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The effect of using sodium di-methyl-dithiocarbamate as a co-collector with xanthates in the froth flotation of pentlandite containing ore from Nkomati mine in South Africa

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Sodium ethyl and potassium amyl xanthates are commonly used in bulk and selective froth flotation of pentlandite ores respectively. Pulp pH plays a significant role in pentlandite flotation and xanthates are sensitive to pH. Consequently, more stable collectors have to be used in the froth flotation of pentlandite ores. The dithiocarbamates are possible replacement as they are believed to be stable in a wider range of pH and their use yields a faster flotation rates than xanthates. However, it may be uneconomical to use dithiocarbamates as pure collectors due to their cost. The present study explored feasibility of using di-C1-DTC to replace or partially replace PAX and SEX in nickel flotation. The tested molar ratios were 90:10 and 70:30; with xanthates as the abundant constituent in all the mixtures. This study showed that the using di-C1-DTC as co-collector was beneficial as the mixtures *30di-C1-DTC:70SEX* and *10di-C1-DTC:90PAX* improved nickel recovery and grade respectively. Furthermore, there were no significant differences in cumulative mass and water recoveries obtained with all the mixtures therefore differences in nickel recoveries were due to the differences in the selectivity properties of the collectors and not physical processes viz. physical entrapment and hydraulic entrainment.

1. Introduction

Nickel sulphide processing industry needs to be more efficient and cost effective to be sustainable as there is a growing demand for nickel, there are strict environmental constraints especially on sulphur emissions and there is a challenge posed by nickel oxide ores as primary source of nickel. Currently, nickel sulphide mineral ores amounts to more than 50% of all commercial nickel (Senior et al., 1995). There is a growing demand for nickel and it is projected that the current nickel sulphide reserves may be depleted by 2030 (Tundermann et al., 1996). Furthermore, nickel sulphide ore reserves are declining and the available ores are mostly of low nickel content. Sodium ethyl xanthate (SEX) and potassium amyl xanthate (PAX) are respectively used in bulk and selective froth flotation of nickel sulphide mineral ores. Xanthates collectors are generally strong collectors and least selective compared to the other thiol collectors. Furthermore, pulp pH plays a significant role in pentlandite flotation and xanthates are sensitive to pH. This may be problematic when grades continue to decline as the xanthates may not be able to efficiently concentrate the available complex, low grade ores (Senior et al., 1995). Consequently, more selective and more stable collectors should be used in their froth flotation. Sodium di-methyl-dithiocarbamate (di-C1-DTC) may replace the xanthates as dithiocarbamates are believed to be stable in a wider range of pH and their use yield a faster flotation rates than xanthates. Dithiocarbamates were discovered in 1850 (Lotter and Bradshaw, 2010). They have strong bonding properties with metal as they have the lone pair of electrons on both nitrogen and sulphur and consequently, they have a higher collecting power. Furthermore, they are known to form insoluble metal-thiolate agglomerates. Their maiden use as a collector however only came nine and half decades after their discovery (Lotter and Bradshaw, 2010). Dithiocarbamates never gained the popularity as they cost more than xanthates. Therefore, it may not be economically feasible to use di-C1-DTC alone due to its higher cost compared to the xanthates.

The use of pure PAX and SEX yielded higher nickel grades and recoveries respectively than the use of di-C1-DTC (Ngobeni and Hangone, in preparation). They concluded that pure di-C1-DTC may not be able to fully replace xanthates as collectors in froth flotation of pentlandite ores. In an attempt to solve these problems; mixtures of collectors has been proposed to partially replace xanthates with di-C1-DTC. The use of the mixture of collectors is not a new concept and dates back to 1958 and it has become a

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common phenomenon in froth flotation (Marabini et al., 2007). The collector constituents in the mixture may be of either same functional group or different functional groups. The use of mixtures of collectors in most cases yield higher recoveries and higher grades than the use of single collectors. These higher recoveries and grades may be attributed to either synergistic effect between the collectors in the mixture or the linear summation of constituents' characteristics (Bradshaw and O'Connor, 1994; Zhang and Somasundaran, 2006).

Xanthates adsorb to the mineral surface via charge transfer between the collector and the mineral surface while dithiocarbamates adsorb via the formation of metal-thiolate on the mineral surface. Therefore, when a xanthate and dithiocarbamate collectors are mixed, the mixtures may have improved adsorption characteristics as the mixture may encompass the adsorption characteristics of both collectors resulting in an improved mineral surface coverage (Bradshaw, 1997; Makanza et al., 2008). The literature provides enough evidence of the benefits associated with the use of collector mixtures over pure collectors (Rao and Forssberg, 1997; Sis and Chander, 2003; Vidyadhar and Rao, 2007; Filippov et al., 2010; Makanza et al., 2008; Bradshaw and O'Connor, 1994; Liu and Peng, 1999). The present study investigated effects of using di-C1-DTC as a co-collector with either PAX or SEX on nickel grades and recoveries. The following mixtures were tested in this work *90SEX:10di-C1-DTC*; *90SEX:10di-C2-DTP*; *70SEX:30-di-C1-DTC*; and *70SEX:30di-C2-DTP*.

2. Experimental

2.1. Mineralogy of the ore

Pentlandite (1.3%) was identified as the major form of nickel sulphide present in the ore. The other minerals present were:

Sulphide gangue: Pyrrhotite (10.7%), pyrite (3%), chalcopyrite (1%).

Non-sulphide gangue: Clinopyroxene (18.8%), tremolite (10.7%), chromite (9.4%), serpentine (8.8%), chlorite (6.0%).

2.2. Grinding of ore samples

Each of the 1 kg ore samples was wet milled, with 60% water by mass, in a rod-mill for 35 min to give P_{80}-75 μm. The rod mill was charged with 30 stainless steel rods of which 20 were 25 mm × 300 mm and 10 were 20 mm × 300 mm. The total charge weight was 25 kg.

2.3. Reagents

The PAX; SEX and di-C1-DTC collectors used in this work were of analytical grade. The xanthates were received as powder while di-C1-DTC was received as liquid. All collectors were dosed at 80 g/t.

Analytical grade calcium hydroxide was used to increase and maintain the pulp pH at 10.

Calcium chloride, at 80 g/t, was used as an activator of pentlandite.

The frother, SAS froth 94, was dosed at 30 g/t and was received in liquid from. It was prepared immediately before the flotation.

2.4. Flotation procedure

(1) 1 kg wet milled ore sample was poured into a 3 l batch froth flotation cell and flotation was carried out with a pulp density of 30%. The impeller speed of the flotation cell was maintained at 850 rpm.
(2) Calcium hydroxide was added to raise pH to 10 and the slurry was aerated for 5 min before further conditioning. A 20 ml feed sample was drawn using a syringe.
(3) The pulp was conditioned for 2 min with calcium chloride to activate the pentlandite mineral surface. It was then conditioned for a further 2 min by adding 80 g/t of collector or collector mixture. The collector mixtures were pre-mixed before they were added to the pulp.
(4) The frother at 30 g/t of ore was added and allowed to condition for one minute. The total conditioning time was 10 min i.e. 5, 2, 2 and 1 min for pH modifier, activator, collector and frother respectively. Air was introduced into the cell and its flow rate was maintained at 7 l/min.
(5) Five concentrates were collected with, a scrape interval of 10 s, after 1, 2, 3, 4 and 5 min respectively. This was analogous to rougher, cleaner and scavenger flotation sequences in the industrial operation.
(6) After 15 min the air was switched off and concentrates were weighed, filtered, dried and analysed.
(7) The experiments with each collector or collector mixture were repeated.

3. Results and discussion

The core output of this work is given in Table 1 below and it shows the cumulative concentrate mass; cumulative water recoveries; cumulative nickel recoveries; cumulative nickel grades obtained when using pure collectors and their mixtures thereof. The results showing the effects of using pure di-C1-DTC, PAX, SEX and mixtures *30di-C1-DTC:70PAX*; *10di-C1-DTC:90SEX* and *30di-C1-DTC:70SEX*; are discussed in this section. Rate of nickel recovery, cumulative nickel grades versus cumulative nickel recoveries and cumulative mass recoveries versus cumulative water recoveries were used to quantify these results. The cumulative mass recoveries obtained with the use of pure di-C1-DTC and its mixtures were not significantly affected hence the observed differences on cumulative nickel recoveries were attributed to the differences on the selective properties of the collectors and their mixtures and contribution of physical entrapment and hydraulic entrainment were insignificant or minimal. However, there was significant difference between the mass recovery obtained with the use of pure SEX and PAX. Mass recovery increases with water recovery. Therefore, the difference in mass water recovery could be attributed to the difference in the water recovery obtained with the use of these collectors.

3.1. The effects of pure di-C1-DTC, PAX and SEX on the rate of nickel recovery

A plot of the rate of nickel recovery versus flotation time showed that the rate of nickel recoveries decreased in the following order with the collectors used:

SEX > di-C1-DTC > PAX

The long chained collectors have slower reaction rates on mineral surfaces than their shorter chained counterparts (Wills and Napier-Munn, 2006; Lotter and Bradshaw, 2010). Therefore, the reaction between ethyl xanthate and mineral surface may have been faster than the reaction between amyl xanthate on the mineral surface. Consequently, the rate of nickel recovery obtained with the use of SEX was higher than that obtained with the use of PAX. Generally, the use of dithiocarbamates is believed yield faster flotation rate than xanthates. However, the use of di-C1-DTC yielded a slower rate of flotation than the use of SEX (Fig. 1); it is difficult to discuss the observed differences in the rate of nickel recovery due to structural differences between the xanthates and