SULPHIDE PRECIPITATION AND ION EXCHANGE TECHNOLOGIES FOR COST EFFECTIVE REMOVAL OF SELECTED METALS IN WASTEWATER

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ABSTRACT

New "clean technologies" to treat mining and metallurgical effluents containing dissolved metals have been successfully applied at mine sites in North America and Asia, treating water flows up to 24,000 m^3/day. These clean technologies offer significant benefits compared to conventional alternatives and provide a sustainable solution that eliminates residual waste sludge, improves water conservation, generates revenues from wastewater, and delivers overall improvements to the environment. This paper will profile these technologies, and provide best practice case study examples of their application at mining operations, including data for water chemistry, flows, water quality, capital and operating costs, and life cycle costs of treatment.

INTRODUCTION

The BioSulphide® and ChemSulphide® processes developed by BioteQ Environmental Technologies represent advanced precipitation technologies that use biological and chemical sources of sulphide respectively to selectively precipitate dissolved metals, producing saleable metal by-products and clean water that can be safely re-used or discharged[1]. These technologies can remove and recover up to 99% of dissolved valuable metals such as Cu, Zn, Ni and Co from mining effluents, and meet discharge limits for the most toxic metals such as Cd, As, Pb and Hg in the parts per billion range. Revenues from the sale of recovered metal products can offset treatments cost and deliver significantly lower life cycle costs for water treatment compared to conventional lime treatment. Ion exchange (IX) processes can be effectively combined with sulphide precipitation to deliver cost-effective recovery of valuable metals from large flows of wastewater containing relatively low concentration of metals.

BioteQ in a 50/50 joint venture with Jiangxi Copper Corporation (JCC) of China, designed, built and commissioned a 1,100 m^3/hr water treatment plant at JCC's Dexing copper mine using BioteQ's ChemSulphide® process. The copper recovery plant, built in 2008, recovers copper from surface water run-off, mixed with drainage from waste dumps and low grade stockpiles using the ChemSulphide® process upstream of a high density sludge (HDS) lime neutralization plant that is used for the removal of aluminum and final neutralization of the effluent prior to discharge into the environment.

During the construction and operation of the copper recovery plant, nickel and cobalt (Ni/Co) were found in the ChemSulphide® plant effluent at concentrations ranging between 5 and 8 mg/L for each metal. Given the total amount of flow being treated (600 to 1,100 m^3/hr), a decision was made to evaluate the possibility of recovering Ni and Co from the copper recovery plant discharge, upstream of the HDS plant, using selective ion exchange. With the Dexing mine wastewater composition being dominated by elevated levels of Fe and Al, and the experience by resin manufacturers, the use of IX for the recovery of Ni and Co from the Dexing wastewater represents a novel application with several technical challenges that have been overcome by the BioteQ IX process. Following successful onsite pilot testing, BioteQ designed a treatment plant using an IX process to concentrate the Ni/Co solution and using carbonate precipitation to make the final Ni/Co product. Commissioning of the plant commenced in April 2011 and is schedule to be operational by July 2011.

MINE WASTEWATER TREATMENT PROCESS DESCRIPTION & RESULTS

The Dexing mine wastewater treatment flowsheet is comprised of the existing copper recovery plant, the newly built IX plant for nickel and cobalt recovery, and the HDS lime neutralization plant. The overall schematic of the treatment is shown in Figure 1. Each of the treatment stages is described in more detail below.

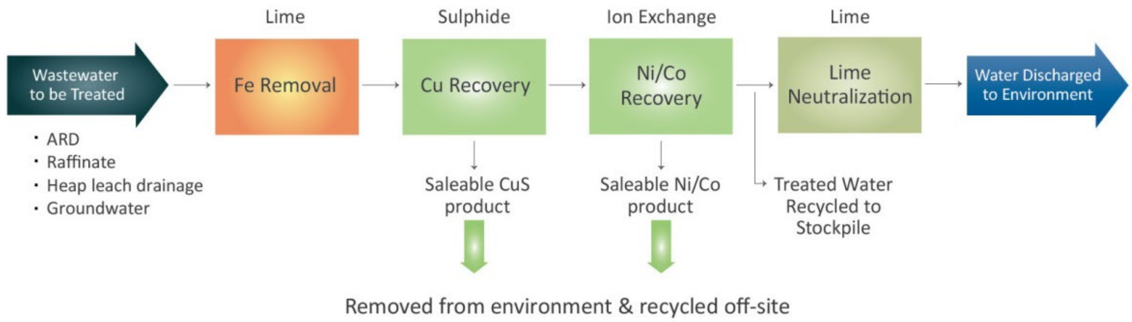

Figure 1 – Process diagram for wastewater treatment at the Dexing copper mine

Copper Recovery Plant

The copper recovery plant was built in 2007 and includes a ferric iron removal stage followed by a copper recovery stage (ChemSulphide®). The design flow is 1,000 m^3/hr, however, the plant often treats in excess of 1,100 m^3/hr during the wet season. The average parameters for the feed and discharge are shown in Table 1.

Table 1 – ChemSulphide® Water Chemistry

Parameters	Average Feed Chemistry	Average Effluent Results
pH	2.2 to 2.6	3.0
Copper	149 mg/L	< 3 mg/L
Fe^{3+}	909 mg/L	126 mg/L
Fe^{2+}	386 mg/L	536 mg/L

Ferric Iron Removal Stage

In the ferric removal stage, lime slurry is added to the feed water based on the pH in order to precipitate ferric iron as ferric oxy-hydroxide prior to the recovery of copper.

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 + 2H_2O \rightarrow 2Fe(OH)_3 \downarrow + 3CaSO_4{*}2H_2O\downarrow \qquad (1)$$

The ferric iron/gypsum sludge reports to the iron stage thickener underflow and is discharged into a storage area. The solids-free overflow from the ferric removal stage thickener reports to the copper recovery stage.

Copper Recovery Stage

The feed water from the ferric iron removal circuit flows by gravity to the copper contactor, where the copper in solution reacts with NaHS precipitating copper sulphide as per reaction (2). NaHS is dosed into the process based on ORP.

$$2NaHS + 2CuSO_4 \rightarrow Na_2SO_4 + H_2SO_4 + 2CuS\downarrow \quad (2)$$

The resulting CuS precipitate settles to the bottom of the clarifier where it undergoes thickening followed by dewatering in a conventional plate-and-frame filter press with the addition of flocculent. A portion of the clarifier underflow is recycled to the copper precipitation reactor as seed to promote particle growth. The copper clarifier overflow reports to a water splitter tank, before it reports either to the HDS circuit or to the Zhujia Heap Leach. The copper recovery during this stage reaches an average of 98% removal.

Sludge Reduction

One of the secondary benefits of copper recovery upstream of HDS lime neutralization is the reduction in the amount of waste sludge produced by lime neutralization and in the potentially mobile heavy metal content of this sludge. This is due to the fact that copper recovered as CuS in the copper recovery plant does not precipitate out as $Cu(OH)_2$ in the HDS plant. Consequently, based on the annual copper production of 2 million pounds/year, the sludge tonnage and volume reduction is estimated to be approximately 1,400 dmt/year and 4,650 m^3/year respectively, assuming 30% w/w solids content in the waste sludge produced by the HDS plant.

HDS Lime Neutralization Plant

The existing HDS lime neutralization plant was built in 2008 and represents a state of the art facility with sludge recycle and conditioning stages achieving sludge densities between 25% and 30% solids. The feed to HDS passes through two continuously stirred tank reactors where the mixture of conditioned sludge and milk of lime is added into both reactors based on pH. The target pH set point in the second reactor is pH 8. Lime precipitates the residual divalent and trivalent metals as respective metal hydroxides as per reactions (3) and (4):

$$MSO_4 + Ca(OH)_2 + 2H_2O \rightarrow M(OH)_2 + CaSO_4{*}2H_2O \quad (3)$$

$$M_2(SO_4)_3 + 3Ca(OH)_2 + 2H_2O \rightarrow 2M(OH)_3 + 3CaSO_4{*}2H_2O \quad (4)$$

Floc is added to the lime reactors overflow drop-box that feeds the clarifier centre well feed pipe. In the clarifier, the metal-hydroxide/gypsum sludge settles to the bottom and metal free water overflows the weir of the clarifier into the treated water circuit for either recycle or discharge into the Dawu River.

Newly Constructed IX Plant for Cobalt and Nickel Recovery

The IX Plant is designed to operate downstream of the existing copper recovery plant and upstream of the existing HDS plant. Given the seasonal flow variations (600 to 1,100 m^3/hr), the design capacity for the Ni/Co Plant was selected to be 800 m^3/hr to optimize the utilization of the plant due to variable flows during the year and to minimize the tie-in adjustment from the existing Dexing water treatment plant. The design feed concentrations of Ni and Co is 6.2 mg/L and 7.4 mg/L respectively. As can be seen in Table 2, in addition to Ni and Co, the effluent from the copper plant also contains large amounts of other metals with little or no value, including a high concentration of aluminum and ferrous iron compared to Ni and Co. This has previously made selective and cost effective Ni and Co recovery a challenge in that high concentrations of Al and Fe (II) typically negatively interfere with Ni and Co recovery.

Table 2 - Metal concentrations in the Copper Recovery Plant effluent

Date	Ni (mg/L)	Co (mg/L)	Al (mg/L)	Fe (mg/L)	Ca (mg/L)	Mg (mg/L)	Cu (mg/L)	pH
2008	5.76	6.13	1136	718	602	1347	4.41	3.5
2009	6.2	7.84	772	795	-	-	2.99	3.21
Feb – March 2010	5.08	6.46	486	368	389	558	1.02	3.01

The recovery of Ni and Co is a two stage process. In the first stage IX resin is used to remove Ni and Co from the large flow of the diluted wastewater stream and concentrate it into a small volume of solution rich Ni and Co. In the second stage, Ni and Co carbonates are precipitated from the concentrated metal solution using sodium carbonate.

Loading

The first step to recover Ni and Co from the copper recovery plant effluent is to concentrate Ni and Co from the effluent stream using the IX process with a chelating resin WP-2, which was selected amongst the resins tested during the piloting effort based on the WP-2 resin operating parameters, the resin performance, and its impact to the project economics. The plant includes six IX columns with a total resin inventory of approximately 19.2 m^3 (total bed volume or BV). A bank of nine bag filters in parallel are installed between the IX feed pumps and the IX columns to remove any solids that might pose a problem to the IX operations. As the loading time is five times longer than the total regeneration time, the columns are operated in a carousel mode such that one column is regenerating while the other five will be loading.

Table 3 – Specification of WP-2 from Purity Systems International

Bulk density (g/L)	700
Mean bead size (mm)	0.5
Functional groups	Iminoacetic acid
Matrix	Modified hydrophilic polymers grafted to amorphous silica gel

Resin loading cycle consists of loading and backwash (BW). During the loading stage Ni and Co, along with some other metals, will be loaded onto the resin while the effluent discharges to the HDS Plant. During the BW step, flow from the effluent of the other columns in loading is redirected through the column to remove any solid particles trapped in the resin.

Regeneration

During the regeneration stage, 8% sulphuric acid (the regenerant) will be pumped through the column to strip Ni and Co off the resin to make a concentrated Ni/Co solution. Due to the weak affinity of Ni and Co to the resin functional groups at low pH these metals are stripped off the resin relatively quickly during regeneration. Online pH and conductivity probes are installed on each column to monitor the effluent and optimize the duration of the initial regeneration step. Before the next loading cycle, the column will be rinsed by 2 BV of feed water to recover the residual spent regenerant still enclosed in the void space of the resin bed. The residual spent regenerant will contain some residual acid and some Ni and

Co. The initial 0.6 - 0.8 BV of rinse water will be recovered as make-up water for regenerant preparation and the remaining portion of the rinse water will be discharged to the HDS Plant.

The spent regenerant solution contains elevated concentrations of nickel and cobalt. This solution is further processed to make a final saleable mixed Ni/Co product. The composition of the spent regenerant solution based on the pilot data is presented in Table 4 below.

Table 4 - Composition of Spent Regenerant Solution

Ni (mg/L)	Co (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	Al (mg/L)	Cu (mg/L)	Ca (mg/L)	Mg (mg/L)
770	860	650	269	946	26	288	148

<u>pH Adjustment Prior to Carbonate Precipitation</u>

The average Ni and Co concentrations in the product solution are estimated to be 770 mg/L and 860 mg/L, respectively. The Ni/Co concentrated solution needs to be further processed to make a final product. In order to precipitate Ni/Co ions as Ni/Co carbonate, the removal of iron and aluminum is crucial. The post IX process includes two stages, a pH adjustment stage and a nickel and cobalt precipitation stage.

In the pH adjustment stage, limestone powder and hydrogen peroxide are added. The addition of hydrogen peroxide helps oxidize ferrous into ferric iron. The limestone raises the solution pH to pH 3.5, and precipitates out iron and some aluminum. The mixed solution then overflows to a second pH adjustment tank where flocculent is added. The iron and aluminum precipitation reactions are summarized below.

Oxidation of Fe^{2+} to Fe^{3+}:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \qquad (5)$$

pH adjustment and precipitation of Fe^{3+}& Al^{3+}:

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \qquad (9)$$

$$CO_3^{-2} + H_2O \rightarrow HCO_3^- + OH^- \qquad (10)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow \qquad (11)$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \downarrow \qquad (12)$$

The discharge from the limestone reactors is then pumped to the first centrifugal decanter to separate solids from the solution pregnant with nickel and cobalt. The solution discharged from the first decanter is pumped via a polish filter to the Ni/Co contactor. The sludge stream produced from the first decanter is mixed with wash water and pumped to the second centrifugal decanter. The solution discharged from the second decanter is also pumped via a polish filter to the Ni/Co contactor. A portion of the sludge produced by the second decanter will be recycled back to the limestone reactor tank to act as seed. The remaining portion of the sludge will be pumped out for disposal. Less than one percent of the Ni and Co will be lost in the wasted sludge.

Carbonate Precipitation and Solid-liquid Separation

In the Ni and Co precipitation stage, soda ash is used to make Ni/Co carbonate. The soda ash solution is dosed to the Ni/Co condition tank and Ni/Co contactor. The rate of soda ash addition is controlled by the pH measurement in the contactor. The precipitate is separated by a clarifier. The nickel and cobalt carbonate precipitation reactions are summarized below.

$$Ni^{2+} + Na_2CO_3 \rightarrow NiCO_3 \downarrow + 2Na^+ \quad (13)$$

$$Co^{2+} + Na_2CO_3 \rightarrow CoCO_3 \downarrow + 2Na^+ \quad (14)$$

The overflow of the clarifier is directed back to the HDS plant. The Ni/Co carbonate sludge is continuously recycled to the sludge conditioning tank to provide seeding. A portion of the Ni/Co sludge from the clarifier will require further dewatering with a filter press to produce the final nickel and cobalt carbonate product.

Table 5 – Ni and Co recovery in the IX plant

Overall Recovery Ni	65.80%
Overall Recovery Co	65.10%

The solids from the filter press are the final Ni/Co concentrate.

Sludge Reduction

One of the secondary benefits of Ni and Co recovery upstream of HDS lime neutralization is the reduction in the amount of waste sludge produced by lime neutralization and in the potentially mobile, heavy metal content of this sludge. This is due to the fact that nickel and cobalt recovered in the mixed carbonate product do not precipitate out as $Ni(OH)_2$ and $Co(OH)_2$ in the HDS plant. Consequently, based on the annual nickel and cobalt production of 62 thousand and 72 thousand pounds/year respectively, the waste sludge tonnage and volume reduction is estimated to be approximately 96 dmt/year and 318 m^3/year respectively, assuming 30% w/w solids content in the waste sludge produced by the HDS plant.

COST ANALYSIS & DISCUSSION

The wastewater treatment plant at the Dexing mine is expected to treat five to ten billion litres of wastewater per year and recover 2 million lbs of copper, 62 thousand lbs of nickel, and 73 thousand lbs of cobalt per each year of operation for the next fifteen years. While the capital costs of all three stages of treatment are known, the actual metal production and operating costs are available only for the Copper Recovery plant and the HDS plant as these have been operating since 2008. The metal production forecast is based on historic trends in wastewater flow and composition. The capital and operating costs, revenues from the sale of metals, and the Net Present Values (NPV) of each treatment stage are discussed below.

Copper Recovery Plant

The capital cost for the 1,000 m^3/hr ChemSulphide® plant was $3.6 million US. The revenue of the plant comes from the sale of the recovered copper sulphide. The relatively low operating cost and high revenue resulted in a payback of less than three years. The actual revenues and OPEX for the years 2008, 2009, and 2010 are shown in Table 6 in US dollars.

Table 6 – Actual Revenue for the Copper Recovery Plant in $ US

Year	Revenue ($)	Opex ($)	Net Cash Flow ($)
2008	3,249,564	2,282,542	967,022
2009	4,343,784	2,850,742	1,493,042
2010	6,456,224	3,074,824	3,381,400

The revenue for the following twelve years was calculated based on 2,000,000 lbs of recovered copper per year with an 85% net smelter return (NSR). Given the drop in copper price to $1.50 US/lb in late 2008, the current prices of over $4.00 US/lb, and the climbing trend in commodity prices, $3.00 US/lb seems a fair and conservative estimate for the prices of copper over the next twelve years. The revenues are expected to be $5,100,000 US per year, and the OPEX will be $2,800,000 US/year. The fifteen year NPV is $19,200,000 US, providing a net positive return.

Cobalt and Nickel Recovery IX Plant

The final Ni and Co grades in the concentrate will be approximately 11.6% and 13.8%, respectively. Based on the commercial evaluation of this product by several local smelters, the NSR of this concentrate is expected to be 65% for both Ni and Co. The total capital cost for the Ni/Co Plant (equipment and resin) is $3 million US. The annual production is projected to be 28 metric tonnes Ni and 33 metric tonnes Co, with a total annual operating cost of $442,000 US.

Table 7 – Revenue and Opex for the IX Plant

Nickel Recovered (lbs/yr)	61,600
Cobalt Recovered (lbs/yr)	72,600
Nickel Price (US $/lb)	10.90
Cobalt Price (US $/lb)	18.20
Revenue (US $/yr)	1,295,294
Opex (US $/yr)	442,000

This paper presents a case scenario that uses very conservative estimates for the price of nickel and cobalt over the fifteen year period, using the current price. Given the overall long-term upward trend for Ni and Co pricing, this price fluctuation will have a positive impact on the economics of the project. Based on these conditions, the IX plant will have less than four years of payback time on capital, and a positive return of $5,900,000 US after fifteen years.

HDS Plant

The capital cost of the HDS lime neutralization plant was $1,200,000 US in 2008. Since the HDS plant does not generate any revenue from the sale of recovered metals, the operating cost of the HDS plant represents a negative cash flow. Table 8 below displays the annual operating cost of the HDS plant since the plant start-up in 2008. As can be seen from this table, the annual operating cost gradually increased to approximately $1.5 million US per year. The cost increase over the first two full years of operations was primarily due to the gradual increase in the volume of water treated through the plant resulting in a corresponding increase in lime consumption. For the purpose of determining the 15 year NPV, the annual operating cost for the next twelve years is assumed to remain $1.5 million US which reflects the fact that in 2010 the plant reached the maximum design throughput capacity.

Table 8 – Opex for the HDS plant

Year	Revenue ($)	Opex ($)	Yearly Cash Flow ($)
2008	0	318,841	(318,841)
2009	0	1,341,176	(1,341,176)
2010	0	1,447,612	(1,447,612)

Total Life Cycle Cost (15- year NPV) of Mine Wastewater Treatment at Dexing Mine

The total 15 year NPV of mine wastewater treatment at the Dexing mine and the comparison of individual NPV values for the three treatment stages is presented in Table 9. The NPV values were calculated using the discount rate of 5% and the capital costs, revenues, and operating costs discussed above.

Table 9: Fifteen (15) year NPV of Wastewater Treatment at the Dexing Mine

	ChemSulphide™	IX	HDS	Total
Capital cost (US $)	3,600,000	3,000,000	1,200,000	7,800,000
Forecasted Revenue (US $/yr)	5,100,000	1,300,000	0	6,400,000
Opex (US $/yr)	2,800,000	442,000	1,500,000	4,800,000
Yearly Cash Flow (US $)	2,300,000	850,000	(1,500,000)	1,700,000
15 Year NPV (US $)	19,200,000	5,900,000	(15,500,000)	9,600,000

As can be seen from Table 9, the ChemSulphide® copper recovery plant will be the most profitable with an NPV of over $19 million US. The NPV of the Ni/Co recovery IX plant is expected to be approximately $5.9 million US. In contrast to the ChemSulphide® and IX plants, the HDS lime neutralization stage plant will produce a negative NPV of $15.5 million US dollars for the same period of time. The total 15 year NPV of mine wastewater treatment at Dexing which is the sum of the three NPVs for the individual treatment stages is $9.6 million US.

The HDS lime neutralization process is the most common treatment method used by the industry worldwide. The figures presented in Table 9 show that the recovery of copper, nickel and cobalt upstream of the HDS plant can turn wastewater treatment from a cost centre costing as much as $15.5 million US in NPV over 15 years into a profit centre generating a positive return of $9.6 million US in NPV over the same period. This has the following implications for the Dexing mine:

- Mine wastewater treatment no longer represents a long-term financial liability in that the treatment generates revenues, and ultimately a profit.
- The production of saleable metal concentrates from wastewater is expected to continue for decades and extend beyond the life of the mine.

- The profit from wastewater treatment can be used to offset mine reclamation and ultimate closure costs while providing stable employment for the local community.
- Sludge reduction at the HDS plant is further increased, contributing to greater overall improvements to the environment.
- The recovery of metals from wastewater improves resource recovery and enhances the overall sustainability profile of the Dexing mine.

CONCLUSIONS

BioteQ is a service provider specializing in the field of wastewater treatment and metal recovery, providing clean technology solutions that help convert waste into value. The main benefits of BioteQ's approach to wastewater treatment include: significant reduction of long-term environmental and economic liabilities, compliance with new stringent regulations for effluent discharge into the environment, improved resource recovery, and contribution to enhancing the overall sustainability profile of mining and metal extraction projects. As such, mine operators can apply BioteQ's clean technologies to comply with the tightening regulatory environment, address corporate social responsibility, adopt greater sustainable mining practices, and benefit from increased commodity prices.

In the case of the Dexing mine, the implementation of BioteQ's technologies turned wastewater treatment from a long-term cost centre with an estimated 15 year NPV of $15.5 million US into a profit centre with a positive NPV of $9.6 million US by recovering up to 2 million pounds of copper, 62 thousand pounds of nickel, and 73 thousand pounds of cobalt annually. The sludge produced by the HDS lime plant no longer contains toxic heavy metals and is considered non-hazardous. In addition, the recovery of metals from mine wastewater upstream of the HDS lime neutralization plant reduces the sludge volume produced by the HDS by approximately 5,000 m^3/year.

REFERENCES

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