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Trithiocarbonates for PGM flotation

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Small replacements of C₁₂-trithiocarbonate (C₁₂-TTC) for dithiocarbonate (DTC)/dithiophosphate (DTP) in a reagent suite for the flotation of platinum group metals (PGM) have significantly improved the rejection of gangue. Coupled to this is an improvement in kinetics, grade and recovery of PGMs. In a pilot-plant trial, after a 5 mole per cent replacement of the current DTC/DTP collector combination by C₁₂-TTC, large opaque bubbles were replaced by small clear ones. In addition, a similar flotation response was realized with one-third of the current depressant dosage.

During a preliminary plant trial on underground UG2 ore, the initial rougher concentrates were characterized by higher PGM concentrate grades and this was in part due to improved chromite rejection. The concentrate produced from the TTC trial also exhibited a much finer particle size distribution. The overall circuit performance, which included secondary regrind and flotation, showed an increase in concentrate grade of approximately 44% while the tailings grade remained unchanged

Introduction

An increase in the beneficiation of UG2 ore is central to Impala Platinum's strategic plan for increasing its platinum production in 2006/07. Beneficiation of this chromite rich ore, however, poses certain problems and challenges. High recovery of valuable minerals from UG2 is accompanied by high chrome recoveries to the concentrate and this is detrimental to the downstream smelting process. This is due to spinel formation, which is an insoluble species in respect to the conditions that prevail in the smelter at Impala Platinum. Furthermore, these species are of intermediate density (between matte and slag) and form a mushy layer at the matte-slag interface (Adams, 2006).

The presence of high amounts (> 1.5%) of chromite in the smelter feed for extended periods of time will eventually lead to the build-up of high-chrome accretions in the furnace hearth, which leads to operational problems (Adams, 2006).

The associated problems with even small quantities of chromite in the smelter feed include:

- Spinel build-up in the furnace hearth, which leads to the reduction in smelter capacity and lock-up of PGMs in the furnace
- Suspended spinel in the slag will reduce the efficiency of the matte/slag separation due to an increase in slag viscosity
- High quantities of chrome also increase slag resistance, which increases slag temperatures. This will increase refractory wear and power consumption.

Merensky concentrate contains far less chromite and is used to dilute chromite fed to the smelter from the UG2 concentrator. To ensure the highest Merensky concentrate grade possible, large amounts of depressants are added to the rougher flotation banks in an attempt to reduce the mass pull to the smelter.

To further address grade and chromite content in the concentrate sent to the smelter, Impala initiated an extended reagent strategy. This involves reagent suppliers and selected tertiary institutions. The goal of this research strategy is to improve Impala's flotation reagent suite in terms of cost, metal recovery and concentrate grade. Collector optimization forms a small, but vital part of this programme.

Collector optimization

The use of co-collectors, or promoters, in mineral flotation has been well established in the minerals processing industry (Pugh, 1986; Bradshaw *et al.*, 1994; Choi *et al.*, 1993; Lui *et al.*, 1999; Monte *et al.*, 2004; Grobler *et al.*, 2005) and such uses have often resulted in reduced collector costs without affecting the metallurgical performance (Crozier and Klimpel, 1989; Leja, 1989). In bulk PGM flotation, the collectors of choice for many years have been dithiocarbonates (DTC), better known as xanthates, and dithiophosphates (DTP) (Grobler *et al.*, 2005; Wiese *et al.*, 2005a) and much research has been focused on this collector combination (Wiese *et al.*, 2005 a, b; Bulatovic, 2003; Sweet, 1999).

Helbig *et al.* (2000) concluded that the role of DTP was to enhance the adsorption of xanthate onto sulphide minerals and it has also been reported (Wiese *et al.*, 2005b) that the use of DTC/DTP mixtures increased the recovery of pyrrhotite from a Merensky Reef sample. DTP itself, however, does not show very strong collection properties when used alone (Helbig *et al.*, 2000).

Research to improve on the existing collector suite at Impala Platinum on short-chain trithiocarbonates (TTCs), with less than six carbon atoms in the hydrophobic tail, have been under investigation as early as the mid 1980s (Slabbert, 1985). Indications from laboratory flotation tests on PGM bearing Merensky Reef samples repeatedly showed TTCs, and in particular the iC₃-TTC and iC₄-TTC,

to be more effective collectors than the current DTC/DTP mixture (Slabbert, 1985; Steyn, 1996). The high volatility of these short-chain TTC decomposition products (mercaptans), however, produces a very unpleasant odour and this restricted their use on full-scale plant trials. Further test work was thus placed on hold.

In spite of the odour problem, the introduction of short-chain TTCs into the thiocarbonate collector series has been very informative from a fundamental point of view. The added collector molecule to the carbonate series allowed for a better understanding of molecular structural effects on flotation. For example, the use of thermodynamic principals for liquid-liquid equilibrium made it possible to calculate and compare the surface activity coefficients of adsorbed collector molecules and water (Steyn, 1996; Davidtz, 1999). It was possible to quantify and explain the increased hydrophobic state that results from the third sulphur atom in TTCs.

Experimental results supported by theory revealed a direct relationship between the calculated Gibbs excess free energy (G^{ex}) and flotation activity (rate of recovery) (Steyn, 1996). The G^{ex} calculations for the interaction of collector and water at the interface where water and collector mix were based on the UNIFAC group contribution method (Sandler, 1997). Activity coefficients of water and collector molecules at the interface of interaction were calculated for this collector/water binary system. It was concluded that when all three sulphur atoms in TTCs bond to the mineral surface, an increased hydrophobicity resulted when compared to xanthates where the oxygen does not bond to the surface. Instead the more polar oxygen directly interacts with water, and reduces surface hydrophobicity (Steyn, 1996; Davidtz, 1999).

In early work by Steyn (1996) on the effect of nitrogen flotation gas on Merensky Reef samples, it was found that pyrrhotite, chalcopyrite and pentlandite in the flotation tails were significantly lower with iC_3 -TTC than with a DTC/DTP mixture.

An extensive study on the flotation chemistry of thiocarbonate collectors on auriferous pyrite by Du Plessis (2003) highlighted some very distinct differences between the traditional xanthate collectors and trithiocarbonates. Her work illustrated the importance of collector functional group as well as the importance of collector hydrocarbon chain length in a systematic manner. One of the significant findings was that it appeared qualitatively, that at the same collector concentration, the TTC was able to produce a higher adsorption density on pyrite compared to DTC. Although the dithiolate of the TTC would form under conventional flotation conditions, it appeared that the formation of the dithiolate was not the lone factor in the TTC's ability to render the mineral hydrophobic. An adsorbed mercaptide was proposed.

With this continued research at the University of Pretoria and the University of Utah further contributions to the

development of long-chain TTC (C_{12}) collectors have been made. This molecule is completely water soluble and kinetically very active. It also addresses the odour problem associated with short-chain TTC decomposition. This new insight into the chemistry of TTC collectors, along with the developments on C_{12} -TTC, renewed interest from Impala Platinum. This all led the way to an intensive research and development programme to quantify and apply C_{12} -TTC as a ternary collector along with the traditional DTC-DTP mixture at Impala Platinum.

The experimental format has been:

- Laboratory flotation work by Vos (2004) where it was shown that when small amounts of C_{12} -TTC were added to DTC-DTP mixtures during milling, an improvement in PGM recovery and final concentrate grade was obtained
- Pilot plant trials on Merensky ore and
- Preliminary plant trials on UG2 underground ore.

This paper deals with studies that included a pilot plant trial on Merensky ore and a preliminary plant trial on UG2 underground ore.

Methodologies

Pilot plant investigation

Because the Merensky flotation section is running on a high depressant dosage, the pilot-plant trial was designed to evaluate C_{12} -TTC (at low depressant dosages only) against the standard collector suite running at both high and low depressant dosages.

The pilot-plant testing was done with a floatability characterization test rig (FCTR) at the Impala Platinum Merensky plant site. This pilot plant consists of 6 x 150ℓ rougher cells in series and is fed from the cyclone overflow from one of the Merensky mills by diverting the whole overflow to a 4-m³ feed tank, from where it is pumped to the pilot plant.

To ensure high statistical confidence, sufficient data for the TTC trial was collected by running continuously for two weeks. On a 24-hour basis, feed, concentrate, and tailings samples were collected. The TTC was dosed along with DTC and DTP at the mill feed hopper, while the remainder of the chemicals were added at the pilot-plant conditioning tank.

Preliminary plant trial

Section 20/21 of Impala's MF2 plant concentrator treats UG-2 underground material in a traditional primary-secondary milling and flotation configuration.

TTC was dosed to the mill feed with no changes made to the rest of the reagents. The DTC-DTP mixture was fed at the conditioning tank with the activator at the surge tank and the depressant and frother at the head of the float bank.

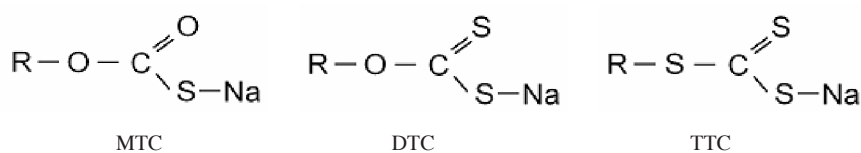


Figure 1. Molecular structure of the family of thiocarbonate collectors

Results and discussion

Pilot-plant investigation on Merensky ore

Over the trial period a total of twenty-four data-sets were collected and the average head grade assays for the three trials are reported in Figure 2.

No significant difference was observed in the head grades for all three trial runs. This allows for further metallurgical comparisons.

Effect on froth phase

The presence of stable froth phases is very problematic during froth flotation. Gangue minerals such as talc with non-polar or hydrophobic basal planes and polar edges influence froth properties. The polar edges that interact with the water phase and aggregates of these gangue particles increase the interlamellar viscosity. The result is poor interlamellar drainage and increased bubble stability which increases mass recovery and ultimately, poorer grade or selectivity.

Fast floating gangue such as talc and chlorite competes with valuable minerals for bubble space. This effect has a detrimental effect on flotation kinetics and concentrate grades. Gangue depressants on the Merensky floats have been used since the start (~1969) but since then, many changes have been made in depressant type and dosage rate.

One way of reducing the amount of floatable gangue that reports to the concentrate is to increase the amount of depressant, and Impala has implemented this since 2004. The result has been an increase in concentrate grade and valuable mineral recovery. Apart from the improved metallurgical performance, the addition of high quantities of depressant also had an effect on the froth phase. Previously, where the froth phase was typically characterized as having fairly large and stable bubbles, high depressant addition produced smaller bubbles and a highly mineralized froth.

Figure 3 is an image of the froth phase taken from the first rougher cell during the three pilot-plant tests.

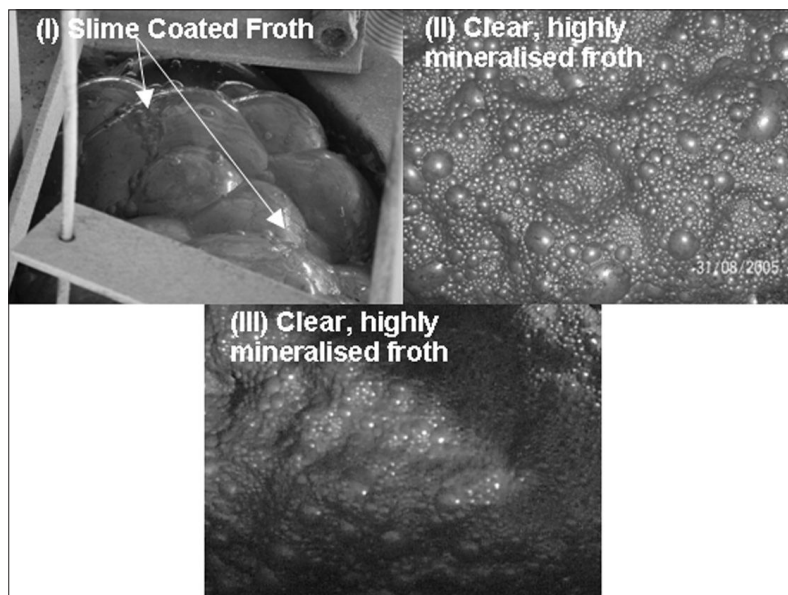


Figure 3. Very stable froth phase from low depressant dosages with DTC-DTP (I), a reduction in froth phase bubble size with the addition of TTC at low depressant dosages (II) and high amounts of depressant with DTC-DTP (III)

From Figure 3 it can be seen that the addition of TTC has a similar effect on the froth phase when compared to DTC-DTP with high depressant dosages. The reduction in froth phase bubble size and stability resulted in lower gangue mineral recovery, as can be seen from Table I.

Although the addition of TTC did not produce as high an initial concentrate grade as with high depressant dosages, the increase of approximately 46% (Table I) is very significant if it is kept in mind that only a very small amount of TTC was required for this and at only a fraction of the current depressant dosage. No significant difference in initial recovery was observed.

Overall performance

A summary of the metallurgical performances for the three tests is given in Table II.

For both the high-depressant dosage and the addition of TTC, there was an improvement in both grade and recovery compared to the low-depressant test. The high-depressant tests did yield the lowest mass pull, which resulted in the highest concentrate grade.

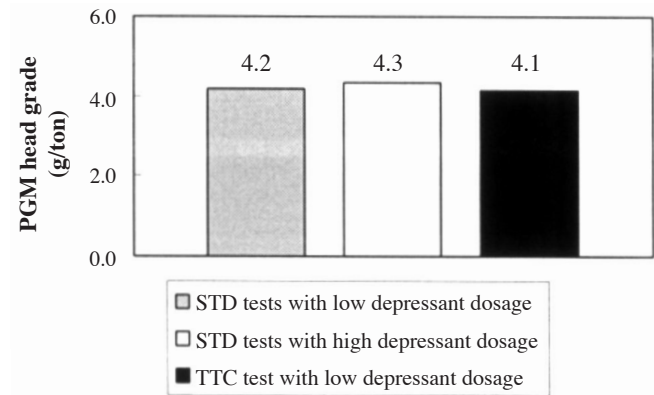


Figure 2. Normalized average head-grade comparisons for pilot-plant trial

No difference was detected between the recoveries and final tailings grade for the high-depressant tests and the TTC tests.

Table I
Concentrate grade comparison from first rougher cell

Collector combination	Concentrate grade (g/ton PGM)	Relative increase (%)
Xanthate/DTP (100 g/ton depressant)	~120	--
Xanthate/DTP (350 g/ton depressant)	~200	~ 67%
Xanthate/DTP/TTC (100 g/ton depressant)	~175	~ 46%

Table II
Overall performance comparison for pilot-plant testing—normalized values

	Tails grade	Rougher concentrate grade	Mass recovery	PGM recovery
	(g/ton)	(g/ton)	(%)	(%)
Standard with low depressant	0.50	60.0	6.2	88.8
Standard with high depressant	0.44	89.6	4.4	90.2
Addition of TTC with low depressant	0.42	77.1	4.8	90.3

Table III
Feed grade (g/ton PGM) and size gradings from shift results

	Cumulative % Retained in Size Fraction				Feed (g/ton)
	+300 μ m	+150 μ m	+75 μ m	-75 μ m	
Standard reagent suite	8.8	32.9	56.4	43.6	4.2
Addition of TTC	9.9	33.0	56.5	43.5	4.1
Absolute difference	1.1	0.1	0.1	-0.1	-0.1
Confidence in difference	85.3%	53.7%	52.8%	52.8%	70.6%

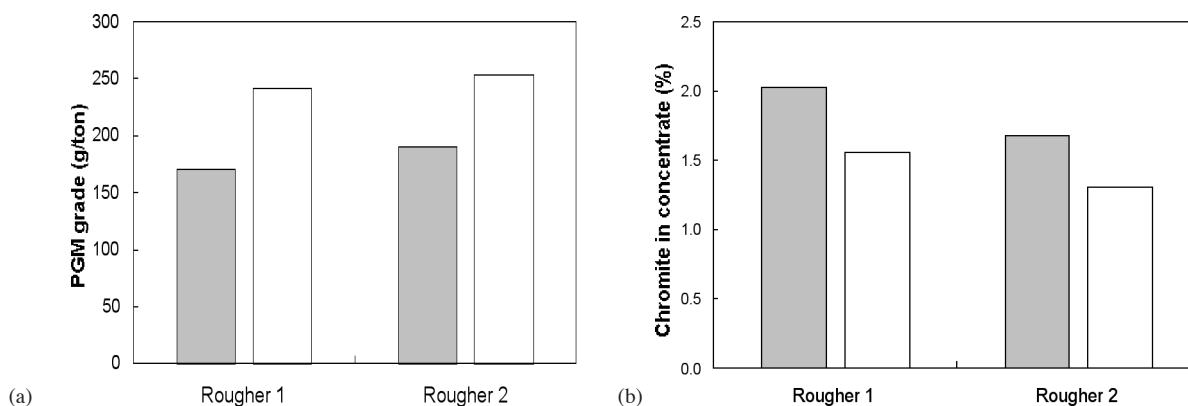


Figure 4. The effect of TTC on initial PGM (a) and chromite (b) grades in the concentrate. The white bars indicate the tests containing TTC. Normalized data

Preliminary plant trial on UG-2 ore

Table III shows the float feed PGM grade and size gradings from the shifts used in this evaluation. It is seen that there was no significant difference between the two test conditions with regard to these parameters.

Approximately one week prior to starting the TTC trial a step change in the PGM feed grade was observed. However, from the time the trial was initiated until completion no further changes in PGM feed grade were detected.

This allows for valid comparisons of metallurgical performances between the two sets of data.

Initial concentrate grade

Figures 4a and 4b indicate the change in PGM and chromite grades (normalized data) for the first two primary rougher concentrates, respectively, when the TTC was introduced.

Similar to the pilot-plant trial on the underground Merensky ore, the concentrates from the first two primary roughers were significantly higher in PGM grade after TTC was introduced. This was in part due to a reduction in the amount of chromite recovered to both concentrates.

The reduction in chromite content in the concentrate is very important for optimization during the beneficiation of UG2-type ores. Not only does the reduction in chromite reduce the mass of concentrate sent to the smelter but it also improves the smelting process. Chromite is known to form spinels during smelting, which have very high melting points. As a consequence the furnace temperature has to be increased to compensate. This again has a detrimental effect on the furnaces due to higher refractory wear and increase in power consumption.

Table IV is a summary of the results from the particle size analyses done on the two concentrates with and without TTC in plant testing at MF2.

Table IV
Results of particle size analyses on rougher concentrates

Screen aperture (µm)	% Retained on screen			
	Cell 1		Cell 2	
	Standard	TTC	Standard	TTC
300	0.37	0.28	2.51	1.03
212	0.52	0.24	1.25	0.57
150	0.85	0.28	1.50	0.55
106	1.75	0.34	2.25	0.67
75	3.52	0.63	3.61	1.31
53	5.98	2.50	5.30	2.87
38	8.28	6.15	6.86	5.37
10	43.43	49.95	38.03	44.82
Sub 10	35.30	39.63	38.69	42.80

It is seen that, from 53 µm upwards, the concentrate samples from the TTC trial had less material in the corresponding size fractions. It would appear that in this initial stage of rougher flotation a large portion of composite particles was rejected when the TTC was used.

Table V shows that for the +53 µm fraction a significant improvement was achieved in both chromite and siliceous gangue rejection when the TTC was introduced. This resulted in a substantial improvement in PGM concentrate grade.

For the -53 µm fraction the concentrates from the TTC trial had equal or higher chromite and siliceous gangue content than the samples from the standard trial. The PGM grade was still higher although not by the same margin as the +53 µm fraction.

Overall performance

Analysis of the first two concentrates from the primary roughers indicates that a reduction in chromite recovery can be achieved if the TTC is used in combination with the current DTC-DTP mixture. This effect is more prominent for coarser size fractions.

A summary of the two-week plant trial is given in Table VI. Unlike the individual concentrate samples taken from the primary roughers, no difference was seen in the

overall (primary and secondary float section as a whole) chromite content to the concentrates. The PGM recovery also remained similar.

What was realized, however, was an overall reduction in solids' recovery and hence an improvement in final PGM concentrate grade.

Summary and conclusions

Previous flotation research involving the long-chain trithiocarbonate has shown that a significant improvement in PGM flotation kinetics and initial concentrate grade can be achieved. This was by adding approximately 10 g/ton of the trithiocarbonate as a spike just before flotation. Despite this, the overall effect was similar to the traditional xanthate-DTP collector combination. By adding the new collector along with the current xanthate-DTP mixture to the mill, an improved method for trithiocarbonate has been developed with potentially significant economic benefits.

For both Merensky and UG2 underground ores the addition of small amounts of TTC has led to an improvement in the PGM flotation process. Investigation of the concentrate samples from the first rougher cells for both the pilot-plant trial and full-scale plant trial has shown a significant improvement in selectivity.

On Merensky ore it was established that an improvement in gangue rejection can be achieved with the addition of TTC and that this improvement is realized at only a fraction of the current depressant dosage. Simplistic cost calculations, which include the reduction in depressant usage and the added cost from including the TTC as a ternary collector, indicate that a substantial saving of approximately 10 million rand per annum is possible, even if no recovery benefit is taken into account.

During concentration of PGMs from high chromite UG2 ores the increase in PGM grade in the concentrate is almost always coupled with a reduction in chromite recovery. This is due to the high amount of chromite (25%–35%) in the feed, compared to only 2% for Merensky ores. The data presented in Tables IV and V, however, suggest that the increase in concentrate grade is not solely due to improved chromite rejection but it is thought that this improvement is from improved rejection of siliceous gangue as well.

Table V
Summary of the normalized assay values obtained for the concentrate samples for the +53 µm and -53 µm size fractions respectively

	Rougher 1			Rougher 2		
	PGM (g/ton)	Cr ₂ O ₃ (%)	SiO ₂ (%)	PGM (g/ton)	Cr ₂ O ₃ (%)	SiO ₂ (%)
Standard +53 µm	150	1.0	40.0	160	2.50	50.0
With TTC +53 µm	394	0.9	35.8	294	0.73	37.3
Standard -53 µm	152	1.2	40.2	175	1.79	50.6
With TTC -53 µm	218	1.2	48.6	188	2.12	49.8

Table VI
Overall comparison between TTC and conventional collector suite in plant testing at MF2—normalized values

	Head grade (g/ton)	Conc grade (g/ton)	Tails grade (g/ton)	Recovery (%)	Cr ₂ O ₃ in conc (%)	Mass pull (%)
Standard	4.2	90	1.00	77.0	2.04	3.6
With TTC	4.1	129	0.94	77.6	2.23	2.5
Difference	-0.1	39	-0.06	0.6	0.2	
% Confidence	78.0	97.7	72.5	78.6	64.8	

The improvement in chromite rejection from UG2 concentrates could have great potential benefits for downstream smelting. Furthermore, Impala's primary grind on UG2 ore is very coarse to minimize chromite recovery in the primary rougher and scavenger cells. By improving chromite rejection during rougher flotation with the addition of TTC, the option of improving liberation from the primary mills now becomes possible and a viable option for further evaluation.

For UG2, if the PGM grade in the first concentrate increases and the chrome grade decreases then there could be a case for taking this concentrate to final concentrate, if not already the case.

The way forward

A comprehensive investigation of the effect of long-chain trithiocarbonates on the flotation of Merensky ore has been undertaken since 2004 and the next step in the application of the long-chain trithiocarbonate on Merensky ore will be to continue to a full-scale plant trial.

The effect of the trithiocarbonate on the froth phase (as can be seen from Figures 3 I-III) is believed to be in part due to a change in the collector-frother interaction. This is another part of the optimization programme that will be addressed in an attempt to optimize the reagent suite.

For UG2 ores no formal investigation has been undertaken to date but the preliminary plant trial data suggests that a positive contribution can be made here as well. A similar approach will be followed as was used for the Merensky ore investigations. A series of laboratory batch flotation tests will be undertaken to determine the optimum trithiocarbonate dosage, followed by pilot plant verification and finally a plant trial.

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References

ADAMS, D. Metallurgical Engineer, Impala Platinum, Smelter Technical Department, Private Communications, 2006.

BRADSHAW, D.J. and O'CONNOR, C.T. The flotation of pyrite using mixtures of dithiocarbamates and other thiol collectors, *Minerals Engineering*, May–Jun, vol. 7, nos. 5–6, 1994. pp. 681–690.

BULATOVIC, S. Evaluation of alternative reagent schemes for the flotation of platinum group minerals from various ores, *Minerals Engineering*, Oct, vol. 16, 2003. pp. 931–939.

CHOI, I.-K., WEN, W.-W., and SMITH, R.W. The effect of a long chain phosphate on the adsorption of collectors on kaolinite, *Minerals Engineering*, Nov, vol. 6, no. 11, 1993. pp. 1191–1197.

CROZIER, R.D. and KLIMPEL, R.R. Frother: Plant practice, *Minerals Processing and Extractive Metallurgy Review*, vol. 5, 1989. pp. 257–279.

DAVIDTZ, J.C. Quantification of flotation activity by means of excess Gibbs free energies, *Minerals*

Engineering, May, vol. 12, no. 10, 1999. pp. 1147–1161.

DU PLESSIS, R. The thiocarbonate flotation chemistry of auriferous pyrite, PhD Thesis, University of Utah, Salt Lake City, Utah, USA, 2003.

GROBLER, W.A., SONDASHI, S., and CHIDLEY, F.J. Recent developments in flotation reagents to improve base metal recovery, The South African Institute of Mining and Metallurgy, Third Southern African Conference on Base Metals, In Press (2005).

HELBIG, C., BRADSHAW, D.J., HARRIS, P.J., O'CONNOR, C.T., and BALDAUF, H. The synergistic interactions of mixtures of thiol collectors in the flotation of sulphide minerals, Presented at XXI *International Mineral Processing Congress*, Rome, Italy, 2000.

LEJA, J. Interactions of surfactants. *Minerals Processing and Extractive Metallurgy Review*, vol. 5, 1989. pp. 1–22.

LIU, Q. and PENG Y. The development of a composite collector for the flotation of rutile, *Minerals Engineering*, Dec, vol. 12, no. 12, 1999. pp. 1419–1430.

MONTE, M.B.M. and OLIVEIRA, J.F. Flotation of sylvite with dodecylamine and the effect of added long chain alcohols, *Minerals Engineering*, March, vol. 17, 2004. pp. 425–430.

PUGH, R.J. The role of the solution chemistry of dodecylamine and oleic acid collectors in the flotation of fluorite, *Colloids and Surfaces*, May, vol. 18, no. 1, 1986. pp. 19–41.

SANDLER, S.I. *Chemical Engineering Thermodynamics*, 2nd edn., 1997.

SLABBERT, W. The role of trithiocarbonates and thiols on the flotation of some selected South African sulphide ores. M.Eng Thesis, Potchefstroom University for Christian Higher Education, Potchefstroom, South Africa, 1985.

STEYN, J.J. The role of collector functional groups in the flotation activity of Merensky Reef samples, M.Eng Thesis, Potchefstroom University for Christian Higher Education, Potchefstroom, South Africa, 1996.

SWEET, J.A. Investigation of a methodology to decouple physical and chemical effects for flotation circuit performance evaluation, M.Sc. thesis, Faculty of Engineering and Built Environment, University of Cape Town, South Africa, 1999.

VOS, C.F. Senior Metallurgist, Impala Platinum, Concentrator Technical Department, Internal Report, 2004.

WIESE, J., HARRIS, P., and BRADSHAW, D. The influence of the reagent suite on the flotation of ores from the Merensky reef, *Minerals Engineering*, Feb, vol. 18, no. 2, 2005a. pp. 189–198.

WIESE, J., HARRIS, P., and BRADSHAW, D.J. Investigation of the role and interactions of a dithiophosphate collector in the flotation of sulphides from the Merensky reef, *Minerals Engineering*, July, vol. 18, no. 8, 2005b. pp. 791–800.