



Synergistic effects among dithiocarbonates (DTC), dithiophosphate (DTP) and trithiocarbonates (TTC) in the flotation of Merensky ores

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Synopsis

Traditionally, dithiocarbonates (xanthates) have been the preferred collectors for the flotation of platinum-bearing sulphides. However, collector development has led to trithiocarbonates (TTC), which have proven to be very effective bulk sulphide collectors. The interest in TTC flotation behaviour is currently focused on the interaction of these collectors with other collectors, specifically the dithiocarbonates. Batch-flotation research has shown synergism to exist among dithiocarbonate, dithiophosphate and trithiocarbonate collectors. Increased sulphide recoveries, both for the first-minute and final concentrate, were realized using mixtures of these collectors relative to the standard.

Introduction

The xanthates (dithiocarbonates) have been the workhorse of sulphide mineral flotation since their introduction in the early 1920s. Further research in collector development has led to trithiocarbonates (TTCs). Bench-scale flotation research has indicated TTCs to be very effective sulphide mineral collectors¹. They are currently used in the flotation of copper ores in the USA and Spain and gold ores in South Africa.

Essentially the difference between the two reagents is the three bivalent sulphur atoms bound to the carbon atom of the functional group of the trithiocarbonates, compared to the two bivalent atoms of the dithiocarbonates (indicated by Figure 1).

Initial research conducted by Slabberts² on Merensky ore using iso-propyl-trithiocarbonates (iC₃-TTC) indicated a 2 per cent increase in recovery relative to the xanthate-dithiophosphate mixture. The inherent disadvantage of the short chain TTCs is the unpleasant odour associated with the decompositional products, i.e. short chain mercaptans, and as a result further research was discontinued. Instead research was focused on the development of long-chain (C₁₀-C₁₂) TTC, which does not share the same unpleasant odour of its predecessor due to low associated vapour pressures.

Research carried out by Du Plessis³ and Van Rensburg⁴ indicated that the TTC collector class should be more effective at recovering auriferous pyrite, than the conventional dithiocarbonate collector under conventional and N₂TEC flotation conditions. This patented technology is based on the flotation of auriferous pyrite under an inert atmosphere (i.e. nitrogen atmosphere)³.

The interest in TTC flotation behaviour is currently focused on the interaction of these collectors with other collectors (dithiophosphate and dithiocarbonates), rather than the good bulk-sulphide flotation behaviour of the pure, and more expensive, TTCs. The enhanced flotation behaviour (grades and recoveries), also called synergism, of mixtures of collectors is no new concept to the mineral flotation industry. Bradshaw⁵ has quantitatively indicated that synergism exists between dithiocarbonates and dithiocarbamates. Increased recoveries and grades were realized using the mixture of collectors compared to pure individual species.

The mechanism by which a mixture of collector reagents enhances the flotation response is not fully known and is the subject of continuous research. Nevertheless, many South African platinum concentrators employ a mixture of xanthate and dithiophosphate for this purpose. Despite the obvious advantages associated with the combined collector suites, secondary effects such as excessive frothing can impact negatively on the flotation process.

The flotation of auriferous pyrite using a mixture of the dithiocarbonates and trithiocarbonates has proven to be very successful both on bench and plant scale. The use of this combination of flotation reagents at AngloGold's Vaal River operations has substantially increased the gold and uranium

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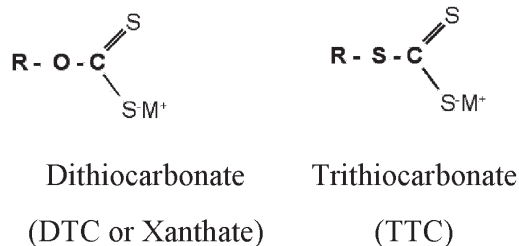


Figure 1—Collector structure of collectors investigated

recovery and the sulphur grade over a ten-month period⁶. These chemicals now form part of the permanent collector suite. The strong synergistic effect is evident from the relatively small amounts (less than 25 molar %) of TTC mixtures needed to improve the flotation behaviour (recoveries and grades)⁶.

The potential application of trithiocarbonate collectors for PGM recovery was demonstrated by a series of batch-scale flotation tests performed with pure TTCs (n-dodecyl trithiocarbonate)¹. The results indicated the more selective nature of these collectors, in pure form, compared to the standard reagent suite, by improving the grade substantially. Despite these results, no tests were performed on batch-scale to investigate whether any synergistic effect exists between dithiocarbonate and trithiocarbonate collectors, as was evident in auriferous pyrite flotation. The aim of this test work was to investigate the effectiveness of dithiocarbonate and trithiocarbonate collectors on the flotation of platinum-bearing sulphides, i.e. Merensky ore.

Experimental

A 500 kg Merensky ore sample was received as crushed material from Implats, Rustenburg. The -10 mm +3 mm fraction was subsequently crushed in a cone crusher to render a product before splitting of less than 3 mm. The bulk ore sample was split into 4 kg samples using a rotary splitter. The ore was milled in a Bond Index rod mill to establish the milling curves in order to simulate the in-plant particle size distribution, as supplied by Van Vuuren⁷ of Implats. Flotation tests were carried out in an 8-litre modified Denver cell with automatic level control to ensure a froth height of 30 mm. The ore was conditioned at 33 per cent solids (by mass) with an impeller speed of 1100 rpm at a pH of 8.4 for 3 minutes. The air flowrate was at 3 l/min and a froth build-up of 60 seconds was allowed for before the first concentrate was collected. The froth scraping interval was kept constant at 15 seconds and four concentrates were collected at intervals of 1 (0–1 min), 5 (1–6 min), 10 (6–16 min) and 14 minutes (16–30 min). The average sulphur grade of the feed was 0.24% S.

The standard Implats collector flotation suite, consisting of iso-butyl xanthate (SIBX) and dithiophosphate (DTP), 1:1 mass-ratio, was employed as the reference basis. The total reagent consumption, supplied by Van Vuuren⁷, expressed in g/ton of ore, was re-calculated as molar dosages. Different pure collectors and collector mixtures were compared to this molar dosage, which was kept constant.

It is worth mentioning at this stage, that TTC (n-dodecyl trithiocarbonate) substituted only equal moles of SIBX; the total molar amount of DTP was kept constant. Thus, for the

sake of convention, the standard basis refers to the standard Impala collector mixture, consisting of SIBX and DTP. The 7.5% n-C₁₂ TTC substitution refers to the substitution of 7.5% (mol basis) of TTC for SIBX in the standard Impala collector mixture, while keeping the molar amounts of DTP constant. The 100% TTC substitution refers, in fact, to a mixture of TTC and DTP where all the SIBX was replaced with equal molar amounts of TTC.

CuSO₄ was added first and the pulp was conditioned for 5 minutes before the introduction of the collector reagents. In the case where no TTC was used, the standard collectors were added, after CuSO₄, and the pulp conditioned for 3 minutes. But, in the case where TTC was added, the TTC was added after the CuSO₄ and conditioned for two minutes before the rest of the collectors were added. It is proposed that TTC enhances xanthate adsorption and packing, hence the addition of TTC first. Most tests were carried out in triplicate. Water balances were performed after drying the concentrates and tails at low temperatures.

TTCs used in all experiments were prepared by first reacting sodium hydroxide with the mercaptan (obtained from Phillips Mining Chemicals). Subsequently, carbon disulphide was added drop by drop over a period of 20 minutes. Fresh TTCs were prepared every 2 to 3 days and kept cool to minimize decomposition.

A single-cell Leco sulphur analyser was used to perform the sulphur analysis. The inherent drawback of a single sulphur cell is the difficulty of analysing both the tailings and concentrate samples accurately. More modern dual-cell sulphur analysers compensate for this by using different cells for the high and low grade concentrates. The single-cell analyser used was far less accurate in analysing high sulphur levels than low sulphur levels, with a typical standard deviation of 0.13% for the 29.6% standard. The tail sulphur assay, according to Bradshaw⁵, is usually the largest potential source of error due to the lower detection limits of the Leco.

The Leco sulphur analyser was calibrated daily using pyrite standards supplied by Mintek. Different standards (i.e. 29.6%, 13.5% and 0.5% S) were used according to the sulphur content of the samples to be determined. Routine checks on the standards were performed (i.e. every 7th sample) to ensure accuracy of results. Sulphur balances were determined to ensure accuracy of each test. All mass and mineral balances reported were better than 94.9%. Table 1 summarizes the maximum errors for sulphur balances performed on triplicate flotation tests. Major and trace element analysis was performed using an ARL9400XP spectrometer. The samples were first ground in a tungsten carbide grinding vessel, before being briquetted. Flotation tests done in triplicate were analysed.

Table 1

Maximum errors for the sulphur balances performed in triplicate flotation trials

% TTC	Sulphur balances (max errors)
0	3.5%
4.5	2.8%
7.5	5.1%
12.5	3.0%
25	1.0%
50	2.4%
100	0.4%

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Results and discussion

Figure 2 summarizes the performance obtained for pure TTC and the standard (0% TTC) compared to different molar substitutions of TTC. Mixtures of 7.5% and 12.5% TTC outperformed the standard as well as the 100% TTC substitution and significantly higher cumulative sulphur recoveries were realized. The error bars refer to the standard deviation of the tests performed in triplicate. The broken line represents the linear contribution of TTC for the 0 to 100% TTC mixtures (the same convention as mentioned above). The higher sulphur recovery realized compared to the linear contribution suggests synergism. The results suggest that a critical amount of TTC is necessary to achieve synergism. The detrimental effect of higher proportions of TTC (25% and 50%) on the recovery of sulphur is not clearly understood.

TTCs are renowned for their good frothing abilities and as a result a very stable froth with poor drainage properties was produced. The high froth stability was not nearly as severe for the low percentage substitutions as for the 100% substitution. The excess frothing of the TTC at high substitutions influences the mass pulls significantly, resulting in low concentrate grades. The secondary effect of frothing on the mass pulls makes it difficult to compare collector efficiencies. This effect can be minimized by controlling the mass-pull for the batch flotation cells. Nevertheless, Figure 3 compares the cumulative sulphur recovery for different TTC mixtures as a function of the cumulative mass pull expressed as percentage of the feed, while Figure 4 indicates the mass pull as a function of time. Figures 3 and 4 clearly show the effect of the froth stability on the mass pull of the 100% TTC substitution. It is further evident that the mass pulls for the 4.5%, 7.5% and 12.5% substitution compare well, while the mass pull for the standard is consistently lower.

The recovery of first-minute concentrate indicates the higher rates of flotation, implying shorter residence times

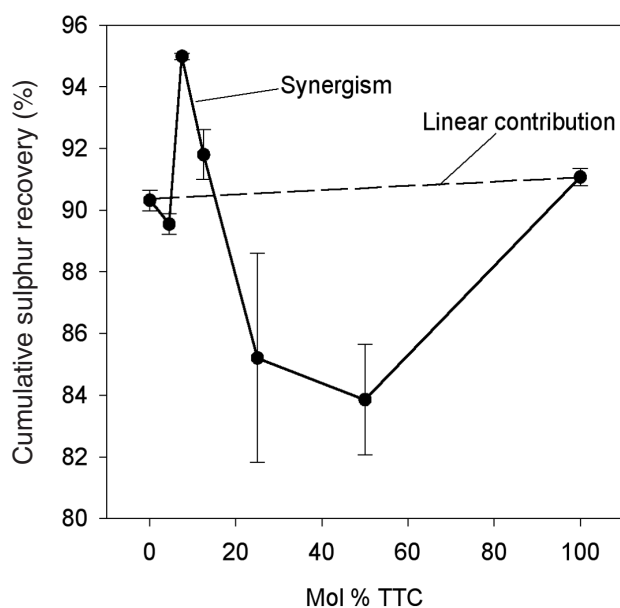


Figure 2—Sulphur-recovery relationships evaluating different mixtures of iso-butyl dithiocarbonate and n-C₁₂-trithiocarbonate and that of the pure species

and increased throughput in industrial operations. The recovery obtained for the first minute using 7.5% TTC was 66% compared to the 56.9% for the standard. This difference is reflected by the rate constants summarized in Table II for the batch flotation tests evaluated using the Klimpel model⁸ given below:

$$r = R \left\{ 1 - \left(\frac{1}{kt} \right) [1 - \exp^{-kt}] \right\} \quad [1]$$

with r = sulphur recovery at time t (%)
 R = infinite time recovery (%)
 k = rate constant (min⁻¹)

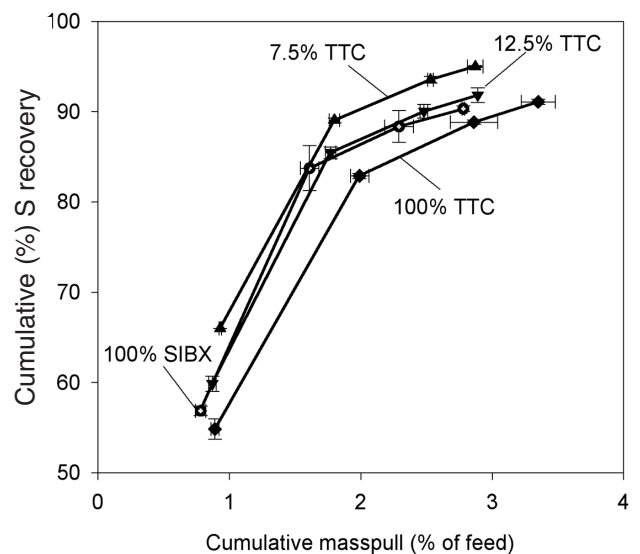


Figure 3—The influence of mass pull on the sulphur recovery of selected mixtures of iso-butyl dithiocarbonate and n-C₁₂-trithiocarbonate and that of the pure species

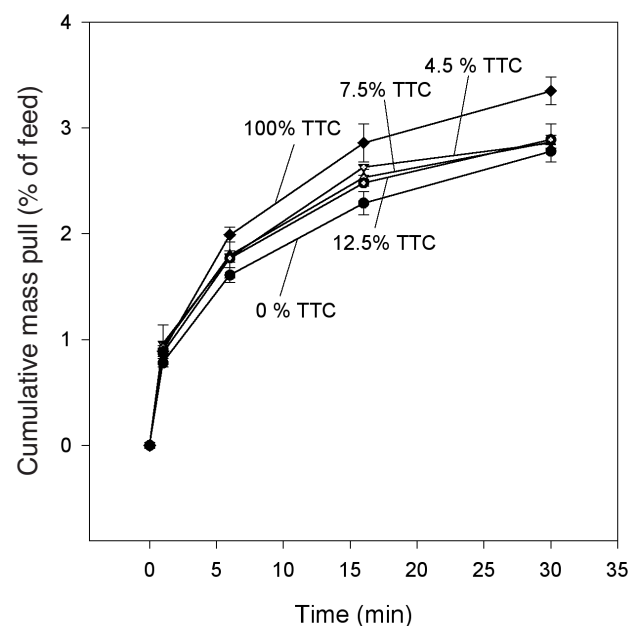


Figure 4—Mass pull as a function of time for selected mixtures of iso-butyl dithiocarbonate and n-C₁₂-trithiocarbonate and that of the pure species

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Table II

Summary of batch flotation results obtained on Merensky ore

Collector mixture	Rate constant (k) (min ⁻¹)		Ultimate recovery (%S)	
	Average	95% Confidence	Average	95% Confidence
0 % TTC	2.44	0.03	89.71	2.12
4.5% TTC	3.0	0.69	89.8	0.44
7.5% TTC	3.1	0.03	95.27	0.36
12.5% TTC	2.63	0.04	92.24	0.80
100% TTC	2.21	0.17	91.31	0.28

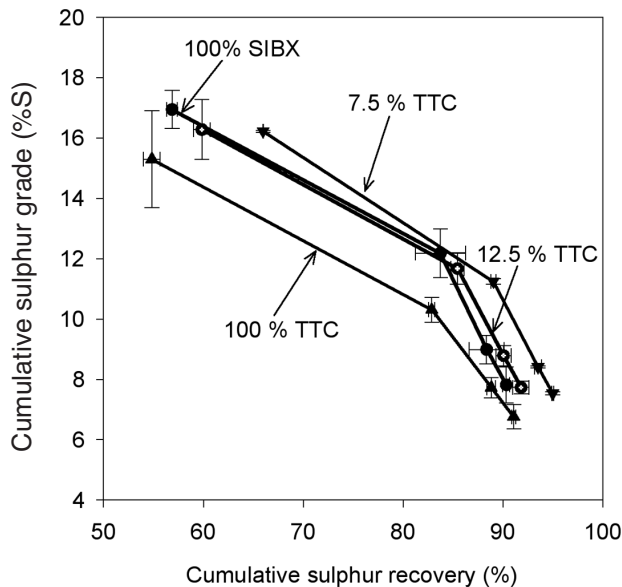


Figure 5—Grade-recovery relationships of selected mixtures of isobutyl dithiocarbonate and n-C₁₂-triisobutyl dithiocarbonate and that of the pure species

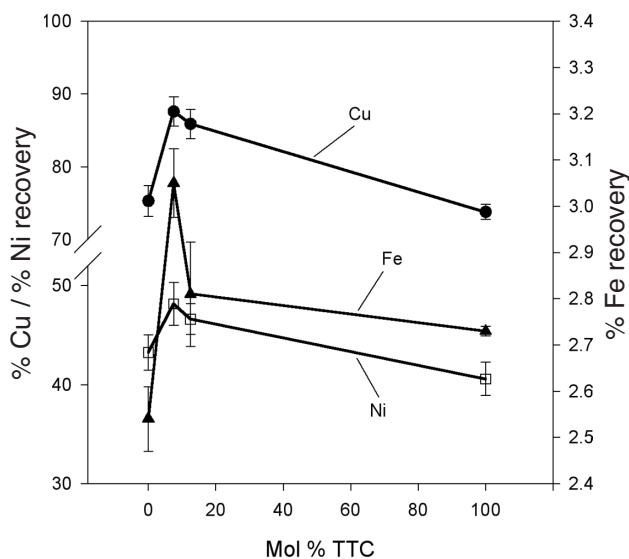


Figure 6—Recovery of selected base metals to the first concentrate

The large standard deviation of the rate constant for the 4.5% TTC substitution, given in Table II, is attributed to the grade variations encountered for the first-minute concentrates.

The higher sulphur recoveries were not at the expense of the concentrate grade as indicated by Figure 5. Figure 5 shows the standard deviations, for the tests performed in triplicate, to indicate that the difference in curves is significant. The final grade of the 12.5% substitution was 7.5% compared to the standard of 7.8%.

Although the first concentrate of the batch-flotation test is usually prone to inconsistencies, it was nevertheless decided to determine the recoveries of selected base metals to this concentrate due to the much improved results obtained with the trithiocarbonate mixtures. Figure 6 summarizes the recoveries of the base metal sulphides to the first concentrate based on chemical compositions determined by X-ray fluorescence. The error bars refer to the standard deviation of the tests performed in triplicate. The much improved recoveries of Cu and Ni are evident from these results. This indicates the strong interaction of these collectors with the Cu-bearing chalcopyrite (CuFeS₂) and Ni-bearing pentlandite (Ni,Fe)₉S₈.

An interesting aspect, which is not dealt with in this work, is the possible effect of the TTCs on the recovery of especially pyrrhotite. It is well known that pyrrhotite oxidizes readily and forms a major portion of the base metal sulphides reporting to the tailings. The interaction of the trithiocarbonate with the oxidized mineral needs to be investigated, especially looking at improving pyrrhotite recovery from the concentrator tails.

Conclusions

These results demonstrate the utility of TTC collectors for PGM-bearing sulphide recovery. Mixtures of TTC and DTC collectors achieved better overall flotation response by increasing the recovery and rate without negatively affecting the concentrate grade. Much improved recoveries of especially Cu and Ni were realized during the first minute of flotation, indicating improved flotation kinetics.

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