

Effects of a Thio Collector Mixture for Optimising Recovery of a Low-Grade Carbonatite Copper Ore using Senfroth 38 Frother

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A laboratory froth flotation experiment was conducted on a low-grade carbonatite copper ore sample obtained from Phalaborwa in the Limpopo province of South Africa. The sample was a homogenous hydrocyclone overflow which serves as the feed to the flotation cells at Palabora Mining Company (PMC). The sample has an average copper assay of 0.59% with predominant copper-bearing minerals being chalcopyrite, bornite and cubanite. The carbonatite nature of the ore comes from the high content of calcium (28.85%) and magnesium (6.84%) minerals. Collectors used were sodium diethyl dithiocarbamate and potassium ethyl xanthate alongside Senfroth 38 supplied by Senmin. The results showed that at 200 g/t mixture of collectors (50:50), an optimum grade of 8.03% Cu in the rougher flotation concentrate was achieved at 74% recovery, while during the second flotation, 24.65% Cu was obtained at 74.4% recovery using a Senfroth 38 dosage of 6 L/t with 100 g/t mixed (50:50) collectors. The particle size and pH value of the pulp played a significant role in that the mixed collectors performed efficiently at pH above 8.3 and at room temperature while particle sizes greater than 53 μm were well concentrated when compared with those of less than 53 μm .

INTRODUCTION

The need for copper ore concentration research is on the rise as a result of the depletion of deposits and the advent of low-grade copper ores. Although most copper ore deposits have other valuable minerals that support their economic extraction, the increase in technological innovations as regards copper usage and applications has increased the demand for copper. Several factors influence concentration results in a froth flotation column, of which the reagent used is most influential.

Collectors are chemical reagents that selectively adsorb onto the surface of particles to form a monolayer so as to induce hydrophobicity (Wills & Napier-Munn, 2006). Collectors can be chemically bonded to particle surfaces (chemisorption) or can be held on the surface by physical forces (physical adsorption) but recently, their influence on froth has been investigated (Bradshaw, 1997). Over the years, the use of xanthate and dithiol compounds individually as collectors in the flotation process has received a huge boost due to their efficiency and affordable cost. Xanthates collectors are very good for sulphide ores while thiocarbamates are very selective for other copper ores (Hangone et al., 2005). Both xanthates and dithiol are anionic collectors and, according to Albijanic et al. (2012), the functional group of the thio collector makes underpotential deposition (chemisorption) quite interesting and effective. Mixtures of collectors have been used extensively for many years, especially in sulphide mineral flotation (Lotter & Bradshaw, 2010), but the selection of collector combination and appropriate dosage has been based on experience and contextual knowledge. The advantages of using mixed

collectors have been identified to include lower dosage when compared to a single collector, which, in turn, accounts for lower cost and better performance in terms of grade and recovery of minerals (Mclvor & Finch, 1991; Bradshaw, 1997).

Other reagents which affect froth flotation include frothers, activators and depressants as well as pH modifiers. Frothers are added to the system to change the bubble characteristics and stability of the foam/froth. Commonly used frothers are pine oil, methyl isobutyl carbinol (MIBC) and polyglycols. Flotation technology is always evolving in terms of reagent usage in which new developments are made. The development of better collectors and frother matching are on the rise. The chemistry of reagents has also been studied to understand the effect and mechanism of actions between mixed collectors and addition of frothers in a flotation cell. In the field of bubble generation, attempts are made to generate more micro bubbles. Decreasing the bubble size increases the efficiency of flotation.

A low-grade copper ore is classified as an ore with less than 1% copper (Wills & Napier-Munn, 2006). Most copper ore has associated minerals which makes it economical exploitable but a carbonatite copper ore is unique in that it has high calcium and magnesium carbonates and associated minerals in large quantities alongside copper-bearing minerals and other metals. This is a feature peculiar of the Phalaborwa copper deposit in the Limpopo province of South Africa.

EXPERIMENTAL

Materials and Reagents

The copper ore samples were obtained from Palabora Mining Company (PMC). The sample is cyclone overflow which serves as the flotation feed to the industrial plant. The feed sample assay is 0.59% copper and other gangue, as shown in Table I. The copper-bearing minerals detected were chalcopyrite, cubanite and bornite. Other minerals presents are magnetite, dolomite, calcite apatite and biotite, as analysed through X-ray fluorescence and X-ray diffraction analysis. The samples were dried and a homogenous sample was obtained using a laboratory quartering splitter. After subjecting the whole sample to quartering to obtain a homogenous sample, particle size analysis was carried out to classify the sample grains and analyse their individual effects on the flotation performance, as shown in Figure 1. Collectors used for this research work were sodium diethyldithiocarbamate (Na-Di-DTC) and potassium ethylxanthate (KEX), both having a purity of about 95% and supplied by Sigma Aldrich. The frother was Senfroth 38 from Senmin. According to the data sheet prepared by Fourie (2010), it contains alcohol (85%) and a resin blend, is a flammable liquid with strong odour, with a boiling point of 133 °C, flash point of 46 °C, flammability of 1.4 to 11.2 %, density of 0.835 g/mL, is miscible with water and lower alcohols and ketones. The additions of acid may liberate heat due to the presence of ammonia. The frother is incompatible with some synthetic rubbers because swelling may occur.

Table I. Elemental assay of the copper ore sample (%).

Ca	Fe	Si	Mg	Na	P	Al	Cu	S	K	Ti
28.85	16.78	5.41	6.84	0.47	2.22	1.57	0.59	0.39	0.75	0.43
Sr	Mn	Cl	Ba	Zr	Ce	Nd	Co	Ni	V	Zn
0.42	0.15	0.23	0.09	0.06	0.04	0.03	0.02	<0.01	0.02	<0.01

Batch Flotation Procedure

A mechanical batch flotation cell (Denver D12) was used. 500 g of homogeneous sample was weighed and floated for each flotation procedure. The conditioning time was set at 5 min and a pulp density of 35.7% was maintained for each froth flotation test. The measured pH was adjusted using NaOH (for basic pH) and HCl (for acidic pH). The impeller speed was set at 1200 rpm. Senfroth 38 was added to the flotation pulp after 5 min of conditioning and 15 L/min air was introduced through diffuser

placed at the bottom of the flotation cell while the samples were concentrated. Manual scrapping was used to collect the concentrate every 30 s, after which the concentrate and the tailing were dried and weighed. The experiment was repeated for different dosages of Senfroth 38 and at different pH values. The experiment was repeated three times for each factor under consideration to establish the average value of results. Although the mass percentage of the samples and products are not presented in this paper, Cu assay was measured in the concentrate based on the associated sizes of particles.

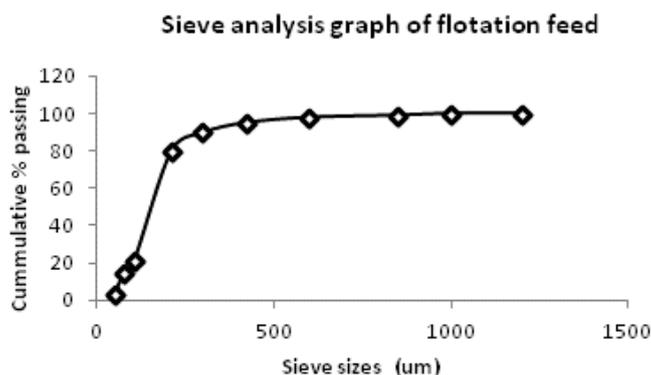


Figure 1. Sieve analysis of the homogenous sample.

RESULTS AND DISCUSSION

Effects of Collector Mixture and Dosage Optimisation

The performance of the reagents is based on the recovery and grade of copper in the concentrates. When no collector was added to the pulp, the grade was 3% Cu and recovery was 89%. This shows the natural hydrophobic properties of some of the minerals present in the ore, especially the carbonates and pyrite. Also, sulphide being an electronic conductor can act as a source for electrons and support electrode reactions at the mineral surface (Woods, 1976; Wang, 1989). Figures 2 and 3 respectively show the rougher flotation results with the use of a single collector at a time and when the two collectors were mixed together. KEX demonstrated better recovery of copper-bearing minerals, confirming the efficacy of xanthate collectors when compared with other thio collectors due to their shorter hydrocarbon chain which give higher adsorption density on sulphides (Lotter & Bradshaw, 2010; Wills & Napier-Munn, 2006). At collector dosages above 200 g/ton, a decline in Cu grade of the concentrate was observed for the two collectors individually and when they were mixed.

The decline in Cu grade as the collector concentration increases may be due to excess coating on the material surface and also entrapment of pyrite and calcite minerals which, in turn, lowers the amount of Cu present in the concentrate. Senfroth 38 was used at a 4 L/t. The laboratory temperature was 21 °C. Xanthates collectors worked efficiently alone when compared with dithiocarbamate, however, dithiocarbamate shows a higher recovery in Figure 3 as a result of its selectivity for sulphide minerals. Although the selectivity properties of dithiocarbamate have been argued by Hangone et al. (2005), the nitrogen in sodium dithiocarbamate is an electron acceptor and less electronegative than oxygen, which has a higher tendency to donate electrons, resulting in better selectivity on sulphide ores as well as other copper ores (Bhaskar & Forsling, 1991). The mixture of both collectors at a dosage of 200 g/t (50:50 ratio) gave the best concentration performance for the first rougher flotation at 8.03% Cu with a recovery of 74%. Xanthates adsorb on the sulphide mineral surface and react with metal ions to form hydrophobic metal xanthates (Somasundaran, 1993). Since oxygen is the xanthate electron donor, while the nitrogen is the dithiocarbamate electron acceptor, oxygen in the xanthate has strong electron-withdrawing effects. These characteristics of KEX make it a good copper inhibitor (Scendo, 2005).

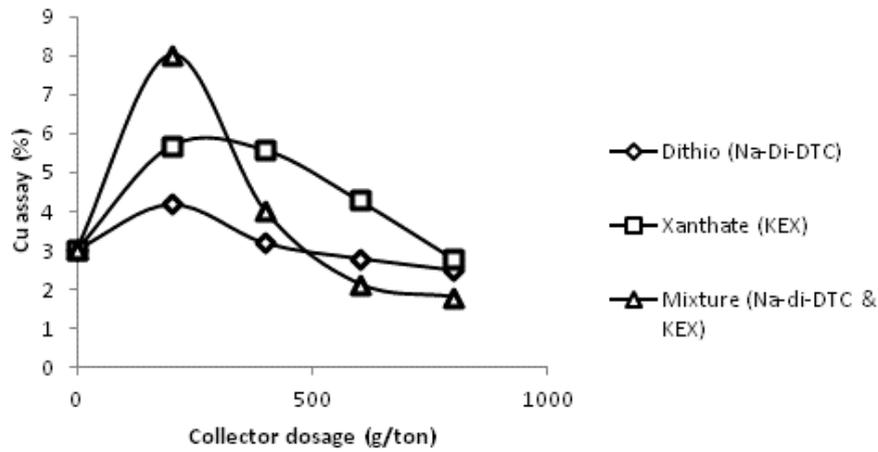


Figure 2. Cu grades in concentrate at different dosage of collectors.

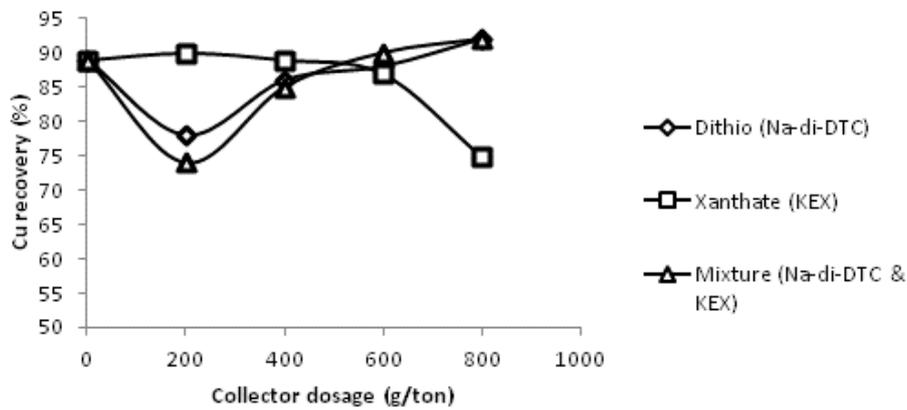


Figure 3. Cu recovery and concentrate grade at different dosage of collectors.

Effect of Particle Sizes on Recovery and Copper Concentrate Assay

According to researchers, particles sizes appropriate for froth flotation range from 20 μm to 150 μm . Particle sizes of about 53 μm to 106 μm are appropriate for sulphide ores, as seen in Table II, to avoid entrainment and entrapment of fine particles and prevent minerals from being floated because adsorbing flotation reagents cover the surfaces of the minerals.

Table II also shows the average Cu assay in the particle sizes obtained after the rougher flotation process. It was observed that more Cu minerals were recovered within the +106 μm and +53 μm apertures, which suggests that effective liberation took place within these sizes. Bigger particles break up the froth and reduce recovery while finer particles cause entrapment during flotation.

Table II. Sample particle sizes and their corresponding copper assay before and after froth flotation.

Grain sizes (μm)	Cu assay (%)	
	Before flotation	After flotation
+ 212	0.2	6.23
+106	0.45	6.87
+75	0.55	7.32
+53	0.68	8.53
-53	0.72	5.41

Effects of pH on Collector Mixtures and Concentrate Recovery

Most anionic collectors decompose in acid as shown in Equation 1. This reduces the efficiency of flotation, thus lowering recovery and Cu grade in the concentrate, as shown in Figure 4. The initial pH of the slurry before reagent addition was 8.3 (basic) and can be accounted for by the presence of calcium- and magnesium-bearing minerals which are basic in nature. After the addition of the reagents, a slight change of pH to 8.5 was observed. For the second flotation, to obtain a cleaner concentrate, a collector mixture of Na-di-DTC and KEX were added together at 100 g/t (50:50) with sodium silicate depressant (50 g/t). The calcium and magnesium contents in the concentrate reduced significantly due to the attachment of these minerals to silica, as seen in Figure 5. No activator was added and a final Cu grade of 24.72% at 74% Cu recovery was achieved.

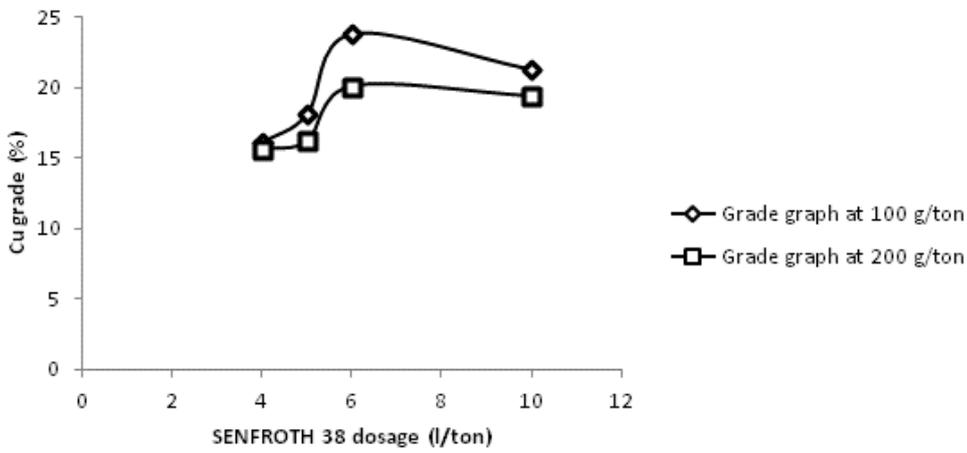


Figure 4. Effect of frother dosage on grade of Cu in concentrate.

Effects of Senfroth 38 on Grade and Recovery Optimisation

At a dosage of 4 L/t, the bubbles were observed to be small, however, as the frother dosage increased, the bubbles became bigger and more uniform, which facilitates better recovery and a good Cu grade. At dosages above 7 L/t, bigger bubbles were noticed with faint yellowish bubbles becoming irregular. This causes coalescence of particles and entrapment of gangue minerals as analysed in the concentrate mineralogy. As seen in Figures 4 to 6, an increase in dosage of both the frother and the mixed collectors increased the recovery and the grade up to a certain point, after which a decline in flotation performance was noticed.

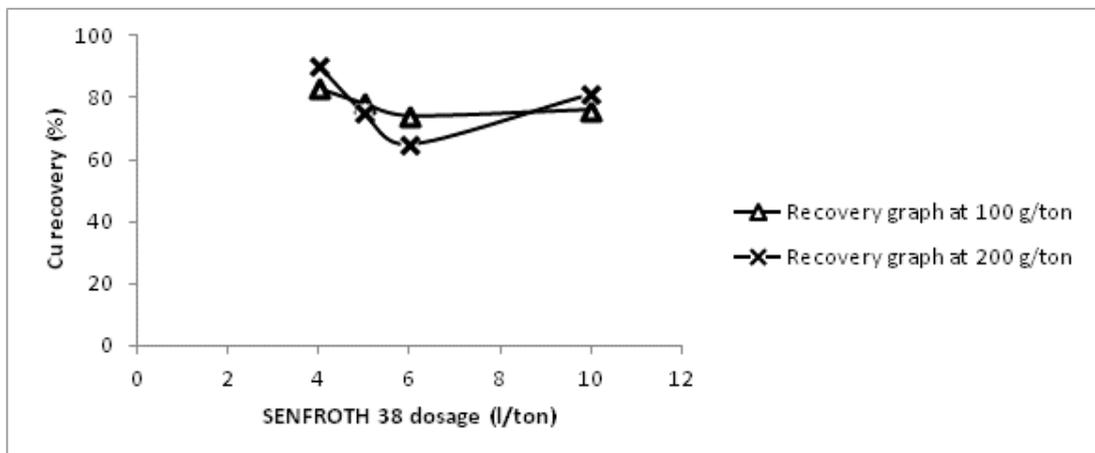


Figure 5. Effects of frother dosage on recovery of Cu in concentrate.

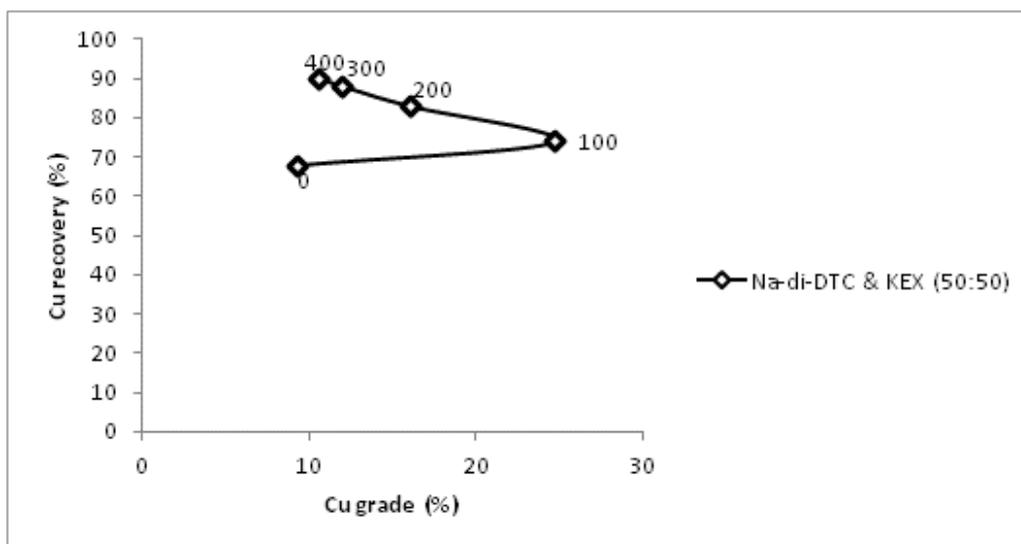


Figure 6. Cu grade vs Cu recovery for the second flotation test at various collector dosages.

CONCLUSIONS

This work analysed the effects of mixed collectors on the recovery of copper from low-grade carbonatite ore obtained from the Phalaborwa region of Limpopo, South Africa. The flotation performance was based on the optimum dosage of reagents used which presents a better recovery at a saleable copper grade. The two collectors used (potassium ethyl xanthate and sodium diethyl dithiocarbamate) were effective in upgrading the copper-bearing minerals in the ore in the presence of Senfroth 38 frother within a pH range of 8.5 to 10. The best performance was seen at a dosage of 200 g/t (50:50) during the rougher flotation, giving a Cu grade of 8.03% with a 74% recovery. The second cleaner flotation, in which a depressant was added, gave a Cu grade of 24.7% at 74.4% recovery. The experiments used a pulp density of 37.7%. The optimised recovery which has the best obtainable grade was observed at pH 9.0 and a frother dosage of 6 L/t. The Senfroth 38 frother used forms a stable and uniform froth below 8 L/t dosage. Efforts can still be made to improve the grade and recovery of this ore although particles of less than 53 μm can be effectively concentrated by flotation. Further research is still needed to explain the chemistry of frother and collector selectivity based on sulphide ore types and nature.

ACKNOWLEDGEMENT

We acknowledge the support of Tshwane University of Technology and the Palabora Mining Company Metallurgical Department crew.

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