

FLOTATION AND ADSORPTION STUDIES OF CHALCOPYRITE WITH CUPFERRON

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ABSTRACT

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Flotation tests were conducted in a Hallimond tube on chalcopyrite, with a collector system of cupferron and fuel oil. The reagent concentration, pH and conditioning time were studied as variables. The necessity of the fuel oil was verified by conducting experiments without it. Contact-angle measurements have been conducted by the captive-bubble technique. From the results it was found that fuel oil is necessary to promote adhesion of the conditioned mineral particles to the air bubbles. Adsorption experiments were carried out in a column apparatus under similar conditions as in flotation, except for the addition of fuel oil. The adsorption density and flotability were high at weakly acidic range where the reagent complexes the metal ions effectively in an aqueous medium.

INTRODUCTION

Chelating agents have received attention in the past for their potential use as collectors with high selectivity for minerals. Vivian (1927) reported the use of cupferron, an analytical chelating agent, as a good collector for flotation of cassiterite. Dewitt and Batchelder (1939) described the oximes (good chelating agents for metals) as flotation reagents. Since then there have been several reports (Gutziet, 1946; Peterson et al., 1965) of the use of chelating agents as floataids. Rinelli and Marabini (1973), Marabini and Rinelli (1973) and Marabini (1975) studied flotation of metallic minerals by means of collector systems, consisting of a chelating agent reacts with the cations of the mineral surface to form an insoluble metal chelate, to which the hydrocarbon oil which is necessary to ensure flotation adheres by physical adsorption. They described 8-hydroxy quinoline (Rinelli and Marabini, 1973), cupferron (Marabini and Rinelli, 1973), salicylaldehyde (Marabini, 1975) as collectors for various oxide minerals. Recently, Nagaraj and Somasundaran (1976) reported the use of LIX reagents as collectors for oxide copper minerals. Marabini (1978) studied the adsorption of salicylaldehyde on cassiterite to understand the reaction mechanism between the

chelating agent and mineral surface. Lenormand et al. (1979) studied the flotation of Malachite with potassium octylhydroximate as collector, and described the reaction mechanism by studying the adsorption, PZC measurements and IR. Further, Nagaraj and Somasundaran (1979) have shown the correlation of adsorption and flotation for oximes-copper minerals system.

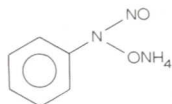
The work done so far was only on oxide minerals but not on sulfide minerals. Even though sulphide ores are easily floated by xanthates, in the case of complex sulphide ores it is very difficult to separate the individual sulphides effectively.

The advantage of using chelating agents lies in the possible selectivity or the specificity that they may possess for metal ions. This advantage is based on the assumption that they do adsorb or form a chelate on surfaces of minerals with selectivity or specificity similar to that exhibited in aqueous solutions.

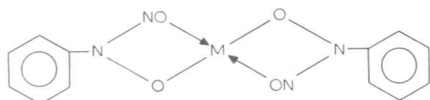
MATERIALS AND METHODS

The chalcopyrite sample used in all the experiments was obtained from Chitradurga Copper Mines (Karnataka, India). It was subjected to a series of concentration procedures such as froth flotation, heavy media separation and isodynamic separation and only the -72+100 BSS mesh portion from dry screening was selected. The selected material was treated with hot 1.0 N H_2SO_4 , filtered, washed with water thoroughly, dried and preserved carefully. The assay of this sample which was used in the tests described in this paper was Cu = 30.14%, Fe = 32.62%, S = 34.45% and SiO_2 = 1.22%.

Cupferron (ammonium nitrosophenyl hydroxylamine) is an organic reagent, which is readily soluble in water, forms insoluble chelate complexes with metal ions both in weakly and strongly acidic solutions. Cupferron salts are presumably of the inner-complex type. The solubility of the copper cupferrate in water is 0.7 mg/lit and iron cupferrate 0.02 mg/lit. The structure of cupferron is shown as:



Cupferron forms four-membered ring complexes with the metal ions shown in the figure:



In the present work, cupferron, Analar grade, was recrystallized prior to the experiments. pH adjustments were made with HCl and NaOH solutions. All the flotation experiments were carried out in a modified Hallimond

tube with flotation time of two minutes, with nitrogen gas flow as 0.2 l/min, 1.0 g mineral and 0.1 g/l fuel oil was used in all the experiments. The effect of concentration, pH and conditioning time were studied.

Adsorption experiments were carried out in a column apparatus, varying the reagent concentration and pH. The fuel oil was not used in the adsorption experiments.

The column apparatus for adsorption was used by Mellgren and Subbarau (1962) followed by Subramanyam (1979). The same apparatus with slight changes was used by Bogdanov et al. (1960) for their studies on 'Kinetics of flotation reagent sorption'. In the present work the apparatus used was similar to that of Subramanyam (1979). In this apparatus the adsorption cell is a sintered-glass filter tube with a porous disc. The adsorption cell is attached to the outlet of a graduated 800 ml separating funnel.

The effluent samples were collected every 60 seconds, keeping a flow rate of 0.013 l/min and analysed by a Carl-Zeiss double beam spectrophotometer at a wave-length of 301 nm, which is λ_{\max} for cupferron solutions. The adsorped quantity of the reagent is calculated from the concentrations of the effluent and the feed and the volume of reagent solution passed through 1.0 gm mineral bed.

The specific surface area of chalcopyrite sample was determined from the sieve analysis (Pryor, 1965) and was found to be 98.68 cm²/g.

For contact angle measurements, the sample was prepared by the method described by Ramachandra Rao (1960) and the measurements were done by captive-bubble technique.

RESULTS AND DISCUSSION

Effect of concentration

Figure 1 shows that by increasing the concentration of the reagent the flotability also increases gradually to certain extent. Beyond 0.06 g/l no further change in the flotability was observed. A similar trend was observed in adsorption, also shown in the same figure. It could also be seen from the Fig. 2 that the increase in adsorption is very small beyond 0.06 g/l concentration.

The adsorption density was plotted against time as shown in Fig. 2. The experiments were carried out for various concentrations at same flow rate. The nature of these curves indicates a hyperbolic relationship between adsorption-density and time. In the earlier work of Subbarau (1963) on the adsorption of xanthate on galena and Subramanyam (1979) on the adsorption of xanthate on chalcopyrite, a similar relationship is found to be valid, but in the case of the present study with cupferron the adsorption density is relatively high. This may be due to the formation of surface chelate. Collector action of the reagent can be visualized as the result of probable surface chelation shown in the simple schematic diagram, Fig. 3. A similar mechanism has been

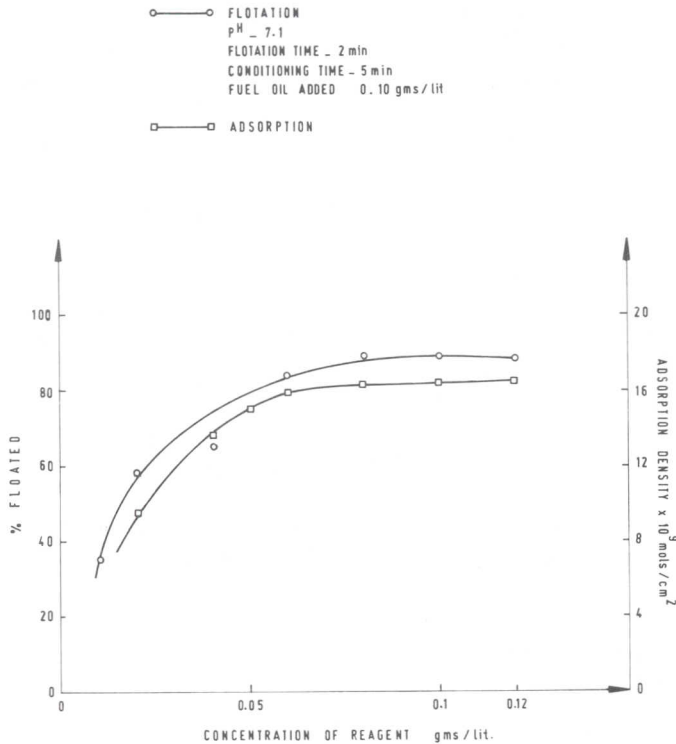


Fig. 1. Correlation of adsorption and flotation-varying reagent concentration, Chalcopyrite-Cupferron system. Vertical axis indicates wt % floated.

suggested by Nagaraj and Somasundaran (1976). It may be recognised that this chelate need not be identical with the metal chelate formed in the aqueous solutions.

Effect of pH

The adsorption density is plotted against time as shown in Fig. 4 at various pH values with 0.05 g/l of cupferron concentration and 0.013 l/min as flow rate. It is seen from the figure that at pH 4.04 the adsorption density is comparatively high because cupferron chelates metal ions effectively in the same pH range in aqueous medium. Figure 5 shows the superposition of the adsorption and flotation curves. Flotability shows a peak at pH 4. The adsorption density also decreases from pH 4 to pH 8. Measurements of adsorption below pH 4 were not practicable. At pH 2, the flotability was less than that at pH 4 due to the partial decomposition of the reagent, thereby the concentration of the reagent was decreased. This effect is also observed to create difficulty in attempts to measure adsorption at pH 2.

In basic medium the NH_4 group in the reagent is not released and the structure of the compound remains the same, which is not favourable for

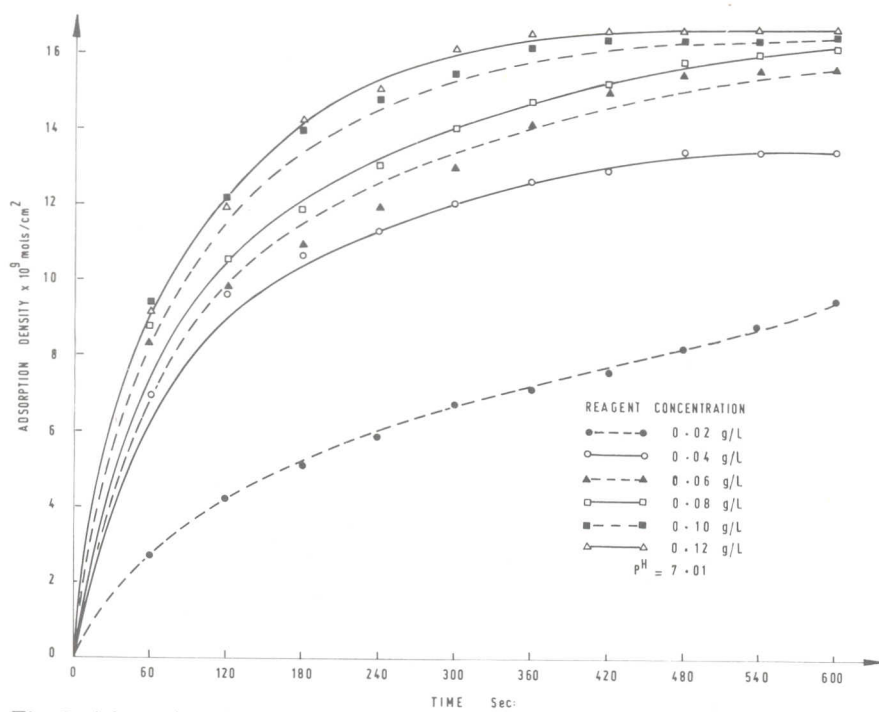


Fig. 2. Adsorption time curves-varying concentration.

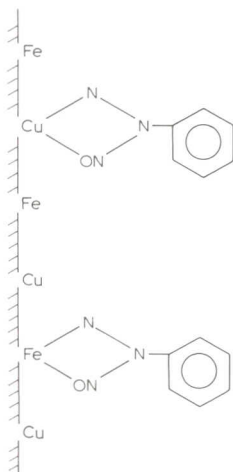
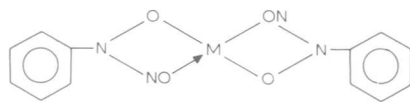


Fig. 3. Bulk chelate and proposed surface chelate structure.

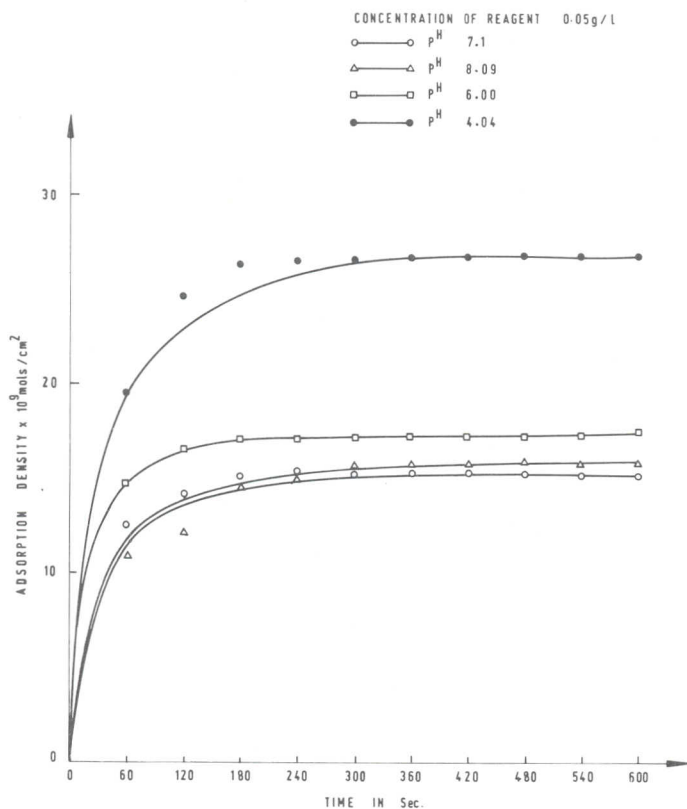


Fig. 4. Adsorption-time curves at different pH values.

complexation of metal ions. This is why both the flotability and adsorption density are less in this range.

Effect of conditioning time

From Fig. 6 it is observed that there is no appreciable change in flotability by increasing the conditioning time. From the adsorption studies, Fig. 4 illustrates that the saturation state of the reagent sorption was attained within a short period. One may suggest surface chemical action like the formation of a surface-chelate.

Contact angle studies

The contact angle of the system without fuel oil was found to be $35 \pm 2^\circ$ and with fuel oil it was $60 \pm 2^\circ$. The contact angle for the system without reagent and with fuel oil only was observed to be $60 \pm 2^\circ$. This shows that the contact angle may be controlled by the fuel oil when the reagent fuel oil mixture is used. However, flotation tests with oil and no chelating agent yield quite low flotability.

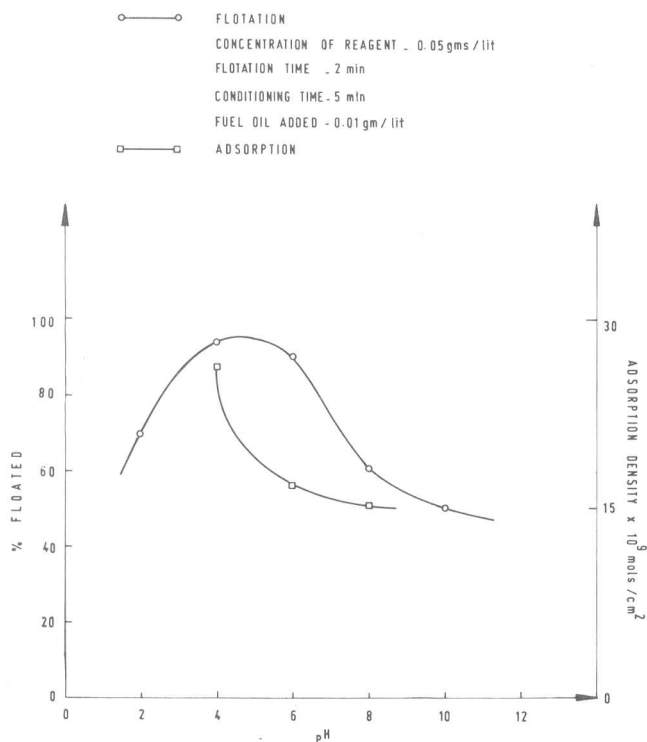


Fig. 5. Correlation of adsorption and flotation at various pH values. Vertical axis represents wt % floated.

In the chalcopyrite cupferron system (without fuel oil), it was observed that the contact angle is independent of concentration and pH. The reagent does not render the mineral surface hydrophobic enough to obtain good contact between the mineral and the bubble. This aim is fulfilled by adding fuel oil which creates hydrophobicity.

It would thus be seen that cupferron can act as a collector for chalcopyrite in the presence of oil and shows a reasonable correlation between adsorption and flotation behaviour. The possibility of surface chelate formation and other structural effects obviously need further study.

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CHALCOPYRITE - CUPFERRON	
CONCENTRATION	0.05 g/l
p ^H	NEUTRAL
FLOTATION	2 min.
FUEL OIL	0.1g/l

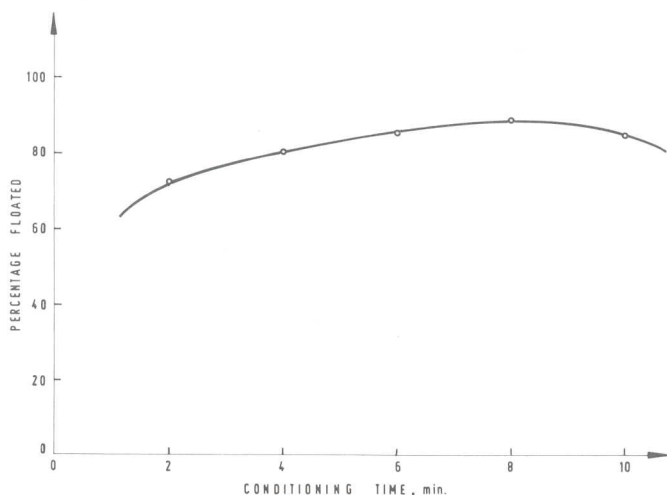


Fig. 6. Effect of conditioning time on the flotability of chalcopyrite. Vertical axis indicates wt % floated.

REFERENCES

- Bogdanov, O.S., Podnek, A.K., Hainman, V.J. and Nikhailova, N.S., 1960. Kinetics of flotation reagent sorption. *Int. Miner. Process. Congr., Inst. Min. Metall., London*, pp. 221-232.
- Dewitt, C.C. and Batchelder, F.V., 1939. Chelate compounds as flotation collectors, *J. Am. Chem. Soc.*, 61: 1247-1250.
- Gutziet, G., 1946. Chelate forming organic compounds as flotation reagents. *Trans. Am. Inst. Min. Metall. Pet. Eng.*, 169: 212-215.
- Lenormand, J., Salaman, T. and Yoon, R.H., 1979. Hydraxomate flotation of Malachite. *Can. Metall. Q.*, 18: 125-129.
- Marabini, A.M. and Rinelli, U.L., 1973. Flotation of pitch blende with a chelating agent and fuel oil. *Inst. Min. Metall. Trans. Sect. C*, 82: C 225-228.
- Marabini, A.M., 1975. New collector for cassiterite. *Inst. Min. Metall. Trans. Sect. C*, 84: C 177-178.
- Marabini, A.M., 1978. Study of adsorption of salicylaldehyde on cassiterite. *Inst. Min. Metall. Trans. Sect. C*, 87: C 76-78.
- Mellgren, O. and Subbarau, M.G., 1962-1963. Adsorption of ethyl xanthate on galena. *Bull. Inst. Min. Metall.*, 72: 425-442.
- Nagaraj, D.R. and Somasundaran, P., 1976. Chelating agents as flotoids, LIX-Copper mineral systems. *AIME Centennial Annual Meeting, San Francisco*.
- Nagaraj, D.R. and Somasundaran, P., 1979. Chelating agents as collectors in flotation, oximes-copper mineral systems *AIME Centennial Annual Meeting, San Francisco*. 1979, preprint number 79-76.

- Peterson, H.D., Fuerstenau, N.C., Richard, R.S. and Miller, J.D., 1965. Chrysocolla flotation by the formation of insoluble chelate. *Trans. Soc. Min. Eng., AIME*, 232: 389-394.
- Pryor, E.J., 1965. *Mineral Processing*. Elsevier, Amsterdam, 150 pp.
- Ramachandra Rao, S. and Patel, C.C., 1960. Behaviour of xanthates on Iron pyrite surface in the presence of oxygen-carbondioxide and their mixture. *J. Mines, Metals Fuels*, 8 (7): 18-23.
- Rinelli, U.L. and Marabini, A.M., 1973. Flotation of zinc and lead oxide sulphide ores with chelating agents. 10th Int. Miner. Process. Congr., Inst. Min. Metall., London, pp. 493-521.
- Subbarau, M.G., 1961. Studies in adsorption of Potassium Ethyl Xanthate on Galena. Diss., University of London, London, 161 pp.
- Subramanyam, T.V.S., 1979. Studies on Flotation and Adsorption of Chalcopyrite with Potassium Ethylxanthate. Diss., Indian Institute of Technology, Madras, 180 pp.
- Vivian, A.C., 1927. Flotation of tin ores. *Min. Mag.*, 36: 348-352.