

**EVALUATION OF BLENDED COLLECTORS FOR IMPROVED
RECOVERY OF PGEs FROM WESTERN BUSHVELD UG2 DEPOSIT**



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DECLARATION

I, Malebogo Gloria Moja declare that the contents of this thesis, submitted to the Vaal University of Technology for the degree of Magister Technologic (M-tech) in Metallurgical Engineering, are original and have not been submitted prior to this for an academic examination towards any qualification at this university or any other institution.

Name of Candidate: Malebogo Gloria Moja

Signed.....

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LIST OF ABBREVIATIONS

PGE	Platinum group elements
PGM	Platinum group minerals
EPL	Eastern Platinum Limited
WPL	Western Platinum Limited
JV	Joint venture
X	Xanthate
SNPX	Sodium n-propyl xanthate
SIBX	Sodium iso-butyl xanthate
DTP	Dithiophosphate
DTC	Dithiocarbamate
IPETC	Isopropyl-N-ethyl thionocarbamate
ABTC	S-alkyl-N-butyl thionocarbamate
CMC	Carboxyl methyl cellulose
CuSO₄	Copper sulphate
MSDS	Material safety data sheet
SEM	Scanning electron microscopy

XRD	X-Ray diffraction
ICP-MS	Inductively coupled plasma-Mass Spectrometry
C1	First concentrate collected from 0th to 1st minute
C2	Second concentrate collected from 1st to 3rd minute
C3	Third concentrate collected from 3rd to 8th minute
C4	Fourth concentrate collected from 8th to 20th minute

ABSTRACT

Lonmin mining company located in the Bushveld Complex of South Africa is one of the main platinum group elements (PGEs) producers in the world. Its core operations are made up of 11 shafts and inclines. There are resources of 181 million troy ounces of 3PGE + Au, and there are reserves of 32 million ounces of 3PGE + Au.

One of the ore type produced at Lonmin is UG2 ore which is dominated by the high presence of chromite. The UG2 ore is also associated with PGE assemblages divided into sulphides and non-sulphides, and it is beneficiated through the froth flotation technique. Froth flotation is a physico-chemical process that is used for separation of desired valuable minerals from the gangue minerals by utilising the difference in surface properties.

The process has been achieving lower recoveries with P4 (shaft name) UG2 ore compared to Eastern Platinum Limited (EPL) UG2 ore when using similar reagents suite, this leads to loss of valuable minerals to the tailings, both ores were from Lonmin. The first step was to conduct the mineralogical analysis conducted using Scanning electron microscopy- energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), and optical microscopy to study the mineral composition of the two ores, and to identify any differences between them (two ores) considering that EPL UG2 ore is a blend of P1, P2, P3 (shaft names) and P4 UG2 ores while P4 UG2 ore is not blended with any other ores. The mineralogical results showed the presence of chromite, plagioclase, enstatite and sulphide minerals. The PGEs could not be detectable by any of the techniques used due to their small size and rarity. However, X-ray diffraction detected differences in concentrations of minor gangue constituents such as talc, muscovite, chlorite and actinolite and these results suggest that reagent consuming gangue mineralogy may have contributed to the differences in PGE recoveries by flotation.

Batch flotation tests were also conducted. The existing reagent suite consisted of CuSO_4 as an activator, Sodium n-propyl xanthate (SPNX) as a collector, carboxymethyl cellulose CMC as a depressant, and Senfroth 200 as a frother, and this was a single collector system. Therefore it was imperative to conduct flotation n investigation on alternative collector blends in order to improve the recovery of P4 UG2 ore. SNPX was used as the primary collector and it was blended with the following co-collectors: alkyl dithiocarbamates (DTC), two formulations of S-alkyl-N-butyl

thionocarbamates (ABTC C1 & ABTC C2), and two formulations O-isopropyl-N-ethyl thionocarbamate (IPETC 30 & IPETC 31), one co-collector at a time. The first test incorporated the SNPX at dosage of 150 g/t without a blend and this dosage was selected based on the current optimum practice used at Lonmin and to use as a benchmark for the project. Trying to maintain the same dosage of 150 g/t of collectors, SNPX + co-collector were blended at two different dosages of 100 g/t + 50 g/t, and was also due to the fact that the co-collectors were highly concentrated and small dosages were expected to perform very well with SNPX. Lastly, the SNPX + co-collector at dosages 100 g/t + 125 g/t, here the dosage of co-collector was very high compared to 50 g/t and this was to check the effect of high dosages of highly concentrated collectors on the performance of the ore.

The flotation results showed that the use of 50 g/t of co-collectors yielded optimum PGEs + Au recoveries and grades, while the dosage of 125 g/t decreased recoveries and grades. The high dosage quantities of collectors do not necessarily mean they will yield improved recoveries and grades. Different chain structures can be used to alter the behaviour of a collector, and these may increase or decrease their capabilities to cause higher recoveries. By using a collector with a longer hydrocarbon chain the flotation limit may be extended without loss of selectivity, consequently bringing about greater water repulsion, instead of increasing the concentration of a shorter chain collector.

At 100 g/t of SNPX and 50 g/t of co-collector i.e. SNPX + IPETC 30 yielded improved 3PGE + Au recovery of 85.7 % at 3PGE + Au grades of 60.14 g/t, compared to the unblended SNPX (150 g/t) which yielded 3PGE + Au recovery of 81.1 % but insignificantly higher grade of 60.53 g/t. On the other hand, SNPX + IPETC C1 blend yielded low 3PGE + Au recoveries compared to SNPX + IPETC 30 and SNPX + IPETC 31 blends, but it achieved the highest grade of 76.1 g/t. Evidently, this proves that the relationship between recovery and grade is a trade-off.

The results have also shown the synergic effects, especially for SNPX blended with IPETC 30, and SNPX blended with IPETC 31 at dosage of 100 g/t (SNPX) and 50 g/t (IPETCs). It can be concluded that the different interaction obtainable from the thionocarbamate (ROCSNHR), effectively complement that from the xanthate ion (ROCS_2^-) to achieve more collector interaction at surface sites otherwise interactable for xanthate only. Therefore the collector

blends rendered the mineral of interest hydrophobic and as a result the minerals were recovered to the concentrate.

On the other hand, too much of collectors may not be beneficial. At the dosage of 100 g/t of SNPX and 125 g/t of collectors, SNPX + DTC attained lower recoveries compared to SNPX, SNPX + IPETC 30, SNPX + IPETC 31, however the grade was higher than achieved SNPX + IPETC 30, SNPX + IPETC 31 and SNPX + ABTC C1. Nevertheless, comparing these results to the dosage of 50 g/t of the co-collectors, the 125 g/t did not perform well at all. The dosage of 125 g/t of co-collectors lead to loss of collecting power and selectivity, especially for SNPX + IPETC 30, SNPX + IPETC 31, and SNPX + ABTC C1 blends. It is therefore wise to conduct an optimisation test to determine the correct dosing rate.

In addition, the chromite entrainment was below the smelter limit and is very beneficial since chromite is detrimental to the furnace.

Therefore, it is concluded that the blends of SNPX with IPETC 30 and IPETC 31 at a dosage 50 g/t have shown satisfying recoveries and the FeCr_2O_4 recovery is less than 1 % meaning there will not be any smelter penalties for FeCr_2O_4 content. Therefore, these are the recommended collector blends.

It is recommended that further mineralogical study of the ores be conducted so that it may provide deeper insight into the causes of low recoveries under SNPX only. The system of blended collectors and its optimisation would be beneficial and can be practiced. The Chemisorption studies between the minerals and co-collectors used will provide more specific insight and details into the actual interaction synergy that gave the improved recoveries.

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1 INTRODUCTION

1.1 Background information

Lonmin PLC is a mining company located in the Bushveld Complex of South Africa and it is one of the largest companies in the world that produces Platinum Group Elements (PGEs). It is listed on the London Stock Exchange and Johannesburg Stock Exchange. The productive operations of Lonmin are located in South Africa with additional PGE mineral resources in Canada. Lonmin core operations in the Bushveld Complex are made up of 11 shafts and inclines.

Almost 80 % of the global platinum group mineral resources are hosted in South Africa. The mine has been granted with Mining Licence from South African government for the core operations which will run to 2037 and it is renewable to 2067. There are resources of 181 million troy ounces of 3PGE + Au, and there are reserves of 32 million ounces of 3PGE + Au (Lonmin, 2018).

PGEs are found in the UG2 reef, Merensky reef and Platreef, all of which are in the Critical Zone (Cawthorn, 1999). The mineralogy of these three reefs varies; the UG2 reef is a chromitite band dominated by chromite, the Merensky reef is a megacrystic pyroxenite layer dominated by pyroxene and some plagioclase (Penberthy and Merkle, 1999; Penberthy *et al.*, 2000; Schouwstra *et al.*, 2000) and Platreef comprises pyroxinites, serpentinites and calc-silicates (McFadzean *et al.*, 2015).

The UG2 is a chromitite layer in the upper critical zone enriched in PGEs. Chromitite is a rock containing chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) as its primary constituent and in the chromite there is 40-50 % of Cr_2O_3 (Hay and Roy, 2010; Muzenda *et al.*, 2011). The chromitite layer extends for nearly the length of 400 km of the eastern and western limbs of the Bushveld Complex (Mondal & Mathez, 2007).

The UG2 chromitite layer also consists of PGEs assemblage divided into sulphide and non-sulphide. Laurite (RuS_2), cooperite (PtS) and braggite ($(\text{Pt}, \text{Pd})\text{NiS}$) are the examples of sulphides minerals containing PGEs. The non-sulphide PGEs are Pt-Fe and (Pt_3Fe) alloys, tellurides and bismuthinides. The occurrence of platinum group minerals in UG2 is generally fine grains (average 12 microns), associated with base metal sulphides, silicate gangue and/or

chromite grains (Kinloch, 1982; McLaren and De Villers, 1982; Gruenewaldt *et al.*, 1986; Penberty *et al.*, 2000). The mineralogy of UG2 is complex and mineral liberation is difficult and consequently it is challenging to extract PGEs from UG2 (Valenta and Mapheto, 2011).

One of the main gangue constituents in UG2 is chromite and it is imperative that the amount of chromite reporting to the concentrate is minimized during flotation for better operations of downstream processes i.e. smelting (Wesseldijk *et al.*, 1999). This problem is due to the fact that chromite is a spinel mineral and forms species that are stable at 2000°C (Wesseldijk *et al.*, 1999). The efficiency of the smelting process is therefore affected by these stable species (McKenzie, 1996). A smelter can tolerate a maximum of 3% of chromite from flotation concentrates (McFadzean *et al.*, 2015; Wesseldijk *et al.*, 1999). Wesseldijk *et al.* (1999) states that, due to chromite's hydrophilic nature it can be assumed that it reports to the concentrate during froth flotation by entrainment and not because chromite is hydrophobic in nature.

1.2 Problem statement

The Lonmin mine has 11 shafts which are in operation. The P4ⁱ (P-names for the shafts were changed for confidential reasons) shaft produces UG2 ore and it is one of the shafts that supply the Eastern Platinum (EPL) concentrator with about 80 % of its ore and the rest goes to the other concentrator called EPC. The EPL concentrator is not only supplied by the P4 shaft with ore but also receives ore from P1, P2 and P3 shafts.

The main beneficiation technique that is utilised at the Lonmin concentrators for minerals is froth flotation. Currently PGEs recovery from P4 UG2 ore is at 82 % while higher recoveries were expected. Therefore, it would be interesting to identify the mineralogical peculiarity of the Lonmin P4 UG2 ore responsible for this lower recovery.

This research entails a study of the ore from the P4 shaft and EPL concentrator to identify mineralogical difference peculiar to the ore. Towards improving the recovery, investigation of variety of collector + co-collector blends will be considered. The specific collector + co-collectors blend that will give best recovery can then be reconciled with mineralogical peculiarity of the P4 UG2 ore.

The reagents used in this work were from the product range of Senmin International. Senmin International is company that manufactures mineral beneficiation chemicals for various ores and

it is located in Sasolburg. This study was done as a collaboration between Department of Metallurgical Engineering (Vaal University of Technology) and Senmin International.

In this project, combinations of these collectors were investigated to evaluate their performance on the ore to achieve maximum recovery and grade levels. The concept of combination or blending of collectors in froth flotation is not new. Glembotskii (1958) conducted test work which showed that a mixture of weaker collector and a stronger collector resulted in a recovery gain of 2-5 % relative to the single strong collector system. Glembotskii (1958) further stated that due to the synergic effect generated between the two different collectors, the performance by the mixed collectors was improved. The larger the difference in structure and composition, the larger the synergic effect as explained Glembotskii (1958).

1.3 Hypothesis

Based on this research the following hypotheses are put forward:

- I. The behavior and interaction of the ore with chemical reagents are affected by the mineralogy of the ore.
- II. Blending two collectors during froth flotation results in synergistic effect on valuable minerals.

1.4 Aim and Objectives

1.4.1 Aim

The aim of this research work was to attain improved PGEs recovery and grade in the froth flotation of the Lonmin P4 (from western limb of Bushveld igneous complex) UG2 ore. The general objective of the project was therefore to investigate the effect of blended collectors on the UG2 ore through froth flotation technique.

1.4.2 Specific Objective

The specific objectives are to:

- I. Carry out mineralogical analysis to identify features specific to the Lonmin UG2 ore that can limit achievable flotation recovery, relative to the data in other part of the UG2.

- II. Conduct flotation tests utilizing blends of various Senmin collectors on the Lonmin UG2 ore, so as to obtain the collector blend which give improved recovery for the P4 ore without grade compromise.
- III. Evaluate the process chemistry for the reagent that gave the best recovery to reconcile the mineralogy to the flotation chemistry.

The specific collectors which were used were: Sodium n-propyl xanthate (SNPX), alkyl dithiocarbamates (DTC), S-alkyl-N-butyl thionocarbamates (ABTC C1 & ABTC C2), and O-isopropyl-N-ethyl thionocarbamate (IPETC 30 & IPETC 31). The rationales for these choices are discussed in Section 2.4.3 of literature review.

1.4.3 Scope of the study

This study covered the usage of different reagents, ore variation and flotation chemistry. Other parameters which affect flotation such as grain size were not investigated but the parameters were adopted from established plant data.

1.5 Benefits of the Research

This research will give more insight into varieties of flotation behaviours of diverse mineralogy of the BIC UG2 ore bodies. With improved PGEs recovery for the Lonmin UG2 P4 ore, value loss to tailings will be minimised, and the economics of operation will improve.

2 LITERATURE REVIEW

2.1 Platinum group elements mining in the Bushveld Complex

Platinum group elements also known as PGEs, are a chemically related group of elements or metals which are found in nature and these are platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru) and osmium (Os). The PGEs possess extraordinary physical and chemical properties such as catalytic properties, and resistance to wear and tarnish. Other properties that characterise PGEs include stable electrical properties, resistance to chemical attack and excellent high-temperature characteristics leading them to be extensively used in industrial applications.

The Bushveld Complex hosts major occurrences of PGEs (Cawthorn, 1999). The Bushveld Complex underlies parts of the North West, Limpopo and Mpumalanga provinces in South Africa. The complex is divided into the western (North West province), eastern (Mpumalanga province) and northern (Limpopo province) limbs (Schouwstra *et al.*, 2000). The Bushveld Complex is a layered intrusion comprising the Rustenburg layered Suite, Rashoop Granophyre Suite, and the Lebowa Granite Suite. The Rustenburg Layered Suite is divided into the Lower Zone comprising ultramafic cumulates of olivine and pyroxene, Critical Zone consisting of a succession of interlayered ultramafics (pyroxenites and anorthosites) and chromititic bands, the Main Zone made of gabbro, and the Upper Zone comprising ferrogabbros and magnetite bands.

PGEs are found in the UG2 reef, Merensky reef and Platreef, all of which are in the Critical Zone (Cawthorn, 1999). The mineralogy of these three reefs varies; the UG2 reef is a chromitite band dominated by chromite, the Merensky reef is a megacrystic pyroxenite layer dominated by pyroxene and some plagioclase (Penberthy and Merkle, 1999; Penberthy *et al.*, 2000; Schouwstra *et al.*, 2000) and Platreef is comprises pyroxenites, serpentinites and calc-silicates (McFadzean *et al.*, 2015).

The UG2 ore is characterised by the high contents of chromite, which can cause detrimental effects in the furnaces. Therefore, it is imperative that the amount of chromite reporting to the concentrate during flotation be minimized for better operations in the downstream processes i.e. smelting (Wesseldijk *et al.*, 1999). Chromite (FeCr_2O_4) is a spinel mineral and has high melting

point. As a result, the smelters have strict specifications regarding the percentage of chromite which can be tolerated from the concentrators (Wesseldijk *et al.*, 1999).

The UG2 is a chromitite layer in the upper critical zone enriched in PGEs. Chromitite is a rock containing chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) with a 40-50 % Cr_2O_3 content as its primary constituent (Hay and Roy, 2010; Muzenda *et al.*, 2011). The chromitite layer extends for nearly the full length of 400 km of the eastern and western limbs of the Bushveld Complex (Mondal and Mathez, 2007). The UG2 chromitite layer also contains an assemblage of platinum group minerals divided into sulphides and non-sulphides, as well as alloys, summaries in Table 2-1. The platinum group minerals in UG2 generally occur as fine grains (average 12 microns) associated with base metal sulphides, silicate gangue and/or chromite grains (Kinloch, 1982; McLaren and De Villers, 1982; Von Gruenewaldt *et al.*, 1986; Penberty *et al.*, 2000). The mineralogy of UG2 is complex, mineral liberation is difficult and consequently it is challenging to extract PGEs from UG2 (Valenta and Mapheto, 2011).

Further understanding of the PGEs can be drawn from various PGEs mining operations, their locations and assays reported from geological data. The annual average production of South African, Zimbabwean and other PGE operations are shown in Table 2-2, and Figure 2-1 shows the map of the PGE mining operations in the Bushveld Complex. Table 2-2 shows the company names and the projects they are involved in, the amount of ore produced per year, and their assays. This project is based on the UG2 ore from Lonmin mine in the Marikana operations.

Table 2-1. PGE assemblage minerals (adapted from O’driscoll and González-Jiménez, 2016)

Platinum group minerals					
Sulphide minerals	Chemical formula	Non-Sulphide minerals	Chemical formula	PGE alloy	Chemical formula
Erlichmanite	OsS_2	Genkinite	$(\text{Pt}, \text{Pd})_4\text{Sb}_3$	Chengdeite	Ir_3Fe
Hollingworthite	$(\text{Rh}, \text{Pt}, \text{Pd})\text{AsS}$	Geversite	$\text{Pt}(\text{Sb}, \text{Bi})_2$	Hongshiite	PtCu

Xingzhongite	$(\text{Pb,Cu,Fe})(\text{Ir,Pt,Rh})_2\text{S}_4$	Stumpflite	$\text{Pt}(\text{Sb,Bi})$	Tetraferroplat inum	PtFe
Laurite	(RuS_2)	Insizwaite	$\text{Pt}(\text{Bi,Sb})_2$	Niggliite	PtSn
Kashinite	$(\text{Ir,Rh})_2\text{S}_3$	Maslovite	PtBiTe	Rustenburgit e	$(\text{Pt,Pd})_3\text{Sn}$
Cuproiridsite	CuIr_2S_4	Oosterboschite	$(\text{Pd,Cu})_7\text{Se}_3$	Isoferroplatin um	Pt_3Fe
Daomanite	CuPtAsS_2	Palladseite	$\text{Pd}_{17}\text{Se}_{15}$	Tulameenite	Pt_2FeCu
Prassoite	$(\text{Rh}_{17}\text{S}_{15})$	Merenskyite	$\text{Pd,Pt}(\text{Te,Bi})_2$	Nielsenite	PdCu_3
Braggite	$(\text{Pt,Pd,Ni})\text{S}$	Kotulskite	$\text{Pd}(\text{Te,Bi})$	Atokite	$(\text{Pd,Pt})_3\text{Sn}$
Bowieite	$(\text{Rh,Ir,Pt})_2\text{S}_3$	Telluropalladinit e	Pd_9Te_4	Cabriite	Pd_2SnCu
Cuprorhodsite	$(\text{CuFe})\text{Rh}_2\text{S}_4$	Palladoarsenide	Pd_2As	Taimyrite	$(\text{Pd,Cu,Pt})_3\text{Sn}$
Cooperite	PtS	Arsenopalladinit e	$\text{Pd}_8(\text{As,Sb})_3$	Paolovite	Pd_2Sn
Malanite	$\text{Cu}(\text{Pt,Ir,Co})_2\text{S}_4$	Palladodymite	$(\text{Pd,Rh})_2\text{As}$	Stannopalladi nite	$(\text{Pd,Cu})_3\text{Sn}_2$
Moncheite	$(\text{Pt,Pd})(\text{Te,Bi})_2$	Sudburyite	$(\text{Pd,Ni})\text{Sb}$		

Maslovite	PtBiTe	Froodite	PdBi ₂
Sperrylite	PtAs ₂	Michenerite	(Pd,Pt)BiTe
Vysotskite	(Pd,Ni,Pt)S	Palladobismutha rsenide	Pd ₂ (As,Bi)
Vasilite	(Pd,Cu) ₁₆ (S,Te) ₇	Plumbopalladini te	Pd ₃ Pb ₂

Mineral resources, such as PGEs, are harvested, but cannot be regrown and are eventually depleted. The PGEs in an ore body may run out, a mine may become unsafe to excavate, or the operations may become costly, causing the mine to close down (i.e. the lifespan of a mine is always finite).

The lifespan for each mine depends on the quantity and quality of the mineral pursued; the health and safety of the public and employees; and the environmental effects. A mine will stay operational until the cost of extraction exceeds the value of what is extracted. For example, in June 2012, Everest and Marikana operations which both belong to Aquarius Platinum were suspended because of the weak platinum prices and high operational cost. Even though at that time Marikana reserves had 10 years' life remaining, during the first quarter of 2012 it was already operating at a loss (South Africa's Mineral Industry, 2012).

It was stated in the Wesizwe website that Bakubung Platinum Mine had its first blast of the mine ventilation shaft in 2012 and that the mine's lifespan will be 30 years (Wesizwe, 2017). Tharisa mine located south-western limb of the Bushveld Complex, is a shallow and open pit PGE and chrome mine, with an estimated 18 years lifespan, and an estimated further 40 years as an underground operation (Tharisa, 2017).

According to the annual Mineral Resource and Mineral Reserve Statement (2016) the two Lonmin sections located in the western limb of Bushveld Complex called Eastern Platinum Limited (EPL) and Western Platinum Limited (WPL) have been permitted to mine the PGEs and

the associated metals and minerals until 2037, but renewable up to 2067 (Lonmin Annual reports and accounts, 2016).

Table 2-2. The annual average production of South African, Zimbabwean and other PGM projects (adapted from Glaister and Mudd, 2010).

Company	Project & mine type	Mt ore/yr	4E g/t	t Pt	t Pd	t Rh	t Au	t PGM^{6E}
AngloPt^{50%-} Bafokeng^{50%}	Bafokeng-Rasemone (UG)	2.518	4.36	5.834	2.393	0.384	0.349	9.359
AngloPt^{100%}	Lebowa (UG)	1.509	4.54	3.112	2.095	0.323	0.176	6.158
AngloPt^{100%}	Potgietersrust (OC)	4.830	3.62	5.670	5.952	0.385	0.630	12.416
AngloPt^{100%}	Amandelbult (UG)	6.602	5.46	18.584	8.504	2.134	0.612	32.974
AngloPt^{100%}	Rustenburg (UG)	11.457	4.26	25.584	12.164	2.810	1.116	44.971
AngloPt^{85%}	Union (UG)	5.717	3.79	9.656	4.307	1.503	0.167	18.020
AngloPt^{100%}	Twickenham (UG)	0.142	4.77	0.259	0.262	0.043	0.008	0.618
AngloPt^{50%-} Xstrata^{37%}	Mototolo JV(UG)	1.314	3.46	1.918	1.133	0.283	0.027	3.850
AquariusPt^{100%}	Everest (UG ^{70.2%})	1.988	2.96	2.539	1.355	0.411	0.039	5.212
AquariusPt^{50%-} AngloPt^{50%}	Kroondal JV(OC ^{93.7%})	4.843	3.62	6.042	2.887	1.056	0.049	15.158
AquariusPt^{50%-}	Marikana	1.490	4.30	1.836	0.787	0.249	0.023	4.149

AngloPt^{50%}	JV(OC ^{77.8%})							
African	Modikwa	2.408	4.11	4.012	3.941	0.821	0.116	-
Rainbow								
Minerals^{41.5%}	JV(OC ^{93.3%})							
AngloPt^{50%}								
African	Two Rivers (UG)	2.205	4.11	2.901	1.662	0.476	0.039	6.074
Rainbow								
Minerals^{55%}								
Impala^{45%}								
Lonmin^{82%}	Marikana	13.237	4.88	25.10	11.31	3.299	0.612	44.109
Incwala^{18%}	(UG ^{87.2%})							
Lonmin^{100%}	Limpopo(UG)	0.608	3.74	-	-	-	-	-
Lonmin^{42.5%}	Pandora	0.523	5.06	-	-	-	-	-
Anglo^{42.5%}	JV(OC ^{62.7%})							
AquariusPt^{50%}	Mimosa	1.406	3.67	2.028	1.512	0.159	0.272	5.010
Impala^{50%}	(UG ^{98.2%})							
Impala^{86.9%}	Zimplats(OC ^{73.4%})	2.059	3.49	2.779	2.315	0.250	-	6.015
Impala^{86.3%}	Impala (UG ^{96%})	15.593	4.84	33.03	15.022	3.839	-	60.059
EastPlat^{85%}	Crocodile	0.844	4.66	1.026	0.455	0.162	0.011	2.021
	River(UG)							
Impala^{73%}	Manila (UG)	1.043	3.88	1.360	1.384	0.285	-	3.573
Northam^{100%}	Northam (UG)	1.993	5.57	6.041	2.880	0.599	0.207	11.009

Norilsk	Stillwater,	1.068	19.39	3.919	13.17	-	-	-
Nickel^{100%}	USA(UG)							
North America	Lac de lles,	4.770	2.17 ^{Pd}	0.666	7.347	-	0.589	-
Palladium^{100%}	Canada(OC)							
	Totals	94.9	4.41	164.1	110.2	19.47	5.63	290.8

^{xyz%} denotes ownership.

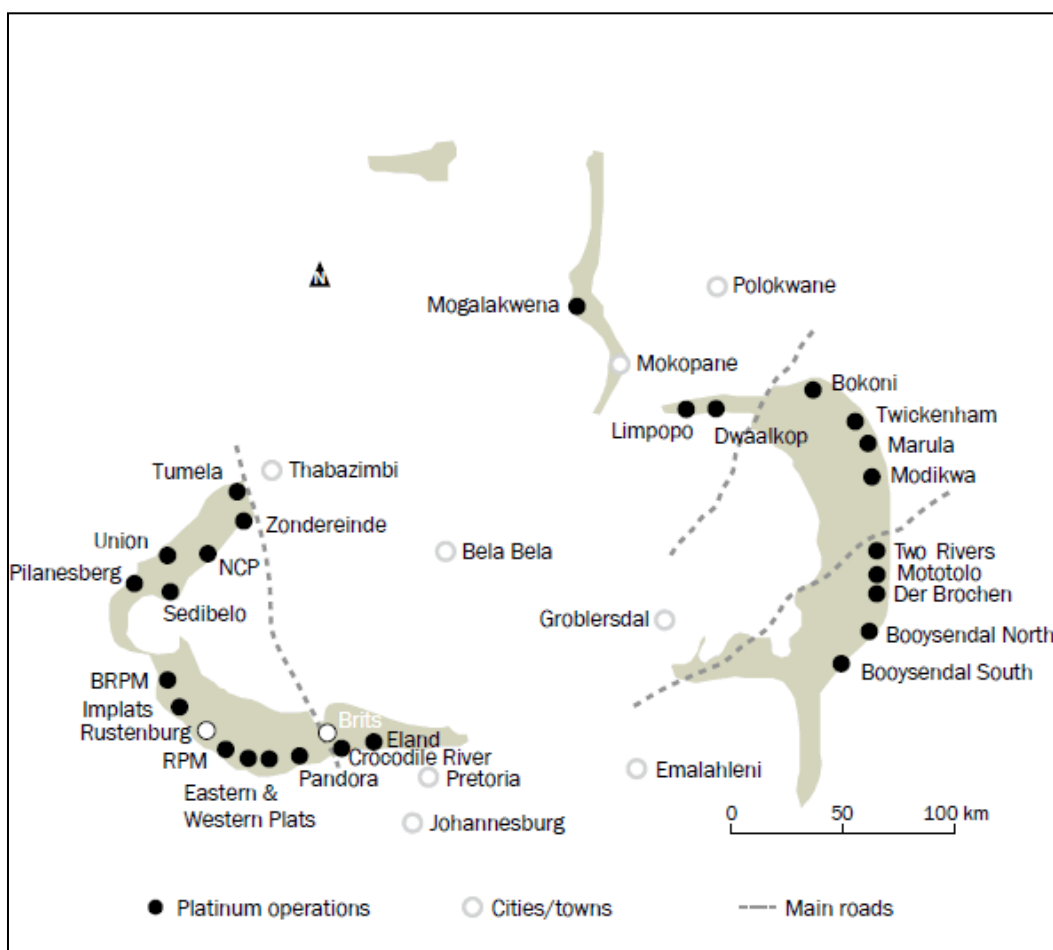


Figure 2-1. The Bushveld Igneous Complex map (www.chamberofmines.org.za)

2.2 Lonmin operation in the western limb of the Bushveld Complex

The Lonmin Marikana operations are made up of Western Platinum Limited and Eastern Platinum Limited. They are located in the Marikana district which is in the eastern side of

Rustenburg in the North West province of South Africa. Four of the primary vertical shaft complexes, namely K3, K4, Saffy and Rowland accounted for the largest portion of the 2015 Mineral Reserves (Lonmin, 2015). On the other hand, Newman, Pandora E3 Joint Venture and W1, Hossy, East 1 (E1) and East 2 (E2) shafts are reaching the end of lives and as a result production has declined. The above mentioned Marikana operation sites are shown in Figure 2-2. Furthermore, Table 2-3 shows the total proved and probable mineral reserves from Lonmin attained in 2016 for further understanding.

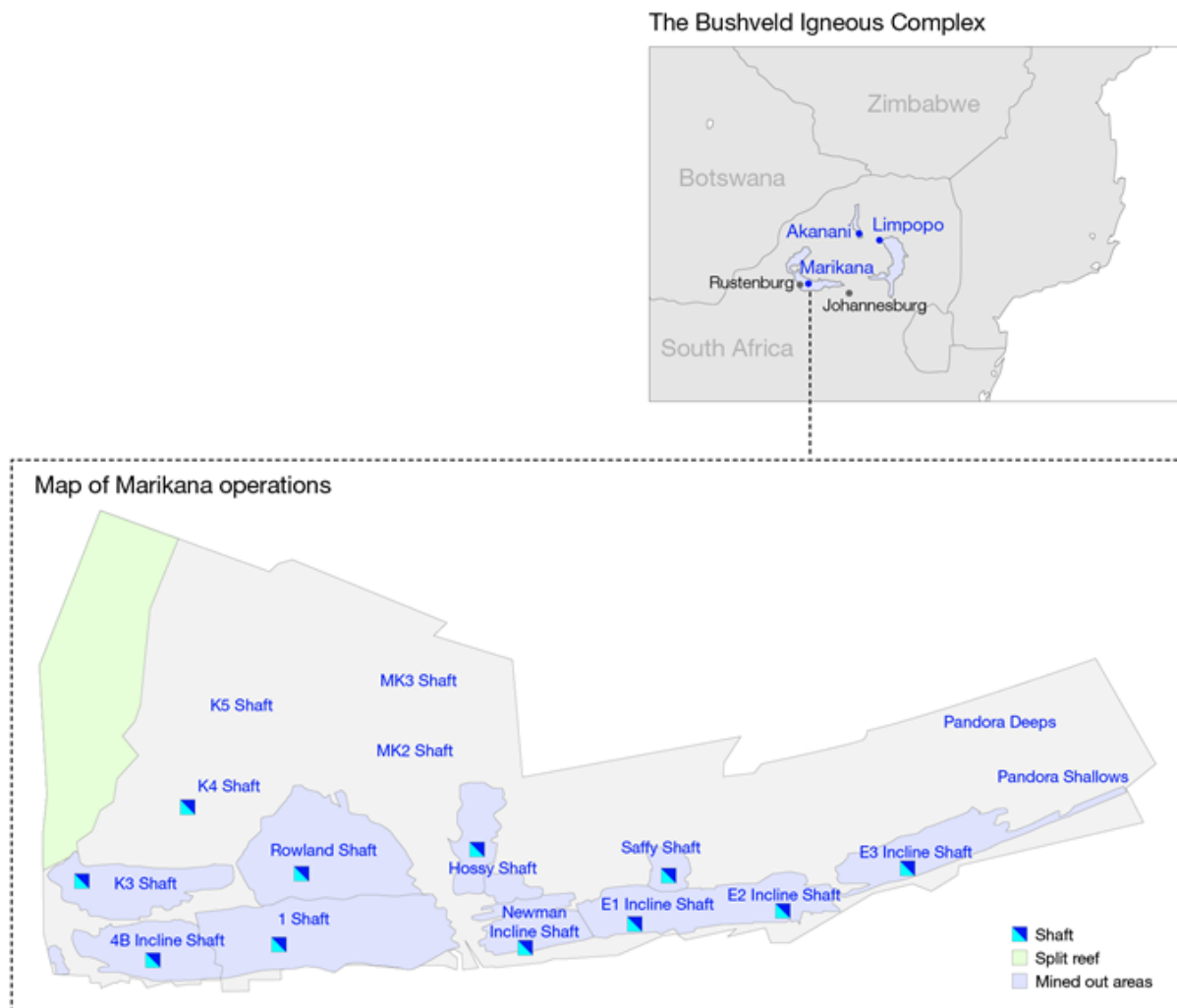


Figure 2-2. Lonmin operations (Lonmin website, accessed 31/08/2016).

Table 2-3. Total proved and probable mineral reserves from Lonmin (adapted from Lonmin Mineral Resource and Mineral Reserves Statement, 2016).

Ore Source	30 September 2016				30 September 2015			
	Mt	3 PGE + Au		Pt	Mt	3 PGE + Au		Pt
		g/t	Moz	Moz	Moz	Moz	Moz	Moz
Marikana	230.9	4.06	30.1	18.3	263.8	4.10	34.7	21.2
Pandora	6.1	4.2	0.8	0.5	6.6	4.09	0.9	0.5
JV								
Tailings dams	21.1	1.10	0.7	0.5	21.2	1.10	0.7	0.5
Total	258.2	3.82	31.7	19.2	291.5	3.88	36.4	22.2
Mineral Reserves								

*Tailings Dams exclude Au, due to assay values below laboratory detection limit, and therefore are reported as 3PGE.

For further discussion in this context, the names of the shafts were changed for confidential reasons. The ore from four different shafts in the Lonmin mine Marikana operation feeds EPL concentrator and the ore from one of the shafts was tested without being mixed with any other ore. These shafts are named P1, P2, P3 and P4 for ethical reasons. Considering the importance of mineralogy, the blending of ores clearly introduces the mineralogical differences as compared to a single shaft ore being fed to a concentrator. At the same time, the P4 ore is also purely treated on its own without being blended with other ores, now this raised the question of the recovery effect. The recovery attained from the EPL (ore blend) concentrator was higher than the recovery of P4 concentrator (single ore). The mineralogical differences between the two feeds may be one of the factors that have contributed towards the differences in the recovery.

Moreover, the reagents have to be taken into consideration because clearly one reagent regime used for a blend of ores can be different to the one used for single ore.

The typical PGEs recovery of the UG2 ore throughout the Bushveld Complex ranges from 75 % to +90 %. There are number of factors which contribute towards the variation of flotation recoveries including the differences in mineralogy, plant capacity and operating philosophy (Valenta, 2007). In this case, mineralogical differences could be the cause of the recovery differences. This theory is based on the fact that EPL concentrator is made up of ores from P1, P2, P3 and P4, while P4 is purely made up of ore from a single shaft, which is P4.

The main beneficiation technique for valuable minerals that is utilised at the Lonmin concentrators is froth flotation. Currently PGEs recovery from P4 UG2 ore is at 82 % while higher recoveries were expected. Therefore, there is interest in identifying the mineralogical peculiarity of the Lonmin P4 UG2 ore responsible for this lower recovery, while it is also necessary to achieve increased recovery through a suitable reagent regime.

2.3 Improving PGEs recovery through froth flotation

2.3.1 The principle of froth flotation

There are various ways to improve the recovery of PGEs. Froth flotation is a commonly used technique for ore beneficiation, and it can be defined as a physico-chemical process that is used for separation of desired valuable minerals from the gangue minerals by utilising the difference in surface properties (Wills and Napier-Munn, 2006).

There are three mechanisms which normally occur during the process of material being recovered by flotation: a) selectivity of attachment to air bubbles (or true flotation); b) Entrainment; and lastly c) Physical entrapment between particles in the froth attached to air bubbles (Wills and Napier-Munn, 2006). The most crucial mechanism is the attachment of the valuable mineral to air bubbles so that the majority of the particles that are represented are recovered to the concentrate. Apart from true flotation being a common mechanism for the recovery of valuable mineral, the separation efficiency between the gangue and valuable mineral is also dependent on the degree of entrainment and entrapment (Wills and Napier-Munn, 2006).

Sometimes particles float to the surface because they are entrained between the air bubbles, and not because they are hydrophobic in nature.

For flotation to take place, attachment of a particle to a bubble should occur with the assistance of chemical reagents and rise to the water surface. This is illustrated by the principle of flotation in a mechanical cell, see Figure 2-3.

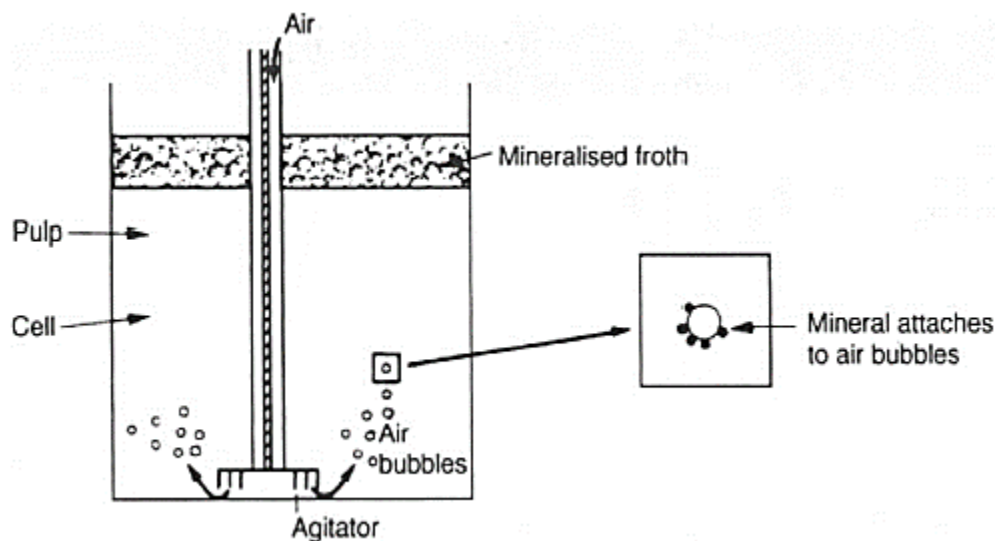


Figure 2-3. Typical principle of froth flotation (adapted from Wills and Napier-Munn, 2006).

The agitator shown in Figure 2-3 is used to provide sufficient turbulence to promote collision between particles and bubbles and to ensure that there is an even distribution of the air bubbles (Wills and Napier-Munn, 2006). Air is introduced at the bottom of the cell, as the air moves up, the hydrophobic particles attach to the upward moving air bubbles and move from the pulp phase through to froth phase where they are collected as concentrate, leaving the hydrophilic particles in the pulp or tailing. The valuable or desirable minerals are rendered hydrophobic by the flotation reagents, although some of them are hydrophobic by nature, so that they attach themselves to the rising air bubble and accumulate in the froth. The non-valuable minerals which are also known as gangue may be hydrophilic and only report to the froth zone by entrainment or entrapment, but sometimes they are hydrophobic by nature and need to be depressed by reagents.

This technique is only applicable to relatively fine particles, because the adhesion between too coarse particles and the bubble will be less than the weight of the particle causing the bubble to

burst before it reaches the froth zone. For successful flotation, there is an optimum size range, usually below 100 μm (Trahar and Warren, 1976; Crawford and Ralston, 1988; Finch and Dobby, 1990; Manono, 2012).

Wills and Napier-Munn (2006) stated that “the activity of a mineral surface in relation to flotation reagents in water depends on the forces which operate on that surface”. Figure 2-4 shows the forces which tend to separate a bubble and a particle. The contact angle is developed between the mineral surface and the bubble surface by tensile forces. At equilibrium,

$$\gamma_{s/a} = \gamma_{s/w} + \gamma_{w/a} \cos\theta \dots\dots\dots \text{Eq. 1}$$

$\gamma_{s/a}$, $\gamma_{s/w}$, and $\gamma_{w/a}$ are the surface energies between the solid and air, solid and water and water and air respectively and θ is angle of contact between the mineral surface and the bubble.

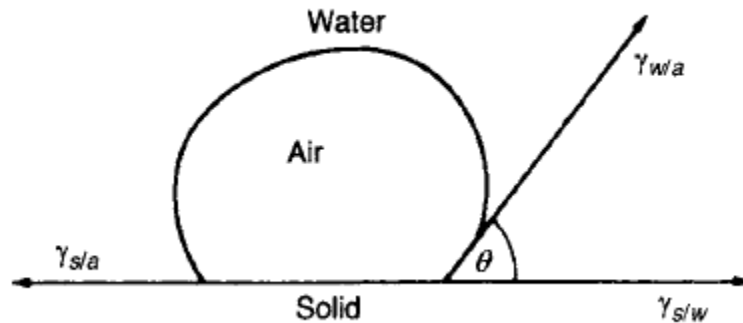


Figure 2-4. Diagram of contact angle between bubble and particle in an aqueous medium (Wills and Napier-Munn, 2006; Chau et al., 2009).

There are three main components of flotation system to be considered for optimal performance of froth flotation namely; chemistry, operational parameters and equipment (Kawatra, 2011). These are summarised in Figure 2-5.

The chemistry component is made up of collectors which impart hydrophobicity on the mineral; frothers which stabilise the froth; and modifiers/regulators are used to control the pH and they can also be used to either activate(activator) or depress(depressant) mineral attachment to air bubbles (Wills and Napier-Munn, 2006).

The operational component addresses the issue of feed rate, mineralogy, particle size, pulp density and temperature. Lastly, the equipment component which comprises of cell design, agitation, air flow, cell bank configuration and cell bank control. Different approaches have been explored and investigated over the years taking into consideration every component of flotation system.

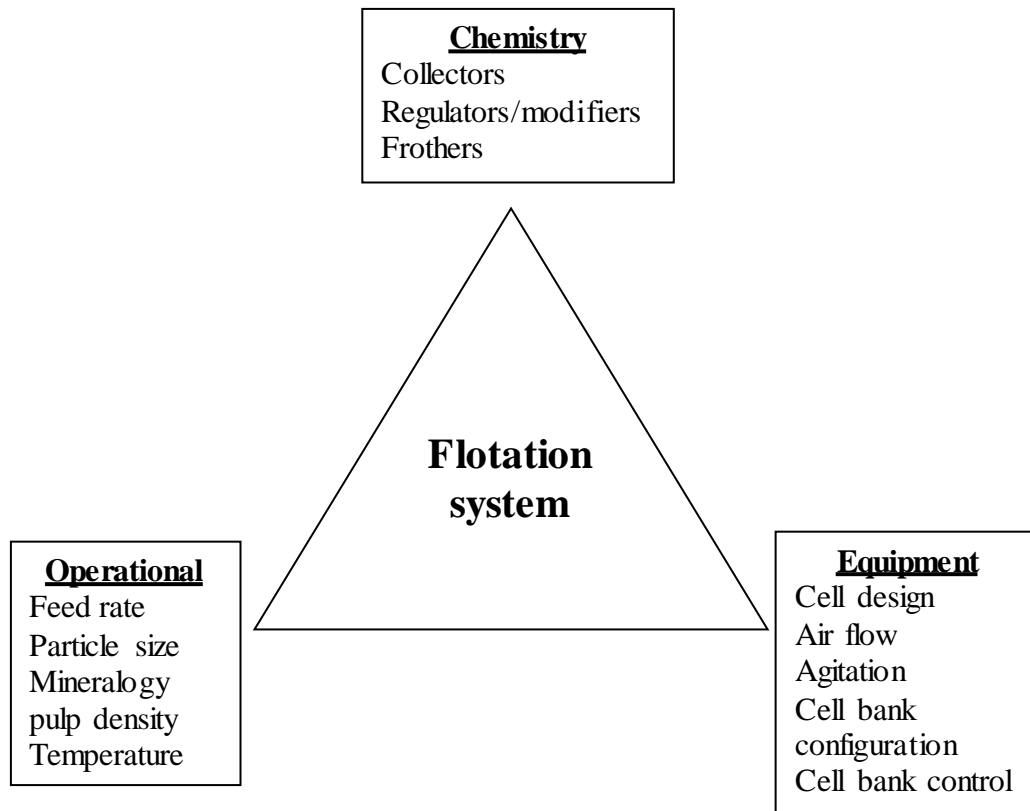


Figure 2-5. Summary of the variables in the flotation system (Klimpel, 1984; Kawatra, 2011)

2.3.2 Approaches used to improve the recovery of PGEs

Ore beneficiation is about understanding and knowing the kind of ore that is being dealt with. It is like cooking a meal; one needs to know and understand the ingredients before cooking. The same analogy applies for the beneficiation of the ore, know and understand the mineralogy otherwise the valuable minerals and desired results may not be achieved, and sometimes this factor may be overlooked.

Van Tonder *et al.* (2010) conducted a study on UG2 ore from four different shafts (Salene, Waterval, Paardekraal and Townlands) by blending them. These authors concluded that factors such as mineralogical hosting of platinum group elements and platinum group minerals, sulphide and discrete platinum group mineral grain size, and silicate and oxide alteration are usually what distinguish the metallurgical behaviour of ores. For example, the UG2 ore mined at the Union mine in Limpopo province will not have the same mineralogical composition as the one mined in Two Rivers in Mpumalanga province.

Van Tonder *et al.* (2010) blended UG2 ores from four different shafts (Salene, Waterval, Paardekraal and Townlands) in order to determine the effect between linear grinding and flotation characteristics, and non-linear effects, i.e. synergistic/antagonistic effect will be displayed. According to the grinding results there was no indication of non-linear grinding characteristics for blends of ores. The binary blends of the Salene ore with other ore types have shown a significant antagonistic effect in flotation results. However, a synergistic effect resulted with the ternary/quaternary blends of ores. The study concluded that when there are large differences in metallurgical properties between the ore types, the blends of platinum ore display non-linear characteristics (Van Tonder *et al.*, 2010).

The environment in which the ore is milled plays an important role as well, and dictates the performance of the ore. The type of material used to mill the ore sample may contaminate it (ore) and affect its floatability. Maksimainen *et al.* (2010) evaluated the effect of grinding environment on two Finnish PGE ores with low sulphur content, namely Ore A ~2.3 % and Ore B ~0.06 %. The grinding atmosphere (CO₂, N₂ and air) and grinding media were the variables which were studied. It was found that mild steel grinding as an alternative to stainless steel or autogenous grinding has the effect of creating a more reducing pulp environment, reducing its dissolved oxygen content. However, it has been reported that flotation performance may be benefited by a slightly reducing environment, especially the low sulphide platinum group mineral ores (Bradshaw *et al.*, 2006). The study showed that PGE grade and recovery in flotation of the ore with 0.06 % sulphide content were improved when grinding in CO₂ atmosphere. The selectivity of platinum was improved as well with the 2.3 % sulphide content ore, but recovery was the same (Maksimainen *et al.*, 2010).

The agitation effect can be looked into together with particle size effect. The floatability of the ore depends on how fine or coarse the particle size is. With the correct particle size greater flotation rates can be achieved, while incorrect size may yield poor flotation results.

The majority of platinum concentrators in South Africa use mechanically agitated flotation cells which operate with high power intensity. This is due to the belief that increasing power intensity is beneficial to flotation of finer particles. Deglon (2005) has illustrated that indeed increasing the power intensity increases the flotation rate of platinum ore, but this was accompanied by the decrease in concentrate grade.

According to Deglon (2005), the benefits of high power intensity on flotation of finer particles are constrained by the effect of other particle. For example, Feng and Aldrich (1999) conducted a study on the sulphide ore from Merensky reef in South Africa where it was found that smaller bubbles were attained with medium sized particles rather than with finer and coarse particles, and as a result higher recovery rates were achieved (Feng and Aldrich, 1999).

There are innumerable studies which were and still are being conducted on the chemistry of flotation. For example, Muzenda *et al.* (2011) conducted a study investigating the effect of pH on the recovery of PGEs and base metal sulphides (BMS) on the UG2 ore from Bushveld complex. The correct pH level among other things is considered vital in order to achieve the desired recovery and grade. The study has shown that a pH of 9 yielded the highest recovery compared to the pH levels of 6, 8, 10 and 11 which were also experimented on. However, the highest grade was not achieved at the same pH level as that of the recovery, but rather at a pH of 6 which is quite acidic since collectors which were used in this study (xanthates) are more stable in alkaline medium (Muzenda *et al.*, 2011).

The correct amount of copper sulphate and depressant added to the flotation of PGEs can improve the recovery. Copper sulphate activates the valuable minerals to facilitate collector-mineral adsorption and promote bubble attachment. Similarly, depressants such as guar gum or carboxyl methylcellulose (CMC) can be used to depress naturally hydrophobic gangue minerals such as talc (Mailula *et al.*, 2003).

In addition to operational and chemistry components which play crucial role in flotation, there is an equipment component. Ramlall and Loveday (2015), using the UG2 ore from the eastern limb of Bushveld Complex compared flotation cell models for recovering minerals and concluded that the best model was the one that considers entrainment. The investigation showed that the modified Kelsall model with entrainment yielded the best results. The indication given by the model is that the floatable platinum group minerals can be demonstrated as a fast and slow floating fraction together with entrainment (Ramlall and Loveday, 2015). These approaches of improving the recovery of PGEs are summarised in Table 2-4.

Table 2-4. Summary of various approaches used to improve the recovery of PGEs.

Operations	Approaches	Recovery improvement achieved	References
UG2 ore from Salene, Waterval, Paardekraal and Townlands shafts.	Blending four UG2 ores	Antagonistic effect for binary blends with Salene, synergistic effect with ternary and quaternary blends.	Van Tonder <i>et al.</i> (2010)
Sulphide poor PGE ores.	Grinding environment.	CO ₂ atm and mild stainless steel improved PGM grade and recovery	Maksimainen <i>et al.</i> (2010)
Merensky and UG2 ores.	Investigating the influence of agitation on flotation.	Agitation increases flotation rate, but decreases concentrate grade.	Deglon (2005).
Sulphide ore from Merensky	Effect of particle size	Medium particles yield smaller bubbles and higher recovery rate.	Feng and Aldrich (1999).

UG2 from Bushveld Complex.	Variation of pH.	pH of 9 gave the highest PGE recovery compared to pHs of 6,8,10 and 11.	Muzenda <i>et al.</i> (2011).
UG2 ore in the Eastern limb of Bushveld Complex.	Varying batch flotation models.	The modified Kelsall model with entrainment is the best.	Ramlall and Loveday (2015).

With all of these studies and more conducted in the PGEs field, Lonmin is no exception. Its operations and ore have been studied over the years, but as it is well known that the mineralogy may change and this may require operational regime to change as well, if not just reagent regime. Considering that EPL ore has been performing well and yielding the desired recovery over the years, and now that P4 ore has been tested on its own and it has shown the undesired results, the major change which has come into the equation is the difference in the ore. Therefore, the mineralogy of the two ores has come into question. Because EPL ore is the blend of P1, P2, P3 and P4 ore, while on the other hand P4 ore is not a blend at all, it is then suspected that the mineralogy is indeed different and it may also be due to the differences in the grinding methods used at the different shafts. The question is, what exactly is or not in EPL ore that is not or is in P4 ore which is leading to the differences in the recovery. Consequently, the mineralogy of the two ores was studied. Furthermore, due to these differences in the ore, the reagent regime was affected and as a result this study focused on blending the collectors in order to improve the recovery.

2.4 Improving PGE flotation via reagent modification

The improvement of recovery and grade through flotation also relies on a suitable reagent regime. With a suitable combination of collectors, frothers and modifiers higher recoveries and grades can be achieved. Moreover, the selection of reagents varies from operation to operation across the reef.

UG2 ore poses quite a challenge for metallurgists during flotation because of its high chromite content. However, different combinations of reagents are used to overcome such challenges and this further includes achieving high PGE recoveries and grades. It is either a modification of collectors, frothers or modifiers (regulators), used in different molar ratios, dosages and blends. This may also be referred to as the chemistry of the reagents.

The chemistry component includes the utilisation of different chemical reagents. The optimisation of the reagent regime is crucial because the recovery and grade of the valuable minerals highly depends on it. As mentioned earlier, the reagents are made up of: collectors, which adsorb on the mineral surfaces making them hydrophobic so that they attach to and float with bubbles; frothers which stabilise the froth; and modifiers/regulators are used to control the pH and they can also be used to either activate (activator) or depress (depressant) mineral attachment to air bubbles (Wills and Napier-Munn, 2006).

2.4.1 The effect of frothers on froth flotation

The purpose of frother is to stabilize froth during flotation (Wills and Napier-Munn, 2006). Frothers lower the surface tension of water and possess the ability to adsorb on the air bubble–water interface. The film strength of the air bubbles is increased by the presence of frothers in the liquid phase, therefore providing better attachment of hydrophobic particles to the bubbles (Bulatovic, 2007). It has been found that by increasing frother dosage, low mass pulls and PGM + Au recovery can be improved (Wiese *et al.*, 2010; Valenta, 2007). Furthermore it was found that with an increase in frother dosage water recovery was increased, which lead to an increase in the mass reporting to the concentrate (Wiese *et al.*, 2010). This improvement in recovery was due to an increase in solids recovery through entrainment (Valenta and Harris, 1999). Entrainment can however be detrimental to the concentrate grade.

2.4.2 The effect of modifiers on froth flotation

The modifiers are also known as regulators and are divided into three groups which are: activators, depressants and pH regulators. The major function of these reagents is to modify the chemical nature of the mineral surfaces and as a result govern the selectivity of the flotation

system (Wills and Napier-Munn, 2006; Bulatovic, 2007). The collector tends to adsorb only on the targeted particles for recovery in the presence of regulators (Bulatovic, 2007).

2.4.2.1 The effect of activators on froth flotation

Activators react directly with the surface of the mineral (e.g. copper sulphate with sphalerite) and as a result provide conditions for interaction of this mineral with the collector (Bulatovic, 2007). The commonly used activator in the PGEs ores is copper sulphate. Care should be taken when using the activator though. For example, the main gangue constituent found in the UG2 ore is chromite, which is naturally hydrophilic and this is a good thing considering that the smelters have low tolerance of it (chromite), but Mailula *et al.* (2003) has found that high dosages of copper sulphate activates chromite while low dosages of copper sulphate does not activate the chromite.

2.4.2.2 The effect of depressants on froth flotation

Depressants can be briefly defined as modifiers that prevent an adsorption of a collector onto a mineral. They also increase selectivity by rendering unwanted gangue minerals hydrophilic (Kawatra, 2011). There are different types of depressants that are used for each ore type, and it should be noted that just because a reagent is a depressant for one mineral/collector combination, it does not necessarily mean that it is a depressant for the other combinations (Kawatra, 2011).

Norilose 8058 is a depressant manufactured by Senmin International that was used in this project and it is carboxymethyl cellulose (CMC). Wiese *et al.* (2010) stated that the CMC molecule possesses a high negative charge density and that the adsorption of CMC at high concentrations results in a strong negative charge on the particles causing significant dispersion.

2.4.2.3 The effect of pH on froth flotation

The pH modifiers change the concentration of the hydrogen ion in the pulp in order to regulate the ionic composition of the pulp. As a result the collector interaction is improved with the selected mineral and collector interaction with unwanted minerals is reduced (Bulatovic, 2007). Wills and Napier-Munn (2006) mentioned that, where possible, flotation is carried out in an alkaline medium because collectors like xanthates are stable under these conditions. Lime, sodium hydroxide or ammonia is commonly used to maintain the alkalinity of the pulp. On the

other hand, the addition of sulphuric acid or sulphurous acid is used for lowering the pH (Muzenda, 2011).

2.4.3 Collector types

Since the collectors have to impart hydrophobicity onto the mineral of interest, they are added to the pulp and allowed some conditioning time during agitation for adsorption (Wills and Napier-Munn, 2006). Wills and Napier-Munn (2006) states that collector molecules may be divided into two compounds which are: ionising compounds, they dissociate into ions in water; and non-ionising compounds which are insoluble and they cover the mineral surface with a thin film therefore rendering it (mineral) water-repellent. This research focused specifically on thiol collectors. Figure 2-6 shows the collectors according to their classification.

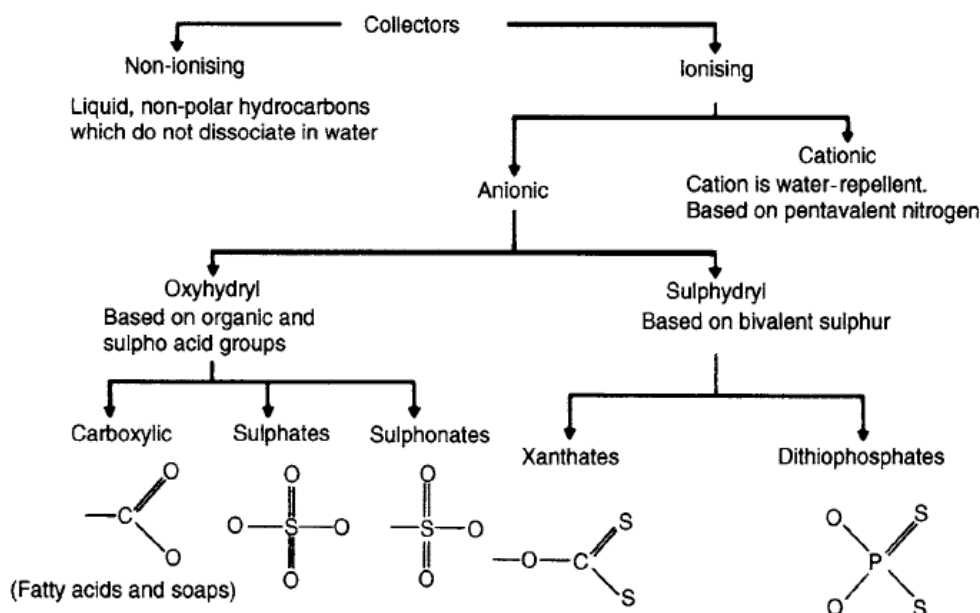


Figure 2-6. Classification of collectors (adapted from Glemboskii et al., 1972)

Thiol collectors have been around for over 100 years and they are still relevant in the froth flotation industry. They can be defined as compounds containing a –SH group in combination with an organic radical (Bulatovic, 2007), and they play a significant role during flotation of valuable minerals. Thiol collectors, which are also known as sulphydriyl collectors, are widely renowned for being selective and powerful in the flotation of sulphide minerals (Wills and Napier-Munn, 2006). The typical thiol collectors and their molecule structures are illustrated in Figure 2-7.

The different molecule structures of the collectors are shown in Figure 2-7 and the behaviour of the donor oxygen (O), nitrogen (N) and phosphorus (P) atoms contributes towards the different behaviours of the collectors (Nagaraj *et al.*, 1988). The bonding to the mineral surface and the interaction with water is affected by the electronegativity of these elements (O, N and P) according to Pauling scale. The electronegativity decreases in the following order:

$$\text{O (3.5)} > \text{N (3.07)} > \text{P (2.06)}$$

Oxygen is the most polar atom of the three. It has a lone pair of electrons and, as a result, it has a tendency of giving away or donating electrons while nitrogen tends to accept electrons. Therefore, the presence of oxygen in the xanthate and dithiophosphate molecules provide strong electron withdrawing effects (Bradshaw, 1997). This property, in conjunction with the phosphorus which is more electropositive than the carbon in the xanthate, leads to dithiophosphates being stronger acids and more selective, but weaker collector (Nagaraj *et al.*, 1988).

With regards to dithiocarbamate, nitrogen is less electronegative than oxygen and it is more likely to give away electrons, bringing about a stronger but less selective collector (Bhaskar Raju and Forsling, 1991). In summary, the collector strength and selectivity towards the sulphide minerals can be listed in the following orders (Bradshaw, 1997), where DTC = dithiocarbamate, X = xanthate and DTP = dithiophosphate:

Collector Strength DTC > X > DTP

Selectivity DTP > X > DTC

This comparison applies when or if metal-thiolate forms on the mineral surface, although, oxidation of the collector may occur which would change the relationship. The dithiocarbamate and dithiophosphate have advantage over xanthate because they have the potential of an additional alkyl group in the structure, which contributes towards greater hydrophobicity. This comparison would be applicable for the collectors forming metal-thiolate, but may not in the case of the xanthate forming the dithiolate (Bradshaw, 1997).

The lower collecting strength of short chain collectors like dithiophosphates is usually compensated for by increasing their dosage, and there is optimum dosage for each system. However, too high a dosage is detrimental (Sutherland and Wark, 1955).

Xanthate, dithiocarbamate and thionocarbamates were the selected collectors for this study. Xanthate was used as a primary collector, while dithiocarbamate and thionocarbamates were used as secondary collectors, also called co-collectors.

Xanthates, dithiocarbamates and thionocarbamates are the commonly used collectors, and they are at times modified to improve the overall performance (Bulatovic, 2007). The adsorption mechanisms of these reagents are reviewed further.

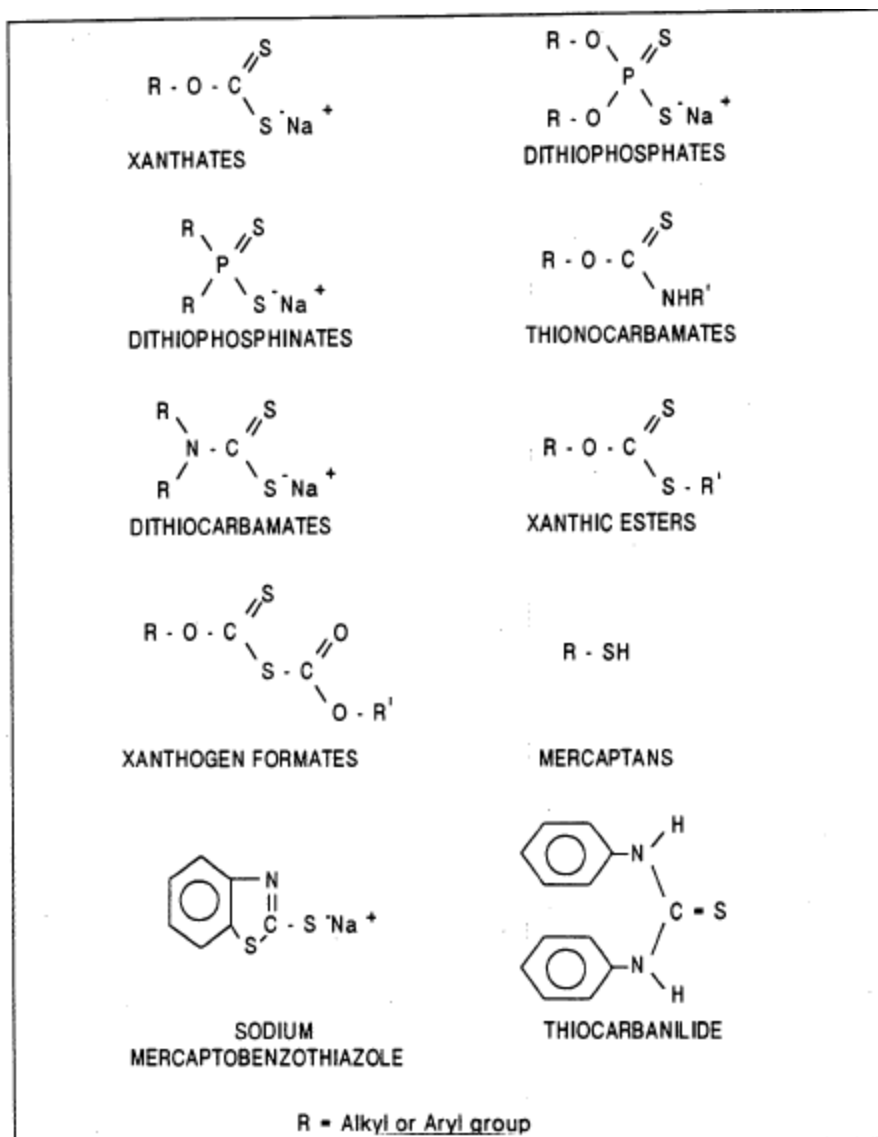


Figure 2-7. Typical examples of thiol collectors and their molecule structure (Adapted from Adkins and Pearse, 1992).

2.4.3.1 Xanthates collectors and their adsorption mechanism

Xanthates are commonly used thiol collectors for sulphide minerals because of their availability and cost effectiveness compared to other classes of collectors (Ngobeni, 2013). Xanthate hydrolyses and forms unstable xanthic acids in the presence of moisture; it further decomposes into carbon disulphide and alcohol, as shown in equation 2 (Bulatovic, 2007; Fuerstenau, 1982a).



In solution, xanthate decomposition increases with a decrease in pH, and xanthates are stable in alkaline media (Bulatovic, 2007; Wills and Napier-Munn, 2006). The length of the carbon radical determines the dissociation of xanthates in an acid medium, and xanthates with a shorter hydrocarbon radical dissociate faster than those with longer carbon chains (Bulatovic, 2007; Fuerstenau, 1982b). Furthermore, xanthates possess intermediate selectivity and collecting power (Ngobeni, 2013).

Sodium or potassium is used as cation in the xanthates structure. It is also known that xanthates adsorb on sulphide mineral surface because of the chemical interactions between the surface and the polar group, consequently resulting in insoluble metal xanthates, which are strongly hydrophobic (Wills and Napier-Munn, 2006). The xanthate used in this study was sodium n-propyl xanthate (SNPX).

According to Ngobeni (2013), the flotation of various minerals with xanthate type of collectors depends on the surface products formed on the mineral surfaces by the collectors. Some minerals are floated by the formation of metal-thiolates, while others are floated by the formation of dixanthogens on the mineral surfaces. For example; sulphide minerals such as bornite and pentlandite are floated by the formation of metal-xanthate, and minerals such as chalcopyrite, pyrite, pyrrhotite and covellite are floated by the formation of dixanthogens (Hangone *et al.*, 2005; Lotter and Bradshaw, 2010).

Depending on the redox condition of the pulp, xanthates can form two surface products. This is the reason pH is considered important when using xanthate collectors, and it is therefore crucial to control the pH based on the mineral to be floated. Commonly, xanthates form dixanthogens in acidic pulps, and metal-xanthate in alkaline pulps (Fuerstenau, 1978).

The mechanism of xanthate adsorption is made up of two-step process i.e. a catalytic oxidation step followed by a chemical adsorption step. In catalytic oxidation, electrons are donated to the mineral by a collector molecule and adsorbed onto the mineral surface. The electron transfer between the collectors and the mineral surface is called electron deposition. The transferred electrons then move to an oxygen rich spot on the surface and reacts with oxygen. The mineral acts as the catalyst in the catalytic stage (Crozier, 1991; Ngobeni, 2013). In the final stage, which is called chemical adsorption, the mineral surface and the collector bond chemically by sharing of electrons between the sulphur atoms on both the mineral surface and the collector molecule.

The bond between the mineral surface and the collector is between the sulphur atom on the mineral and sulphur atom on the collector (Cozier, 1991; Ngobeni, 2013). The two reactions below show possible surface reactions between mineral surfaces and xanthate molecules. Equation 3 demonstrates the formation of dixanthogens, while the equation 4 shows the formation of metal-thiolate, where M is heavy metal:



2.4.3.2 *Dithiocarbamate collectors and their adsorption mechanism*

Dithiocarbamates have similar properties to xanthates, but are more expensive, hence they are used as secondary collectors. They are stable over wide range of pH (from pH 5–12) and can achieve flotation rates which are faster than xanthates (Bulatovic, 2007; Ngobeni and Hangone, 2013). Dithiocarbamate is a product of reacting carbon disulphide and amine (R-NH₂). The lower solubility of the dithiocarbamate salts attributes to faster adsorption of the dithiocarbamates on to the mineral surface compared to xanthate, hence the faster flotation rates (Sutherland and Wark, 1955). Furthermore, dithiocarbamates are more effective at lower dosages than xanthates at higher critical pH (Bradshaw, 1997).

Unlike xanthate collectors, the dithiocarbamate collectors consist of one adsorption mechanism, which is the formation of metal-thiolate bond. The metal-thiolate bond formed by dithiocarbamate is stable across a wide range of redox potential (Lotter and Bradshaw, 2010; Ngobeni, 2013). The equation 5 illustrates the reaction between the metal and dithiocarbamate:



2.4.3.3 *Thionocarbamate collectors and their adsorption mechanism*

Thionocarbamates belong to the family of xanthates and dialkyldithiocarbamates, due to the similarity of the surface coordinating solidophilic groups in these compounds. They are selective and good collectors for copper sulphides, but exhibit weak collective capability. Previous work done has shown that this is due to the presence of the amino group (NH) (Figure 2-7) and the frothing properties also depends on the alkyl chain lengths (Sheridan et al., 2002).

They are stable in acid media down to a pH of 4 (Ackerman *et al.*, 1984; Jiwu *et al.*, 1984; Wills and Napier-Munn, 2006). The thionocarbamates have an outstanding selectivity against pyrite and pyrrhotite (Nagaraj, 1988; Liu, 2004).

The thionocarbamates are colourless to dark brown in colour, and they are insoluble in liquids. In certain petroleum sulphonates they can be dispersed and as a result they form a white milky liquid (Bulatovic, 2007). The performance of these collectors relies heavily on the purity of the reagent. When these reagents contain impurities they produce voluminous froth and are non-selective. The thionocarbamates used for this study were two S-alkyl-N-butyl thionocarbamates (ABTC) at two different concentrations, and two O-Isopropyl-N-Ethyl thionocarbamates (IPETC) at two different concentrations. The general molecular structure of thionocarbamate is shown in Figure 2-8.

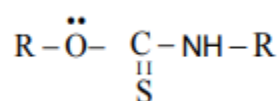


Figure 2-8. The general molecular structure of thionocarbamates.

Thionocarbamates are described as effective collectors for all types of copper mineralisation and zinc that offer improved selectivity over pyrite. Apart from the kind of ores IPETC should be used on, there are various studies which have been conducted on the interaction of dialkyl thionocarbamates with Cu metal, Cu sulphide minerals and pyrite, but the extent of adsorption, the collector species adsorbed and the mechanism of their adsorption are not yet understood (Buckley *et al.*, 2003). The adsorption mechanism of IPETC is still uncertain, despite research efforts. According to an infrared (IR) spectroscopic study IPETC, its Cu salt, and its interaction with chalcopyrite and a Cu metal film, it was concluded that the thionocarbamate attached to the surface of a Cu film in an ionic form but by ‘chemisorption’ in molecular form to the surface of chalcopyrite (Bogdanov *et al.*, 1976; Buckley *et al.*, 2003; Buckley *et al.*, 2014).

The adsorption of thionocarbamates on the sulphide minerals is faster than the adsorption of the xanthate (Fairthorne *et al.*, 1997). Glembotskii (1977) stated that the electron density at the reactive centre of the molecule was proportional to the collecting power of thionocarbamates through applying Pearson’s hard and soft acid-base theory (Pearson, 1963). As a result, collector

performance was improved by electron-donating substituents due to increasing electron density, while electron accepting substituents had the reverse effect.

Oxidation of the collector will take place if the redox potential of the system is higher than oxidation potential of the thiolate to the dithiolate (Finkelstein and Poling, 1977), namely, for xanthates:



Moreover, Fairthorne *et al.*, (1997) conducted a study on increasing flotation of the sulphide minerals, galena, chalcopyrite and pyrite by determining the ability of O-isopropyl-N-ethyl thionocarbamate (IPETC), O-isobutyl-N-ethoxycarbonyl thionocarbamate (IBECTC) and butyl ethoxycarbonyl thiourea (BECTU) collectors. For all these collectors, flotation rate constant, the flotation characteristics of these minerals and maximum flotation recovery, were calculated from the data acquired and compared as a function of pH and collector concentration. The overall results showed that the flotation performance of these collectors was stronger for chalcopyrite than for galena and pyrite (Fairthorne *et al.*, 1997). Flotation increases with collector concentration and decreasing pH values. For chalcopyrite, BECTU has indicated a slightly better collector performances compared to IPETC, but more superior to those of IBECTC, particularly at low collector concentrations or at high pH values (Fairthorne *et al.*, 1997). By blending some of these collectors with the primary collector may lead to even more improved flotation performance.

2.4.4 The effect of collector alkyl group

The behaviour of the collector is affected by alkyl. The stability of xanthates in solution was affected by the alkyl group of the xanthate and the stability increased in the following order (Harris, 1984):



The concentration of the collector needed for effective flotation and the solubility of the metal salt formed decreases with an increase in alkyl chain length (Taggart, 1945; Kakovsky, 1957).

Ackerman *et al.* (1984) studied the effect of different alkyl substituents on the performance of thionocarbamates and it was found that the collecting power increases with the number of carbon

atoms in the alkyl groups. Moreover, it was suggested that the presence of O-alkyl and N-alkyl substituents in the traditional dialkyl class of thionocarbamates, influenced hydrophobicity and steric accessibility, respectively (Ackerman *et al.*, 1984). These collectors chemically interact with copper in solution or on the surface of copper sulphide minerals forming more stable complexes than xanthate collectors (Basilio, 1989; Yoon and Basilio, 1993).

There are different chain structures used to alter the behaviour of a collector, and these may increase or decrease the recovery. By using a collector with a longer hydrocarbon chain the flotation limit may be extended without loss of selectivity, thus bringing about greater water repulsion without increasing the concentration of shorter chain collectors (Wills and Napier-Munn, 2006). On the other hand, chain length is commonly limited to two to five carbon atoms. Since the solubility of a collector in water reduces quickly with increasing chain length even though there is a corresponding decreases in solubility of the collector products and for chemisorption to occur on the mineral surface it is necessary for the collector to ionise in water (Wills and Napier-Munn, 2006).

It is not only the chain length but also the structure of the chain affects solubility and adsorption (Smith, 1989); straight chains have lower solubility than branched chains.

Kim *et al.* (2000) looked into the characteristics of xanthate with relation to its hydrocarbon chain length. A calculation for the free energy associated with one $-\text{CH}_2$ group in the homologous group of xanthates was done based on the standard redox potential of dioxanthogen/xanthate (X_2/X)- couple and solubility products of transient metal xanthates. It was established that the estimated free energy was 690-920 cal and 799-824 cal, respectively, and it was in good agreement with that for various homologues (Kim *et al.*, 2000).

2.4.5 Collector blends

Collectors can be used either as a single reagent or in a mixed system. Glembotskii (1958), Lotter and Bradshaw (2010), and Ngoben and Hangone (2013) have proven that it is beneficial to blend or mix collectors. These benefits included faster kinetics, increased carrying capacity of the froth phase, and recovery of middling and coarse particles (Lotter and Bradshaw, 2010). It has been found that the summation of different collectors enhanced the flotation performance compared to a single collector (Bradshaw, 1997).

Numerous tests have been done in the past and are still continuing to be conducted on the collector blends. The chemical reaction that takes place when two collectors are blended may improve the flotation performance. Sometimes, as in this case specifically with the UG ores, collectors may be blended to achieve higher recoveries and grades with low chromite content.

It is hoped that better results will be achieved through the synergistic effect brought upon by the blends of two or more collectors. However, this does not necessarily mean that by blending two or more collectors' higher recoveries or grades would be achieved, sometimes the opposite occurs and in that case it will not be recommended to use two or more collectors, but to rather use a single collector system.

The blending of collectors may be of either the same functional group i.e. xanthate with another xanthate, or dithiophosphate with another dithiophosphate or different functional group i.e. xanthate with dithiophosphate (Ngobeni, 2013). Many studies have mentioned that by blending collectors higher recoveries and higher grades may be achieved (Glembotskii, 1958; Lotter and Bradshaw, 2010; Ngobeni and Hangone (2013). The performances may be due to either synergistic effect between the collectors in the blend or a linear summation of constituents' characteristics (Bradshaw and O'Connor, 1994; Zhang and Somasundaran, 2006).

Ethyl xanthate and amyl xanthate combination and xanthates and diethyl dithiophosphate combinations were investigated in the mass ratios of 2:1 for the flotation of arsenopyrite and galena (Plaskin *et al.*, 1954). The results showed an improvement that was greater than a summation of the properties of the pure constituent collectors especially for the recovery of coarse fraction (100-150 μm). In all cases the mixtures of collectors improved the kinetics of the recovery. The improved flotation performance attained with the use of blended/mixed collectors was attributed to the better adsorption characteristics on the inhomogeneous mineral surfaces (Bradshaw, 1997; Makanza *et al.* (2008).

Synergistic effect is the surface phenomenon where by two or more collectors interact with each other in a blend/mixture to ensure that the performance of flotation is greater than the sum of the individual collectors in the blend/mixture (Ngobeni, 2013). This phenomenon is complex because it depends on the chemical nature and adsorption properties of the constituents in the blend (Zhang and Somasundaran, 2006; Ngobeni, 2013). Furthermore, it is believed that synergistic effect is more prominent at lower dosages and it depends on both the ratio and the

structure of the collector constituents (Bradshaw, 1997; Zhang and Somasundaran, 2006; Ngobeni, 2013). The linear summation is a linear addition of the input of each constituent in the blend.

2.4.5.1 *The adsorption mechanisms in the collector blends*

The dominant mechanism between thiol collectors and sulphide mineral surfaces is chemical adsorption (Buckley *et al.*, 2003; Ngobeni, 2013). Xanthate collectors adsorb onto the mineral surface by means of charge transfer, and dithiocarbamates adsorb through the formation of metal-thiolate. Thionocarbamates' adsorption mechanism remains unresolved. When two or more collectors are blended, improved adsorption characteristics may be achieved as the blend may possess the adsorption characteristics of both collectors (Bradshaw, 1997; Makanza *et al.*, 2008; Ngobeni, 2013).

The concept of co-adsorption describes an instance whereby one collector in the blend chemically adsorbs onto the mineral surface. In turn a site on the mineral surface is then created by the adsorbed collector for easy adsorption of the second collector. The overall hydrophobicity of the mineral surface is therefore improved by this process (Mellgren, 1966; Makanza, 2008; Ngobeni, 2013).

Based on this information, the synergistic enhancement of the performance of flotation experienced is due to improved adsorption characteristics of the blended collectors on the mineral surface as compared to those of the pure collectors (Bradshaw, 1997). Plaskin and Zaitseva (1960) proposed that different collectors form a more evenly dispersed surface film than the pure collectors. It was also found that chemisorbed collector species were more evenly distributed on the mineral surface compared to physisorbed species (Woods, 1994). A blend may bring about a balance of better distributed and more strongly held chemisorbed species, and more hydrophobic neutral physisorbed dithiolates, and this could result in the formation of a multilayer surface product that is more strongly attached to the mineral surface (Bradshaw, 1997).

2.4.6 Collector dosages

Deciding on the dosage of collectors, or any reagent is as important as selecting the correct collectors. Thorough research has to be done to determine the dosage. This may include long

hours conducting experiments, testing different dosages, together with the other reagents such as activators, depressants and frothers so that a suitable reagent suite is achieved. Furthermore, the mineralogy of the ore should be well understood in order to determine the suitable reagent suite and also for the reagents to be effective and efficient.

Wiese et al. (2005) further show the effect of blending reagents and the dosages on the flotation rate. Wiese *et al.* (2005) have used three different reagent suites on the Merensky reef ore which were sampled at two different parts of the reef in the Bushveld complex. The ores were labelled: ore A which was characterised by significantly higher sulphur content; and ore B which had lower sulphur content compared to ore A. The tests were conducted using the reagents suites shown in Table 2-5.

For both ores there was significant increase for water recovered using “SIBX/DTP, CU” reagent suite than with the other two suites. The mass of solids between the two ores showed the significant difference, and ore B obtained almost double the mass of concentrate compared to ore A. The mass material reported to the concentrate via entrainment and true flotation.

Changing the reagent suite did not have much influence on the copper recoveries and the addition of copper sulphate did not enhance the recovery either as it was expected. The change in reagent suite did not show much influence on the recovery of copper as is normally expected, the addition of copper sulphate did not enhance the recovery at all. The lower grades of copper and nickel were achieved using ore B, where greater masses of solids were recovered. This was also consistent with the increase in the amount of naturally hydrophobic gangue present in ore B (Wiese et al., 2004).

Table 2-5. Reagent suites used to evaluate the flotation performance of two Merensky ores.

Reagent suite	Reagents	Dosages (g/t)
SIBX/DTP/CU	CuSO ₄	40
	SIBX/DTP	37.5/37.5
	CuSO ₄	40
	KU 47	100
	Dow 200	40

SNPX/CU	CuSO ₄	40
	SNPX	150
	CuSO ₄	40
	Depramin 267	100
	Dow 200	40
SIBX/DTP	SIBX/DTP	40/40
	KU 9	100
	Dow 250	40

On a different type of an ore, the blending of collector continues to show effects. Makanza *et al.*, (2007) mixed trithiocarbonate and SIBX in the flotation of auriferous pyrite. It was found that flotation responses of gold and uranium were improved by the mixture of the two collectors than by SIBX alone, but this had no effect on sulphur recoveries. Based on the mineralogical analysis of flotation concentrates, gold and uranium were also hosted by kerogen. As a result, the improved recoveries were proposed to be due to higher kerogen rather than synergism pyrite flotation.

Addition of sodium di-ethyldithiophosphate (DTP), which is used as a co-collector, to sodium isobutyl xanthate (SIBX) in the platinum group mineral (PGM) flotation was done to investigate a synergistic effect of the mixture (Bulatovic, 2003). Various flotation tests were conducted using single collectors as well as numerous mixtures of the collectors at different but constant total molar concentrations. Furthermore, the concentrates were analysed size-by-size in all cases. After all these tests were conducted, the results showed that there was no conclusive evidence of a synergistic effect when utilising mixtures (Bulatovic, 2003). However, the DTP increased the recovery of fine particles (<25µm) and this was due to its effect on the behaviour of the froth phase. As a result, Bulatovic (2003) concluded that effect of DTP stabilised the froth phase and that this was not a result of any synergistic interaction between the SIBX and DTP, but rather a parallel reaction.

Improving the recovery of the Lonmin ore was investigated using the following collectors: SNPX, DTC, ABTC and IPETC. These collectors were selected because of their good interaction with sulphide minerals and base metal sulphides, and these minerals are associated with PGEs.

They are also powerful and selective collectors for the mentioned minerals, especially when xanthates are blended with dithiocarbamates or thionocarbamates. The mineralogical differences between the two ores were also established.

3 RESEARCH METHODOLOGY

3.1 The sample preparation

3.1.1 Ore Sampling

The P4 and EPL UG2 ores were delivered to Senmin International facilities each weighing 1 ton. The ores were crushed to 2 mm particle size separated into smaller portions and each bag weighed 2 kg.

3.1.2 Particle size distribution

In order to successfully perform flotation the size of the particles should be known and be suitable. The particle size distribution was conducted using the sieves of different sizes and a screen shaker. First, a rotary splitter (Figure 3-1) was properly cleaned, that is; the feeder, the rotating table and the cups. The inspection was conducted to verify that the splitter is working by turning the rotating table and the vibrating feeder on for 1 minute and they were stopped. After completing the cleaning and inspection, the rotary splitter was turned on and 2 kg sample was poured into a splitter to split sample into 8 equal masses of 250 g.

As the rotary splitter was busy, 10 sieves and a receiving pan (Figure 3-1) were selected and stacked in a descending order using the $\sqrt{2}$ rule with the top size of 2000 μm , afterwards the sieves were placed on a sieve shaker. When the sample was finished in the feeder the rotary splitter was turned off and the cups were taken out to weigh the sample on the scale and verify the masses. The 250 g mass of P4 UG2 ore was weighed on a balanced laboratory scale and poured on top of the stack of sieves. The top sieve was closed with a lid and properly sealed with sieve knots so that the sample does not spill during shaking.

The sieve shaker was then plugged on the socket on the wall, the timer was adjusted to 10 minutes and the sieve shaker was switched on. After 10 minutes period had lapsed the sieve shaker was stopped, the sieve knots were untied and the sieves were removed from the shaker. The mass of sample left on each sieve was weighed and recorded. Due to different sizes and shapes of the particles, some particles got stuck between the meshes of the sieves and this contributed towards mass loss. The rotary splitter and the sieves were then cleaned.



Figure 3-1. Rotary splitter and sieves on the sieve shaker.

This procedure was conducted on P4 and EPL ore. Figure 3-2 shows the cumulative mass percentage versus particle size. The figure shows that 75 % of particles reported to the 355 μm and lower sieves.

3.1.3 Milling curve generation

A milling curve was generated in order to determine the time the mill would take to achieve particle size of 75 % passing 75 μm . The 2kg samples were milled at three different times which were 30, 45 and 65 minutes. A stainless steel mill and rods were used. The rods weighed 13 kg and their sizes are shown below in Table 3-1.

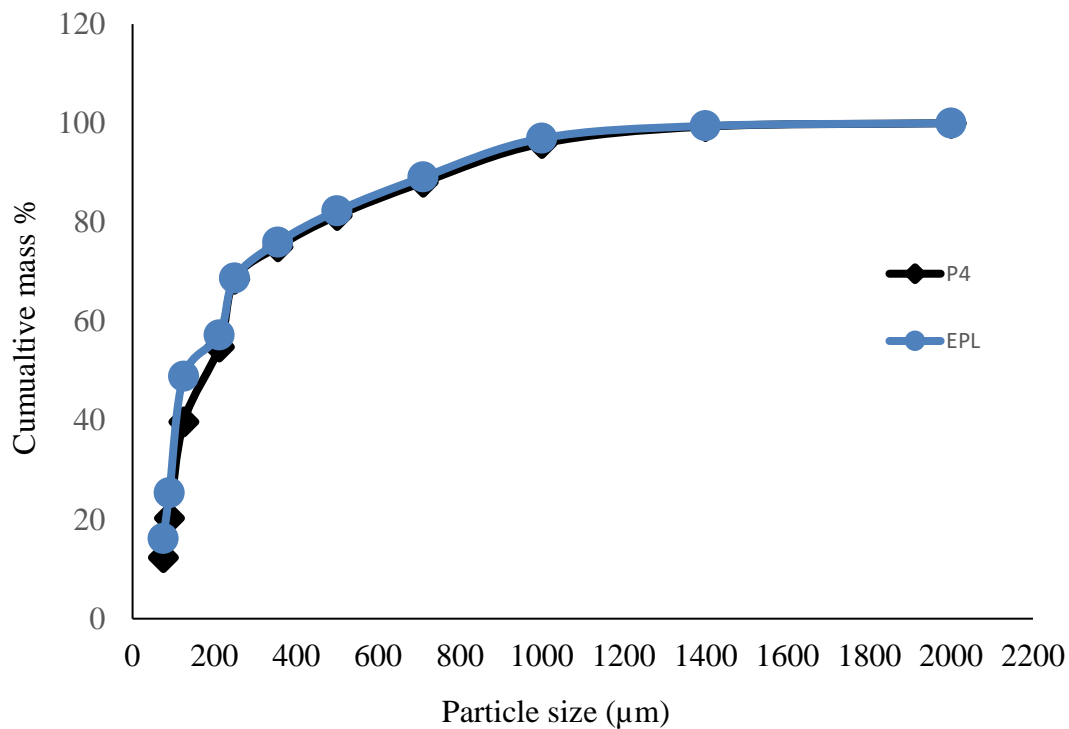


Figure 3-2. Cumulative mass percentage versus particle size of EPL UG2 ore and P4 UG2 ore.

The 2 kg sample was poured into a mill and 1 litre of water was added. The mill was tightly closed with a lid to ensure that the sample would not spill during the rotation of the mill. The samples were wet milled to achieve 67% solids by mass. As it was mentioned earlier, the timer was set and changed three times and the start button was pressed to start the mill. Safety was always priority, so the guard cage of the mill was closed to protect anyone should the lid of the mill open (Figure 3-3).



Figure 3-3. Rod mill with guard cage.

On completion of milling, the samples were taken out of the mill and rinsed out with water together with the rods into a bucket. The samples were dried in an oven, weighed, screened with just 75 μm sieve and recorded. This procedure was conducted on EPL and P4 ore and similar results were achieved, hence only one set of results were shown, see Figure 3-4.

Table 3-1. Stainless steel rod sizes

Quantity	Length (cm)	Diameter (cm)
10	31	2
10	31	1.5
8	32	0.9

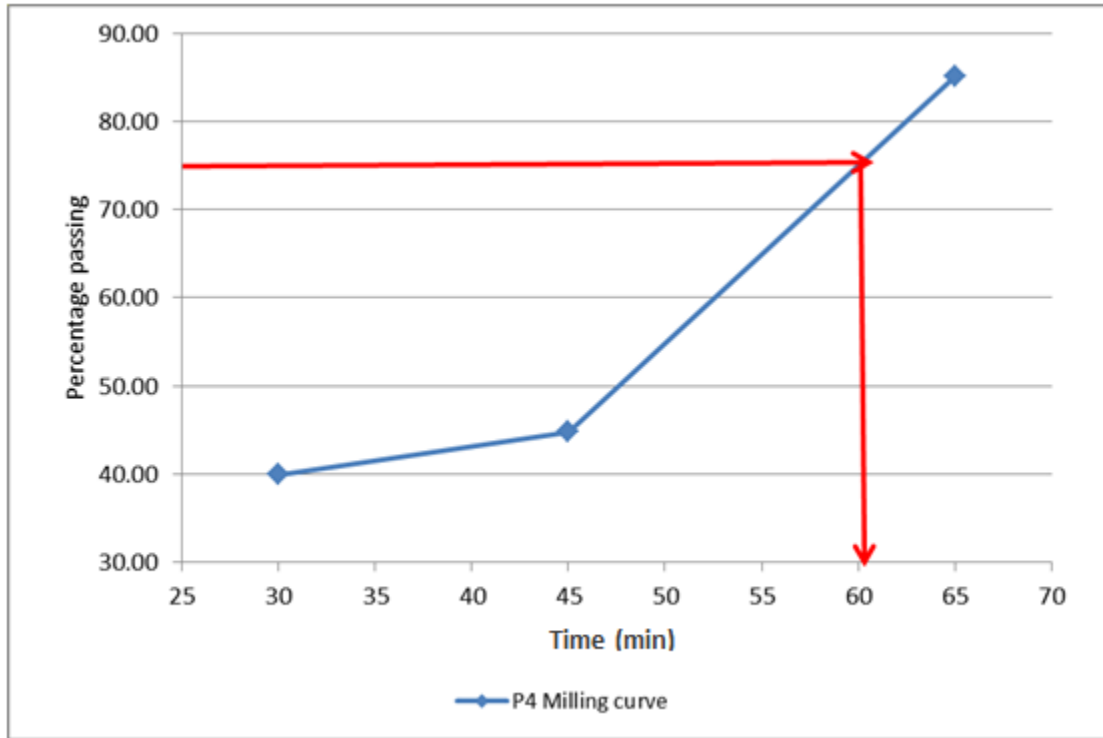


Figure 3-4. The milling curve for P4 type of ore.

3.2 Mineralogical analysis

The mineralogical studies were conducted on P4 and EPL ore in order to understand the characteristics of the two ores. The types of analyses which were used were: optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), fire assay and inductively coupled plasma Mass spectrometry (ICP-MS). All these equipment is available at Vaal University of Technology except for fire assay and ICP-OES which were done at Mintek.

3.2.1 Sample preparation for optical microscopy and scanning electron microscopy (SEM)

The samples analysed with optical microscopy were later analysed with SEM. The samples were prepared in the following manner:

The P4 and EPL ores were categorised according to their particle size, refer to Figure 3-2, so the samples for the optical microscopy and SEM were prepared using those sizes. The particles ranged from 2000 μm to -90 μm . Each particle size was mounted differently.

The mounting machine was inspected to ensure that it was in a good working condition and safe to use, and switched on. The tap connected to the machine was opened to ensure that the water cooled down the machine during the operation. The moulding closure and chamber were cleaned to avoid contamination. Then a small portion of ore, or basically a tip of spatula followed by a Polyfast resin (mounting media), were poured into a moulding chamber (see Figure 3-5). The chamber was closed tightly with a moulding closure. The operating temperature of 180 $^{\circ}\text{C}$, a force of 30 kN, heating time of 8 minutes and cooling time of 3 minutes were set on the machine. Start button was pressed and the samples were mounted. All the particle sizes acquired for P4 and EPL ores were mounted.

The mounted samples were then grinded with 800 and 1200 mesh sizes, and polished with 3 μm Kemet diamond liquid until they could be seen properly under the microscope.

The samples were then analysed with the optical microscopy, followed by SEM.



Figure 3-5. Metallurgical mounting machine used to prepared samples for optical microscopy and SEM analysis.

3.2.2 Principle of Optical Microscope

Optical microscope used a lens close to the object being viewed to collect light (called the objective lens) which focuses a real image of the object inside the microscope. That image was then magnified by a second lens or group of lenses (called the eyepiece) that gave an enlarged inverted virtual image of the object.

3.2.3 The Scanning electron microscopy (SEM)

Two samples were analysed with SEM. One was EPL ore sample of a particle size of 1400 μm , while the other sample was of P4 ore at a particle size of 212 μm . The two particle sizes were chosen based on their well-polished finish and visibility. The samples were carbon coated to avoid any surface charging before they were loaded into the SEM machine.

During the SEM analysis, a beam of electrons was focused on one particular area of the specimen, and as a result energy was transferred to the area. These electrons are also referred to as primary electrons and released electrons from the specimen itself. The released electrons, which also are called secondary electrons, were translated into a signal through being attracted and collected by a positively biased grid or detector. The electron beam was swept across the area being inspected producing many such signals to produce the SEM image. These signals from the inspected topography were then intensified, analysed, and translated into images. Finally, the image was shown on the monitor (Mustafa, 2017).

3.2.4 X-ray diffraction (XRD)

The X-ray diffraction machine was used to analyse the P4 and EPL ores. The two ores were screened and divided into different particle sizes but only the following sizes were analysed: -90 μm , +90 μm , 125 μm , 212 μm and 250 μm . Water supply and computer were connected to The XRD machine, and they were all switched on. The XRD machine was opened and six aluminium sample holders were taken out and cleaned with paper towel acetone. The ore samples were poured into the sample holders and flattened. The sample holders were labelled with a marker, placed back into the XRD machine and the door was closed. The start button was pressed and the ore samples were analysed. The computer connected to the XRD displayed the results on the monitor, and the results were saved after the analysis was completed (Scintag, 1999).

3.2.5 Fire assay and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

The flotation concentrates and tails were analysed by fire assay and ICP methods at Mintek. According to Mintek the analyses procedure is as follows:

For fire assay fusion, a suitable amount of sample was weighed on a scale, mixed with lead collection flux to a homogenous state and loaded into a fusion furnace at 1150 °C for 50 minutes. The reducing conditions converted litharge (lead oxide) to a metallic lead button that formed a lead and three of the PGE (Pt, Pd, Rh) and Au complex. After the lead button was hammered into a form of cube it was loaded into a cupellation furnace at 1000 °C for an hour. The lead was absorbed by the cupel and some was oxidized because of the atmospheric oxygen in the furnace.

When the cupellation was complete the PGEs & Au and Ag (added as silver nitrate) prill were left on a hollow surface of the cupel.

The PGEs and Au held by the silver prill were transferred by the forceps into a borosilicate glass tube and aqua regia was added. The tube was then sealed and transferred into a metal housing and placed into dissolution oven. The tube containing the PGEs and Au and aqua regia solution was left in an oven at 220 °C for 8 hours. The tube was popped and the PGE and Au solution was transferred into the volumetric flask, internal standard was added, made up to volume and assayed on the ICP-MS (Mintek, 2018).

3.3 Froth flotation investigation

This research was based on using collector blend in order to improve the recovery of PGEs from the UG2 ore from Western Bushveld Complex. The first test was conducted only on the primary collector which was SNPX before blending it with secondary collectors also known as co-collectors. By so doing, one can be able to tell whether the co-collectors bring any change when blended with SNPX or not. The results will further illustrate if there is any synergistic or antagonistic effect.

It should be noted that the reagent suite and dosages used in this study for the activator, frother, depressant and SNPX were according to Lonmin standard procedure, only the collectors were varied for blending investigation.

3.3.1 Flotation reagents

This section briefly describes the chemical reagents which were used in this study. The physical description, the form in which the reagents were acquired, and their preparation method are also discussed. The reagents used were: activator (copper sulphate), collectors (SNPX, dithiocarbamate, and four types of thionocarbamates), depressant (CMC) and frother (Senfroth 200). Tap water was used and all the reagents were supplied by Senmin.

3.3.1.1 *Copper sulphate as activator*

Copper sulphate was the activator used. It was found in a form of blue granules and it was dosed at 40 g/t. It was freshly prepared everyday before flotation test-work were conducted.

3.3.1.2 Collectors

The collectors used were of analytical grade. The following collectors were used: SNPX, dithiocarbamate and four thionocarbamate. Dithiocarbamate and four different thionocarbamate formulations were used as co-collectors, having different active contents of 40 % and 100 %. The material safety data sheets (MSDS) of these reagents are provided in Appendix A.

SNPX was received in powder form while the other collectors were in liquid form. When SNPX was dosed as a single collector it was dosed at 150 g/t, but when it was blended with the other co-collectors it was dosed as SNPX: co-collector at 100:50 g/t, then followed by the dosage of 100:125 g/t.

3.3.1.3 Carboxyl methylcellulose (CMC) as a depressant

The CMC was used as a depressant and received as white fine granules. It was dosed at 60 g/t. Like copper sulphate, CMC was prepared prior to every flotation test-work.

3.3.1.4 Senfroth 200 as frother

Senfroth 200 was used as frother and it was received in a liquid form. It was dosed at 22 g/t

3.3.2 Experimental design

The experimental design used for this project was factorial, i.e. 2^5 . Where base number 2 represent the levels at which the active content were tested and exponent 5 is the number of different co-collectors which were tested. This helped predicting how many tests would be conducted. Table 3-2 shows the six different sets of tests which were performed for both SNPX with each co-collector at present (+) or not present (-)

Table 3-2. Experimental design matrix

	SNPX	DTC	ABTC C1	AB TC C2	IPETC30	IPETC31
1	+	-	-	-	-	-
2	+	+	-	-	-	-
3	+	-	+	-	-	-

4	+	-	-	+	-	-
5	+	-	-	-	+	-
6	+	-	-	-	-	+

3.3.3 Experimental procedure

The 2 kg samples were wet milled at 67 % solids by mass in a laboratory rod mill for 60 minutes to achieve the grind of 75 % passing 75 μm . The milled ore and rods were washed out of the mill with water and into the bucket below the mill to ensure that none of the particles were lost.

The wet milled slurry was transferred into a 5 litre Denver batch flotation cell (Figure 3-6), and flotation was carried out at a pulp density of 35 % solids. In total, this was obtained by adding 2 kg of ore to 2.900 litres of water. The impeller was lowered into the cell and operated at a speed of 1200 r/min throughout the test.



Figure 3-6. Denver batch float machine.

The conditioning times for the reagents were in the following order: copper sulphate at 40 g/t for 5 minutes; followed by either SNPX at 150 g/t, or SNPX: co-collector at 100 g/t: 50 g/t, for 2 minutes; depressant (CMC) at 60 g/t for 2 minutes; and lastly A frother (Senfroth XP200) at 22

g/t for 1 minute. So the total conditioning time was 10 minutes. Thereafter, air was introduced into the cell at a constant flow rate of 5 l/min.

Four concentrates (C) were collected into four different dishes by scraping off the froth at the intervals of 15 seconds for 20 minutes with collection times as follows: C1 = 0-1 minute (1 minute total collection time); C2 = 1-3 minutes (2 minutes total collection time); C3 = 3-8 minutes (5 minutes total collection time); and C4 = 8-20 minutes (12 minutes total collection time). After the collection of the concentrates, the air was switched off. The collected concentrates and the tailings were weighed, filtered, dried, and weighed again. . Each experimental condition was run in triplicates. To ensure procedural precision, mass pulls were compared and any runs that deviated by more than 5 % were rejected and repeated. The dried concentrates and tailings were sent to Mintek to be analysed for 4E (Pt, Pd, Rh and Au) and chromite. Since the focus of this study was on blending collectors, all other reagents and their dosages were kept constant during the tests.

The first experiment which was also a benchmark entailed the use of EPL ore and P4 ore with exactly the same reagents and dosages. The conditioning times for the reagents were in the following order: copper sulphate at 40 g/t for 5 minutes; followed by either SNPX at 150 g/t, for 2 minutes; depressant (CMC) at 60 g/t for 2 minutes; and lastly A frother (Senfroth XP200) at 22 g/t for 1 minute.

3.4 Data Processing

The flotation results were captured and processed using excel. The concentrate grades which analysed were used to calculate the masses, recoveries, cumulative grades and cumulative recoveries of the 3PGEs + Au and chromite. The water recovery was also calculated.

The recoveries of PGEs were calculated using equation 7 to 9.

$$M_{PGEs} = M_s \times Assay_{PGEs} \dots \dots \dots Eq. 7$$

$$R = \frac{M_{PGEs}}{Total\ M_{PGEs}} \times 100 \dots \dots \dots Eq. 8$$

$$R_{final} = Sum\ of\ PGEs\ recoveries \dots \dots \dots Eq. 9$$

Where:

M_{PGEs} - Mass of PGEs in each concentrate mass collected (g)

M_s - Mass of concentrate solids in each concentrate collected (g)

$Assay_{PGEs}$ - Assay of the PGEs analysed in each concentrate collected (g/t)

R - Recovery in each concentrate collected (%)

R_{final} – Sum of recoveries from each concentrate collected (%)

$Total_{M_{PGEs}}$ = Total/sum of PGEs from concentrate 1 to concentrate 4 (g)

The recoveries of chromite were calculated using equation 10 to 12.

$$M_{Cr2O3} = M_s \times Assay_{Cr2O3} \dots \dots \dots \text{Eq. 10}$$

$$R = \frac{M_{Cr2O3}}{Total_{M_{Cr2O3}}} \times 100 \dots \dots \dots \text{Eq. 11}$$

$$R_{final} = \text{Sum of } Cr2O3 \text{ recoveries} \dots \dots \dots \text{Eq. 12}$$

Where:

M_{Cr2O3} - Mass of chromite in each concentrate mass collected (g)

M_s - Mass of concentrate solids in each concentrate collected (g)

$Assay_{Cr2O3}$ - Assay of the chromite analysed in each concentrate collected (%)

R - Recovery in each concentrate collected (%)

R_{final} – Sum of recoveries from each concentrate collected (%)

$Total_{M_{Cr2O3}}$ = Total/sum of chromite from concentrate 1 to concentrate 4 (g)

The cumulative recovery of PGEs and chromite was calculated by adding the first concentrate recovery to the next, from concentrate 1 until concentrate 4. For example:

Cumulative recovery after fourth concentrate = recovery 1 + recovery 2 + recovery 3 + recovery 4.

The cumulative grade of PGEs was calculated using equation 13.

$$\text{Cumulative grade} = \frac{\text{Mass of PGEs in concentrates collected up to that instance}}{\text{Mass of concentrate solids collected up to that instance}}$$

.....Eq. 13

The recovery of water was calculated using equation 14.

$$R_{\text{water}} = \frac{\text{Water retained from each wet concentrate collected}}{\text{Total water in the flotation cell}}$$

.....Eq. 14

4 RESULTS AND DISCUSSION

4.1 Mineralogical analysis for P4 and EPL ores

4.1.1 Scanning electron microscopy- energy dispersive spectroscopy (SEM-EDS) analysis

Two mounted and polished samples of EPL and P4 ore were analysed with SEM and illustrated in Figures 4-1 to 4-5, and Figures 4-6 and 4-7 respectively. Figure 4-1 to Figure 4-5 are from one EPL sample at a particle size of 1400 μm , and Figure 4-6 and 4-7 are from one sample of P4 at a particle size 212 μm . Different elements/minerals were identified and shown on the figures below.

Figure 4-1 and Figure 4-2 are showing the backscattered image and EDS map respectively. The backscattered image in Figure 4-1 shows a large olivine grain with inclusions of Ca-pyroxene and Fe-oxides. The EDS map in Figure 4-2 shows the distribution of Si in a large olivine grain. The dark spots are oxide inclusions.

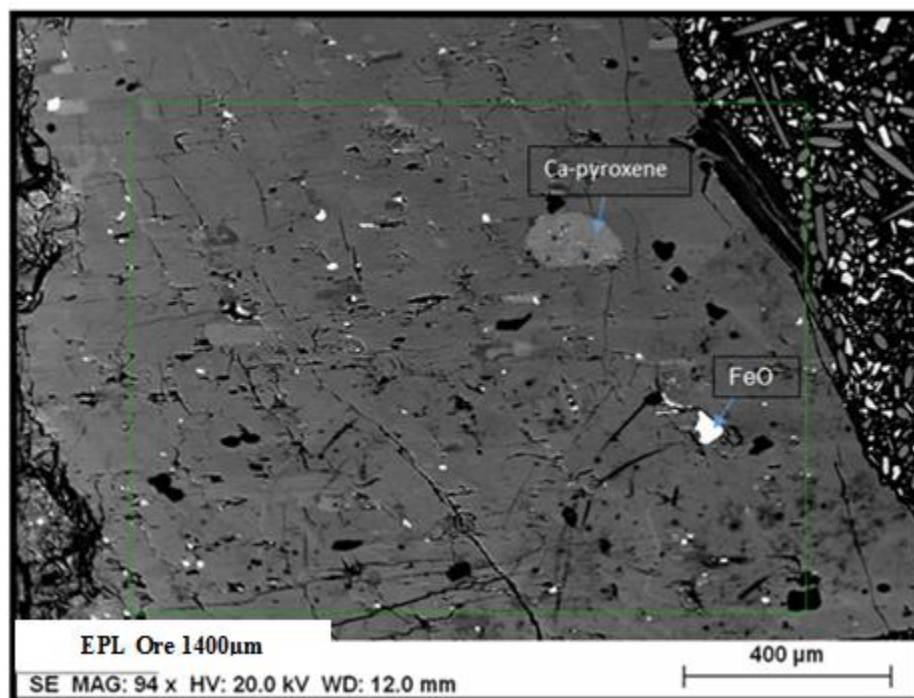


Figure 4-1. Backscattered image of EPL ore at a particle size of 1400 μm .

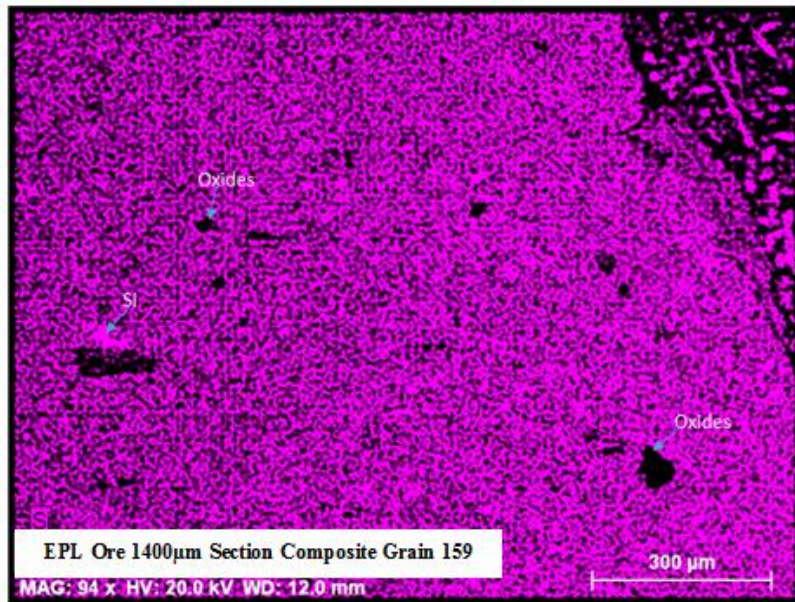


Figure 4-2. EDS map of EPL ore at a particle size of 1400 μm showing the distribution of Si.

EDS map in Figure 4-3 shows the distribution of Fe, Mg and Cr in an olivine grain. The blue coloration maps represent Fe-oxide inclusions and the white coloration in the map represents chromite inclusions.

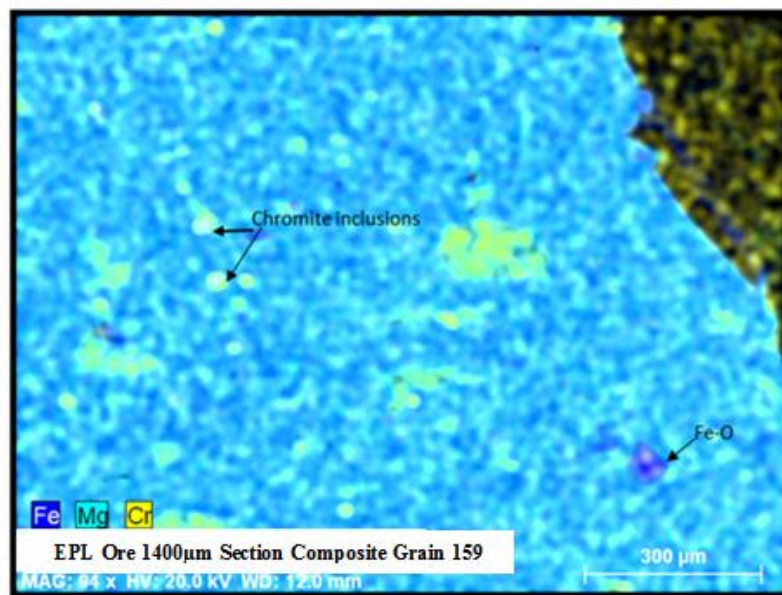


Figure 4-3. EDS map of EPL ore showing the distribution of Fe, Mg and Cr in an olivine grain.

EDS map in Figure 4-4 shows Mg and Ca distributions. The green areas are pyroxene inclusions within the olivine grain.

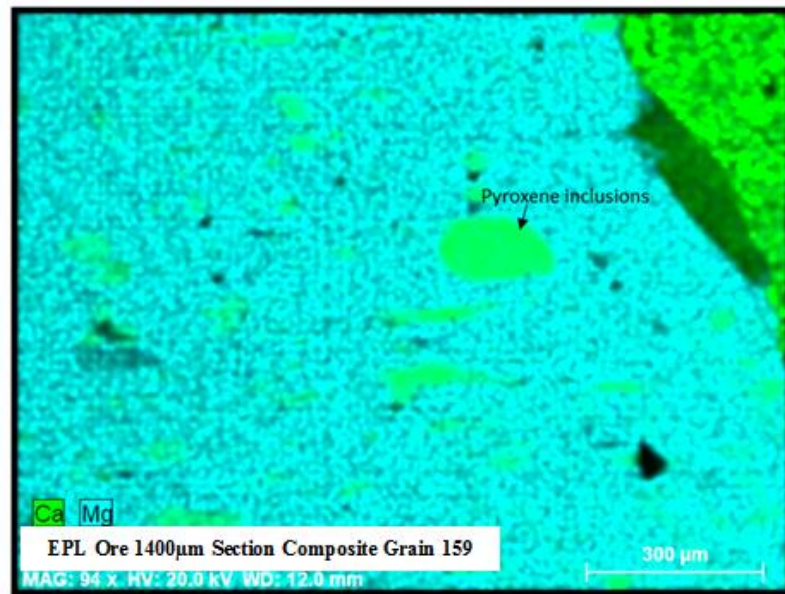


Figure 4-4. EDS map showing Mg and Ca distributions.

EDS map in Figure 4-5 shows the following: the blue coloration maps represent Fe-oxide, yellow indicates chromite, red is sulphur and green is Nickel. There are two small grains of Ni-bearing pyrrhotite (green spots with red haloes). Small green spots are scattered within the enclosing silicate grain, indicating the presence of Nickel in solid solution within the silicates.

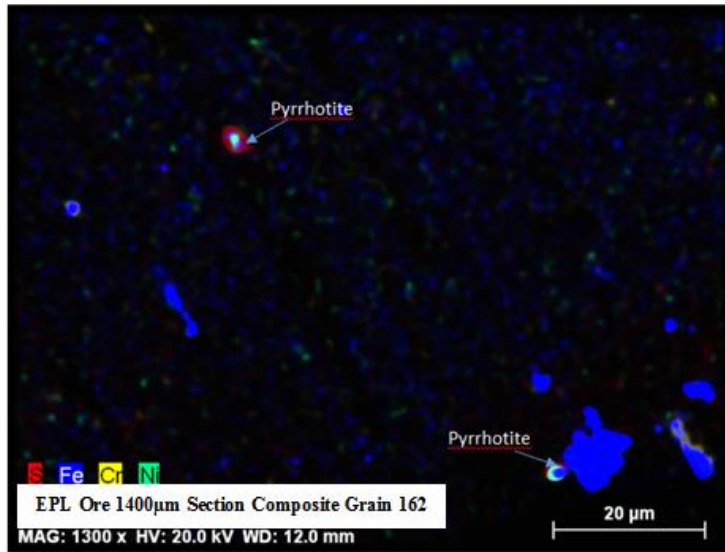


Figure 4-5. EDS map showing the distribution of S, Fe, Cr and Ni.

As mentioned above Figures 4-6 and 4-7 represents 212 µm of P4 ore. The backscattered image on Figure 4-6 shows large grain of Cr and silicates. The EDS map in Figure 4-7 shows Cu, Cr and Si.

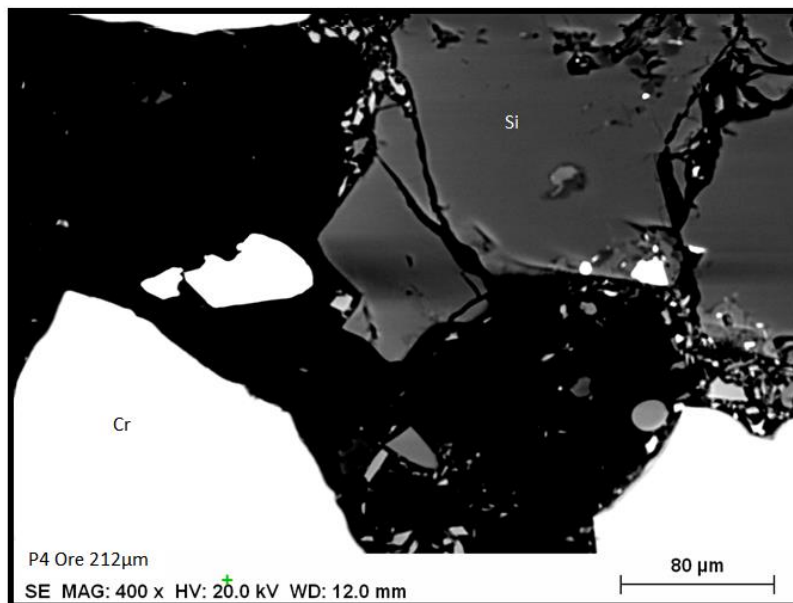


Figure 4-6. The backscattered image of P4 ore at a particle size of 212 µm.

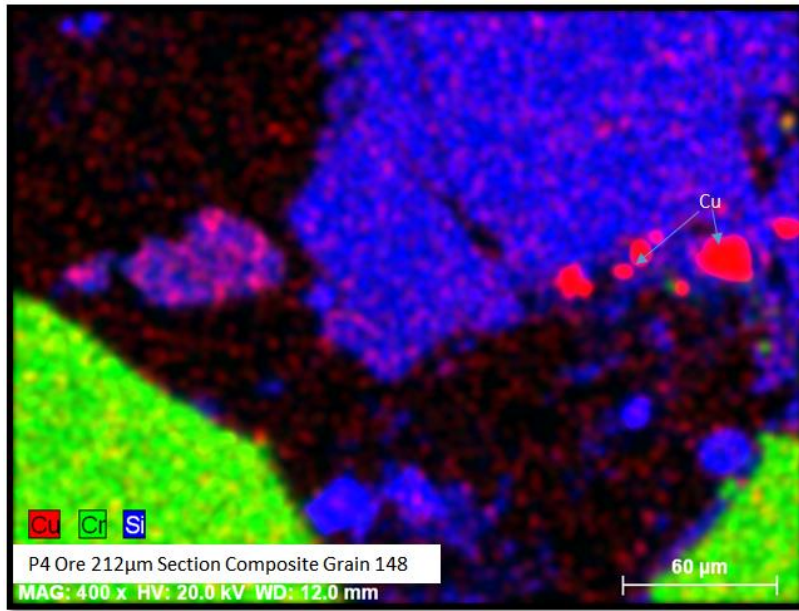


Figure 4-7. The EDS map showing Cu, Cr and Si.

Sulphides are minute and enclosed in silicates and as a result they are not visible in these results figure, however the presence of the Cu indicate the presence of the sulphides. Some particles looked like sulphides under polarized optical microscope, but under SEM they were found to be Fe-oxides.

4.1.2 Optical microscopy analysis

Figure 4-8 and Figure 4-9 show the optical microscopy results.

The photomicrographs of EPL and P4 ore show that there are sulphide minerals (goldish and glittering maps) in the ores, but they are enclosed in gangue minerals, see Figure 4-8. This supports Figure 4-5 which indicates the presence of the sulphides in the ore. The figure shows that though the sulphide minerals are present, they are not fully liberated. The occurrence of platinum group minerals in UG2 is generally fine grains (averaging 12 microns), and are also associated with base metal sulphides, silicate gangue and/or chromite grains (Kinloch, 1982; McLaren and De Villers, 1982; Von Gruenewaldt *et al.*, 1986; Penberty *et al.*, 2000). The platinum group minerals are not observable in these photomicrographs because of their small size and rarity. It is for this reason that this mineralogical study has not shed any light on the ore mineral differences between the EPL and P4 ores that might explain the differences in recoveries between the two ores.

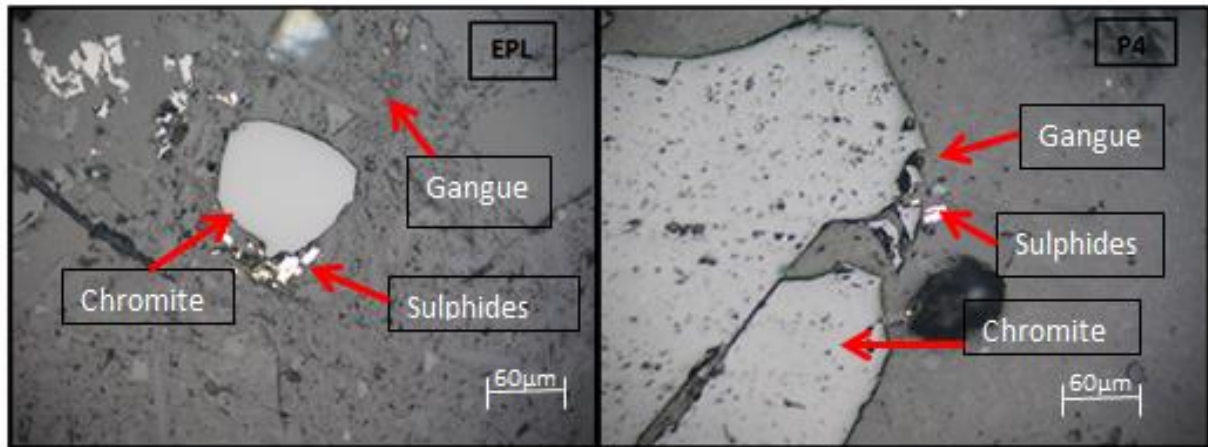


Figure 4-8. Photomicrograph of EPL and P4 ore at a particle size of 355µm.

Figure 4-9 indicates that chromite grains are large and liberated sulphides are smaller locked in gangue though they are more exposed compared to Figure 4-8.

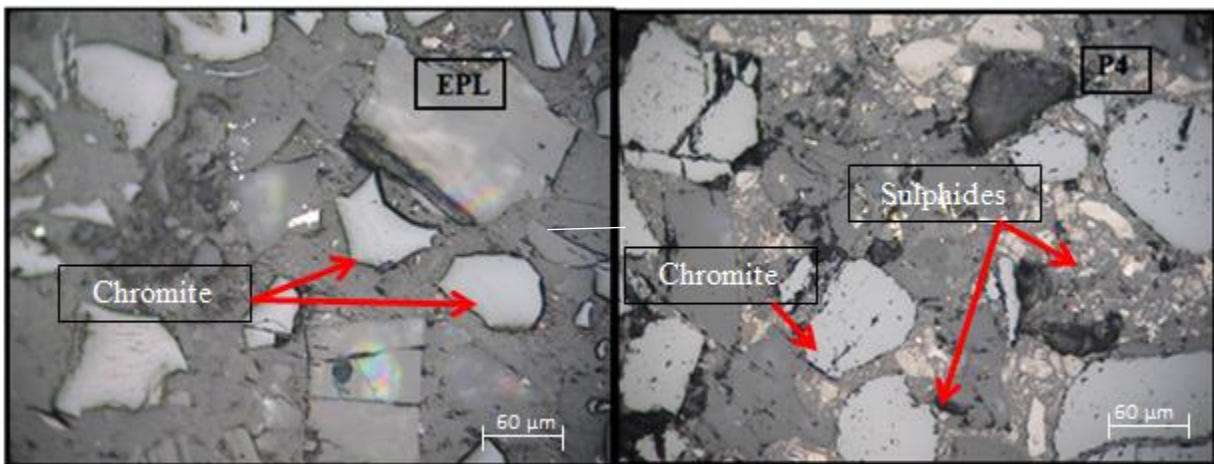


Figure 4-9. Photomicrograph of EPL and P4 ore at a particle size of 125µm.

4.1.3 X-ray diffraction (XRD) analysis

The XRD analysis was done at the university and other samples were also sent to XRD Analytical and Consultant cc which is the external service provider. The results presented here are from the XRD Analytical and Consultant cc.

Figure 4-10 and Figure 4-11 indicate the major minerals which are present in concentrations of >1% in P4 and EPL ores. Chromite, plagioclase and enstatite are the dominating minerals in both ores. Higher chromite content lies in the 212 μm size of the ores.

Other minerals like talc, muscovite, actinolite, and quartz are present in smaller quantities (Figure 4-10). However, these minerals (except quartz), as well as chlorite, are reagent consumers and may be the problem, and may lead to higher reagents dosage. It is also important that they are depressed during flotation process. The major difference between these two ores is that in the -90 μm fraction lies more chlorite and quartz in the P4 ore than EPL ore, so this can be one of the significant differences between these ores. These data suggest that the differences in recoveries between the EPL and P4 ores may be a result of differences in the characters of the gangue mineral components rather than the ore mineral components. However, the data are insufficient to prove this.

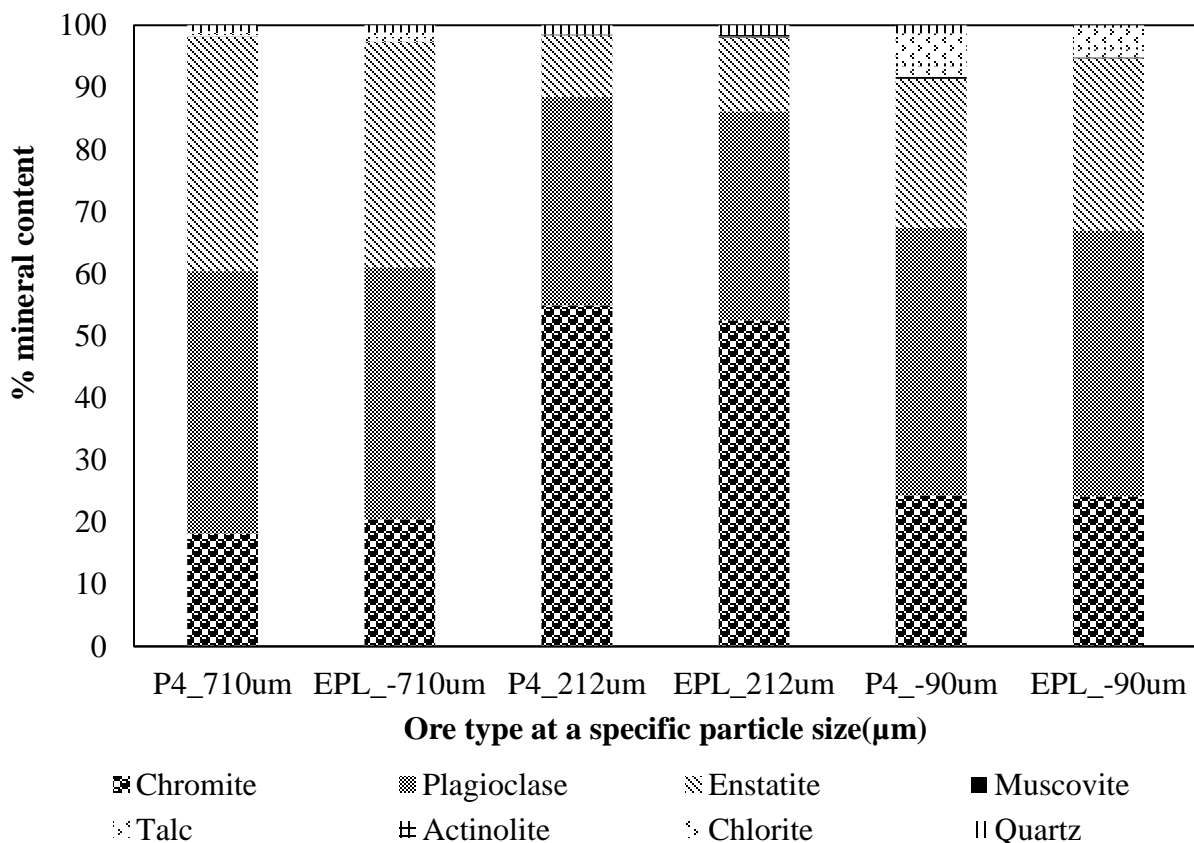


Figure 4-10. XRD analysis of minerals in the P4 UG2 ore according to the particle size.

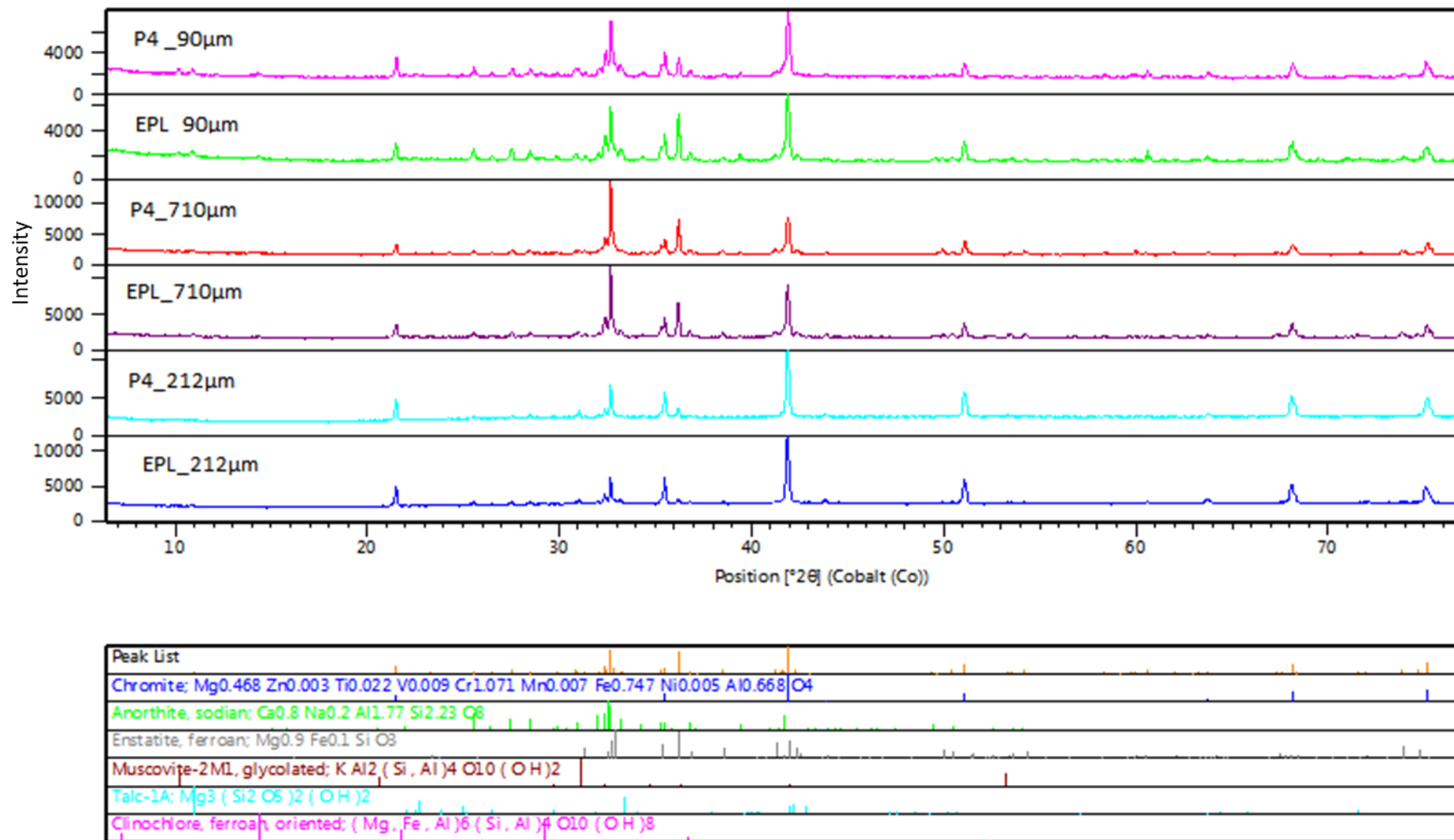


Figure 4-11. XRD results of P4 and EPL ore at different particle sizes.

4.2 Froth flotation results using SNPX and its blends

This section covers the flotation responses; grade/recovery and chromite and water recovery achieved during the batch flotation of EPL and P4 ore at the dosage rates of 50 and 125 g/t of co-collectors. The EPL ore test was conducted to establish the benchmark together with P4 (using only SNPX) before blending the co-collectors. The raw data is available in Appendices B and C.

4.2.1 Flotation response of EPL ore against P4 ore: benchmark performance

This section presents the benchmark flotation results obtained when comparing the behaviour of EPL ore to P4 ore under similar flotation conditions using SNPX only as the collector as described in Section 3.5. The raw data is available in Appendix B.

Table 4-1. The summary of the results obtained when floating EPL ore and P4 ore at the same reagent suite.

Ore	Collector	Dosage (g/t)	Cumulative concentrate mass (%)		Cumulative water (%)		Cumulative 3PGE + Au recovery (%)		Cumulative 3PGE + Au grade (g/t)	
			1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min
EPL	SNPX	150	0.8	4.6	2.1	17.1	40	77.6	191.82	67.98
P4	SNPX	150	1.2	18.4	3.2	18.6	41.4	69.8	147.44	58.72

Figure 4-12 shows that the EPL ore achieved faster kinetics compared to P4 ore.

On the other hand, P4 ore started off at slightly higher recovery on the 1st minute, although as the flotation time proceeded the recovery increased, but it was lower than that of EPL ore. The EPL ore achieved the cumulative recovery of 77.6 % while P4 achieved 69.8 %. Figure 4-10 has shown that there is higher average content of chlorite in the P4 ore at 1.76 %, while EPL ore had lower average chlorite content of 1.27 %. Since chlorite is one of the minerals which consume reagents it explains the lower recover obtained by P4 ore.

The average chromite difference of 32.47 % for P4 ore and 32.35 % for EPL ore, and average plagioclase difference of 39.61 % for P4 ore and 38.99 % of P4 ore may also have contributed towards the recovery difference. Evidently these results show that the mineralogical differences between the two ores seem to be the factor that is causing the recovery differences. It is therefore desirable to improve the recovery of the P4 ore to be like that of EPL ore or even greater.

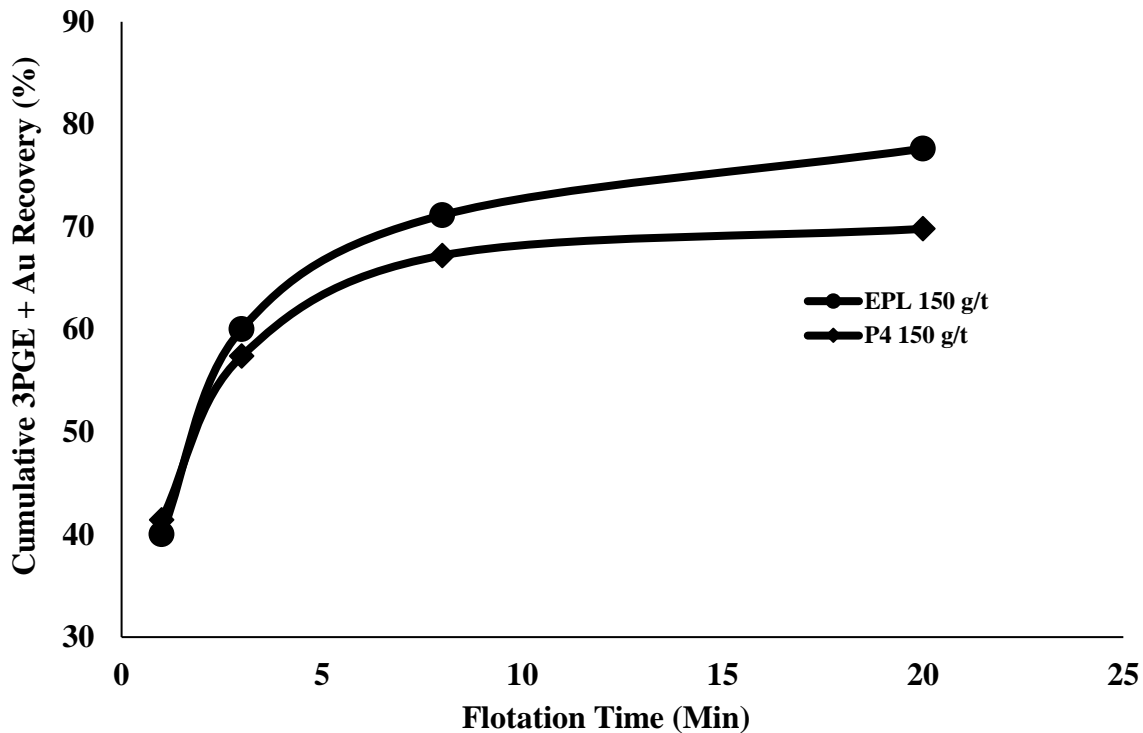


Figure 4-12. Flotation responses of EPL and P4 ores with usage of SNPX at 150 g/t.

Figure 4-13 shows the cumulative grade against cumulative recovery graph of EPL and P4 ore when using the standard reagent suite with SNPX at a dosage of 150 g/t.

The relationship between grade and recovery is usually inversely proportional. As cumulative recovery of EPL ore has showed that it is greater than that of P4 ore, the cumulative grade was 67.98 g/t which is greater than P4 ore at 58.72 g/t. The high presence of chlorite in P4 at 5.29 % (Figure 4-10) ore has hindered it from achieving higher grades, as a result the adsorption of the collector on the EPL ore was more selective than on the P4 ore. Since the reagent suite is exactly the same for both tests, therefore the mineralogical difference must be the only reason different flotation response is recorded for these 2 ore types.

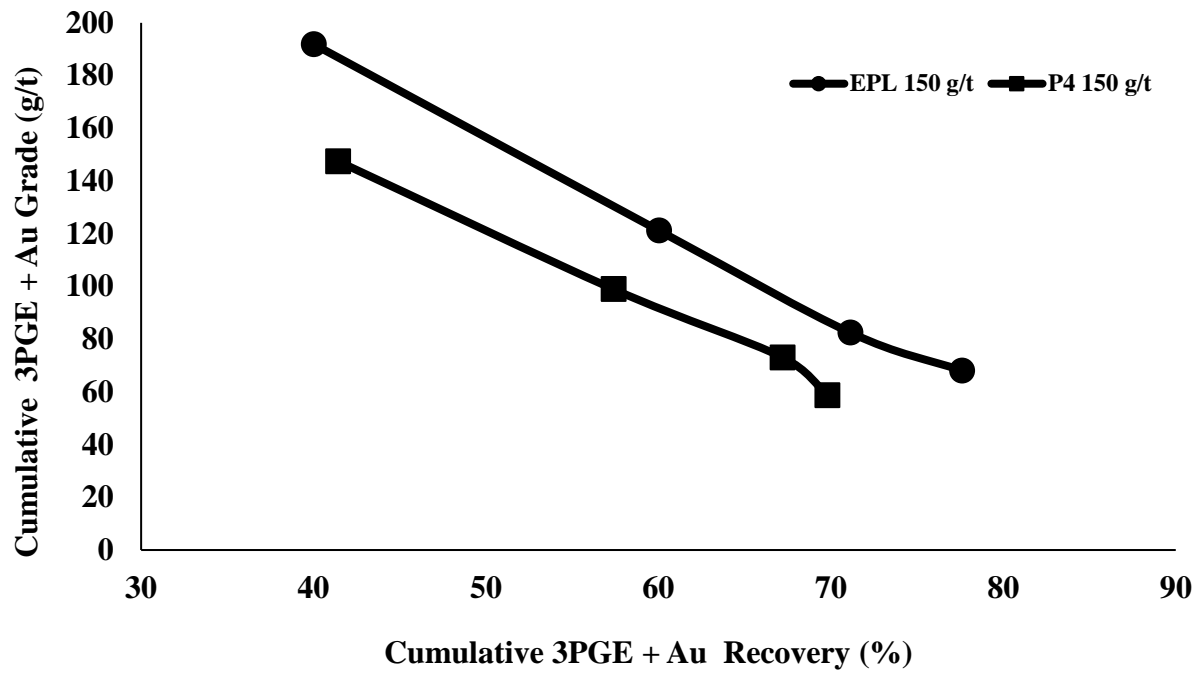


Figure 4-13. The cumulative grade against cumulative recovery of EPL and P4 ore when using the standard reagent suite with SNPX at a dosage of 150 g/t.

Figure 4-14 shows water and chromite recovery from the flotation of EPL and P4 ore using the same reagent suite for each concentrate collected. The figure indicates that chromite increases with water except on the last/four concentrate whereby the chromite decreased more than water. This shows that on the forth concentrate chromite was reporting there through entrainment. Chromite and water were highly recovered on the third concentrate for both ores. The cumulative water recovery for EPL and P4 ore was 17.1 % and 18.6 %, while the cumulative chromite recovery was 0.949 % and 0.985 %, respectively.

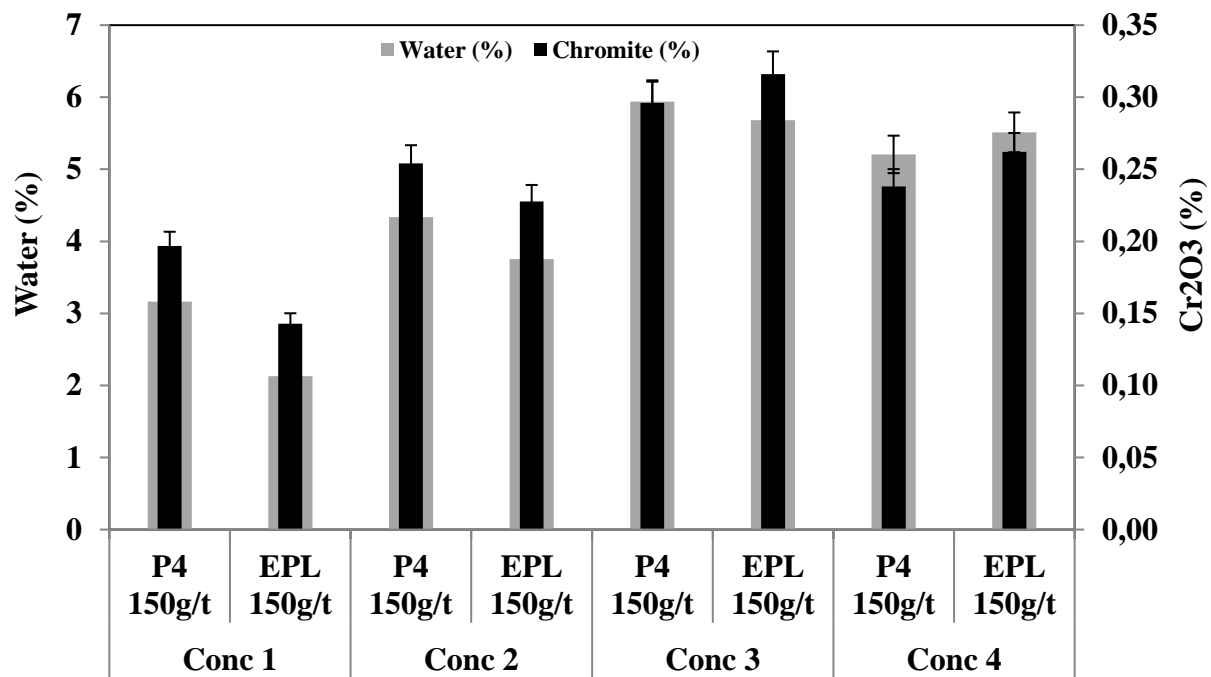


Figure 4-14. Water and chromite recovery for EPL and P4 ore when using the standard reagent suite with SNPX at a dosage of 150 g/t.

4.2.2 Flotation responses of P4 UG2 ore under SNPX with co-collectors

Table 4-2 shows the summary of the results obtained when floating P4 ore with different collector blends. The raw data is on Appendix C. The flotation test using SNPX was repeated after the benchmark tests were conducted because the flotation machine and the cell were changed due to the renovations the laboratory had to go through and as a result the results on Table 4-1 is different to that one on Table 4-2.

Table 4-2. The summary of the results obtained when floating P4 ore with different collector blends.

Collector	Dosage (g/t)	Total dosage (g/t)	Cumulative concentrate mass (%)		Cumulative water (%)		Cumulative 3PGE + Au recovery (%)		Cumulative 3PGE + Au grade (g/t)		Cumulative Chromite recovery (%)	
			1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min	1 min	20 min
SNPX	150	150	1.2	4.7	3.5	20.7	49.56	81.14	144.4	60.53	0.24	0.99
SNPX + DTC	100 + 50	150	1.4	5.1	4.8	25	51.7	80.72	139.15	60.24	0.26	1.12
SNPX + DTC	100 + 125	225	1	4.3	3.4	20.2	49.2	76.49	153.71	56.01	0.17	0.83
SNPX + ABTC C1	100 + 50	150	1.3	4.6	5.3	26.4	38.73	77.36	145.65	76.1	0.23	0.93
SNPX + ABTC C1	100 + 125	225	1.6	5	5.5	26.3	42.53	75.39	83.92	48.87	0.34	1.06
SNPX + ABTC C2	100 + 50	150	1.6	6.1	4.6	26.5	37.43	78.64	88.3	50.04	0.43	1.45
SNPX + ABTC C2	100 + 125	225	2.3	6	16.3	32.6	6.12	61.76	5.95	23.07	0.48	1.4
SNPX + IPETC 30	100 + 50	150	2.1	5.9	5.7	27.8	58.16	85.69	113.81	60.14	0.41	1.26
SNPX + IPETC 30	100 + 125	225	7.5	9.9	13.7	30.1	67.77	83.85	34.03	31.76	1.56	2.11
SNPX + IPETC 31	100 + 50	150	1.9	5.8	6	28.2	48.42	80.68	110.39	60.63	0.41	1.3
SNPX + IPETC 31	100 + 125	225	7.6	10.1	14.9	21.5	67.81	83.74	33.26	30.77	2.61	3.18

4.2.2.1 The flotation kinetics of 3PGE +Au obtained with the use of SNPX and SNPX blends with co-collectors at 50g/t and 125g/t on the P4 UG2 ore

The usage of SNPX at 150 g/t (total collector dosage) has proven that the information given by the Lonmin correspondents that it yields higher recovery for EPL ore than for P4 is true as shown in Figures 4-13 and 4-14. Therefore SNPX at 150 g/t graph will be used as a benchmark throughout the study. The section of results is based on only P4 ore.

The flotation kinetics of 3PGE +Au obtained with the use of SNPX, and SNPX blends with co-collectors at 50 g/t and 125 g/t are graphically illustrated in Figure 4-15 and Figure 4-16, respectively.

The SNPX: IPETC 30 blend at 50 g/t yielded faster 3PGEs + Au kinetics compared to the SNPX and other SNPX blends. From the 3rd minute until the 20th it showed superior qualities, see Figure 4-15. The recovery increased in the following order:

SNPX + ABTC C1 < SNPX + ABTC C2 < SNPX + DTC = SNPX + IPETC 31 < SNPX < SNPX + IPETC 30

$$77.4 \% < 78.6 \% < 80.7 \% < 81.1 \% < 85.7 \%$$

The recovery for SNPX + DTC was equivalent to SNPX + IPETC 31.

With SNPX at a dosage of 150 g/t the recovery of 3PGEs + Au increased rapidly until 8th minute, and thereafter increased gradually until the 20th minute when the last concentrate was collected at an overall cumulative recovery of 81.1 %, which is almost the same as the overall cumulative recovery of SNPX + DTC, and SNPX + IPETC 31 blends. This may be due to the fact that SNPX is a short hydrocarbon chain xanthate, and therefore the reaction between the xanthate and the minerals may have been faster than with the SNPX-DTC blend but slower than the SNPX-IPETC 30 blend. Short chain hydrocarbon is known to show faster kinetics than long chain hydrocarbon, because the solubility of the collector in water reduces quickly with increasing chain length (Wills and Napier-Munn, 2006; Lotter and Bradshaw, 2010).

On the other hand, SNPX + ABTC C1 and SNPX + ABTC C2 started off slower than the other collectors and even the overall recovery was lower at 78.6 and 77.4 % respectively, the graphs show that they will keep on collecting more if given more time.

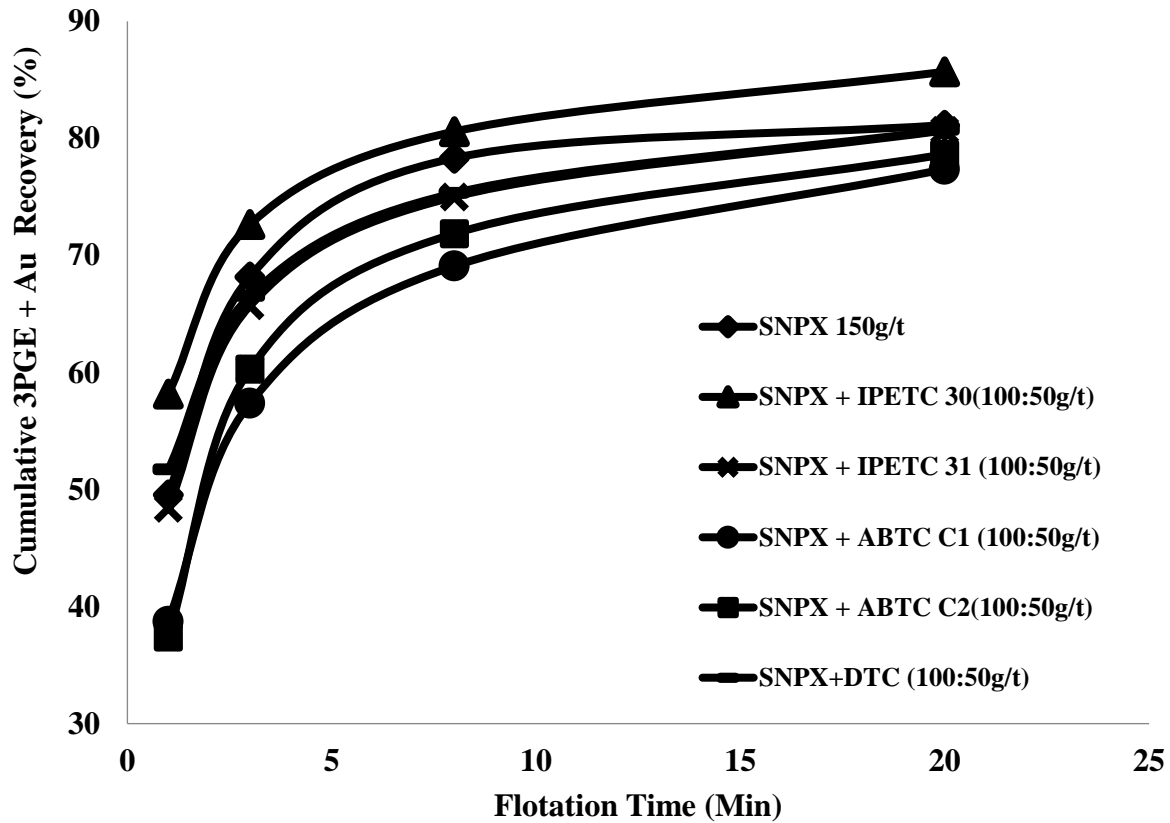


Figure 4-15. Flotation responses of 3PGE +Au obtained from the P4 UG2 ore with the use of SNPX and SNPX blends with co-collectors at 50 g/t.

According to Glembotskii (1958), and Lotter and Bradshaw (2010), blending xanthates and DTCs exhibit synergistic effects. However, SNPX + DTC blend achieved overall cumulative recovery similar to that of SNPX alone (Figure 4-15). By twenty minutes, the maximum recovery was attained for the SNPX condition, and additional floating time was not going to improve the recovery (as indicated by the asymptote), while SNPX + DTC, SNPX + ABTC C1 and SNPX + ABTC C2 blend curves were continuing in inclination which was an indication that should the floating time have been increased the recoveries were going to keep increasing as well. This increasing recovery, compared to SNPX alone, is the evidence of synergistic effect.

However, such further increase in recovery generally compromises grade disproportionately (see discussion on Figure 4-17).

It is also notable that the kinetics under SNPX alone is faster than that under SNPX + DTC. This agrees with known effects of chain length and branching of the hydrocarbon group in the collector ion. The linear and shorter group in SNPX gave higher reaction rate compared to the dialkyl structure in $R_2NCS_2^-$ from DTC. The DTC blending therefore does not present clear indication of improvement in flotation performance.

The SNPX + IPETC 30 blend however, gave improved overall cumulative recovery of 85.7 %, which is 4.6 % higher compared to SNPX results. This improved recovery is also accompanied with higher recovery rate over the entire duration.

Similar performance of co-collector at 50 g/t was also observed with co-collector dosage of 125g/t, as shown in Figure 4-16.

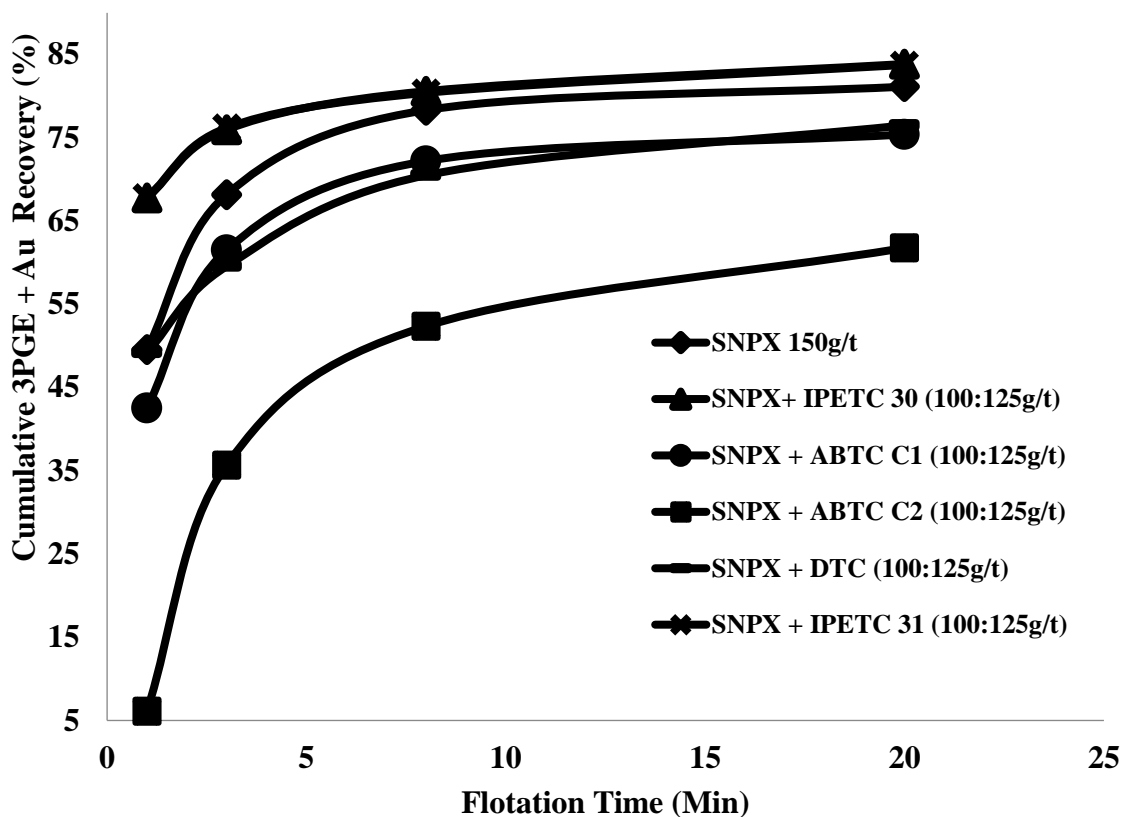


Figure 4-16. Flotation response of 3PGE +Au obtained from P4 UG2 ore with the use of SNPX and SNPX blends with co-collectors at 125 g/t.

The only difference was that SNPX + IPETC 31 and SNPX + DTC were no longer equal. The recovery of SNPX + IPETC 31 increased from 80.7% at 50 g/t dosage to 83.74 % at 125g/t dosages, but SNPX + IPETC 30 decreased from 85.7% at 50g/t dosage to 83.85 %. The recovery increased in the following order:

SNPX + ABTC C2 < SNPX + ABTC C1 < SNPX + DTC < SNPX < SNPX + IPETC 31 < SNPX + IPETC 30

$$61.76 \% < 75.39 \% < 76.49 \% < 81.1 \% < 83.74 \% < 83.85 \%$$

In essence, the addition of high dosage of co-collector at 125 g/t lead to decrease of recoveries and grades of all SNPX and SNPX blends except for SNPX + IPETC 31 which only increased by 3.04%. This shows that the blends reached their optimum performance and further addition of

co-collectors to the high dosage of 125 g/t lead to the opposite undesired antagonistic effect, whereby instead of recovery and grade increasing they decreased, as seen in Section 4.2.2.2.

4.2.2.2 Cumulative 3PGE + Au grade versus cumulative 3PGE + Au recovery of the P4 ore at SNPX dosages of 50 g/t and 125 g/t.

Figure 4-17 and Figure 4-18 illustrate the cumulative 3PGM +Au grade versus cumulative 3PGM + Au recovery for SNPX and its blends, at a dosage of 50 and 125 g/t of co-collectors respectively.

The 3PGE + Au grades at co-collectors dosage of 50 g/t increase in the following order:

SNPX + ABTC C2 < SNPX + IPETC 30 < SNPX + DTC < SNPX < SNPX + IPETC 31 < SNPX + ABTC C1

$$50 \text{ g/t} < 60.14 \text{ g/t} < 60.2 \text{ g/t} < 60.53 \text{ g/t} < 60.53 \text{ g/t} < 76.1 \text{ g/t}$$

The SNPX + IPETC 30 and SNPX + DTC blend shows overall grade of 60.14 g/t and 60.2 g/t respectively, while SNPX show higher grades of 144.4 g/t from the start of flotation until this dropped remarkably to 60.53 g/t after recovery stagnated between the 12th and 20th minutes (Figure 4-17).

SNPX + IPETC 30, SNPX + IPETC 31 < SNPX + ABTC C1 shows that an improved recovery would have been achieved should the floating time have been extended according to the graphs seen in Figure 4-17. The recovery improvements are positive indicators of desired synergistic effects from a collector blend. It can be inferred that the different interaction obtainable from the thionocarbamate (ROCSNHR), effectively complement that from the xanthate ion (ROCS₂⁻) to achieve more collector interaction at surface sites otherwise interactable for xanthate only. A recent study (Bu *et al.*, 2018) indicated IPETC is able to remove hydroxide ions from mineral surface and interact at such freshly activated site. Such should be complementary interactions of the thionocarbamates that improve the recovery. The SNPX + ABTC C2 on the other hand achieved low grade of 50 g/t, at a higher recovery of 78.6 % compared to that of SNPX + ABTC C1. This should be due to the difference in the chemical composition between ABTC C2 and ABTC C1. However, the differences are not indicated in the MSDSs, they are only written that

the active ingredient in both ABTC C1 and ABTC C2 is S-alkyl-N-butyl thionocarbamates and that their chemical family is carbamate esters.

Moreover, the extension of time for SNPX + IPETC 30, SNPX + IPETC 31 < SNPX + ABTC C1 show that it was going to be accompanied by grade compromise. It is well known fact that the grade/recovery relationship is a trade-off and it is unsettling to the metallurgists because one has to decide on what to sacrifice, grade or recovery. It is always desired to attain increase in both grade and recovery simultaneously.

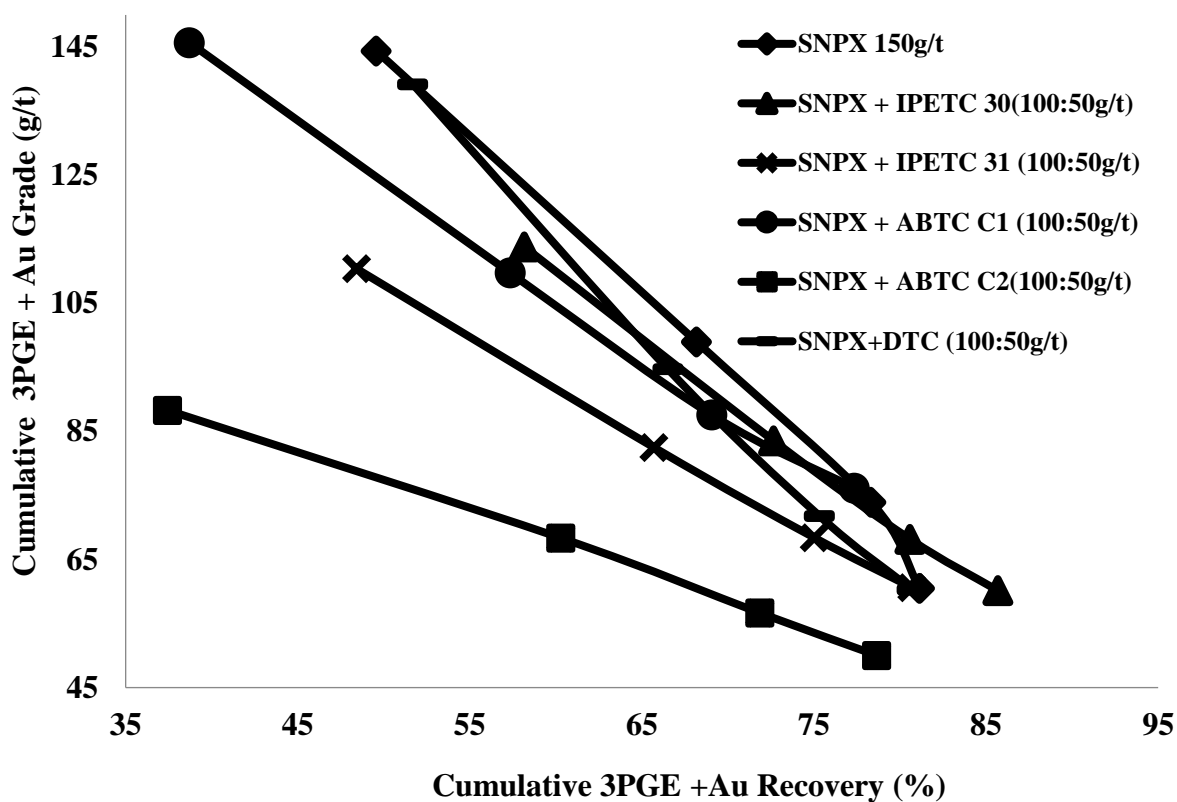


Figure 4-17. Cumulative 3PGE + Au grade versus cumulative 3PGE + Au recovery from P4 UG2 ore obtained with the use of SNPX and SNPX blends with co-collectors at 50 g/t.

Bhaskar Raju and Forsling (1991) stated that because dithiocarbamate loses electrons easily, resulting in a stronger and less selective collector, xanthate can be more selective than DTC. This can explain the cumulative grade of SNPX-DTC lying below the other conditions in Figure 4-17.

IPETC on the other hand has advantage over xanthate due to its higher selectivity for base sulphide metals and long-term storage stability, yet it is not considered a powerful collector (Nagaraj *et al.*, 1986) due to the presence of the amino group (NH) and its frothing properties which depend on the alkyl chain lengths (Sheridan *et al.*, 2002). But SNPX + IPETC 30, SNPX + IPETC 31 < SNPX + ABTC C1 blends achieved higher overall cumulative grades and overall cumulative recovery than the other conditions, the thionocarbamate blends clearly perform better for improving PGE beneficiation from this ore.

Figure 4-18 graphically illustrates the cumulative 3PGM + Au grade versus cumulative 3PGM + Au recovery for SNPX and SNPX blends with co-collectors at a dosage of 125 g/t. The recovery increased in the following order:

SNPX + ABTC C2 < SNPX + ABTC C1 < SNPX + DTC < SNPX < SNPX + IPETC 31 < SNPX + IPETC 30

The cumulative 3PGE + Au recoveries obtained with these use of co-collectors were:

$$61.76\% < 75.39\% < 76.49\% < 81.1\% < 83.74\% < 83.85\%$$

The final cumulative 3PGE + Au grade increased in the following order:

SNPX + ABTC C2 < SNPX + IPETC 31 < SNPX + IPETC 30 < SNPX + ABTC C1 < SNPX + DTC < SNPX

$$23.07 \text{ g/t} < 30.77 \text{ g/t} < 31.76 \text{ g/t} < 48.87 \text{ g/t} < 56.01 \text{ g/t} < 60.53 \text{ g/t}$$

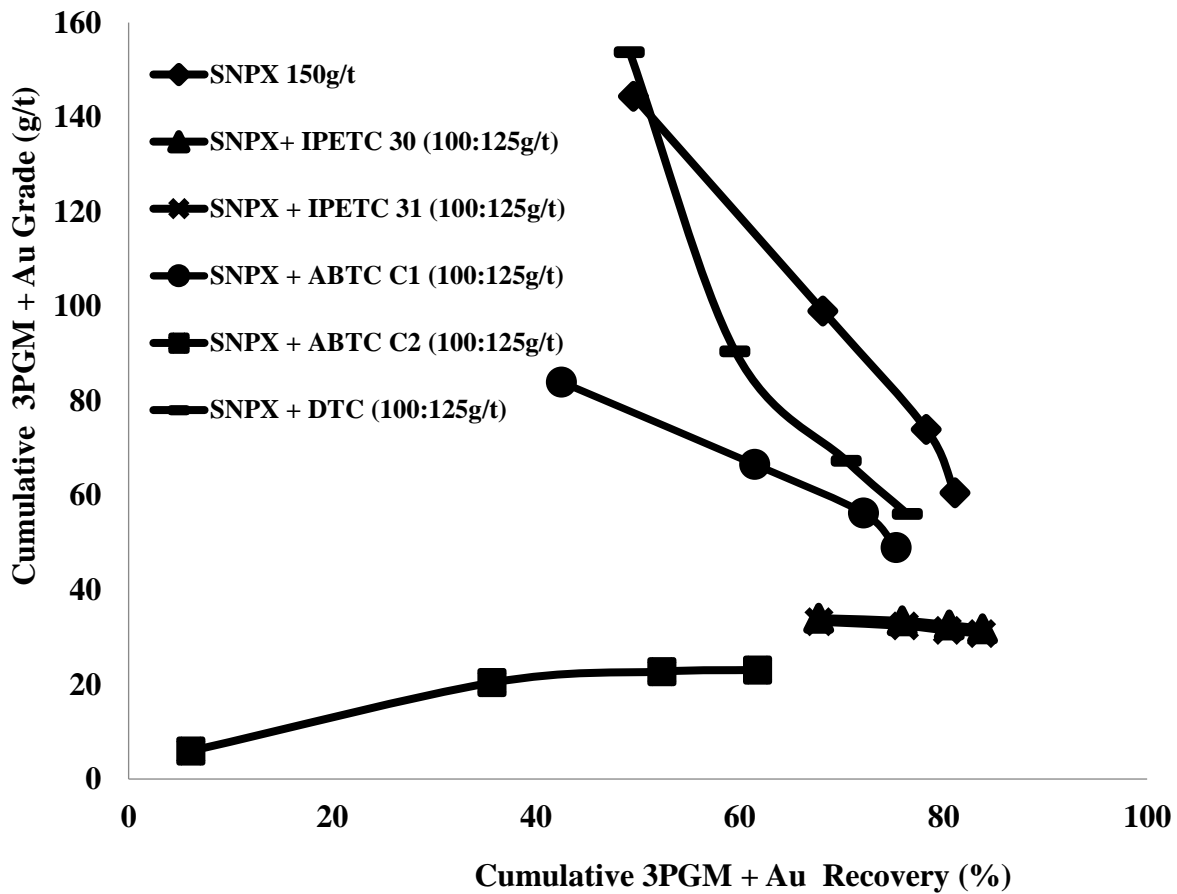


Figure 4-18. The cumulative 3PGE + Au grade versus cumulative 3PGE + Au recovery obtained from P4 UG2 ore with the use of SNPX and SNPX blends with co-collectors at 125 g/t.

SNPX + DTC blends started off at a high grade of 153.71 g/t and reduced to 56.01 g/t. Though it may have attained lower recoveries compared to SNPX, SNPX + IPETC 30, SNPX + IPETC 31, the grade was higher than SNPX + IPETC 30, SNPX + IPETC 31 and SNPX + ABTC 19. So lower recoveries and higher grades were attained for SNPX + DTC blends. However, comparing these results to the dosage of 50 g/t of the co-collectors, the 125 g/t performed poorly. The dosage of 125 g/t of co-collectors ended up losing collecting power and selectivity, especially for SNPX + IPETC 30, SNPX + IPETC 31, SNPX + ABTC C1 blends. It is therefore wise to conduct an optimisation test to determine the correct dosing rate.

The froth phase can determine the grade of the mineral obtained from the flotation process by facilitating removal of entrained gangue minerals without losing the attached valuable minerals

and there is an optimum froth stability required to achieve this (Bradshaw, 1997). For example, if the froth is too stable the gangue minerals do not drain back into the pulp leading to low grades. This is evidently shown in Figure 4-18 whereby grades (23.07 to 56.01 g/t) dropped drastically when the ore was floated at a co-collector dosage of 125 g/t, while at a co-collector dosage of 50 g/t float grades were ranging from 50 to 76.1 g/t. However, if the froth is not stable enough, the froth will breakdown causing the loss of mineral from the froth back into the pulp phase, consequently reducing recovery.

Although all the other blends showed the grade-recovery trade off, SNPX + ABTC C2 blend was doing the opposite, with recovery and grade were actually increasing together. At the very low level of recovery, the blend was very selective, and grade was not yet being compromised.

The short chain collectors which possess lower collecting strength like dithiophosphates are usually compensated for by increasing their dosage, and there is optimum dosage for each system, however too high dosage is detrimental (Sutherland and Wark, 1955). In this case the dosage of 125 g/t indicates that it is over the optimum dose, hence the antagonistic effect was experienced.

The other factor that may have led to bench mark lower grades is the presence of reagent consumers such as actinolite, muscovite and talc. They could have consumed the reagents before they had enough time to be adsorbed on the minerals.

4.2.2.3 Chrome recovery versus water recovery obtained with the use of SNPX and SNPX blends.

Figure 4-19 and Figure 4-20 illustrate the relationship between the chromite and water recoveries at each stage of flotation with SNPX and its blends at 50 and 125 g/t of co-collectors, respectively. The raw data is available in appendix B.

Figure 4-19 shows the average percentage chromite recovery with the use of SNPX and SNPX blends at 50 g/t increasing in the following order:

SNPX = SNPX + ABTC C1 < SNPX + DTC < SNPX + IPETC 30 < SNPX + IPETC 31 < SNPX + ABTC C2

0.25 % < 0.28 % < 0.3 % < 0.32 % < 0.37 %

The SNPX and SNPX + ABTC C1 attained equal percentage chromite recovery of 0.25 %.

The mass percentage of water with the use of SNPX and SNPX blends at 50 g/t increased in the following order (Figure 4-19):

SNPX = SNPX + ABTC C1 < SNPX + DTC < SNPX + ABTC C2 < SNPX + IPETC 30 < SNPX + IPETC 31

6.61 % < 6.25 % < 6.62 % < 6.95 % < 7.04

The first and second concentrates only had short duration of floating, i.e. one and three minutes, respectively, compared to the third and fourth concentrates which were floated for 8 and 12 minutes, respectively, and the water recovery by mass therefore increased by that order stated. Moreover, the first two concentrates recovered higher percentages of chromite. Chromite was mostly entrained and recovered together in sizes with finer particles, but over time chromite recovery decreased. Generally chromite is not naturally hydrophobic and it reports to the concentrate by entrainment. Higher mass pull rates or recoveries thus enhance chromite entrainment. All these blends performed very well regarding the recovery of chromite. The percentage chromite recoveries are below 2.5 % which is the limit of the smelter requirements.

In addition, the presence of talc may be small (see Figure 4-10) in the ore, but it also possesses disproportionate effect on concentrate grade by enhancing froth stability and increasing the entrainment of other gangue minerals. Therefore, other hydrophilic minerals like chromite and pyroxene also ends up reporting to the concentrate (Martinovic, 2004).

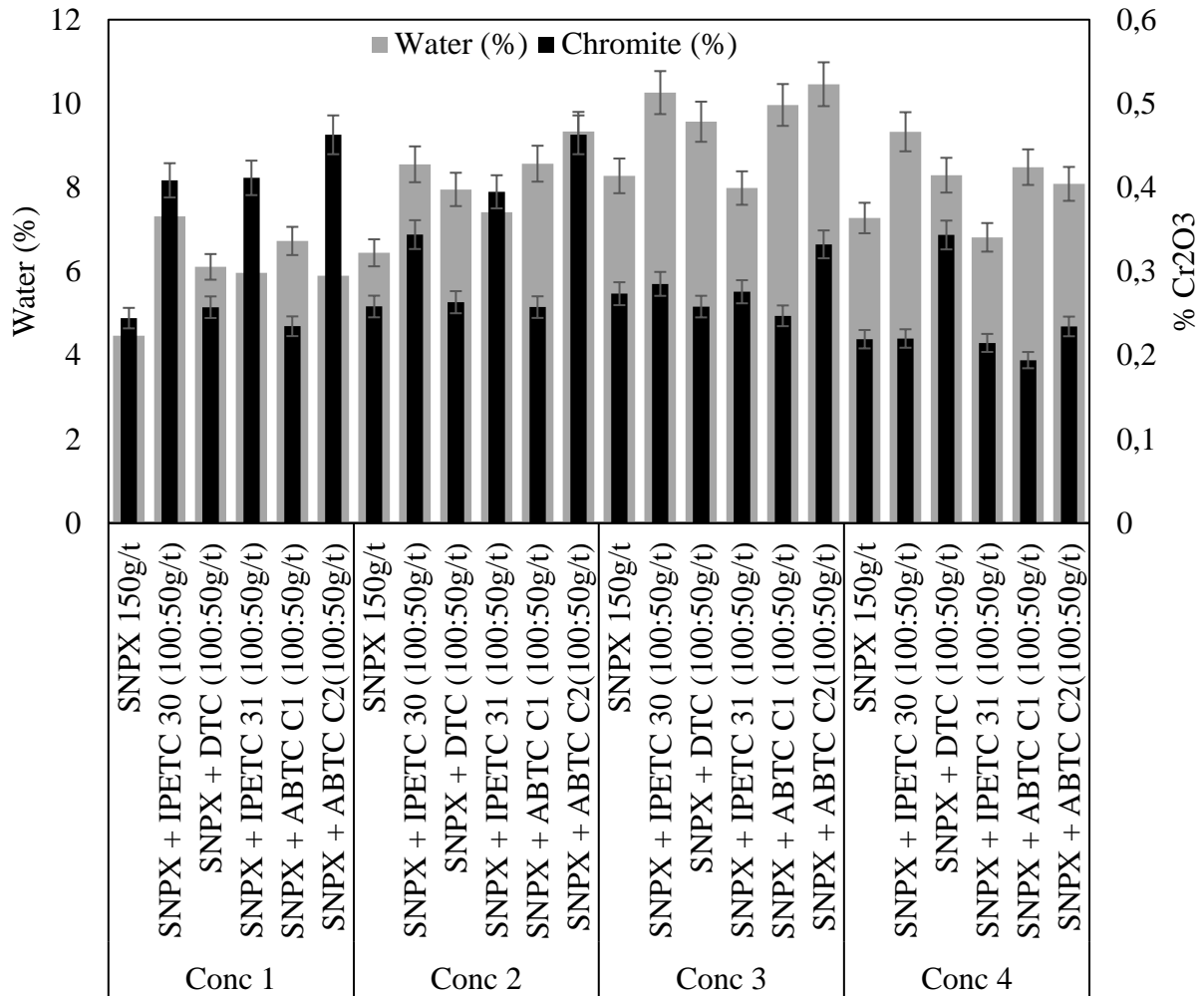


Figure 4-19. Chrome recovery versus water recovery obtained with the use of SNPX and SNPX blends with co-collectors at 50 g/t.

SNPX and its blends at a dosage of 125 g/t of co-collector show average percentage (Conc 1 to Conc 4) chromite recovery increase in the following order (Figure 4-20):

SNPX + DTC < SNPX < SNPX + ABTC C1 < SNPX + ABTC C2 < SNPX + IPETC 30 < SNPX + IPETC 31

0.21 % < 0.25 % < 0.26 % < 0.35 % < 0.5 % < 0.79 %

The percentage mass of water recovery with the use of SNPX and SNPX blends at 125 g/t increased in the following order (Figure 4-20):

SNPX + DTC < SNPX < SNPX + ABTC C1 < SNPX + IPETC 30 < SNPX + IPETC 31 < SNPX + ABTC C2

6.45 % < 6.61 % < 8.39 % < 9.60 % < 10.05 % < 10.40 %

SNPX + IPETC 31 yielded higher average chromite recovery of 0.79 % than SNPX and its other blends. And the lowest chromite recovery was 0.21 % for SNPX + DTC. Like the recovery of chromite at a dosage of 50 g/t for co-collectors ranging from 0.25 % to 0.37 %, the overall chromite recovery for SNPX and its blends at a dosage of 125 g/t for co-collectors were less than 1 % and ranging from 0.21 % to 0.79 %. The high dosages of co-collector lead to high recovery of chromite. The water recovery increased with time, while the chromite recovery was decreasing and becoming less entrained.

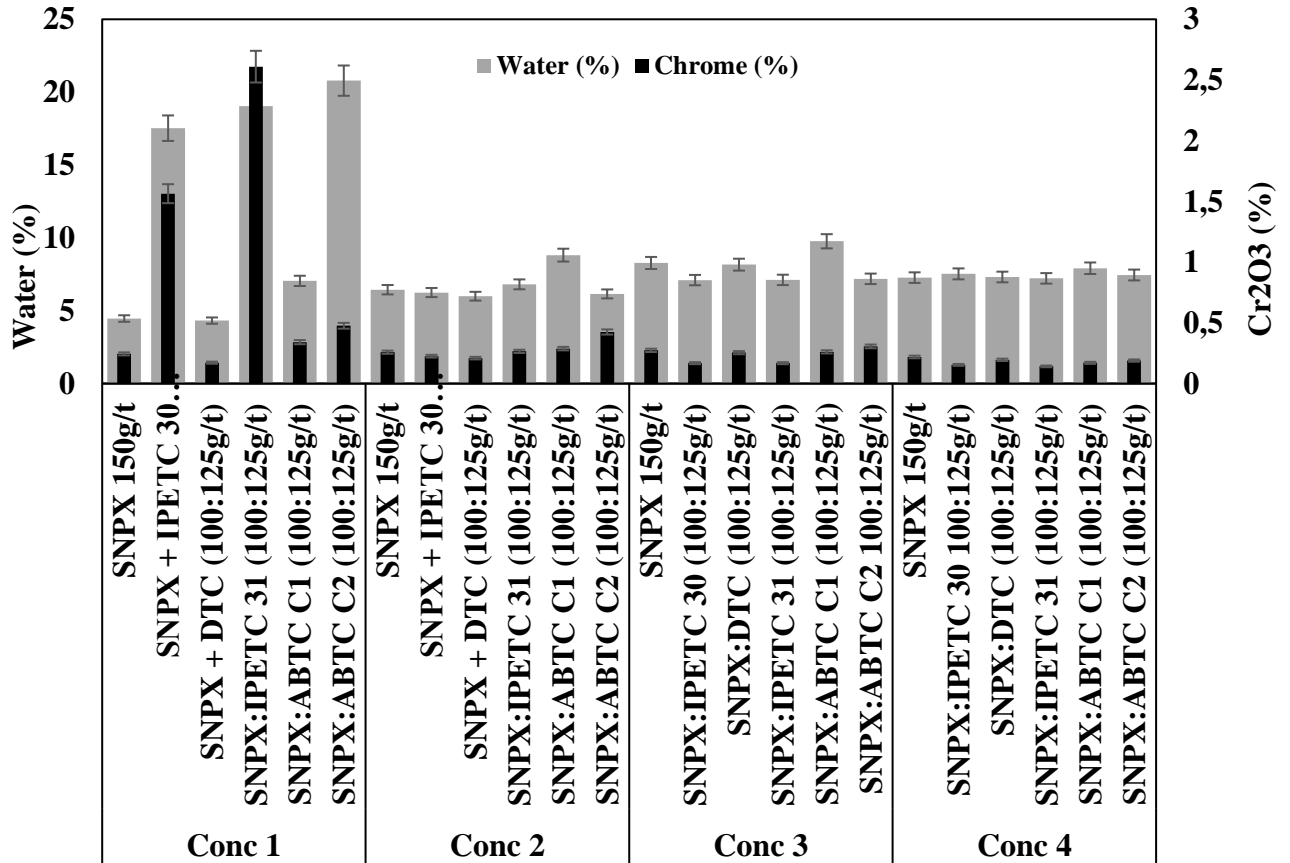


Figure 4-20. Chrome recovery versus water recovery obtained with the use of SNPX and SNPX blends with co-collectors at 125 g/t.

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Different secondary collectors, also known as co-collectors were evaluated in this study in order to improve the recovery of platinum group elements (PGEs) from a UG2 ore from the western limb of Bushveld Complex. Mineralogical study of the ore was conducted using Scanning electron microscopy- energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), and optical microscopy and results showed the presence of chromite, plagioclase, enstatite, sulphide minerals. The PGEs were not detectable by any of the techniques used because of their small size and rarity. Consequently, compositional or textural differences in the ore mineralogy between the two feed sources (EPL and P4) could not be evaluated. However, differences in concentrations of minor gangue constituents such as talc, muscovite, chlorite and actinolite that were discerned by X-ray diffraction suggest that reagent consuming gangue mineralogy may have contributed to the differences in PGE recoveries by flotation.

The main technique used for beneficiation of PGEs is froth flotation, and the batch floats tests were conducted using the primary collector which was sodium n-propyl xanthate (SNPX) and the SNPX + co-collector blends. The co-collectors used were two formulations of S-alkyl-N-butyl thionocarbamate (ABTC C1 and ABTC C2), two formulations of O-isopropyl-N-ethyl thionocarbamate (IPETC 30 and IPETC 31) and lastly one dithiocarbamate (DTC). The total primary collector when it was used without the blend was 150g/t and when blended with co-collectors it was varied between 100:50 g/t and 100:125 g/t.

The flotation results showed that the use of 50 g/t of co-collectors yielded optimum PGEs + Au recoveries and grades, while the dosage of 125 g/t decreased recoveries and grades. The high dosage quantities of collectors do not necessarily mean they will yield improved recoveries and grades. Different chain structures can be used to alter the behaviour of a collector, and these may increase or decrease the recovery. By using a collector with a longer hydrocarbon chain the flotation limit may be extended without loss of selectivity, consequently bringing about greater water repulsion, instead of increasing the concentration of a shorter chain collector (Wills and Napier-Munn, 2006).

At 50 g/t of co-collector SNPX + IPETC 30 and SNPX + IPETC 31 yielded improved 3PGE + Au PGEs recoveries of 85.7% at 3PGE + Au grades of 60.14 g/t compared to unblended SNPX (150g/t) which yielded 3PGE + Au recovery of 81.1 % but insignificantly higher grade of 60.53 g/t. On the other hand, SNPX + IPETC C1 blend yielded low 3PGE + Au recoveries compared to SNPX + IPETC 30 and SNPX + IPETC 31 blends, but it achieved the highest grade of 76.1 g/t. Evidently, this proves that the relationship between recovery and grade is a trade-off.

The results have shown the synergic effects, especially for SNPX blended with IPETC 30, and SNPX blended with IPETC 31 at dosage of 100 g/t (SNPX) and 50 g/t (IPETCs). It can be inferred that the different interaction obtainable from the thionocarbamate (ROCSNHR), effectively complement that from the xanthate ion (ROCS_2^-) to achieve more collector interaction at surface sites otherwise interactable for xanthate only. Therefore the collector blends rendered the mineral of interest hydrophobic and as a result the minerals were recovered to the concentrate.

At a 125g/t of co-collector SNPX + DTC attained lower recoveries compared to SNPX, SNPX + IPETC 30, SNPX + IPETC 31, however the grade was higher than SNPX + IPETC 30, SNPX + IPETC 31 and SNPX + ABTC C1. So lower recoveries and higher grades were attained for SNPX + DTC blends. However, comparing these results to the dosage of 50 g/t of the co-collectors, the 125 g/t performed poorly. The dosage of 125 g/t of co-collectors ended up losing collecting power and selectivity, especially for SNPX + IPETC 30, SNPX + IPETC 31, SNPX + ABTC C1 blends. It is therefore wise to conduct an optimisation test to determine the correct dosing rate.

In addition, the chromite entrainment was below the smelter limit and is very beneficial since chromite is detrimental to the furnace.

5.2 Recommendations

The blends of SNPX with IPETC 30 and IPETC 31 at dosage 50g/t have shown overall satisfying recoveries and the chromite recovery is less than 1 % meaning there will not be any smelter penalties for chromite content. Therefore, these are the recommended collector blends.

The following are recommendations for further work:

- Further mineralogical study of the ores may provide deeper insight into the causes of low recoveries under SNPX only.
- Lonmin and other companies may start using these co-collectors for improved recovery of the PGEs.
- Further flotation tests may be conducted by exploring the co-collectors dosages between 50g/t going to 125g/t just in case an intermediate value may yield even better results.
- Chemisorption studies between the minerals and co-collectors used will provide more specific insight and details into the actual interaction synergy that gave the improved recoveries

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LIST OF APPENDICES

APPENDIX A

Reagent dosage calculation for flotation test

$$X_{ml} = \frac{Y(kg) \times 100 \times Z(\frac{g}{t})}{1000 \times N\%}$$

Where:

X – Dosage of reagent in ml

Y – Mass of the dry sample in kg

Z – Dosage required for the test in g/t

N – Strength of the reagent if percentage

Chemical and physical properties of SNPX

Properties	CuSO ₄	Norilose 8058	Senfroth 200	SNPX
Appearance	Powder	Dry powder or granules	Liquid	Hygroscopic crystalline solid
Colour	Blue	White to yellowish	Colourless	Shades of yellow, pale yellow when pure
Odour	No data available	Odourless	Mild	Disagreeable odour, unpleasant
Active ingredients	Cupric sulfate	Sodium Carboxy Methyl Cellulose	2-[2-(2-butoxyethoxy)ethoxy]ethanol; TEGBE; triethylene glycol monobutyl ether;butoxytriethylene glycol	Sodium n- propyl xanthate
pH value	No data available	6-10 (1% solution)	7	Strong alkaline
Melting point	200	-	Not applicable	75
Boiling point	No data available	Not applicable	277	Not applicable, it composes on heat.
Density	3,103 g/mL (Relative density)	0.55-0.67	0.992	Bulk 05-0.8
Flash point (°C)	No data available	No data available	138	No flash point for solid (30 on contact with moisture.
Solubility in water	No data available	Very soluble (gel formation)	Completely soluble	Soluble

Properties	Dithiocarbamate (DTC)	S-alkyl-N-butyl thionocarbamate (ABTC C1)	S-alkyl-N-butyl thionocarbamate (ABTC C2)	Isopropyl-N-ethyl thionocarbamate (IPETC)	Isopropyl-N-ethyl thionocarbamate (IPETC)
Appearance	Aqueous solution	Clear liquid	Clear liquid	Clear oily liquid	Clear oily liquid
Colour	Yellow to red-orange	Yellow-orange	Yellow-orange	Amber to orange	Amber to orange
Odour	Amine	Garlic	Garlic	Pungent	Pungent
Active ingredients	Dithiocarbamate/Sodium hydroxide	S-alkyl-N-butyl thionocarbamate	S-alkyl-N-butyl thionocarbamate	Isopropyl-N-ethyl thionocarbamatecollectors	Isopropyl-N-ethyl thionocarbamates
pH value	11	Not applicable	Not applicable	No data available	No data available
Melting point	No data available	Not applicable	Not applicable	No data available	No data available
Boiling point(°C)	100-110	Not applicable	Not applicable	82	82
Density (g/ml)	1,1	1,04	1,04	0,85	0,85
Flash point (°C)	> 95	94,2	94,2	62	62
Solubility in water	No data available	Negligible	Not applicable	Negligible	Negligible

APPENDIX B

The raw data obtained when floating EPL ore and P4 ore at the same reagent suite.

Product	EPL 150 g/t				P4 150 g/t			
	Assay		Mass		Assay		Mass	
	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)
C 1	191.82	4.43	50.3	236.1	147.44	4.49	69	351
C 2	69.75	5.13	69.2	416.6	53.37	5.44	73.5	481.1
C 3	30.21	5.56	88.6	630.7	28.85	5.58	83.5	659.1
C 4	23.27	6.08	67.2	611.9	9.66	5.69	65.9	577.9
Tails	5697.9	14902.6	5697.9	9204.7	1.303333	27.4	5688.6	9030.9

APPENDIX C

The raw data of the tests conducted with co-collectors at dosages of 50 g/t and 125 g/t. These results show the concentrate assays and masses of solids and water.

Product	P4 150 g/t				SNPX:IPETC 30 (100:50g/t)			
	Assay		Mass		Assay		Mass	
	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)
C 1	144.40	5.25	73.00	388.40	113.81	5.10	126.90	635.70
C 2	53.87	5.51	73.50	560.40	40.41	6.12	89.00	744.00
C 3	27.41	5.45	78.70	720.00	25.39	5.82	77.60	892.70
C 4	10.01	5.74	59.90	632.60	21.03	5.78	60.30	811.50
Tails	0.70	27.10	5732.10	6398.60	0.63	27.73	5641.10	8016.10

Product	SNPX:IPETC 31 (100:50g/t)				SNPX:IPETC 19 (100:50g/t)			
	Assay		Mass		Assay		Mass	
	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)
C 1	110.39	5.63	115.30	661.90	145.65	5.43	77.70	585.00
C 2	48.29	6.62	94.10	822.60	72.51	6.16	70.60	745.30
C 3	31.04	5.52	78.80	886.40	44.00	5.71	71.20	867.10
C 4	24.21	5.50	61.60	756.00	36.40	5.26	57.60	738.10
Tails	0.90	27.60	5642.90	7973.10	1.04	28.10	5726.50	8164.50
Product	SNPX:DTC (100:50g/t)				SNPX:IPETC 21 (100:50g/t)			
	Assay		Mass		Assay		Mass	
	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)
C 1	139.15	4.85	84.30	531.30	88.30	6.80	98.80	512.80
C 2	44.78	5.57	75.10	691.90	49.89	6.84	106.80	812.10
C 3	25.36	5.21	78.70	832.30	29.94	5.82	90.10	910.10
C 4	18.59	8.28	65.90	721.40	22.36	5.24	70.60	703.40
Tails	0.77	27.53	5704.00	8323.10	0.89	27.70	5616.20	8161.60

Product	P4 150 g/t				SNPX:IPETC 30 (100:125g/t)			
	Assay		Mass		Assay		Mass	
	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)
C 1	144.40	5.25	73.00	388.40	34.03	5.33	448.60	1524.90
C 2	53.87	5.51	73.50	560.40	29.31	5.46	63.10	543.60
C 3	27.41	5.45	78.70	720.00	22.68	5.61	45.80	617.80
C 4	10.01	5.74	59.90	632.60	19.78	6.32	37.20	654.80
Tails	0.70	27.10	5732.10	6398.60	0.67	27.57	5428.70	5358.90

Product	SNPX:IPETC 31 (100:125g/t)				SNPX:IPETC 19 (100:125g/t)			
	Assay		Mass		Assay		Mass	
	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)
C 1	33.26	9.11	454.40	1657.00	83.92	5.40	98.40	613.20
C 2	26.68	6.01	70.60	592.40	45.41	5.53	81.10	766.90
C 3	20.34	5.78	46.10	619.00	29.68	5.81	70.00	849.60
C 4	20.69	6.21	36.10	628.20	12.39	5.32	53.00	688.60
Tails	0.66	27.97	5501.20	5203.40	0.84	27.00	5710.80	5781.70
Product	SNPX:DTC (100:125g/t)				SNPX:IPETC 21 (100:125g/t)			
	Assay		Mass		Assay		Mass	
	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)	PGM(g/t)	Cr203 (%)	Solid mass(g)	water mass(g)
C 1	153.71	4.41	59.70	375.90	5.95	5.48	139.30	1808.70
C 2	30.59	5.07	63.70	521.70	41.00	6.98	97.60	535.30
C 3	28.09	5.37	72.40	710.00	30.16	6.56	74.80	625.40
C 4	18.89	5.04	59.20	636.30	25.12	6.00	50.60	648.10
Tails	0.77	26.77	5659.70	6456.10	0.91	27.90	5616.20	5082.50

ⁱ P-names changed for confidential reasons