GALVANIC CEMENTATION : A novel technique for Winning Pure Copper from Chalcopyrite leached with Ferric Chloride Solution

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A study of the practical aspects of large scale galvanic deposition of copper has revealed that the rate of deposition depends on anolyte acidity, catholyte composition (ferric and cuprous ion concentrations), areas of anode and cathode, and cell resistance.

Small inter-electrode distance, low ferric and high cuprous ion concentrations in the catholyte, and unit anode-to-cathode area ratio are some of the operating conditions which lead to high rate of galvanic deposition of copper of purity over 99.9%.

The large cell comprising of six independent galvanic couples of electrode area 200 sq. cm. each produced about 200 grams of copper powder in 24 hours from a catholyte of 18.2 gpl copper.

INTRODUCTION AND CELL ASSEMBLY

The results of small scale experiments on galvanic deposition were so encouraging that the possibility of winning pure copper from chalcopyrite leached with acidic ferric chloride solution in a semi-pilot scale was investigated. Laboratory scale rectangular cell experiments carried out earlier established the optimum operating conditions [1].

In the present work a rectangular teak wood cell 150 × 25 × 28 cms (lbh) was used. A porous diaphragm housed lengthwise at the centre forms two compartments of capacity 42 lits each. Previous experiments with different diaphragm materials has proved the suitability of microporous rubber because of its suitable porosity, low resistivity, selectivity, wettability and reasonable resistance to chemical attack[2]. The ribbed microporous rubber diaphragms available in standard size of 50 × 10 × 0.1 cms were joined with araldite and cut to size before fixing in the cell groove with molten pitch.

The chalcopyrite concentrate analysing 26% copper was leached with acidic ferric chloride as outlined by Nagaraj [3]. The leaching conditions were so adjusted as to have low ferric ion concentration and copper in the cuprous form in the solution as per the reaction:

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

The decanted leach solution was diluted to 15 lits (catholyte) and run into one of the compartments. The other compartment was filled simultaneously with 20 lits of dilute hydrochloric acid (anolyte). This larger volume of anolyte gives a higher level, thus minimizing the transport of cuprous ions from cathode to anode compartment. The mild steel sheets were pickled in 10% hydrochloric acid using Rhodine 50 as inhibitor (supplied by Agromore Ltd., Bangalore), dried with acetone and weighed before being used as anodes. Copper sheets polished with emery paper, washed and dried, were used as cathodes. The anode and cathode, placed close to each other with diaphragm separating the two, were to be short circuited to mark the start of galvanic deposition (Fig.1).

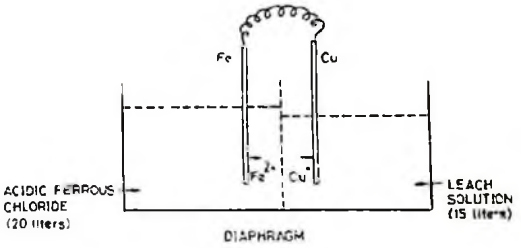


Fig 1 GALVANIC CEMENTATION CELL (Showing a single galvanic couple)

The main reactions that occur are:

Anodic: $Fe = Fe^{2+} + 2e$

Cothodic: $2Cu^{+} + 2e = 2Cu$.

The efficiency of galvanic deposition is expressed by the ratio Cu/Fe (copper/deposited iron dissolved) and has a value 2.28 at 100% efficiency. This ideal value is never realised in practice because of various side reactions that occur and are listed under the heading 'Excess Iron Consumption'.

The present work is concerned with winning of pure copper at a fast rate with minimum iron consumption.

WINNING OF COPPER

An initial experiment was carried out to determine the variation of cell resistance with inter-electrode distance. The two compartments were filled with 15 lits each of leached solution (pH=0.1) and 0.001M ferrous chloride solution (pH=0.8). An external potential was applied across two stainless steel electrodes (9.5×3×0.1cms) placed in the diaphragm cell. Current and voltage drop were recorded at various inter-electrode distances (Table 1),

TABLE—I

Variation of Cell Resistance with Inter-Electrode Distance.

Inter-electrode distance (Cms)	Potential Drop (Volts)	Current (Amps)	Resistance (Ohms)
4	1	0.79	1.27
6	1	0.72	1.39
10	1	0.62	1.61
18	1.10	0.52	2.11
23	1.15	0.42	2.74

Copper winning experiment was first carried out with four mild steel sheets of total length 126 cms and two copper sheets of total length 40 cms (A_a/A_c, anode to cathode area ratio=3.15). On short circuiting the anode and cathode, a current of 0.6 amp was recorded: 91.3 gms of copper deposited in 47 hrs at a rate of 1.94gms/hr. Anodic copper or direct cement copper obtained was 14.5 gms. In this experiment the ferric and cuprous ion concentrations in the catholyte were 38gpl and 12 gpl respectively.

Next, the deposition was carried out with an arrangement of three couples of A_a/A_c ratios of 1,1.5 and 2 under an initial ferric ion concentration of 22 gpl in the catholyte. The variation of Cu^+ and Fe^{3+} ion concentrations in the catholyte shown in Fig. 2 and Table 2 gives the data on galvanic deposition.

In another experiment six galvanic couples each of A_a/A_c unity was used with catholyte containing lower ferric ion concentration (6.8gpl). Table 3 summarizes the data obtained at the end of 24 hrs. The experiment was continued with copper depleted solution for the next 24 hrs and the results obtained are recorded in Table 4.

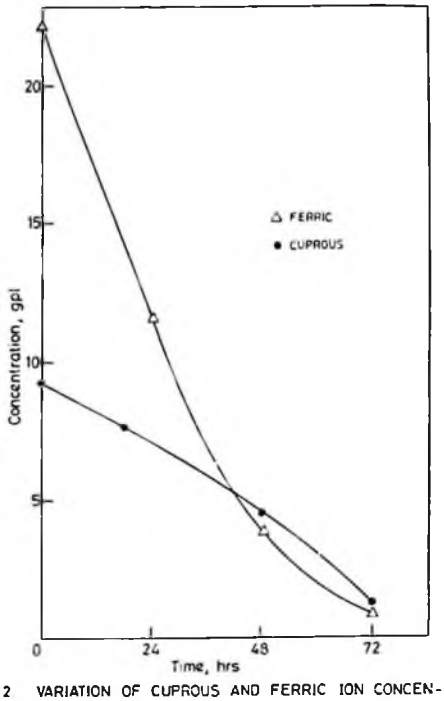


Fig 2 VARIATION OF CUPROUS AND FERRIC ION CONCENTRATIONS IN THE CATHOLYTE

TABLE—II

Galvanic Deposition of Copper From Catholyte of High Ferric ion Concentration.

*A_a/A_c	A_a (cm^2)	Copper Recovery in 72 hrs. (gms)	Iron dissolved in 72 hrs. (gms)	Cu/Fe
1	200	21.3	64.6	0.33
1.5	600	26.8	81.1	0.33
2	400	32.9	79.5	0.41

Catholyte Analysis:
$(Cu^+)_{t=0}$ = 9 2gpl
$(Fe^{3+})'_{t=0}$ = 22.2 gpl.
$(Cu^+)_{t=72hrs}$ = 1.3 gpl
$(Fe^{3+})_{t=72hrs}$ = 1 1 gpl

Inter-electrode distance = 5cms
Overall efficiency, Cu_{total}/Fe_{total} = 0.36

Total Galvanic Copper deposited = 81.0gms
Overall rate of copper deposition = 1.12 gms/hr

Total Iron consumed = 225.2gms
Direct Cement Copper (Cu^+diffusion from catholyte)obtained at the anode = 33 gms.

*A_a/A_a : Area of Anode/Area of Cathode.

TABLE—III

Galvanic Deposition of Copper from Catholyte of low Ferric ion Concentration using a area ratio of Unity ($A_a = A_c = 200 Cm^2$)

Galvanic Coupe No.	Copper Recovery in 24 hrs(gms)	Iron Lost in 24 hrs (gms)	Cu — Fe
1	27.9	19.5	1.43
2	33.1	22.8	1.45
3	27.8	19.5	1.43
4	28.9	19.8	1.46
5	28.2	21.3	1.34
6	31.9	22.2	1.44

Catholyte Analysis.
$Cu^+)_{t=0}$ = 18.2 gpl
$(Fe^{3+})_{t=0}$ = 6.8 gpl
$(C^+)_{t=24\ hrs}$ = 4.7 gpl
$(Fe^{3+})_{t=24hrs}$ = 2.2 gpl

Inter-electrode distance = 4 cms
Overall efficiency Cu_{totel}/Fe_{total} = 1.49

Total Copper deposited = 186gms Purity (unreduced) = 99.1%
Overall rate of copper deposition = 7.73 gms/hr

Total Iron lost = 124.8 gms
Galvanic cnrrent per couple (at the start of expt.) = 0.73 amp.

TABLE—IV

Deposition from Copper Depleted Catholyte of previous experiment using same Assembly

Total Copper Recovery in 24 hrs (gms)	Total Iron lost in 24 hrs (gms)	$\frac{Cu_{total}}{Fe_{total}}$
34.9	57.0	0.61

Catholyte Analysis :
$(Cu^+)_{t=0}$ = 4.7 gpl
$(Fe^{3+})_{t=0}$ = 2.2 gpl
$(Cu^+)_{t=24hrs}$ 1·7gpl
$(Fe^{3+})_{t=24hrs}$ = 1·9gpl

Rate of Copper deposition at Cathode = 1.45 gms/hr
Direct Cement copper obtained at anode after 48 hrs = 8.5 gms.

The last experiment was carried out with copper enriched catholyte (27.3 gpl) using various A_a/A_c ratios. The unit was run for 24 hrs and the data obtained is presented in Table-5. The experiment was continued for another 15 hrs. using copper depleted catholyte and yielded data in Table-6.

All the above experiments were carried out at room temperature without agitation of either the anolyte or catholyte.

TABLE—V

Galvanic Deposition from Solution of High Copper Concentration

Galvani Couple No.	$\frac{A_a}{A_c}$	A_a (Cm^2)	Copper Recovery in 24 hrs. (gms)	Iron lost in 24 hrs (gms)	Cu — Fe
1	$\frac{1}{2}$	50	22.2	13.8	1.61
2	1	100	31.2	19.8	1.58
3	1	100	29.2	19.1	1.53
4	1	200	40.2	27.2	1.48
5	1	200	47.2	32.1	1.47
6	1	200	44.6	29.7	1.50
7	2	200	27.4	20.3	1.35

Catholyte Analysis :
$(Cu^+)_{t=0}$ = 27.3 gpl
$(Fe^{3+})_{t=0}$ = 9.1 gpl
$(Cu^+)_{t=25hrs}$ = 8.5 gpl
$(Fe^{3+})_{t=24hrs}$ = 3·3 gpl

Inter-electrode distance = 5cms
Overall efficiency Cu_{total}/Fe_{total} = 1.63

Total copper deposited = 265gms
overall rate of copper deposition = 11gms/hr

Total iron lost = 162 gms
Powder purity (H_2 reduced) = 99.9 +

TABLE—VI

Deposition from Copper Depleted Catholyte of Previous Experiment using same Assembly.

Total Copper Recovery in 15 hrs (gms)	Total iron Lost in 15 hrs (gms)	$\frac{Cu_{total}}{Fe_{total}}$
95.3	108.5	0.88

Catholyte Analysis :
$(Cu^+)_{t=0}$ = 8 5 gpl
$(Fe^{3+})_{t=0}$ = 3.3 gpl
$(Cu^+)_{t=15hrs}$ = 2.2 gpl
$(Fe^{3+})_{t=15hrs}$ = 3.2 gpl

Rate of Copper deposition = 6.4gms/hr
Direct Cement Copper obtained at anode after 39 hrs = 69 gms

RESULTS AND DISCUSSION

1. Effect of Cell Resistance

The rate of galvanic deposition indicated by the magnitude of galvanic current depends to a large extent on the cell resistance. It is observed from Table 1 that for maximum galvanic current (which is possible at low cell resistance), the inter-electrode distance should be small and therefore it was maintained at 4 or 5cms in all experiments,

2. Anolyte Acidity

The anolyte used should fecilitate a high degree of electrochemical corrosion of iron. From an earlier study, 9 gpl hydrochloric acid (20ml Conc. HCl per lit) was found to be best [2] and used in the present large scale investigation; the total amount of acid should be sufficient to keep all the dissolved iron as $FeCl_2$ in solution.

3. Effect of Ferric and Cuprous ions in the Catholyte

The ferric ions are reduced at a faster rate than cuprous ions when their concentration is high (Fig.2) resulting in a slow rate of copper deposition. In the last two experiments higher rate of copper deposition has been achieved by decreasing the ferric ion concentration in the copper-rich catholyte. Ferric ions can affect the rate by consuming electrons to get reduced to ferrous and/or leaching out deposited copper. In either case that effect leads to decreased efficiency.

The galvanic current increases with cuprous ion concentration in the catholyte. Thus, the deposition rate which was high at the start of the experiment comes down with progress in copper deposition. Experimentation with copper-depleted solutions has always yielded sluggish deposition rate and poor efficiency. Hence a cut-off point (cuprous ion concentration in catholyte) can always be defined from the economical or production point of view.

It has become possible to increase the rate of deposition from 1.12gms/hr to 11gms/hr by controlling the ferric and cuprous ion concentrations in the catholyte.

4. Effect of electrode area

Table-5, illustrates that copper deposition is maximum when A_a/A_c is unity $A_a/A_c = 1$ and large electrode area are the conditions for large currents. However, an optimum area exists beyond which there is no proportional increase in current. Six galvanic couples, each of unit A_a/A_c ratio, anode area of 200 cm^2 and catholyte $(Cu^+)_{t=0} = 18.2$ gpl generated a total current of 4.38 amps (Table-3).

The reason of maximum current at $A_a/A_c = 1$ can be explained along the lines of Stern [4].

Consider the Tafel relationships:

$\phi_c^1 = \phi_c - \beta_c \log (I_c/A_c i_{oc})$ ..... (1).

$\phi_a^1 = \phi_a + \beta_a \log (I_a/A_a i_{oa})$ ..... (3).

where subscripts a and c refer to anode and cathode respectively, ϕ^1 is the polarized potential, ϕ is the open circuit potential, β is the Tafel slope, I is the current density, A_a is the fraction of surface that is anode such that $A_a + A_c = 1$ and i_{oa} and i_{oc} are the exchange currnt densities for the anode and cathode reoctions, respectively. At steady state,

$\phi_c^1 = \phi_a^1 = \phi_{cor}$ and $I_a = I_c = I_{cor}$, then

$\beta_c \log I_{cor} = \phi_c - \phi_{cor} + \beta_c \log A_c I_{oc}$.

and subsitituting for ϕcor in eq 3,

$$\phi cor = \phi_a + \beta_a \log I_{cor} - \beta_a \log A_a i_{oa} \ldots\ldots\ldots\ldots (4)$$

$$\log I_{cor} = \phi_c - \phi_a/\beta_c + \beta_a + \beta_a/\beta_c + \beta_a \log A_a i_{oc} + \beta_c/\beta_c{}^* \beta_a . \log A_c i_{oc}$$

Since $A_a = 1 - A_c$,

$$d \log I_{cor}/dA_c = -\beta_a/2.3(\beta_c + \beta_a) . 1/(1-A_c) + \beta_c/2.3 (\beta_c + \beta_c) 1/A$$

$$= \beta_c(1-A_a) - \beta_a A_c/2\text{-}3(\beta_c + \beta_a) A_c A_a \ldots\ldots\ldots (5)$$

maximum I_{cor} occurs at $d \log I_{corros}/dA_c = 0$

or when the numerator of eq (5) equals zero. This occurs at $A_c = \beta_c/\beta_c + \beta_a$. If $\beta_c = \beta_a$, which is frequently observed, the maximum corrosion rate occurs at $A_a = \frac{1}{2}$ or at an anode-cathode area ratio of unity. At any other anode-cathode area ratio, the corrosion current is less.

If the area of anode is more than that of cathode, part of anode which is not in parallel to cathode undergoes chemical dissolution without contributing to the galvanic deposition, resulting in decreased efficiency. This point is clearly seen from Table-5., for couples of $A_a = A_c = 100 cm^2$ and $A_a = 200 cm^2$, $A_a = 100 cm^2$ have comparable copper recovery but the efficiencies are respectively 1.53 and 1.35.

5. Excess Iron Consumption

When galvanic deposition is the only process taking place the ratio of copper deposition to Fe dissol-

ved is 2.28. The highest value obtained in the present investigation is 1.63 and falls much short of ideal value. The low efficiency recorded is due to the following side reactions at the anode: a) dissolution of iron due to direct cementation of the diffused copper from catholyte, $2Cu^{+} + Fe = Fe^{2+} + 2Cu$; b) dissolution due to hydrogen liberation, $Fe + 2H^{+} = Fe^{2+} + H_2$: c) dissolution due to reduction of ferric ion, $Fe + 2Fe^{3+} = 3\ Fe^{2+}$, d) effect of contact resistance

Table-3 reveals that under identical conditions, the copper deposition varies from 27.8 gms to 33.1gms. This variation has been attributed to varying contact resistance

7) The Morphology and Purity of Powder

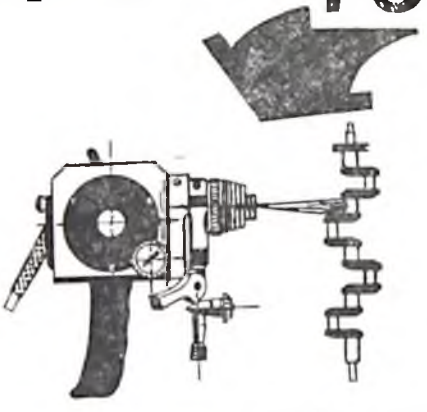
Dendritic deposit is common with copper-rich catholyte while copper-depleted catholyte gives adherent coating. In both cases, the deposit build-up was on front face only. The moist power deposit is prone to oxidation during open-air drying, but it can be avoided by initial acetone drying followed by vacuum-oven drying at 100°C. Hydrogen reduced copper powder, analysed spectrographically was 99.9 + pure, with Fe, As, Pb, Mg, Ni and Al at ppm levels.

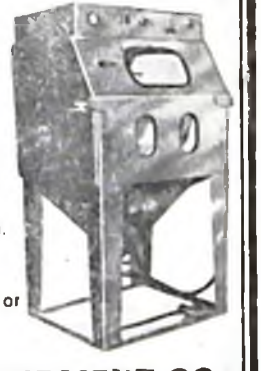
Fine powder of directly cemented copper on the iron anode was found almost entirely at the bottom of the cell. It is less pure than the galvanic copper.

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