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

<table>
<thead>
<tr>
<th>State</th>
<th>Deposit</th>
<th>Reserves in Million tonnes</th>
<th>Grade %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANDHRA</td>
<td>Bandala mottu</td>
<td>1.04</td>
<td>1.42</td>
</tr>
<tr>
<td>PRADSHI</td>
<td>Nalla Konda</td>
<td>3.14</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>Mailaram</td>
<td>0.99</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>Dukhonda</td>
<td>2.15</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>Gani-Kalara</td>
<td>0.43</td>
<td>1.37</td>
</tr>
<tr>
<td>KARNATAKA</td>
<td>Ingaldhal</td>
<td>1.48</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>Kalyadi</td>
<td>3.04</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>Aladahalli</td>
<td>1.76</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>Kalasapura</td>
<td>0.16</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Masanikera</td>
<td>6.38</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>Kallur</td>
<td>2.47</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Machanur</td>
<td>1.91</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>Tagadur</td>
<td>17.00</td>
<td>0.70</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>41.95</td>
</tr>
</tbody>
</table>

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 melting 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 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 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

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Process</th>
<th>Leach system</th>
<th>Recovery</th>
<th>By-products</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Treadwell Process</td>
<td>Concentrated H₂SO₄ at 200°C</td>
<td>Copper precipitated as CuCN and reduced by hydrogen</td>
<td>Elemental sulphur</td>
<td>The plant was shut down</td>
</tr>
<tr>
<td>2.</td>
<td>Arbiter Process</td>
<td>Low pressure oxygen and ammonia</td>
<td>By solvent extraction and electrowinning</td>
<td>Ammonium sulphate</td>
<td>Proved costly and hence shut down</td>
</tr>
<tr>
<td>3.</td>
<td>Hecla Process</td>
<td>Concentrate subjected to sulphation roasting and water leach</td>
<td>Electrowinning</td>
<td>Sulphuric Acid</td>
<td>Operated only for two years</td>
</tr>
<tr>
<td>4.</td>
<td>Sherritt-Cominco Process</td>
<td>Three step leaching H₂SO₄/CuSO₄/H₂SO₄ (O₂)</td>
<td>Electrowinning</td>
<td>Elemental sulphur</td>
<td>Pilot demonstration plant operated for one year</td>
</tr>
<tr>
<td>5.</td>
<td>Lurgi-Mitterberg Process</td>
<td>High pressure oxygen and H₂SO₄</td>
<td>Electrowinning</td>
<td>Elemental sulphur</td>
<td>Pilot plant operated for two years</td>
</tr>
<tr>
<td>6.</td>
<td>Cyprus Cyret Process</td>
<td>Hot ferric chloride-cupric chloride solution</td>
<td>CuCl crystals reduced to metallic copper by hydrogen</td>
<td>Elemental sulphur</td>
<td>Pilot plant in operation</td>
</tr>
<tr>
<td>7.</td>
<td>Duval “CLEAR” Process</td>
<td>Hot ferric chloride solution</td>
<td>Electrowinning to get copper powder</td>
<td>Elemental sulphur</td>
<td>Commercial plant in operation</td>
</tr>
</tbody>
</table>

(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.


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

1. Size: 100% — 325 mesh
2. FeCl₃/CuFeS₂ 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:

\[
\text{CuFeS}_2 + 3 \text{FeCl}_3 \rightarrow \text{CuCl} + 4 \text{FeCl}_2 + 2 \text{S}
\]

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...
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, Ingaidhal, Chitradurga.

**REFERENCES**

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