ELECTROWINNING OF COPPER & RECOVERY OF SULPHUR FROM MATTE : FERRIC CHLORIDE PROCESS

J. Balachandra,

Dept. of Metallurgy, Indian Institute of Science Bangalore-560 012.

(Received and accepted Dec. 1977)

In the usual industrial practice of obtaining electrolytic copper from matte, the matte is converted and cast into anodes and electrolyzed to obtain copper as cathode sheets. In the pyrometallurgical step, sulphur is eliminated as SO_2 which is fixed up as sulphuric acid.

Several hydrometallurgical treatment processes for chalcopyrite concentrates have been reported (1-3). In one of the processes Ferric Chloride has been considered as an efficient leachant for extraction of copper (4-7). The leaching is carried out at 100-110°C with 4 Molar Ferric Chloride and the copper extracted from the process liquor preferably by cementation. One of the attractive features is the recovery of sulphide sulphur in the elemental form obviating any atmosphere pollution. The ease of storage and transport of sulphur as against sulphuric acid is another advantage. In this treatment copper is obtained as powder which finds a ready market.

It is well known that sulphides of metals like Nickel, Cu., behave almost like metal anodes in electrolysis. The recovery of Ni from sulphide anodes is well established. In the present investigation electrowinning of copper from cast copper matte anodes using $FeCl_3$ as the anolyte has been attempted. The process is carried out at room temperature, (except for rise in cell operating temperature during electrolysis) in a diaphragm cell, copper is recovered as powder in the cathode compartment and elemental sulphur is retained in the anode compact crust from which it can be extracted.

EXPERIMENTAL :

Copper matte supplied by M/s Hindustan Copper has been melted and cast under controlled conditions into anode shapes ($10 \times 1\frac{3}{4} \times \frac{1}{4}$") $25.4 \times 3.81 \times .637$ cms. No special precautions need be taken during cooling of the cast anodes as is required in the case of Nickel Sulphide anodes. The anodes are however brittle and have to be handled with care. The anodes analyze 40.56% Cu. A diaphragm cell of 2 litre capacity (1 litre in each compartment) with microporous rubber diaphragm has been used to observe the difference in behaviour of the diaphragms. Sheet copper was used as cathode. The anolyte was stirred mechanically. The catholyte was in all experiments 4 Vol% HCl. The inter electrode distance was maintained at 17·78 cms (7"). The matte anode was weighed initially and after scraping off the crust and cleaning at the end of the experiment and the loss in weight has been recorded as anode weight loss. The scraped material has been washed dried and weighed and reported as anode sludge. There was negligible amount of sludge collected in the anolyte as the crust on the anode was compact, though cracked. The cathode was weighed before and after the experiment and the weight recorded. The copper powder in the cathode compartment was collected washed dried and weighed. During the handling, the fine copper powder oxidised.

Two different concentrations of $FeCl_3$ in the anolyte (Viz : 5 and 10 Wt% $FeCl_3$) were used. The effect of several variables such as volume of electrolyte, duration of electrolysis, concentration of anolyte, and current density on the copper deposit and also on the copper concentration in the anolyte and catholyte at the end of the experiment was studied. Since the copper powder has tendency to oxidize during washing and drying the powder obtained in several experiments was analyzed for copper content. The copper content was observed to be 86% and this value has been taken for calculating the copper content of the deposit. No iron has been detected in the copper deposit on chemical analysis.

Flotation of Sulphur from a few samples of anode crust (washed and dried) has been attempted, as also dissolution and recovery by treatment with Tetra Chloroethylene.

A chemical analysis of the copper deposit, in a few experiments has been made. The ratio of actual copper content taken into solution based on the anode loss to the theoretical amount based on ampere hours passed has been calculated indicating the ampere hour efficiency.

RESULTS & DISCUSSION:

Table I gives complete experimental data on the process. The copper content mentioned in Column (16) has been computed from the actual weight of the deposit recorded in Column (9) taking the copper content to be 86% of the deposit weight because as mentioned earlier the deposit oxidizes during handling. It is observed from Column (12) and (13) that the copper content in the anolyte is generally by far greater than that in the catholyte at the end of the experiment indicating rapid depletion of copper transported to the cathode compartment. The cell voltage has a tendency to rise because of the build up of the anode crust. With development of cracks in the crust during the run of the cell, voltage decreases. However, in spite of the formation of the crust, the anode is observed to be uniformly dissolved and no break up of the electrode is observed. The temperature rise is dependent on the current (and current density) and duration of electrolysis.

Table-II summarises the effect of variables on the copper deposition. It is observed from the copper material balance that the copper dissolved from the matte anode as indicated in Column (4) is accounted for by the sum of the Copper deposit (actual copper content) and the concentration in the anolyte and catholyte.

The effect of C. D. and duration of electrolysis on the ratio of copper deposited in the cathode compartment to the copper dissolved from the matte (expressed as a percentage) termed "deposition ratio" is shown in Column (6) for each of the concentrations of the anolyte. The anolyte concentration was either 0.6 or 0.3 M $FeCl_3$ (corresponding to 10 or 15%).

The anolyte and catholyte compositions for the three sets of experiments were as indicated at A, B and C. A is a 5% $FeCl_3$ solution with 500 cc as anolyte; B a 10% $FeCl_3$ solution with 500 cc as anolyte; and C a 10% solution with 800 cc as anolyte. The anolyte and catholyte volumes were identical.

EFFECT OF C. D:

In the first set of experiments increase in C. D. shows a slightly higher deposition ratio in column 6 for electrolysis of 6 hours duration and a slight decrease in 24 hours runs. It also shows that for the same C. D. the deposition ratio decreased with time. In the second set of experiments also, for 6 hours and 24 hours runs the deposition ratio (column 6) increases with C. D. In the third set of runs the same effect is observed.

EFFECT OF $FeCl_3$ ANOLYTE CONCENTRATION AND DURATION OF ELECTROLYSIS:

From experiments of sets A & B it is seen that a higher concentration (0.6M $FeCl_3$) as in set B compared to 0.3M $FeCl_3$ in A gives better deposition ratio and more so for longer duration of electrolysis.

From sets B & C, for the same concentration viz., 10% $FeCl_3$ (0.6M) a larger volume of anolyte (cell capacity) gives a higher deposition ratio because the operating C. D. can be higher owing to a greater immersion depth of the anode though for the same C D. the ratio will be lower for 6 hour runs. This is possibly due to the time involved in cracking up of the crust to enable the electrolysis to proceed satisfactorily.

A plastic diaphragm was used in place of microporous rubber diaphrgam in expt. 9 (Serial No.7) and comparing experiments 9 and 13 it is seen, all experimental conditions being the same the deposition ratio is higher when microporous rubber diaphragm is used.

AMPERE HOUR EFFICIENCY OF ANODE DISSOLUTION:

The theoretical amount of copper to be dissolved in divalent condition for the ampere hours passed is shown in Column (12). The actual amount dissolved is given in Column (4). The ratio of actual amount dissolved to the theoretical is shown in Column (13). It shows certain features.

For the same ampere hours passed (18 amp. hrs.) as in experiments 15, 16 & 17 from sets A, B and C the ratio as in column (13) is of the same order. Similarly for 27 amp. hours passed as in 14, 19 and 18 in sets A, B & C the ratio is almost alike. This holds good for ratio obtained for 36 amp. hours as in experiments 12, 13 and 8 and for 72 amp. hrs for experiments 20, 21 and 6. This shows that the dissolution rate is almost identical for the total ampere hours passed irrespective of the anolyte composition, and is in the range 40 to 55%.

TABLE I

EXPERIMENTAL DATA

	ANOLYTE		CATHOLYTE		
Solution Composition	A 80 gms $FeCl_3$ 32cc HCl 800cc water	B 50 gms $FeCl_3$ 20cc HCl 500cc water	C 25 gms $FeCl_3$ 20cc HCl 500cc water	D 32cc HCl 800 cc water	E 20cc HCl 500 cc water

Anode-Cathode spacing 17.78 Cms (7"). Diaphragm ; microporous rubber. in all experiments, except for plastic in experiment .9. *The actual copper content was 86% of the deposited copper (as analysed)

Sl No.	Exp. No.	Matte Anode Wt. gm	Ano-lyte	Catho lyte	Current amps.	Current Den. Amp/ dm^2.	Duration of Elect-rolysis	Copper powder dep. gms.	*Copper content gms.	Anode Sludge gms.	Copper in ano-lyte at end of expt. gms.	Copper in Catho-lyte at end of expt. gms.	Cell voltage. V.	Tempera-ture. °C.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	6	92.7	A	D	3.0	6.20	24	28.37	24.6	33.5	11.22	1.50	6.5 to 10.2	45
2	7	163.0	A	D	5.0	10.34	24	53.0	45.58	47.94	17.17	2.38	9.8 to 12.0	55
3	8	58.3	A	D	1.5	3.10	24	18.0	15.61	26.22	4.53	3.14	4.0 to 6.4	35
4	9	48.0	B	E	1.5	4.65	24	5.73	4.92	21.75	12.71	1.33	5.8 to 10.0	35
5	12	53.0	C	E	1.5	4.65	24	9.04	7.78	28.37	13.58	0.25	5.5 to 9.0	45
6	13	44.5	B	E	1.5	4.65	24	7.74	6.65	25.27	9.95	1.10	6.4 to 9.5	45
7	14	36.3	C	E	4.5	13.95	6	8.07	6.94	12.25	6.96	0.54	16 to 17	68
8	15	24.9	C	E	3.0	9.30	6	5.06	4.35	9.69	4.28	1.17	12 to 15.0	55
9	16	25.7	B	E	3.0	9.30	6	5.91	5.08	6.56	3.67	1.59	10 to 12	45
10	17	25.8	A	D	3.0	6.20	6	2.44	2.10	7.90	5.18	3.37	8.5	45
11	18	37.3	A	D	4.5	9.30	6	4.34	3.73	10.24	7.78	2.89	10 to 12	55
12	19	38.3	B	E	4.5	9.30	6	9.85	8.47	10.12	5.22	1.70	15	55
13	20	83.0	C	E	3.0	9.30	24	13.07	11.23	20.00	17.37	1.93	6 to 12	45
14	21	88.5	B	E	3.0	9.30	24	23.59	20.27	23.04	13.03	2.00	6 to 12	45

TABLE – II

EFFECT OF VARIABLES ON COPPER DEPOSITION

SET A. ANOLYTE			25 gms ($FeCl_3$ Solution) 20cc HCl. 500cc Water		Deposition ratio			CATHOLYTE	20cc HCl. 500cc Water		Copper content of matte 40.56%	
Sl. No.	Expt. No.	Matte dissolved gms.	Copper dissolved from matte. Gms.	Copper deposited. gms.	% Ratio of 5 to 4	Copper in anolyte. gms.	Copper in catholyte gms.	Duration of electrolysis	C. D. amps/dm^2	Amp. hrs. passed.	Cu. to be dissolved as Cu^{++} (Theo) gms.	Cu Dissolved (4) Theo. Cu^{++} to be dissolved. (12). %
1	2	3	4	5	6	7	8	9	10	11	12	13
1	15	24.9	10.10	4.35	43.06	4.28	1.17	6	9.30	18	21.49	47
2	14	36.3	14.72	6.94	47.15	6.96	0.54	6	13.95	27	32.20	45.7
3	12	53.0	21.50	7.78	36.20	13.58	0.75	24	4.65	36	42.98	50.0
4	20	83.0	33.67	11.23	33.40	17.37	1.93	24	9.30	72	85.96	39.1
SET B. ANOLYTE:			50 gms $FeCl_3$ (10% Soln.) 20cc HCl, 500cc Water					CATHOLYTE.	20cc HCl 500cc Water			
5	16	25.7	10.42	5.08	48.7	3.67	1.59	6	9.30	18	21.49	48.5
6	19	38.3	15.53	8.47	54.6	5.22	1.70	6	13.95	27	32.20	48.2
7	9	48.0	9.47	4.92	25.2	12.71	1.33	24	4.65	36	42.98	45.3
8	13	44.5	18.05	6.65	36.8	9.95	1.10	24	4.65	36	42.98	42.0
9	21	88.5	35.90	20.27	56.4	13.03	2.00	24	9.30	72	85.96	41.7
SET C: ANOLYTE:			80 gms $FeCl_3$; 32cc HCl 800cc Water					CATHOLYTE:	32c.c. HCl, 800cc Water			
10	17	25.8	10.46	2.10	20.0	5.18	3.37	6	6.20	18	21.49	48.7
11	18	37.3	15.13	3.73	24.6	7.78	2.89	6	9.30	27	32.20	47.0
12	8	58.3	23.65	15.61	66.0	4.53	3.14	24	3.10	36	42.98	55.0
13	6	92.7	37.6	24.6	65.4	11.22	1.50	24	6.20	72	85.96	43.7
14	7	163.0	66.12	45.58	68.8	17.17	2.88	24	10.34	120	143.3	46.2

SIEVE ANALYSIS OF THE POWDER DEPOSITED:

Sieve analysis of the copper deposited from a few experiments shows the powder to be in the range −100 + 150 mesh size.

SULPHUR RECOVERY:

The anode scrapings from a few runs have been subjected to flotation to recover sulphur. Conditions for the rougher were

KCN 0.5 grams.
Sodium Silicate: 0.5 ml.
Terpineol: 1.56 ml.
pH 11 and conditioning for 5 minutes.

In the cleaner no KCN was used. About 65% of the anode scraping has been floated as elemental sulphur. Dissolution of anode scraping in Tetrochlorethylene and recovery of Sulphur yielded poorer recoveries of Sulphur though the product was crystalline and pure.

CONCLUSION:

From the study it is seen that copper can be extracted satisfactorily as powder from the matte anode at room temperature electrolytically using the $FeCl_3$ as the anolyte the concentration being fairly low compared to the direct leaching process. Sulphur can also be floated from the anode scrapings. The regeneration of the $FeCl_3$ as in the chemical leaching process does not prove a problem in the process. The efficiency of operation is likely to improve on continuous operation. The optimum operating conditions appear to be:

10% $FeCl_3$ with 4 Vol% HCl as anolyte.
4 Vol% HCl as Catholyte.
C. D. -9.30 to 13.95 amps/dm^2.

My thanks are due to Prof. K. I. Vasu for helpful suggestions and discussions and to Dr. U. B. Naik for data on flotation of Sulphur.

REFERENCES

1. Burkin AR., Met. Rev. 16 (1971) 47.
2. Monhemius A.J., Chem. Processes Eng. 51, 1, (1970) 65.
3. Paynter J.C., J.T.A. Inst. of Min. & Met. Nov. 73, 158.
4. U.S. Bu of Mines RI 8007, 1975.
5. U.S. Bu. of Mines IC 8699, 1976.
6. U.S. Bu. of Mines RI. 7474, 1971.
7. D. R. Nagaraj, M. S. Thesis IISc, 1974.

WITH BEST COMPLIMENTS FROM :

ACCUMULATOR FABRICS

FACTORY :
67-B, Industrial Suburb
Yeswantpur
Bangalore-560 022

OFFICE :
21-22, Muniswamy Road
Queen's Road Cross
Bangalore-560 051

Manufacturers of Microporous PVC Battery Separators for all sizes of Lead Acid Batteries and Glaspol Tubular Bags for Tubular Batteries

Asian Paints' Research and Development are more than surface deep

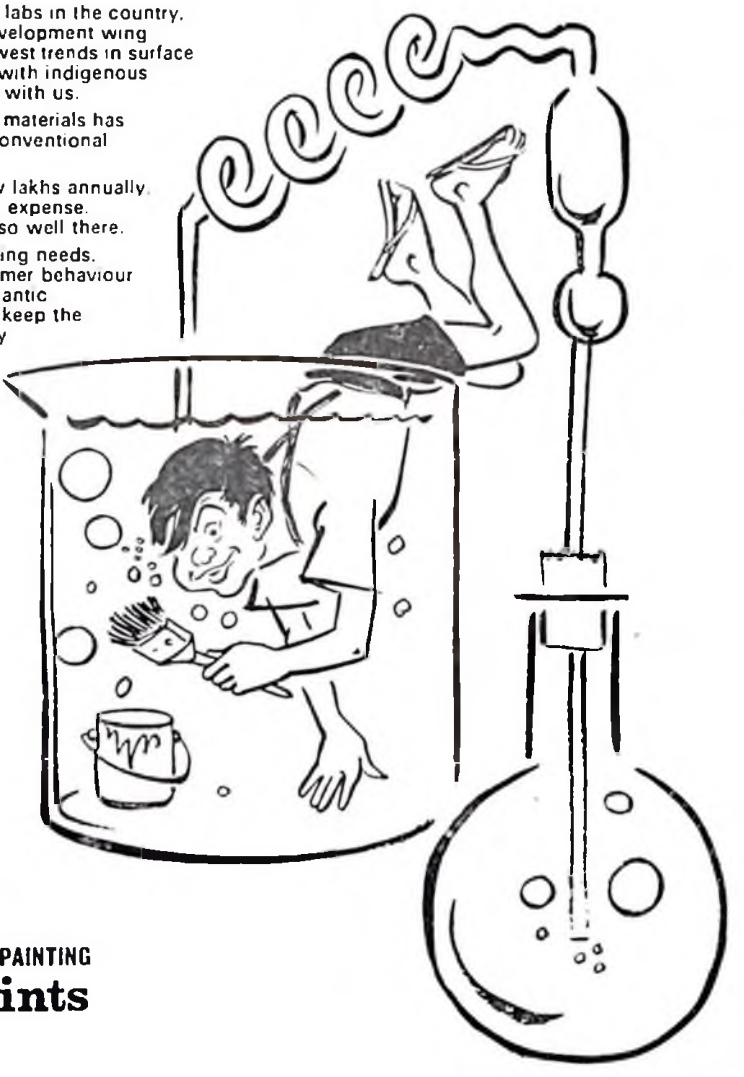
Equipped by one of the finest labs in the country, our technical research and development wing keeps in close touch with newest trends in surface coatings. Import substitution with indigenous materials has been a tradition with us.

Fundamental research on raw materials has resulted in putting to use unconventional materials available in India.

This costs the Company a few lakhs annually. But then we don't grudge the expense. Our research boys are doing so well there.

Projecting tomorrow's marketing needs, analysing the trends of consumer behaviour for this country's size, is a gigantic job. Professionals in the field keep the facts at fingertips. EDP facility makes the task easier.

Development of materials for mass markets is our commitment.



ANY SURFACE THAT NEEDS PAINTING
NEEDS asian paints

AIYARS-A. 178