

Expanding Sulphide Use for Metal recovery from Mine Water

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Abstract Sulphide precipitation has long been known as an effective tool for removing metals from waste water, but its use has been limited by reagent cost and operational challenges. This paper describes some initial results from laboratory work aimed at developing a new integrated system for metal recovery from waste waters and process streams using a biogenic sulphide reagent. Results described here are focused on the metal precipitation, recovery and water treatment side of the process, and concludes that with low enough net sulphide generation costs, recovery of multiple valuable products would be possible from many waste streams.

Key Words Sulphide precipitation, metal recovery, biogenic sulphide, water treatment

Introduction

Acidic mine drainage is considered to be one of the most challenging environmental issues facing the mining industry. Currently, the most common approaches attempt to prevent or minimize metal contaminated mine drainage, but when it does occur it is handled as a problem waste requiring treatment. In most cases treatment consists of some form of chemical neutralization, usually using lime, to neutralize acidity and precipitate dissolved metals and gypsum as a mixed sludge, which itself must be treated as a waste product requiring safe disposal. This treatment method is simple and predictable, but provides no recovery of metal value, results in substantial production of waste sludge and may not be sufficient to meet strict water quality targets for some heavy metals (SENES 1994).

Sulphide precipitation is an effective method of removing many dissolved heavy metals from solution as highly insoluble metal sulphide compounds, but reagent cost and practical operating considerations have limited its use for mine water treatment applications. Certain anaerobic bacteria have the ability to generate sulphide and alkalinity from oxidized forms of sulphur such as sulphate, and this has been identified as a way to make sulphide precipitation a practical option for mine water treatment. This has included the development of constructed wetlands for passive water treatment, as well as the use of bioreactors to treat more substantial streams. Successful applications of biological-based sulphide precipitation initially involved recovery of a single valuable metal, and relatively expensive biological treatment of the entire waste stream (Scheeren 1992).

Active biological water treatment using sulphide precipitation has mainly been developed as a chemical-biological system, allowing investigation of sequential sulphide precipitation to recover multiple metals into separate products of sufficient value to be recovered (Hammack 1994, Rowley 1997). This approach has the potential to open a range of flowsheet options that treat mine water as a resource rather than a pollution problem, but to date successful commercial applications remain limited to a few plants recovering a single high value metal, often as an add-on to an existing lime treatment plant.

In 2009 Kemetco Research Inc. began laboratory work aimed at commercializing a new approach to metal recovery from waste water and process streams that incorporates metal sulphide precipitation with biogenic sulphide. Kemetco's 'Biometals Process' includes several distinct process components with the overall objective of lowering the net process input costs, allowing increased economic recovery of metal values in a given process stream. An important part of this work is to determine the potential for recovery of lower-value components from existing waste streams. Work described below focuses specifically on batch testing of multi-product sequential precipitation of metals and other dissolved solids from two very different examples of mine drainage obtained from closed North American minesites.

Methods and Materials

Test Samples

Sample A was obtained from a former underground mine that continues to discharge more than 10,000 m³/day of slightly acidic drainage that carries significant levels of copper, zinc and cadmium along with minor amounts of other metals (Table 1). Sample B is from a former open pit mine, where post-closure remediation left a continuing flow of 2500 m³/day requiring on-going treatment. This is a high acidity stream with high metal loading, including high sulphate, aluminum, iron and manganese, in addition to substantial copper and zinc (Table 1). Both sites currently have a lime treatment plant in operation.

Test Procedures

Treatment results described are from batch tests carried out in closed flasks using 1 or 2 litres of mine water sample from the indicated site. Flasks were continuously stirred and fitted with gas inlet and outlet tubes to allow continuous feed of bioreactor off-gas for sulphide addition stages. Bioreactors operate continuously and produce a gas stream normally containing 0.5 – 1.0% H₂S in a gas mixture that also contains residual H₂, CO₂ and CO. For each stage pH and ORP were monitored intermittently, and where required, pH was adjusted by the batch addition of the chosen chemical reagent or a measured volume of bioreactor discharge (alkalinity approximately 10 g/L CaCO₃ equivalent). Chemical reagents were slurried with water prior to addition to improve reaction efficiency.

Following each stage, precipitated solids were removed by settling and/or filtration, and a filtered solution sample was collected for analysis. All solutions were analyzed using ICP-ES, providing a 33 element scan.

Results

Sample A – High Flow

Tests on this sample used relatively simple flowsheets. The significant values, as well as the principal contaminants, are copper and zinc, with a small amount of cadmium that is also an important pollutant. Precipitation of copper sulphide followed by zinc sulphide is a straightforward procedure, but in this case the separation is complicated by the relatively high initial pH of the mine water. At pH levels below 3, copper sulphide forms readily, but zinc sulphide will not form with the sulphide levels being used. With the higher pH of Sample A, sulphide addition needs to be carefully controlled in the first stage to prevent zinc from precipitating into the copper product. In practise, this can be done using ORP measurement, as there will be a sharp drop in ORP when there is no copper in solution to react with free sulphide ions.

Copper sulphide precipitation causes a small drop in solution pH, and the pH will further drop in the second stage as zinc sulphide is formed. To obtain complete zinc removal, therefore, it was necessary to increase the pH in the second stage. This was achieved through addition of a small amount of bioreactor discharge solution (in the results shown in Table 2, this required less than 0.4% of the sample volume) Cadmium is effectively removed as a sulphide in this flowsheet, and can be precipitated preferentially into the copper or zinc product by carefully controlling the sulphide addition into the first stage. In this sequential recovery flowsheet a third stage is required to further adjust the pH to a suitable neutral level, and thereby remove the aluminum content and any iron present (there was no iron in the samples collected from this site, but often it is present at low levels).

An example of Sample A results with this three-stage flowsheet is presented in Table 2. Values indicate the degree of metal removal (as a per cent) for each metal in each stage. A value of 100% removal indicates that the content for that metal was below the detection limit for the analysis.

Table 1 Analysis of mine drainage samples collected for testing (metal values in mg/L, flow in m³/day)

Sample	Flow	pH	Cu	Zn	Co	Ni	Cd	Al	Fe	Mn
Sample A – High Flow	12,000	4.3	14.3	17.8	<0.1	<0.1	0.09	13.3	0.4	3.65
Sample B – High Strength	2,500	2.7	67	181	4.65	9.68	1.37	950	872	184

Table 2 Sample A – Three product configuration, 1 litre test (metal values indicate % removal from solution)

Stage	pH	Reagents Added	Addition (g/l)	Cu (%)	Zn (%)	Cd (%)	Al (%)
Feed	4.3	-	-	0	0	0	0
Copper Recovery	3.7	H ₂ S	-	98	0	56	0
Zinc Recovery	4.0	H ₂ S/bd	bd: 3.7	100	98	100	5
pH Adjustment	6.2	bd	70.4	100	100	100	98

In the example shown, all pH adjustment used alkaline discharge from the sulphide-generating bioreactors. In practise the bioreactors would only be used to generate enough sulphide for the required precipitation, so the alkalinity generated would be sufficient to maintain the feed pH after sulphide precipitation, but not necessarily for aluminum precipitation. This may require a small addition of chemical reagent such as lime or limestone.

For this stream, one option being investigated is to utilize material from the growing stockpile of lime neutralization sludge. While use of this material would likely add some further complexity to the circuit, it would have the positive effects of increasing the value of metals recovered, avoiding the cost of buying an alkaline reagent, and reducing the mass and potential toxicity of the existing waste sludge by removing heavy metals. When re-using waste sludge, it would be added as a first stage, raising the pH to approximately 5.0–5.5 to remove aluminum and iron, while solubilising copper, zinc and cadmium. These metals would then be recovered in the subsequent sulphide precipitation stages. Bioreactor alkalinity would then be sufficient to raise the final pH to a neutral level for discharge.

Sample B – High Strength

Mine water from site B is more typical of sites where multi-product sequential precipitation has strong economic potential, but so far has not been tried on a large scale due to the complexity of the solution and the high levels of low-value contaminants present. In this batch work a number of possible treatment/recovery flowsheets are being investigated. A simple approach would be to precipitate copper as a single stage prior to the existing lime treatment plant to recover the highest value component only. One challenge even for this scenario is the variable amount of ferric iron present in the stream, which will consume sulphide reagent while reducing the iron to the ferrous state without removing it from solution. This increases costs and reduces the grade of the resulting copper product by adding elemental sulphur. Low cost sulphide would therefore be important for this scenario as well as the more complex flowsheets.

Sample B mine water also carries significant zinc value, and results for a copper and zinc recovery flowsheet are presented in Table 3. In this case a separate stage is added to remove gypsum and aluminum with limestone, which is effective at low pH and can be an order of magnitude lower cost than lime. A minor amount of zinc is lost to this precipitate, but contamination of the zinc product in the third stage is also reduced. Another option for zinc recovery is to control the pH around 3.5 with a non-calcium reagent and precipitate the zinc without removing aluminum and sulphate.

Table 3 Sample B – Four stage, three product configuration, 2 litre test (metal values indicate % removal from solution)

Stage	pH	Reagent Added	Addition (g/l)	Cu (%)	Zn (%)	Co (%)	Ni (%)	Cd (%)	Al (%)	Fe (%)	Mn (%)
Feed	2.6	-	-	0	0	0	0	0	0	0	0
Copper Recovery	2.4	H ₂ S	-	100	0	0	0	100	0	0	0
Al/CaSO ₄ Removal	5.0	CaCO ₃	5.0	100	4	0	0	100	99	0	1
Zinc Recovery	3.0	H ₂ S	-	100	97	0	0	100	98	0	1
Final Treatment	7.8	CaO	4.5	100	100	98	99	100	100	100	42

Table 4 Sample B –Multi stage configuration for minor recovery, 2.1 litre test (metal values indicate % removal from solution, bd – bioreactor discharge solution)

Stage	pH	Reagent Added	Addition (g/l)	Cu (%)	Zn (%)	Co (%)	Ni (%)	Cd (%)	Al (%)	Fe (%)	Mn (%)
Feed	2.7	-	-	0	0	0	0	0	0	0	0
Copper Recovery	2.3	H ₂ S	-	100	0	0	0	100	0	0	0
Al/CaSO ₄ Removal	5.1	CaCO ₃	5.3	100	9	0	0	100	99	1	0
Zinc Recovery	3.0	H ₂ S	-	100	95	0	0	100	99	1	0
Co-Ni Recovery	5.1	H ₂ S/CaCO ₃	0.21	100	100	53	71	100	99	1	0
Iron Removal	7.7	CaO	1.9	100	100	99	99	100	100	100	81
Mn Recovery	8.3	bd	57	100	100	98	99	100	100	100	95

With Sample B mine water more substantial multi-stage sequential metal recovery scenarios are also being investigated. These are aimed at maximizing the recovered values as well as testing the full potential of selective metal recovery. Table 4 shows results from one of these tests, which includes separate stages for Co-Ni recovery and Mn recovery. Cobalt and Nickel are present at very low levels relative to other metals, but due to the high value of these metals, together they represent almost as much potential revenue as the zinc. Manganese is somewhat lower value, but using the dissolved carbonate in the bioreactor discharge to precipitate manganese carbonate is an effective way to achieve the required discharge water quality while minimizing lime addition and generating a potentially marketable product.

While these results have not yet been fully optimized, relatively clean precipitates have been produced for all of the targeted metals. This flowsheet also has the effect of isolating aluminum and iron into separate precipitates that could potentially be reprocessed to generate marketable industrial products. While this may not be practical for all sites, it could be particularly important where sludge disposal is a major cost. Another effect of this type of flowsheet is that most of the pH adjustment can be done in low pH solutions. This would allow the substitution of limestone for lime as the principal source of alkalinity, which could result in substantial cost savings.

Conclusions

Initial batch testing of multi-stage sequential metal removal from complex mine drainage has shown good potential for selective recovery resulting in high product quality. Both minor high-value metals and abundant low-value metals can be recovered selectively. If combined with effective product handling and low net-cost biological sulphide generation, this approach would have economic potential for many sites. The strongest economics may correspond to sites where long term sludge disposal is a major cost or environmental concern.

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