

STUDIES ON THE BENEFICIATION OF COPPER OXIDE MINERALS

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SUMMARY

Bench scale experiments on the beneficiation of copper oxides were conducted using different chelating agents, viz. Cupferron, 8-Hydroxyquinoline, α -Benzoin oxime and sodium diethyldithiocarbamate. Among the four collectors tried, diethyldithiocarbamate was found to be effective in achieving good recovery and grade. Also the consumption of the reagent was less compared to other collectors. All the collectors have exhibited excellent selectivity towards copper and fairly good concentrate was obtained. Adsorption studies revealed that the adsorption of the collector on the mineral surface follows a true chemical reaction. Investigation on the nature of complexation with diethyldithiocarbamate has indicated that each copper atom on the surface will be complexed with two diethyldithiocarbamate molecules. Variables like reagent concentration, pH of the pulp, impeller speed, etc. were studied.

INTRODUCTION

The gradual depletion of high grade sulphide mineral deposits has turned the attention of the mineral industry to the recovery of metals from the oxides and silicates. Although it is general practice to treat oxide type copper ores through hydrometallurgical methods, beneficiation by flotation is done after sulphidization treatment using xanthates as collectors. The sulphidization stage is critical because either too little or too much sodium sulphide results in poor recoveries. In spite of the rigorous efforts towards the close control of sulphidization process by using various special electrode systems (ref.1) its industrial application was seriously restricted due to the critical requirements in the procedure.

Consequently many attempts have been made in search of suitable collector systems for the beneficiation of copper oxide minerals. The most obvious general class of reagents for this purpose would seem to be the organic chelating agents. A few investigators have reported methods of floating the oxide copper minerals, without sulphidization, in which strong complexing reagents are invariably used as collectors (Table-1).

Most of the above investigations, carried out on pure (Natural/synthetic) or concentrated minerals, suggest that organic compounds offer considerable promise for concentrating all copper ores irrespective of their forms.

TABLE 1

| Mineral | Reagent | Optimum Conditions | Reference |
|-----------------------------------------|--------------------------------------------------------------------|---------------------------------------------|-----------|
| Malachite | Potassium Octylhydroxamate | pH : 6-10 Recovery : 95% | ref.2 |
| Malachite + Azurite | Monoalkyl dithiocarbamates (Butyl, octyl, cyclohexyl) | pH : 9.5 Recovery : 93% | ref.3 |
| Chrysocolla | Potassium Octylhydroxamate | pH : 6-10 Temp. : 58°C Recovery : 76% | ref.4 |
| Chrysocolla | Alkyl substituted malachite green dyes (Butyl, hexyl, octyl) | pH : 7.7-8.0 Recovery : 68% | ref.5 |
| Sulphide/oxide/ carbonate mixture | Salicylaldoxime and its isomers | pH : 4.8 Recovery : 97% | ref.6 |
| Sulphide/oxide/ carbonate mixture | Hydroxy benzaldoxime, heptal- doxime and octaldoxime | pH : 4.8 Recovery : 96.5% | ref.7 |
| Tenorite | Salicylaldoxime | pH : 2.5 & 9.0 Recovery : 90% | ref.8 |
| Chrysocolla | 2-hydroxy benzophenone oxime | pH : 5.0 Recovery : 90% | ref.8 |
| Cuprite | LIX 65N (substituted benzo- phenone oxime) | pH : 6 & 10 Recovery : 100% | ref.9 |

The present investigation was undertaken to study the flotation response of oxidized copper ore, over 5.5 million tons from Malanjkhand Copper Mine (Hindustan Copper Limited, India), which is presently stockpiled in need of suitable beneficiation process. Based on the analytical chemistry of copper complexes, different class of reagents, viz. Sodium Diethyldithiocarbamate (DTC), Cupferron, 8-Hydroxyquinoline (Oxine) and α -Benzoinoxime (Oxime) were used as collectors directly to beneficiate the above mentioned copper oxide ore.

MATERIALS AND METHODS

The copper oxide ore used in the present investigation was obtained from Malanjkhand mine of the Hindustan Copper Limited, India. About 90% of Malanjkhand ore occurs in a hydrothermally mineralized quartz reef that was emplaced in precambrian granites. The remaining 10% is in granite near the reef contact. Metadiorite dykes and apatite bodies have intruded both the reef and granite. In the primary ore zone pyrite and chalcopyrite are the principal minerals. Chalcocite, covellite and bornite are placed in the zone of secondary enrichment and malachite, azurite, tenorite and cuprite occur in the oxidized cap. The latter material is currently being stockpiled. (ref.10).

The representative portion of the sample was crushed to 10 mesh using jaw crusher followed by roll crusher; the output of which was further ground in a ball mill. The final product with the size distribution shown in Fig.1 was directly used in the flotation experiments.

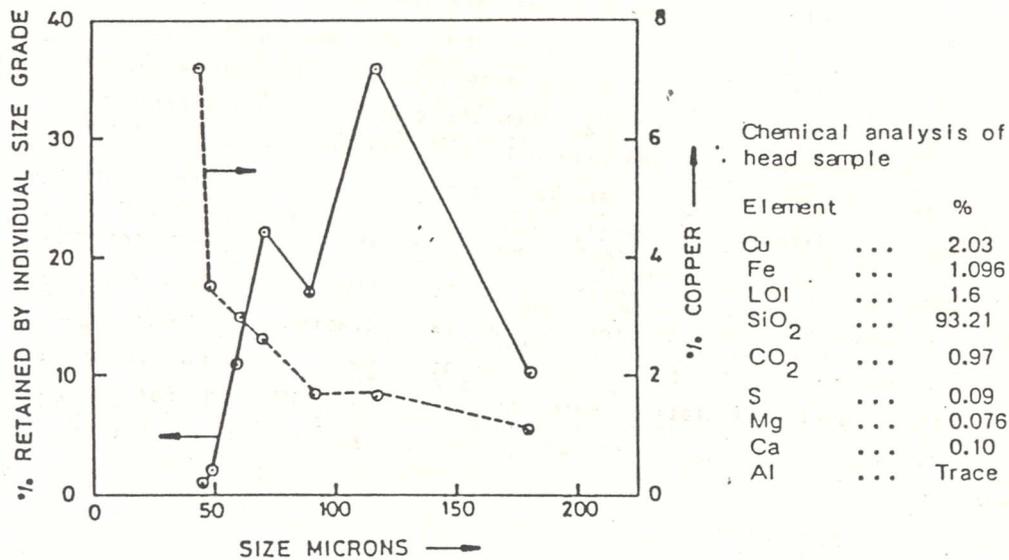


Fig.1 Sieve analysis of head sample

From the liberation analysis it was found that the mineral grains are free from the gangue below the size of 150 microns. The microscopic examination of the material revealed that about 91% of the copper is present in the form of malachite and about 6% in the form of azurite and the rest as cuprite and tenorite. The chemical analysis of the head sample given above clearly states that most of the gangue is present in the form of silica.

All the reagents viz. DTC, cupferron, oxime and oxine were of Analar grade and sodium silicate and pine oil were of commercial quality. pH was adjusted with AR sodium hydroxide and AR acetic acid.

All the flotation experiments were conducted in a Denver Laboratory flotation cell, with 0.5 kg of the material in each experiment. pH of the pulp was adjusted with dil. NaOH and dil. Acetic acid, after conditioning with depressant sodium silicate for 180 seconds. Before the addition of frother the material was conditioned with collector for 120 seconds and continued further 60 seconds with frother. 30% solids were maintained in the pulp. Flotation experiments were conducted using 3 kg/ton of sodium silicate and

0.05 kg/ton of pine oil which are found to be optimum from the preliminary experiments. The froth collected was filtered, washed and dried under IR lamps. The float was analysed for copper with Atomic Absorption Spectrophotometer, Varian AA 575.

The adsorption of DTC on the surface of the mineral was conducted by shaking method. 10 g of the material was taken and conditioned with the reagent (the amount of reagent, pH of the pulp and % solids were the same as in flotation), filtered, washed with water thoroughly and the same was quantitatively estimated both in the filtrate and on the material. The reagent adsorbed on the material was extracted with CCl_4 , then the copper ions were stripped into the aqueous solution by treating with dil. HNO_3 and analysed for copper. The amount of reagent adsorbed on the material was back calculated. The amount of reagent in the filtrate was directly analysed with spectrophotometer at λ_{max} of 280 nm. Where the reagent cannot be analysed directly, copper solution was added and the complex formed is extracted with CCl_4 and quantitatively estimated with spectrophotometer at λ_{max} of 460 nm. Surface products formed during flotation were analysed with IR and Far I.R. Spectrophotometers. I.R. was taken using KBr pellet and Far IR using polythene disc.

RESULTS AND DISCUSSION

Flotation

Initially a few experiments were conducted using conventional collector,

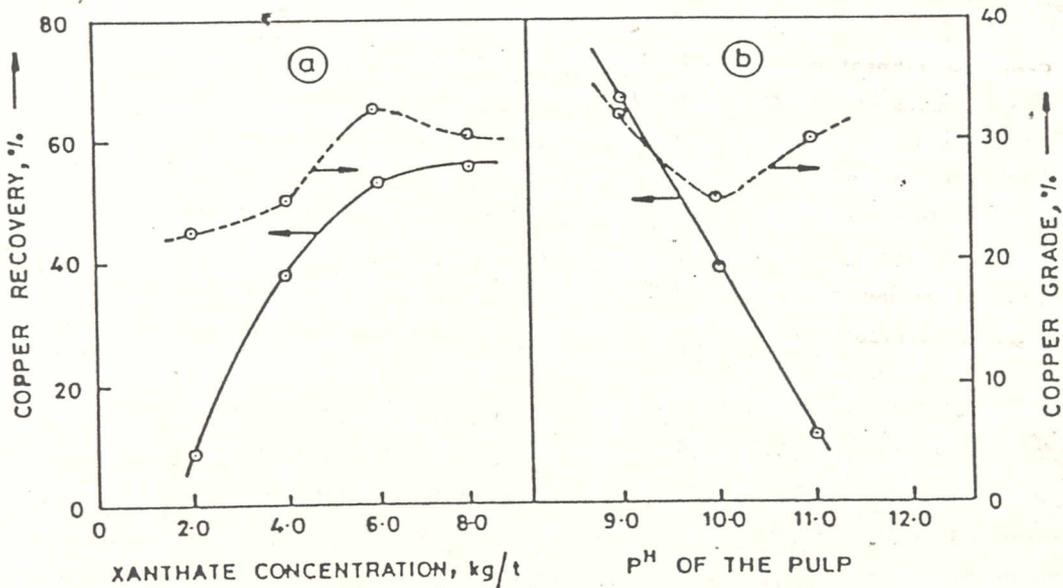


Fig.2 Floatability with xanthate as a collector a) effect of concentration at pH 10.0 b) effect of pH at 6 kg/t of xanthate.

potassium ethyl xanthate. Results of the same shown in Fig.2 indicate that the recovery 62% is low, though the grade (32%) is satisfactory. Further the requirement of collector dosage is prohibitively high compared to the circuits of sulphide flotation. pH of the pulp has got marked effect both on the recovery and grade of copper. pH 9.0 is found to be optimum for this system.

Further, strong copper complexing organic reagents such as cupferron, oxine, oxime and DTC were tried as collectors. At various concentrations of cupferron and pH of the pulp, floats were collected, the analysis of which is shown in Fig.3. These results indicate that cupferron gives better recovery, but

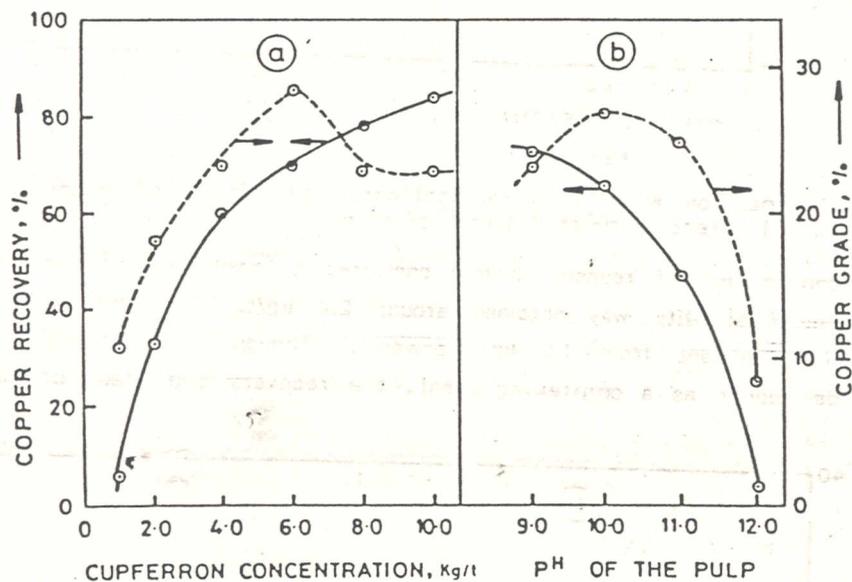


Fig.3 Flotation with cupferron as collector a) effect of concentration at pH 10.0 b) effect of pH at 6 kg/t of cupferron.

the consumption of the reagent is prohibitively high. The pulp pH has shown pronounced effect both on the recovery and grade of copper, the best results being obtained at pH 10.0. This could be attributed to the undissociated NH_4 group restricting the oxygen atom to participate in the complexation reaction. Further the complex of copper-cupferrate will slightly decompose in alkali solutions. In fact, the complexing ability of cupferron is high in mild acidic conditions, where the reagent can be dissociated into cupferrate ion and NH_4^+ . In the present investigation all the experiments were conducted only at and above pH 9.0, and the reason for such a restriction is indicated later.

Floatability of copper oxides with oxine as collector is shown in Fig.4.

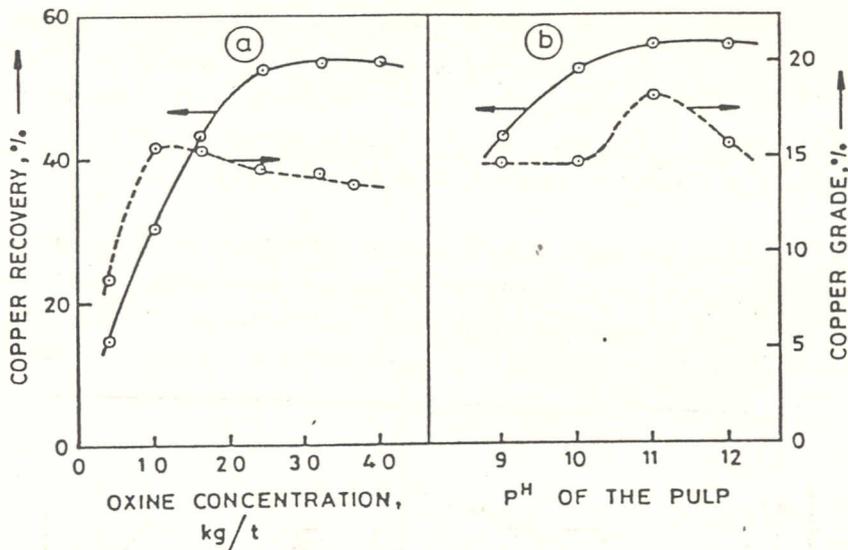


Fig.4 Flotation with oxine as collector a) effect of concentration at pH 10.0 b) effect of pH at 2.4 kg/t of oxine.

The consumption of reagent is less compared to xanthate and cupferron. The optimum floatability was obtained around 2.4 kg/t. The grade of the float remained constant from 1.0 kg/t onwards. Though oxine is highly selective towards copper as a complexing agent, the recovery and grade of the copper

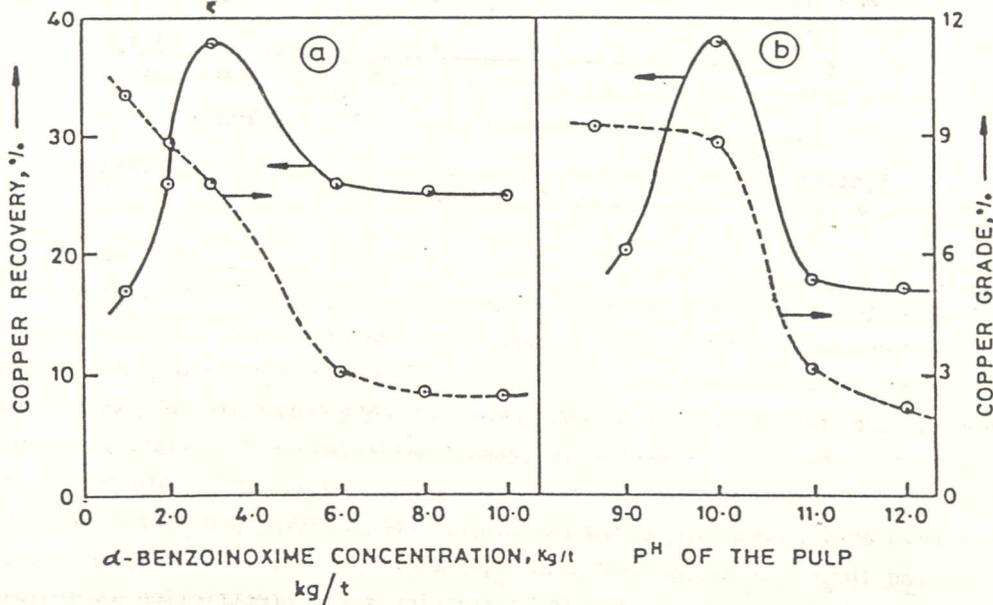


Fig.5 Oxime as collector a) effect of concentration at pH 10.0 b) effect of pH at 3 kg/t of oxime.

are still on the lines of xanthate only. It may be attributed to insufficient hydrophobic character of the reagent as observed earlier by Prabhakar et.al. (ref.11). The recovery can be enhanced by the addition of hydrocarbons like fuel oil, in which case the grade will be affected. No significant changes were observed with regard to pH of the pulp, because of the broad pH range (5.3 to 14.5) of oxine for copper complexation.

α -Benzoinoxime is selective towards cupric ions in ammoniacal solutions, but the results of the same as collector, shown in Fig.5, are however rather disappointing. The reagent consumption is low compared to other collectors and xanthate. This can be explained by the fact that it mostly reacts with the metal ion in equimolar proportions, forming acyloin oxime configuration (ref.12). Because of this singular activity towards copper, it was designated by a trivial name cupron. This type of complexation may help lower reagent consumption. The poor performance of oxime as a collector in this case is not clearly understood.

Among the four collectors studied, DTC has shown a positive response in all aspects like reagent consumption, recovery and grade of the mineral (Fig.6), with recovery upto 90% and grade upto 45% copper. Though DTC belongs to a category of xantates, thiouride group in DTC 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

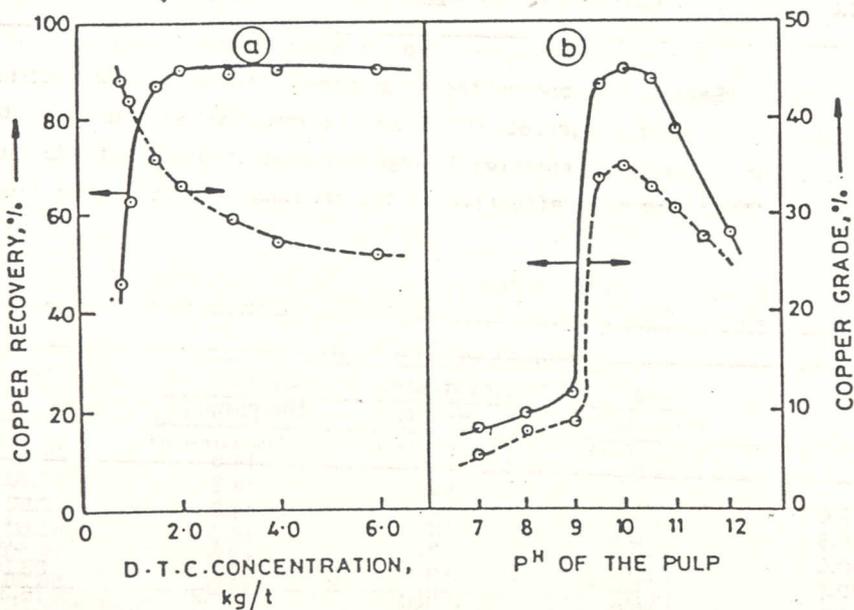


Fig.6 Flotation with DTC as collector a) effect of concentration at pH 10.0 b) effect of pH at 1.5 kg/t of DTC.

strong coordinate covalent bond with metal ion. Also the reagent is stable both in alkali and acid compared to xanthates. Since the results were highly encouraging, further variables were studied in detail with this reagent alone.

In the preliminary investigations, dissolution of copper was noticed below pH 9.0 (15% of copper at pH 7.0 and 5% at pH 8.0). Because of this dissolution high dosage of reagent is essential to achieve better floatability. Below pH 9.0, precipitate was seen in the float with all the reagents. This fact coincides with the work of PZC of malachite (pH 9.4) reported by Attia (ref.13).

Adsorption of DTC at various concentrations was studied and the results are given in Table 2. Good correlation was found between the reagent adsorbed

TABLE 2

Amount of DTC adsorbed on mineral surface at various DTC concentrations

| DTC Conc. kg/t. | Amount of DTC (mg) | | | Cu Recovery % |
|--------------------|-----------------------------|--------------------------------|----------------------------|------------------|
| | Before (feed) adsorption | After (filtrate) adsorption | Adsorbed on the mineral | |
| 0.8 | 8.0 | 0.0 | 8.0 | 46.6 |
| 1.0 | 10.0 | 0.0 | 10.0 | 64.2 |
| 1.5 | 15.0 | 0.0 | 15.0 | 87.5 |
| 2.0 | 20.0 | 0.04 | 19.5 | 89.2 |
| 3.0 | 30.0 | 0.25 | 29.8 | 88.9 |
| 4.0 | 40.0 | 9.80 | 30.2 | 90.0 |
| 6.0 | 60.0 | 28.5 | 31.3 | 91.2 |

and flotation. Beyond the concentration of 3 kg/t, there is no increase in the amount of reagent adsorbed. Table 3 shows the amount adsorbed at different pH values at 1.5 kg/t of DTC concentration. It was found that the adsorption of DTC is equally effective in the pH range studied. The flotation

TABLE 3

Adsorption of DTC at various pH values

| pH of the pulp | Amount of DTC (mg) | | | Cu Recovery % |
|-------------------|--------------------|----------------------|----------------------------|------------------|
| | Feed solution | Filtrate solution | Adsorbed on the mineral | |
| 9.0 | 15.0 | Nil | 14.8 | 22.70 |
| 9.5 | 15.0 | Nil | 14.9 | 87.20 |
| 10.0 | 15.0 | Nil | 14.9 | 88.60 |
| 10.5 | 15.0 | Nil | 15.0 | 88.00 |
| 11.0 | 15.0 | Nil | 14.9 | 76.30 |
| 12.0 | 15.0 | Nil | 15.0 | 56.86 |

results at various pH values correlate well with this observation.

The high consumption of the reagent can be attributed to a true complex reaction where the ratio of the reagent to metal is 1:1 or 2:1. Further the material has undergone size reduction in the flotation cell because of its high friability, causing more reagent consumption. This effect can be clearly seen from Table 4 where the sieve analysis of feed, float and tailings is stated, along with surface areas of malachite (calculated).

TABLE 4
Sieve analysis of feed, float and tailings

| Sieve Mesh BSS | Feed* | | Float** | | Tailings*** | |
|----------------------|-------------------|------|-------------------|-------|-------------------|--------|
| | Wt. % retained | % Cu | Wt. % retained | % Cu | Wt. % retained | % Cu |
| +100 | 10.66 | 1.14 | 2.85 | 28.09 | 11.92 | 0.1760 |
| -100+150 | 35.98 | 1.69 | 10.15 | 36.08 | 24.55 | 0.0511 |
| -150+200 | 17.22 | 1.62 | 4.94 | 41.99 | 7.91 | 0.0568 |
| -200+240 | 22.18 | 2.62 | 6.84 | 39.59 | 10.22 | 0.0682 |
| -240+300 | 10.81 | 2.98 | 5.06 | 41.75 | 10.60 | 0.0737 |
| -300+340 | 2.08 | 3.50 | 3.19 | 33.58 | 5.90 | 0.1310 |
| -350 | 1.07 | 7.23 | 66.97 | 22.06 | 28.90 | 0.4200 |

* Surface area of malachite present in 500 gms of feed = 3327 cm²

** Surface area of malachite present in float = 4271 cm²

*** Surface area of malachite present in tailings = 271 cm²

The optimum dosages of sodium silicate and pine oil were found to be at 3.0 kg/t and 0.05 kg/t respectively. Among the various frothers tried like MIBC, Naphthenic acid and pine oil, pine oil was found to be effective. Froths collected at different impeller speeds (Table 5) showed a poorer grade of the mineral at high impeller speeds. Under conditions of high agitation

TABLE 5
Effect of impeller speed at 1.5 kg/t DTC concentration

| Impeller Speed | Cu. Grade | Cu. Recovery |
|----------------|-----------|--------------|
| 620 | 35.70 | 65.8 |
| 820 | 34.63 | 90.51 |
| 1050 | 29.89 | 73.34 |
| 1280 | 29.93 | 73.16 |
| 1460 | 24.05 | 55.92 |

in a mechanical cell, the high centrifugal forces prevailing in the agitated pulp tend to separate large floating particles from their bubbles. The

decrease in grade can be explained due to the mechanical entrapment of the gangue particles.

Adsorption mechanism

Generally it was observed that all the reagents studied have exhibited the complex formation on the surface of the mineral. The colour of the froth with the reagents tried as collectors is similar to the colour of their respective pure copper complexes. This physical observation indicates the

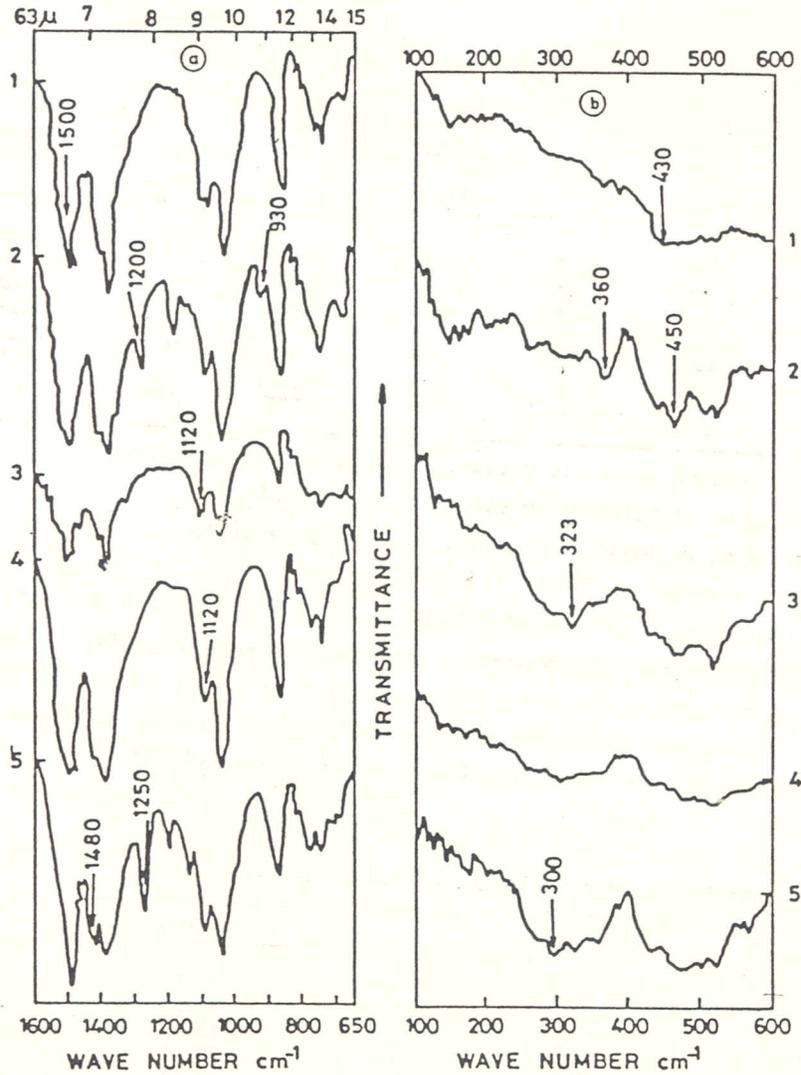
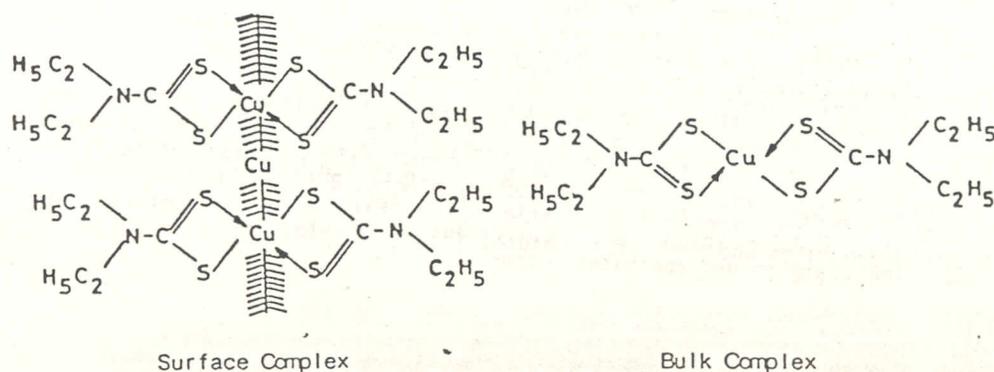


Fig. 7 Spectra of a) IR and b) Far IR : (1) Malachite concentrate (2) Float with cupferron as collector (3) Float with oxine as collector (4) Float with oxime as collector (5) Float with DTC as collector.

complex formation on the surface of the mineral.

The IR and Far IR spectra of the froths after thorough washing along with malachite concentrate are shown in Fig.7. In the spectrum of malachite (Fig.7.1) concentrate, the characteristic carbonate band at 1500 cm^{-1} (ref.2) is observed in all the spectra and the band at $400\text{-}500\text{ cm}^{-1}$ is accounted for the stretching vibrations of Cu-O in malachite (ref.14). Spectrum of the float with cupferron as collector (Fig.7.2) shows a band at 930 cm^{-1} which corresponds to the vibrations of Cu-O bond (ref.15) and the band at 450 cm^{-1} is attributed to the Metal-Nitrogen stretching mode (ref.14). The band at 1200 cm^{-1} could be assigned to C-N vibrations. The appearance of the band at 1120 cm^{-1} (ref.16) for the spectrum of float with 8-hydroxyquinoline as collector (Fig.7.3) is the characteristic peak for the metal oxinates, which is due to the diatomic vibrations of C-O group. Fig.7.4 shows the spectrum for the float with oxime as collector where no specific characteristic bands were obtained. The spectrum of the float with DTC as collector is shown in Fig.7.5. A band at 1500 cm^{-1} (ref.17) is characteristic of copper DTC complex, although it is masked by the carbonate band of malachite. The band at 300 cm^{-1} which is due to Cu-S stretching vibrations (ref.14) is a strong indication for the surface complexation besides the C-N band at 1250 cm^{-1} . The above IR analyses compared with the respective pure copper complexes of the reagents (spectra not shown in fig.) indicate the presence of the reagent on the mineral surface via a chemical reaction with copper.

The surface compound formed during the flotation with DTC (at 1.5 kg/t) was extracted with CCl_4 and subjected to spectrophotometric analysis. This spectrum is identical with the pure copper DTC complex. Further, this surface complex was stripped into an aqueous layer and analysed for copper. The quantity of copper present is exactly coinciding (total adsorbed amount of DTC, ref. Table 2) with 1:2 metal to reagent ratio, similar to that of bulk complexation. Hence the adsorption mechanism can be visualised from the following schematic diagram.



CONCLUSIONS

Among the four different chelating agents and xanthate tried as collectors, DTC was found to be effective for the flotation of copper oxides. Consumption of the reagent is also less compared to the other reagents used. The nature of collector adsorption on the mineral was found to be a surface chemical reaction. The investigation revealed that each copper atom on the surface of the mineral was complexed by 2 DTC molecules.

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