ELECTROMETALLURGY OF CHALCOPYRITES—III
FERRIC CHLORIDE LEACHING

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(Received Jan. 1977; accepted Oct. 1977)

Of the oxidizing-type leachants, ferric chloride is highly promising for sulphidic copper ores, an important feature being the recovery of Sulphur in the elemental form. The leaching proceeds according the reaction,

$$CuFeS_2 + 3\ FeCl_3 \longrightarrow CuCl + 4\ FeCl_2 + 2S$$

Perhaps also as:

$$CuFeS_2 + 4\ FeCl_3 \longrightarrow CuCl_2 + 5\ FeCl_2 + 2S$$

Laboratory Scale study on ferric chloride leaching of chalcopyrite concentrates (64% $CuFeS_2$) established the following conditions for 97% copper extraction in about 3 hours:

Temperature: 105—110°C
Concentration of leachant: 600 gpl $FeCl_3$ (~4M)
Particle size: Around 200 mesh
$FeCl_3/CuFeS_2$ Wt. Ratio: 3.00
Suitable agitation

Roughly, 64% of sulphur was converted to the elemental form. Scaling-up trails on 10 Kg samples indicated copper extractions up to 95% in about 5 hours at a feed pulp density between 1.55 and 1.6.

The conventional pyrometallurgical extraction of copper from sulphide concentrates consists essentially of: (1) roasting the concentrates to remove pyritic sulphur (2) smelting to produce a liquid matte (3) converting the iron sulphide in the matte to an iron silicate slag (4) converting the "white metal" so produced to blister copper and (5) electro-refining of blister copper. In such a process all the sulphur from the concentrates are converted to gaseous sulphur dioxide. Unless part of the sulphur is fixed in the form of sulphuric acid, or other compounds, all the sulphur dioxide must pass out into the atmosphere as waste gases. A great deal of work has been done on the removal of SO_2 from the waste gases in the last several years. One of the principal reasons for this is the fact that SO_2 discharged into the atmosphere in sufficient quantity is harmful to the surrounding vegetation[1]. The physiological effects of SO_2 is given in Table-1[2].

Because of these pollution problems and the increased necessity of using low-grade ores, a number of hydrometallurgical processes have been developed to extract copper[3]. Hydrometallurgy offers hope to setup plants near relatively small deposits and extract the metal economically, independent of large smelters.

Hydrometallurgy can be conveniently divided into three broad areas: namely, the dissolution of the desired element into solution, the clarification of the resulting solution,

TABLE 1. Relation of odour intensity and physiological effect to concentration of SO_2 in Air.

Conc of SO_2 by volume ppm.	Physiological effect
3 to 5	Faintly detectable by smell or taste.
8 to 12	Slight throat irritation and tendency to cough.
20	Very distinct throat irritation, coughing, constriction of chest, and smarting of eyes.
50	More pronounced irritation of eyes, throat and chest, but possible to breathe several minutes.
150	Extremely disagreeable, but may be endured for several minutes.
500	Causes sensation of suffocation even with first breath.

and finally, the recovery of the desired metal, often in elemental form, from the purified leach liquor.

Types of Leaching reactions:

There are mainly two types of leaching reactions (a) those in which the mineral may simply dissolve in a suitable reagent and (b) those which need the presence of an external oxidizing agent. Although most base-metal oxides are readily soluble in mineral acids, the corresponding sulphides require the presence of an oxidizing agent to effect their dissolution. Further, the leachant itself may perform the operation of oxidation and dissolution. Chalcopyrite ($CuFeS_2$), for example, can be leached with ferric chloride (oxidant-leachant) or with ammonia (solvent) in the presence of oxygen (oxidant). Only the ferric chloride leaching is considered in detail.

Ferric Salt Lixiviant: The theory.

Some idea about the nature of and requirements for the oxidation of the sulphide minerals can be

obtained from the Eh-pH diagrams, which at present are available only for metals and simple compounds [4-6]. From the Eh-pH diagram of simple copper sulphides[7], it can be seen that if the simple sulphides like CuS and Cu_2S should go into solution as Cu^{2+}, an oxidising agent is necessary. In acid media, both CuS and Cu_2S are stable under neutral or slightly oxidising conditions. At low pH values, oxidizing potentials between 0.2 and 0.4 volts are required to convert the copper sulphides into sulphur species and soluble copper. In neutral or basic solutions, insoluble oxide-type products are formed.

From the Eh-pH diagram of $S-H_2O$ system[7] elemental sulphur is found to be stable in acid solutions under slightly oxidising conditions, and at a potential above 0.3V, it becomes unstable with respect to bisulphate or sulphate formation depending on the pH.

The Eh-pH diagram for iron[7] shows the stability domains of the metastable iron hydroxides, Fe^{2+} and Fe^{3+}. When a metal sulphide, MS is immersed in an acidified ferric solution (potential, 0.77V), the following reaction should occur, thermodynamically:

$$MS + 8Fe^{3+} + 4H_2O \rightarrow M^{2+} + SO_4^{2-} + 8H^+ + 8Fe^{2+} \quad \ldots (1)$$

However, in practice, only elemental sulphur is formed and its further oxidation to SO_4^{2-} occurs only to a negligible amount :

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S \quad \ldots (2)$$

Even though the oxidation of this sulphur to sulphate is thermodynamically feasible, the reaction is kinetically unfavourable, probably because of the hydrophobic nature of sulphur[7]. Hence, elemental sulphur, once formed, enjoys an extraordinary stability under a wide range of conditions and at temperatures as high as its melting point.

The action of ferric ion on $CuFeS_2$ essentially involves the oxidation of S^{2-} to S^0 by Fe^{3+}, whereby it is itself reduced to Fe^{2+}, as given by the reaction :

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S \quad \ldots (3)$$

The partial reactions are : $2Fe^{3+} + 2e \rightarrow 2Fe^{2+}$; and $S^{2-} - 2e \rightarrow S$.

The process, involving the two redox couples, will proceed until the changes in their concentrations bring the two potentials equal at equilibrium :

$$E(Fe^{3+}, Fe^{2+}) = E(S^{2-}, S)$$

or at 25°C.

$$0.771 - \frac{0.059}{2} \log \frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} = -0.51 + \frac{0.059}{2} \log \frac{[S]}{[S^{2-}]}$$

At equilibrium, therefore :

$$\frac{[S]}{[S^{2-}]} \frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} \approx 10^{43}$$

This suggests that the reaction (3), representing the leaching of chalcopyrite with ferric chloride, is highly in favour of the forward direction and attains near completion at equilibrium.

Advantages of Ferric chloride :

Having established the usefulness of ferric ion in leaching of sulphide minerals, the next step is to find out a suitable ferric salt for this purpose. Of the various ferric salts, ferric chloride is undisputably the best from the following points of view: (a) availability (b) cheapness (c) higher reactivity (d) ease of regeneration from ferrous chloride by electrolytic oxidation or chlorination (e) high stability (f) very high solubility, both of itself and ferrous chloride, the product of the leaching reaction and (g) the fact that cuprous chloride complexes are stable in the leached liquor. Also, elemental sulphur is produced as a useful by-product in ferric chloride leaching whereas most of the sulphur is oxidised to sulphate in ferric sulphate leaching[7].

Ferric Salt Lixiviant: The practice

The first recorded use of ferric chloride seems to be the Doetsch process[8] for copper sulphide ores at Rio Tinto in 1859. Doetsch and Frohlich[9] in 1882 leached CuS by dissolving in a ferric chloride solution. An attempt was made in 1913 to revive the Doetsch - Frohlich process under the name of the Slater process[10], essentially involving the regeneration of the ferric chloride which the originators had not envisaged.

The first systematic study of the dissolution of copper sulphide ores in both ferric sulphate and ferric chloride was carried out by Sullivan[11-14] and Brown[15, 16]. They noted that ferric chloride was a better leachant for chalcopyrite than ferric sulphate, and the rate of dissolution increased rapidly with temperature.

It was in 1930 that Pike et al[17] studied the dissolution of chalcopyrites in ferric chloride on both bench and pilot - plant scales. A 150 Kg/day pilot plant was run for about four months which gave recoveries of 85 - 90% for copper and 60 - 70% for

sulphur. Ironically, all the interest given to commercialise ferric chloride leaching for copper ores seems to have died down for sometime, except for occasional investigations[18—22], until the beginning of 1960's which fortunately marked a systematic reconsideration of the ferric chloride leaching[23—29].

The lost interest in the ferric chloride route was revived in 1971 when Haver and Wong[30] reported a pollution - free copper, iron and sulphur recovery process from chalcopyrite concentrates, using a highly concentrated ferric chloride solution. Parameters like temperature, agitation, $FeCl_3/CuFeS_2$ ratio and particle size were all investigated. Parabolic kinetics was observed and this was attributed to mass transfer through the constantly thickening sulphur layer formed on the surface of the chalcopyrite during leaching. That the Haver and Wong's process created a lot of interest is demonstrated by the development of the CYMET process[31], which is essentially an electrochemical process combining the anodic dissolution and the ferric chloride leaching of chalcopyrites. Many are believed to be developing a ferric chloride leach process for treating chalcopyrite concentrates or other copper - bearing materials[32, 33].

Laboratory - scale experiments:

50 gm. samples of the sized concentrates were leached with calculated amounts of ferric chloride in a one litre pyrex conical flask on a hot plate. The pulp was mildly agitated (at about 200 rpm) with a glass impeller, and there was provision for controlling the speed of rotation of the impeller. Evaporation losses were compensated throughout the experiment. At definite intervals, the leach solution was sampled out for analysis to study the progress of leaching. The pulp during leaching was held at the boiling point of the solution in all the experiments, and the ore concentrate was added when the solution was at the boiling point. Elemental sulphur in the residue was recovered by extraction with carbon disulphide.

(a) **Effect of particle size:**

Leaching involves a heterogenous reaction and therefore, the finer the particle size, the larger the surface area to weight ratio, the faster the rate of leaching and better the efficiency of copper extraction. Table-II summarises the result obtained in laboratory scale studies. As evident from Table-II, there was not much advantage when leaching a —300 mesh sample compared with the —200, +300 sample, so as to warrant an additional grinding step; the as-received concentrate, containing 77% —200 mesh, can be directly used for leaching without loosing efficiency or percentage of copper extraction.

TABLE II. **Effect of particle size on copper extraction**

50 g. chalcopyrite concentrate (20.3% Cu); $FeCl_3/CuFeS_2$ wt. ratio: 3.89; Temp: 108°C; Agitation: 200 rpm; Volume of solution: 200 ml

Time, Min	% copper extraction		
	—300 mesh	—200, +300	—150, +200
30	80	52	41
60	92	70	60
120	95	88	76
180	97	96	84

TABLE III. Effect of $FeCl_3/CuFeS_2$ weight ratio on copper extraction.

—200, +300 concentrate; 50 g samples, 108°C, agitation at 200 rpm.

Time, Min	% copper extraction for $FeCl_3/CuFeS_2$ ratio of		
	3.89	3.02	2.56
30	52	48	41
60	70	60	52
120	88	80	72
180	96	95	81

(b) **Effect of leachant concentration:**

The effect of $FeCl_3/CuFeS_2$ ratio on copper extraction is evident from table III. It is found that higher $FeCl_3/CuFeS_2$ ratio is associated with a higher rate of copper extraction, the effect being very little above the ratio 2.66 corresponding to the reaction:

$$CuFeS_2 + 3\ FeCl_3 \rightarrow CuCl + 4\ FeCl_2 + 2S$$

(c) **Effect of agitation:**

For any heterogeneous dissolution reaction, agitation enough to keep the particles in suspension, should be envisaged. The nature and extent of agitation depend on the size and shape of the leaching

vessel and on the type of agitator used. In this work, only paddle agitator was used, and considering the leaching conditions, agitation at 200 rpm was found suitable.

(d) **Effect of temperature :**

In all the present investigations, the leach slurries were held at 105 – 110°C, since this ensured maximum advantage of temperature. Room temperature leaching extracted only about 7 to 10% copper in about 4 hours. The temperature effect is not significant until about 55°C,[7] while above 55°C, the mechanism of dissolution changes in favour of faster kinetics. Even though temperature is the most important variable in determining the reaction rate, too high a temperature creates complications due to the low melting point of sulphur (110°C).

(e) **Sulphur recovery :**

In the laboratory experiments, the sulphur in the residue is easily extracted with carbondisulphide or perchloroethylene. The recovery in the elemental form averaged about 64%.

SCALING-UP OF LEACHING :

The leaching Tank :

Ferric chloride at higher temperatures is exceedingly corrosive and together with copper chloride only complicates the problem. Most of the common materials for fabricating the process equipment therefore fail in this case. The iron group of materials fail mainly because of the electrochemical action of copper and Fe^{3+} in the solution. Only non-metallic materials offer any hope.

The large-scale leaching trials were carried out in a rectangular FRP tank, 40 litres capacity, placed inside a larger mild steel shell, the space between being stuffed with insulators. The tank was equipped with agitation and heating arrangements.

Agitation :

The agitators or impellers were made from quality teak wood and fixed on to the shaft from a pulley system driven by a ½ H. P. motor. The speed of agitation could be controlled either through the pulley system or by controlling the speed of the motor with a dimmerstat-autotransformer. Under suitable agitation speed, no caking or segregation of the ore particles occurred at the corners of the rectangular tank.

Heating :

Perhaps the heating of the leach-pulp is the most difficult part of the process. Obviously, no metal or alloy heating elements could be directly introduced, and no metal or alloy sheath can protect them.

Silica-sheathed nichrome spirals were found suitable and withstood even the rough handling several trials. Dimmerstat-autotransformers were used to regulate the temperatures.

However, these silica sheathed heaters were slow in heating the solution. Hence, various possibilities were tried to heat the solution rapidly; these include heating with heated air, superheated steam or direct electrode heating, as in salt bath furnaces. It was found that "electrode heating" was the best. The principle is, when an A. C is passed through two electrodes dipped in an electrolyte, the electrode and consequently the stirred electrolyte gets heated up depending on (a) their resistivity (b) the resistivity of the electrolyte and (c) the current capacity of the electrodes.

Two silicon carbide or graphite rodes separated by about 10–15 cm on a non-conducting frame were immersed in the leach tank and an A.C was passed at a low voltage, the depth of immersion was about 15 cm. Heating was rapid and in about half-hour's time, the solution attained a temperature of about 100°C. No heat loss is possible with such an arrangement, but some disintegration of the electrodes occurred after constant use.

Leaching Experiments :

Calculated amount of ferric chloride was charged into a PVC vessel, and with slight warming and flow agitation, water was added till all the ferric chloride dissolved. About 8–10 gpl conc. hydrochloric acid was also added to prevent hydrolysis. The solution was finally made up to required volume so as to give a ferric chloride concentration of 600 gpl. A major portion of the leachant was poured into the tank and heated to about 105°C.

The calculated amount of the chalcopyrite concentrate (10 Kgs) sufficient to give a pulp density between 1.5 and 1.6, was made into a paste with the

remainder of the ferric chloride solution, added in batches. The pulp was agitated at approximately 150–200 rpm. The "electrode heating" was used for the initial rapid heating and was removed when a temperature of 150°C was attained. Temperature was maintained around 105°C by silica - sheathed heaters.

Some results of the large-scale experiments are given in Table-IV. It is seen that about 95% extraction of copper is possible in 5½ hrs, under optimum conditions.

The progress of leaching in a typical experiment is presented in Table V. The results confirm the parabolic kinetics. The accumulation of solid sulphur on the surface of the chalcopyrite particles separates the reactants. This separation introduces additional diffusion steps for the reaction to take place and hence the rate of leaching will depend on the nature, porosity, and stability of the continuously thickening sulphur film on the surface of the chalcopyrite.

PILOT PLANT CALCULATIONS:

Considering the leaching reaction to be,

$$CuFeS_2 + 3\ FeCl_3 \rightarrow CuCl + 4\ FeCl_2 + 2S.$$

One ton of the chalcopyrite concentrate analysing about 25% copper will require 2,000 kgs of anhydrous ferric chloride to be dissolved in 3,000 lits of water. About 80 lits of concentrated HCl should be added to prevent iron from hydrolysing.

The pulp should be leached in a tank of about 7,000 litres capacity at 105 – 110°C. Agitation should be provided in the tank at about 200 rpm. Leaching should be carried out from 4-6 hrs, total time being decided by the chemical analysis of the leach liquor.

TABLE V. **Progress of a leach experiment**

Concentrate: 10 Kgs (Cu: 22.4%); $FeCl_3/CuFeS_2$ weight ratio: 3.80; Temp. of leaching: < 105°C; Volume of pulp during leaching: 33.0 lits; Agitation: 200 rpm.

Time, hrs.	COPPER		
	In leach solution, gpl	gms. of Cu from concentrate	%extraction
1	34.6	1142	51.0
2	43.6	1438	64.2
3	50.2	1657	74.0
4	54.8	1809	80.7
5	57.7	1903	85.0
6	61.3	2020	90.3

CONCLUSION:

Ferric chloride has been proved to be a promising leachant to extract copper by a hydrometallurgy route. Conditions have been established for the leaching of chalcopyrites, firstly on a laboratory scale and then scaled up for 10 Kg samples, essentially with a view to develop the technological infra-structure for pilot plant trials and for final commercialization of the process.

Note: Pilot Plant trials on this process are now being conducted at Chitradurga Copper Company, Karnataka.

TABLE IV. **Some Results of Large-scale Leaching**

Concentrate Quantity Kgs.	%Cu	Volume of leachant, lit	$FeCl_3/CuFeS_2$ Wt. ratio	Volume of pulp during leaching Lits	Leach Temp., °C	Duration of leach, hrs.	Final volume, lits.	Residue, weight Kg.	Leach solution analysis, gpl		%Copper extraction
									Cu	Fe	
1.5	23.0	5.0	3.01	6.0	90	5	8.0	0.8	26.0	181.0	60
3.0	24.8	12.5	3.49	15.6	95	5	21.0	1.1	32.6	165.8	92
8.0	22.0	30.0	3.49	31.0	110	5	47.0	3.5	35.2	172.5	94
10.0	20.1	26.5	2.64	30.0	100–105	5½	35.0	5.0	54.6	260.0	95

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