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Nickel-Cobalt-Copper Keynote Address

ARE WE ANY CLOSER TO HYDROMET OVERTAKING SMELTING FOR COPPER SULPHIDE CONCENTRATES

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ABSTRACT

Where primary copper concentrates contain little in the way of deleterious elements and transport or government royalties for export of untreated concentrates do not present significant commercial issues, smelting of primary copper concentrates remains the route of choice. Opportunities for technically viable hydrometallurgical treatment routes ultimately turn on commercial viability and an assessment of risk for hydrometallurgical options.

While pyrometallurgical treatment of concentrates is capital intensive and has stringent environmental controls, smelting technology also continues to evolve to address these issues, so it is unlikely that primary sulphide concentrate treatment will move significantly away from smelting unless concentrate compositions change significantly. However, increases in the proportion of concentrates produced with high levels of impurities will increasingly open opportunities for hydrometallurgical flowsheets to be considered.

Most primary hydrometallurgical options for treating both clean and dirty primary copper concentrates remain commercially unproven. There are, however, an increasing number of process plants treating primary and secondary copper concentrates where the hydrometallurgical process can add value to the project that cannot be achieved via a concentrate smelting route.

For secondary copper concentrates, the alternatives are much more open, with a significant number of hydrometallurgical plants in operation treating both concentrates and run of mine ores ROM. Whole ore treatment is prevalent as a result of difficulties in obtaining good flotation recoveries.

This paper will explore the basis of flowsheet selection, in cases where alternatives other than smelting have been considered for copper sulphide concentrate treatment.

INTRODUCTION

The demand for copper, strong up to 2014, has fallen away as a result of the global financial crisis. However like most cycles, this situation will ultimately reverse and the developing economies will continue to require copper to address their future needs for infrastructure and power generation.

Of the current demand, hydrometallurgical production provides for approximately 20% of the current demand, predominantly from secondary copper sources, which has been relatively stable at this level for the past decade; only a small proportion of this production is attributable to treatment of primary sulphides.

Copper ores being mined today are typically too low grade (0.5 to 2% Cu) and require some form of concentration, typically flotation, prior to concentrate treatment. Copper concentrates of between 20 and 30% copper grade are targeted to maximize smelting efficiency and to minimise offsite costs. In many cases this approach also concentrates impurities that create issues for smelting, and that particular issue is only expected to become increasingly more a concern over time.

Taking this consideration into an evaluation of hydrometallurgical options, a range of criteria including this issue need to be satisfied before a hydrometallurgical process would be technically and commercially applicable to treat copper concentrates in place of smelting. The generalized criteria proposed are:

- High Impurity levels which limit smelter applicability,
- Comparable copper and precious metal recoveries and cathode quality versus smelting,
- Minimise sulphate production, except where low grade acid can be utilised,
- Minimise technological risk through use of proven unit operations,
- Accessible low cost reagents,
- By-products produced safe for disposal as non-hazardous waste,
- Low energy footprint,
- Process simplicity rugged and resistant to upset conditions,
- Competitive capital and operating costs versus smelting.

Ultimately, commercial considerations and risk assessment are the key criteria which determine whether a hydrometallurgical flowsheet is a viable alternative. Satisfying these criteria also offers the potential to treat lower grade materials which in turn increases concentrator recoveries, compared to recovery levels that would be optimal for smelting.

As a result of the expected increase in demand in the future for copper, many new mines must be brought on line as high grade, metallurgically clean ores are progressively worked out. Consideration will need to be given to resources that are low grade, complex and typically contain significant impurity levels. Sufficient clean easily smeltable concentrates will not always be available for blending down impurity levels and traders who offer this facility extract a significant price for the service.

So what are the alternatives?

- There are concentrates in production that are unacceptable to smelters, so the normal smelter toll treatment schedules are not relevant.
- A pre-treatment approach may be applied which results in a product that is amenable to a smelter and a waste stream containing the majority of the impurities in an environmentally acceptable form. Roasting is one such process that follows this route.
- A hydrometallurgical process which treats concentrates without any pre-treatment.

Each concentrate needs to be considered on its merits and all available treatment routes need to be considered; both from a technical and commercial standpoint.

South America has for many years been the major source of copper concentrates and, Peru and Chile for example, have significant copper/arsenic resources. To date these not been exploited to any significant extent because of the difficulties in obtaining a separation between copper and arsenic

BACKGROUND

The three tables below present an overview of the current and future situation which informs flowsheet decisions for concentrate treatment. In the first instance, we need to consider the production tonnage, elemental and mineralogical composition of the range of concentrates produced worldwide.

Tonnage because there are constraints on smelting capacity in terms of the ability of individual smelters to accept different impurity levels up to their specified limits. Smelters apply limits to maximum impurity levels which are detailed below.

The elemental composition of concentrates determines the ability of a smelter to handle specific impurity levels and to address their environmental discharge limits.

The importance of concentrate mineralogy pertains more to the concentrate upgrade options and to hydrometallurgical options for concentrate treatment than to treatment through a smelter.

Copper Reserves and Resources

Data on copper resources current and future has been extracted from United States Geological Survey⁽¹⁾ (USGS) data and are presented in Table 1 below. North and South America currently contain a large majority of the known reserves (60%). However, the expectation is that this dominant position will change over time to approximately half of its current value (33%), and that those resources will likely come from a number of other sources with no dominant region identified.

It is clear from Table 1 that the vast majority of current and future copper resources are igneous in origin and are held in porphyry type deposits and these deposits typically tend to be of lower copper grade (0 – 2.0% Cu). Many are South American deposits prone to the presence of significant impurity levels, particularly arsenic; the Cu-As association in porphyry copper deposits is well known.

While there is a wide range in potential impurity levels, one of the more ubiquitous impurities is arsenic, which poses a number of environmental disposal issues.

Figure 1 below illustrates the location of copper deposits on a worldwide basis.

Figure 1: Global Locations of Copper Deposits`

Concentrate Elemental Composition

Table 1 does not however, offer insight into the concentrate compositions produced from treating these resources and for this data we need to look to extracts from the European Copper Institute publications⁽²⁾ that detail statistical data for elemental and mineralogical composition of copper concentrates in Table 2 and 3 below. These data take into consideration the range of mineralogical compositions of the concentrates and contained gangue.

Concentrate Mineralogy

In order to assess the potential options for concentrate production, upgrade and hydrometallurgical treatment of concentrate, knowledge is required of the concentrate mineralogy. From Table 3 below two key issues can be identified.

- Base metals comprise a significant proportion of concentrates reflecting the output of mines treating complex sulphides. Smelter maximum limits for zinc and lead are relatively high at 3% each but nonetheless it is clear that significant zinc and lead contamination of concentrates exist.
- Arsenic and antimony contamination are the other main impurity group with significant representation in concentrate production. Antimony impurity maximums are higher than arsenic for smelting, as shown in the smelter schedules below.

There are clearly two avenues where smelting of concentrates is problematical, the first is complex base metal concentrates and the second is treatment of concentrates containing arsenic levels exceeding either smelter capacity or grade limitations.

Table 3: Concentrate Mineralogy

Many of the large undeveloped copper deposits have significant impurity issues, for example:

- Salobo, Brazil High Fluorine
- La Granja, Peru High Arsenic
- Tampakan, Philippines High Arsenic
- Nena, PNG High Arsenic

It is clear from data presented by Brook Hunt⁽³⁾ in Figure 2 below, that future concentrate production will include increasing proportions of arsenic bearing concentrates and increases in arsenic grade in the immediate future. Opportunities for blending high arsenic concentrates with clean concentrates to bring arsenic levels within smelter limits will not be sufficient on its own to control the increasing levels of arsenic in concentrates. Other methods of control will need to be sought as sale of concentrates to traders for blending increases off site costs, and the blending will need to be carried out before the concentrate reaches a port in China.

Figure 2: Arsenic Content in Concentrates

CONCENTRATE TRANSPORT

The sea transport of copper concentrates from mine site to smelters is shown in Figure 3 below, and the line weighting shows the magnitude of concentrate movement. There are no current constraints on concentrate composition for shipment. Shipment of concentrates is covered by the new International Maritime Organization guidelines which provide a more systematic hazard assessment for solid bulk cargoes. The two relevant regulations that suppliers/shippers of solid bulk materials need to comply with are, firstly, MARPOL Annex $V^{(4)}$, designed to prevent pollution of the marine environment, which applied from the $1st$ January 2013 and secondly, the International Maritime Solid Bulk Cargoes Code $(MSBC)^{(5)}$, set up to ensure the safe transport of solid bulk cargoes.

Residues of cargoes that are considered toxic can only be carried if discharge facilities at the incoming port have facilities for dry and wet discharge of residues. High arsenic concentrates and concentrates high in secondary copper sulphides fall into this category, and are categorized as harmful to the marine environment (HME) which require the discharge port to have facilities for cleaning the holds of the transport vessel that do not involve discharge of the washings to the marine environment.

Treatment of concentrates containing arsenic is largely carried out in China and Japan although limited facilities do exist in South America and Africa for treating high arsenic concentrates, The World Copper Fact Book 2015⁽⁶⁾

Figure 3: Concentrate Shipment

SMELTING

Historically, arsenic has either been avoided in the mining operation to the extent necessary to hold concentrates produced to below the arsenic limits in the smelter schedule of terms and the remaining arsenic is then eliminated in the smelter. Alternatively, blending of concentrates by traders such as Glencore has been applied to limit arsenic concentrations, and can equally be applied to minimise base metal concentrations such as lead and zinc. Arsenic remains the key impurity.

During smelting, the majority of the arsenic is volatilised and must be recovered by the gas handling train at the smelter. Arsenic reports to the smelter offgas as either arsenic sulphide or trioxide which are trapped by either dry or wet gas cleaning methods. A small proportion of arsenic reports to the slag, matte and blister products. Since 2006, the concentration of certain penalty elements in concentrates imported into China have been restricted as outlined in Table 4.

Table 4: Upper concentration limits for importing copper concentrates into China

These restrictions do not apply internally to China as higher arsenic content concentrates are produced and treated. Outside China, most smelters will not process concentrates with arsenic exceeding 0.2%, and there are expectations of tighter environmental constraints in the future both globally and in China. Tighter controls will lead to a reduction in the current arsenic maximum in smelter schedules, placing tighter constraints on pre-treatment flowsheets prior to smelting. Further pressure will be applied to finding alternative treatment routes as blending is unlikely to be sufficient to address high penalty element concentrations.

Historically significant lead and arsenic contamination has been identified at a number of existing smelter and roaster sites, particularly older decommissioned sites, and further environmental legislation is considered probable leading to tightening of existing emission limits. Sulphur dioxide emissions are also an ongoing environmental concern. Offgas cleaning efficiencies are updated by evolving technology in existing and future smelter and roaster installations to ensure that the offgas

treatment meets best available technology (BAT) constraints. A typical smelter specification for concentrates is presented in Table 5 below. This particular schedule is typical of Chinese smelters and places a 0.5% arsenic limit on concentrates.

The current generation of smelters employing state of the art smelting and converting technologies together with gas handling trains and acid plants provide the benchmark for comparing hydrometallurgical plant alternatives.

Table 5: Smelter Specification

The smelter specification is the starting point for the analysis of the economic differences between smelting and hydrometallurgical treatment of concentrates. Within technical constraints, the preferred concentrate treatment option will be the one that returns the highest IRR for the project. Table 6 below provides a typical spread of smelter charges across a range of concentrate mineralogies.

Freight rates for bulk concentrate shipment to smelters in China and Japan has fallen significantly in the last few years as a result of an oversupply of bulk carriers built following the GFC. This is reducing the overall cost of smelting concentrates to miners and also reducing the differential between smelting costs and hydrometallurgical treatment costs which impacts the ability to repay capital committed on hydrometallurgical plants. While a longer term view needs to be taken the current investment climate is not attractive, with freight rates down to perhaps 50% of previous years. Lower fuel prices are also contributing to the fall in freight rates.

The freight costs used in Table 6 below are an estimate of costs for freight from South America to China.

Table 6: Smelting Costs

Smelter Payment Schedule

Pay copper less one unit at LME settlement averaged over Q/P

A dirty concentrate as detailed in Table 6 above will not be acceptable to the majority of smelters, Fountain^{(7)}. The impurity levels present are above the maximum levels for most penalty elements. A number of observations can be made:

- Lead is typically not a penalty element.
- Zinc penalties are a significant penalty cost across a wider range of concentrates compared to low to medium arsenic levels which are acceptable to a smelter.
- Antimony and arsenic levels are only limiting for a small proportion of concentrate produced at this point. High arsenic concentrates are not smeltable without pre-treatment.

Hydrometallurgy is equally suited to treatment of clean or dirty concentrates; however the commercial opportunities for hydrometallurgy clearly lie in the treatment of dirty concentrates which comprise approximately 10% of current concentrate production worldwide. This proportion is expected to rise in the future as more of the known resources with high impurity levels need to be

treated to meet copper demand. The opportunities for hydrometallurgical treatment of concentrates lie in the treatment of concentrates with penalty element levels unacceptable to smelters.

Environmental issues will also play a more dominant role, as tighter emission controls are placed on smelters and roasters. It is clear that even with the best available technologies, smelter and roaster emissions do contain levels of impurities that spread as a halo of contamination around existing facilities. The literature contains many examples of current and past contamination halos around smelters and roasters that increasingly will not be tolerated by society, particularly when dirty concentrates are treated.

PROCESSES FOR SELECTIVE REMOVAL OF IMPURITIES FROM CONCENTRATES

Hydrometallurgical treatment of complex concentrates or concentrates high in impurity levels is an alternative. Although a large range of hydrometallurgical options have been proposed by various researchers, to date, only a limited number have been applied commercially, which has been a major stumbling block to a broader application of hydrometallurgy to treatment of copper concentrates.

Cost, as will be shown later is a key factor in the decision making process. Hydrometallurgical processes can address high impurity levels of all the key contaminants identified in Table 3 above, and can also be used as an adjunct to conventional flotation to improve overall project economics.

A range of flowsheet options are briefly described that may be used to selectively remove arsenic from a copper sulphide concentrate to produce a saleable copper concentrate which will incur normal smelting charges. It should be noted that options to produce an arsenic depleted concentrate product does require further off site treatment to produce copper and gold, but smelting charges for arsenic depleted concentrates are acceptable. These realisation costs need to be considered in any comparison of processes to ensure a valid comparison is provided of the overall costs of copper and gold production.

Blending

Blending currently remains a suitable option for reducing arsenic, zinc and lead levels in copper concentrates but is increasingly unlikely to be a solution for arsenic in concentrates as sufficient clean concentrates will not be available in the future to control the projected increase in average arsenic content of copper concentrates globally.

For example at the Toromocho mine in Peru, published data indicates that arsenic levels in concentrate have been reduced from more than 1% to 0.7% during production which has resulted in a reduction in the concentrate grade from 28% to 22%. Even at 0.7% arsenic the concentrate cannot be imported to China so the solution has been to sell concentrate at a discount to traders such as Glencore who can blend the dirty concentrates with clean concentrates prior to sale to a smelter.

Grade Control Opportunities in Conventional Flotation

Flotation concentrators are constrained by the grade/recovery relationship in the flotation circuit and the grade and the impurity limits of the smelter. Hydrometallurgy provides a means to break that constraint and offers an opportunity to increase overall copper production, reduce plant operating costs and increase net revenue from existing flotation concentrators by recovering additional copper lost in flotation tailings. Removal of the recovery constraint on the flotation concentrate allows shipped concentrate grade to a smelter to be increased to the maximum possible, thus reducing transport and TC charges, however cleaner losses will increase as a result of this strategy. Hydrometallurgy can then be used to recover the majority of the copper reporting to the cleaner tailings streams. Rejection of zinc and lead can be improved if copper recovery is not an economic consideration.

However an alternative flowsheet option is proposed here which minimizes the impact of the recovery constraint by providing a revenue stream which is in the main independent of smelter charges. The concept requires a different approach to the operation of a flotation concentrator demonstrated in Figure 4 below.

Figure 4: Clean Concentrate Treatment Options

The cleaning circuits within a flotation concentrator are constrained to operate on a grade recovery curve with the final concentrate grade adjusted to match a target copper recovery from the concentrator. Maximum grade and maximum recovery are mutually exclusive targets and typically result in a 2 to 4% copper loss between roughing and cleaning stages in a concentrator. It is this copper loss that the proposed hydrometallurgical flowsheet targets together with any copper losses attendant on maximizing concentrate grade. Substantial reductions in freight costs and TC charges for concentrate can be targeted by this approach, which is independent of smelter costs.

Hydrometallurgical processes with low levels of pyrite oxidation such as Galvanox⁽⁸⁾ or Albion can be utilized to allow a flotation concentrator to be operated in order to maximize final concentrate grade, thus allowing the hydrometallurgical circuit treating cleaner tailings at the same time to increase overall copper recovery. Applying hydrometallurgy to the cleaner tailings allows both recovery losses between rougher and cleaner concentrates and any additional cleaner recovery losses to be substantially extracted as copper cathode.

The major component of the revenue from application of this approach is then generated from copper which would not comprise smelter feed. Hence the net revenue after operating costs from the hydrometallurgy circuit is substantially larger than that generated by comparing smelter net returns with hydrometallurgical returns on similar streams.

Hydrometallurgy has been proposed to date for high grade concentrate streams however the proposed approach above presents a very commercially viable and low risk alternative that could provide better economics than treating the entire concentrate stream by hydrometallurgy. The hydrometallurgical plant is significantly smaller and does not place the entire concentrate revenue at risk with a new process, yet generates a copper revenue stream currently lost to tailings.

Impurity Reduction in Differential Flotation

Differential flotation to separate arsenic containing copper sulphides from chalcopyrite is an alternative where the copper arsenic minerals are not dominant in the concentrate. CSIRO in particular, and research organisations in China and South America are actively pursuing studies in differential flotation of copper and copper arsenic sulphides. A review of current status is presented by Bruckard et al.⁽⁹⁾. Control of flotation pH, Eh, depressants and collectors has been used with some success to separate copper sulphides from copper arsenic sulphides. However, separation of a copper flotation concentrate into high arsenic and low arsenic copper products, does not completely address the issue, as the high arsenic product still has to be treated to recover the contained copper and to produce a stable arsenic product for storage.

While a large proportion of the sulphide product should then be suitable for shipment to a smelter, there remains a significant proportion of the mine production tied up in a high arsenic concentrate that will require treatment to recover the contained copper and to product an arsenic product in an environmentally acceptable form. This treatment can be either roasting or hydrometallurgy. Differential flotation is seen as a low cost, relatively low risk first step in releasing the metal values from a mine containing high arsenic values.

For example, flotation testwork reported by Bruckard et al.⁽¹⁰⁾ on North Parkes arsenic containing ores recovered 87% of the arsenic into a concentrate containing 48% of the copper. The remaining 52% of the copper was contained in a low arsenic concentrate (0.26% As) which is a suitable smelter feed. However the remaining high arsenic concentrate still requires treatment to recover the contained copper. Options are presented in Figure 5 below.

Figure 5: Differential Flotation and Product Treatment

Reductive Roasting

Reductive roasting provides a means of removal of arsenic from copper concentrates. The process has an industrial track record and a number of flowsheet alternatives exist for roasting concentrates, however the alternative currently favoured is a selective roast to remove sufficient arsenic to meet a smelter schedule while retaining sufficient sulphur in the roaster product to meet a smelter energy demand.

Smelters typically prefer a minimum sulphur level in a concentrate of 20%. This may be an issue for a partial roast on some concentrates if the concentrate sulphur level is too low to support the partial removal of sulphur from that concentrate. Selective mining and differential flotation can also be used to minimise roaster feed as a proportion of total production to contain costs.

Roasting has been successfully used in the past to treat copper concentrates from the El Indio mine which contained over 6% arsenic, producing a saleable copper-gold concentrate. Xstrata's Altonorte smelter is still believed to toll treat high-arsenic concentrates through a roaster.

Currently the Ministro Hales (formerly Mansa Mina) mine deals with a high-arsenic deposit and is being commissioned with treatment of the high arsenic concentrate through a selective roasting process to produce an arsenic depleted copper concentrate with a specification suitable for smelter treatment.

The Codelco approach suggests that reductive roasting is a viable approach for high arsenic concentrates. However, it should be noted that this decision may depend on the flowsheet requirements and operating costs associated with the arsenic disposal flowsheet selected. Current trends suggest that a scorodite product, rather than a calcium arsenate product should be produced from the flowsheet and this can have significant capital and operating cost implications. Increasing

The objective of the Ministro Hales flowsheet is to selectively remove over 90% of the arsenic during reductive roasting in fluidised-bed reactors operated at ~680°C. During the roasting process enargite is converted to covellite and any pyrite contained in the concentrate is also oxidised to provide part of the heating requirements, while chalcopyrite is left essentially unreacted.

Arsenic is volatilised from the copper concentrate as As_2S_3 gas. The high temperature off-gas from the roaster passes through cyclones before dilution air is added in a combustion chamber to oxidize As₂S₃ to As₂O₃ with further formation of SO₂. The main purpose of the As₂S₃ oxidation is to avoid post-combustion in the dry electrostatic precipitators downstream. From the cyclones, the offgas is cooled to 350-380ºC in an air-cooled heat exchanger before dust is removed in a dry electrostatic precipitator (ESP). Dust from the roaster and the ESP are routed to the calcine cooler to form a combined roaster calcine product. This arsenic-depleted product is then sold to smelters.

The As₂O₃ gas is condensed and scrubbed from the off-gas stream in a scrubber, which leaves the remaining gas to be cleaned and sulphur dioxide to be recovered as sulphuric acid in a sulphuric acid plant. The solution from the gas cleaning circuit containing the arsenic is then treated in a hydrometallurgical plant, where the arsenic is first oxidised to the As(V) state using hydrogen peroxide and then precipitated with addition of calcium hydroxide to produce a calcium arsenite in a waste product that is stored in a lined storage facility.

A key issue for roasters remains the ability of the gas cleaning train to meet environmental standards and historically roasters do not have a good track record in preventing an arsenic contamination halo from developing around roasters. Roasters such as La Oroya in Peru have historically been a source of lead, arsenic and cadmium contamination although steps are being taken to reduce current emissions to environmentally acceptable levels. Nonetheless a significant contamination issue exists, despite high levels of arsenic capture in the gas handling train.

Alkaline Sulphide Leaching

The ASL process as applied to enargite containing concentrates has been outlined by Anderson⁽¹¹⁾. The heart of the process is an alkaline sulphide leach in which arsenic is selectively leached from the concentrate in a caustic environment with sodium sulphide as the active agent, according to the following reaction:

$$
2Cu3ASS4 + 3Na2S \rightarrow 3Cu2S + 2Na3ASS4
$$

A modified flowsheet for the ASL process proposed by Baxter et $al.$ (12) proposes atmospheric leaching at elevated temperature (~90-100ºC) with addition of caustic soda and sodium sulphide. High arsenic recovery to the leach solution is expected with relatively short residence times of 2-6 hours. A significant proportion of the gold also dissolves under these conditions, but the gold can be removed selectively from the solution using a resin based process. The flowsheet also includes steps for reagent recovery from the spent leach solution via H₂S formation and re-absorption. The flowsheet includes a small HTPOX autoclave utilising pyrite-rich cleaner concentrate to provide iron and heat into the arsenic precipitation step. This results in production of the desired scorodite precipitate, while also producing steam and acid to be used elsewhere in the process. The pressure oxidation of the copper-containing pyrite cleaner tailings also introduces additional copper into solution, which is recovered using a small solvent extraction and electrowinning circuit.

The ASL leach process has been considered for use on high arsenic concentrates to be produced from the Tampakan deposit Indophil⁽¹³⁾, and a modified alkaline leach as detailed below has been piloted recently.

Toowong Process

The Toowong Process has been developed by Core Resources based on an alkaline sulphide leach to preferentially remove arsenic and antimony from copper concentrates. The patented Alkaline Leaching (AL) process selectively leaches arsenic and antimony from copper concentrates. Copper, lead and nickel are not leached in the process. The final product from the process is a cleaned saleable copper concentrate with minimal penalty elements

This process addresses the issues with reagent consumption and recycle and can be expected to show lower operating costs. Arsenic and antimony are precipitated as stable residues for storage at the mine site.

This process has been piloted by Core on Tampakan concentrates subsequent to the above work on ALS and the Toowong Process has shown the capability of reducing the arsenic concentration in

a concentrate from 1.1% to 0.1%. The process has not yet been applied commercially. The leach reagents are mostly regenerated and recycled, minimising the operating costs of the process, which has been a key issue in earlier iterations of the process.

Copper Metathesis

This process has its genesis in work carried out by Sohn et al.⁽¹⁵⁾ in 1984 which has been initially explored in a single stage autoclave pilot plant campaign carried out by Anaconda Minerals Company. The process involves the generation of copper sulphate from primary copper sulphide breakdown followed by replacement of iron in copper sulphide minerals with copper, to produce a concentrate comprised of secondary copper sulphides the reactions occurring in a high temperature autoclave. Grades of up to 60% copper have been achieved by this process.

The initial objective of this process was to upgrade copper concentrates to reduce transport and smelting costs but latterly interest has been shown in the process for removal of radionuclides from copper concentrates in parallel with the copper grade improvement.

A different two stage autoclave flowsheet has been proposed by Dunn et $al^{(16)}$ to achieve the impurity removal. Arsenic removal is partial with an approximately even split between arsenic in the upgraded concentrate and arsenic in solution, with the iron leached. The impurities removed can be precipitated into a stable residue for storage at the mine site leaving a clean high grade concentrate for toll treatment at a smelter.

COMPLETE HYDROMETALLURGICAL PROCESSING

Applying a complete hydrometallurgical processing solution to the treatment of concentrates containing high impurity levels is to leach the copper minerals and to produce a saleable copper product and a disposable impurity-containing residue. The most likely impurity to be removed based on the above concentrate compositions is arsenic.

Gold is either extracted during the copper leach or in a subsequent leach on the residue, typically using cyanidation. Where gold is a significant contributor to the revenue, particular attention should be paid to the mineralogical occurrence of the gold and the economics of its recovery.

Dreisinger⁽¹⁷⁾ reviewed the available options for leaching of primary copper sulphides. A large number of processes were considered in the review, from atmospheric leaching to total pressure oxidation. It is conceivable that each of these processes may be adapted to treat arsenic containing copper-gold concentrates; however only a selection of the more prominent processes suitable specifically for treatment of high-arsenic copper-gold concentrates is briefly described below. While the sulphide leaching step may be regarded as the heart of each process, each process requires an integrated flowsheet consisting of a unique combination of steps to effect optimal copper extraction and recovery, gold recovery and arsenic precipitation and residue disposal.

Table 7 summarises the key features of a range of primary sulphide treatment processes.

Table 7: Hydrometallurgical Leaching Processes

Each of these flowsheets is comprised of a number of common elements:

- Feed Preparation
- Leaching
- Solid/Liquid Separation
- Solvent Extraction
- **Electrowinning**

The majority of the unit operations in each flowsheet are similar and are in commercial operation regardless of the novelty of the leaching process applied by each technology. The Outotec Hydrocopper process is the one exception to this scenario. The focus of each process is an alternative leaching process for primary copper sulphides. A number have reached demonstration plant level but only one, total POX, is utilised commercially, although the Albion process is also used to treat smelter dust.

The key issues for consideration of hydrometallurgical flowsheets are:

- Smelting costs for the majority of the range of concentrates produced do not allow hydrometallurgical processes, which generally have lower operating costs, sufficient financial margin between smelter costs and hydromet operating costs to repay the capital of a hydrometallurgical plant when treatment of clean concentrates is considered.
- This situation may not hold true for dirty concentrates which are outside the penalty element limits of smelters and do constitute a potential niche market for hydrometallurgy in competition with partial treatment processes.

The key issues for implementing a hydrometallurgical flowsheet are:

- There is a high level of technical risk associated with most primary sulphide treatment processes, centred on the leaching process, and no commercial operations are available to minimise that risk, except in one case.
- Sulphur oxidation in any standalone hydrometallurgical process (oxygen and neutralisation costs) is the main differential component of operating costs between competing processes. Low grade acid production from a leaching process requires either neutralisation or acid consumption in secondary leaching processes to improve project economics.
- Technical viability of a hydrometallurgical process must be coupled with commercial considerations in determining the relative economics between competing processes.
- Process operating cost differentials are largely controlled by the level of sulphide sulphur oxidation in the leaching process and the ability to utilise generated acid in secondary leaching processes, which is a project specific issue.
- Precious metal recovery is variable across the processes depending on the presence of elemental sulphur and whether the leaching process is above or below the melting temperature of sulphur.

Pressure Leaching

While a large number of processes with these characteristics are available, the more prominent processes associated with treatment of copper arsenic containing concentrates and currently receiving the most attention for development are the high temperature pressure oxidation process (HTPOX), the medium temperature pressure oxidation process (MTPOX), the nitrogen species catalysed process (NSC) and the CESL process.

HTPOX

High temperature (or total) pressure oxidation (HTPOX) is often the first choice and the benchmark used to determine maximum extraction from total oxidation of all sulphide minerals. It was originally developed and has been extensively used commercially for oxidation of refractory sulphide gold concentrates and ores. This technology has been applied on a commercial scale on copper concentrates at Sepon, Kansanshi and Bagdad. Essentially, the autoclave engineering in these applications is identical to an equivalent refractory gold autoclave leaching pyrite.

The application of this process, which is typically performed in horizontal agitated multicompartment autoclaves at temperatures of 220-230°C, has been recommended for concentrates with enargite Ferron et al.⁽¹⁸⁾, as copper recoveries are high (>95%) and an environmentally acceptable arsenic precipitate, scorodite, is produced. Pressure oxidation of enargite can suffer from lower recoveries as a result of unwanted side reactions which produce copper arsenic ferrites, but otherwise the remaining copper sulphides are readily treated to produce copper recoveries of the order of 99%.

The POX process applied to chalcopyrite is expected to result in almost total recovery of copper in a leach time of 60-120 minutes without the requirement for fine grinding of the concentrate feed. The leach residue can also be expected to be amenable to cyanide leaching, providing high gold extractions at a relatively low gold leaching reagent cost, which is contingent on achieving good control of low concentrations of basic ferric sulphate in the leach residue.

The process relies on oxygen injection into the autoclave under pressure to achieve essentially complete oxidation of all sulphide sulphur in the autoclave feed. Due to the total oxidation of the sulphide sulphur to sulphuric acid the process consumes large quantities of oxygen and the acid produced has to be neutralised with limestone or otherwise utilised. If copper oxide resources are available in the area, this disadvantage can be reversed as the acid can be used to leach additional copper at low cost to the project and provide an additional revenue source. This process has typically been employed industrially in flowsheets where the acid generated can be used elsewhere.

MTPOX

Pressure oxidation at medium to low temperatures up to 160ºC has the aim of reducing the consumption of oxygen through part production of part elemental sulphur and part production of sulphuric acid in the leach. The process produces 65 – 70% elemental sulphur. This approach results in lower oxygen consumption and neutralisation costs which in turn reduce overall operating costs.

Freeport Mc Moran spent 8 years developing this process which resulted in a demonstration plant being built at Bagdad Arizona to treat clean copper concentrates. This work is reported by Marsden et al.⁽¹⁹⁾⁽²⁰⁾⁽²¹⁾⁽²²⁾ The commercial demonstration plant was initially designed to operate as a HTPOX plant and following successful operation in this mode the plant was converted in 2005 to run as a combined medium temperature autoclave leach with direct electrowinning (MT-DEW-SX Process) to produce 16 000 t LME Grade A copper per annum. Concentrate feed to feed the medium temperature autoclave circuit was pretreated by fine grinding to 12-15 microns.

The CESL Process

The CESL Process has been refined over many years and many pilot and demonstration plant runs on a range of concentrate types and is marketed by CESL Limited, a subsidiary of Teck Corporation.

The CESL copper process was initially designed to treat copper concentrates but the scope of the process has been expanded to prove up the process on all copper sulphides including the more refractory copper arsenic sulphides. The process typically operates at 150ºC and at a chloride concentration of 10-15 g/L in solution. Further detail on the various iterations of the flowsheet can be found in Mayhew et at.⁽²³⁾⁽²⁴⁾. Teck and Aurubis have formed a strategic alliance to pursue treatment of copper concentrates with particular reference to copper arsenic and copper gold concentrates.

The process is expected to achieve good copper extraction treating copper arsenic concentrates and the production of a scorodite precipitate in the leach, although optimal copper extraction from enargite may be expected to involve a trade-off between extraction, regrind size and leach time. Optimisation of the leach conditions is an important aspect in assuring acceptable recoveries.

While the process has not been installed in a commercial plant, a 10 000 t/a copper demonstration plant was operated by Vale at its Sossego Mine in Brazil Deffreyne et al.⁽²⁵⁾. The plant is now shut down.

The CESL copper leach produces significant elemental sulphur, resulting in reduced oxygen and neutralisation costs when compared to total pressure oxidation.

As with all the medium temperature processes that produce elemental sulphur, gold recovery from the POX leach residue is an issue, as conventional atmospheric cyanidation will typically result in high cyanide consumptions, mainly due to side reactions with elemental sulphur. The resultant SCN⁻ is also difficult to destroy and Caro's acid detoxification is the most likely process to be applied.

CESL have overcome this issue by developing a pressure cyanidation process, coined the CESL Gold Process. This process is reported to reduce cyanide consumptions to acceptable levels when used in conjunction with a cyanide recovery process.

The presence of chlorides in the process liquors from the CESL process requires special attention to materials of construction and poses a risk of chloride transfer to the electrowinning tankhouse via the solvent extraction circuit. It allows for use of saline water in the process, but control of chloride levels in the circuit is an important parameter to ensure high extractions.

The NSC Process

The NSC process has been proposed by Anderson et al.⁽²⁶⁾ as a means of treating a copper concentrate containing significant molybdenum and rhenium credits without the need for a separate molybdenum flotation circuit with multiple cleaning stages and attendant molybdenum recovery losses. Treatment of a bulk concentrate will significantly improve overall molybdenum recoveries.

The process involves an autoclave leach using nitric and sulphuric acid at 155ºC and 6.2 bar overpressure to leach both copper and molybdenum. After solid/liquid separation, molybdenum is recovered by adsorption onto activated carbon and sulphuric acid is also recovered and recycled to the autoclave. Copper is recovered by conventional SXEW.

Sulphur oxidation to sulphuric acid is estimated at 60% so precious metal recovery from the POX residue is an issue. It is proposed to leach the elemental sulphur in the POX residue in a separate step with sodium hydroxide. Approximately 50% of the POX residue is recycled to the autoclave to increase copper and molybdenum recovery. The economics presented in the above paper look attractive for the case detailed however there are no commercial applications of the process as yet.

The process relies on the increased copper, molybdenum and rhenium recoveries to offset the increased cost of copper production relative to smelting. Conceptually this approach can be applied to other applications where by-product recovery is used to offset the cost of copper cathode production. Typically the issue is capital cost repayment.

Atmospheric Sulphate Leaching

Three patented processes that utilise atmospheric leaching are described below. The Albion process is a relatively simple process that has undergone significant development and commercialisation. The GalvanoxTM process is a more recent technology that also requires a small high temperature pressure oxidation circuit. Gold is typically recovered from leach residues by cyanidation and one of the features of the low temperature leach where the elemental sulphur is not melted would appear to be lower cyanide consumptions relative to those processes where the sulphur has been melted.

The Albion Process

The Albion Process has been developed by Xstrata Technologies and includes ultrafine grinding using the IsaMillTM technology followed by atmospheric leaching in agitated tanks with oxygen injection. The process was initially developed to treat high-arsenic concentrates from the Frieda River mine Hourn et al.⁽²⁷⁾ and has subsequently been commercialised at Mt Isa treating arsenic containing smelter flue dusts Hourn et al.⁽²⁸⁾ to recover the contained copper. The process has also been used commercially in a number of other applications treating zinc sulphide concentrates and refractory gold concentrates.

In order to achieve acceptable copper recoveries from an enargite-containing copper concentrate using the Albion process, fine grinding to ~10 micron is usually required followed by atmospheric leaching near the boiling point for 24 hours together with oxygen injection.

During the atmospheric leaching process, which is executed under controlled acidic conditions, iron and arsenic are also leached. The leach slurry is then neutralised with limestone, which allows iron and arsenic precipitation as ferric arsenate. The solids are separated by thickening and filtration and washed to enable copper recovery from the PLS. The washed residue is amenable to gold recovery from the residue using cyanidation. High gold recovery is usually achieved at acceptable cyanide consumption levels, although gold associated with unreacted pyrite will not be recovered. Copper is recovered through solvent extraction and electrowinning and the acidic raffinate is returned to the leach.

The Albion Process has been tested at laboratory scale on numerous arsenic containing copper concentrates. It has been used successfully by Xstrata at their Mt Isa plant to leach arsenic containing smelter dusts and has found full scale commercial application in gold (2) and zinc (3) processing. The projected advantage of the Albion process is the relatively low process risk of the unit processes involved and lower operating cost due to the ability to control elemental sulphur formation. Precious metals are not encapsulated in sulphur as the process is conducted below the melting point of sulphur.

The Galvanox™ Process

The Galvanox™ process was invented by Professor David Dixon of UBC and co-workers Dixon et al.⁽²⁹⁾. The Galvanox™ process was originally targeted at the processing of chalcopyrite, but has been shown to be applicable to enargite as well Dixon et al.⁽³⁰⁾. The heart of the process is the atmospheric leach at elevated temperature (80°C) where the presence of pyrite is required to provide the catalytic galvanic effect. The process preferentially leaches any copper sulphides within 12–24 hours depending on the specific project mineralogy. Pyrite is essentially unreacted (passivated) in the leach and can be recycled to the leach process from the leach residue to provide the required pyrite to copper mineral ratio. This aspect of the process is largely unique to this process and facilitates an ability to treat cleaner concentrate streams from copper concentrators to increase overall copper recovery.

A small pressure leach circuit operates in parallel to the atmospheric leach circuit, treating approximately 10% of the feed as a minimum, and uses a solution bleed stream as autoclave dilution to precipitate the arsenic and iron as disposable scorodite and hematite respectively. The autoclave also provides acid and heat to the atmospheric leach circuit.

The Galvanox™ process has been shown to be potentially more economical than other hydrometallurgical processes when applied to chalcopyrite concentrates Dixon et al.⁽³¹⁾. This is mainly due to maximisation of the formation of elemental sulphur in the atmospheric leach. Excellent gold recoveries have also been achieved on combined leach residues at manageable cyanide consumption levels. In a flowsheet treating arsenic containing concentrates, two separate residues can be produced; an arsenic-containing residue comprising largely scorodite and gypsum, and a sulphide and elemental sulphur containing residue. These residues can be separately leached for gold in CIL circuits and stored separately, thereby removing the risk of interaction of sulphide residue affecting arsenic stability of the scorodite precipitate.

The Galvanox™ process is known to be more effective on some ores than others. Testwork is essential to determine the amenability of a specific concentrate.

The ROL Process

The ROL Process developed by FLSmidth first published in 2015 employs an initial atmospheric leach followed by sequential grinding using the FLSmidth Stirred Media Reactor and further atmospheric leaching to achieve copper leaching in a short time frame (6 hours) without observed passivation issues with chalcopyrite. The leaching step is followed by solid liquid separation and SXEW for copper recovery. The leaching process is carried out at 80 °C and copper recoveries are expected to be in the range 97-99%. The grinding steps are largely a polishing operation to remove surface layers from the chalcopyrite.

Leaching is by an initial oxidative leach step followed by a reductive leaching step to complete copper leaching. Sulphur yield from the leach is estimated at 85 – 95%. Three recent papers by FLSmidth, Chaiko et al.⁽³²⁾⁽³³⁾ and Eyzaguirre et al.⁽³⁴⁾ provide significant detail on the process, which has only been tested at batch and small scale piloting at this stage. Leaching times for enargite are approximately double that of chalcopyrite.

In Dec 2015 FLSmidth signed an agreement with BASF to exploit the ROL technology.

Atmospheric Chloride leaching

The most prominent of the more recent chloride technologies have been the Outotec HydroCopper® and Intec Copper processes. These companies have recently entered into a technical co-operation agreement to better exploit similarities and synergies in their processes. Both technologies make use of the leaching of sulphide concentrates in chloride media under atmospheric conditions. The HydroCopper® process is described below.

The HydroCopper® Process

The HydroCopper® process has been developed by Outotec, Hyvärinen et al.⁽³⁵⁾. This process has been primarily developed and extensively demonstrated on chalcopyrite concentrates. The process has been piloted for the Erdenet project, but remains to be commercialised. The process is significantly different from the other options above and is based on chloride metallurgy. The high chloride brine environment provides for high mineral reactivity during atmospheric leaching with lower energy requirements for copper extraction and recovery than in sulphate systems.

Outotec have developed a flowsheet to recover copper and gold from an arsenic-containing copper concentrate and produce a scorodite and elemental sulphur containing residue. The process has been engineered and recently demonstrated on the Zangezur concentrate in Outotec's demonstration plant in Pori, Finland.

The HydroCopper® process is performed in a concentrated chloride brine in a 3-stage countercurrent leach in which gold is also leached and recovered by absorption onto resin. The process uses chlor-alkali cells to regenerate caustic soda, chlorine, hydrogen and hydrochloric acid, which are all used in the process. Copper is continuously removed from the process by precipitation as cuprous oxide. The high purity cuprous oxide is then treated in a reduction melting process to produce copper which is cast into copper wire rod. The rod product may receive a premium over LME grade copper cathode. Hydrogen used in the reduction melting processes is also generated in the chlor-alkali plant.

Bacterial Leaching

Bacterial leaching of sulphide minerals has been practiced in many forms. The most widespread application of bacterial leaching is in the processing of refractory gold concentrates with the BIOX® process the front-running commercial application. The bacterial leaching process that has undergone the most complete development for leaching of copper concentrates leaching is the BioCOP™ process, developed by BHP Billiton in South Africa, Batty et. al.⁽³⁶⁾.

The BioCOP™ Process

The BioCOP™ process uses thermophile bacteria to oxidise and leach copper from sulphide concentrates. The thermophilic bacteria oxidize sulphide minerals to metal sulphates and sulphuric acid at temperatures of $~80$ °C. In contrast to the mesophilic leaching of refractory gold concentrates at ~40°C which use air as an oxidant, the BioCOP™ process uses oxygen in the leach.

The Alliance Copper joint venture group (BHP Billiton and Codelco) has commercialized the BioCOP™ process at Chuquicamata in Chile in a 20,000 tpa Cu demonstration plant. The plant was specifically used in this application to treat high- arsenic concentrates and is integrated with a heap leach circuit to allow for an acid credit back to the bioleach plant. The process is proprietary and although little has been published on the extent of chemical reactions in the BioCOP™ process, the reaction is understood to proceed to full oxidation of the sulphides similar to the high temperature total pressure oxidation process described above. The major difference is that additional limestone is required to assist with neutralisation during the leach and ferric arsenate precipitation. Dreisinger⁽¹⁷⁾ conducted a comparison of the BioCOP™ and HTPOX processes and found the former to have the higher operating cost. The successful completion of the Alliance Copper project in Chile has validated the BioCOP™ technology at a significant scale but further commercial exploitation of the process has not eventuated.

FLOWSHEET SELECTION

Flowsheet selection takes into consideration a number of fundamental aspects of project development that include both technical and financial considerations. The objective in flowsheet development is to define a result that has an acceptable technical risk at the maximum financial return. Elements to consider cover a range of disciplines and include:

- Developing a thorough understanding of the resource mineralogy and internal variability
- Project Throughput
- Flowsheet Technical Risk
- Process Robustness
- Project Logistics
- Operating Costs
- Capital Costs

Different aspects of each process are compared qualitatively in a matrix in Table 8 below.

Full-scale commercial plant using this technology successfully.

* Proven at least at pilot scale operation on similar high-arsenic copper-gold concentrate at time of writing.

Such a matrix can be expanded and each aspect weighted and rated to give a comparison that is quantitative and based on priority issues. When it is considered that the cost of concentrate processing may be expected to be of the order of 20-30 % of the total development cost of a project, selection of a process based on its robustness rather than absolute cost considerations becomes important.

Evaluation of process options using such a method without adequate supporting testwork should only be used to prioritise processes for further testwork and development.

CASE STUDIES

Three cases are presented for flowsheet options that are considered to be technically feasible and have viable economics.

- Case 1 explores the option of treating cleaner tailings from a conventional flotation concentrator where the majority of the copper in concentrate passes to a smelter. A small hydrometallurgical circuit is used to increase copper recovery and to allow production of higher grade concentrate for the smelter.
- Case 2 explores the option of treating a copper concentrate with intermediate levels of arsenic above the 0.5% limit of a smelter. Differential flotation is used to produce a concentrate suitable for smelting and a concentrate requiring treatment on site to remove the arsenic from the high arsenic flotation product. Pre-treatment can be a partial roast or an alkaline sulphide leach, and total treatment can be any of the range of available hydrometallurgical processes described above. Any requirement for precious metal recovery and acid availability for secondary processing impacts the economics of this decision.
- Case 3 explores the option of treating the entire concentrate stream where arsenic levels are above a concentration where differential flotation can be considered as a means of reducing the size of the concentrate treatment circuits. As for Case 2 pre-treatment can be a partial roast or an alkaline sulphide leach, and total treatment can be any of the range of available hydrometallurgical processes described above. Any requirement for precious metal recovery and acid availability for secondary processing impacts the economics of this decision.

Case Study 1 – Clean Concentrate Option

Overview

While most of the focus in application of hydrometallurgy lies toward treatment of dirty concentrates, there is a hydrometallurgical application to flotation concentrators that warrants more attention. Flotation concentrators are constrained to operate on a grade recovery curve with the operating point determined by a balance between copper recovery and off site processing costs.

A flowsheet option that removes this constraint can provide significant financial benefits to existing operations. The objective of the concept is to increase copper grade in the cleaner concentrate treated offsite to minimise transport and TC charges. The cleaner tailings will contain more of the copper and is then treated to recover the increased copper losses resulting from the change in operating philosophy. As the cleaner tailings will also typically contain significant quantities of pyrite only the Galvanox technology is applicable to this case; Figure 4 above refers.

Basis of Option

In order to quantify the potential economic benefits of the concept introduced above, a typical flotation concentrator has been chosen and the costs (both capital and operating) have been developed to illustrate the economics and potential of the concept. The base case chosen is as follows:

- 112,000 tpa copper in concentrate
- Concentrate Moisture 9%
- 28% Cu grade or 32% Cu Grade
- Concentrate shipped to smelter
- Transport charges \$47.50/tonne
- Treatment charges \$100/tonne
- Refinement Charges \$10/tonne

Offsite Treatment Charges have been estimated for two concentrate grades based on the assumptions specified above.

Offsite Smelting Economics

These data are presented in Table 9 below for a medium size copper concentrator. It is estimated that a reduction in smelter treatment charges of the order of 3.3c/lb copper should be possible through increasing the concentrate grade by 4%. These savings are based on the above assumptions transport and TC charges. These savings do not provide the complete picture as treatment of the cleaner tailings increases the overall copper recovery and the net revenue to the operation.

The data presented in Table 9 incorporates a base case for conventional smelting where the entire concentrate stream passes directly to the smelter and an alternative where the cleaner tailings is subject to hydrometallurgical treatment. Cleaner losses can largely be recovered economically.

Three cases for cleaner losses of copper (2.5%, 3.0% and 3.5%) impact the copper concentrate tonnage passing to smelting so the generated revenue will vary with the extent of cleaner losses within the range detailed below. In order to assess the overall revenue consideration then needs to be given to assessing copper recovery from the cleaner tailings. Table 9 needs to be read in combination with Table 10.

Table 9: Smelter Costs

A hydrometallurgical plant can be applied to the notional cleaner tails stream from a conventional copper flotation concentrator using the Galvanox technology which has the unique ability to minimally oxidise the pyrite in the cleaner tailings allowing process streams typically rich in pyrite and low in copper to be economically treated. Data from several low grade porphyry copper flotation copper concentrators has been used to estimate a range of typical cleaner losses to be expected and the grade of a cleaner tailings stream which is available for treatment. It should be noted that Galvanox has shown the capability to recover copper effectively from process streams under 1% copper which makes it ideally suited to implementing this option.

A proportion of the high grade concentrate is also treated in this option through a total POX autoclave to provide a source of heat and acid for the Galvanox circuit.

Copper leached in the Galvanox circuit and the autoclave is recovered by conventional solid liquid separation and SXEW. The only novel commercially unproven unit operation in this circuit is the

Galvanox leach which is carried out in an atmospheric leach circuit. The engineering of the leach circuit has commercially proven applications, so only the leach chemistry in the atmospheric leach is novel.

A Metsim model, design criteria and operating costs were developed for this case and extracted data have been used in part in Table 10 below. Table 10 presents an estimate of the increase in net revenue that can be achieved by treating the cleaner tailings and part of the cleaner concentrate through a small hydrometallurgical facility.

In developing the option economics, recovery assumptions have been made based on both flotation and hydrometallurgical pilot plants operations run on similar materials.

Table 10: Concentrator Hydrometallurgical Add On Economics

A payback period of approximately 2.5 years is indicated across the range of cases makes this type of addition to a conventional copper concentrator an commercially attractive proposition. While the economic parameters of each concentrator will differ, conceptually this approach should be economically viable in most cases.

The flotation concentrator can then be run to maximise concentrate grade, allowing the cleaner tailings to be treated in a hydrometallurgical facility which then recovers the majority of the cleaner losses. Projects with higher cleaner losses as a result of project specific issues would be even more attractive propositions for the application of this flowsheet modification. The leach extraction used in the example is considered to be conservative, and may well be higher.

Case Study 2 – Intermediate Arsenic Grades

Case Study 2 looks at options for treating a copper concentrate containing arsenic in excess of 0.5% which is the maximum arsenic level acceptable to Chinese smelters. Arsenic grades in excess of 0.5% need treatment of some type to meet the smelter limits.

Blending can be used if sufficient clean concentrate is available however it is unlikely that this alternative can be used in every case and a more suitable alternative sought. For example Ministro Hayles have contracted to blend their high arsenic concentrates on an as needs basis and 10-15 times the concentrate output is required in clean concentrates to achieve the required arsenic levels

to allow the concentrate to be treated through a smelter. This approach is not sustainable in the longer term if a number of mines seek a similar approach.

Differential Flotation

Differential flotation can be used to produce a low As product for treatment in a smelter and a high As product requiring further treatment. Differential flotation of copper iron and copper arsenic sulphides requires more control as the separation is difficult to achieve because of the similar flotation characteristics of the copper sulphides are similar. However with the correct flotation regime a reasonable separation can be achieved, across a limited range of arsenic grades immediately above the maximum smelter limit for arsenic. Differential flotation is a viable option across the low end of the arsenic concentration range, up to about 2.5% As to 3.0% arsenic. Experience indicates that the mass of clean concentrate produced is at the high end of this range is reaching a level where treatment of the entire concentrate stream is a more robust option.

Table 11 is indicative of the limitations of differential flotation and treatment of the high arsenic product to provide a useful separation as the arsenic grade of differential flotation increases. Limited flotation data was available from which to construct this table and a number of assumptions have been made with regard to concentrate composition and flotation recoveries. However the table does serve to illustrate two key issues

- The mass split between high arsenic and low arsenic concentrates tend to limit differential flotation to the low end of the arsenic concentration range
- The arsenic concentration in the low arsenic product tends to rise as the flotation feed arsenic grade increases to a point where blending of this product with a treated high arsenic product may be required to hold the blended concentrates within the smelter arsenic limit.

The flowsheet comprises separation of a bulk concentrate into a high arsenic and low arsenic product stream. The high arsenic stream can then be treated to selectively remove arsenic and both streams recombined to provide a smelter feed. Treatment of the removed arsenic is separately addressed.

High Arsenic Flotation Concentrate Pre-treatment

Figure 5 above details the options for treatment of a high arsenic flotation product. A pre-treatment approach using partial roasting or an alkaline sulphide leach using the ASL or Toowong technologies can be explored. The partial treatment product can then be combined with the low arsenic product and the combined product treated in a smelter. Alternatively the high arsenic flotation product can be treated by one of a number of available hydrometallurgical options to produce copper cathode and a stable arsenic product for disposal. For the purposes of this analysis it is assumed that no acid requirement external to the treatment process exists so hydrometallurgical treatment options with maximum elemental sulphur generation will be preferred in terms of capital and operating cost. The feed to this flowsheet contains 2.5% arsenic.

Table 12: Medium Grade Arsenic Options

Case Study 3 – Copper Arsenic Concentrates

A case study is presented for a toll treatment hydrometallurgical facility for copper arsenic concentrates where the arsenic grades are in the high end of the range detailed in Table 2 above.

No commercial processes are available other than the POX process which is the basis of the leaching unit operation in this example. While this process is not the lowest operating cost process of the available range it is one of the lowest technical risk. Consideration can be given to siting the plant at a location where the acid produced in the autoclave can be used to leach additional copper or near existing underutilised SXEW facilities both of which impact positively on the project economics.

In addition, experience has shown that this type of concentrate tends to be high in precious metals, particularly silver which, together with gold can be recovered from the autoclave discharge.

Basis of Comparison

The conceptual study was conducted without the benefit of specific comparable testwork on a specific concentrate and the assumptions that were made have been based on previous experience with similar concentrates, including that of the various technology providers involved in the study. The following consistent basis was chosen for all options:

The main sulphide minerals in the concentrate were chalcopyrite (6.4%), enargite (44%) and pyrite (34%).

For the proposed flowsheet, a process model was compiled including mass and energy balances, were generated from design criteria which included a range of assumptions on copper, gold and silver recoveries. Preliminary equipment lists were developed and operating costs and factored capital cost determined at an accuracy of ±35%.

Refinery Design Basis

The following criteria comprise the design basis for a hydrometallurgical refinery to treat dirty copper concentrates. Table 3.5 below details the key design data for the concentrate treatment plant.

Table 13: Refinery Design Basis

The proposed flowsheet has a number of advantages which minimise technical risk:

- Arsenic can be precipitated as scorodite which is environmentally acceptable for disposal
- Copper extraction levels are good typically in the range 96-99% copper
- Precious metals can readily be extracted from the autoclave residues, and is a key requirement given the likely PM content of the tpe of concentrates treated.
- The autoclave residues are environmentally inert given the complete nature of the oxidation process.
- The low grade acid production can be an advantage of secondary copper leaching opportunities are available, particularly those with high carbonate content.

The commercial analysis below will provide a basis for determining the POX flowsheet viability relative to alternatives.

Operating Cost

The operating costs for the proposed POX flowsheet are given in Table 14 below. The operating costs of the SXEW circuit are shown separately, to identify the cost distribution between leaching and recovery and it is also clear that the major cost of the leaching process is consumable quantities, the majority of which are oxygen and limestone for acid neutralisation.

Table 14: Copper Operating Costs

Preliminary Economic Analysis

The technical viability of this flowsheet should not be at issue given the data available from existing operating plants. The commercial viability is at issue as the total POX process is at the high end of the operating and capital cost range for the available processes.

The cost basis for this process is not connected in any way to smelting processes, although there is limited smelting capacity available in the marketplace for concentrates containing this level of arsenic, in reality there is little competition to set pricing benchmarks.

The data presented in Table 15 below present a high level analysis of the flowsheet economics.

If an entire hydrometallurgical facility is required as an addition to a flotation plant then a treatment cost of the order of 103 US c/lb is indicated as required to repay capital within an acceptable time frame

If SXEW facilities are available at an existing mine site with sufficient capacity to treat the autoclave output, then the indicative cost/t of 75 US c/lb is not unreasonable for a concentrate of the above composition.

This analysis is based on commercially proven unit operations and represents the high end of the operating cost range. If a higher level of technical risk is acceptable then operating cost savings of the order of 20 US c/lb and a lower capital cost should be achievable using a leaching process that provides for a lower level of sulphur oxidation. The proposed scenario reflects opportunities that exist in South America where falling copper production is freeing up SXEW capacity and low grade materials are available to leach if acid can be supplied at little or no cost.

The recovery of precious metals is a separate exercise, which requires a separate circuit and Merrill Crowe plant to treat the expected high silver content of this type of concentrate.

		Cu High As	
Parameter	Units	Cost	Cost
		Per Tonne	Per Annum
Concentrate Characteristics			
Concentrate Production	dmt		530,000
Moisture	$\%$		9.0
Concentrate Grade			
-Copper	$\%$		28.0
-Zinc	$\frac{0}{0}$		2.81
-Lead	$\%$		1.48
-Arsenic	$\%$		8.84
- Antimony	$\%$		0.042
Hydromet Plant			
Copper Hydromet Recovery	$\%$		97.0
Recovered Copper	t/a		143,948
Copper Revenue	\$US/a		986,951,536
Hydromet Operating Cost	\$US/a		139,950,363
Net Revenue	\$US/a		847,001,174
Hydromet Capital Cost	\$US		750,000,000
Repay	vears		4
Required Revenue	\$US/a		187,500,000
Operating Cost	c/lb		59.1
Capital Repayment	c/lb		44.1
Refinery Income Required	c/lb		103
Leaching Capital Cost	\$US		390,000,000
Repay	years		4
Required Revenue	\$US/a		97,500,000
Operating Cost	c/lb		30.7
Capital Repayment	c/lb		44.1
Refinery Income Required	c/lb		74.8

Table 15: Cash Flow Analysis

CONCLUSIONS

Hydrometallurgy is unlikely to take over from smelting as the primary means of producing copper from clean sulphide concentrates, however there are niche applications where hydrometallurgy is a serious technical and commercial option for consideration.

Improvements to existing copper flotation concentrators is a neglected opportunity that can increase overall recovery and profitability and while this involves increased flowsheet complexity it is worth consideration for the financial rewards that can be garnered.

Treatment of complex and high arsenic concentrates is the niche application where hydrometallurgy can compete both technically and commercially with smelting. For concentrates high in arsenic in particular, smelter limits on maximum arsenic content of copper concentrates will fall as environmental constraints on smelter emissions tighten in the future. Roasting is a serious alternative to hydrometallurgy for the treatment of high arsenic concentrates, however roaster emissions will also be subject to tightening environmental constraints and in the longer term may not be the technically preferred option as hydrometallurgical options find commercial application.

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