Froth flotation of a Merensky Reef platinum bearing ore using mixtures of SIBX with a dithiophosphate and a dithiocarbamate

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abstract

The Bushveld Igneous Complex (BIC) in northern South Africa has the largest deposit of platinum group elements (PGEs) in the world. In trace amounts, these are closely associated with base metal sulphides (BMS). Froth flotation is used as a bulk sulphide recovery to beneficiate these PGE ores. To maximise the recovery of the PGEs it is required to improve the recovery of the BMS. The chemical additives used largely determines the performance of the froth flotation process. Consequently, mixtures of collectors were used in batch froth flotation tests in an attempt to improve concentrate grades and recoveries of BMS from a Merensky Reef platinum ore. The mixtures consisted of a xanthate (SIBX) with a dithiophosphate (DTP) or a dithiocarbamate (DTC). Each mixture was tested at mole ratios of 80:20 and 60:40, with the xanthate the major component. An increase in nickel recovery was observed with all mixtures relative to pure SIBX at the expense of concentrate grade. The mixtures of DTC with SIBX increased the cumulative nickel recovery by 11%, while the mixtures with DTP increased it by 10%. Copper recovery increased by 6% with the DTP mixtures. No significant improvements in the copper recoveries and grades were observed with the mixtures of SIBX with DTC compared to pure SIBX.

1. Introduction

South Africa has the largest known deposits of platinum group elements (PGEs) in the world. These are located in the Bushveld Igneous Complex (BIC) in the northern part of the country and have been commercially mined since 1925. They contribute about 73% to the world’s PGE production (Loferski, 2012; Matthey, 2014). Currently, the Merensky Reef, the Upper Group 2 (UG2) chromitite layer and the Platreef are the deposits within the complex that are mined. The PGE deposits of the Merensky Reef are strongly associated with base metal sulphide (BMS) minerals of copper, nickel and cobalt. The PGEs are present as either discrete platinum group minerals (PGM) included or attached to the sulphides, or in solid solution with the sulphides (Bulatovic, 2010; Osbahr et al., 2012; Wiese et al., 2006). The BMS minerals present in the Merensky Reef are pyrrhotite, pentlandite, chalcopyrite and traces of pyrite (Bulatovic, 2010; Osbahr et al., 2012).

Froth flotation, as a bulk sulphide recovery process, is used to separate the BMS minerals containing the PGE’s from the gangue minerals. It is required to optimise the recovery of the BMS minerals in order to maximise the recovery of the PGE’s. The flotation process largely depends on differences in hydrophobicity of the various mineral surfaces. Hydrophobic particles are separated as a froth concentrate from the hydrophilic gangue that remains in the pulp. To achieve effective separation, various operational, chemical and equipment variables require optimisation (Kawatra, 1995; Wills and Napier-Munn, 2006). Chemical variables that include collectors, frothers and modifiers are vital for effective separation as they are responsible for inducing hydrophobicity, increasing froth stability and creating favourable pulp conditions. Also, they are the easiest variables to control and optimise (Urbina, 2003; Bulatovic, 2010).

Xanthates and dithiophosphates are used to impart hydrophobicity to BMS minerals in the concentration of PGE ores. Although novel collectors may be available, patent ownership limits their application and restricts open research on their optimal use. This has motivated research into the use of mixtures of available collectors (Urbina, 2003). In the flotation of BMS, improvements in grade and recovery, rate of flotation, the flotation of coarse particles and ratios (Hangone et al., 2005; McFadzean et al., 2013; Nyambayo, 2014; Ngobeni and Hangone, 2013). Since the PGE’s are closely associated with BMS present in the Merensky Reef, similar benefits were expected with the use of collector mixtures in the froth flotation of this ore.

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This study evaluated the use of mixtures of thiol collectors in the froth flotation of a Merensky Reef PGE bearing ore. The collectors considered were: sodium isobutyl xanthate (SIBX), sodium diethyl dithiophosphate (DTP) and sodium diethyl dithiocarbamate (DTC).

2. Materials and methods

An ore from the western section of the Merensky Reef in the BIC was prepared for use in batch froth flotation tests. It had a mean copper and nickel mass percentages of 0.06% and 0.14% respectively. The sulphide mineral distribution of the ore is presented in Table 1.

The ore was split into dry, representative samples of approximately 1 kg each. A slurry of 60% solids was charged to a stainless steel laboratory rod mill containing 20 kg of rods. A grind of 60% passing 75 μm was achieved. The milled slurry was transferred to a 3 L batch froth flotation cell and water was added to produce a pulp density of approximately 35% solids. An agitation speed of 1200 rpm and an airflow rate of 7 L/min were used. The froth height was maintained at 20 mm with the addition of water during the tests. Calcium hydroxide was added to the pulp before each test to raise the pH to 10. Owing to economic consideration, it is favourable to use calcium hydroxide as opposed to the conventionally employed sodium hydroxide. Previous studies have reported a successful utilisation of calcium hydroxide to alter the pH (Ngobeni and Hangone, 2013; Muzenda et al., 2011). The dosages of calcium hydroxide required to raise the pH to 10 in this study were not significant enough to render silicates hydrophobic (Muzenda et al., 2011).

The collectors and frother were supplied by Senmin and standard solutions of the reagents were prepared prior to each test. The collectors used in batch flotation tests were sodium isobutyl xanthate (SIBX), sodium di-ethyl dithiophosphate (DTP) and sodium di-ethyl dithiocarbamate (DTC). SIBX was received as a powder while DTC and DTP were received as solutions. The total standard solutions of the reagents were prepared prior to each test. The dosage used in each of the tests was 0.3 mmol/t (equivalent to 50 g/t of SIBX as determined by dosage tests) and this was directly injected into the cell. The frother, Senfroth 200, was added to the cell at a dosage of 40 g/t. The tests were conducted in duplicate, without the addition of a depressant or an activator.

Feed and tailings samples of 25 ml were taken from beneath the surface of the pulp before and after each test. Concentrates were collected after 2, 6, 12, and 20 min after the air was allowed into the cell. The froth was manually scraped into the collection trays with a scrape interval of 15 s. Once dried, the feed, concentrates and tailing samples were analysed with an XRF spectrophotometer. Mass, water, copper and nickel recoveries, grades and rates of flotation were used to assess the performance of the collectors and their mixtures.

A summary of the results of the experiments performed is given in Table 2.

3. Results and discussion

3.1. The effects of pure SIBX, DTC and DTP on cumulative mass and water recoveries

A froth should be stable enough to allow for concentrate transfer into a launder, while still allowing for the drainage of hydrophilic particles. Without sufficient drainage, the levels of entrainment are high, resulting in low concentrate grades. Water recovery is a strong indicator of entrainment due to froth stability. To investigate these phenomena, the cumulative concentrate mass recoveries versus cumulative water recoveries for no collector, pure SIBX, DTC and DTP are presented (Fig. 1).

Xanthate and dithiocarbamate collectors have insignificant frothing properties compared to dithiophosphates, which have an alcohol as a synthesising reactant (Stamboliadis, 1976). The addition of both SIBX and DTC however increased both the mass and water recoveries compared to no collector (Fig. 1). The mass and water recoveries may have been increased due to the added hydrophobicity imparted to the sulphide mineral particles with the addition of collectors. The higher mass and water recoveries observed with DTP over pure SIBX, DTC and no collector suggest that it contributed to the formation of froth and its stability. This may be due to the excess alcohol, associated with the DTP, which promoted the stability of the froth (Stamboliadis, 1976).

3.2. The effects of pure SIBX, DTC and DTP on cumulative copper recoveries and grades

The final cumulative copper recoveries decreased in the following order; DTP > SIBX = DTC no collector, with 96%, 90%, 90%, and 88% respectively (Fig. 2). The cumulative copper grades decreased in the following order; no collector SIBX DTC > DTP, with 0.43%, 0.41%, 0.38% and 0.14% respectively.

Previous studies (Ngobeni and Hangone, 2013; Bulatovic, 2010) showed the decreasing order of collector selectivity, of which grade was an indicator, has DTC > Xanthate > DTP > no collector. However, in this study it was observed that the absence of a collector produced a final copper grade and recovery not significantly different from those obtained with DTC and SIBX (Fig. 2). This
may have been due to the natural hydrophobicity and flotability of chalcopyrite; the only copper mineral present in the ore. The low water recovery with no collector indicated that the froth was sufficiently unstable to allow for adequate drainage of the entrained hydrophilic minerals while keeping the chalcopyrite (Fig. 1). This may have contributed to a higher copper grade (Table 2). DTP collected 96% of the copper present, but at a low grade. This indicated that the copper may not only have floated by true flotation, but in addition reported to the concentrate via entrainment.

3.3. The effects of pure SIBX, DTC and DTP on cumulative nickel recoveries and grades

The majority of the PGEs in the Merensky Reef are associated with pentlandite (Bulatovic, 2010; Jones, 1999). Therefore an increase in nickel recovery is desirable. Pentlandite is not sufficiently naturally hydrophobic and the addition of collectors is required for its recovery by froth flotation.

The cumulative nickel grades obtained decreased in the order SIBX > DTC > DTP no collector, while the cumulative nickel recovery decreased in the order DTP > DTC > SIBX > no collector (Fig. 3) i.e. the addition of a collector gave significant increases in both nickel recoveries and grades except for DTP, which increased only the nickel recovery.

The frothing property of DTP, evident from the higher water and mass recoveries over that obtained with SIBX and DTC, led to the higher nickel recovery (64%) at a lower nickel grade (0.30%) (Table 2 and Fig. 3). DTC produced a recovery of 59% with a grade of 0.55% and SIBX produced a recovery of 54% with a grade of 0.58%. The increased nickel recovery with DTC compared to SIBX may have been due to its greater selectivity as the larger water recovery obtained was not accompanied by a significantly larger mass recovery than obtained with SIBX (Fig. 1).

3.4. The effects of mixtures of SIBX and DTC on cumulative mass and water recoveries

The performances of mixtures of 80:20 and 60:40 M ratios of SIBX to DTC, were compared to those of pure SIBX and DTC (Figs. 4 – 7).

The mass and water recoveries obtained with the mixtures of SIBX and DTC were not significantly different to those obtained with pure DTC. However, pure DTC and the mixtures gave higher mass and water recoveries than pure SIBX (Fig. 4).

3.5. The effects of mixtures of SIBX and DTC on cumulative copper and nickel recoveries and grades

The cumulative copper grades and recoveries obtained with no collector, SIBX and mixtures of SIBX and DTC were not significantly different (Table 2 and Fig. 5). This may have been due to the natural flotability of chalcopyrite.

However, the cumulative nickel recoveries and grades for both mixtures of SIBX and DTC were similar to those obtained with pure DTC (Table 2 and Fig. 5). The nickel recoveries obtained with the mixtures and pure DTC were significantly higher than that obtained with pure SIBX (54%). However, the grade of nickel was 0.58% with SIBX and 0.54% with the mixtures and pure DTC. This indicates that an addition of DTC to SIBX may increase the recovery of nickel. The majority of the PGE’s in Merensky ores are closely associated with pentlandite, either within the grains or at the...
Fig. 6. The Klimpel rate constants for copper and nickel recovery obtained with SIBX, DTC, SIBX 80:20 DTC and SIBX 60:40 DTC.

Fig. 7. Cumulative mass recoveries versus cumulative water recoveries obtained with SIBX, DTP, SIBX 80:20 DTP and SIBX 60:40 DTP.

Fig. 8. Cumulative copper and nickel grades versus cumulative copper and nickel recoveries obtained with SIBX, DTP, SIBX 80:20 DTP and SIBX 60:40 DTP.

pentlandite - gangue grain boundary (Jones, 1999). Therefore, nickel recovery should be maximised to improve PGE recovery. The differences in nickel recoveries obtained with SIBX and DTC and its mixtures depend on the mechanism of adsorption of the collector on the minerals. Dithiocarbamates adsorb at a higher rate thiolate complex than xanthates (Nyambayo, 2014).

3.6. The effects of mixtures of SIBX and DTC on the rates of copper and nickel recovery

The Klimpel rate constants for copper and nickel recovery with DTC and its mixtures with SIBX (4.6 – 5.6 min\(^{-1}\) for copper and 1.8 – 2.2 min\(^{-1}\) for nickel) were higher than that of pure SIBX (3.8 ± 0.03 min\(^{-1}\) for copper and 1.8 ± 0.13 min\(^{-1}\) for nickel). There pure DTC (4.6 ± 0.07 min\(^{-1}\) for copper and 1.9 ± 0.04 min\(^{-1}\) for nickel) and mixtures of DTC with SIBX (4.7 ± 0.90 min\(^{-1}\) for copper and 2.0 ± 0.2 min\(^{-1}\) for nickel). This suggests that the addition of DTC to SIBX may increase the rate of flotation, but the rate does not depend on the amount of DTC in the mixture (Fig. 6).

3.7. The effect of mixtures of SIBX and DTP on cumulative mass and water recoveries

The froth flotation performances of mixtures of 80:20 and 60:40 M ratios of SIBX to DTP were compared to those obtained with pure SIBX and DTP. SIBX has insignificant frothing properties and recoveries obtained with it are mostly due to true flotation. However, DTP has strong frothing properties as illustrated by the use of the SIBX 80:20 DTP mixture. The addition of DTP to SIBX increased the final water recovery by 30% relative to SIBX. Thus leading to added entrainment, mass recoveries and lower grades (Figs. 7 and 8). A test was conducted with pure SIBX and double frother dosage. The increased frother dosage resulted in increased water recoveries. This resulted in a subsequent increase in the mass recoveries and a decrease in the grades. Identical increased mass and water recoveries accompanied by lower grades were observed with the SIBX 80:20 DTP mixture. This indicates that the frothing properties of DTP may have been the primary contributor to metallurgical results.

3.8. The effect of mixtures of SIBX and DTP on cumulative copper and nickel recoveries and grades

The cumulative copper recovery obtained with SIBX (90%) was lower than that with DTP (96%) (Fig. 2 and Table 2). The mixtures of these collectors gave the same copper recoveries of 97% that were higher than those of the individual pure collectors. The differences in cumulative copper recoveries between pure DTP and the mixtures of DTP and SIBX were not significant (Table 2 and Fig. 8).

SIBX offered a significantly higher cumulative copper grade (0.41%) than DTP (0.14%) and the mixtures SIBX 80:20 DTP and SIBX 60:40 DTP (0.26% and 0.22%) (Table 2 and Fig. 8). SIBX obtained the highest copper grade with the lowest cumulative copper recovery, while pure DTP gave the highest copper recovery with the lowest grade. The mixtures SIBX 80:20 DTP and SIBX 60:40 DTP gave cumulative grades intermediate to those obtained with the pure collectors. As the concentration of DTP increased, the final cumulative copper grade decreased (Fig. 8). This may be attributed to the added froth stability associated with an increase in DTP concentration.
The cumulative nickel recovery obtained with pure DTP was 64%, while the recoveries obtained with SIBX 60:40 DTP and SIBX 80:20 DTP were 61% and 58% respectively (Fig. 8). These were higher than that of pure SIBX (53%). However, SIBX gave the highest nickel grade of 0.58% (Fig. 8). The increase in nickel recovery may in economic terms outweigh the decrease in grade, as nickel is closely associated with the valuable PGE’s. SIBX gave the highest cumulative grade and therefore appeared to be the more selective collector. DTP gave a higher cumulative recovery with a lower grade which may be attributed to its frothing properties (Fig. 8). Also, not all the nickel present in the ore was from pentlandite, and the entrained non-sulphide nickel may have added to the high nickel recoveries.

Similar trends in the cumulative recoveries and grades for copper and nickel were observed (Fig. 8) i.e. as the concentration of DTP increased, the final cumulative grades decreased and the final cumulative recoveries increased. Pure SIBX gave the highest cumulative grades and lowest cumulative recoveries of copper and nickel, while pure DTP gave the highest cumulative recoveries and lowest cumulative grades (Fig. 8).

DTP floated particles indiscriminately due to its strong frothing properties; it is therefore not possible to comment on its selectivity.

3.9. The effects of mixtures of SIBX and DTP on the rates of copper and nickel recovery

The Klimpel rate constants for copper recovery with SIBX and SIBX 80:20 DTP were the same (3.8 ± 0.20 min⁻¹). However, SIBX 60:40 DTP and pure DTP had significantly higher rates of 5.7 ± 1.01 and 6.3 ± 0.21 min⁻¹ respectively. This indicates that the addition of DTP to the mixture may increase the rate of copper flotation if the molar composition of DTP in the mixture is greater than 20% (Fig. 6).

The Klimpel rate constants for nickel recovery obtained were 1.8 ± 0.13, 2.3 ± 0.05, 3.3 ± 0.08 and 4.3 ± 0.50 min⁻¹ for pure SIBX, SIBX 80:20 DTP, SIBX 60:40 DTP and pure DTP respectively. The rate constants increased with increasing molar composition of DTP in the mixtures. This indicates that the rate of nickel flotation may be dependent on the amount of DTP in the mixture (Fig. 6).

4. Conclusions

Chalcopyrite, which is naturally hydrophobic, was the only copper mineral present in the ore. Consequently, most of the copper reported to the concentrate, regardless of the collector or collector mixture used. However, the addition of a collector increased the rate of copper flotation. Pure SIBX produced the highest copper grade, while pure DTP and its mixtures produced highest recovery. The addition of collectors improved nickel recovery. This is important as platinum group elements are closely associated with pentlandite. Pure SIBX produced the highest nickel grade while DTP and its mixtures produced the highest nickel recovery.

DTP and its mixtures promoted froth stability which resulted in larger recoveries of copper and nickel at a lower grade compared to pure SIBX. The mixture of SIBX 80:20 DTP increased the copper and nickel recoveries in comparison to that obtained with pure SIBX, indicating that an addition of DTP may improve recovery. The use of DTC and its mixtures improved the nickel recovery over that of pure SIBX without a significant decrease in grade. The use of mixtures of SIBX and DTC produced concentrate grades and recoveries comparable to those obtained with pure DTC. This indicates that an addition of DTC to SIBX may improve the recovery relative to that obtained with pure SIBX.