_3^{1-}	0.32
Cl^{1-}	16.0
Na^{1+}	213
K^{1+}	3,532

Table 7. Potential economic impact/benefit

Process	Capital cost (MMS)	Cash flow per year (MMS/year)	Cost savings per year (MMS/year)	Payout time (years)
1. ROD 2 stage lime precipitation[a]	9.4	−4.5	0	Infinity
2. SSP copper and zinc only[b]	14.4	−2.1	2.4	2.1
3. SSP copper, zinc, aluminium, iron and manganese recovery[c]	19.5	10.5 to 24.8	15.0 to 26.9	0.37-0.67

[a] The ROD process consists of a 2 stage lime precipitation plant with secured subtitle D disposal of the wastes.

[b] SSP with recovery of copper and zinc only, with secured subtitle D disposal of the other metals wastes.

[c] SSP copper, zinc, aluminium, iron, and manganese recovery.

Table 8. Summary of 6-stage precipitation process operating conditions

Stage number	Operating conditions
Influent liquid flow rate = 15 mL/minute	
Sodium hydroxide solution used to increase pH between stages	
1	Temperature = 10 °C
(Copper sulfide)	pH = Influent pH of acid mine water
	Hydrogen sulfide gas mixture sparged
2	Temperature = 25 °C
(Ferric hydroxide)	pH set point = 4.5
	Nitrogen gas sparged
3	Temperature = 25 °C
(Zinc sulfide)	pH set point = 4.5
	Hydrogen sulfide gas mixture sparged
4	Temperature = 25 °C
(Aluminum hydroxide)	pH set point = 6.0
	Hydrogen sulfide gas mixture sparged
5	Temperature = 25 °C
(Ferrous sulfide)	pH set point = 6.0
	Hydrogen sulfide gas mixture sparged
6	Temperature = 25 °C
(Manganese sulfide)	pH set point = 8.0
	Hydrogen sulfide gas mixture sparged

Table 9. Metal recoveries obtained during continuous process operation

Metal	Week 1	Week 2	Week 3	Week 4	Week 5
Al	99.1	98.1	98.6	99.4	99.8
Cd	98.6	99.4	100	−1.8	99.7
Co	−3.7	99.8	98.4	103.6	99.1
Cu	100	99.1	99.4	99.3	99.8
Fe	98.8	97.4	95.1[a]	96.8	97.1
Mn	89.4	88.6	81.4	75.4[b]	87.4
Ni[c]	49.1	50.4	45.6	42.4	47.8
Zn	102	98.4	99.8	99.9	100

[a] Ferric hydroxide precipitate is difficult to settle and requires additional settle time.

[b] Manganese precipitation is greatly affected by pH in the final stage.

[c] Nickel exhibited low recoveries but its concentration in the infludent is less than 2 ppm.

tems for metal precipitation as metal sulfides in the sequential separation-precipitation systems.

The four stage selective sequential batch type metal precipitation process was able to separate the metal sulfides and hydroxides at reasonably high recoveries and precipitate purities. Copper sulfide and zinc sulfide are precipitated in Stage 1. Aluminum hydroxide is precipitated in Stage 2. Ferrous sulfide is precipitated in Stage 3. All the remaining metals are precipitated in Stage 4. Several problems were overcome in terms of metal separation and ability to precipitate the fine particles using the inclined plate precipitators. Purities for iron sulfide were not consistently high in initial experiments, mainly due to lack of proper mixing of the hydroxide solution, which resulted in localized regions of high pH and consequently co-precipitation of manganese sulfide. The presence of oxygen in these stages initially also adversely affected the ability to achieve pure sulfide precipitates.

Table 10. Precipitate purity[a] results for each precipitate obtained during the first week of operation of the continuous process

Metal	Precipitate 1 (copper sulfide)	Precipitate 2 (ferric hydroxide)	Precipitate 3 (zinc sulfide)	Precipitate 4 (aluminium hydroxide)	Precipitate 5 (ferrous sulfide)	Precipitate 6 (manganese sulfide)
Al	2.2	0	0	95.6	0	9.6
Cd	0.3	0	0	0.8	0.2	0.1
Co	0	0	0	0.2	1.1	0.3
Cu	82	3.8	2.2	0	0	0
Fe	4.1	81.5	0	2.0	92.1	15.0
Mn	4.2	0	0	1.0	6.0	75.0
Ni	0	0	0	0.4	0.6	0
Zn	7.2	14.7	97.8	0	0	0

[a] Metals that were below detection limit in the precipitate were assumed to be 0 concentration in the calculation of % purity.

Table 11. Precipitate purity[a] results for each precipitate obtained during the fourth week of operation of the continuous process

Metal	Precipitate 1 (copper sulfide)	Precipitate 2 (ferric hydroxide)	Precipitate 3 (zinc sulfide)	Precipitate 4 (aluminium hydroxide)	Precipitate 5 (ferrous sulfide)	Precipitate 6 (manganese sulfide)
Al	3.5	0	0	92.85	0	11.7
Cd	0.33	0	0.45	0	0.77	0
Co	0	0	0.38	0.47	0.94	0.67
Cu	82.14	2.35	3.99	0	0	0
Fe	2.73	86.9	0	4.22	92.07	12.69
Mn	1.65	0	0	2.10	5.89	74.94
Ni	0	0	0.33	0.36	0.33	0
Zn	5.65	10.75	94.85	0	0	0

[a] Metals that were below detection limit in the precipitate were assumed to be 0 concentration in the calculation of % purity.

However, the precipitation process was able to demonstrate high overall metal removals and produced final effluent water which could be considered as a valuable product.

Operating conditions for the sequential metal precipitation and biorecovery process were optimized for the development of the six stage continuous type selective sequential precipitation, biorecovery and purification of metals process. This process is able to sequentially precipitate copper sulfide in Stage 1, ferric hydroxide in Stage 2, zinc sulfide in Stage 3, aluminum hydroxide in Stage 4, ferrous sulfide in Stage 5 and manganese sulfide in Stage 6. The process was able to demonstrate very high metal recoveries and precipitate purities, separation of the ferric and ferrous metals as hydroxides and sulfides respectively in separate stages and high purities of the ferrous and ferric metals. Problems associated with improper mixing of hydroxide solution to produce co-precipitation of metal sulfides and with the presence of oxygen in the four stage process, were entirely eliminated in the six stage process. The produced effluent water as the final product contained only calcium and magnesium in trace concentrations and both sulfate and metal sulfide concentrations were below detectible limits. The water quality met EPA's Gold Standard criterion and thus the effluent water produced in these systems is judged to be a valuable product for agricultural and other environmental uses.

Metals are an integral part of the U.S. economy and throughout the world. Innovative and alternative techniques that facilitate the economic control and recovery of metal values is one alternative that leads itself not only to protection of human health and the environment, but also to the recovery of valuable commodities (i.e., metals and pigment products) and resource conservation. Accordingly, AMD rich in valuable heavy metals should be considered not only as a serious environmental problem, but as an important resource of metals and pigments of considerable value to many industrial concerns. Newly developed metal recovery processes from AMD and other acidic streams can thus enable us to recover and recycle these metals cost effectively. An effective process methodology for recovery and separation of the individual metal sulfides and hydroxides is unique, since it is capable of achieving high metal purities and an agriculturally usable water.

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