

# THE DEVELOPMENT AND IMPLEMENTATION OF NEW TTC FLOTATION CHEMICALS

GERHARDUS PETRUS VILJOEN

B.Eng. (Chemical)

Submitted in partial fulfilment of the requirements for the degree of

MASTER OF ENGINEERING (Chemical)

In the School for Chemical and Mineral Engineering at the

POTCHEFSTROOM UNIVERSITY

FOR

CHRISTIAN HIGHER EDUCATION

Supervisor Prof. J.C. Davidtz

Potchefstroom

1998

*This document is the property of Biliton SA Limited, Chemfit Mining Chemicals (Pty LTD) and the Potchefstroom Mining Chemicals Research group and contains confidential, proprietary information which must not be disclosed to or discussed with anyone outside these above-mentioned companies or group.*

*This document is confidential until declassified by the sponsors.*

## ABSTRACT

Batch floats were done on Merensky ore from Section 10 at Impala Platinum. The ultimate objective of this project was a pilot plant trial and certain questions had to be answered before the trial could be conducted. To circumvent decomposition of trithiocarbonates (TTC's) in water, tablets, solvents and emulsions were prepared and tested as carriers of TTC's in the flotation system. The emulsion gave the best result.

The decomposition rate of short chain ionic and covalent collectors in water were measured. In water  $iC_3$ -TTC was less stable and decomposed faster than the corresponding xanthates.

Long and short chain ionic TTC's, covalent TTC and long chain mercaptans were evaluated and compared to the standard collector.  $iC_3$ -TTC dosed in an emulsion showed significant improvement on the standard at Impala Platinum. Combinations of the collectors also showed good results. Mineral potential data for the TTC's differed from xanthates. The TTC dosed as a powder or in emulsion showed a two step drop in potential. At this stage the only conclusion from this is that xanthates and TTC have a different mechanism of adsorption.

Three collectors were chosen for testing on a continuous 60 liter cell at Impala Platinum.  $iC_3$ -TTC dosed in water and the emulsion were compared to the standard collector. A 2.8% and 5% improvement on PGM and nickel recovery was observed with the emulsion.

## UITTREKSEL

Flotasie-eksperimente is gedoen met Merensky erts van Seksie 10 van Impala Platinum. Die hoofdoelwit van die projek was 'n aanlegproefloop en sekere vrae moes beantwoord word. Trithiokarbonate (TTC's) is as tablette, oplosmiddels en emulsies voorberei en die ontbinding van TTC's in water is met die verskillende draers getoets. Die emulsiesisteme het die beste resultate gelewer.

Die ontbindingstempo van kortketting ioniese en kovalente kollekteerders in water is gemeet. In water was  $iC_3$ -TTC minder stabiel en het vinniger opgebreek as die ooreenstemmende xantate.

Lang- en kortketting ioniese TTC's, kovalente TTC en langketting merkaptane is getoets en vergelyk met die standaard kollekteerder.  $iC_3$ -TTC gedoseer as 'n emulsie toon aansienlike verbetering op die standaard by Impala Platinum. Kombinasies van die kollekteerders het ook goeie resultate gelewer. Mineralepotensiaaldata vir die TTC's verskil van xantate. Die TTC gedoseer as poeier of emulsie toon 'n dubbele daling in potensiaal. Die enigste gevolgtrekking op hierdie stadium is dat xantate en TTC verskillende adsorpsiemeganismes toon.

Drie kollekteerders is gekies om verdere toetse met 'n kontinue 60 liter flotasiesel by Impala Platinum te doen.  $iC_3$ -TTC is gedoseer in water en as emulsie en vergelyk met die standaard kollekteerder. Verbeterings van onderskeidelik 2.8% en 5% op PGM en nikkelerwinning is verkry met die emulsie.

## ACKNOWLEDGEMENTS

I hereby wish to extend my appreciation and gratitude to the following people and organisations:

Prof. J.C. Davidtz, my supervisor for his able and willing guidance in this project. I have learned a great deal from his way of thinking and ideas of life.

Impala Platinum for funding this project. I want to thank all the people at Mineral Processing for their support and the knowledge that they shared with me. During my stay there with the 60l cell tests the plant staff were eager to assist me with mechanical and electrical problems. The following people need to be mentioned:

Dave Marshall for organising this project and the tests at Impala Platinum.

Johan Theron for assisting me with the data analysis.

The Chemical Engineering Department at UCT. I enjoyed my visit to Cape Town very much. In particular I want to thank the following personnel:

Dr. Peter Harris, Dee Bradshaw and Martin Harris for their interest and assistance.

Mark Buswell and the Min. Proc. Lab assistants.

All my new friends who showed me around in Cape Town.

Billiton Process Research for helping me with the ore preparation and flotation tests.

My parents, family and friends who stood by me all the way. Lastly, but certainly not least, my Father in Heaven who gave me this opportunity to further my studies and who helped me through this project.

# TABLE OF CONTENTS

|   |      |
|---|------|
| ABSTRACT .....  | ii   |
| UITTREKSEL .....  | iii  |
| ACKNOWLEDGEMENTS .....  | iv   |
| TABLE OF CONTENTS .....   | v    |
| TABLE OF FIGURES .....  | xi   |
| LIST OF TABLES .....  | xiii |
| CHAPTER 1 INTRODUCTION.....                                       | 1    |
| CHAPTER 2 LITERATURE SURVEY .....                                 | 3    |
| 2.1 Mechanism and reactions of sulphide mineral flotation.....    | 3    |
| 2.1.1 The effect of grinding on collector oxidation.....          | 3    |
| 2.1.2 Self-induced or natural flotation .....                     | 4    |
| 2.1.3 Specific cases of collector-induced flotation .....         | 5    |
| 2.1.3.1 Xanthate .....  | 5    |
| 2.1.3.2 DTP.....  | 6    |
| 2.2 Electrochemistry of sulphide flotation.....                   | 8    |
| 2.2.1 Mixed and rest potentials .....                             | 8    |
| 2.2.2 Measurement of pulp potential.....                          | 11   |
| 2.2.3 Eh-pH diagrams .....  | 13   |
| 2.3 The basic TTC molecule .....                                  | 16   |
| 2.3.1 Copper collection .....                                     | 17   |
| 2.3.1.1 The effects of chain length on recoveries and rates ..... | 19   |

|  |    |
|--|----|
| 2.3.1.2 The effect of sulphur content of collector molecules on rates and recoveries | 19 |
| 2.3.1.3 Isomers  | 20 |
| 2.3.1.4 Valleriite-rich copper sulphide ore  | 21 |
| 2.3.1.5 Long chain collectors  | 22 |
| 2.3.2 Platinum containing ores   | 22 |
| 2.3.2.1 PGM collecting with short chain collectors                                   | 22 |
| 2.3.2.2 PGM flotation with long chain collectors                                     | 24 |
| 2.3.2.3 TTC's and DTCB's on Merensky and UG2 ore                                     | 25 |
| 2.3.2.3.1 Nitrogen gas flotation   | 25 |
| 2.3.2.3.2 TTC odour  | 25 |
| 2.3.2.3.3 Metal and mineral recovery with short chain collectors                     | 27 |
| 2.3.3 Pyrite   | 29 |
| 2.3.3.1 Low pH flotation   | 29 |
| 2.3.3.1.1 Short chain collectors   | 29 |
| 2.3.3.1.2 Long chain collectors on gold  | 30 |
| 2.3.3.2 High pH flotation  | 31 |
| 2.3.4 Copper-lead-zinc-iron ore  | 31 |
| 2.3.4.1 Ionic compounds  | 31 |
| 2.3.4.2 Covalent TTC's   | 32 |
| 2.3.4.2.1 Aliphatic derivatives  | 32 |
| 2.3.4.2.2 Allyl and benzyl derivatives   | 32 |
| 2.4 Development of a new flotation theory  | 33 |
| 2.4.1 Energy calculations  | 33 |
| 2.4.2 Rate/Recovery relationship   | 36 |
| 2.4.3 Effect of mole fraction  | 36 |
| CHAPTER 3. PRELIMINARY METHODS   | 38 |

|  |    |
|--|----|
| 3.1 Introduction.....                                      | 38 |
| 3.2 Optimising TTC dosing methods .....                    | 38 |
| 3.2.1 Tablets .....  | 38 |
| 3.2.2 Suspension .....                                     | 40 |
| 3.3 Mercaptan breakthrough .....                           | 41 |
| 3.4 Frother - TTC combinations .....                       | 42 |
| 3.4.1 Materials and methods.....                           | 43 |
| 3.4.2 Results and discussion .....                         | 44 |
| CHAPTER 4 BATCH FLOTATION OF SELECTED TTC's.....           | 46 |
| 4.1 Introduction.....                                      | 46 |
| 4.2 Biliton Process Research - Collector screening .....   | 46 |
| 4.2.1 Materials and methods.....                           | 47 |
| 4.3 Results and discussion.....                            | 48 |
| 4.3.1 Powders .....  | 48 |
| 4.3.2 Suspensions.....                                     | 49 |
| 4.3.2.1 Long and short chain TTC's.....                    | 49 |
| 4.3.3 iC <sub>3</sub> /iC <sub>4</sub> covalent TTC's..... | 50 |
| 4.3.3.1 Materials and methods .....                        | 50 |
| 4.3.3.2 Results and discussion .....                       | 50 |
| 4.3.4 Multiple collector addition.....                     | 51 |
| 4.3.4.1 Materials and methods .....                        | 52 |
| 4.3.4.2 Results and discussion .....                       | 52 |
| CHAPTER 5 MODIFIED LEEDS CELL .....                        | 55 |
| 5.1 Materials and methods .....                            | 55 |
| 5.2 Experimental .....                                     | 56 |

|  |    |
|--|----|
| 5.3 Results and discussion.....                          | 56 |
| 5.3.1 Mass and water recovery.....                       | 56 |
| 5.3.2 Effect of collectors on grades and recoveries..... | 58 |
| 5.3.2.1 Sulphur.....                                     | 58 |
| 5.3.2.2 Copper.....                                      | 59 |
| 5.3.2.3 Nickel.....                                      | 60 |
| 5.3.2.4 Iron.....  | 61 |
| CHAPTER 6. IMPALA 60 litre CONTINUOUS CELL.....          | 63 |
| 6.1 Introduction.....                                    | 63 |
| 6.2 Materials and methods.....                           | 63 |
| 6.3 Experimental.....                                    | 64 |
| 6.4 Results.....   | 66 |
| 6.4.1 Water and Solids Recovery.....                     | 67 |
| 6.4.2 Platinum Group Minerals.....                       | 68 |
| 6.4.3 Copper.....  | 69 |
| 6.4.4 Nickel.....  | 70 |
| 6.4.5 Chromite.....                                      | 71 |
| 6.4.6 Size distribution of feed.....                     | 72 |
| 6.5 Conclusions.....                                     | 74 |
| CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS.....           | 76 |
| 7.1 Methods of dosing.....                               | 76 |
| 7.2 Properties of TTC's.....                             | 77 |
| 7.3 Batch floats.....                                    | 78 |
| 7.3.1 Billiton Process Research flotation tests.....     | 78 |
| 7.3.2 Electrochemistry and Leeds flotation cell.....     | 79 |

|  |     |
|--|-----|
| 7.4 60 litre flotation cell.....                                 | 80  |
| 7.5 Recommendations .....  | 81  |
| CHAPTER 8 BIBLIOGRAPHY .....                                     | 83  |
| APPENDIX A METHODS OF ORE PREPARATION .....                      | 93  |
| 1 Ore sampling .....   | 93  |
| 2 Ore preparation .....  | 93  |
| 2.1 Crushing.....  | 93  |
| 2.2 Splitter .....   | 94  |
| 2.3 Milling.....   | 94  |
| Appendix B Multiple collector addition in batch cells.....       | 96  |
| Appendix C Results of batch floats conducted at UCT .....        | 100 |
| 1 Metallurgical results - Graphics.....                          | 100 |
| 2 Metallurgical results - Tables .....                           | 103 |
| Appendix D Operating procedure of continuous 60 liter cell ..... | 105 |
| Appendix E Viscosity of TTC suspension.....                      | 107 |
| 1. Materials and methods.....                                    | 107 |
| 2. Results .....   | 107 |
| Appendix F Decomposition of collectors .....                     | 110 |
| 1 Materials and methods.....                                     | 110 |
| 2 Experimental .....   | 111 |
| 3 Results and discussion .....                                   | 112 |
| 3.1 Half-life times .....  | 112 |
| 3.2 Toxic gases.....   | 114 |
| Appendix G Electrochemical measurements .....                    | 115 |

|  |     |
|--|-----|
| 1 Buffered aqueous solutions.....          | 116 |
| 1.1 Materials and methods .....            | 116 |
| 1.2 Results and discussion .....           | 117 |
| 1.2.1 Ionic collectors in solution.....    | 117 |
| 1.2.1.1 Pyrrhotite probe.....              | 117 |
| 1.2.1.2 Pyrite probe .....                 | 120 |
| 1.2.1.3 Chalcopyrite probe .....           | 120 |
| 1.2.2 Covalent collector .....             | 120 |
| 2 Mineral Potentials in batch floats ..... | 121 |
| 2.1 Materials and methods .....            | 121 |
| 2.3 Results and discussion .....           | 122 |

## TABLE OF FIGURES

|   |    |
|---|----|
| Figure 2.1 Flotation recovery of sulphide minerals as a function of potential (Richardson and Walker, 1985) ..... | 9  |
| Figure 2.2 A schematic diagram showing currents for anodic and cathodic reactions (Chander 1999).....             | 10 |
| Figure 2.3 The basic TTC molecule .....   | 16 |
| Figure 2.4 Recovery as a function of the hydrocarbon chain length at PMC (Slabbert, 1985).....                    | 18 |
| Figure 2.5 Initial rate as a function of the hydrocarbon chain length at PMC (Slabbert, 1985).....                | 18 |
| Figure 2.6 PGM recovery of the standard and iC <sub>3</sub> -TTC at 45g/t (Slabbert, 1985).....                   | 23 |
| Figure 2.7 Recovery vs time for PGM (Steyn, 1997).....  | 28 |
| Figure 2.8 $\Delta G^{ex}/RT$ vs Recovery for singular collectors (Steyn, 1997).....                              | 35 |
| Figure 2.9 $G^{mix}$ vs mole fraction (x) for the system organic molecule / water (Steyn, 1997) .....             | 37 |
| Figure 5.1 Mass recovery vs time .....  | 57 |
| Figure 5.2 Water recovery vs time .....   | 57 |
| Figure 5.3 Grade recovery curve of sulphur.....   | 58 |
| Figure 5.4 Grade recovery curve of copper.....  | 59 |
| Figure 5.5 Grade recovery curve of nickel .....   | 60 |
| Figure 5.6 Grade recovery curve of iron.....  | 62 |
| Figure 6.1. Flotation section at Impala Platinum .....  | 65 |
| Figure 6.2. 60 litre cell at Impala Platinum .....  | 66 |
| Figure 6.3 Size distribution of feed to the 60 litre cell.....  | 73 |
| Figure A1 Milling curve.....  | 95 |

|   |     |
|---|-----|
| Figure C1.1 Water recovery vs solids recovery.....  | 100 |
| Figure C1.2 Sulphur recovery vs time .....  | 100 |
| Figure C1.3 Copper recovery vs time.....  | 101 |
| Figure C1.4 Nickel recovery vs time.....  | 101 |
| Figure C1.5 Iron recovery vs time .....   | 102 |
| Figure E1 Viscosity vs. TTC % for various speed levels .....                              | 108 |
| Figure E2 Viscosity vs. rate of shear.....  | 109 |
| Figure F.1 Decomposition and solubility product apparatus .....                           | 112 |
| Figure F.2 Absorbance peaks of collectors.....  | 113 |
| Figure G.1. Scematic of experimental set-up (Buswell, 1998) .....                         | 117 |
| Figure G.2. Mineral potentials of platinum in aqueous solution.....                       | 118 |
| Figure G.3 Mineral potentials for different minerals in aqueous solution.....             | 119 |
| Figure G.4 Mineral potentials of covalent collectors.....                                 | 121 |
| Figure G.5 Mineral potential of pyrrhotite in flotation system .....                      | 123 |
| Figure G.6 Mineral potential of pyrite in flotation system.....                           | 123 |
| Figure G.7 Mineral potential of chalcopyrite in flotation system .....                    | 124 |
| Figure G.8 Mineral potential of pentlandite in flotation system.....                      | 124 |
| Figure G.9 Mineral potential of platinum as reference electrode in flotation system ..... | 125 |

## LIST OF TABLES

|   |    |
|---|----|
| Table 2.1 Recoveries and initial rate values (Slabbert, 1985) .....                   | 29 |
| Table 3.1 Frothing properties of $iC_3$ -TTC at different concentrations .....        | 41 |
| Table 3.2 Mercaptan breakthrough .....  | 42 |
| Table 3.3 Chemical dosage and conditioning times .....                                | 43 |
| Table 3.4 $iC_3$ -TTC with different frothers .....                                   | 45 |
| Table 4.1 Metals recovered without suspensions .....                                  | 48 |
| Table 4.2 Combinations of $iC_3$ -TTC and $C_{12}$ -TTC - Various concentrations..... | 49 |
| Table 4.3 Covalent collectors tested in nitrogen and air .....                        | 51 |
| Table 4.4 Recovery after 20 minutes for 20g/ton (25%) initial collector dosage. ....  | 52 |
| Table 4.5 Recovery after 20 minutes of 40g/ton (50%) initial collector dosage.....    | 53 |
| Table 4.6 Recovery after 20 minutes of 60g/ton (75%) initial collector dosage.....    | 54 |
| Table 5.1 Collectors tested with modified Leeds cell .....                            | 55 |
| Table 6.1. Chemical dosage levels with 60 litre cell .....                            | 64 |
| Table 6.2 Water and Solids Recovery on 60 litre cell.....                             | 67 |
| Table 6.3 PGM recovery and grades on 60 litre cell .....                              | 68 |
| Table 6.4 Copper recovery and grades.....   | 70 |
| Table 6.5 Nickel recovery and grades.....   | 71 |
| Table 6.6 Chromite recovery and grades .....  | 72 |
| Table 6.7 Size range for the 60 litre continuous cell .....                           | 74 |
| Table A1 Calculating the milling time for Merensky ore .....                          | 95 |
| Table B1 PGM results for multiple collector addition at BPR .....                     | 96 |
| Table B2 Copper results for multiple collector addition at BPR.....                   | 97 |
| Table B3 Nickel results for multiple collector addition at BPR.....                   | 98 |
| Table B4 Chromate results for multiple collector addition at BPR.....                 | 99 |

|   |     |
|---|-----|
| Table C1. Sulphur results of batch floats at UCT .....    | 103 |
| Table C2. Copper results of batch floats at UCT .....     | 103 |
| Table C3. Iron results of batch floats at UCT .....       | 104 |
| Table C4. Nickel results of batch floats at UCT .....     | 104 |
| Table E1 Viscosity at different TTC concentrations .....  | 108 |
| Table F.1 Half-life times for different pH and gases..... | 113 |