A review of copper hydrometallurgy

by J. C. PAYNTER*, B.Sc. (Chem. Eng.) (Visitor)

SYNOPSIS
Copper hydrometallurgy is discussed with special reference to the treatment of chalcopyrite concentrates under South African conditions. The following processes are described and illustrated: Arbiter Process, sulphuric acid pressure leaching, roasting processes, the Cymet Process, and the ferric chloride process developed at the National Institute for Metallurgy. These processes are then compared with respect to the form of sulphur produced (elemental sulphur or sulphate), the character of the iron product, and the handling of different types of ore.

SAMEVATTING
Koperhidrometallurgie word bespreek met spesiale verwysing na die behandeling van chalcopyrietkonsentrate in Suid-Afrikaanse toestande. Die volgende prosesse word beskryf en gellustreer: Sherritt Gordon se ammoniaksstruklogging, die Arbiter-proses, swaveluurduiklogging, roosterprosesse en die ferrichloorprosesse wat by die Nasionale Instituut vir Metallurgie ontwikkel is. Hierdie prosesse word dan vergelyk ten opsigte van die vorm van die swaai wat geproduceer word (elementale swaai of sulfaat), die aard van die ysterprodukt en die hantering van die verskillende soorte erse.

INTRODUCTION
In giving a review of the hydrometallurgical processes for copper, I am conscious of its being a subject that is widely discussed1-3. Not being an expert, I shall not attempt to provide a better review than those already available. However, as a result of discussion with my colleagues at the National Institute for Metallurgy (NIM) and with metallurgists in industry, I have come to realize that, instead of having a clear picture of the direction in which copper processing is moving, particularly processes employing hydrometallurgical techniques, most metallurgists are becoming increasingly confused, myself included. It is hoped that this paper, although saying very little that is new, will provide a suitable basis for discussion so that benefit can be obtained from the wealth of experience and judgment available and so that the picture can be clarified just a little.

I intend to discuss copper hydrometallurgy with special reference to South African conditions because I believe that conclusions drawn for conditions elsewhere, for example in Arizona, U.S.A., are unlikely to be the same as those arrived at for a plant situated in South Africa. Even within Southern Africa, what applies to a plant located in a remote desert area does not necessarily apply to a plant located in the Witwatersrand area. I also hope to highlight those areas in which research can probably lead to cheaper and improved processes.

WHY HYDROMETALLURGY?
It is perhaps difficult to provide a conclusive reason for the upsurge of interest in hydrometallurgical processes during the past five years. I expect that many persons would cite the fact that, whereas the 1960s felt the impact of the computer in almost every sphere of life, the 1970s are destined to experience the impact of the environmentalist. 'Clean environment' campaigns are already a reality of life, and environmental considerations have forced the cancellation of construction plans for power stations, the closing down of copper and zinc smelters, the wrestling of power from the motor giants of Detroit, and last, but not least, the clean-up of the air in cities like London, which visitors now say has air superior to that we breathe in our own modern metropolis. Sulphur dioxide pollution from smelters has perhaps been the strongest driving force behind the recent massive expenditure on research and development in hydrometallurgy. However, there are probably other factors that have contributed towards this trend.

(a) It has been predicted that an increasing percentage of new copper production will come from non-sulphuric sources and mixed sulphide ores (e.g., copper-zinc). For a variety of technical and economic reasons, these ores often cannot be processed by normal flotation and pyrometallurgical techniques. Differential-flotation processes for mixed sulphides seldom give as clean a separation as desired, and in some instances flotation is quite unpractical.

(b) The successful industrial application of the copper-selective solvent LIX4.5, though used in the treatment of oxide ores, provided the most significant breakthrough in copper hydrometallurgy since that achieved by Sherritt Gordon in their successful development of pressure-leaching techniques.

(c) Many of the basic chemicals required for hydrometallurgical processes are produced in large tonnages at low prices (e.g., oxygen, ammonia, chlorine, hydrochloric acid). Of course, if your process requires sulphuric acid, a smelter may pay you to take it away by the 1980s!

(d) Suitable materials of construction, e.g., titanium, fibreglass, and plastics, have been developed at reasonable prices.

(e) The ever-increasing cost of transport and the tendency for concentrates to be processed locally possibly mean that smelters, whose processing costs are favoured by very large units, are less competitive with hydrometallurgical plants for the smaller tonnages often applicable to new discoveries (e.g., 5000 to 30 000 tonnes of copper
annually). Many local companies have recently found that the cost of transporting concentrates, custom smelting, and refining has risen so much that the need to consider their own processing facilities is becoming increasingly pressing.

(f) As the price of copper has risen, the importance of working capital tied up in copper inventory has increased, and it is believed that virtually all hydrometallurgical processes will have a lower inventory than that of conventional pyrometallurgical processes.

Despite the enormous effort being directed to research in hydrometallurgical processes, an equal, if not larger, effort is being devoted to the following:

(i) improvements in existing pyrometallurgical processes, with special emphasis on the control of sulphur dioxide pollution, and

(ii) developments in new pyrometallurgical processes in which the smelting and converting steps are integrated into one continuous operation (or sequence of operations), and which produce a steady high-quality stream of sulphur dioxide gases, thus making the manufacture of sulphuric acid easier and cheaper (e.g. Mitsubishi, Noranda, and WORCRA processes).

The various new processes being investigated are well summarized in a recent issue of *Engineering & Mining Journal*.

The cost of bringing sulphur dioxide pollution under control will vary from region to region, depending on the regulations in force, but, for conditions in the U.S.A., the cost has been estimated as anything from 3.5 to 9.0 South African cents per kilogram of copper. These costs are significant when it is realized that the custom processing of concentrates to refined copper in a large smelter may cost about 15 South African cents per kilogram of copper, direct operating costs being as low as 7 to 10 cents.

The philosophy that, because many smelters are situated in remote areas, particularly in a country like South Africa, the abatement of sulphur dioxide pollution is not very important is unlikely to carry much support in the future. The erection of smelters must involve the development of a township for persons working at the smelter, and such persons are entitled to breathe clean air when away from work, even though they may have to accept a certain discomfort while at work. A partial solution to pollution by sulphur dioxide does not seem to be acceptable.

**PRODUCTION OF SULPHURIC ACID**

It is interesting to consider what increase in sulphuric acid production from smelter gases could be absorbed by other industries during the next decade. The 1972 production of sulphuric acid in South Africa was approximately 1 400 000 tonnes of 100 per cent H₂SO₄, of which 22 per cent was used by the mining industry (mainly in uranium processing), 67 per cent in the manufacture of fertilizers, and 11 per cent by other consumers.

The quantity of sulphuric acid that could be recovered from smelter gases currently going into the atmosphere is approximately 120 000 tonnes per annum. The air-pollution authorities are already taking certain steps about persuading most of these operators to recover and use this sulphur dioxide.

It is estimated that, if all new copper, zinc, lead, and platinum mining operations smelt their own concentrates and are required to recover the sulphur dioxide from their smelting operations, the production of sulphuric acid in South Africa would be an extra 1 000 000 to 1 500 000 tonnes per annum by 1985. This is likely to be more than the local mining and fertilizer industries would require, unless major new uses for sulphuric acid are found. Unfortunately, most of the new smelter capacity is likely to be located in the north-western Cape and South West Africa, which are near neither to the source of phosphates at Phalaborwa nor to the main farming areas. It is fairly generally accepted that it is uneconomic to transport acid more than 100 to 200 miles.

There is a very good opportunity for the export of fertilizers, especially to South America, and the opening up of Saldanha Bay may make it worth while to site smelters near Saldanha Bay so that the sulphuric acid produced can be reacted with phosphate from Foskor or from the deposits at Langebaan, near Saldanha Bay. It is a well-known fact that apatite (phosphate ore) is almost as cheap a neutralizing agent for sulphuric acid as lime.

These facts highlight the importance of co-operation between the mining and fertilizer industries in co-ordinating, as far as possible, future expansion in smelter and fertilizer plants. The recently announced plans of Impala and Omnia to get together to produce phosphoric acid using sulphuric acid produced from Impala’s stack gases is an encouraging move in this direction.

The cost of producing sulphuric acid from smelter gases depends on the size of the plant and the type of smelter, but it is likely to lie between R20 per tonne for small plants and R5 per tonne for very large plants. In most instances, it is probable that this byproduct acid will be sold at a negligible profit, and, in an assessment of pyrometallurgical routes versus hydrometallurgical routes, it seems sensible to neglect any credit from the sale of the sulphuric acid over and above the production cost.

**HYDROMETALLURGICAL PROCESSES FOR COPPER**

There are many excellent publications reviewing the hydrometallurgy of copper, and Subramanian and Jennings recently discussed, concisely and clearly, the various alternatives that are being investigated for the treatment of chalcopyrite. Dasher recently critically assessed the ability of hydrometallurgy to compete with pyrometallurgy. In this paper, I wish to discuss only those processes that appear to be attracting major attention or appear to be promising. Some may regard the omission of bacterial leaching as serious, but too little is known about the engineering of these processes on a large scale to permit a critical assessment.

Discussion will be mainly limited to the treatment of chalcopyrite concentrates since chalcopyrite is
both the most-abundant copper mineral and the most difficult to leach. Any process that is to be successful must therefore be capable of treating chalcopyrite. A good deal has been written about hydro-metallurgical processes for the treatment of oxide ores, and these will not be discussed here. After the various processes have been briefly described, they will be compared with respect to certain key factors, namely, the degree of oxidation of the sulphur (elemental sulphur or sulphate), the character of the iron product, and the ability to handle mixed sulphides. The comparison strictly applies only to chalcopyrite, and quite different conclusions can be drawn if, for example, chalcocite is being considered.

**Sherritt Gordon’s Ammonia Pressure-Leaching Process**

Sherritt Gordon Mines were pioneers in hydrometallurgy, and much of the credit for advancing the technology of pressure leaching must be given to them. They use pressure-leaching processes for treating nickel concentrates, and they have licensed, among others, Western Mining in Australia and Impala Platinum to use their technology. In laboratory and pilot-plant tests on chalcopyrite, a 95 per cent extraction of copper has been achieved. Most of the unleached copper can be floated from the residue and recycled.

Their flowsheet for the treatment of copper-zinc concentrates is shown in Fig. 1. The basic equations for the dissolution reactions are as follows:

$$2\text{CuFeS}_2 + 8\text{H}_2\text{O} + 12\text{NH}_3 + 2\text{O}_2 \rightarrow 2\text{Cu} (\text{NH}_3)_4\text{SO}_4 + 2\text{Fe}_2\text{O}_3 + 6\text{H}_2\text{O}$$

$$\text{ZnS} + 2\text{O}_2 + 4\text{NH}_3 \rightarrow \text{Zn} (\text{NH}_3)_4\text{SO}_4$$

It will be noted that all the sulphide sulphur is converted to sulphate, and, where there is a market for ammonium sulphate, the process has a definite attraction. In South Africa, where ammonia is used for fertilizer purposes, it is sold at a lower price than ammonia used for industrial purposes. Ammonia would have to be purchased at the fertilizer price before the ammonium sulphate could be sold competitively. As it is unlikely that there will be a large market for ammonium sulphate, the process economics must normally be assessed on the basis that the ammonia will be regenerated using lime and the calcium sulphate will be disposed of.

Sherritt Gordon Mines found that pressures of at least 100 lb/in² or 690 kPa (gauge) were necessary for leaching. Copper was recovered as a metal by precipitation with hydrogen at high pressures, and zinc was recovered by precipitation with carbon dioxide at high pressures. All these high-pressure operations result in an expensive plant requiring careful maintenance and operation. For the reasons given above, these processes are unlikely to find much application in copper processing.

**The Arbiter Process**

The Arbiter Process (Fig. 2), developed by Anaconda, is essentially a modification of the Sherritt Gordon Process. It uses ammoniacal processing but eliminates the use of high pressures. In the leaching step, oxygen, instead of air, is used (tonnage oxygen makes this possible in certain locations) with special agitation techniques that result in good dispersion of the oxygen in the slurry and with proper control of the reaction by some undisclosed means. The availability of the liquid-liquid-extraction reagent LIX has permitted the extraction of copper by liquid-liquid extraction and electrowinning. Techniques are also now available for the recovery of zinc and nickel without resort to the high
pressures used by Sherritt Gordon. It will be noted from Fig. 2 that, as with high-pressure leaching, copper recovery is not complete and unreacted copper has to be floated from the residue.

The Arbiter Process was developed by Professor Arbiter of Anaconda, after a thorough review of all the possible hydrometallurgical processes, as the process that required the least development and was most likely to produce the cheapest copper for Anaconda. A large plant having a capacity of 100 tonnes of copper per day is being erected in Arizona, and Anaconda have claimed that the capital cost is only half that of a smelter.

The process still suffers from the major disadvantage that either ammonium sulphate must be sold or ammonia must be recovered by neutralizing with lime. Where precious metals are not of any account, Arbiter suggests that the lime should be added to the leach because this eliminates one step in the liquid-solid separation and improves the filtration characteristics of the iron oxide in the leach residue.

Because very few metals form ammine complexes, all ammoniacal leaching processes have the advantage of being very selective. This is particularly advantageous in avoiding the extraction of iron, which is almost invariably present in all copper concentrates.

Liquid-liquid extraction using LIX in ammoniacal systems has the advantage over acid systems that the solvent can take higher loadings of copper. A disadvantage, however, is that LIX is less selective for copper over nickel and zinc than in acid systems, but there are techniques for overcoming this problem.

Ammoniacal processes are ideal when the gangue minerals are acid-consuming (e.g., calcareous or dolomitic).

The economics of the process are clearly critically dependent on the availability of cheap oxygen, lime, and ammonia. The losses of ammonia will probably be finally known only when a large-scale plant is in operation but should be less than in the Sherritt Gordon process. These aspects will be discussed in greater detail later in the paper.

One further potential advantage of the ammoniacal system is that copper can exist in the cuprous form, which makes the possibility of direct electrowinning of the copper from the leach liquor rather attractive, since the power cost would probably only be about 50 per cent of that from cupric solutions and the cost of liquid-liquid extraction would be eliminated. This, however, represents a major research project in electrochemical engineering, and the purity of the copper might be lower than that recovered from the strip liquor of a liquid-liquid-extraction plant.

*Salphoric Acid Pressure-Leaching Processes*

Complete oxidation of sulphide concentrates can be achieved in the relatively short time of 1 to 2 hours if temperatures in the range of 140 to 200°C and high pressures of air or oxygen are used. However, the equipment is expensive, and the costs of heating the slurry and compressing the oxidant are considerable. Sulphate is formed under these conditions, and the costs of oxidant and lime are therefore the same as in the ammoniacal processes.

A lower-temperature process operating below the melting point of sulphur in the temperature range 100 to 120°C is to be preferred, since the engineering problems are not nearly so severe, and the costs of heating and compressing the oxidant are also much less. A further major advantage is that, at these temperatures, elemental sulphur, rather than sulphate, is formed. This means that a possible salable by-product is produced instead of the sulphate, which requires lime for neutralization. In addition, the cost of oxidizing the concentrate is only about 30 per cent of that for the higher-temperature process where sulphate is produced. The difference is shown by the following two simple equations:

\[
2 \text{CuFeS}_2 + 2.5 \text{O}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{CuSO}_4 + \text{Fe}_2\text{O}_3 + 4 \text{S} + 2 \text{H}_2\text{O},
\]

and

\[
2 \text{CuFeS}_2 + 5.5 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{CuSO}_4 + \text{Fe}_2\text{O}_3 + 2 \text{H}_2\text{SO}_4.
\]

The leach liquor, after removal of the copper by liquid-liquid extraction or electrowinning, is returned to the process for further leaching. The sulphuric acid shown in the left-hand side of the first equation is therefore recycle acid, and the process has a very low net acid consumption. In fact, it appears that about 5 per cent of the sulphur will be converted to sulphuric acid, thus providing the necessary make-up of acid.

These pressure-leaching processes have the advantage that iron is precipitated as a ferric hydroxide oxide, which reports in the residue. The quantity of iron remaining in solution is a function of the acidity and of the time and temperature of leaching, but, because the solution is recycled to the leach after the removal of the copper, all the iron will eventually report in the residue. It is almost certain that the actual oxidation attack on the mineral is by ferric iron, and a small quantity of dissolved iron is therefore necessary.

Owing to the relatively low level of iron in the leach liquor, direct electrowinning of copper from the leach liquor can be considered, thus saving the costs of the liquid-liquid-extraction plant.

The effect of various operating parameters on the leaching process have been studied extensively by Vizsolyi et al., and Fig. 3 is a flowsheet of the process suggested by them. Under the optimum conditions of a temperature of 115°C and an oxygen partial pressure of 300 to 500 lb/in² or 1380 to 3450 kPa (gauge) on a concentrate that had been ground to 99.5 per cent minus 325 mesh, the percentage copper extraction was only about 65 per cent after 2½ hours. After removal of the sulphur, the undisolved chalcopyrite was floated and recycled for further leaching. Although many of the hydrometallurgical processes being considered appear to require flotation of the leach residue for the recovery of undisolved mineral, such a low percentage dissolution as 65 per cent appears to be unacceptable, especially when it is considered that very intense leaching conditions were used.

Vezina studied this problem in greater depth on a chalcopyrite-
Fig. 2—Simplified flowsheet of the Arbiter Process (according to Price)1)

Fig. 3—Example of a pressure-leaching scheme for chalcopyrite (according to Vizsolyi et al.14)

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pentlandite-pyrrhotite concentrate and showed that the degree of grinding is critical to the achievement of high copper extractions. On a product that was ground to 93 per cent minus 20 \(\mu\)m, the copper extraction was 91 per cent after 8 hours at an oxygen pressure of 80 lb/in\(^2\) or 550 kPa (gauge). Analysis of the residue showed that the extraction for particles less than 20 \(\mu\)m exceeded 95 per cent.

The importance of grinding was taken one step further by Gerlach et al.\(^{14}\). It was found that the subjection of chalcopyrite to a milling action involving a strong impact (vibration mills are commercially available) resulted in copper extractions of 99 per cent in 1 hour at an oxygen pressure of 2000 kPa and a temperature of 110°C. The degree of grinding is not given. Gerlach et al. attribute this surprising result to the fact that impact milling not only comminutes the mineral substances but also mechanically disturbs the lattice structure of the mineral so as to render it more susceptible to oxidizing chemical attack. This theory is supported by X-ray-diffraction studies and also by electrochemical studies, which showed that the redox potential for activated chalcopyrite was only 320 mV, compared with 550 mV for non-activated chalcopyrite.

The approach being pursued by Gerlach et al. clearly represents a significant advance on the results of previous workers, mainly because complete leaching of the copper in one step now appears to be a possibility. It has been reported that Lurgi are testing the process on a pilot-plant scale, and it must certainly be regarded as one of the contenders for commercial application.

Other investigators have also recognized the importance of activating chalcopyrite to make it easier to leach. Copper\(^{14}\), sulphur\(^{16}\), nitric acid\(^{17}\), and hydrogen\(^{18}\) pre-treatments, among many others, have been tried. These are all described and compared by Subramanian and Jennings\(^8\).

**Roasting Processes**

Roasting processes are well-established and have been extensively described in the metallurgical literature. The basic patent using fluidized-bed reactors was issued in 1957, and successful commercial plants are operating in Zambia and Zaire. Over 300 000 tonnes of copper per annum are produced by this process in Zaire alone.

Most processes involve a sulphation roast, followed by a water or dilute-acid leach of the copper with some dissolution of iron. Copper is recovered by electrolywinning, and the sulphate formed is removed by liming. (This process is often referred to as the R-L-E process.) The temperature of roasting is critical: it is essential to select a temperature that is high enough to decompose Fe\(_2\)(SO\(_4\))\(_3\) but is not high enough to result in the formation of insoluble copper ferrite.

Hecla Mining Company\(^{19}\) recently conducted an extensive experimental programme to develop the R-L-E process for use at its Lakeshore Mine. They operated a pilot plant producing 1 ton of high-purity cathode copper per day. This process has its major attraction when it is required to treat ores of mixed oxides and sulphides, as at Lakeshore, and the flowsheet as developed for Lakeshore is given in Fig. 4. The sulphur eventually all reports as sulphuric acid, which can be used in the leaching of the oxide. It would have been interesting if Hecla had compared the economics of liquid-liquid extraction with those of the sponge-iron process in the production of copper from the oxide leaching circuit.

Hecla made extensive studies on the pilot plant to find the optimum roasting temperature for copper recovery at a minimum production of dissolved iron. By operating in the temperature range 590 to 700°C, they achieved copper dissolutions of 97 per cent and iron extractions of less than 8 per cent.

Other organizations (e.g., CSIRO\(^{20}\), U.S. Smelting & Refining Company\(^{21}\), Dowa Mining\(^{22}\)) have developed alternative methods for the recovery of the copper from solution after roasting and leaching. Most of these alternative processes are designed for the treatment of mixed copper-zinc ores.

Recently, the U.S. Bureau of Mines\(^{23}\) proposed a sulphating roast with lime in the roast to overcome one of the major disadvantages of the conventional R-L-E process, namely the production of a roaster gas containing sulphur dioxide. Where there is no market for acid, the sulphate may as well be converted to gypsum in the roaster rather than later by neutralization, which is known to be a tricky operation. Roasting is done at about 600°C, and, in work done at NIM on this process, extractions exceeding 97 per cent have been achieved. The process appears to have a particular advantage for flotation concentrates containing acid-consuming gangue. It has been shown\(^{24}\) that the quantity of lime required to fix the sulphate can be decreased if...
the concentrate contains calcareous material.

The major problem with roasting processes is the dissolution of iron. If a strongly acid electrolyte is used for the dissolution of the copper, iron dissolution may be excessive, resulting in a neutralization problem and a less pure cathode. If water is used to dissolve the copper, copper extraction may be decreased, and, because of the low acid strength, electrowinning is not so attractive although liquid-liquid extraction now becomes possible. The U.S. Bureau of Mines have recently shown that copper dissolution in the roasting process can be improved by the addition of FeO to the furnace charge, but the results need to be confirmed on a pilot-plant scale.

The Cymet Process

The Cymet Process is one of the many chloride processes being studied. One of the major attractions of chloride processes is that the leach can be operated at atmospheric pressure. It is reported that Duval and Cominco are also developing chloride-leaching processes, but no details have been published.

In contrast, Cyprus Metallurgical Processes Corporation have published the results of their research fairly extensively and are prepared to discuss the possibility of licensing their technology. A pilot plant treating 25 tonnes of concentrate per day is due to become operational during 1973. The plant cost is about $8 million.

Fig. 5 presents the flowsheet developed and the pilot plant tested for chalcopryite. Reactivity is increased by an increase in the surface area, and the flotation concentrate is ground to 95 per cent minus 200 mesh. Leaching with ferric chloride anolyte solution from the iron electrolytic cells produces the following reaction:

\[
6 \text{FeCl}_3 + 2 \text{CuFeS}_2 \rightarrow 2 \text{CuCl}_2 + 9 \text{FeCl}_3 + 4 \text{S}
\]

The countercurrent leaching, which takes place at about 75 to 80°C, employs cyclones between leaching stages to provide maximum efficiency. This results in a negligible concentration of ferric chloride in the leached slurry, which goes to the anode compartment of the electrolytic dissolution cells (diaphragm-fitted cells with a woven, permeable synthetic material that separates anode from cathode compartments). Anodes are made of titanium that is coated with conducting oxides, which permit high current densities (200 A/m²) and also give lower voltage drops. Copper is recovered from the leach and anolyte solutions in the cathode compartment of the cell. The cathodes are round copper rods uniformly spaced and oriented parallel to the anodes in the opposite compartment. Copper is precipitated as a powder and removed as a slurry. The copper powder goes to electrorefining.

According to Cymet, the equations governing the processes in the cell are as follows:

\[
\text{CuCl}_2 + 3 \text{HCl} \rightarrow 3e^- + \text{CuCl} + \text{FeCl}_3 + 2 \text{S} + 2 \text{H}^+, \quad 3 \text{CuCl} + 3e^- \rightarrow 3 \text{Cu}^0 + 3 \text{Cl}^-, \quad 3 \text{H}^+ + 3 \text{Cl}^- \rightarrow 3 \text{HCl}
\]

The solids from leaching are autoclaved at about 135°C for 2 hours to form globules of sulphur, which, on being cooled, can be screened off. The screen underflow is subjected to flotation, the concentrate being recycled for leaching and the tailings being rejected.

The spent copper catholyte is further depleted of copper by cementation with metallic iron. The solution is further purified by zinc cementation so that residual traces of copper and other impurities, such as lead, antimony, bismuth, and arsenic, are removed. Zinc occurring in the feed and added for purification is removed by liquid-liquid extraction with a tertiary amine.

The purified ferrous chloride solution is sent to electrolytic iron cells, which plate massive high-purity iron on iron starter sheets, and ferric chloride is regenerated at the anodes. Because of the imbalance between cathode and anode efficiencies, and the use of iron to cement the copper, an additional amount of iron must be removed from the circuit. This is done by hydrolysis. The reactions occurring at the iron cells are as follows:

\[
3 \text{FeCl}_2 + 6 \text{E}^- \rightarrow 3 \text{FeO} + 6 \text{Cl}^-, \quad 6 \text{FeCl}_2 + 6 \text{e}^- + 6 \text{Cl}^- \rightarrow 6 \text{FeCl}_3
\]

The pilot-plant tests indicate that about 50 per cent of the copper is dissolved in the ferric chloride leaching step and another 30 per cent in the electrolytic cells, and 20 per cent is recycled by flotation. The overall extraction exceeds 98 per cent.

Costs presented by Cymet for a plant producing 80,000 tonnes of wirebars per annum indicate that the operating and capital costs are slightly less than those for a conventional smelter constructed in the U.S.A. If credit is given for the iron and sulphur, the Cymet Process is overwhelmingly cheaper (see Table 1). A better estimate of the costs will be made when the large pilot plant has been operated.

The Cymet Process is very ingenious in its use of electrical energy. No figures for power consumption are given by Cymet, but it is estimated that, allowing for inefficiencies, the power consumption of the two electrolysis steps is probably in the range of 3.3 to 4.5 kWh per kilogram of copper. In addition, about 0.3 kWh per kilogram of copper is required for the electrorefining of the copper. The power consumption for conventional electrowinning from sulphate media is about 2.2 kWh per kilogram of copper. The Cymet Process, in addition to winning copper, also oxidizes the leach liquor and produces metallic iron for the additional 1.4 to 2.6 kWh per kilogram of copper, which makes it very attractive. In fact, if the iron can be sold for the price suggested by Cymet, the cost of iron recovery will be less than half the sales value. The production of this salable iron byproduct appears to be the major advantage of the Cymet Process. There are other chloride and sulphate processes that produce elemental sulphur, so that the Cymet Process's production of elemental sulphur gives it no particular advantage.

Cymet have taken advantage of the fact that, in chloride media, copper can exist in the cuprous
TABLE I

COMPARISON OF COPPER PRODUCTION COSTS, CONVENTIONAL SMELTER VERSUS CYMET PROCESS (U.S. CENTS PER POUND OF RECOVERED COPPER)

<table>
<thead>
<tr>
<th></th>
<th>Conventional pyromelter + electrorefining</th>
<th>Cymet Process + electrorefining</th>
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<tbody>
<tr>
<td>Direct operating costs</td>
<td>10,109</td>
<td>9,069</td>
</tr>
<tr>
<td>Administrative and indirect costs</td>
<td>0,781</td>
<td>1,019</td>
</tr>
<tr>
<td>Total direct and indirect costs</td>
<td>10,884</td>
<td>10,587</td>
</tr>
<tr>
<td>Fixed costs (depreciation)</td>
<td>2,733</td>
<td>2,022</td>
</tr>
<tr>
<td>Total operating costs</td>
<td>13,617</td>
<td>12,609</td>
</tr>
<tr>
<td>Credits*</td>
<td>1,325</td>
<td>5,151</td>
</tr>
<tr>
<td>Gold, silver, lead, and zinc</td>
<td>0,790</td>
<td>0,790</td>
</tr>
<tr>
<td>Sulphur and iron</td>
<td>0,533</td>
<td>4,361</td>
</tr>
<tr>
<td>Total credits</td>
<td>1,325</td>
<td>5,151</td>
</tr>
<tr>
<td>Conversion cost per lb of recovered copper</td>
<td>12,292</td>
<td>7,458</td>
</tr>
<tr>
<td>Conversion cost per lb of total contained copper</td>
<td>12,939</td>
<td>7,590</td>
</tr>
<tr>
<td>Capital costs</td>
<td>1,0 compared with 0,83</td>
<td></td>
</tr>
</tbody>
</table>

* Credits were estimated on the following values: gold at $42.00 per oz tr., silver at $1.45 per oz tr., lead at $0.085 per lb, iron (electrolyte) at $0.05 per lb, sulphur equivalent at $10.00 per long ton, and power cost at $0.0103 kWh.

Conversion cost per lb of recovered copper... 12,292 7,458
Conversion cost per lb of total contained copper... 12,939 7,590
Capital costs... 1,0 compared with 0.83

Conversion cost per lb of recovered copper... 12,292 7,458
Conversion cost per lb of total contained copper... 12,939 7,590
Capital costs... 1,0 compared with 0.83

Costs are low and the byproduct iron can be sold.

Ferric Chloride Leaching and Liquid-liquid Extraction

During the past two years, NIM* has investigated, on a pilot-plant scale, a ferric chloride leaching process involving copper recovery by liquid-liquid extraction with LIX-64N and electrowinning of the copper from the sulphate strip liquor. Because of pressure of work, the research is not complete, but certain basic features of the process have been proven. A flowsheet of one version of the process is shown in Fig. 6.

Laboratory and pilot-plant experience has shown that, for copper extractions to exceed 90 per cent, it is necessary for the concentrate to be ground to 95 per cent minus 400 mesh, thus confirming the experience of other investigators in...
the leaching of chalcopyrite.

Copper extractions have been found to be variable, depending on such factors as age of the concentrate, whether it was stored wet or dry, whether it had been pre-leached with hydrochloric acid for the removal of zinc, etc. Leaching at 95°C for about 8 hours gave copper extractions of 96 to 97 per cent. Leaching vessels lined with hard rubber were used, and these appeared to stand up to the leaching conditions without deterioration. Contrary to statements by other researchers, the amount of sulphur going to sulphate did not exceed 5 per cent of the total sulphur.

Copper was extracted from the leach liquors with LIX-64N, the loaded solvent was suitably scrubbed to reduce the iron and chloride levels, and the copper was finally stripped with spent electrolyte from the electrowinning plant. The copper cathodes produced were of a high quality. Because the loading of copper in LIX from chloride media is lower than that from sulphate media owing to the complexing effect of the chloride ions, it is necessary to operate with moderately high levels of copper in the raffinate. This means, then, that copper must be removed from the bleed stream before the iron is recovered. If the bleed stream is first oxidized to convert ferrous chloride to ferric chloride, the excess hydrochloric acid generated in the liquid-liquid-extraction process is consumed and most of the remaining copper can be extracted in a secondary liquid-liquid-extraction circuit. Various techniques such as iron and zinc cementation can be used to remove the last traces of copper.

A special foam aeration column has been developed and tested on a pilot-plant scale to oxidize ferrous chloride to ferric chloride. This device gives good oxygen efficiency, using air at about 45 lb/in² or 300 kPa (gauge), has no moving parts, and is of cheap and simple construction. Good rates of oxidation are achieved at 95 to 100°C. Oxidation of the leach slurry has also been successfully attempted.

Initial plans for the removal of dissolved iron from the circuit revolved around the use of a pyrohydrolysis technique (well proven for pickle liquors, e.g., the Aman Process), in which iron chlorides are converted to iron oxides by water vapour at high temperatures. This serves to regenerate the chlorides as hydrochloric acid for recycle to the oxidation step of the process. The iron oxide might be a salable byproduct. However, detailed studies have indicated that, except when very cheap fuel is available, the cost of fuel is rather high. Capital costs represent a fairly significant proportion of the total plant cost.
Tests are being done on an alternative route involving the precipitation of FeO-OH by oxidation of the ferrous chloride liquor at about 100°C using the oxidizer previously mentioned. A filterable precipitate has been produced, but so far it has not been possible to reduce the chloride content of the precipitate to a level acceptable for discharging. This process would otherwise be much cheaper.

The remaining alternative is to make electrolytic iron and oxidize ferrous to ferric chloride as is done in the Cymet Process. If the iron can be sold for a reasonable price, this is most likely to be the best route to follow.

A detailed comparison of the Cymet Process with the NIM ferric chloride process has not been undertaken, but it is believed that the NIM process could well be cheaper, especially as the Cymet Process involves the extra step of electrorefining the copper powder. Further pilot-plant testwork is required before the process can be regarded as proven on this scale of operations.

Haver and Wong of the U.S. Bureau of Mines also studied a ferric-leaching process but suggested the production of cement copper, which, in my opinion, is a retrograde step.

DEVELOPMENT IN THE FIELD OF COPPER RECOVERY FROM SOLUTION

The use of LIX liquid-liquid-extraction reagents combined with copper electrowinning in sulphate media is now an industrially proven process. Extremely pure copper cathodes can be produced from these processes, the only problem element being lead, which originates from the lead-antimony anodes used. A lead content of less than 10 p.p.m. is highly desirable, and hence a great deal of attention has recently been devoted to finding a means of reducing the lead value, which in some plants has been as high as 100 p.p.m. It has been found that the addition of very small quantities of cobalt greatly assists in decreasing the lead content.

De Nora of Italy and I.C.I. in Britain both have substantial research programmes aimed at producing titanium anodes coated with precious metal that have a long life in copper sulphate electrowinning circuits. According to present indications, the life of these anodes is not long enough to justify their very high capital cost, but they do permit the use of higher current densities than do conventional anodes, and the voltage drop is slightly less. It is possible that further development will result in their application to copper processing.

Recent work by many workers has demonstrated that it is possible to operate copper-electrowinning plants at much higher current densities (600 A/m²) than previously practised (250 A/m²). This can be done by periodical interruption of the current by specially designed air nozzles to improve the circulation of the liquor, especially near the cathode surface. Others have improved the liquor circulation by various means.

The production of a purer electrolyte when LIX is used makes it possible to operate at higher current densities than when the liquor is impure. It may be possible in certain instances to justify the cost of liquid-liquid extraction by the lower cost of the electrowinning plant. The results of a cost-optimization study indicate that the optimum current density, considering the operating and the capital costs, is in the region of 600 A/m², which appears to be within the bounds of practical application in the near future. The problem of how to control the mist arising from cells operating at these high current densities still requires to be solved. It is worth thinking about the possibility of ducting the oxygen away for use in the leaching step and thus also overcoming the mist problem.

The capital cost of a typical circuit for liquid-liquid extraction and electrowinning is proportioned approximately as follows: liquid-liquid-extraction plant 20 per cent, solvent 20 per cent, and electrowinning plant 60 per cent. Operating at high current densities will mean that the cost of the electrowinning plant will be reduced by about one-third, and the cost of the liquid-liquid-extraction plant and its solvent will then be about equal to the cost of the electrowinning plant. Research to decrease the cost of the liquid-liquid-extraction plant and its solvent inventory is therefore urgently required.

An alternative solvent, KELEX, is selective for copper and under certain circumstances promises to be preferable to LIX, but it does not yet have the advantage of having been used on a large plant. Many commercial firms are actively developing new solvents for copper.

One of the major disadvantages of liquid-liquid extraction is that the leach liquors must be clarified after liquid-solid separation so that the losses of solvent are minimized. With the recent successful development of a continuous ion-exchange technique, new horizons open up, and it is possible to consider the possibility of ion-exchange processes for the recovery of copper from a dilute-leach slurry. This would reduce the costs of liquid-solid separation and also eliminate the need for clarification. The major area of application for ion-exchange processes would doubtless be the leaching of oxide or carbonate ores, where the costs of liquid-solid separation are very high and a dilute copper solution is produced. The ion-exchange step could then be used as a concentrating step, followed by a liquid-liquid-extraction step if necessary. For these objectives to be realized, new and improved resins having properties similar to or better than those of LIX or KELEX must be developed.

COMPARISON OF PROCESSES

The only fully realistic and convincing basis for a comparison of processes is, of course, operating and capital cost. However, when so many processes are available and such a variety of feed materials can be considered, it seems to be important at least to make a rough comparison of the various major features of the processes available. A change in the ‘ground rules’ (e.g., cost of power or lime) can alter a comparison appreciably.

In Table II, eight different processes have been compared, and some of the features of the pro-
Iron Removal, and Oxidation State of the Sulphur Produced

These two features together, more than any other feature, probably distinguish the various processes from one another, and also have the greatest impact on the operating costs. Those processes that form sulphur (nos. 3, 4, 7, and 8) have only about 30 per cent of the oxidation requirement of those processes that make sulphate (nos. 1, 2, 5, and 6). The processes in the first group have the additional advantage that the sulphur byproduct has a potential sales value either domestically or on the export market. The processes in the second group have the disadvantage that the sulphate must be neutralized with lime to form calcium sulphate, which must then be dumped.

In some processes (nos. 1, 2, 3, and 4), the iron is advantageously precipitated during the leach. In others (nos. 5 and 6), the iron is rendered insoluble in the roasting step. The two chloride processes (nos. 7 and 8) are unique in that iron is dissolved, and they thus require an extra step for its removal. However, there is a possibility that a salable byproduct can be recovered, which would mean that these processes have the edge over those in which iron is not recovered.

The cost comparison in Table II serves to bring out the above points more clearly. The following comments can be made:

(1) At the price of oxygen and power assumed, the Arbiter Process has little advantage in the operating cost of the leaching step over the conventional Sherritt Gordon process. Its advantages lie in much simpler equipment and a lower ammonia loss, together with the introduction of the liquid-liquid-extraction/electro-winning step.

(2) Both ammonia leaching processes are considerably more expensive than the other processes. In large measure this is due to the cost of liming, thus demonstrating that these processes have
their major advantage where \((\text{NH}_4)_2\text{SO}_4\) can be sold.

(3) The other processes do not differ very much in cost, and the choice of process must probably be made on the basis of other factors, including capital costs, costs of chemicals, etc.

(4) The sulphuric acid pressure-leaching processes and the chloride processes have the advantage of producing elemental sulphur, which, if sold at R10 per tonne, would provide a credit for these processes of 1 cent per kilogram of copper.

(5) The Cymet Process has the additional advantage that the iron can be sold. Its value is uncertain but would probably be in the range of R15 to R50 per tonne, depending on its purity and end use. This would provide an additional credit of 1.5 to 5 cents per kilogram of copper, which tends to make the Cymet Process very attractive if both iron and sulphur can be sold.

(6) The ferric chloride process using electrolytic recovery of iron (no. 8) is also very attractive if both iron and sulphur can be sold. Its capital cost is likely to be less than that of the Cymet Process.

Copper Recovery from Solution

At least six of the processes listed (all except nos. 1 and 7) have a conventional copper-electrowinning plant. The cost of these plants represents anything from 20 to 40 per cent of the total capital cost and, therefore, although the cost will vary slightly for the different processes because of different electrolyte conditions, in principle all these processes have a common capital and operating cost. The possible advantages of a very pure electrolyte have already been discussed.

As already indicated, the capital cost of an electro-refining plant when the copper inventory is included is not much less than the cost of an electrowinning plant, so that this is a cost common to the Cymet Process and the other processes. The power consumption for electro-refining is, of course, only about 15 per cent of that for electrowinning (about 1.3 cents per kilogram of copper at a power cost of 0.6 cents per unit). The cost in the Sherritt Gordon process of precipitating copper powder by the use of hydrogen is not known, but, at the price of hydrogen in South Africa, it is unlikely to be much less (if any) than the cost of electrowinning. The copper powder produced is a specialty sales product. The fact that Anaconda have chosen liquid-liquid extraction and electrowinning, rather than hydrogen precipitation, suggests that, even in the U.S.A., cathodes are preferable and cheaper.

The purity of copper produced by hydrometallurgical processes using liquid-liquid extraction (nos. 2 and 7, and possibly 4, 5, and 6 if desired) is superior to that from pyrometallurgical processes and from other hydrometallurgical processes not employing liquid-liquid extraction, and under difficult marketing conditions is likely to be a selling advantage.

The cost of solvent make-up is estimated to lie in the range 0.3 to 0.5 cent per kilogram of copper.

Cost of Chemicals

The cost of the lixiviant for the four sulphate-based processes (nos. 3 to 6) can be regarded as negligible.

The price of ammonia in South Africa is very high compared with its price in other industrialized countries, although it is predicted that, with the increasing shortage of oil and natural gas and hence the rising prices, ammonia produced from cheap South African coal will eventually be among the cheapest in the world. No realistic figures are available for the consumption of ammonia in the two processes considered, but it is believed that it should be possible to limit the losses so that the make-up cost will be in the range 1.0 to 2.0 cents per kilogram of copper. The Arbiter Process will probably be lower in cost than the Sherritt Gordon process. As mentioned previously, if \((\text{NH}_4)_2\text{SO}_4\) is to be sold as a fertilizer, ammonia will have to be purchased at the fertilizer producer's price.

No realistic figures for chloride loss are available, but it is expected that the make-up cost would be less than that for the ammoniacal processes (say 0.5 to 1.0 cent per kilogram of copper), because chlorides are volatile like ammonia, and the basic raw-material price (hydrochloric acid) is somewhat lower. Much of the ammonia could be lost with the \(\text{CaSO}_4\), but no \(\text{CaSO}_4\) is produced in the chloride processes.

Type of Concentrate

Where a concentrate contains acid-consuming gangue (e.g., of a calcareous nature), only the ammoniacal and the lime-roast-leach processes are applicable. The lime-roast-leach process (no. 6) seems to be particularly suitable for this purpose, because the presence of calcareous material reduces the operating cost.

The ability of the various processes to treat mixed concentrates (e.g., copper-zinc, copper-zinc-lead, and copper-nickel-cobalt) is of importance because this is a field in which hydrometallurgical processes have a possible major advantage over pyrometallurgical processes. It is believed that adequate processing knowledge is available to solve these separation problems for ammoniacal, sulphate, and chloride processes. Separations can probably be more effectively achieved in ammoniacal and chloride systems, but every case has to be looked at separately. More research is certainly needed to provide improved and cheaper separation processes.

From a survey of the experience of various investigators in the leaching of chalcopyrite, it appears that the reactivity of chalcopyrite varies considerably, and much more attention should be given to an understanding of the reasons for this difference. One investigator even found that, by dissolving the flotation chemicals from a concentrate in an organic solvent, the copper dissolution increased from 90 to 95 per cent.

Recovery of Precious Metals

Sulphide ores always contain some precious metals. The degree to which precious metals will dissolve in the leaching step will depend very much on how they are present in the concentrate, e.g., they can be alloyed with base metals. However, it is fairly certain that, the more intense the leaching conditions and the finer the grind, the greater will be the tendency for the precious metals to dissolve if the leaching conditions permit this. Palladium,
platinum, and silver, for example, are all soluble in ammoniacal
solutions, and under pressure-leach-
ing conditions appreciable quantities of palladium, especially, have been
found to dissolve. Palladium and silver are soluble in sulphate media,
but there is no reported instance of any investigator having detected the
dissolution of these metals in sulphate-leaching tests. All the precious metals are soluble in chloride media, and experience here
seems to vary. Work done at NIM on a local chalcopyrite and copper-
nickel matte showed negligible dis-
solution of precious metals. However, Cymet report recoveries of silver and gold into the copper of 90 per
cent and 60 per cent respectively27. How this took place is difficult to
understand.
Various workers have investigated the recovery of gold and silver from
leach residues using the cyanidation process, and good success has been
achieved. Thiourea processes might also be considered under certain
circumstances.

CONCLUSION
This review has demonstrated that, within a few years, a variety of hydrometallurgical processes will be available that are likely to be
competitive with pyrometallurgical processes when there is no sale for sulphuric acid from the smelter. The selection of the right process will
depend on the character of the feed material, the location and size of the
plants, and the byproducts that can be recovered and sold. In
general, it appears that processes producing sulphur have an ad-
vantage over processes producing sulphate as a reaction product.

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