PROSPECT OF METAL RECOVERY /RECYCLE FROM ACID MINE DRAINAGE[1]

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Abstract: Experimental investigations were conducted to determine the prospect of recovering valuable metals from acid mine drainage (AMD) from a Canadian source. In particular, potential for the recovery of zinc as sulfide for recycling to a zinc roaster has been examined. Several chemical methods were evaluated to selectively precipitate and recover metal ions, and a conceptual flowsheet, consisting of a three-step process, was developed. The process comprised oxidation of Fe(II) and precipitation of iron as ferric hydroxide in the first step, precipitation of Zn and Cu as sulfides in the second step, and the removal of the residual metal ions by lime neutralization in the third step. Alternative methods for selective precipitation that were evaluated included a two-step process in which ferric iron was precipitated with limestone, followed by precipitation of zinc and copper hydroxides and other metals using sodium hydroxide. The precipitation of sulfides was studied using sodium sulfide, sodium hydrosulfide and hydrogen sulfide. The results to date showed that almost 100% iron is precipitated in step 1, more than 90% zinc recovery with greater than 50% Zn grade can be obtained in step 2, and a discharge effluent with less than 1 mg/L heavy metals (Fe, Cu, Mn, Al) is obtained in step 3. The zinc grade was superior to that obtained by other methods evaluated which produced only 30% Zn grade. Economical and technical constraints of the three step process are reagent costs and solid-liquid separation. Acceptability of zinc hydroxide for recycling is uncertain. Alternative approaches for metal recovery based on these findings are suggested.

Additional Key Words: acid mine drainage, metal recovery, selective precipitation.

Introduction

Acid mine drainage (AMD) generated in sulfide-ore-processing regions is a serious environmental concern. The standard treatment is by mixing lime to precipitate the dissolved metals and disposing of the resulting sludge. This practice inevitably results in the loss of metals, some of which, if recovered, could provide revenue to offset in part the treatment and disposal costs while decreasing the sludge volume.

The present project was initiated to investigate methods for the treatment of AMD with the objective of recovering some of the base metals while maintaining or improving the effluent quality. Earlier work was done with AMD from Mattabi Mines Ltd., Ignace, Ontario (Rao and Finch 1992). Precipitation of the metals as hydroxide, sulfide, and by cementation in the case of copper, was investigated. Two multistep treatment options were demonstrated. In both options iron was first precipitated as ferric hydroxide at about pH 3.5. The possible use of this product as feedstock for producing a ferric sulfate coagulent was also considered (Rao et al. 1992). Contamination of the iron hydroxide with Cu and Zn was significantly reduced by introducing dodecylamine, $C_{12}H_{25}NH_2$ (DDA). This had the added benefit of reducing the loss of Cu and Zn. DDA was tried because it is known to adsorb on iron hydroxides (Iwasaki et al. 1960) and thus may act to "block" the adsorption site for metal ions.

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The present work was conducted with AMD from Les Mines Gallen, Rouyn Noranda, Quebec. This contained zinc in high concentration (~14 g/L) and ~30 g/L iron. Concentration of copper was very low (~0.2 g/L) relative to that of zinc. The work was therefore aimed at the recovery of zinc. Precipitation as the sulfide was selected because the precipitation as the hydroxide required raising the pH to about 7, which caused contamination with manganese and calcium sulfate precipitates. Zinc sulfide is also the common feed material to a zinc extraction plant.

The recovery of zinc as sufide was investigated by a three-step process:
Step 1. Removal of iron as hydroxide with preoxidation of Fe(II) to Fe(III),
Step 2. Precipitation of zinc sulfide,
Step 3. Production of a final discharge effluent using lime treatment.

The precipitation of zinc sulfide was studied with hydrogen sulfide, sodium sulfide, and sodium hydrosulfide. Sodium sulfide was chosen as it is a readily available industrial chemical. Hydrogen sulfide was used to study the precipitation at lower pH and investigate the action of lime to set the pH to higher values. Sodium hydrosulfide was used as an alternative to sodium sulfide. It is recognized that the equilibrium concentrations of Na_2S, $NaHS$, and H_2S are a function of the pH only.

This treatment procedure was compared with other options, including straight precipitation of all metals in one step and a two-steps option comprising precipitation of iron as hydroxide at pH 3.5 followed by precipitation of other metals as hydroxides by sodium hydroxide.

Experimental Work

Material Description

The AMD received was a seep water, pH about 1.8. It was diluted five times to correspond to more typical conditions; this is referred to as the "original" AMD (table 1). For experiments involving biological oxidation of Fe(II), the seep water was diluted 23 times.

Table 1. Composition of the original AMD from Les Mines Gallen.

| Metal	mg/L	Metal	mg/L
Fe(II)	16,700	Al	3,520
Fe(III)	13,100	Mg	2,790
Total Fe	29,800	Ca	5.0
Cu	191	Pb	1.8
Zn	13,800	Cd	45.3
Mn	146	As	50.0

Oxidation of Fe(II)

Using Hydrogen Peroxide. The stoichiometric quantity of hydrogen peroxide required to oxidize the iron present as Fe(II) was added as a 30% solution to 20 L AMD. The mixture was stirred for 15 min and left for 12 h to allow for the dissipation of any residual peroxide.

Using Thiobacillus ferrooxidans (Tf bacteria). The bacteria were enriched from waste rock at a mine site using 9K

medium (Payant and Siwik 1987). Then 1.5 L AMD was inoculated with the isolated bacteria, and the nutrients (1.605 g KNO_3 and 0.525 g K_2HPO_4) were added. The solution was agitated for 6 days, samples were drawn for Fe(II) determination initially and after 1, 2, and 6 days.

Treatment Procedure for the Three-Step Process.

The basic experimental approach described before (Rao and Finch 1992) was followed with some modifications. The process flowsheet is shown in fig.1.
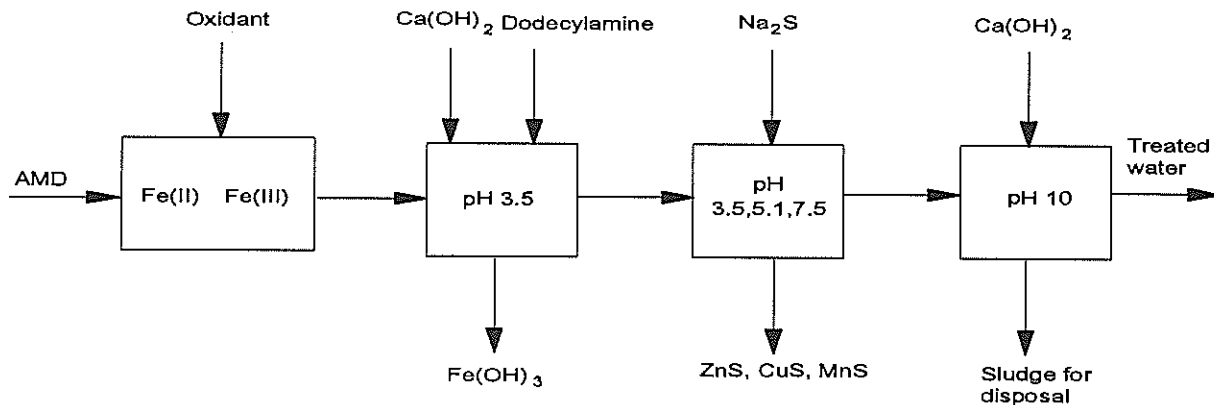
Figure 1. Flowsheet for three-step precipitation process.
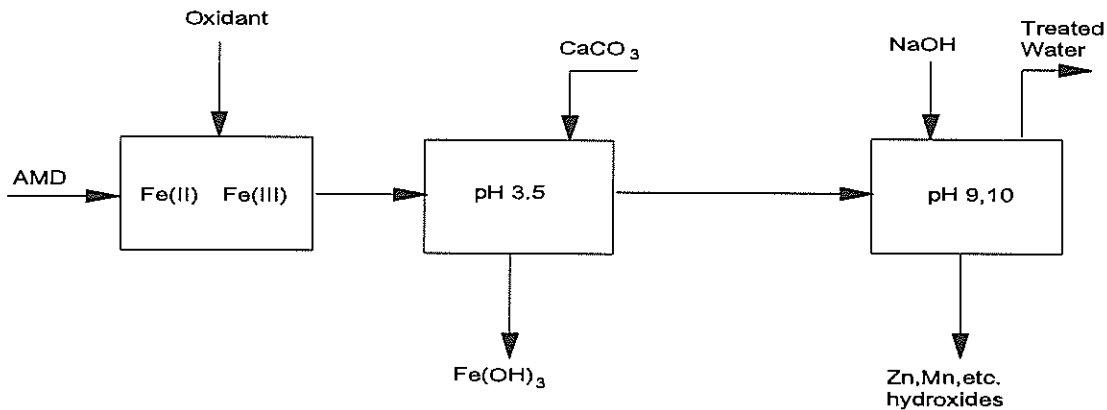
Figure 2. Flowsheet for alternative two-step precipitation process.

Step 1. Removal of iron as the hydroxide. After oxidation, dodecylamine (DDA) in concentrations up to 20 mg/L was added to the AMD. Experiments were conducted in a 1.5- L flotation cell with impeller speed at 800 r/min. Following the mixing of DDA, iron hydroxide was precipitated by adding calcium hydroxide until the pH reached 3.5 to 3.7. The precipitate was allowed to settle, enhanced by adding an anionic flocculant (0.05% solution) at an optimum dosage of 3.75 mg/L AMD, as established by settling rate studies. The precipitate was filtered to retrieve the effluent, which is feed to step 2.

Step 2. Recovery of zinc as the sulfide. Zinc was precipitated from the effluent of step 1 using sodium sulfide, hydrogen sulfide, or sodium hydrosulfide. The pH was adjusted using sodium hydroxide or calcium oxide. A calculated amount

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(stoichiometric to precipitate Zn) of sodium sulfide or hydrosulfide was added from a 10% solution. For precipitation by hydrogen sulfide, the gas was bubbled through 1 L of solution at a rate of 35 mL/min for 2 h.

Treatment with sodium sulfide was studied at pH 3.9, 5.1, and 7.5. Treatment with hydrogen sulfide was conducted at pH 3.5, 5.1, and 7.5. Additional experiments were conducted by treatment with sodium sulfide, followed by the required amount of lime to reach a pH of 4.5. In another modification, sodium sulfide and the lime were mixed and added together to the AMD. The sulfide precipitate in each case was allowed to settle, and the solution was clarified by filtration through 0.45 μm millipore filter.

Step 3. Production of a final discharge effluent by lime treatment. Each effluent from the various step 2 treatments was treated with lime to pH 10.

Two Step Precipitation Process.

The process sheet for this option is shown in fig.2. After the oxidation of Fe(II), ferric hydroxide was precipitated by calcium carbonate; 13.5 g was required to raise the pH of 1 L to 3.5. After the separation of ferric hydroxide as described before, 4N sodium hydroxide solution was added to the filtrate to raise the pH to 9 and 10 in two separate batches. The precipitate of metal hydroxides was flocculated using anionic flocculant and separated by filtration.

Base line Test.

For the purpose of comparison, the pH of the original AMD was raised directly to pH 9.5, as is done in the conventional lime treatment process.

Leachability Tests.

These were conducted on precipitates from steps 1 and 3 according to the Ontario Regulatory Extraction Procedure (1985).

Results

Oxidation of Fe(II) to Fe(III).

A comparison of the three methods of oxidation showed that the residence times required for chemical oxidation were significantly shorter than that required for biological oxidation (table 2).

Table 2. Residence times for the oxidation of Fe(II) to Fe(III) in AMD.

Method	Reagent	Residence time
Chemical	Hydrogen peroxide	15 min- 2 h.
Biological	T. ferrooxidans	2-6 days.

Removal of Iron as the Hydroxide (Step 1).

Effect of Dodecylamine (DDA). The results obtained with different quantities of DDA are shown in table 3, which records the concentration of metal ions in the effluent. The precipitation of iron was virtually complete at pH 3.5; above 5 to 10 mg DDA/L, zinc contamination in the precipitate is reduced.

The DDA created a reddish froth, which retained some solids; analysis showed that they were mainly calcium sulfate with very little ferric hydroxide (despite the color).

Table 3. Precipitation of ferric hydroxide: effect of DDA.

DDA, mg/L	Concentration, mg/L									
	Fe	Cu	Zn	Mn	Al	Mg	Ca	Pb	Cd	As
Original	5,880	38	2,840	29	704	562	1.0	0.4	9.1	10.0
0	10.3	34.3	2,448	28	396	450	244	0.4	8.0	5.5
5	10.8	36.7	2,752	29	426	554	248	0.4	8.1	5.5
10	12.0	47.1	2,750	29	438	556	248	0.4	8.2	5.0
20	12.8	37.1	2,746	29	445	556	248	0.4	8.2	5.0

Table 4. Composition of the ferric hydroxide sludge in step 1.

Reagent	Composition (dry basis),%								
	Fe	Zn	Cu	Mn	Mg	Al	Cd	Ca	As
$Ca(OH)_2$	16.720	1.61	0.03	0.004	0.12	1.00	0.002	0.03	0.019
$Ca(OH)_2$ + DDA, 5 mg/L	18.430	0.64	0.02	0.003	0.09	0.80	0.002	0.02	0.018
$CaCO_3$	18.380	0.03	0.02	0.001	0.001	1.10	0.003	0.02	1.100

Purity of Ferric Hydroxide Sludge. The composition of the sludge produced by various reagents are summarized in table 4. The sludge produced with calcium carbonate had the lowest levels of As, Cd, Mg, Mn, and Zn compared with the sludge obtained with calcium hydroxide. With calcium hydroxide the zinc loss was reduced in the presence of DDA, but it was still higher than that with calcium carbonate. Therefore, calcium carbonate is the most effective reagent for the production of a metal-free ferric hydroxide sludge for disposal or possible reuse.

Recovery of Zinc as the Sulfide.

Effect of pH Adjusted With Sodium Hydroxide. The effluents from step 2 show (table 5) that zinc was selectively precipitated below pH 4. More complete precipitation was observed at higher pH, but the selectivity was reduced. Composition of the precipitates showed that the Zn grade was 55% to 60% at pH<4, decreasing to <50% at pH 7.4, with Al as the main contaminant.

Comparison of Lime and Sodium Hydroxide to Adjust pH. Adjustment of pH with lime in place of sodium hydroxide also produced selective precipitation of zinc but with significantly greater recovery, the effluent showing lower concentration of zinc (table 6). The grade of the precipitate was lower owing to contamination by calcium sulfate.

Two-Step Precipitation Process. When sodium hydroxide was used for the two-step precipitation process, the Zn grade ranged from 27.3% to 29.7% at pH 9 and 10. However, the main advantage of this option is that the step 3 lime treatment may be eliminated, thereby reducing the volume of sludge requiring disposal, and sodium hydroxide precipitation is more easily controlled compared to sulfide precipitation.

Table 5. Step 2- Precipitation of zinc sulfide: Effect of sulfide reagents[1].

Description	Concentration, mg/L									
	Fe	Cu	Zn	Mn	Al	Mg	Ca	Pb	Cd	As
Original	5,880	38	2,840	29	704	562	1.0	0.4	9.1	10.0
Effluent after step 1	10.8	36.7	2,752	29	426	554	248	0.4	8.1	5.5
H_2S: pH 3.5	8.8	ND[2]	965	28	329	554	246	ND	1.0	4.0
pH 5.1	3.1	ND	697	28	10	550	246	ND	ND	4.0
pH 7.4	1.0	ND	4.0	1.9	ND	534	246	ND	ND	3.5
Na_2S: pH 3.9[3]	5.8	ND	542	28	316	556	250	ND	1.0	4.5
pH 5.1	2.1	ND	356	26	11	552	248	ND	ND	4.0
pH7.4	1.0	ND	3.3	11	ND	517	246	ND	ND	3.5
NaHS: pH 3.8[3]	3.9	0.1	1,142	42.4	211	632	423	0.3	11	1.8

[1]Conditions: DDA (10 mg/L) in step 1; NaOH used for pH adjustment.
[2]ND Not detected.
[3] Natural pH.

Base line Test. The effluent from this simulation of the conventional lime treatment of AMD showed metal concentrations similar to those in the effluent of the three-step process.

Sludge Stability.

The leachability test results (table 7) on unfiltered ferric hydroxide sludge from step 1, with and without DDA, showed that it contained Cu and Zn above the regulatory limit of 5 mg/L. In filtered sludge, the level of leached Cu is below the regulatory limit; however, the level of Zn did not meet the regulatory limit. Leaching tests were not conducted for step 1 ferric hydroxide precipitate formed with calcium carbonate. However, the results of the leaching tests on sludges from other tests indicate that filtration of the sludge reduces the degree to which metals are leached from the sludge.

Final Water Quality.

Chemical analysis of discharge water from various process options showed that in each case the water quality was sufficiently good for discharge; total metal levels ranged from 0.1 to 11 mg/L.

Discussion

Oxidation of Fe(II).

In comparing chemical versus biological oxidation for the conversion of Fe(II) to Fe(III), it was found that although residence time required for biological oxidation was excessive (2-6 days), an examination of the economics of the process (to be discussed below) shows the cost of biological oxidation is 72% to 97% lower than that of the options examined for chemical oxidation. To improve the efficiency of biological oxidation, process parameters such as temperature, rate of oxidation, rate of aeration, and inoculum ratio should be examined.

Table 6. Comparison of lime and sodium hydroxide in the precipitation of zinc sulfide.

Description	Zn in products			
	Effluent, mg/L		Precipitate, %	
	NaOH	Lime	NaOH	Lime
H_2S: pH 3.5	965	306	59.2	43.8
pH 5.1	697	2	46.4	21.1
Na_2S: pH 5.1	356	ND[1]	48.3	ND
pH 4.5	ND	1.1	ND	56.4
pH 4.5	ND	2.4	ND	54.8

[1]ND Not detected

Table 7. Sludge stability of ferric hydroxide sludges.

	Leachable metals, mg/L					
	Zn	Fe	Cu	Mn	Al	Mg
Settled sludge:						
no DDA	950	1.98	15.8	10.2	144	207
10 mg/L DDA	830	1.66	10.5	8.4	92	145
Filtered sludge:						
no DDA	130	0.10	2.46	0.91	6.2	18.4
10 mg/L DDA	105	0.10	1.80	0.65	6.0	15.6

Precipitation of Ferric Hydroxide (Step 1).

The results (table 3) showed that while the precipitation of iron as ferric hydroxide was practically complete, the precipitate is contaminated with Cu, Zn and Al ions. The extent of coprecipitation is reduced in the presence of DDA, but the precipitate still failed the leachability test. Of the chemical precipitants tested, calcium carbonate yielded the least contaminated ferric hydroxide precipitate. It is also cost effective; the estimated cost of calcium carbonate is 4 to 22 times lower than that of the other precipitants on cost-per-unit volume basis.

Precipitation of Zinc Sulfide (Step 2).

Sulfide precipitation of zinc at pH 3.5 using sodium sulfide yielded the highest grade of zinc, but the effluent from this process still carried about 1,000 mg/L Zn.

The recovery of zinc at pH 3.5 with hydrogen sulfide is enhanced using lime in place of sodium hydroxide to set the pH. In addition to pH control, the Ca(II) ions precipitate the sulfate ion in solution. This facilitates the dissociation of $ZnSO_4$ to free additional Zn(II) ions, which are then precipitated (Huang and Tahija 1990). The product, however, then contains about 8 to 9% Ca as $CaSO_4$, but remains free of other metals, which confirms the high degree of selectivity.

A possible alternative route is to use sodium sulfide and lime. Setting the pH at 4.5 yielded essentially 100% Zn recovery (table 6) from the effluent of step 1 with high selectivity and a product much lower in Ca than that obtained with hydrogen sulfide and lime. The use of calcium sulfide as a precipiant for zinc has been described (Kim and Amodeo 1983). This will be explored as a cheaper alternative for the precipitation of zinc.

Zinc Recovery as Hydroxide by Two Step Option.

Precipitation of Fe-free effluent from step 1 with sodium hydroxide at pH 10 yielded a sludge with almost 30% Zn with dissolved metals in the overflow that were sufficiently low for discharge. Use of lime to precipitate zinc as hydroxide resulted in a low Zn grade (11 to 20%) owing to contamination by calcium sulfate.

Comparison of the ZnS precipitate formed at pH 3.5 and $Zn(OH)_2$ formed at pH 10 indicates that each has certain advantages. In the latter case, although there is no sludge for disposal, there are concerns of high moisture content and elevated levels of Al and Mg. The impact of moisture content and impurities on recycling to the zinc roasters or in pressure leaching should be determined.

Although the fine nature of sulfide precipitates may result in carryover of material from a zinc roaster, the precipitate would be suitable for pressure leaching. A sedimentation-flocculation-filtration scheme should be considered for solid-liquid separation of the sulfide precipitates. On the basis of economics the feasibility of the process involving calcium carbonate for iron precipitation at pH 3.5 and sodium hydroxide for zinc precipitation at pH 10 depends on the costs associated with solid-liquid separation.

Economics.

Reagent costs. The available costs for the two oxidizing agents tested are , in dollar-per-cubic-meter, 5.85 for hydrogen peroxide and 0.32 for T. ferrooxidans. The costs for various reagent combinations are summarized in table 8. All costs are in Canadian dollars.

Table 8.   Reagent costs for various precipitation steps.

Precipitation step	Reagent	Cost, $/m³
Step 1 Fe precipitation.	$CaCO_3$	0.16
	Na_2CO_3	2.40
	$Ca(OH)_2$	0.75
	CaO	0.65
Steps 2+3 in 2 steps.	Na_2S (pH 3.5) .... $Ca(OH)_2$ (pH 10) .... Total	3.20 0.39 3.59
Steps 2+3 in 1 step.	NaOH (pH 10)	2.78
Step 2+3 in 1 step.	$Ca(OH)_2$ (pH 10)	NA[1]

[1]NA Not available.

The least expensive oxidant is biological catalyst T.ferrooxidans. However, the residence time observed for Fe(II) oxidation in these preliminary tests was 2 to 6 days and must be optimized, and the effect of process parameters (e.g., temperature) must be determined.

For step 1 precipitation of ferric hydroxide, calcium carbonate is the least expensive neutralizing agent. For zinc precipitation and final water treatment, sodium hydroxide is the least expensive reagent.

Lime Treatment versus the Proposed Flowsheet. The operating costs for the 1992 season at Les Mines Gallen plant were $487,000 (P.Godbehere, internal memo, 1992). The costs associated with lime treatment and sludge handling would be eliminated by recycling all of the zinc and iron. Therefore, in conducting a preliminary cost-benefit analysis, a credit for lime and sludge handling will be assumed.

The estimates of reagent costs, reported in table 10 are based on the experimental results for dilute seep water. However, owing to stratification of the rock, the concentration of the pit water increases continuously throughout the operating season, which must be taken into account for an accurate cost-benefit analysis.

Based on the zinc loading during the operating season of the plant (22,221 kg), the zinc credit was calculated as $9,675 assuming 50% of the zinc value, $1,046.72 per mt.

To estimate the feasibility of the project, possible benefits (credits) associated with replacing lime treatment with the costs (debits) of the zinc value recovery process are detailed in table 9.

The costs of chemicals used in full operation will be higher owing to lower efficiency. Also, the cost of solid-liquid separation is not taken into account. Although the credits otherwise outweigh the debits, the feasibility of the proposed value recovery project will depend on the costs associated with soild-liquid separation.

Table 9. Possible credits and debits associated with replacing lime treatment with the two-step recovery process of $CaCO_3$-NaOH.

Description	Credit	Debit
Zn credit (22,221 kg Zn)	$9,675	NAp.[1]
Lime	150,000	NAp.
Sludge handling	55,000	NAp.
Fe credit from $Fe_2(SO_4)_3$ from weak acid plant	120,000	NAp.
$CaCO_3$/NaOH for Fe and Zn precipitation from AMD.	NAp.	$21,477
Total	334,675	21,477

[1]NAp. Not applicable.

Conclusions

The present work has demonstrated on a laboratory scale the technical feasibility of a three step process for recovering zinc from AMD. The three-step process gives superior grade zinc sulfide, but it is less economic, owing to the cost of sodium sulfide, than the two-step process, which gives higher recovery and lower, but still acceptable, grade of zinc hydroxide.

Future work directed toward the following areas for improving the efficiency and economics of the process is recommended in the following areas:

1. Solid-liquid separation studies on ferric hydroxide and zinc sulfide and hydroxide precipitates.
2. Use of calcium sulfide as a precipitant for zinc sulfide.
3. Sulfate reducing bacteria as the sulfide ion source.

4. Separation of zinc sulfide and calcium sulfate by selective flotation.
5. Separation of zinc hydroxide and calcium sulfate by selective flotation.

Sulfide precipitation appears to have a growing application because it yields improved effluent quality compared to lime. The incremental costs of metal recovery by using an alternative, cheaper source of sulfide (e.g., calcium sulfide) should be evaluated. The perception of the mining industry as involved with recycling metals and extending natural resources may have important social and economic consequences.

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