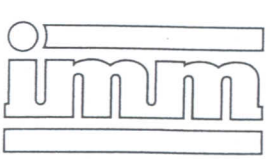
# MINERALS, MATERIALS AND INDUSTRY

Papers presented at the Fourteenth Congress of the Council of Mining and Metallurgical Institutions, organized by the Institution of Mining and Metallurgy and held in Edinburgh, Scotland, from 2 to 6 July, 1990

The Institution of
Mining and Metallurgy



# Studies on the flotation of mixed oxide–sulphide ores of copper from Malanjkhand deposit, India

S. Prabhakar
*National Metallurgical Laboratory Madras Centre, CSIR Madras Complex, Madras, India*
G. Bhaskar Raju
*National Metallurgical Laboratory Madras Centre, CSIR Madras Complex, Madras, India*
V. N. Misra
*Kalgoorlie Metallurgical Laboratory, Chemistry Centre, Department of Mines, Kalgoorlie, Western Australia*
P. R. Khangaonkar
*School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Ipoh, Malaysia*

## SYNOPSIS

Bench scale experiments on the beneficiation of a mixed oxide-sulphide ore of copper from Malanjkhand deposit of Hindusthan Copper Limited, India conducted with certain modifications in collector systems within the limits of existing plant operating conditions yielded better metallurgical results. Sodium isopropyl xanthate (IPX) and sodium diethyldithiocarbamate (DTC) were tried as collectors along with modifiers, such as, sodium silicate, guargum, Magnafloc-140 and Magnafloc-351. All the variables, viz. reagent concentration, pH of the pulp etc. were systematically studied and optimised. Improved metallurgical results were obtained with isopropyl xanthate in combination with sodium silicate and guargum at pH 9.0. The results were also equally good with dithiocarbamate, a chemisorbing collector.

## INTRODUCTION

Hindusthan Copper Limited's Malanjkhand Project (M.P. State), is the biggest open pit base metal mine in India. The project is designed to produce 2 million tonnes of ore per year at its full rated capacity and concentrate the same by flotation. Malachite is the predominant copper mineral in the oxidized capping whereas chalcopyrite and pyrite are the principal minerals in the primary ore zone[1]. In the secondary enrichment zone, where the present mining activities are going on, copper occurs not only as chalcopyrite but also as covellite and chalcocite. Apart from secondary sulphide mineralization, considerable degree of oxide formation was also observed in the ore from this zone. The ore exhibits a copper segregation tendency in the finer sizes.

The ore, at different levels, carries different proportions of primary and secondary copper minerals and oxide copper minerals. The varied nature of the deposit affects the copper recoveries and results in increased tailing losses[2].

To achieve better metallurgical results, specific, more efficient collector systems are needed to float the sluggishly floating covellite and chalcocite and the poorly floating malachite.

The present investigation details certain modifications in the collector systems within the limits of existing operating conditions of the plant.

## MATERIALS AND METHODS

The copper ore used in the investigation was a typical (crushed) sample

containing sulphides and oxides analysing about 3.0% copper, obtained from Malanjkhand Copper Project of Hindusthan Copper Limited, India. The sample was again crushed to 10 mesh using Laboratory jaw crusher followed by roll crusher, the output of which was further ground in a ball mill to get 60% -0.075 mm fraction. The final product with the size distribution shown in Table II was directly used in the flotation experiments. The chemical analysis of the head sample is shown in Table I.

Table I : Chemical analysis of head sample

| | % |
|---|---|
| Copper | 3.06 |
| Iron | 3.22 |
| Silica | 81.34 |
| Sulphur | 4.75 |
| CaO | 2.39 |
| Acid (5% Sulphuric acid) Soluble Copper | 0.34 |

Table II : Sieve analysis of the head sample

| Sl. No. | Size mm | Wt.% | Cu % | Total Cu distribution | % Distribution |
|---|---|---|---|---|---|
| 1 | +0.21 | 1.22 | 0.69 | 0.0084 | 0.27 |
| 2 | -0.21 +0.15 | 6.95 | 1.32 | 0.0920 | 3.01 |
| 3 | -0.15 +0.105 | 16.87 | 1.91 | 0.3222 | 10.53 |
| 4 | -0.105+0.075 | 9.95 | 2.35 | 0.2338 | 7.64 |
| 5 | -0.075+0.063 | 10.76 | 2.30 | 0.2475 | 8.09 |
| 6 | -0.063+0.053 | 10.09 | 3.63 | 0.3663 | 11.98 |
| 7 | -0.053 | 44.16 | 4.05 | 1.7885 | 58.47 |
| | | 100.00 | | 3.0587 | 100.00 |

Some of the reagents used in the investigation viz. sodium silicate, pine oil, guargum, Magnafloc and sodium isopropyl xanthate were of commercial grade whilst sodium diethyl dithiocarbamate, sodium hydroxide and acetic acid were of laboratory reagent grades. All the flotation experiments were carried out in a Dorr-Oliver flotation cell (1 kg capacity) keeping 25-30% solids in a single stage operation. The analysis of copper in the ore, float and tailings was determined with Atomic Absorption Spectrophotometer AA 575. All the experiments were duplicated and the average results obtained are reported.

## RESULTS AND DISCUSSION

As a preliminary step the extent of fines (-0.075 mm) in the as received sample was determined by screening. These fines accounted for about 8% by weight of the sample and analysed 5.8% copper including 1.4% acid (5% Sulphuric acid) soluble copper. This indicates that the generation of fines at the crushing stage itself is substantial.

The chemical analysis of the head sample after grinding shown in Table I, revealed the major gangue to be silica. The sieve analysis of the sample after grinding in a ball mill is indicated in Table II. It is evident that the -0.053 mm fraction accounts for about 45% by weight. The chemical analysis of the individual sieve fractions indicated that more than 50% of the total copper remained in this fraction.

### Preliminary flotation trials

The concentrator plant at Malanjkhand is presently carrying out the flotation of copper ores ground to 50% -0.075 mm using IPX and pine oil at the natural pH of the water available. A few preliminary experiments were carried out with 1 kg of ground ore, 0.06 kg/ton sodium isopropyl xanthate and 0.04 kg/ton pine oil without any modifiers or depressants, i.e. maintaining the same conditions as in the plant except cleaning and scavenging steps. The trials resulted a recovery of 73.4% with a float grade of 14.5% copper.

As the tailings were rich in copper, they were subjected to sieve analysis and the results are presented in Table III. The results indicated that

Table III : Sieve analysis of the tailings

| Sl. No. | Size mm | Wt.% | Cu % | Distribution | % Distribution |
|---|---|---|---|---|---|
| 1 | +0.21 | 1.12 | 0.536 | 0.006 | 0.65 |
| 2 | -0.21 +0.15 | 5.80 | 0.345 | 0.020 | 2.15 |
| 3 | -0.15 +0.105 | 14.95 | 0.482 | 0.072 | 7.74 |
| 4 | -0.105+0.075 | 9.05 | 0.718 | 0.065 | 6.99 |
| 5 | -0.075+0.063 | 10.94 | 0.649 | 0.071 | 7.63 |
| 6 | -0.063+0.053 | 10.12 | 1.344 | 0.136 | 14.62 |
| 7 | -0.053+ | 48.02 | 1.166 | 0.560 | 60.22 |
| | | 100.00 | | 0.930 | 100.00 |

the copper loss in fine fractions, i.e. -0.063+0.053 and -0.053 mm alone accounted for more than 65% of total loss of copper in tailings and were responsible for lower recoveries. Further the low recoveries may be attributed to pH of the pulp, which is near neutral. The earlier work[3] on copper oxides (mainly malachite) from Malanjkhand deposit revealed the dissolution of copper at neutral pH of the pulp. The dissolved copper ions in the pulp was found to create difficulties like gangue activation (low grade float) and high reagent consumption. So a separate set of experiments was carried out to observe the effect of reagent concentration and pH of the pulp.

Effect of reagent concentration

The effect of isopropyl xanthate concentration on the flotation of copper, keeping all the other conditions the same as above is shown in Table IV. The results showed negligible variations in both recovery and grade by increasing the reagent concentration and possibly the collector dosage may not be the cause for poor recoveries at Malanjkhand.

Table IV : Effect of IPX concentration without sodium silicate and without pH control

Conditions : Ore ... 1000 gm
Pine oil... 0.04 kg/ton

| Sl. No. | IPX kg/ton | Grade % | Recovery % |
|---|---|---|---|
| 1 | 0.06 | 14.0 | 73.3 |
| 2 | 0.10 | 16.2 | 79.1 |
| 3 | 0.15 | 16.9 | 80.5 |
| 4 | 0.20 | 18.3 | 81.2 |
| 5 | 0.25 | 18.8 | 80.6 |
| 6 | 0.30 | 17.9 | 79.8 |

Effect of pH

A set of experiments was conducted at different pH values of the pulp at 0.25 kg/ton of isopropyl xanthate and 0.04 kg/ton of pine oil. The results presented in Table V indicate a slight

Table V : Effect of pH without sodium silicate

Conditions : Ore .. 1000 gm
IPX .. 0.25 kg/ton
Pine oil .. 0.04 kg/ton

| Sl. No. | pH | Grade % | Recovery % |
|---|---|---|---|
| 1 | 7.0 | 15.80 | 81.30 |
| 2 | 8.0 | 20.61 | 83.34 |
| 3 | 9.0 | 20.80 | 86.71 |
| 4 | 10.0 | 20.20 | 86.01 |

improvement in both grade and recovery at pH 9.0. This improvement might be attributed to the flotation of malachite present in the ore as the point of zero charge (PZC) of malachite lies at about pH 9.4 as reported by Attia[4]. This fact is in accordance with the findings of the authors' earlier work on the beneficiation of copper oxide minerals[3].

Though the recovery and grade improved to 86% and 20% Cu respectively with the modification in the pulp and pH, the loss of copper in tailings

seriously affects the overall efficiency of the plant. Further the silica in the float can pose other metallurgical problems. From the above experimental results it was concluded that this type of ore needs in depth flotation studies using some modifiers/regulating agents/ selective collectors to reduce tailings losses in the form of fines and to reduce silica in float. Keeping this in view further experiments were carried out using various regulating agents.

Flotation with regulating agents

The flotation experiments were carried out with sodium silicate and other modifiers such as guargum and Magnafloc polymers.

Effect of sodium silicate

The effect of sodium silicate on flotation, at 0.25 kg/ton of isopropyl xanthate, 0.04 kg/ton of pine oil and at pH 9.0 is shown in Table VI. The addition of sodium silicate upto 1.5 kg/ton

Table VI : Effect of sodium silicate quantity

Conditions : Ore ... 1000 gm
IPX ... 0.25 kg/ton
pH ... 9.2
Pine oil ... 0.04 kg/ton

| Sl. No. | Sod.Silicate kg/ton | Grade % | Recovery % |
|---|---|---|---|
| 1 | 0.5 | 21.44 | 84.3 |
| 2 | 1.0 | 23.46 | 85.2 |
| 3 | 1.5 | 25.90 | 84.6 |
| 4 | 2.0 | 25.80 | 84.9 |
| 5 | 2.5 | 25.85 | 85.0 |

was found to result in remarkable improvements in copper grade, without affecting the recovery. The addition of sodium silicate naturally resulted in an increase in pH of the pulp due to its basic nature. To verify the effect of pH in the presence of sodium silicate, a few more experiments were carried out at different pH values of pulp, keeping the other conditions same as above.

Effect of pH in the presence of sodium silicate

The experimental results at different pH values of the pulp are shown in Table VII, from which it is again clear that the optimum pH is 9.0. It was also observed that the quantity of NaOH added to attain the pH 9.0 was not appreciable due to the presence of sodium silicate in the pulp. From the

Table VII : Effect of pH in the presence of sodium silicate

Conditions : Ore ... 1000 gm
IPX ...0.25 kg/ton
Sod. silicate ...1.5 kg/ton
Pine oil ...0.04 kg/ton

| Sl. No. | pH | Grade % | Recovery % |
|---|---|---|---|
| 1 | 7.0 | 17.0 | 78.0 |
| 2 | 7.5 | 17.7 | 80.0 |
| 3 | 8.0 | 19.7 | 85.0 |
| 4 | 8.5 | 21.3 | 84.4 |
| 5 | 9.0 | 25.4 | 85.2 |
| 6 | 9.5 | 23.6 | 85.0 |
| 7 | 10.0 | 20.2 | 86.1 |

above studies it was concluded that the presence of sodium silicate in the pulp and maintenance of pH at 9.0 can yield better copper grades with good recoveries (85%). For still better recoveries it was felt necessary to recover the copper values from the finer fractions of the sample. For this purpose a separate set of experiments was planned and carried out with other regulating agents, consisting mostly of polymers.

Effect of other regulating agents

The flotation experiments were carried out with the addition of reagents (polymers) such as guargum Magnafloc-140

Magnafloc-351 and cellulose xanthate.

The results obtained in the presence of various regulating agents with 0.25 kg/ton of isopropylxanthate, 0.04 kg/ton of pine oil and at pH 9.0 without depressant for silica are shown in Table VIII. Guargum was comparatively

Table VIII : Effect of various regulating agents without sodium silicate to recover fines thereby recovery

Conditions : Ore ... 1000 gm
IPX ... 0.25 kg/ton
pH ... 9.0
Pine oil ... 0.04 kg/ton

| Sl. No. | Name of regulating agent and quantity | Grade % | Recovery % |
|---|---|---|---|
| 1 | Magnafloc-140 0.010 kg/ton | 17.3 | 81.6 |
| 2 | Magnafloc-351 0.010 kg/ton | 18.2 | 85.5 |
| 3 | Cellulose xanthate 0.010 kg/ton | 20.5 | 86.0 |
| 4 | Guargum 0.250 kg/ton | 19.9 | 89.4 |

more effective in obtaining better copper recoveries than other regulating agents.

In the light of the above, further experiments were carried out with guargum at different concentrations both with and without sodium silicate, and pH values of the pulp.

Effect of guargum concentration

The effect of guargum concentration on the flotability with and without sodium silicate is shown in Table IX(a) and IX(b) respectively. There was not much variation in copper recovery with increasing guargum concentration and a dosage of 0.25 kg/ton was found to be more optimum where the copper recovery ranged from 89-90%. It was also observed that the presence of sodium silicate in the pulp improved the grade by more than 2%.

Table IX(a) : Effect of guargum concentration without sodium silicate

Conditions : Ore ... 1000 gm
IPX ... 0.25 kg/ton
pH ... 9.0
Pine oil ... 0.04 kg/ton

| Sl. No. | Guargum kg/ton | Grade % | Recovery % |
|---|---|---|---|
| 1 | 0.05 | 17.3 | 83.2 |
| 2 | 0.10 | 18.7 | 84.1 |
| 3 | 0.15 | 16.6 | 84.5 |
| 4 | 0.20 | 17.6 | 86.8 |
| 5 | 0.25 | 19.9 | 89.4 |
| 6 | 0.30 | 18.5 | 90.3 |
| 7 | 0.35 | 18.3 | 88.7 |

Table IX(b) : Effect of guargum concentration in presence of sodium silicate

Conditions : Ore .. 1000 gm
IPX .. 0.25 kg/ton
Sod. silicate.. 1.5 kg/ton
pH .. 9.0
Pine oil .. 0.04 kg/ton

| Sl. No. | Guargum kg/ton | Grade % | Recovery % |
|---|---|---|---|
| 1 | 0.05 | 21.2 | 84.3 |
| 2 | 0.10 | 22.6 | 84.2 |
| 3 | 0.15 | 22.9 | 88.4 |
| 4 | 0.20 | 22.8 | 88.7 |
| 5 | 0.25 | 23.0 | 89.5 |
| 6 | 0.30 | 23.1 | 88.8 |
| 7 | 0.35 | 22.9 | 90.0 |

Effect of pH in the presence of guargum and sodium silicate

A few experiments were carried out at different pH values of the pulp in the presence of guargum and the results of the same are shown in Table X. A slight reduction in pH of the pulp was noticed after the addition of guargum. However, the results again confirmed the optimum pH to be around 9.0.

Table X : Effect of pH in the presence of both guargum and sodium silicate

Conditions : Ore .. 1000 gm
IPX .. 0.25 kg/ton
Guargum .. 0.25 kg/ton
Sod. silicate.. 1.5 kg/ton
Pine oil .. 0.04 kg/ton

| Sl. No. | pH | Grade % | Recovery % |
|---|---|---|---|
| 1 | 7.0 | 19.7 | 85.5 |
| 2 | 8.0 | 21.1 | 86.2 |
| 3 | 9.0 | 23.0 | 89.5 |
| 4 | 10.0 | 22.1 | 87.0 |

The above studies resulted in some improvement in both grade and recovery by the addition of sodium silicate and guargum at pH 9.0. As discussed earlier the improvement in grade may be due to the addition of sodium silicate, a depressant for silica, and better recovery due to the pH of the pulp and guargum. Flocculation of fines was observed after the addition of guargum but these flocs may not be stable to float completely due to turbulence caused by agitation and further improvement in recovery beyond 90% was not possible. It is suggested that column flotation technique may work in this case, where the agitation turbulence is negligible. Further studies on these lines are currently being investigated in our laboratory.

Flotation with chelating type collector

Chelating agents are powerful, selective and specific collectors in flotation. Many researchers have indicated clearly the possibility of surface chelates for floating otherwise difficult minerals. Earlier work has reported the collector action of sodium diethyldithiocarbamate in the flotation of chalcopyrite[5] and copper oxides mainly malachite[3].

In the present, case since the ore is a mixture of sulphide and oxide minerals of copper (chiefly chalcopyrite and malachite), the flotation efficiency of sodium diethyldithiocarbamate was investigated. The effect of the reagent concentration was studied at pH 9.0 with 1.5 kg/ton of sodium silicate and 0.04 kg/ton of pine oil. The results obtained are presented in Table XI indicative of good grade and recovery of copper.Though dithiocarbamate belongs

Table XI : Effect of DTC concentration

Conditions : Ore .. 1000 gm
Sod. silicate.. 1.5 kg/ton
pH .. 9.0
Pine oil .. 0.04 kg/ton

| Sl. No. | DTC kg/ton | Grade % | Recovery % |
|---|---|---|---|
| 1 | 0.10 | 19.9 | 63.3 |
| 2 | 0.20 | 19.8 | 66.2 |
| 3 | 0.30 | 20.2 | 72.1 |
| 4 | 0.40 | 19.9 | 73.8 |
| 5 | 0.50 | 21.0 | 75.0 |
| 6 | 0.75 | 22.7 | 79.0 |
| 7 | 1.00 | 24.3 | 85.8 |
| 8 | 1.50 | 24.8 | 88.3 |
| 9 | 2.00 | 24.9 | 91.4 |
| 10 | 2.50 | 25.8 | 92.3 |

to a category of xanthates, thiouride group in diethyldithiocarbamate is responsible for high degree of selectivity. Mesomeric electron releasing tendency of $(C_2H_5)_2$-N- group enhances the electron donating ability to metal ions to facilitate strong coordinating bond with metal ion. However, the only setback with the use of sodium diethyldithiocarbamate is its high cost and consumption in flotation.

Flotation with sodium isopropylxanthate followed by sodium diethyldithiocarbamate

Some experiments were conducted at optimum conditions with xanthate followed

by flotation with DTC mainly to reduce the consumption of DTC. Five identical flotation experiments were performed with xanthate 0.25 kg/ton, 0.15 kg/ton sodium silicate and 0.04 kg/ton pine oil at pH 9.0 in the first stage and the tailings were refloated with dithiocarbamate (0.05 kg/ton) only. The average overall grade obtained was 16.8% copper with a recovery of 94.8 %.

## CONCLUSION

The crushing/grinding operations with Malanjkhand ore body generate more fines resulting in poor copper recoveries with lower grades of flotation concentrates. The studies carried out on the ore body have revealed that the pH of the pulp plays a vital role. Flotation with sodium diethyldithiocarbamate yielded better results compared to sodium isopropylxanthate. The addition of modifier viz. guargum, yielded excellent results for both grade and recovery of copper possibly through flocculation of slimes. This technique could be easily adopted for the flotation of Malanjkhand copper ores.

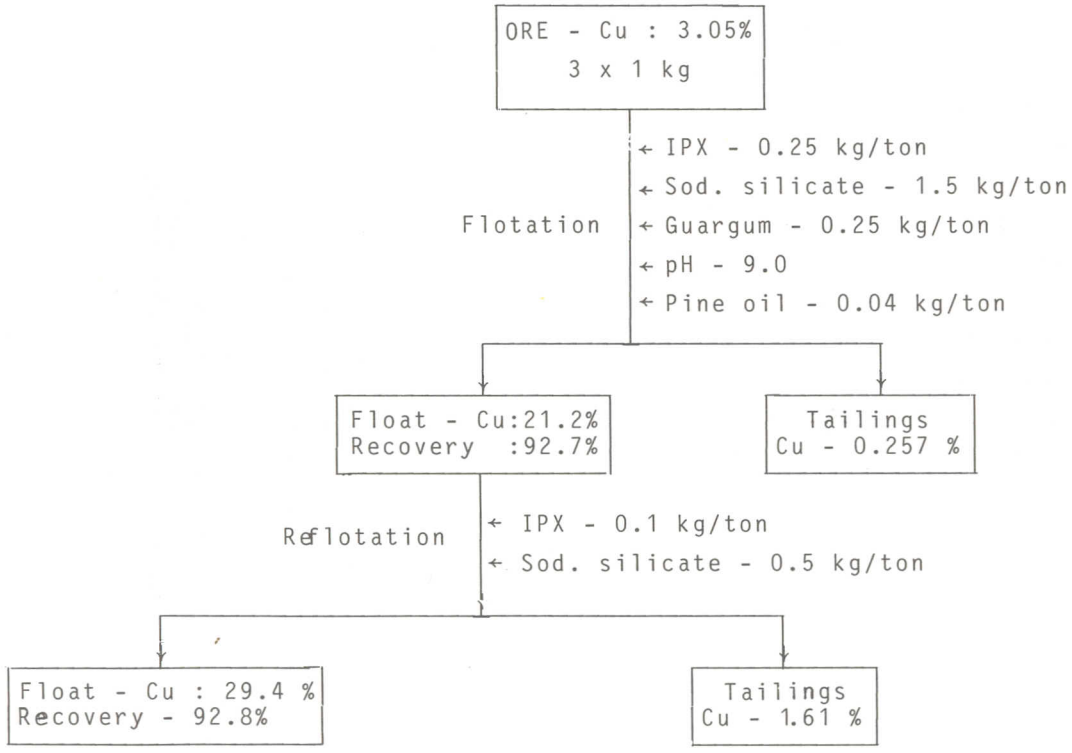



Figure 1

### Trials with sodium isopropylxanthate and guargum

Amongst all the above experiments, the trials with guargum may be considered more economical and easily adoptable in commercial plant practice. Specific experiments were conducted including cleaning of the float to study the limits of grade and recovery of copper. The flow sheet adopted in these trials and the results obtained are indicated in Figure 1.

## REFERENCES

1. Lane White, Hindustan Copper Limited: India's Copper Producer, E&MJ , June 1985,p. 26-42.

2. Ghosh, S., Makode, M.N., Raju, M.S. and Satyanarayana, K. Studies on the investigation of copper losses in the flotation plant tailings of copper concentrator, Malanjkhand Copper Project : Proc. of the Int. Conf. on Base Metal Tech., Nat. Met. Lab., Jamshedpur, India, 1989, p. 283-288.
3. Prabhakar, S., Bhaskar Raju, G. and Khangaonkar, P.R. : Studies on the beneficiation of copper oxide minerals, Proc. XVI Int. Min. Proc. Cong. Stockholm, ed. by K.S. Eric Forssberg, Elsevier, 1988, p. 1267-1278.
4. Attia, Y.A. : Surface chemistry of copper minerals in water, Trans. Inst. Min. Met., Sec. C, Vol. 84, 1975, p. 221-230.
5. Bhaskar Raju, G and Khangaonkar, P.R. : Electroflotation of chalcopyrite fines with sodium diethyldithiocarbamate as collector, Int. J.Min. Process, Vol.13, 1984, p.211-221.