Minerals Engineering 36–38 (2012) 100–104

Contents lists available at SciVerse ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

The role of dithiophosphate as a co-collector in the flotation of a platinum group mineral ore

K.C. Corin *, J.C. Bezuidenhout, C.T. O'Connor

Centre for Minerals Research, Department of Chemical Engineering, University of Cape Town, Rondebosch 7701, South Africa

ARTICLE INFO

Article history:
Available online 26 March 2012

Keywords:
Flotation reagents
Precious metal ores
Froth flotation

ABSTRACT

In the present study the effect of adding sodium di-ethyldithiophosphate (DTP) to sodium isobutyl xanthate (SIBX) as a co-collector in the flotation of a platinum group mineral (PGM) ore was studied with a view to investigating whether there was any evidence of a synergistic beneficial effect resulting from the use of the mixture. Flotation tests were carried out using single collectors as well as various mixtures of the collectors at different but constant total molar concentrations. Size-by-size analyses of the concentrates were carried out in all cases. After deconvoluting the results of the different flotation tests there was no conclusive evidence of a synergistic effect when using mixtures. The DTP was shown to cause an increase in the recovery of fine particles (<25 μm) and this is ascribed to its effect on the behaviour of the froth phase. It was concluded that the effect of the addition of the DTP was to stabilise the froth phase and that this was a parallel reaction and not a result of any synergistic interaction between the SIBX and DTP.

1. Introduction

When two or more collectors are mixed in the flotation process and the outcome is an increase in the recovery of the valuable mineral(s) greater than the proportional contribution of each collector, the collectors are said to be acting synergistically. Bradshaw and O'Connor (2000) and Lotter and Bradshaw (2010) have reviewed the many reports where it has been suggested that such interactions are occurring. It is however often not immediately clear if it is correct to deduce a synergistic effect when mixtures of reagents are shown to result in an unexpected increase in flotation performance. For example, Mingione (1984) investigated the effect of various mixtures of the collectors di-iso-butyl dithiophosphate (DTP) and sodium iso-propyl xanthate (SIPX) on an ore that contained PGMs and reported that the optimum PGM recovery was obtained with an approximately 70% di-iso-butyl DTP/30% SIPX and attributed the improved results to a collector–collector synergistic interaction. However it is possible that sodium di-iso-butyl DTP, which is known to have frothing properties due to the presence of residual isobutyl alcohol from the synthesis process, may have changed the behaviour of the froth phase which may have been the cause of this change in recovery.

It has also been suggested that the heterogeneity of sites of different energies on the surface of a particle will result in different interactions between strong and weak sites and strong and weakly adsorbing reagents and this would give rise to a synergistic effect resulting in an overall increase in hydrophobicity (e.g. Bagci et al., 2006, Bradshaw et al., 1997, Heilbig et al., 2000). Bradshaw and O'Connor (1994) reported on the interaction between potassium n-butyl xanthate and a cyclohexyl dithiocarbamate in the flotation of pyrite at pH = 4. In the batch flotation tests sulphur recovery and grade, water recovery, rate of recovery and image analysis of the surface froth were used to evaluate the effect of the mixture on the overall flotation performance. It was shown that the use of the mixture, as compared to the pure collectors, improved the bubble loading efficiency and thermochemical measurements of the adsorption of the collectors onto the mineral indicated that the mixture of collectors may have shown a greater heat of adsorption than the individual collectors. However recently the adsorption of dithiophosphate onto chalcopyrite using a Setaram microcalorimeter was investigated and it was found that the heat of adsorption was at the limits of detection of the instrument casting some doubt on the earlier results (McFadzean and Auroux, 2011).

With respect to dithiophosphates in particular, apart from the above reports, Plaskin et al. (1960) have suggested that mixing ethyl xanthate, butyl xanthate and diethyl DTP in the flotation of galena resulted in a more even coverage of collector on the mineral surface. Wakamutsu and Numata (1979), using a mixture of butyl xanthate and butyl DTP in the flotation of galena, showed that the DTP adsorbed preferentially from the mixture but this did not affect the mass loaded onto bubbles. Adkins and Pearse (1992), in a study of the flotation of a mixed copper sulphide/oxide ore,

---

* Corresponding author.
E-mail address: Kirsten.Corin@uct.ac.za (K.C. Corin).

0892-6875/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mineng.2012.02.019

showed that a mixture of isopropyl xanthate and dicresyl DTP resulted in enhanced rates and recoveries of copper.

Another example of synergistic effects in flotation is the observation that mixtures of surfactants can cause a greater lowering of surface tension than that predicted for each component in the mixture due to a chemical interaction between the components in the mixture (Finch and Smith, 1972). It should be mentioned that there has been no evidence of any significant chemical interaction taking place between the many different mixtures of thiols studied to date.

In summary, a careful examination of the results of many such investigations questions whether there was indeed a synergistic effect arising from mixing collectors or whether the co-collector played a parallel but advantageous role leading to the ultimate improved metallurgical performance. In the present study the effect of adding sodium di-ethyldithiophosphate (DTP) to sodium isobutyl xanthate (SIBX) as a co-collector in the flotation of a PGM ore was studied with a view to investigating whether there was any evidence of a synergistic beneficial effect resulting from the use of the mixture. The di-ethyl as opposed to the di-isobutyl dithiophosphate was used to ensure that no spurious side effects of frothing would confound the results. Flotation tests were carried out using single collectors as well as various mixtures of the collectors at different but constant total molar concentrations.

2. Experimental

2.1. Ore sample

The ore used in the present study was a typical sample of Platreef ore from the Eastern limb of the Bushveld Complex of South Africa containing PGMs and having low concentrations of base metal sulphides. The mineralogy of the ore is shown in Tables 1a and b and shows the distribution of PGMs in the ore (Chapman, 2010). The base metal sulphides (BMS) contained approximately 25% chalcopyrite, 37% pentlandite and 38% pyrrhotite.

The ore was prepared for flotation by milling to 85% passing 75 μm with approximately 45% passing 25 μm. Batch flotation tests were carried out in a 3 l modified Leeds flotation cell using synthetic plant water, the composition of which has been described elsewhere (Shackleton et al., 2003). Although various xanthates and dithiophosphates were studied in the overall test programme only the results obtained using sodium iso-butyl xanthate (SIBX) and sodium di-ethyldithiophosphate (DTP) are reported here. In all cases the dosage of collector added was 4.09×10^{-4} mol/kg of ore. In a separate study it was shown that sodium di-ethyldithiophosphate had no significant frothing properties (Bezuidenhout, 2011). The frother used was Dowfroth 200 at a dosage of 40 g/t. The pH was the natural value for the ore, viz. 9. All feed, concentrate and tailings samples were assayed for Cu and Ni and the mass of solids and water recovered was measured. In certain cases, as indicated in the results section, the platinum group elements were assayed. Previous studies have shown that measuring the mass of water and solids recovered provides a significant insight into the nature and behaviour of the froth phase (Wiese et al., 2010). The particle size distributions of all concentrates were determined by screen analysis.

Table 1
Mineralogy of ore used in this study and the distribution of PGMs in the sample.

Mineral	Composition (%)	Mineral	Composition (%)
Enstatite	39.1	Diopside	15.1
Feldspar	18.4	Serpentine	6.9
Chlorite	8.2	Amphibole	3.0
Talc	0.8	Mica	0.8
Iron oxides	0.5	Other silicates	2.4
BMS	2.1	Other	2.7
	Area (%)		Mass (%)
Distribution of PGMs in ore			
Pt-sulphide	9.1	Pd-arsenide	0.0
PtPd-sulphide	3.1	Ferroplatinum	6.1
PtRh-sulphide	0.8	Pt-alloys	7.6
Pt-telluride	30.9	Pd-alloys	7.6
Pd-telluride	15.5	PGE-sulparsenides	2.4
Pt-arsenide	12.8	Gold	4.0

In order to determine the respective amounts of floatable and non-floatable gangue reporting to the concentrate by either true flotation or mechanical entrainment, a method previously described in which depressant is added in specified dosages was used (Wiese, 2009). In this procedure three basic assumptions are made: (i) the sulphide minerals in the concentrate samples have an average sulphur content of 36.45%, (ii) essentially all the naturally floatable gangue is depressed at 500 g/t depressant dosage and therefore the only gangue reporting to the concentrate at this depressant dosage is entrained gangue, and (iii) all sulphide minerals are fully liberated from the gangue. The total mass of gangue in the concentrate is thus the mass of the concentrate minus the mass of the sulphide minerals. Finally, the gradient of the curve given by the total gangue versus water recovery at a 500 g/t depressant dosage is used to determine the entrainment factor. This entrainment factor is used to calculate the mass of gangue reporting to the concentrate at 0 g/t depressant dosage and at the 100 g/t depressant dosage.

3. Results

Table 2 presents results obtained when the ore was floated using either pure SIBX or pure DTP or mixtures of these reagents as collectors in the absence of any depressant. A separate set of tests were carried out at 50, 100 and 500 g/t guar to obtain the constants used in the calculations to obtain the mass of total gangue separate from solids recovered. In the first instance it is clear that DTP resulted in a significantly greater overall recovery of both solids and water. The extra solids recovered when using DTP (29 g) is almost equivalent to the increased amount of entrained material recovered (33 g) since the recovery of naturally floatable gangue (NFG) is essentially constant.

Table 3 shows the grade and recovery results obtained when using pure SIBX and pure DTP respectively as well as the results obtained using different mixtures of these reagents. There is a significant decrease in Ni recovery when considering the 41% and 100% DTP ratios; this can be attributed to the fact that DTP alone is not a good collector for Ni. SIBX is the main Ni collector and DTP did not contribute any additional recovery – this is why you have no real difference in nickel recoveries when xanthate is present; as soon as xanthate was completely removed, total nickel recovery dropped.

Fig. 1 shows the effect of the use of DTP on the size-by-size recovery of non-sulphide minerals. It is interesting to note that DTP plays a major role in the recovery of particles in the <25 μm range. SIBX alone with frother only recovers about 10% of the total in this size range whereas the pure DTP recovers 15.5% in this size range and 18.4% in the <10 μm range. When mixed with SIBX, the respective values are 9.7% and 14.7%. The SIBX dominates until the −25 + 10 μm range but below 10 μm the DTP, even at a mole fraction of 0.24, plays a key role in recovering this size fraction. It should also be recalled that 45% of the feed is in the −25 μm size range and hence these results indicate a significant role of the DTP in the overall recovery of non-sulphide minerals. Similar results to those shown in Fig. 1 were obtained when the mass of solids recovered is plotted as a function of size class.