

**FLOTATION OF AURIFEROUS PYRITE USING A MIXTURE OF  
COLLECTORS**

By

**ANTONY TAPIWA MAKANZA**

Submitted in partial fulfilment of the requirements for the degree

**Master of Engineering  
(Metallurgical Engineering)**

in the

Faculty of Engineering, Built Environment and Information Technology  
University of Pretoria

December 2005

---

*...now unto Him that is able to do exceeding abundantly above  
all that we ask or think, according to the power that worketh in  
us....*

*ACKNOWLEDGEMENTS*

First of all, I would like to extend my greatest appreciation to Anglogold Ashanti for providing the financial support for this project. To Sarah Havenga and Professor Chris Pistorius, your commitment cannot be summarised in a few words. Thank you for all the support that you gave me during my time as a student in the department. You will always be remembered for your kindness. Professor John Davidtz, words cannot express how grateful I am for your unwavering support and guidance throughout the project. You've got loads of patience I must say, going through all that nonsense I used to send you and for listening to me all those times I used to make unfounded arguments. It's a quality that many would desire to have, but is often elusive. To Tham, thank you for being a source of inspiration. "I am free at last". To all my friends from His People Church, thank you for all the encouragement in all those times when it looked like the end was endless. Last but not least, I would like to thank my wife Ennie and our daughter Mutsawashe for being there when I needed them and when I desperately did not need them.

*Antony T. Makanza*

*November 2005*

*Pretoria, South Africa*

FLOTATION OF AURIFEROUS PYRITE USING A MIXTURE OF  
COLLECTORS

By

ANTONY TAPIWA MAKANZA

Supervisors: Professor John C. Davidtz  
Doctor Thys (MKG) Vermaak  
Department: Materials Science and Metallurgical Engineering  
Degree: Master of Engineering

**ABSTRACT**

The effects SIBX/C<sub>10</sub> (or C<sub>12</sub>) TTC mixtures on flotation response of pyrite, gold and uranium from AngloGold Ashanti's No 2 Gold Plant feed were investigated. In batch flotation tests where TTC was dosed from aged 1% wt stock solutions, synergism was shown to occur in gold flotation at 25 mole percent C<sub>12</sub> TTC and in uranium flotation at a similar dosage of C<sub>10</sub> TTC. With commercial C<sub>12</sub> TTC, 8 mole percent recorded the highest uranium and gold recoveries. The SIBX/C<sub>12</sub> TTC mixture had a greater effect on gold than on uranium. When C<sub>12</sub> mercaptan replaced the TTC in SIBX mixtures, rates and recoveries decreased at all levels.

Kinetics and recovery with a mixture of 92 mole percent SIBX and 8 mole percent commercial C<sub>12</sub> TTC gave a better flotation activity than obtained with SIBX alone. A combination of SIBX and an aged 1% wt solution of TTC lost activity when compared to that of SIBX and commercial TTC. This was attributed to the hydrolysis of TTC.

Micro-probe analysis, back-scattered electron images, and EDS analysis showed that all the uranium recovered in flotation concentrates was associated with either pyrite, galena or a carbonaceous material (karogen). This was attributed to the flotation of the uranium oxide minerals brannerite and uraninite.

Conditioning at pH values between 1.9-3.7 improved kinetics of gold, sulphur and uranium collection, but sulphur and uranium final recoveries were lower and gold final recovery was higher than the standard.

In the presence of 0.001M cyanide, equivalent to 70g/t copper sulphate failed to activate pyrite at both pH 5.5 and pH 7.2. At a similar molar dosage lead nitrate did activate pyrite at pH 5.5 but not at pH 7.2.

*Keywords:* Froth flotation, Auriferous Pyrite, Trithiocarbonate collectors, Cyanide, Lead nitrate, Copper sulphate, Mineralogy, pH

**TABLE OF CONTENTS**

Acknowledgements	iii
Abstract	iv
Chapter 1 Introduction	1
Chapter 2 Literature Review	3
2.1 Introduction	3
2.2 Operations at No. 2 Gold Plant – An Overview	3
2.3. Mineralogy of No 2 Gold Plant Feed	8
2.3.1 Introduction	8
2.3.2 Mineralogy of the Vaal Reef	8
2.4. Fundamentals of Froth Flotation	13
24.1 An Overview of the Flotation Process	13
2.4.2 Thermodynamic Considerations	14
2.4.3 Contact Angle	17
2.4.3 Flotation Rate	19
2.5. Collectors for Auriferous Pyrite Flotation	23
2.5.1 Xanthate (Dithiocarbonate) Collectors	26
2.5.2 Xanthate – Pyrite Interactions	29
2.5.3 Trithiocarbonate Collectors	31
2.5.4 TTC – Pyrite Interactions	32
2.5.5 Synergism in SIBX/TTC Mixtures	35
2.5.6 Mechanisms of Synergism	35
2.6. Activators for Auriferous Pyrite Flotation	37
2.6.1 Adsorption of Lead (II) Ions on Pyrite	39
2.6.2 Copper Sulphate	42
2.6.3 Adsorption of Copper (II) ions on Pyrite	44
2.6.4 Cyanide and Activation of Pyrite with Copper and Lead Ions	46
2.6.5 Iron ions and Surface Charge	53

---

---

Chapter 3 Materials and Methods	55
3.1 Materials	55
3.1.1 Ore	55
3.1.2 Reagents	57
3.1.3 Apparatus	57
3.2 Methods	59
3.2.1 Single-Point Flotation Tests	59
3.2.2 Release Curve Measurements	60
Chapter 4 Effect of SIBX dosage level on single point batch flotation	61
4.1 Introduction	61
4.2 Results and Discussion	62
4.2.1 Mass Recovery	62
4.2.2 Sulphur	63
4.2.3 Uranium	64
4.2.4 Gold	64
4.2.5 Optimum SIBX Dosage	65
4.2.6 Conclusions	66
Chapter 5 Effect of SIBX/TTC mixtures on single point batch flotation	67
5.1 Introduction	67
5.2 SIBX and C <sub>10</sub> TTC	68
5.2.1 Results and Discussion	68
5.2.1.1 Mass Recovery	68
5.2.1.2 Sulphur	69
5.2.1.3 Uranium	70
5.2.1.4 Gold	72
5.2.1.5 Conclusions	73
5.3 SIBX and C <sub>12</sub> TTC	74
5.3.1 Results and Discussion	74
5.3.1.1 Mass Recovery	74
5.3.1.2 Sulphur	75
5.3.1.3 Gold	76

---

---

5.3.1.4 Uranium	78
5.3.1.5 Conclusions	79
5.4 Auriferous Pyrite Flotation with SIBX/Fresh TTC Mixtures	80
5.4.1 Introduction	80
5.4.2 Results and Discussion	81
5.4.2.1 Water Recovery	81
5.4.2.2 Mass Recovery	82
5.4.2.3 Sulphur	83
5.4.2.4 Uranium	84
5.4.2.5 Gold	86
5.4.2.6 Conclusions	87
Chapter 6 Effect of Diluted and Aged TTC on Sulphur, gold and uranium flotation	88
6.1 Introduction	88
6.2 Results and Discussion	88
6.2.1 Water and Mass recovery	85
6.2.2 Sulphur Recovery	90
6.2.3 Uranium Recovery	91
6.2.5 Gold	92
6.2.6 Conclusions	93
Chapter 7 Effect of Conditioning pH on Sulphur, Gold and Uranium Flotation	95
7.1 Introduction	95
7.2 Results and Discussion	96
7.2.1 Sulphur	96
7.2.2 Uranium	101
7.2.3 Gold	111
7.2.4 Conclusions	113
Chapter 8 Activation of Pyrite by Pb <sup>2+</sup> and Cu <sup>2+</sup> in the Presence of Cyanide	114
8.1 Introduction	114

---



8.2 Results and Discussion	114
8.2.1 Copper Sulphate	114
8.2.2 Lead Nitrate	117
8.2.3 Copper Sulphate at pH 5.5	119
8.2.4 Lead Nitrate at pH 5.5	119
8.2.5 Conclusions	121
Chapter 5 Conclusions and Recommendations	125
References	121
Appendix A – Back-scattered electron images	131

---

---

**LIST OF FIGURES**

Figure 2.1	An XRD pattern for typical No. 2 Gold Plant feed	4
Figure 2.2	Flow sheet of No. 2 Gold Plant flotation circuit	7
Figure 2.3	Conglomerate comprised of pebbles of quartz embedded in a quartz rich matrix.	9
Figure 2.4	Photomicrograph showing uraniferous karogen containing inter- and intra-columnar gold	10
Figure 2.5	The radioactive decay of $U^{238}$ to $Pb^{206}$	12
Figure 2.6	Processes occurring in a flotation cell	13
Figure 2.7	Mineral surface–collector–water interactions	15
Figure 2.8	Initial rate- $G^{ex}$ relationship for DTC's and TTC's on copper	16
Figure 2.9	Relationship between $G^{ex}$ and recovery for covalent TTC collector molecules	16
Figure 2.10	A summary of interacting variables in flotation	17
Figure 2.11	Schematic representation of the equilibrium contact between an air bubble and a solid immersed in a liquid	18
Figure 2.12	Typical curves obtained by fitting recovery-time data to a two parameter model.	21
Figure 2.13	Thiol collectors (a) dithiocarbonates, (b) trithiocarbonates	25
Figure 2.14	Illustration of different surfactant self-assembly structures	26
Figure 2.15	Hydrolysis and oxidation of ethyl xanthate in aqueous solution	27
Figure 2.16	Infrared spectrum of diamyl dixanthogen and pyrite conditioned in the absence and presence of PAX	29
Figure 2.17	Differential IR spectrum of pyrite after reacting with EX at pH 6	31
Figure 2.18	FTIR of (a) $EX_2$ and (b) $Fe(EX)_3$	31

---

---

Figure 2.19	Chemical structure of TTCs	32
Figure 2.20	Oxidation of Trithiocarbonates to their corresponding dimmers	33
Figure 2.21	Comparison between FTIR transmission spectra the n-amyl TTC dimer and that of pyrite treated with potassium n-amyl trithiocarbonate	33
Figure 2.22	Standard reduction potentials for thiocarbonate collectors as a function of alkyl chain length	34
Figure 2.23	Auriferous pyrite grade–recovery curves for DTC and 25% TTC / 75% DTC mixture	35
Figure 2.24	Electrochemically controlled contact angle measurements as a function of lead concentration for pyrite in PAX	37
Figure 2.25	(a) A Pobaix diagram for the Pb-H <sub>2</sub> O (b) Lead (II) speciation at 1 x 10 <sup>-3</sup> M [Pb <sup>2+</sup> ]	38
Figure 2.26	Speciation of cyanide as a function of pH at 2 x 10 <sup>-3</sup> [CN <sup>-</sup> ].	39
Figure 2.27	Effect of copper sulphate on recovery of pyrite	43
Figure 2.28	Effect of copper sulphate on pyrite flotation	43
Figure 2.29	Effect of copper sulphate on gangue recovery	44
Figure 2.30	A Pourbaix diagram for the Fe-S-CN-H <sub>2</sub> O system	47
Figure 2.31	Copper (II) speciation at different pH values.	47
Figure 2.32	Speciation diagram for 2 x 10 <sup>-3</sup> M Fe(III) as a function of pH at 25°C.	51
Figure 2.33	Speciation diagram for 2 x 10 <sup>-3</sup> M Fe(II) as a function of pH at 25°C.	51
Figure 2.34	Effect of pH and reagent addition order on the flotation of pyrite in the absence and presence of Fe <sup>3+</sup> ions	52
Figure 2.35	Effect of pH and reagent addition order on the flotation of ore-pyrite in the absence and presence of Fe <sup>2+</sup> ions	53

---

---

Figure 3.1	Typical particle size distribution of ore samples treated in this investigation.	56
Figure 3.2	A Denver D12 laboratory flotation machine	58
Figure 4.1	Response of mass recovery to different SIBX dosages	62
Figure 4.2	Change of (a) concentrate sulphur grade and (b) the corresponding recoveries with SIBX dosage	63
Figure 4.3	Variation of (a) uranium grade (b) uranium recovery with SIBX	64
Figure 4.4	Variation of (a) gold grade and (b) gold recovery with SIBX dosage	65
Figure 4.5	(a) sulphur, gold and uranium grades and (b) their corresponding recoveries plotted versus SIBX	66
Figure 5.1	Variation of mass recovery with mole percent of C <sub>10</sub> TTC	68
Figure 5.2	Variation of (a) sulphur grade (b) sulphur recovery with C <sub>10</sub> TTC mole ratio	70
Figure 5.3	Sulphur grade-recovery combinations for the different SIBX/C <sub>10</sub> TTC mixtures tested	70
Fig. 5.4	Response of (a) uranium grade and (b) uranium recovery to different SIBX/ C <sub>10</sub> TTC mixtures. (c) Corresponding uranium grade-recovery relationships	71
Fig. 5.5	(a) Gold grade and (b) recovery for SIBX/C <sub>10</sub> TTC mixtures	73
Figure 5.6	Gold grade-recovery relationships for SIBX/C <sub>10</sub> TTC combinations	73
Figure 5.7	Response of mass recovery to increased C <sub>12</sub> TTC mole percent	75
Figure 5.8	Sulphur (a) grade and (b) recovery plotted against C <sub>12</sub> TTC mole percent in the collector mixture	76
Figure 5.9	Response of gold (a) grade, and (b) gold recovery change in C <sub>12</sub> TTC mole percent in the collector	77

---

---

Figure 5.10	Gold recoveries and their corresponding grades for SIBX/C <sub>12</sub> mixtures	77
Figure 5.11	Response of uranium (a) grade and (b) recovery to change in C <sub>12</sub> TTC mole percent	78
Figure 5.12	The response of water recovery to mole percent C <sub>12</sub> TTC	81
Figure 5.13	Variation of mass recovery with mole percent C <sub>12</sub> TTC of the mixture dosed	82
Figure 5.14	(a) Variation of sulphur grade with TTC mole percent and (b) the linear relationship between sulphur grade and mass recovery	83
Figure 5.15	(a) Plot of sulphur recovery versus TTC mole percent (b) Sulphur recoveries and their corresponding grades	84
Figure 5.16	(a) Variation of uranium grade and recovery with C <sub>12</sub> TTC mole percent	85
Figure 5.17	Change in (a) gold grade and (b) gold recovery with mole percent C <sub>12</sub> TTC	87
Figure 5.18	A summary of gold flotation responses for the different collector mixtures tested	87
Figure 6.1	Sulphur recovery-grade curves	91
Figure 6.2	Uranium recovery-grade curves	92
Figure 6.3	Gold recovery-grade curves	93
Figure 7.1	A Pourbaix diagram for the Fe-S-H <sub>2</sub> O system at 25°C	97
Figure 7.2	Sulphur recovery-grade curves	98
Figure 7.3	Speciation diagram for 2 × 10 <sup>-3</sup> M Fe(III) as a function of pH at 25°C.	99
Figure 7.4	Speciation diagram for 2 × 10 <sup>-3</sup> M Fe(II) as a function of pH at 25°C	99
Figure 7.5	Uranium grade-recovery curves for conditioning at pH 1.9 and 7.2	102

---

---

Figure 7.6	A back-scattered electron image of a concentrate recovered with 20g/t SIBX	103
Figure 7.7	EDS spectra of phases in Figure 4.32.	104
Figure 7.8	Lead and uranium recoveries for C <sub>10</sub> TTC/SIBX mixtures	105
Figure 7.9	Lead and uranium recoveries for C <sub>12</sub> TTC/SIBX mixtures	105
Figure 7.10	A dispersion of fine uranium-containing particles embedded in a larger particle	106
Figure 7.11	A BEI taken from the micro-probe analysis of concentrates floated with 20g/t SIBX	106
Figure 7.12	EDS spectra generated from the microprobe analysis of an iron sulphide	108
Figure 7.13	EDS spectra generated from the microprobe analysis of the dark phase found in concentrates	109
Figure 7.14	Gold recovery–grade curves for two conditioning pHs: pH 1.9 and pH 7.5	111
Figure 8.1	A Pourbaix diagram for the Fe-S-CN-H <sub>2</sub> O system	112
Figure 8.2	Copper (II) speciation at different pH values.	115
Figure 8.3	Lead (II) speciation at 2 × 10 <sup>-4</sup> M [Pb <sup>2+</sup> ].	116
Figure 8.4	(a) Sulphur (b) uranium and (c) gold recovery-time graphs recorded for 440mmol/t Pb(NO <sub>3</sub> ) <sub>2</sub> in NaCN	118
		120

---

---

**LIST OF TABLES**

Table 2.1	Typical minerals found in No. 2 Gold Plant Feed	5
Table 2.2	Chemical composition of calcine water	5
Table 2.3	Typical reagent suite used at No. 2 Gold Plant	6
Table 2.4	Vaal Reef pebble cementing matrix	9
Table 2.5	Application of Selected Thiol Collectors	23
Table 2.6	Selected Thiol Collector Structures	24
Table 2.7	Response of sulphide minerals to xanthate collectors	28
Table 2.8	Half-life times for SIBX and iC3-TTC	39
Table 2.9	Basic chemistry of the INCO SO <sub>2</sub> /AIR process	49
Table 3.1	Typical minerals found in No. 2 Gold Plant Feed	55
Table 3.2	Chemical composition of the ore sample	56
Table 3.3	Collectors used in the study	57
Table 4.1	Mass recovery	62
Table 4.2	Sulphur flotation data for each SIBX dosage	63
Table 4.3	Uranium flotation responses for different SIBX dosages	64
Table 4.4	Gold flotation data for each SIBX dosage tested	65
Table 5.1	SIBX/C <sub>10</sub> TTC combinations and reagent volumes	67
Table 5.2	SIBX/C <sub>12</sub> TTC combinations and reagent volumes	67
Table 5.3	Mass recovery	68
Table 5.4	Sulphur flotation responses for SIBX/C <sub>10</sub> TTC mixtures	69
Table 5.5	Uranium flotation responses for SIBX/C <sub>10</sub> TTC mixtures	71
Table 5.6	Gold flotation data for SIBX/C <sub>10</sub> TTC mixtures tested	72
Table 5.7	Mass recovery	74
Table 5.8	Sulphur flotation responses for SIBX/C <sub>12</sub> TTC mixtures	75
Table 5.9	Gold flotation data for SIBX/C <sub>12</sub> TTC mixtures tested	76
Table 5.10	Uranium flotation responses for SIBX/C <sub>12</sub> TTC mixtures	78
Table 5.11	SIBX/C <sub>12</sub> TTC combinations and reagent volumes	80
Table 5.12	Water recoveries	81
Table 5.13	Mass recovery	82

---

Table 5.14	Sulphur flotation responses for SIBX/C <sub>12</sub> TTC mixtures	83
Table 5.15	Uranium flotation responses for SIBX/C <sub>12</sub> TTC mixtures	85
Table 5.16	Gold flotation data for SIBX/C <sub>12</sub> TTC mixtures	86
Table 6.1	Water initial rates and final recoveries	89
Table 6.2	Mass final recoveries and initial rates	89
Table 6.3	Sulphur initial rates and final recoveries	90
Table 6.4	Uranium final recoveries and initial rates	91
Table 6.5	Gold flotation responses for 8 mole percent TTC	93
Table 7.1	Sulphur final recoveries and initial rates	96
Table 7.2	Pulp pH and potentials recorded during conditioning	96
Table 7.3	Uranium final recoveries and initial rates	101
Table 7.4	Gold final recoveries and initial rates	111
Table 8.1	Flotation responses recorded with lead nitrate at pH 5.5	120

---