

HYDROMETALLURGICAL TREATMENT OF COPPER SULPHIDES – ARE WE ON THE BRINK?

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1. INTRODUCTION

Once again, we are in an era of intense interest in the hydrometallurgical treatment of copper sulphides. The previous big push began in the nineteen seventies, but tailed off in the eighties when the copper price dropped.

Historically, commercial applications have been generally limited to special cases such as the treatment of copper/cobalt ores on the African Copperbelt, which successfully used the pyromet/hydromet roast/leach/electrowin route. Other than that, efforts have failed to produce a hydrometallurgical process to displace smelting for primary copper sulphide ores. In recent times, however, significant progress has been made with secondary sulphides. For example, there is a growing list of operations using heap leaching/SX/EW, and, of course, the new Mt Gordon pressure oxidation/ferric leaching plant has now been commissioned here in Queensland

Efforts to conquer the chalcopyrite giant have been redoubled in the nineties, with a new wave of candidate processes. This Symposium is devoted to their current status and future prospects. Hopes appear to be on the rise that we may finally be on the brink of an era of breakthrough.

2. DRIVING FORCES FOR CHANGE

In the nineteen seventies and eighties, the main driving forces were the pressure of more stringent environmental regulations and the successful introduction of SX/EW for producing cathode copper at the mine site. The environmental issues were partially alleviated by development of new and modified smelting processes, and the construction of high efficiency sulphuric acid plants.

Ironically, the resulting availability of abundant cheap sulphuric acid further promoted the use of SX/EW for very large-scale oxide ore leaching operations. Further improvements in SX/EW technology resulted, including the routine production cathode copper of equal or better than electrorefined copper, and SX/EW was embraced by the large copper companies.

A further driving force was the desirability of new technology to treat high impurity, multi-metal and low grade concentrates, for which the flotation/smelting approach was unsuitable or uneconomic.

In the nineties, the environmental issues are still there, and there is ongoing interest in impure and difficult to treat ores. However, the spotlight appears to have shifted to the high cost of concentrate transport and toll smelting, and variations in currency exchange rates (outside of USA), especially among medium and small operations. Also there is growing interest in being "masters of one's own destiny", by producing copper metal at the mine site or at an in-house satellite operation. Depending on copper price and location, total realisation costs for concentrates can be in the range of 30-40% of the copper value for sites with a significant transport component. Delay between production of concentrates and payment can be another significant issue for the miner. Penalties for impure concentrates eat further into the margin.

Success in the hydrometallurgical treatment of gold and zinc sulphides by bio-oxidation and pressure-oxidation has made available commercial scale engineering and equipment expertise for copper recovery processes using similar technology. Thus, engineering and operational risk is seen to be diminished. Parallel impacts are also being felt in nickel/cobalt circles.

Another significant encouragement is the increasingly successful treatment chalcocitic ores by bioheap leaching, which are achieving remarkably high copper recoveries in some cases.

3. PUNDITS AND PIONEERS

Optimism ran high among the hydrometallurgical fraternity in the nineteen seventies. Flushed with the stunning success of SX/EW, and swayed by the changing environmental climate, many pundits confidently prophesied the imminent demise of copper smelting, especially in the USA.

Many organisations launched into extensive R & D program with the hydrometallurgical treatment of chalcopyrite concentrates as a major focus. Some of these pioneers built and operated prototype commercial scale operations. These included the Anaconda Arbiter ammonia leach plant in Montana and the Duval CLEAR chloride operation in Arizona. Other hopefuls reaching various stages of development included the Cuprex, Canmet, Cymet and Minemet chloride processes, the USBM chloride and fluosilicic acid routes, the Sherritt-Cominco pressure leaching process, the Kennecott nitric-sulphuric leach process and the Parker nitrile technology. These have been well documented in various previous papers over the years.

In the early eighties, a commercial copper circuit utilising nitrogen species catalysed pressure-oxidation technology to treat a copper-silver concentrate was installed at Sunshine Mining & Refining, Idaho. Although not a stand-alone copper operation, it represents a successful hydrometallurgical application for a complex sulphide ore. The operation closed down in the mid nineties due to declining silver production.

Interestingly, during this period, a roast/leach/electrowin plant was built by Hecla in Arizona, which used cementation rather than the then emerging SX/EW technology. The operation was never really a success.

Despite all these efforts, and the progress made, smelting remained largely unscathed, and still reigned supreme for chalcopyrite concentrates. Our smelting brethren had also been hard at work, coming up with new or modified, more efficient smelting processes, relieving some the pressure of environmental issues.

4. WARRIORS AND WORRIERS

The nineties have seen a new generation of hydrometallurgical warriors rise up to assault the smelting colossus. Already, we have had the first casualty, at Escondida, where a further development of the ammonia leaching approach was applied - and this only tackled the easier target of chalcocite!

However, others are pressing on with vigour, and this Symposium is a testament to their progress and optimism. Already we have one new plant in operation at Mt Gordon, albeit again on chalcocite. Others warriors, though, are setting their sights directly on chalcopyrite itself. They include low, medium and high pressure oxidation, bio-oxidation, ferric sulphate leaching, chloride/bromide leaching and chloride/sulphuric acid leaching.

Most of these processes will be addressed in detail by later presentations, and have also been the subject of previous papers. This paper is therefore limited to brief review of key aspects, especially the current status and prospects for commercialisation.

4.1 MT GORDON

The feedstock is initially whole high-grade chalcocite ore (typically 7.5% Cu) from the previously untreated Esperanza deposit. Later, chalcocite concentrates will be produced from the nearby lower grade Mammoth deposit and fed to the plant. Formerly, Mammoth ore was bio-leached in-situ and in heaps (Gunpowder operation). The plant is capable of producing 50,000 tpa of LME Grade A cathode copper, and there is the possibility of a future cobalt by-product.

The plant, owned by Western Metals of Perth, employs a ferric leach/low pressure oxidation process, after a moderate grind to 75 microns. Final copper recovery is by conventional SX/EW. An outline flowsheet is given in Fig.1. The process was developed in-house by the previous owners Aberfoyle. The development program included a pilot scale operation at site.

Plant engineering and construction was completed by Bateman Kinhill in July 1998, copper design production was reached in May 1999. Commissioning was lengthy, due to mechanical issues and initial treatment of non-typical ore. The plant is now operating at above design capacity and with high availability. The capital cost was about A\$105M. The operating cost is around US37c/lb copper produced, and it is anticipated that it will come down to US30c/lb.

Laboratory testwork indicates that the process is also applicable to chalcopyrite with the addition of fine grinding, a larger oxygen plant and a bigger bleed stream. No work has yet been done on precious metals recovery, which will be complicated by the presence of elemental sulphur in the leach residue. Mt Gordon ores do not contain precious metals.

A licensing strategy not yet been formulated, but the strategy will probably lean towards gaining participation in projects.

4.2 ACTIVOX PROCESS

This is a low pressure oxidation process operating at about 100C, preceded by ultrafine grinding to 5-15 microns, depending on the particular feedstock. Final copper recovery is via SX/EW. The process is depicted in Fig. 2.

The process is applicable to chalcopyrite and chalcocite, and gold is recovered by cyanidation of the residue. Advantages of the low pressure include lower capital cost for the autoclaves and related equipment, production of elemental sulphur which minimises oxygen consumption, operation below the melting point of sulphur and precipitation of most of the iron as haematite or goethite. Cyanide consumption for gold recovery from the residue is said to be acceptable.

WMT claim that compared with smelting, capital cost is significantly lower and operating cost is similar in areas of reasonable power cost. Metal recoveries are said to be at least as good as smelting/refining, and there is potential to increase flotation recovery, as Activox is relatively insensitive to concentrate grade. Plants as small as 10,000 tpa copper output could be viable in the right economic scenario.

The process is being developed by Western Minerals Technology in Perth. Nickel and gold feed materials have been successfully tested as well as copper. Three pilot plant campaigns have been successfully run on different concentrates, and other runs are planned. Work has also been carried out on peripheral operations in order to improve overall process performance. For example, the use of PSA oxygen has been successfully integrated into the process to facilitate on-site generation of oxygen for smaller projects.

WMT believe that the technology is ready for commercial application. A number of nickel/cobalt/copper projects are being progressed, and WMT are confident that at least one of these will go ahead within the next 12 months. It is understood that the technology is available for license.

4.3 CESL PROCESS

The CESL process is based on medium pressure oxidation at about 150C, with chloride as a catalyst. It is preceded by a light regrind to about 95% passing 45 microns. A second stage atmospheric leach is incorporated to maximise copper extraction. LME grade cathode copper is recovered by SX/EW. An outline flowsheet is presented in Fig.3.

The process is aimed at treating chalcopyrite concentrates in direct competition to smelting. Gold is recovered from the residue by cyanidation following elemental sulphur removal, so that cyanide consumption is reduced. The sulphur is available as a potential by-product. Advantages include the use of a temperature high enough to avoid the need for ultrafine grinding, while still only producing elemental sulphur to minimise oxygen consumption, and precipitation of most of the iron as haematite. The potential problems of operating in the presence of molten sulphur are said to have been overcome. The presence of chloride will require the expense of suitable corrosion resistant materials.

The process is being developed by Cominco Engineering Services Limited (CESL) of Vancouver, and is applicable to nickel concentrates as well as copper. CESL claim that the economic comparison with smelting is favourable, with about half of the capital and lower operating costs. Operating costs are affected by the prevailing cost of power. Metal recoveries are said to be comparable with the smelting route. Economics improve with larger installations.

Extensive fully integrated pilot and demonstration plant campaigns have been successfully undertaken, and the process is said to be ready for commercial application. A number of projects are under consideration. The technology is available for license on a royalty basis.

4.4 DYNATEC PROCESS

This is a medium pressure oxidation process, which operates at 150C after a fine grind to 90% passing 25 microns. Unleached copper is floated from the residue after sulphur removal, and recycled to maximise copper extraction. Copper recovery is via SX/EW, though direct SX is being tested. Gold is recovered from the flotation tailing by cyanidation. The prior removal of sulphur reduces cyanide consumption. The flowsheet is shown in Fig. 4.

The above conditions relate to chalcopyrite concentrates. For chalcocite, the operating temperature is reduced to about 100C. As for the CESL process, the 150C operating temperature minimises oxygen consumption and precipitates the iron. However in the Dynatec process, coal is added to disperse the molten sulphur.

The process is being developed by Dynatec Corporation (Formerly Sherritt International Consultants) of Fort Saskatchewan, Canada. Dynatec state that high copper and gold recoveries have been achieved in miniplant campaigns. An engineering study for a commercial plant is planned.

4.5 NITROGEN SPECIES CATALYSED (NSC) PRESSURE OXIDATION

This process is based on moderate pressure oxidation at 125-155C, catalysed with nitrogen species supplied from sodium nitrite, following an ultrafine grind to 80% passing 10 microns. Silver is solubilised and recovered by precipitation with sodium chloride, alkaline reduction, casting and electrowinning. Copper is then recovered by conventional SX/EW. At the earlier mentioned at Sunshine operation, the feedstock was argentiferous tetrahedrite concentrate, which was first preleached with sodium sulphide to remove and recover antimony by EW. The copper in the residue was in the form of chalcocite. After regrinding, it was treated by NSC pressure oxidation at 155C in batch autoclaves. (Continuous autoclaves could be used, but were felt to be not fully proven at the time.) Molten elemental sulphur was formed, which was converted into 3 mm prills by cooling while maintaining agitation. The prills were then screened out of the residue for use in the antimony section. The copper /silver portion of the Sunshine plant is outlined in Fig.5. Leach extractions achieved were 99% for copper and 96% for silver.

Laboratory testwork has indicated that chalcopyrite concentrate can be treated successfully in the temperature range of 125-155C, with 125 being the preferred temperature. Silver recovery will be as at Sunshine, while novel gold recovery technology is incorporated in which the elemental sulphur is reacted with sodium hydroxide to form sodium polysulphide and thiosulphate. These compounds are used to extract and recover the gold, thus avoiding the issue of cyanidation in the presence of elemental sulphur. Advantages claimed for the process include fast pressure oxidation kinetics and the ability to employ unlined stainless steel autoclaves because of the high solution redox potential resulting from the NO^+/NO couple. The process can also be used at a higher pressure corresponding to 175C at which point the sulphur is further oxidised to sulphate. This yields sulphuric acid for potential use in an associated copper oxide ore leaching operation, at the expense of increased oxygen. In this case, the gold would be recoverable from the residue by cyanidation. Sources of the technology are understood to be The Centre for Advanced Mineral and Metallurgical Processing (Dr Corby Anderson) in Butte, Montana, and Sunshine Mining and Refining. No standard licensing arrangement has yet been developed. Preliminary economics appear favourable. Further work is being done and applications are under consideration.

4.6 HIGH TEMPERATURE PRESSURE OXIDATION

High pressure oxidation generally involves a temperature in the range of 200-225C, with copper recovery by conventional SX/EW. The process is illustrated in Fig.6.

The process is applicable to chalcopyrite concentrates, with gold recovery from the residue by cyanidation after neutralisation.

Sulphur is oxidised to sulphate, which makes acid available for an adjacent copper oxide leaching project, at the expense of increased oxygen consumption and higher cost autoclaves and associated facilities. Advantages include no fine grinding, no catalyst, no elemental sulphur in the autoclaves or leach residue and prior industry experience with gold pressure oxidation.

Compared with smelting, capital cost appears to be significantly lower. Operating cost is also attractive, particularly when the unit power cost is favourable. Economics are favoured at higher throughputs. Metal recoveries are generally in the high nineties.

Development work for chalcopyrite concentrates has been done by a number of organisations. Placer Dome of Vancouver have undertaken pilot plant work and prepared comparative economics with smelting. General Gold of Perth have also carried out successful pilot scale work and a full feasibility study for the Guelb Moghrein project in Mauritania, which is said to be ready to proceed when funding has been obtained.

4.7 BIO-OXIDATION

Bio-oxidation can be carried out at temperatures in the range of 35-70C, utilising various bacteria types depending on the particular temperature selected. Secondary copper minerals such as chalcocite are effectively leached using mesophiles at about 35-45C. For chalcopyrite, moderate thermophiles at 45-50C or extreme thermophiles at 70-80C are more effective. Ultrafine grinding can be considered to enhance performance for chalcopyrite concentrates, though at the expense of higher power consumption and more demanding liquid/solid separation characteristics. Copper is recovered by conventional SX/EW. An outline flowsheet is shown in Fig. 7.

Copper and gold recoveries in the high nineties are achievable. Cyanide consumption will be effected by the amount of elemental sulphur in the residue, which in turn depends on the degree of oxidation. Silver recovery varies with mineralogy. A high degree of oxidation to sulphate makes acid available to treat associated copper oxide ore, at the expense of higher power consumption. A significant amount of limestone can be required for neutralisation and iron precipitation.

The process has the advantages of relatively simple atmospheric pressure equipment, prior commercial operations for gold ores, and the absence of on-site oxygen generation or storage facilities. However, oxygen utilisation from aeration is relatively low, though work is being done to gain improvements. Retention time is affected by mineralogy, but is generally in the order of 4-6 days. Capital cost is significantly lower than smelting, and the process is considered to be viable for relatively small operations. Operating cost is heavily dependent on the cost of power in the area. Bio-oxidation is also being considered for nickel and cobalt feedstocks, and a commercial plant for cobalt has been constructed in Africa.

There appear to two major development efforts to commercialise copper ore bio-oxidation, both of which benefit from prior commercial gold bio-oxidation experience:

4.7.1 Billiton BioCOP Technology

Billiton are conducting parallel programs for mesophile and thermophile bacteria. Mesophile bioleaching at 42-45C is being developed for secondary copper sulphide applications. Depending on mineralogy, the process may include a ferric preleach with recycled SX. Residue flotation can be used for recovering any chalcopyrite component as a concentrate. Gold/silver can be recovered with the flotation concentrate, or by cyanidation of the leach residue. Thermophile bioleaching at 70-80C is being pursued for chalcopyrite, as the mesophile approach suffers from a passivation effect which prevents high copper recovery from chalcopyrite. Billiton do not propose to use ultrafine grinding.

Billiton have operated pilot plants for copper and nickel production. Successful demonstration plant campaigns were conducted in 1998. A demonstration plant to produce 1000 tpa copper is currently under consideration. Commercialisation for copper is about 2 years away for mesophile bacteria, and 3 years for thermophiles. Billiton are not planning to licence the technology, except where they participate in the project.

4.7.2 BacTech/Mintek Technology

After extensive separate development experience, BacTech of Perth and Mintek of Johannesburg are now operating in collaboration. Their test program experience ranges from bioleaching of secondary sulphides with mesophiles at 36-40C, and moderate and extreme thermophiles for chalcopyrite at 45-50C and 70C respectively. Ultrafine grinding is generally included. Mintek also developed of indirect process in which iron bio-oxidation occurs in separate step. This approach yields elemental sulphur rather than sulphates.

BacTech/Mintek have run pilot scale campaigns, including a fully integrated system for chalcopyrite concentrates at Mt Lyell, Tasmania, where low unit power cost results in a particularly favourable operating cost. Nickel concentrates have also been tested. Commercial opportunities are being actively pursued. An agreement has been made to study the application of bioleaching for the Stillwater nickel/copper project in Montana. Another arrangement has been made with Penoles in Mexico to construct and operate a pilot plant, test new reactor designs, undertake a feasibility study and look at possible base metal operations in other Latin American countries. An agreement has been made with Paques Bio Systems in the Netherlands concerning their Circox bioreactor design, which could reduce capital and operating costs by up to 25%.

4.8 NENATECH PROCESS

This involves ferric sulphate leaching at 80C and atmospheric pressure, with oxygen sparging to maintain an adequate level of ferric. The feed is finely ground to 20 microns. Copper recovery is by conventional SX/EW. The flowsheet is depicted in Fig. 8.

Copper recovery is expected to be in the mid to high nineties. Sulphur is largely oxidised to sulphates. Acid generated could be utilised to leach oxide ore. Limestone is required to remove iron and excess acid from solution. Gold can be recovered from the residue by cyanidation without the requirement to remove sulphur. Cyanide consumption should be reasonable. The process has the advantage of relatively simple atmospheric pressure equipment, similar to what has been used in the uranium industry. However it needs on-site oxygen, though this helps to reduce leaching time to less than 24 hours.

Capital cost is significantly lower than smelting, and the technology can be applied to smaller operations. The process was developed by MIM, Brisbane, and Highlands Gold, PNG, for the complex Nena ore in PNG. This project was subsequently expanded to treat the nearby larger Frieda River chalcopyrite deposit. Successful pilot plant campaigns were undertaken at Hydrometallurgy Research Laboratories in Brisbane. The project is now being managed by Cyprus-Amax and Highlands Pacific, and confirmatory testwork has been carried out in the USA. Licensing strategy has not yet been formulated.

4.9 INTEC PROCESS

Involves a four-stage counter-current leach with chloride/bromide solution at 85C and atmospheric pressure. Gold and silver are solubilised along with the copper. Impurities are precipitated with lime, then silver is precipitated with mercury as an amalgam, then produced as a chloride for further processing. Copper is electrowon as high purity dendrites in a special cell, then processed into ingots or briquettes. Gold is recovered from solution on to carbon for further processing. The halx leach solution is regenerated in the EW cells. An outline flowsheet is given in Fig. 9.

Metal recoveries are expected to be in high nineties. Sulphur is formed in the elemental state, and potentially could be recovered as a by-product. Iron precipitates as goethite, and therefore does not require limestone. Other advantages include the absence of fine grinding, integral but separate, gold and silver recovery steps, less than 24 hours leach retention time, no on-site oxygen generation or storage, and copper EW from chloride conditions without chlorine generation. On the other hand, equipment must be designed to resist chloride, and a novel type of EW cell is involved.

The process is being developed by Intec in Sydney supported by a consortium of companies. Following successful operation of a pilot plant in 1996, Intec have been operating a 1 tpd demonstration plant also in Sydney. Intec state that the capital and operating costs are lower than smelting and refining. The process will also be applicable for smaller capacity plants. Intec's aim is to compete directly with smelting for primary copper sulphide concentrates, and their intention is to make the technology available for license on a royalty or other basis.

4.10 CHLORIDE/SULPHURIC ACID LEACHING PROCESS

Leaching is carried out with a sodium chloride/sulphuric acid solution with oxygen sparging at 80-95C and atmospheric pressure. Leach time is under 24 hours. The chloride acts as a catalyst for the oxidation reaction, and allows high copper recovery at a relatively coarse grind size. Copper is recovered by conventional SX/EW. The feed size is about 75 to 100 microns, so that no fine grinding is required. Chloride resistant materials must be used for the equipment. The process is outlined in Fig.10.

The technology has been in commercial operation at BHAS (Pasminco), at Port Pirie, South Australia, for many years for the treatment of copper/lead matte. About 92% of the copper is extracted for a production of around 4000 tpa. Titanium cathode plates are used in EW instead of stainless steel to resist corrosion due to chloride carryover.

The process is being considered to treat highly pyritic chalcopyrite ore by Leadstar for their Labuk project in Malaysia. The Labuk ore does not respond well to flotation, and whole-of-ore treatment is planned. Chalcopyrite is preferentially leached, and the degree of oxidation of pyrite is controlled to suit the heat and acid balances. The precious metals are largely in the pyrite, and are not recovered. Sulphur from the chalcopyrite is converted into the elemental state. Continuous piloting at Hydrometallurgy Research Laboratories, Brisbane, has been undertaken, and a further confirmatory campaign is currently planned along with a definitive feasibility study. The testwork indicates a copper recovery in the upper nineties. Cobalt carbonate is recovered as a by-product. The projected capital cost for a 14,000 tpa process plant, including cobalt recovery but excluding infrastructure, is about US\$2000 per annual tonne of copper. The anticipated operating cost is US\$36c/lb.

While the new generation of hopefuls are full of enthusiasm, there are still many sceptics who worry about such issues as the dependence of the new processes on power for electrowinning, corrosion and maintenance, plant availability, doubts about precious metals recovery, the previous chequered history of hydrometallurgical processes for copper sulphide concentrates and the existence of smelters whose capital has long been repaid as well as new smelters protected by national trade policies.

5. BRAVE NEW WORLD AHEAD?

Despite past failures, there does appear to be a different feeling in the air! Perhaps the time is ripe for hydrometallurgy to succeed. We may after all, like the nickel industry, be on the brink of a "brave new world."

Time will obviously tell. In the meantime, today's warriors are certainly giving the industry something to think about!

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