

ELECTRO-HYDROMETALLURGY OF CHALCOPYRITES — VII AN APPRAISAL OF FERRIC CHLORIDE LEACHING PROCESS

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ABSTRACT

Importance of hydrometallurgical route for processing chalcopyrite recovery of copper is highlighted. Conditions for ferric chloride leaching process have been standardized involving the recovery of copper by galvanic cementation as well as electrolysis in diaphragm cell.

Key words: Chalcopyrites, electrohydrometallurgy, ferric chloride leaching

All the copper produced in India comes from the three groups of mines operated by the Hindustan Copper Limited: The Indian Copper Complex at Ghatsila, Bihar; Khetri Copper Complex in Rajasthan; and Malanjkhand Copper Project in Madhya Pradesh. Annual demand of copper in India is estimated at about 1.2 lakh tonnes [1]. Indigenous production contributes about 50% of this demand while the rest is met by imports.

Apart from the large copper mines owned by Messrs. Hindustan Copper Limited as above, there are a number of small deposits in India which need to be exploited to attain self-sufficiency in copper. The small deposits are spread throughout the country and are far away from the existing smelters. Table I [1-3] gives the location and reserves of copper of such small deposits in South India. Apart from the locations given in Table I,

TABLE I - Copper deposits in South India

State	Deposit	Reserves Million tonnes	Grade %
ANDHRA PRADESH	Bandala mottu	1.04	1.42
	Nalla Konda	3.14	1.82
	Mailaram	0.99	1.80
	Dhukonda	2.15	1.51
	Gani-Kalara	0.43	1.37
KARNATAKA	Ingalldhal	1.48	1.78
	Kalyadi	3.04	0.88
	Aladahalli	1.76	1.03
	Kalasapura	0.16	0.25
	Masanikera	6.38	0.38
	Kallur	2.47	0.85
	Machanur	1.91	0.95
	Tagadur	17.00	0.70
Total		41.95	

possibilities of copper deposits exist in places like Kaiga, Nuggihalli, Harapanhalli and Soranhalli in Karnataka and Mamandur in Tamil Nadu. The total reserves of all small deposits add up to a large value of 41.95 million tonnes. It is necessary to explore and exploit all these small deposits

in order to step up indigenous production of the metal.

There are concentrator plants [4,5] to produce chalcopyrite concentrates at Ingaldhal, Chitradurga and Kalyadi in Karnataka and Mailaram in Andhra Pradesh. The concentrates so produced are transported for over 2000 kms to Ghatsila or Khetri for smelting. In order that these small deposits are made economically viable, the concentrates should be treated to extract the metal values at site itself, instead of transporting to far off smelters. As the concentrate production from such deposits will only be small quantity (10 to 20 M.T./day) it is not economical to establish a smelter to extract the metal. It is at this point one has to think of hydrometallurgical methods of copper extraction.

Hydrometallurgical processes for extraction of copper were primarily developed because of pollution problems associated with copper smelters [6]. The sulphur dioxide emitted from the smelting plants caused air pollution, acid rain and consequent effect on vegetation. Governments all over the world enforced regulations to reduce the sulphur emissions from such smelters. Hydrometallurgical methods of extraction of copper are more relevant to the Indian situation because these could be started on a small scale at the site itself to extract the metal values without pollution. Added to this, hydrometallurgical processes produce valuable by-products.

During the mid - 1970's a 'hydrometallurgy boom' was witnessed — dozens of proposed flow sheets have been published that use a variety of leach solutions and oxidants for solubilizing the copper and assorted means for recovering the copper from solution [7-12]. Only a few of them were investigated on a large pilot scale or applied industrially; these are given in Table II.

Apart from the above processes, the following processes are being extensively tested in the laboratory: (1) Nitric-sulphuric leach process, wherein the concentrates are leached in a single step and at atmospheric pressure in a mix of nitric/sulphuric acid. The clear leach solution is subjected to two pressure reaction steps to remove excess nitrate and iron; and copper is electrowon. (2) Sulphite reduction process, wherein the concentrate is roasted and leached with an acid ammonium sulphate solution, the SO₂ roaster off-gas is scrubbed to produce ammonium bisulphite; combining the bisulphite and leach solutions at elevated temperatures precipitates a fairly pure copper powder. (3) Eimco's electroslurry process feeds a copper concentrate directly to specially designed electrolytic cells. The concentrate is subjected to anodic dissolution while metallic copper is deposited at the cathode.

TABLE II - Hydrometallurgical process for copper extraction

Sl.No.	Process	Leach system	Recovery	By-products	Remarks
1.	Treadwell Process	Concentrated H ₂ SO ₄ at 200°C	Copper precipitated as CuCN and reduced by hydrogen	Elemental sulphur	The plant was shut down
2.	Arbiter Process	Low pressure oxygen and ammonia	By solvent extraction and electrowinning	Ammonium sulphate	Proved costly and hence shut down
3.	Hecla Process	Concentrate subjected to sulphation roasting and water leach	Electrowinning	Sulphuric Acid	Operated only for two years
4.	Sherritt-Cominco Process	Three step leaching H ₂ SO ₄ /CuSO ₄ /H ₂ SO ₄ (O ₂)	Electrowinning	Elemental sulphur	Pilot demonstration plant operated for one year
5.	Lurgi-Mitterberg Process	High pressure oxygen and H ₂ SO ₄	Electrowinning	Elemental sulphur	Pilot plant operated for two years
6.	Cyprus Cymet Process	Hot ferric chloride-cupric chloride solution	CuCl crystals reduced to metallic copper by hydrogen	Elemental sulphur	Pilot plant in operation
7.	Duval "CLEAR" Process	Hot ferric chloride solution	Electrowinning to get copper powder	Elemental sulphur	Commercial plant in operation

(4) Cupric sulphate - acetonitrile technology stabilizes the cuprous ion. Distillation of acetonitrile results in disproportionation of the cuprous ion into cupric and metallic copper powder.

It is clear from Table II that the Duval process which was a ferric chloride leaching medium has been commercialised and is in operation. It is not without reason that the process has been more or less successful and withstood the test of time. It is also significant to note that ferric ion is the very widely studied lixiviant for chalcopyrite [13-21]. Ferric chloride leach of chalcopyrite has the following main advantages over other leachants:

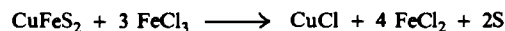
- (1) No pretreatment such as roasting or activation of the concentrate is necessary.
- (2) Leaching proceeds at atmospheric pressure.
- (3) Leaching rates are fast.
- (4) Leaching efficiencies are high.
- (5) Elemental sulphur is a by-product.
- (6) Ferric chloride could be regenerated from ferrous chloride by chlorine, oxygen or electrolysis.
- (7) Cuprous ions are stabilised, thereby reducing the energy consumption in the recovery stage.
- (8) There is a possibility of recovering precious metals from the leach residue.
- (9) The leaching process does not require very rigid controls and is very simple to operate.
- (10) No air pollution, as no gaseous products are liberated during leaching.

An integrated hydrometallurgical process has been proposed [13] for the treatment of chalcopyrite concentrates, using concentrated acidified ferric chloride solutions. Nagaraj & Vasu [20] initiated work in India and they tested the Chitradurga chalcopyrite concentrates. Pasu et al [17] have also presented a systematic study on the leaching of chalcopyrite in ferric chloride.

The leaching conditions for obtaining recovery of over 95% may be summarised as follows:

- | | |
|--|---|
| (1) Size: | 100% — 325 mesh |
| (2) FeCl ₃ /CuFeS ₂ ratio: | 3.0 |
| (3) Temperature: | 106°C |
| (4) Agitation: | 200 rpm |
| (5) Contact time: | Minimum 3 hrs at the above temperature. |

The leaching reaction can be represented by the following equation:



RECOVERY OF COPPER FROM LEACH SOLUTION

Having obtained the copper in solution, the next step will be to treat the clarified liquor to win the metal. There are four possibilities to win copper from ferric chloride leach solution. It is important to note that all these processes produce copper in the powder form.

(1) To crystallise CuCl and reduce the crystals by a current of hydrogen. Cyprus process uses this method to win the metal.

(2) Cementation

Copper can be precipitated from the leach solution by another more electropositive metal such as iron. Haver and Wong, in their original process, used sponge iron and reported that only 0.625 parts of iron was required for one part of copper, as all the copper was in the monovalent state. However, the cementation copper so obtained will be impure and needs further purification steps.

(3) Galvanic cementation

This is a modified cementation process wherein the anodic and cathodic reactions are separated in a diaphragm cell. The anode (e.g.iron) and

cathode (copper) are short-circuited externally when copper deposits from leach solution while iron dissolves (Fig.1). Initial work carried out has shown the possibility of obtaining a pure product. The process is simple, inexpensive and requires minimum control [22-23].

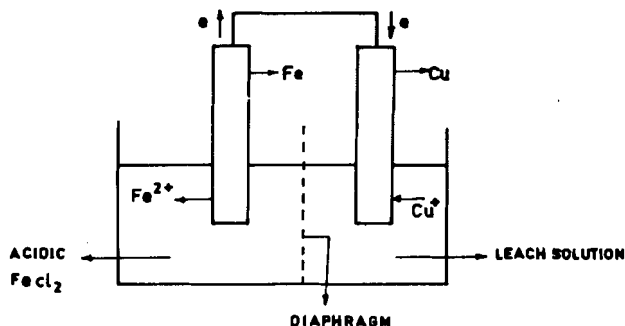


Fig. 1 Galvanic cementation cell

(4) Electrolysis

Electrowinning of copper from leach solutions have to be carried out in a diaphragm cell. Haver and Wong's modified process was an electrowinning step, to produce pure copper powder. The main advantage of electrolysis is that part of the ferric chloride required for leaching can be regenerated at the anode while depositing copper at the cathode.

REGENERATION

The copper-stripped ferrous chloride solution should be regenerated to ferric chloride before being again used for leaching. While the use of chlorine is simple and can be carried out at ambient temperature, oxygen may require higher temperature and sophisticated equipment [24]. In India, rising power costs have made the cost of chlorine dearer, thereby making oxygen regeneration attractive.

CONCLUSION

Ferric chloride still remains the best lixiviant for chalcopyrite concentrates. Methods of recovery and regeneration could be blended and modified to suit the local need and economics. A pilot plant based on the above process is in operation at Chitradurga Copper Unit, Ingaldhal, Chitradurga.

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