

# THIOCARBONATE COLLECTORS IN PYRITE FLOTATION – FUNDAMENTALS AND APPLICATIONS

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## ABSTRACT

Recent results from electrochemical measurements demonstrate that trithiocarbonate (TTC) collectors are more readily oxidized to their corresponding dithiolates than the dithiocarbonate/xanthate (DTC) collectors. Based on the traditional analysis of collector adsorption, trithiocarbonates might then be expected to be effective for bulk sulfide mineral flotation. Previous bench-scale flotation research had shown that TTC collectors are very effective for the flotation of copper sulfide minerals and PGM (platinum group metal) sulfide minerals. More recently, the TTC collectors were evaluated for auriferous pyrite recovery in bench-scale plant scale flotation testing in the United States and in plant tests at AngloGold in South Africa. TTC collectors were also applied in bench-scale testing of a PGM ore. In each case an improved separation efficiency was realized. Fundamental studies at the University of Utah examining the effect of collector structure (functional group, -O-CS<sub>2</sub> versus -S-CS<sub>2</sub>), specifically with respect to auriferous pyrite flotation, are in progress. The effect of collector structure was evaluated with air as well as nitrogen as the flotation gas medium. Experimental techniques utilized included electrochemically controlled contact angle measurements to evaluate mineral hydrophobicity and infrared spectroscopy to explain collector adsorption phenomena at the mineral surface.

Keywords: Pyrite, trithiocarbonate, xanthate, collector, nitrogen, flotation.

## INTRODUCTION

Xanthates (dithiocarbonates) have been the collector of choice for the flotation of sulfide minerals ever since the flotation process was developed and have been studied quite extensively. Although some limited research efforts on alternative sulfhydryl collectors have been undertaken, most research efforts have been focussed on xanthates. This narrow focus has hidden the potential of alternative sulfhydryl collectors, such as trithiocarbonates. Early bench-scale flotation research with trithiocarbonate collectors has shown them to be very effective in bulk sulfide flotation (Coetzer, 1987, Coetzer and Davidtz, 1989; Du Plessis and Davidtz, 1998). More recently fundamental analysis using electrochemical techniques have supported these bench-scale results, illustrating that the trithiocarbonate (TTC) collectors are more readily oxidized to their corresponding dithiolates, than the dithiocarbonate (DTC) collectors, as is shown in Figure 1 (Majima and Takeda, 1968; Winter and Woods, 1973; Du Plessis et al., 2000).

It is generally accepted that in dithiocarbonate flotation with pyrite, dixanthogen (X<sub>2</sub>) is formed at the pyrite surface by the anodic oxidation of the xanthate ion (X<sup>-</sup>); and that this reaction is coupled with the cathodic reduction of adsorbed oxygen, as is illustrated by the following reactions (Allison et al., 1972; Haug and Miller, 1978):



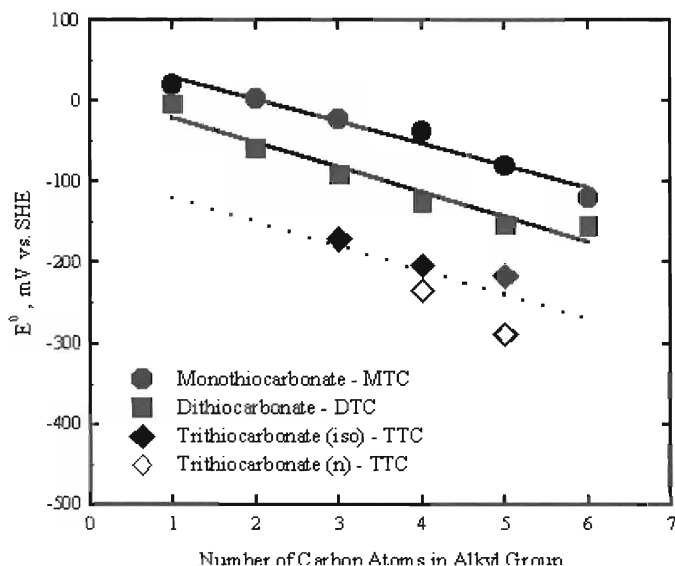


Figure 1. Standard potentials for thiocarbonate collectors, as a function of alkyl chain length (Majima and Takeda, 1968, Winter and Woods, 1973, Du Plessis et al. 2000).

Because the trithiocarbonate molecule is more easily oxidized to its corresponding dithiolate, it can be suggested that the hydrophobic pyrite surface state would be established more easily in the case of trithiocarbonate under conventional sulfide mineral flotation conditions and thus that this collector might be expected to be more effective for bulk sulfide mineral flotation.

One of the objectives of this paper was to examine the fundamental aspects of thiocarbonate flotation of pyrite, with both air and nitrogen, as revealed from electrochemically controlled contact angle measurements and from infrared surface spectroscopy. In addition the application of trithiocarbonates as collectors for various sulfide ores, are compared with dithiocarbonates, particularly with respect to the flotation of auriferous pyrite ores.

## MATERIALS AND METHODS

Electrochemically controlled contact angle measurements were carried out as described previously (Miller et al., 2002) in buffered solutions (sodium acetate (0.49 M) / acetic acid (0.01 M), pH 4.6.8 and sodium borate (0.05 M), pH 9.2).

Mid-IR spectra were recorded using a Biorad-Digilab FTS-6000 FTIR spectrometer, with a wide band MCT liquid-nitrogen cooled detector. The optical system included a high intensity ceramic source and a germanium coated KBr beam splitter. Dried air was used to purge the system, prior to spectroscopic analysis. Liquid cell transmission spectra were taken of prepared dithiolates of potassium n-amyli dithiocarbonate and trithiocarbonate. All transmission spectra were the result of 512 co-added scans ratioed against 512 co-added background scans, at a resolution of  $4\text{ cm}^{-1}$ . External reflection spectra of a polished pyrite electrode surface were obtained at a specular reflectance angle of 30 degrees from the normal with a resolution of  $8\text{ cm}^{-1}$ , after electrochemical treatment using a EG&G PAR 173 Potentiostat/Galvanostat programmed with an IBM PC-XT computer, implementing Model 250 Electrochemical Analysis System software.

Bench-scale flotation experiments, carried out at Newmont Mining Corporation's Technical facility in Denver, Colorado, were evaluated for auriferous pyrite recovery, using the  $N_2TEC$  technology conditions.

The bench-scale flotation procedure was carried out with an auriferous pyrite ore from Lone Tree, Nevada (Simmons, 1997), as described elsewhere (Du Plessis, 2002).

Platinum group metal (PGM) bench-scale flotation experiments were carried out at Impala Platinum in Rustenburg, South Africa according to standard practice at this facility.

## RESULTS AND DISCUSSION

### Flotation Chemistry in Air

Electrochemically controlled contact angle measurements at a pyrite surface, with air as the gas phase, revealed some interesting results, when dithiocarbonate and trithiocarbonate collectors were compared. At high potentials, above the potential for dithiolate formation (eqn. 1), a hydrophobic pyrite surface state could be established for both dithiocarbonate (DTC) and trithiocarbonate (TTC) collectors as can be seen in Figure 2. As expected, at lower potentials the hydrophobic pyrite surface state could not be sustained for dithiocarbonate. However, unexpectedly, the hydrophobic surface state could be sustained at low potentials in the case of the trithiocarbonate collector.

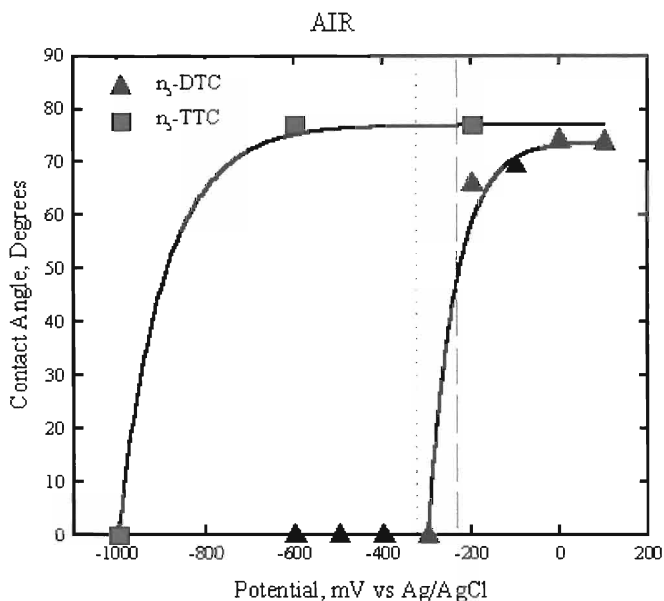


Figure 2. Electrochemically controlled contact angle measurements for pyrite in a  $1 \times 10^{-3}$  M thiocarbonate collector solution, pH 4.68, gas phase composition: air (Dashed line indicates the equilibrium half cell potential for the dithiocarbonate/dithiolate couple at  $1 \times 10^{-3}$  M  $n_3$ -DTC and the dotted line indicates the equilibrium half cell potential for the trithiocarbonate/dithiolate couple at  $1 \times 10^{-3}$  M  $n_3$ -TTC).

The hydrophobic pyrite surface state established by the trithiocarbonate collector, was established well below the potential where the formation of the trithiocarbonate dithiolate is expected to occur. This would indicate that a collector species different from the corresponding dithiolate is responsible for the hydrophobic pyrite surface state under these conditions. It is conceivable that this species may be the corresponding mercaptan.

Trithiocarbonates are known to decompose in solution, and one of the possible decomposition products is the mercaptan, as is illustrated by following reaction:

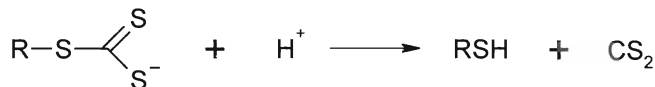


Figure 3. Decomposition reaction for trithiocarbonate collector.

Mercaptans themselves have been found to be one of the more successful non-traditional sulfide mineral collectors, although only the higher homologues have found industrial application (Lovell, 1982).

Mercaptans have been used for sulfide mineral flotation, particularly in South Africa and have been found to be very successful, for the flotation of base metal oxide minerals (Aplan and Fuerstenau, 1984; Aplan and Chander, 1988).

The formation of the dithiolates of the di- and trithiocarbonate collectors under conventional flotation conditions (in air, at higher potentials) was confirmed using external reflection Fourier Transform infrared spectroscopy. External reflection spectra of the pyrite surface, taken after treatment at 0.1 V vs. Ag/AgCl for 15 minutes, in air, and with  $1 \times 10^{-3}$  M thiocarbonate collector, is presented in Figure 4. The bands observed in both cases correspond to the bands assigned to the dithiolates of these thiocarbonate collectors (Allison et al., 1972; Wang, 1995). To illustrate that the assignment of these bands to the respective dithiolates is indeed correct, these spectra are compared with thin film transmission spectra of the synthesized dithiolates of n-amyl di- and trithiocarbonates. This confirms that it is indeed the dithiolates of the di- and trithiocarbonates that form under these more conventional pyrite flotation conditions.

The interesting finding obtained at low potentials for the trithiocarbonate collector, with air as the gas phase, is still under investigation with infrared spectroscopy and various other techniques to understand the nature of the adsorbed collector.

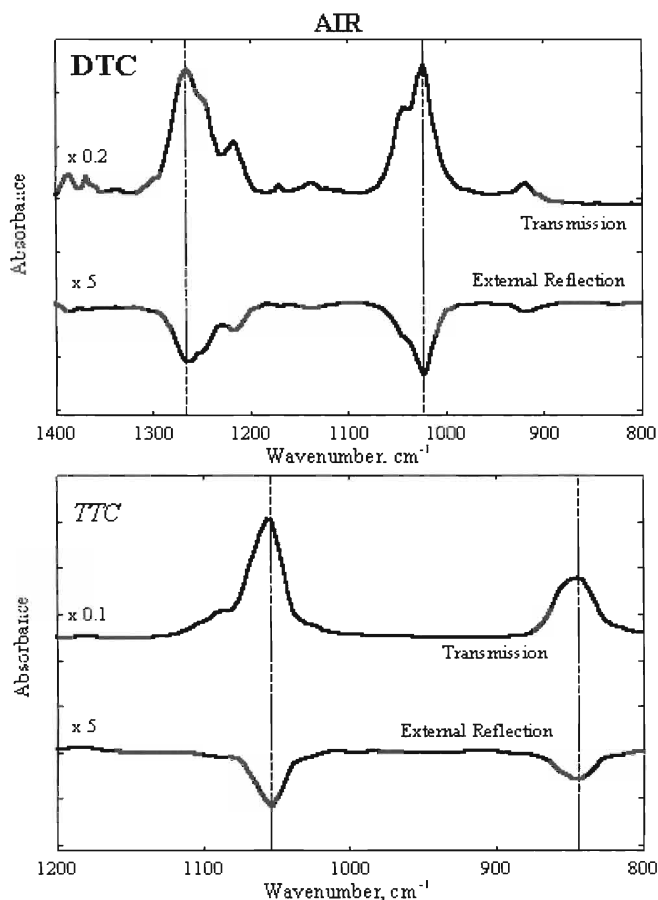


Figure 4. Comparison of the infrared spectrum of the dithiolate (transmission) and external reflection spectrum (s polarized) of a treated single crystal pyrite electrode (treated with  $1 \times 10^{-3}$  M thiocarbonate collector at pH 4.7, 0.1 V vs. Ag/AgCl for 15 minutes) for potassium n-amyl dithiocarbonate and potassium n-amyl trithiocarbonate (Du Plessis et al., 2002).

## Flotation Chemistry in Nitrogen

Although interesting results were obtained using trithiocarbonates in air, at low potentials, even more interesting results were obtained when thiocarbonate collectors were evaluated, at low potentials, with nitrogen as the gas phase. These results are part of a research program involving the investigation of the fundamental aspects of the patented N<sub>2</sub>TEC process (Gathje and Simmons, 1997; Simmons and Gathje, 1998). This process was recently implemented by Newmont Mining Corporation at the Lone Tree Mine in Nevada. Basically it was discovered that auriferous pyrite recovery from low-grade refractory gold ores is significantly improved by grinding and floating under an inert (nitrogen) atmosphere (Simmons, 1997; Simmons *et al.*, 1999). In the N<sub>2</sub>TEC process, air is replaced by nitrogen as the flotation gas and potassium amyl xanthate (PAX) is used as collector in the potential range -0.1 to -0.5 V vs. Ag/AgCl (0.122 to -0.278 V vs. SHE) (Simmons, 1997).

As is illustrated in Figure 5, using potassium n-amyl dithiocarbonate as collector, in a nitrogen atmosphere the hydrophobic surface state for pyrite could be extended to low potentials, where dixanthogen is not expected to occur. This improvement in pyrite hydrophobicity (recovery of auriferous pyrite) at low potential in nitrogen, was ascribed to a cleaner pyrite surface being available for collector adsorption, although the exact mechanism of collector adsorption under these conditions has not yet been established (Miller *et al.*, 2002).

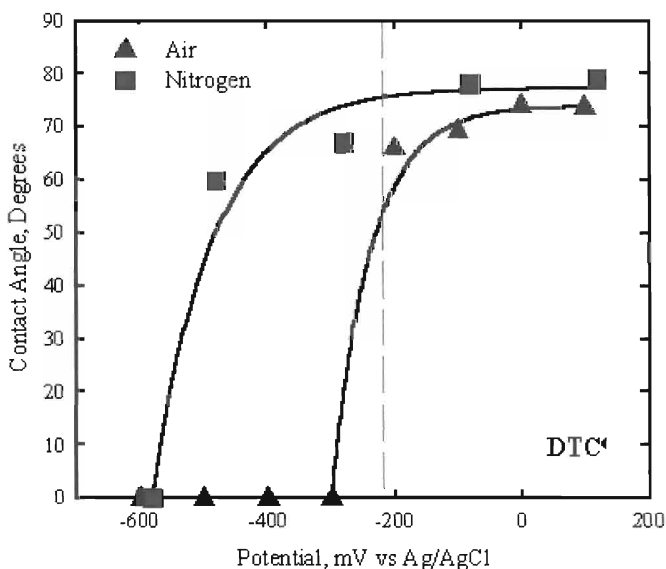


Figure 5. Electrochemically controlled contact angle measurements for pyrite in a  $1 \times 10^{-3}$  M PAX solution, pH 4.68 (Dashed line indicates the equilibrium half-cell potential for the X<sup>-</sup>/X<sub>2</sub> couple at  $1 \times 10^{-3}$  M PAX) (Miller *et al.*, 2002).

In the case of trithiocarbonate, the electrochemically controlled contact angle measurements were independent of gas phase composition; the hydrophobic pyrite surface state could be established at low potentials in both air and nitrogen.

When external reflection infrared spectroscopy experiments were undertaken to establish which species is responsible for creating the hydrophobic pyrite surface state under low potential, nitrogen conditions, the spectra were somewhat unclear. This is probably due to a very low surface coverage of collector species at the pyrite surface. Current research is focussed on optimizing the sensitivity of external reflection FTIR measurements, so that more definite conclusions can be reached regarding the collector adsorption mechanism under these conditions.

When comparing the effectiveness of trithiocarbonates collectors and dithiocarbonate collectors under nitrogen conditions, no significant difference was seen at low pH (pH 4.70). However, at higher pH (pH 9.20), a notable difference in pyrite hydrophobicity was seen, as is demonstrated in Figure 6. It is apparent

from Figure 6, that when the pH increases, a hydrophobic pyrite surface state can only be established at considerably higher potential values for the dithiocarbonate collector, whereas in the case of the trithiocarbonate collector, a hydrophobic pyrite surface state could be sustained at low potential values. This demonstrates that under nitrogen conditions, the trithiocarbonate collector should be more effective than the dithiocarbonate collector for auriferous pyrite recovery under more alkaline conditions.

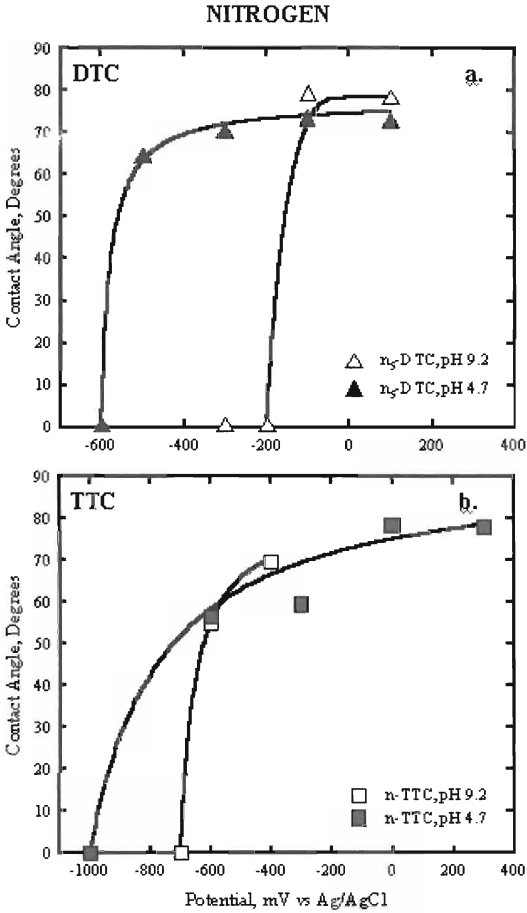


Figure 6. Electrochemically controlled contact angle measurements for potassium n-amyl dithiocarbonate and trithiocarbonate collectors as a function of applied potential for pH 4.7 and 9.2 (Gas phase composition: Nitrogen, Collector concentration:  $1 \times 10^{-3}$  M), (Du Plessis et al., 2002).

**Auriferous Pyrite Bench-Scale Flotation in Nitrogen**

The electrochemically controlled contact angle results were supported by bench-scale flotation results obtained for auriferous pyrite recovery under nitrogen conditions, at Newmont’s Technical Facility, located in Englewood, Colorado, in the United States. In Figure 7, the most significant results obtained in an extensive bench-scale flotation program for flotation feed from the Lone Tree plant (2.6 g Au/ton) are presented as grade/recovery curves at different pH values. Each curve in the figure represents the average cumulative results of two bench-scale experiments, with two concentrates, taken at 5 minutes and 10 minutes respectively and for a collector dosage of 0.15 kg/ton of the n-decyl derivatives of potassium di- and trithiocarbonate. The data points at 100 % sulfide recovery represents the feed grade.

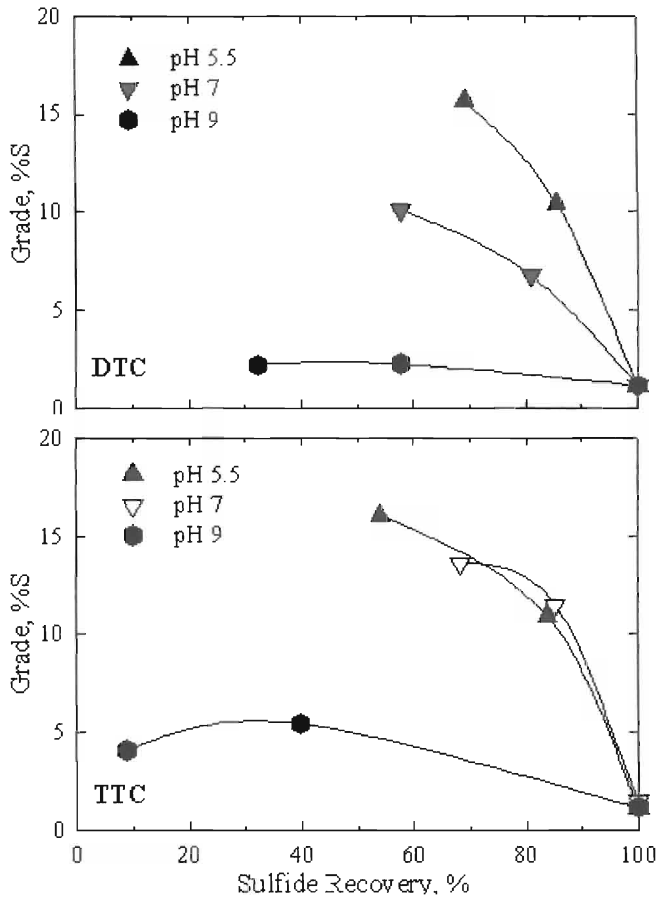


Figure 7. Comparison of grade-recovery curves for dithiocarbonate and trithiocarbonate collectors, using nitrogen as the flotation gas medium, with a potassium n-decyl thiocarbonate collector dosage of 0.15 kg/tonne at pH 5.5, 7 and 9.

At pH 5.5, as is shown in Figure 7, similar auriferous pyrite grades and recoveries were obtained using di- and trithiocarbonate collectors, using nitrogen as the flotation gas medium. For this auriferous pyrite ore, when air was used as the gas phase, again similar results were found using di- and trithiocarbonates, although these grades and recoveries were significantly lower, than those obtained under nitrogen conditions. In particular the results obtained with air, are somewhat unexpected because fundamental analysis, as discussed in the background section and revealed using electrochemically controlled contact angle measurements, indicated that trithiocarbonate collector should be more effective under these conditions, so improved grades and recoveries were expected when using trithiocarbonate collectors under conventional flotation conditions in air.

A possible explanation lies in the complexity of the bench-scale flotation process. While it is easy and convenient to control the pyrite potential when electrochemically controlled contact angle measurements are being carried out, it is much more difficult to control the pulp potential during the bench-scale flotation process. Thus, the pulp potential could vary, in which case solution chemistry conditions could arise which are not as conducive to effective pyrite flotation with trithiocarbonate collectors under conventional flotation conditions (with air as the flotation gas). Also, the solution chemistry of the bench-scale process is a lot more complicated than for fundamental analysis. For example, due to the many minerals present in the slurry during bench-scale flotation, galvanic interactions may occur. Metal ions might also be present in solution, which could lead to unintended depression or even unexpected activation.

However, auriferous pyrite recovery improved drastically using trithiocarbonate collectors under more alkaline conditions, compared to equivalent experiments carried out using the corresponding dithiocarbonate.

For the standard N<sub>2</sub>TEC technology conditions, the sulfide mineral flotation grade and recovery illustrated in Figure 7, corresponds to a gold grade of 22 g Au/ton and a recovery of approximately 70%, obtained for both di- and trithiocarbonates at pH 5.5. When the trithiocarbonate collector is used under natural pH conditions (pH 7), it is clear that similar sulfide grades and recoveries are obtained as was the case for pH 5.5, while for the dithiocarbonate collector there is a significant decrease in sulfide mineral grade, indicating a loss in selectivity. At even higher pH conditions (pH 9), the auriferous pyrite recoveries obtained using the trithiocarbonate collector, falls quite drastically, as does the auriferous pyrite grade. However, this drop in auriferous pyrite grade is not as extreme, as was the case using the dithiocarbonate collector under these alkaline conditions (pH 9). The reason for this extreme drop in auriferous pyrite grade and recovery is probably due to surface oxidation and hydrolysis of pyrite under these conditions (Chander, 1991; Miller et al., 2002). The surface hydrolysis leads to a hydrophilic pyrite surface state, on which it is conceivable that collector attachment is limited and thus this ultimately leads to a loss in auriferous pyrite recovery.

The benefits of using trithiocarbonate collectors could also be seen in the quality of the froth generated. With the trithiocarbonate collector, the froth appearance after the second concentrate was taken, was quite clean, which was not always the case with the dithiocarbonate collector. Under more alkaline conditions (pH 9), the froth generated was not as stable as at lower pH values (pH 5.5 and pH 7), and was also clearly of a substantial lower sulfide grade. The experimental results at pH 9, also varied more than those obtained for lower pH values, probably due to the more unstable froth generated. This then is the cause for the atypical result in the TTC grade recovery-curve for pH 9.

These results certainly demonstrate the possible utility of trithiocarbonate under more alkaline conditions, with nitrogen as the flotation gas medium, and suggest that the trithiocarbonate collectors should be particularly successful under these conditions. In addition to these bench-scale results, initial plant trials at AngloGold in South Africa over a period of 9 months, showed that by using dodecyl trithiocarbonate in addition to the traditional collector (sodium iso-butyl xanthate), a 37.5% increase in U<sub>3</sub>O<sub>8</sub> recovery and a 4.5% increase in gold grade could be obtained.

### **PGM Bench-Scale Flotation in Air**

For platinum group mineral (PGM) recovery by flotation in air (more conventional sulfide mineral flotation conditions), the trithiocarbonate collector proved to be effective. The results from duplicate bench-scale experiments are presented as grade-recovery curves in Figure 8. In this case, four concentrates were collected for each bench-scale flotation experiment. Again it seems that trithiocarbonates improve the separation efficiency. Although the overall PGM recovery increased only slightly with the use of the trithiocarbonate collector (94.5% compared to the standard recovery of 93%), the concentrate grade increased significantly (43 ppm compared to the standard grade of 38 ppm). This would suggest that the trithiocarbonate collector is more selective for PGM recovery than the standard collector (sodium-iso-butyl xanthate (SIBX)).

### **SUMMARY**

Fundamental analysis of thiocarbonate collectors, using electrochemically controlled contact angle measurements and infrared spectroscopy revealed that trithiocarbonate collectors could be expected to be more effective at auriferous pyrite recovery under conventional flotation conditions in air. The formation of the corresponding dithiolate, at high potentials in air, was confirmed for both di- and trithiocarbonates using external reflection FTIR spectroscopy. The beneficial effect of using nitrogen as the flotation gas medium was demonstrated for both di- and trithiocarbonates. These electrochemically controlled contact angle measurements revealed that there should be some benefit to using trithiocarbonates for auriferous pyrite flotation under more alkaline conditions.

Bench-scale flotation experiments demonstrated that improved auriferous pyrite grades could be obtained using trithiocarbonates under more alkaline conditions. Trithiocarbonate collectors were shown to improve separation efficiency for auriferous pyrite recovery as well as PGM recovery.

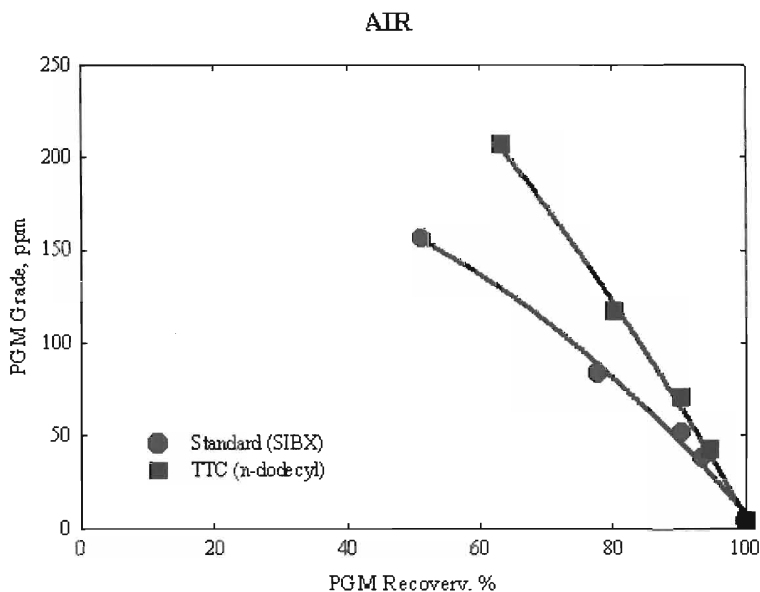


Figure 8. PGM grade-recovery curve comparing the flotation response using air as the flotation gas medium, with a collector dosage of 0.01 kg/tonne at natural pH.

## ACKNOWLEDGEMENTS

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