

GREEN TECHNOLOGIES FOR SULPHATE AND METAL REMOVAL IN MINING AND METALLURGICAL EFFLUENTS

Oscar Lopez,

BioteQ Water (Chile) SpA, Chile

David Sanguinetti, Michael Bratty and David Kratochvil

BioteQ Environmental Technologies Inc, Canada

ABSTRACT

Metal and sulphate contaminated wastewater, produced by acid mine drainage and mineral processing, occurs at an estimated seventy percent of the world's mine sites, making it one of the mining industry's most significant environmental and financial liabilities. Historically, resource companies have typically used lime treatment to reduce the concentrations of metals and sulphate in wastewater; however, lime treatment can require additional process steps to produce water that complies with regulations, and can create a metal-laden sludge that requires on-going storage and management, creating a long-term environmental liability for site owners.

In recent years, sulphide-based process technologies for metal removal have been successfully implemented at mine sites in Canada, the US, Mexico, Australia, and China and new ion-exchange technologies for reduction of sulphate have been extensively piloted in Canada and Chile. These technologies offer significant benefits compared to conventional alternatives as they remove metals and sulphate to very low levels, eliminate the production of contaminated sludge, produce clean water that meets regulatory standards for discharge or re-use, remove metals in a saleable form that can off-set the cost of water treatment, and deliver savings for both capital and operating costs. This unique approach provides a sustainable business model that generates revenues from waste, reduces corporate liability for customers and delivers overall improvements to the environment.

This paper will profile these technologies, and provide case-study examples of their application at mining operations.

INTRODUCTION

It is estimated that more than 70% of the world's mine sites have acid mine drainage or metal contaminated wastewater, numbering in the thousands of sites. Because the resulting metal contaminated solution is toxic to the environment, the water is fully regulated in most jurisdictions, and mining companies are required by environmental regulators to treat the water. In recent years the discharge limits for a number of metals, as well as anionic species such as sulphate, have been made stricter in many jurisdictions. In addition, many jurisdictions, such as the U.S., Canada, and Australia, are requiring mining firms to post bonds that guarantee long-term clean up costs. As environmental regulations tighten globally, leading mining companies are proactively looking for ways to enhance the sustainability of their mine operations, and reduce potential long-term liabilities. To assist these companies, BioteQ has developed the

This paper was presented at Enviromine 2009, in Santiago, Chile

BioSulphide® and ChemSulphide® technologies for the removal and recovery of metals and the Sulf-IX™ technology for the removal of Ca/Mg hardness and sulphate.

DISCUSSION

Description of Sulphide Precipitation Processes

The BioSulphide® Process (Lawrence et al, 2005, Lawrence et al, 2007, Bratty et al 2006) has both a biological and a chemical stage, as shown in Figure 1.

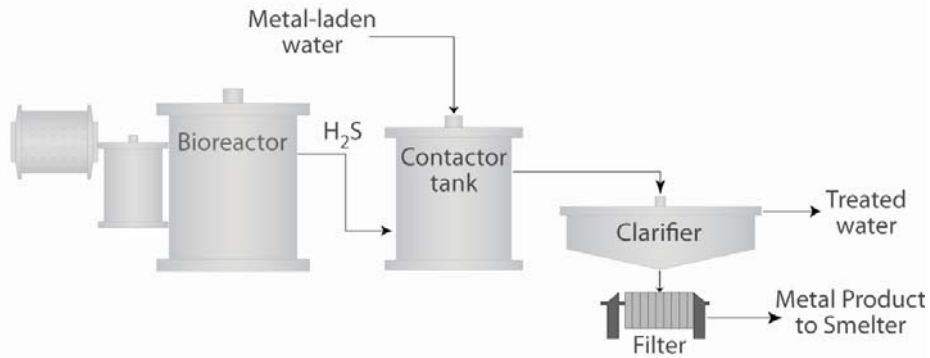


Figure 1: BioSulphide® Process

In the biological stage sulphur-reducing bacteria contained in an anaerobic bioreactor produce hydrogen sulphide gas (H₂S). The gas is transferred to a contactor tank that contains the contaminated water to be treated. In the chemical stage, the solution chemistry in the tank is adjusted to selectively precipitate metals as pure metal sulphides. The precipitated metals and treated water are pumped to a clarifier tank where the water is separated from the metal solids and discharged or recycled. The metal solids are filtered to remove excess water, producing a high grade metal product suitable for refining. To recover multiple types of metals, separate contactor and clarifier tanks are set up in series.

The ChemSulphide® Process follows a similar process, shown in Figure 2, but rather than using biologically generated hydrogen sulphide, the process uses chemical sulphide reagents.

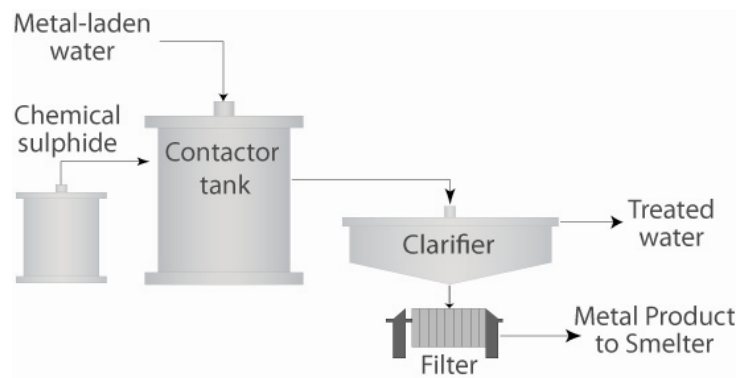


Figure 2: ChemSulphide® Process

Sulphide Precipitation versus Lime

Sulphide precipitation processes and precipitation with lime have both been used successfully to treat metal-contaminated acid water. While the two methods are effective in reducing metal loadings and acidity, sulphide precipitation has proven that it can have significant advantages compared to lime treatment in terms of environmental impact and cost savings, based on operating results from eight plants. Specifically, compared with lime, sulphide precipitation:

- Removes dissolved metals from the environment by selectively recovering individual metals as sulphide by-products that can be sold to offset treatment costs, and recycled into useful products. Metals that can be recovered include copper, nickel, cobalt, zinc, arsenic, antimony, lead, cadmium, selenium, and manganese. Recovery rates can exceed 99%.
- Can produce water that meets strict water quality regulations for re-use or discharge to the environment, consistently proven by bioassay testing of trout and daphnia in undiluted treated water.
- Reduces long-term environmental liabilities by removing toxic metals from the environment, and does not produce any residual sludge waste that requires ongoing storage and monitoring.
- Can lower sulphate loadings on the environment compared to lime treatment for metals such as zinc and cadmium, as lime treatment for these metals requires elevating the pH to a level of 10 -11 which exceeds the usual maximum discharge level of 9.0 or 9.5 and thus requires re-acidifying (frequently with sulphuric acid).
- When combined with lime treatment, sulphide precipitation reduces lime consumption, with concurrent reduction of greenhouse gas emissions and improved “carbon footprint” of the site. The reduction in lime consumption varies with composition of the feed water.
- Yields a lower capital cost than an equivalent lime-based system because faster process kinetics and better settling rates for metal sulphides result in smaller vessels and a smaller plant footprint. Capital cost savings can be up to 50% for sulphide precipitation processes compared to lime treatment.
- Delivers lower operating costs by reducing or eliminating sludge volumes and the associated handling and disposal costs. Cost savings are site specific, depending on the toxicity of the sludge.

Wellington Oro Case Study

The construction of a water treatment plant using ChemSulphide® technology at the Wellington Oro Mine site has been reported in earlier papers (Bratty et al, 2008). The plant is now in operation and actual operating results can be reported.

The Wellington Oro Mine site is a closed silver-zinc mine located near Breckenridge, Colorado, USA. The ChemSulphide® technology was selected from an international call for proposals as the best technology to address metal contaminated water at the Wellington Oro site after a review by the US Environmental Protection Agency (US EPA).

The water treatment plant is successfully treating mine drainage containing cadmium, zinc, and other trace metals, removing dissolved metals to meet strict effluent specifications set by Colorado Water Quality Standards (shown in Table 1).

Table 1: Wellington Oro water chemistry

Parameter	Feed Chemistry	Effluent Targets	Actual Results
pH	6.19	6.5 to 9.0	6.65
Cadmium	0.112 mg/L	0.004 mg/L	< 0.0005 mg/L
Zinc	270 mg/L	0.225 mg/L	< 0.10 mg/L

The ChemSulphide® precipitation process was selected instead of lime treatment for application at the Wellington Oro site because it does not generate a waste sludge that would otherwise require disposal and ongoing monitoring. An equivalent capacity lime plant would have produced an estimated 1.5 million litres of metal-laden sludge annually, leaving an environmental liability and adding to long-term operating costs, as shown in Table 2.

Table 2: Comparison of Design Specifications for Treatment Options

	Lime Treatment (at maximum flow and load)	Sulphide Precipitation (at maximum flow and load)
Plant Capacity	150 USGPM (35 m ³ /h)	150 USGPM (35 m ³ /h)
Volume of sludge product	390,000 US gallons/yr (1,500 m ³ /yr)	0
Saleable zinc recovered	0	178,000 pounds /yr (81,000 kg/yr)
Zinc content of output	8.5%	61%
Potential zinc revenue	0	US\$50,000 /yr
Capital cost (estimate)	US\$2.6 million	US\$1.7 million
Estimated annual operating cost	US\$150,000 /yr	US\$132,000 /yr
Metal-laden sludge storage cost	variable	0

Instead, the sulphide precipitation plant produces a saleable zinc-cadmium sulphide product, which can be sold to off-set treatment costs, and recycled into useful products.

In addition to delivering operating cost savings, the capital cost of the sulphide precipitation plant for this site was estimated to be approximately 33% less than a lime plant with equivalent capacity.

Dexing Case Study

The ChemSulphide® Process has also been used at Jiangxi Copper's Dexing copper mine, located near Dexing City in southeastern China, which at 120,000 tonnes of copper per year is the largest open pit copper mine in China. The water treatment plant at Dexing operates at a maximum flow of 1,000 m³/h and treats surface water run-off and drainage from waste dumps and the low grade stockpile. In this application of ChemSulphide®, it is being used for copper precipitation and recovery upstream of an HDS lime plant. This configuration results in a number of benefits versus using only a conventional HDS lime plant, some of which are summarised in Table 3.

Table 3: Benefits achieved by ChemSulphide® at Dexing Mine

Parameter	Benefit vs. Lime Treatment Alone
Copper recovered	580 tonnes per year
Lime use reduction	1,240 tonnes per year
Reduction in lime sludge produced	6,000 m ³ per year

From a short term perspective, the revenue generated from the recovered copper supplemented by the savings in lime consumption mean that instead of being a cost, Dexing's water treatment facility generates a profit for the mine. In the longer term, the copper removed in the ChemSulphide® plant is copper that won't report to the lime plant sludge, and as a result the long term liability to the mine due to the storage of the lime plant sludge is considerably reduced. Of course, the reduction in metals reporting to the lime plant also reduces the quantity of sludge produced, resulting in a smaller requirement for storage of sludge and reduces the associated construction and monitoring costs for storage.

BioSulphide® Benefits vs. Alternative Technologies

Further environmental and cost benefits, beyond those offered by ChemSulphide®, can be achieved by using the BioSulphide® Process. A simple schematic illustrating the production of sulphide reagent as hydrogen sulphide gas through the biological reduction of elemental sulphur is shown in Figure 3.

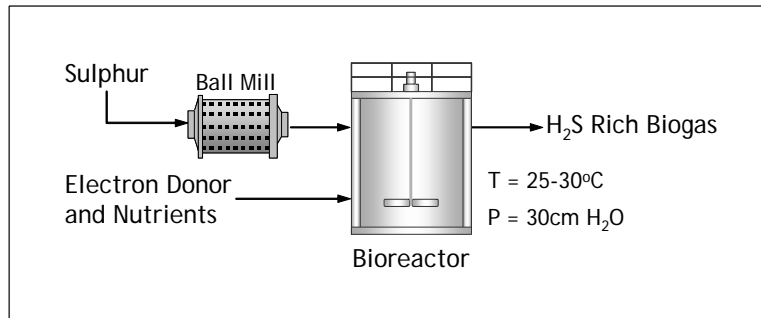


Figure 3: Biological generation of hydrogen sulphide gas

The sulphide reagent is produced by reacting elemental sulphur in a bioreactor with an electron donor, such as acetic acid, in the presence of sulphur-reducing bacteria under anaerobic conditions according to reaction (1).



The sulphur-reducing bacteria act as a catalyst enabling reaction (1) to proceed at 25° C and at a system pressure of +30 cm WC. A continuous production of H₂S is achieved by removing the gaseous products of the reaction (1) from the bioreactor. Since elemental sulphur is used as the sulphur source for making H₂S, instead of sulphate, no process water other than that contained in the reagents required for reaction (1) enters the bioreactor. Thus the bioreactor is a true stand-alone H₂S generator.

Using biological H₂S generation instead of chemical sources of sulphide gives a number of environmental as well as financial benefits, including:

- Low cost of sulphide compared to the cost of Na₂S, NaHS, or H₂S;
- Minimal hazards and increased safety on site primarily due to the low system pressure and low inventory of H₂S. At any point in time the amount of H₂S stored in the bioreactor(s) is a small fraction of the daily H₂S production. This allows the avoidance of special environmental permitting for sulphide reagent storage;
- Reduced environmental risk associated with transportation since elemental sulphur and the most frequently used electron donors (acetic acid and ethanol) pose lower hazards than chemical sulphide sources;
- Low capital cost mainly due to the ambient temperature and pressure in bioreactors that are designed as conventional stirred tanks compared to pressure vessels with expensive agitator seals;
- Easy to scale-up and down over a wide range of H₂S production capacities.

Sulphate Removal Technology

As reported previously (Bratty et al, 2008), the Sulf-IX™ Process which uses ion-exchange technology was developed to remove sulphate from wastewaters and industrial process effluents to meet new environmental discharge regulations for sulphate. The process uses cationic and anionic resins to remove calcium and sulphate, respectively, and employs low cost reagents, namely sulphuric acid and lime, for resin regeneration. The products of the process are clean water, below 250 mg/L sulphate, and clean gypsum solids. A key environmental benefit of the process is that there is no spent regenerant for disposal. The process offers significant technical advantages compared with all other available technologies, including reverse osmosis, and promises to be the most cost effective method for sulphate removal.

A feature of sulphate contaminated waste water in mining is that the metal cations are nearly always balanced by the sulphate anion (SO₄²⁻). This is due to the fact that most metals are won from ore bodies containing minerals that contain sulphur atoms that oxidize to sulphate during the metal extraction process or due to natural oxidation processes in the waste rock and tailings. Furthermore, sulphur-containing reagents such as sulphuric acid are often added to the metal extraction process. For example, the extraction of copper by leaching with sulphuric acid is widely practiced on a very large scale in many countries. The winning of 1 kg of copper can result in the addition of up to 3 kg of sulphate or more, depending on the degree of additional sulphate-producing reactions taking place in mining wastes due to oxidation of residual sulphide minerals.

The fundamental requirement of any process to remove sulphate from water is that it has the capability to meet the regulatory limits imposed. Traditionally, metals and the associated acidity in wastewater have typically been removed by precipitation and neutralisation by adding lime, normally as calcium hydroxide. Reaction with lime removes metals by precipitation as hydroxides and also causes the removal of sulphate as gypsum dihydrate (CaSO₄·2H₂O). However, the effluent from a lime plant will always contain soluble sulphate, usually in the range 1,600 – 1,800 mg/L, due to the solubility of gypsum. Consequently, lime plants cannot produce effluents with a sulphate concentration lower than 1,600 mg/L, well in excess of current regulated values for sulphate in many jurisdictions. Figure 4 shows a simple schematic of the Sulf-IX™ Process.

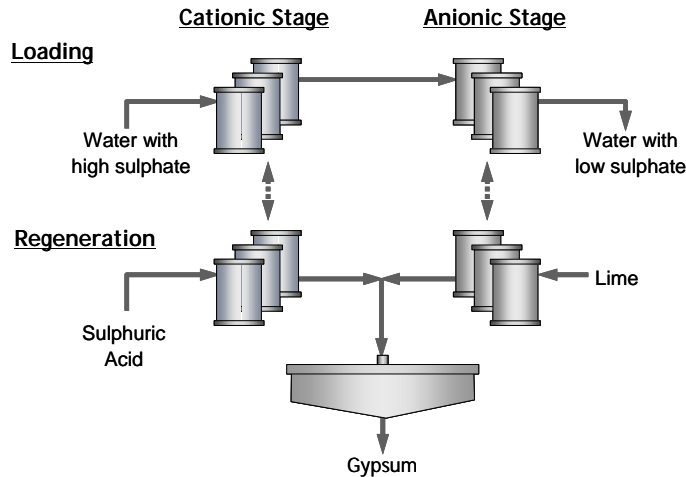


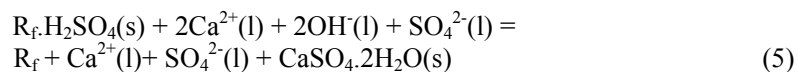
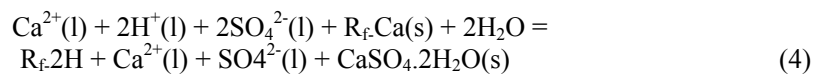
Figure 4: Simple schematic of the Sulf-IX™ Process

The process is particularly suited for the removal of sulphate from lime plant effluent but is applicable for the treatment of any process stream, groundwater, or wastewater high in Total Dissolved Solids (TDS) and Ca/Mg hardness. The complete process cycle includes resin loading, regeneration and rinsing. Feed water is first passed through a series of contactors containing cation exchange resin to remove primarily calcium and magnesium by loading the cations onto the resin, and then through contactors containing anion exchange resin to remove sulphate (equations 2 and 3).



Where, (s) and (l) represent solid and liquid phases, respectively, and R_f depicts the resin functional groups.

Ion exchange resins have finite capacities to remove ions from feed water hence must periodically undergo regeneration (equations 4 and 5).



As can be seen from reaction (4), sulphuric acid is used for cationic resin regeneration. Solid gypsum dihydrate formed during regeneration is separated from the spent regenerant solution in a clarifier and, following the addition of H_2SO_4 , the “refreshed” regenerant solution is 100% recycled to resin regeneration in subsequent resin cycles. Similarly, reaction (5) shows that lime is used for anionic resin regeneration, with gypsum formed and separated in a clarifier. Following the addition of $\text{Ca}(\text{OH})_2$, the “refreshed” regenerant solution is 100% recycled to resin regeneration in subsequent resin cycles.

The technology was initially based on the GYP-CIX technology developed in South Africa (Robertson et al, 1993), which also uses sulphuric acid and lime for resin regeneration. The

Sulf-IX™ Process, however, overcomes difficulties of the GYP-CIX process associated with limited process flexibility for varying feed chemistry, mechanical entrainment of gypsum in the regeneration stage, and limitations on sulphate removal when magnesium is present in significant concentration in the feed water. These and other process developments have resulted in a significant reduction in the estimated costs of constructing and operating a commercial plant. Estimates carried out on a number of potential applications indicate that the operating cost to reduce sulphate from the concentration of a typical lime plant effluent to less than 500 mg/L will be in the range US\$0.60 to US\$6.00 per m³ depending on several site specific factors, including the scale of the plant flow and the concentration of magnesium in the feed. Magnesium can also load on the cationic resin but its removal is much lower than calcium due to the high solubility of magnesium sulphate relative to calcium sulphate and can therefore build up in the cation resin regeneration circuit. If this is the case, treatment of a bleed from the cation regeneration circuit is required to remove magnesium from the circuit, and is part of the Sulf-IX™ technology.

Environmental Benefits of Sulf-IX™ Process

In addition to being cost competitive, there are environmental benefits to the Sulf-IX™ Process:

- No hard to dispose of brine is produced as a by-product. The only by-product of the process is clean gypsum, which can be sold as a construction material or safely disposed of in a conventional land-fill.
- Reduced electricity consumption. Case study comparisons have indicated that the electricity consumption can be less than half of that for a membrane process to treat the same flow.

Pilot Results of the Sulf-IX™ Process

Pilot results which have been previously reported (Bratty et al, 2008) demonstrate that the process is capable of meeting low effluent targets, while the formation of solid gypsum during the regeneration step can be controlled, and blinding of the resin beads can be avoided, resulting in long resin life. More recent testing has continued to confirm Sulf-IX™'s capabilities, including a detailed study of the use of the cationic stage of Sulf-IX™ as a stand-alone softening step which demonstrated calcium effluent concentrations below 20 mg/L.

Sulf-IX™ Used for Water Softening

One of the advantages of the Sulf-IX™ technology is that in the right application the cationic and anionic stages can be operated independently. For example, the cationic stage can be used as a stand-alone water softening system for the removal of calcium or the anionic stage can be used to treat a stream of dilute waste sulphuric acid. Using either the full Sulf-IX™ Process or one of the stages independently has the benefit of reducing the TDS of the treated water without producing a concentrated liquid waste stream.

Metal Refinery Case Study

An intensive piloting study was run on the waste water from a metal refinery with the intent of replacing the soda ash softening circuit with a cationic stage Sulf-IX™ circuit. When compared to a conventional soda ash softening circuit this offers a number of benefits, particularly upstream of a membrane process. Reviewing reaction (2) above, it can be seen that the calcium ions which are removed by the system are replaced by hydrogen ions, resulting in a lowering of the pH. Since membranes generally require acid addition in order to lower the feed pH, this pH adjustment due to Sulf-IX™ is a benefit to the system. Conversely, a soda ash circuit replaces the calcium ions with sodium ions. The sodium ions do nothing to reduce the pH, and since the charge balance requires replacing every calcium ion with two sodium ions the TDS contribution

in mg/L is increased by a factor of 1.15 from the calcium to the sodium. Thus, as a result of replacing the soda ash softening with Sulf-IX™, the TDS loading on the membrane is lowered, resulting in longer membrane life, less brine production, and the elimination of the acid addition for pH adjustment. The net operating savings for a 68 m³/hr facility are calculated to be approximately US\$4.20/m³.

CONCLUSIONS

As environmental regulations for the mining industry become stricter while commodity prices soften, industry leaders are seeking new technological approaches in order to stay competitive. Two significant water treatment technology platforms have been developed that can enhance environmental compliance and deliver lower life cycle costs for water treatment, namely: 1) the BioSulphide Process® and ChemSulphide® Process for water treatment and concurrent base metal recovery and 2) the Sulf-IX™ group of technologies for Ca/ Mg hardness and sulphate removal from mining wastewaters for water discharge or for recycle. These technologies can provide environmental and economic benefits compared to conventionally used technologies. The BioSulphide® and ChemSulphide® processes produce saleable metal products and clean water that can be re-used or safely discharged while reducing or eliminating the quantity of waste sludge produced. The Sulf-IX™ technology removes sulphate from wastewater without the production of waste brine and with reduced electricity consumption.

The sulphide-based processes have been demonstrated at eight operating commercial plants with flow rates up to 1,000 m³/hr and sulphide demand up to 3.7 T H₂S per day. The sulphate removal processes have been demonstrated under extensive pilot testing over several years. The sulphide and sulphate technology platforms may be integrated with conventional lime treatment, to provide a sustainable water treatment alternative to conventional practice.

REFERENCES

- Bratty, M., Lawrence, R.W., Kratochvil, D. (2008).** Reducing water treatment costs while meeting the challenge of environmental compliance for the mining industry. *Proc. WIM 2008 – 1st International Congress on Water Management in the Mining Industry*. Santiago, Chile, July 9-11, 2008.
- Lawrence, R.W., Kratochvil, D., Ramey, D. (2005).** A new commercial metal recovery technology utilizing on-site biological H₂S production. *Proc. HydroCopper 2005 – 3rd International Workshop on Copper Hydrometallurgy*. Santiago, Chile, November 23-25, 2005.
- Lawrence, R.W., Marchant, P.B., Bratty, M., Kratochvil, D. (2007).** Applications for biogenic sulphide reagent for copper recovery in copper and gold hydrometallurgical operations. *Proc. Cu2007, the 6th Copper/Cobre Conference*, August 25-30, 2007, Toronto, Canada.
- Bratty, M., Lawrence, R.W., Kratochvil, D., Marchant, P.B. (2006).** Applications of biological H₂S production from elemental sulphur in the treatment of heavy metal pollution including acid rock drainage. *Proc. International Symposium on Acid Rock Drainage (ICARD)*, St. Louis, March 26, 29, 2006.
- Robertson, A.M., Everett, D.J., Du Plessis, N.J. (1993).** Sulfates Removal by the Gyp-Cix Process Following Lime Treatment. *Hazardous Materials Control Resources Institute, 1993 Superfund XIV Conference and Exhibition*. Washington DC, USA, November 30 to December 2, 1993.