Sulphide Precipitation and Ion Exchange Technologies to Treat Acid Mine Drainage

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Abstract

The need for effective and environmentally compliant technologies to treat metal and sulphate laden water, produced by acid mine drainage, is one of the most significant issues faced by the mining industry. In many jurisdictions, ever tightening regulations apply not only to the discharge of treated effluent into the environment but also to the disposal of waste by-products generated during the treatment process. Within the last decade, sulphide precipitation technologies for selective metal recovery have been developed and successfully applied at mine operations in Canada, the US, Australia and China to cost effectively treat large flows of acidic wastewater. More recently, ion exchange processes have been developed and applied to reduce metal and sulphate concentrations. These technologies remove metals and sulphate to comply with regulations, reduce or eliminate the production of waste sludge, produce clean water meeting strict criteria for re-use or safe discharge, recover value-added by-products from wastewater, and deliver savings in both capital and operating costs. This paper will profile commercial application of these technologies in mining operations.

Key Words: acid rock drainage, wastewater treatment, heavy metals, sulphate, environmental compliance, metal recovery

Introduction

All heavy industrial activities have environmental impacts requiring mitigation and rehabilitation; mining and mineral processing are not an exception. In spite of (or because of) an increase in the global appetite for mining commodities, these impacts are coming under greater scrutiny in both the developed and developing nations.

One of the most common environmental issues at mine sites is acid rock drainage (ARD). This occurs when water, oxygen, bacteria and sulphide minerals interact and oxidize the minerals into dissolved metal salts and sulphuric acid. The drop in pH associated with the acid generation assists with the dissolution and liberation of the metal species. This type of uncontrolled leaching can lead to metal pollution and acidic conditions in receiving waters, causing dead zones and long-term issues with bio-accumulated metals. Mitigation of the impacts of ARD would typically occur in the form of water treatment during and after the production life span of the mine. This can introduce significant costs to the mine owner well beyond the horizon of the operating revenue stream. Alternately, if the mine owner/operator cannot afford to treat the water, or if, in the case of legacy mines, the owner/operator no longer exists, the water liability can become the responsibility of governments bodies and of society.

Waters affected by ARD are usually treated by low-density or high-density sludge (LDS or HDS) lime plants, whereby lime is mixed with the contaminated water, effectively neutralizing the acid and precipitating the soluble metals as metal hydroxides. However, as effluent metal discharge limits become stricter, it is becoming more difficult for a simple lime plant to meet these regulations. This is due to the solubility of metal hydroxides being strongly pH dependent, and with the pH of the lowest metal solubility being different for the various heavy metals. For example, peak removal of copper using lime would require a pH of approximately 8.5; however, peak removal of lead requires a pH closer to 10.5 (Liu and Laskowski, 1989). Therefore, treating for multiple metals with strict discharge limits using lime alone could have limitations.

In addition to the water effluent quality and targets being difficult to meet, the hydroxide sludge products generated by LDS and HDS plants are challenging, and often expensive, to manage long-term. While the sludge products may be stable under ideal conditions, they are effectively weak bases that can re-solubilize under acidic conditions, typically the same conditions that led to the generation of ARD in the first place. In addition, the physical characteristics of metal hydroxide sludge products render them difficult to dewater and unsuitable as mill or smelter feedstock.

Although lime treatment of acid waste water remains the industry standard, the industry is pushing to identify new processes for improved metals removal, lower operating costs and a reduction in the overall life cycle costs, including waste sludge disposal. One of the most promising methods to achieve this goal is through sulphide precipitation. A general metal-sulphide precipitation reaction is shown in equation 1.

$$Me^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow MeS_{(s)} \qquad (1)$$

Metal sulphides are known to have exceptionally low aqueous solubility and are generally not as susceptible to re-dissolution when exposed to acid conditions. Because of these properties, the concept of sulphide precipitation for metals in ARD waste streams has existed for decades. However, the control challenges of executing rapid metal-sulphide reactions on a large scale (resulting in either inefficient reagent consumption and/or formation of colloidal metal-sulphide particles that are difficult to settle), coupled with high sulphide costs and low metal prices, have effectively dampened the industry taste for treating waters in this manner in the past.

BioteQ Environmental Technologies has developed two sulphide precipitation process technologies to meet these challenges. ChemSulphide® uses purchased sodium hydrosulphide (NaHS) reagent for the removal of base metals from contaminated wastewaters, while the BioSulphide® process utilizes biologically generated hydrogen sulphide (H_2S) gas for the same purpose. For both processes, the metal – sulphide precipitation reaction is controlled in a similar fashion in order to ensure high metal removal rates and effective solid-liquid separation. BioSulphide® is generally used for high metals loading and higher sulphide demand due to a lower operating cost per tonne of sulphide required.

In addition to sulphide precipitation processes, BioteQ has also developed ion exchange (IX) water treatment processes for the selective removal of metals from waste water. The IX process is suitable for removing low concentrations of metals from large flows of waste water without high power consumption and without treating/removing all other water constituents (as in the use of membrane technology).

In this paper, we showcase two BioteQ plants that have successfully employed sulphide precipitation and IX process technologies for the cost effective removal of dissolved metals from ARD streams. The Wellington Oro mine near Breckenridge ChemSulphide® plant was constructed and commissioned in 2008 in order to meet strict effluent discharge targets for zinc and cadmium. The Dexing mine in China treated ARD water using an HDS plant, resulting in substantial lost metal opportunity and high costs. Both sites now have operating ChemSulphide® plants (and Dexing has an additional IX plant) for metals recovery and for meeting specified effluent limits.

Site #1 – Wellington Oro Mine, USA

The Wellington Oro mine site near Breckenridge, Colorado had been closed for over thirty years prior to the realization that the site had a water seep acting as a source of acid, zinc and cadmium into local receiving waters. To mitigate this negative impact on the surrounding creeks and rivers, the US Environmental Protection Agency (EPA) issued an international call for proposals for the treatment of this metal contaminated water. While a lime plant may have achieved the strict effluent limits set by the EPA, the performance of such a plant was difficult to guarantee. In addition, the sludge generated from a lime plant would not have had a home, including the abandoned underground mine which has limited space for sludge storage long-term, as the site is located in an area of high land values and intensive recreational use. This indicates that any sludge generated would have had to be disposed of, likely as hazardous waste, off-site. For a legacy mine with no revenue, this was considered cost prohibitive.

As an alternative, BioteQ’s ChemSulphide® was selected as a best available technology (BAT) to manage the environmental legacy to the limits prescribed by the EPA. A schematic of the process flowsheet for the Wellington Oro water treatment plant is shown in Figure 1.

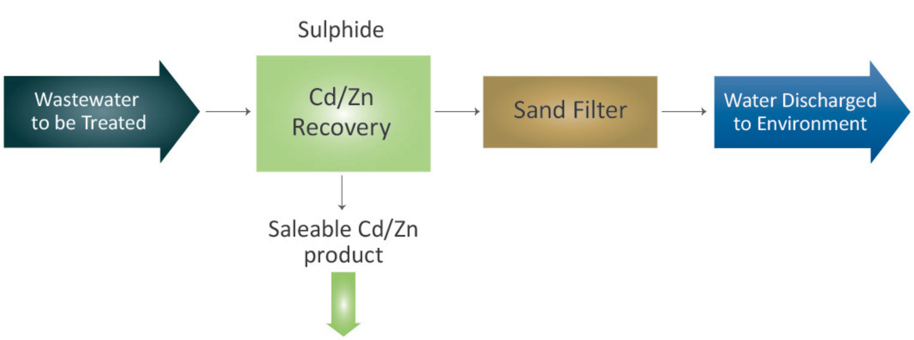

Figure 1: Wellington Oro water treatment plant flowsheet

The feed, target and effluent water quality data from the 820 m^3/day plant are shown in Table 1.

Table 1: Wellington Oro mine water chemistry

Parameter	Feed	Effluent target	Actual effluent
pH	6.2	6.5 – 9.0	6.65 to 7.00
Cadmium	0.12 mg/L	0.004 mg/L	<0.0005 mg/L
Zinc	135 mg/L	0.225 mg/L	<0.090 mg/L

In addition to the exceptional water quality achievable by the ChemSulphide® plant, elimination of sludge was also achieved. A typical lime plant treating the Wellington Oro waste water is estimated to generate approximately 150 million litres per year of metal hydroxide semi-solid sludge waste that would require shipping and disposal. By contrast, the ChemSulphide® plant generated approximately 30,000 lbs per year of zinc and cadmium concentrate, all of which is shipped to a US smelter for refining. The storage and monitoring costs for sludge management were thereby removed from the water management balance sheet.

Due to the overall low metals loading rate, the small quantity of concentrate is collected by a smelter for free; no shipping or handling expenses are incurred to the water treatment plant operators for this transaction. While the zinc/cadmium concentrate by-product is not sold for revenue at the Wellington Oro mine, the primary objective of eliminating the requirement for long-term sludge storage was the more important consideration for the stakeholders.

The capital expense of the ChemSulphide® plant was estimated to be approximately 33% lower than that estimated for a conventional lime HDS plant. This is due to the efficiency of the sulphide precipitation reaction, which occurs quickly enough that a ChemSulphide® plant typically only needs a single precipitation reactor, whereas an HDS lime plant requires a series of multiple lime reactors. As well, mixing and handling NaHS does not require the same infrastructure as does lime slaking, mixing, suspension and circulation. These equipment savings more than offset the extra expense of gas detectors, scrubbers and other safety equipment required for handling of sulphide reagents.

Comparing the operating expenses of the two plants is more challenging, as the true lime consumption, sludge disposal and monitoring costs for the equivalent lime plant were not determined. However, on a stoichiometric basis for metals removal, one can estimate and compare the lime and NaHS consumptions. This comparison is shown in Table 2.

Table 2: Wellington Oro mine water treatment reagents

Reagent/Item	Quantity (DMT/a)	Unit price ($US/DMT)	Operating Expense ($US/a)
Lime	50	$200	$10,000
Sludge disposal	90,000	$20	$1,800,000
NaHS	35	$1,400	$49,000

Clearly the use of sulphide precipitation on a stand-alone basis, where no metal revenue is realized, can result in higher operating costs than lime alone. However, sulphide precipitation coupled with other water treatment considerations (such as sludge disposal in this case) can yield compelling savings and a successful project for the local stakeholders.

Site #2 – Dexing Mine, China

The Dexing mine site near Dexing, Jiangxi province, China, is the largest copper producer in China. This site experienced ARD and successfully managed water treatment using a HDS lime plant to meet effluent targets prior to discharge into the Dawu river. The HDS plant had only a limited capacity (10,000 m^3/day) to treat the total quantity of water (over 24,000 m^3/day during the rainy season), and the remaining untreated water reported to the tailings pond for mixing with alkali material from elsewhere on the site.

The combination of high water flow rates and high copper concentrations was identified by BioteQ and the mine's chief engineer as a lost opportunity. By using the ChemSulphide® process as a complement to a new upsized HDS plant, the mine now recovers the copper in solution prior to neutralization of acid and discharge treated water discharge. A schematic of the process flowsheet for the Dexing copper mine is shown below in Figure 2.

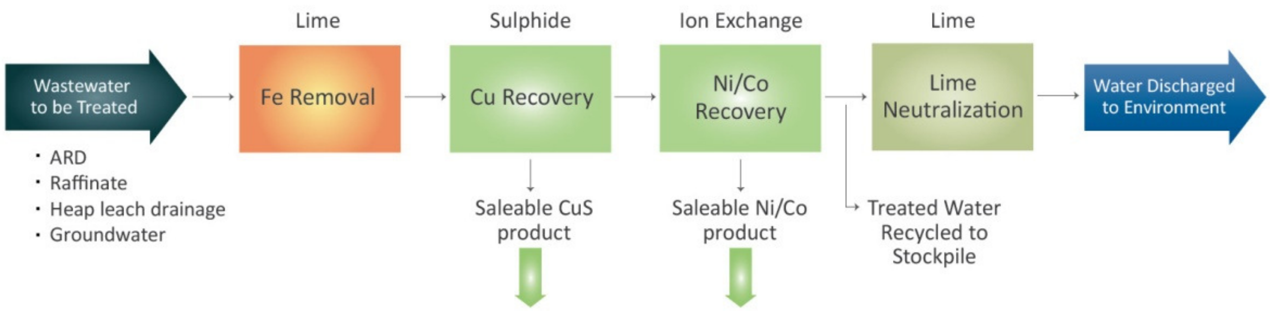

Figure 2: Dexing water treatment process flowsheet

The 24,000 m^3/day ChemSulphide® plant was built in 2007, and consists of a ferric iron removal stage prior to the copper recovery stage. The ferric iron is removed to reduce the NaHS consumption associated with ferric to ferrous iron reduction. Typical influents and effluents for the copper recovery plant are shown in Table 3.

Table 3: Dexing ChemSulphide® water chemistry

Parameter	Feed chemistry	Copper effluent chemistry
pH	2.2 – 2.6	3.0
Copper	149 mg/L	<3 mg/L
Ferric iron	909 mg/L	126 mg/L
Ferrous iron	386 mg/L	536 mg/L

In addition, nickel and cobalt are also recovered from a waste water slipstream via an IX circuit operating downstream of the ChemSulphide® plant and upstream of the HDS plant. In this circuit, the nickel and cobalt are loaded from the large, dilute slipstream flow onto a selective resin. During regeneration, sulphuric acid is applied to the resins to strip the metals into the solution. This low volume, high concentration nickel/cobalt solution also contains aluminum and iron that needs removal prior to selective precipitation of the nickel and cobalt as carbonates. This Al/Fe removal is performed by oxidation of ferrous iron to ferric using hydrogen peroxide, then by addition of limestone to raise the solution pH to 3.5. At this pH, most iron and some aluminum will precipitate as hydroxides, and these solids are removed in a clarifier and sent to the HDS lime plant.

Following the iron/aluminum removal, the nickel/cobalt is removed by addition of sodium carbonate, precipitating the high value metals as nickel carbonate and cobalt carbonate, respectively. The solids are again separated in a clarifier and dewatered in a conventional filter press, while the metal barren solution reports to the final HDS stage prior to discharge.

The 800 m^3/hr IX plant for nickel/cobalt recovery was built and commissioned in 2010/2011. The influent to the IX plant (effluent from ChemSulphide® plant) and concentrated regenerant stream data are shown in Table 4.

Table 4: Nickel/Cobalt IX plant water quality data

Stream	Ni (mg/L)	Co (mg/L)	Al (mg/L)	Fe (mg/L)	Cu (mg/L)	Ca (mg/L)	Mg (mg/L)
Influent	5.1	6.5	486	370	1.02	389	558
Regenerant	770	860	946	919	26	288	148

The overall nickel and cobalt recoveries (from ARD source to final HDS feed stream) are both approximately 65%.

The capital expenses for the three water treatment circuits (ChemSulphide® copper recovery, IX nickel/cobalt recovery and HDS acid neutralization) are shown in Table 5.

Table 5: Water Treatment Capital Expenses

Plant circuit	ChemSulphide®	Ion Exchange	HDS
Capital cost ($US millions)	$3.6	$3.0	$1.2

Not only does the number of water treatment stages drive up the capital cost at this site, but one can see that the cost of ChemSulphide® and IX plants is greater than that of the HDS plant. This is due largely to the extra unit operations required within each water treatment stage (ferric iron removal prior to copper recovery, and iron/aluminum removal prior to nickel/cobalt precipitation). However, in this scenario, the high capital cost is justified by the value of the metals recovered.

The metal concentrates from the copper and nickel/cobalt recovery stages are all of high enough quality and quantity that they are sold back to the mine concentrator, generating revenue to offset the cost of water treatment. The summary of revenues, operating expense and net cash flow for each of the three stages (ChemSulphide® copper recovery, IX for nickel/cobalt recovery and HDS for final acid neutralization) are shown in Table 6 (adapted from Consigny and Kratochvil, 2011).

Table 6: Operating costs and revenues for three stage water treatment at Dexing mine

Plant stage	Revenue ($US)	Operating expense ($US)	Net cash flow ($US)
*ChemSulphide® (Cu recovery)	$5,100,000	$2,800,000	$2,300,000
§Ion-exchange (Ni/Co recovery)	$1,300,000	$442,000	$858,000
*HDS lime plant	$0	$1,500,000	($1,500,000)
Total water treatment	$,6,400,000	$4,742,000	$1,658,000

Note: * = based on 2010 operating data, § = projected values based on commissioning data

As shown in Table 6, the sum of the water treatment stages is a net positive cash flow for the mine site, effectively turning the required water treatment from a cost-centre into a revenue-centre for the mine owner. Application of a 5% discount rate and using the capital costs and net profits for all three stages results in a 15 year NPV of approximately US $9.6 million.

Unlike the case of Wellington Oro, where sludge reduction was a major driver for water treatment, the Dexing mine does not have any such constraints. However, based on the metals removal rates at the mine, the sludge reduction at the HDS plant can be computed, and are presented in Table 7.

Table 7: HDS sludge reduction per water treatment stage

Plant circuit	ChemSulphide®	Ion Exchange
Sludge reduction (DMT/a)	1,400	96

Although the sludge savings may not be a consideration for the Dexing mine, the substantial reduction in mass and volume, which preserves tailings storage capacity, is also complemented by a reduction in sludge toxicity due to removal of heavy metals. This means that, in the case of any future requirements for sludge handling and disposal, the Dexing mine is already proactively ready to address these waste management issues.

Conclusions

Acid rock drainage is a common environmental liability at active and historic mine sites. The uncontrolled liberation of metals and free acid into the environment can cause damage to water ways and receiving bodies. While these types of pollutant streams have historically been treated with lime to neutralize acid and precipitate metal hydroxides, this method of treatment has fundamental limitations, namely borderline performance when facing new strict water quality targets and the production of (usually) valueless metal-laden sludge that can readily re-dissolve under acidic conditions, requiring dedicated disposal, storage and long-term monitoring.

This paper outlines the experience of two mine sites with ARD issues that could not be solved by lime treatment alone. The Wellington Oro site could not use a water treatment process that generated toxic sludge due to lack of disposal space in the mine area. The Dexing mine used lime treatment, at great expense, to meet their water quality targets. In both cases, a BioteQ ChemSulphide® plant resolved these water treatment issues. The Dexing mine has further enhanced its metals recovery and revenue by addition of an IX process for selective nickel/cobalt recovery.

These two plants demonstrate that treating water need not be a net cost to the mine operators. The case studies show that one can comply with tight regulations and become more sustainable while either turning a profit, or, at a minimum, reducing long-term site life cycle costs below the status quo.

References

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Acronyms

BAT	Best available technology
HDS	High density sludge
IX	Ion Exchange
LDS	Low density sludge