Recovery of PGMs from an oxide ore by flotation and leaching

Msc Research Thesis

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September, 2018

ABSTRACT

Froth flotation is the process used in the Platinum Group Metal industry to upgrade the run-of-mine ore for subsequent processes such as smelting and hydrometallurgical PGM refining. The PGM concentrator plants achieve high PGM recoveries (>85%) when treating prestine (unweathered) sulphide ores. However, the depletion of prestine sulphide PGM bearing minerals has triggered interest in exploration of techniques for PGM recovery from near surface oxidised PGM ores. All earlier attempts to process the oxidised PGM ores by conventional flotation methods achieved poor recoveries (typically less than 50 %) hindering the commercial exploitation of these resources.

The characterisation of the non-sulphide PGM ore used in this study indicated that the ore is enriched in oxide iron minerals as a result of weathering. In the flotation work, the maximum PGM flotation recoveries achieved using the sulphide co-collector schemes were 55.1% 3E (Pt, Pd and Au). Application of the hydroxamate oxide collector improved the flotation performance to recoveries of 74.7% 3E. The superior PGM recoveries achieved with hydroxamates probably lies in their ability to form complexes with metals such as iron. Hydroxamates co-collectors have been proven to improve recoveries without any adverse effects on performance of primary collectors such as SIBX.

In this study the non-sulphide PGM ROM ore was leached directly using different acids. Low PGM extractions were recorded for hydrochloric acid (36.6% Pt and 8.8% Pd) and nitric acid (34.5% Pt and 7.1% Pd). The best leaching results of 48% Pt and 24.5% Pd were obtained using aqua regia solution though it is non-selective. Leaching of ROM ore is generally not preferable as it leads to high reagent consumptions. In this study it was postulated that leaching of low grade flotation concentrate would be preferred. Experiments were conducted to leach the concentrate that had the highest PGM recovery with sulphuric acid in order to target the base metals and further concentrate the PGMs in the residue. The base metal recovery from flotation concentrate using sulphuric acid was only efficient for copper and nickel while poor iron recoveries were achieved.

DECLARATION

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2. I have used the Harvard referencing system for citation and referencing. Each significant contribution to, and quotation in this report from the work or works of other people have been duly referenced.

3. This thesis is my own work.

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ACKNOWLEDGEMENTS

I would like to thank the following individuals who contributed immensely towards the completion of this project and the thesis write-up.

Firstly I thank my supervisor Prof Vusi Sibanda for his patient guidance, encouragement, constructive criticism and suggestions throughout the course of this project. His supervision made this masters project a fulfilling learning experience. I would also like to thank my colleague Mr. Katlego Sekgarametso for all the technical discussions of experimental work, data analysis and publication collaborations.

The support provided by the Lab managers and the administrative staff at the School of Chemical and Metallurgical Engineering by ensuring that all the resources were available when required is greatly appreciated.

My sincere appreciation goes to my family especially my aunt Lydia Ntokoane for the financial support she provided to start this project. The continued emotional support and encouragement provided by my three brothers and father helped this work to be feasible. ‘Sentle ke ho boea le thebe le marungoana Bafokeng!’.

Acknowledgements also go to The National Research Foundation (NRF) for financial support, Chemquest and Axis House for supplying the flotation reagents.

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NOMENCLATURE

AAS	Atomic Absorption Spectroscopy
AM810	Hydroxamate co-collector
Au	Gold
BIC	Bushveld Igneous Complex
BMS	Base Metal Sulphides
Ca^{2+}	calcium ions
CO_2	carbon dioxide gas
CPS	controlled potential sulfidisation
Cu	copper
Fe-OCO_2 H	Iron bicarbonate
FLOMIN C5460	sulphide co-collector (DTP + IPETC)
FLOMIN C7133	sulphide co-collector (Xanthoge formate + IPETC)
H_2CO_3	Carbonic acid
HCl	Hydrochloric acid
H^+	Hydrogen ion
H_2 O	Water
HCO_3^-	Bicarbonate
H_2SO_4	sulfuric acid
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

MSZ	Main Sulphide Zone
NaHS	sodium hydrogen sulphide
Ni	nickel
OH^-	Hydroxide ion
Pd	palladium
PGE	Platinum Group Elements
PM230	modified xanthate
PPM	Pilanesburg Platinum Mine
Pt	platinum
$PtAs_2$	sperrylite
(Pt,Pd,Ni)S	cooperate
(Pt,Pd)(Bi,Te)	(Pt,Pd)-bismuthotellurides
QEMSCAN	Quantitative Evaluation of Minerals by Scanning electron microscopy
Rh	Rhodium
SIBX	Sodium Isobutyl Xanthate
wt%	weight percent

1. INTRODUCTION

1.1 Background

Platinum Group Metals (PGMs) possess unique properties such as high conductivity, catalytic activity and corrosion resistance which make them suitable materials for use in a wide range of applications which include manufacture of electronic components, catalysts for chemical processes, vehicle catalytic converters and hydrogen fuel cells (Xiao & Laplante, 2004). The worlds' largest deposit of Platinum Group Metals (PGMs) is the Bushveld Igneous Complex (BIC) in South Africa followed by the Main Sulphide Zone (MSZ) of the Great Dyke in Zimbabwe. The Bushveld Complex comprises of three main reefs, the Merensky reef, Upper Group 2 (UG2) reef and the Platreef. The Merensky reef has been the most exploited because it has relatively higher PGM grades. The UG2 reef exhibits similarly high PGM content as the Merensky but lower levels of nickel and copper minerals. Additionally, UG2 reef contains high concentrations of chromite for which stringent limits and penalties are imposed by smelters because of operational problems such as blocking of the kilns that result from roasting of chromite ores (Liddel & Adams, 2012; Little, et al., 2016). The Platreef has lower PGM values and it is enriched in palladium and base metals (Jones, 2005).

The economical reserves of PGMs in the Main Sulphide Zone in Zimbabwe are currently mined at the Ngezi, Unki and Mimosa mines. The sulphide-rich BIC and MSZ mostly have underground mines that produce ore that is treated by conventional metallurgical processes such as grinding, milling, flotation, smelting and production of a matte and chemical refining (Oberthur, et al., 2013). The achieved successes of PGM concentration by flotation from these pristine (unweathered) sulphide ores is largely due to the occurrence of PGMs in close association with base metal sulphides minerals like chalcopyrite, pentlantite and pyrrhotite which are easily floatable. Platinum recoveries achieved during flotation of pristine ores are generally greater than 85% (Rule, 1998; Locmelis, et al., 2010).

However, the fast depletion of sulphide PGM bearing minerals has triggered interest in exploring possibilities for recovery of the PGMs from near surface oxidised PGM ores, which have

proved to be more difficult to process by conventional means, as an alternative source to sustain PGMs production (Cramer, 2001).

Earlier attempts to process the oxidised PGM ores by conventional flotation methods achieved poor recoveries (typically less than 50 %) hindering the commercial exploitation of these resources. Work performed by Zimbabwe Platinum Mines (Zimplats) on flotation of oxidised MSZ ores from the Ngezi Mine and work conducted at the Old Wedza mine and at the Hartley Mine yielded recoveries of 15 – 30 % (Locmelis, et al., 2010). Attempts made in the South African Bushveld Complex UG2 Reef at Smokey Hills mine, Impala Platinum mine in the western Bushveld and at the Pilanesburg Platinum Mine (PPM) to process oxidized PGM ores by flotation also resulted in low and erratic recoveries (typically < 40%) (Becker et al, 2014; Oberthur, et al., 2013)

1.2 Mineralogy of oxidized PGM ores

Only a few studies exist on oxidised PGM ores from the Bushveld Igneous Complex in South Africa (Ramonotsi, 2011; Becker et al, 2014; Musonda, 2015), but substantial research is documented on the oxidised PGM ores of the MSZ from the Great Dyke of Zimbabwe (Duyvesteyn et al, 1994; Evans, 2002; Locmelis et al, 2009; Oberthür et al, 2013; Kraemer et al, 2015). Oxidised PGM ores which typically exist near the surface i.e. 15 – 30 m deep are altered and oxidised as a result of exposure to atmospheric conditions and acidic ground waters. The major process occurring during oxidation of PGM ores is thought to be the decomposition of base metal sulphides and formation of iron oxyhydroxides. Consequently, the PGE in oxidised ores exist (i) as relict primary PGM, (ii) as secondary PGE alloys, (iii) in solid solution with relict base metals (BMS) (iv) as PGM oxides/hydroxides and (v) as PGE hosted by secondary oxides/hydroxides or silicates (Evans, 2002; Oberthür et al, 2013);.

Alteration and oxidation of base metal sulphides (BMS) affect the particle surface chemical properties, and hence reduce the ability to interact and react with flotation reagents such as sulphide collectors. Moreover, the Pd remobilization in oxidised PGM ores is also believed to reduce flotation efficiency by changing Pt:Pd ratio which is the key metric for PGM flotation (Becker et

al, 2014). Remobilization of Pd refers to removal of palladium from the upper part of the weathered zone and its enrichment in the lower zone. The Pt:Pd ratios rise from 1.7 in pristine ores to about 2.3 in oxidised ores as a result of Pd mobilization (Hey, 1999). Table 1 shows the composition of Main Sulphide Zone (MSZ) ore and the associated oxidised ore.

Table 1: Proportions (by number of grains n, in %) of discrete PGMs observed on polished pristine MSZ and in oxidised MSZ ore concentrates. **(Oberthür et al, 2013)**

Ore type	Discrete PGM grains (n)	PGM phases identified (%)					
		(Pt,Pd)(Bi,Te)*	$PtAs_2$	(Pt, Pd, Ni)S	Pt &Pt-Fe alloys	PGE-sulpharsenides	others
Pristine sulphide MSZ	801	50.1	19.0	8.5	2.4	11.9	8.7
Oxidised sulphide MSZ	1293	11.4	57.2	28.3	3.1	0	0

Table 1 shows that the oxidized PGM ore contains much more sperrylite ($PtAs_2$) and cooperate ((Pt,Pd,Ni)S) minerals and significantly lower (Pt,Pd)-bismuthotellurides mineral compared to the pristine PGM ore sample, showing evidence of alteration.

1.3 Resource estimates of oxidized pgm ores

The oxidised PGM ores present lucrative prospects for future mining of PGMs because the resource estimates of oxidised PGM ores which are either unmined, mined and stockpiled or discarded as overburden waste in South Africa and Zimbabwe are over 500 million tonnes. At the current platinum prices of approximately US$970 per ounce, the value of platinum alone in these ores amounts to about US$10 – 20 billion. The economic benefits that could be realized by developing an alternative and effective processing techniques is so immense that it is motivating research efforts to investigate processing routes for oxidised PGM ores (Oberthur, et al., 2013). The additional advantage is that the oxidised PGM ores can be mined through relatively lower cost open pit mining processes such as one employed in Pilanesburg Platinum Mines (PPM) in South Africa because the ore occurs close to the surface (Becker et al, 2014).

1.4 Problem statement

PGM Mine Concentrator plants fail to meet the plant extraction specification of PGMs in the flotation tailings when treating oxidised or non-sulphide PGM ores. This has been attributed to some PGM values that are within the floatable size range that do not float and subsequently report to the tailings (Ramonotsi, 2011). Studies suggest that poor flotation recoveries achieved are as a result of alteration that happened to the original pristine sulphide ore due to weathering/oxidation. The mineralogy study of the oxidised PGM ore showed that the ore has low base metal sulphides (BMS) content, typically about 0.2 wt% and exhibits a lack of PGM association to the BMS (Becker et al, 2014). Attempts to improve PGM flotation recoveries from PGM oxidised ores have so far been unsuccessful, hence there is no commercial process for recovery of PGM's from such ores. The scope of this current study was to undertake an extensive review of research work that has been done on processing PGM oxidised ores and from this review identify potential beneficiation route/s and perform the preliminary and exploratory test-work to obtain a high level evaluation of the promising process route.

1.5 Objectives

The objectives of this research were to;

1. Undertake an extensive review of research work that has been done on processing PGM oxidised ores.
2. Conduct reagent scouting flotation test-work on the PGM oxide ore using various reagent suites to select appropriate reagents and conditions for improving flotation recoveries from oxidised PGM ore.
3. Optimise the selected reagent suite to achieve the highest possible PGMs flotation recovery.
4. Investigate the hydrometallurgical recovery of PGMs from ROM ore by leaching test work
5. Investigate the feasibility of upgrading the recovered concentrate by leaching the base metals with sulphuric acid

6. Evaluate the hydrometallurgical processing and the flotation routes in terms of the recoveries achieved by each, in order to propose a possible process route for the PGM oxide ore material under study.

1.6 Key questions

1. Can the PGM flotation recovery from the oxidised PGM ore be improved by using co-collectors such as;
    - hydroxamates,
    - mixture of Dithiophosphates and IPETC and
    - mixture of xanthogen formate and IPETC?

2. Can the low grade flotation concentrate be upgraded by leaching base metals with sulphuric acid?
3. Can the hydrometallurgical processing of ROM PGM oxidised ore be an alternative to the conventional flotation route?

2. LITERATURE REVIEW

2.1 Principles of froth flotation

Froth flotation is a selective physico-chemical process which relies on differences in surface properties of valuable minerals and gangue minerals. Preferential attachment of valuable mineral particles to air bubbles (hydrophobicity) and retention of gangue mineral particles to water (hydrophilicity) are used to achieve separation in a water-mineral slurry (Wills & Napier-Munn, 2006). The hydrophobic particles are carried to a froth phase at the top of the flotation cell while hydrophilic gangue remains in the pulp and reports to the tailings as summarised in Figure 1. Bubble attachment to target minerals is enhanced by conditioning with reagents such as collectors, frothers and modifiers (Nagaraj & Farinato, 2016).

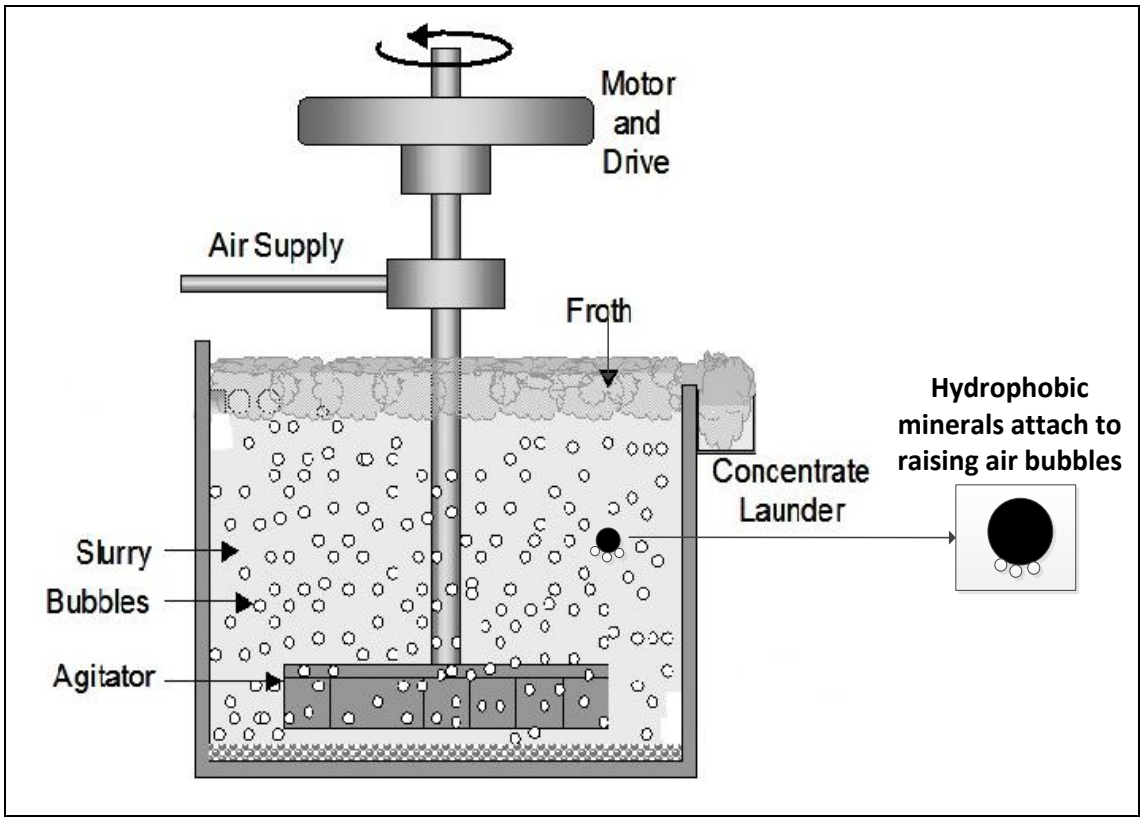


Figure 1: Schematic of batch flotation (adapted from Wills & Napier-Munn, 2006).

2.2 Flotation reagents

2.2.1 Collectors

Collectors are reagents used to impart hydrophobicity on targeted mineral particles through selective adsorption of molecules or ions onto the mineral surface. The collector molecular structure is divided into a water-repellent non-polar hydrocarbon radical which is oriented towards the water phase and a polar part which attaches to the mineral surface during adsorption. This orientation ensures the formation of a hydrophobic monolayer around particle surfaces (Bulatovic, 2007). The formation of a hydrophobic monolayer is influenced by the type and concentration of the collector used because it is generally accepted that excessive collector concentration increases operating costs and reduces valuable mineral recovery by formation of collector multi-layers on particle surfaces (Wills & Napier-Munn, 2006).

Collectors are classified into two broad groups which are insoluble non-ionising compounds and ionizing compounds which dissociate into ions in water as summarised in Figure 2. Ionizing collectors are divided into anionic and cationic collectors depending on the kind of ion that induces hydrophobicity on the mineral surface. Anionic collectors are further subdivided into non-thio compounds and thio-compounds, the latter which are used extensively as sulphydryl collectors in PGM concentrator plants for bulk flotation of base metal sulphides minerals which are normally associated with PGMs (Becker et al, 2014; Kloppers et al, 2016).

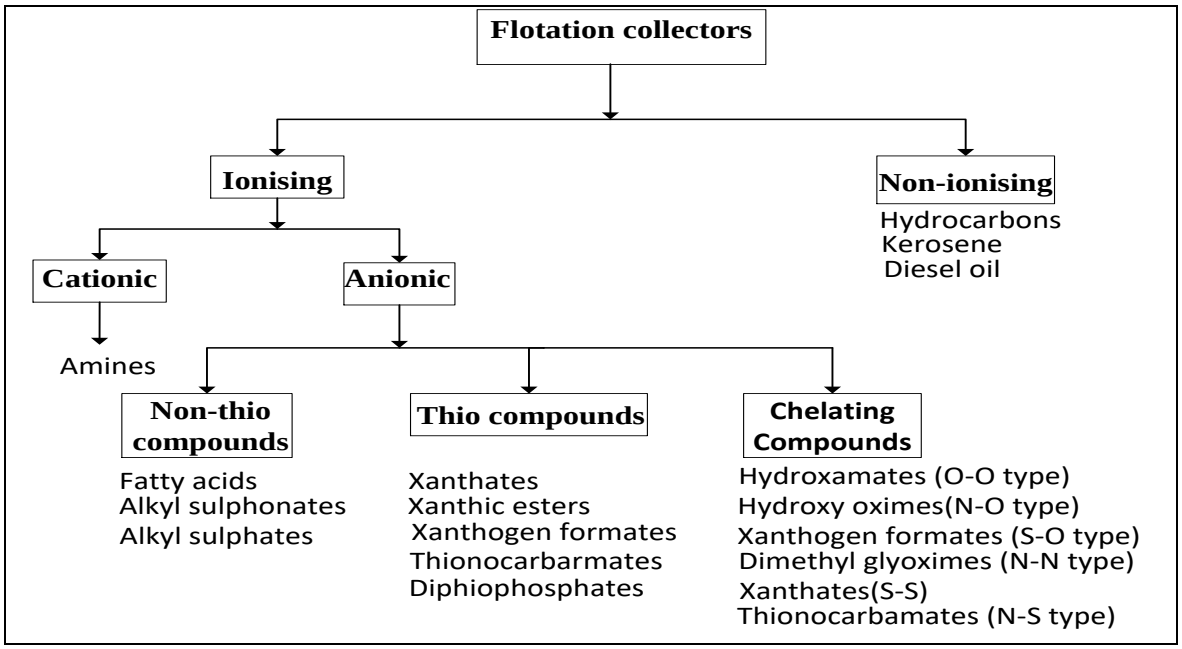


Figure 2: Classification of flotation collectors (adapted from Laskowski, 2010).

2.2.2 Frothers

Frothers are surface active reagents used to stabilize air bubbles in the slurry. This ensures efficient transport of hydrophobic mineral particles to the froth phase and selective drainage of entrained gangue particles (Rao, 2013). The commonly used frothers are heteropolar compounds containing a polar group (OH, COOH, C=O, OSO_2, SO_2OH) and a hydrocarbon radical. The heteropolar structure of the frother molecules enables them to be adsorbed on the air-water interface and reduce the surface tension thereby stabilizing the air bubble (Wills & Napier-Munn, 2006).

2.2.3 Activators

Activators improve the selectivity of flotation process by reacting with the valuable mineral surface to form precipitates which enhance adsorption of collectors. Copper sulphate is extensively used as an activator for the xanthate flotation of sulphide ores (Finkelstein, 1997). A classical example of sulphide mineral activation is the sphalerite activation by copper sulphate which was initially proposed to proceed via an ion exchange process summarized by equations 1 (Fuerstenau, et al., 2007).

$$ZnS\ (s) + Cu^{2+} \rightarrow CuS\ (s) + Zn^{2+} \quad 1$$

However, subsequent works (Ralston, et al., 1981; Wang, et al., 1989d; Prestidge, et al., 1994) suggest that the ion exchange mechanism is oversimplified and instead propose that activation involves further oxidation of sulphide mineral by Cu(II) and reduction of the activator to Cu (I). A more complex mechanism is proposed by Gerson et al (1999) who investigated sphalerite activation by copper sulphate using X-ray absorption fine structure (XAFS) spectroscopy and secondary ion mass spectrometry (SIMS). The results of this study suggest replacement of bulk Zn cations by bulk Cu atoms instead of the initially suggested simple replacement of surface Zn by Cu. This bulk replacement of Zn cations however, is a possible explanation of the two step activation kinetics observed in earlier experiments by other workers (Finkelstein, 1997; Chandra & Gerson, 2009).

2.2.4 Depressants

Flotation concentrate grades are improved by conditioning the pulp with depressants that inhibit flotation of gangue mineral particles. Depressant reagents selectively suppress flotation of gangue minerals by adsorbing on their particles to form a hydrophilic layer that ensures their minimum attachment to rising air bubbles. The major gangue minerals (in decreasing order of abundance) for PGM ores are reported by several studies as orthopyroxene, naturally floatable talc, clinopyroxene and plagioclase (Becker, et al., 2009; Oberthür et al, 2013). The generally used polymer depressants for flotation of sulphide minerals in the PGM industry are carboxymethylcellulose (CMC) and modified guar gum (Corin & Harris, 2010). The flotation efficiency is hugely dependent on the type of depressants, dosages and the mineralogy of the ore. Hence, the high concentrations of talc in complex ores such as oxidised PGM ores dictate the need for unconventionally high depressant dosages as indicated by some workers (Nashwa, 2007; Ramonotsi, 2011; Becker et al, 2014).

2.2.5 pH Modifiers

Flotation efficiency is highly dependent on pulp pH because xanthate collectors are stable in alkaline medium. Pulp alkalinity in flotation is controlled by addition of pH modifiers such as lime or sodium hydroxide while sulphuric acid is added when a decrease in pH is required (Wills & Napier-Munn, 2006). Pulp pH affects flotation recovery by influencing the pulp potential (potential difference of a mineral-solution interface, Eh) which has been proven to be closely related to flotatibility of sulphide minerals (Natarajan & Iwasaki, 1972; Chander, 2003). The work of Natarajan and Iwasaki (1972) showed that in prolonged aeration with oxygen, the Eh measured by a platinum electrode was related to pH according to the equation 2.

$$Eh = Ea - 0.059*pH \quad (2)$$

Where: Ea was 0.85 V in oxygenated acid solutions and 0.95 V in oxygenated alkaline solutions.

Goktepe, (2002) also observed that pulp potential was linearly dependent on solution pH for each of the electrodes that were used in micro flotation experiments. With reference to the PGM flotation, Muzenda et al (2011) observed pH to have a significant effect on the PGM recovery from UG-2 reef and the grades of the PGM concentrates. In this study the highest PGM recovery using SIBX collector was obtained at a pH of 9 while the highest PGM grade was obtained at a pH of 6. Test work by Bulatovic (2003) also indicated that acidic pH (pH 5.5 and 6.5) significantly increased the PGM concentrate grade in the flotation cleaning stages. However, changes in pH were observed to have no significant effect on PGE recoveries in this study.

2.2.6 Mechanisms of PGM ore oxidation

The processing challenges associated with oxidised PGM ores through the conventional flotation reagent schemes can be better understood by considering the effects of weathering on PGM host sulphide minerals as reviewed below. Numerous accounts exist on the alteration mechanisims of the main PGM host base metal sulphides which are pentlandite [$(Fe,Ni)_9S_8$], pyrrhotite ($Fe_{1-x}S$) and chalcopyrite ($CuFeS_2$). The work of Legrand et al (2005a) suggests that oxidation of both pentlandite and pyrrhotite involves diffusion of iron from the bulk lattice to the

surface where it is oxidised. There is concensus that the chalcopyrite oxidation proceeds through a similar mechanism involving migration of iron from the bulk sulphide mineral to the surface (Legrand, et al., 2005; Buckley & Woods, 1984; Vaughan, et al., 1997; Mielczarski, et al., 1996).

The oxidation product is the hydrophilic iron (III) oxyhydroxide (FeOOH) that precipitates on the base metal surfaces rendering them less responsive to suphide flotation collectors. The other alteration products observed by Legrand et al (2005b) on the pentlandite surface were traces of violarite ($FeNi_2S_4$), nickel hydroxide [$Ni(OH)_2$] and nickel sulphate ($NiSO_4$). Prolonged oxidation leads to consumption of all violarite leaving $NiSO_4$ and FeOOH as the only thermodynamically stable products. The study goes on to explain that pyrrhotite surface oxidises more rapidly than pentlandite surface.

Becker (2009) proposed a different oxidation mechanism which involved anodic oxidation of sulphide minerals when exposed to dissolved oxygen or atmospheric air. However, pyrrhotite was still observed to oxidise more readily compared to other base metals sulphides. In this study the author attributed higher oxidation rates for pyrrhotite to its superior metallic conducting properties compared to other BMS.

2.3 Flotation of oxidised/non-sulphide pgm ores

2.3.1 Geological setting – Origin of ore

Mimosa Platinum Mine is located on the Great Dyke of Zimbabwe, which is a 550 km long and 11 km maximum width layered intrusion containing several hundred million tonnes of Platinum Group Elements (PGEs) (Wilson, 1996). Mimosa Platinum Mine is situated on the southern part of the Wedza Geological Complex of the Great Dyke and is 32 km west of Zvishavane and 150 km east of Bulawayo as depicted in Figure 3. The mine is a joint venture shared equally by Impala Platinum and Aquarius Platinum. Mining of pristine PGM ore at Mimosa mine starts at a depth of 60 m below surface and extends to a depth of approximately 200 m. During the 2016 financial year alone 2.64 Mt of pristine ore with a head grade of 3.93 g/t platinum, palladium, rhodium, iridium, ruthenium and gold (6E) were milled at Mimosa Mine. Beneficiation using conventional flotation achieved a recovery of 78%, producing 119 700 ounces of platinum

in concentrate form (Implats, 2016). Currently, the processing of oxidised PGM ore at Mimosa mine and other platinum mines in the MSZ and the Bushveld Complex is not economic and hence such ore is stockpiled or discarded as waste. However, the indicated fast depletion of sulphide minerals is reinvigorating efforts to explore alternative processing routes for oxidised PGM ores in order to sustain PGM production in future (Oberthür et al, 2013).

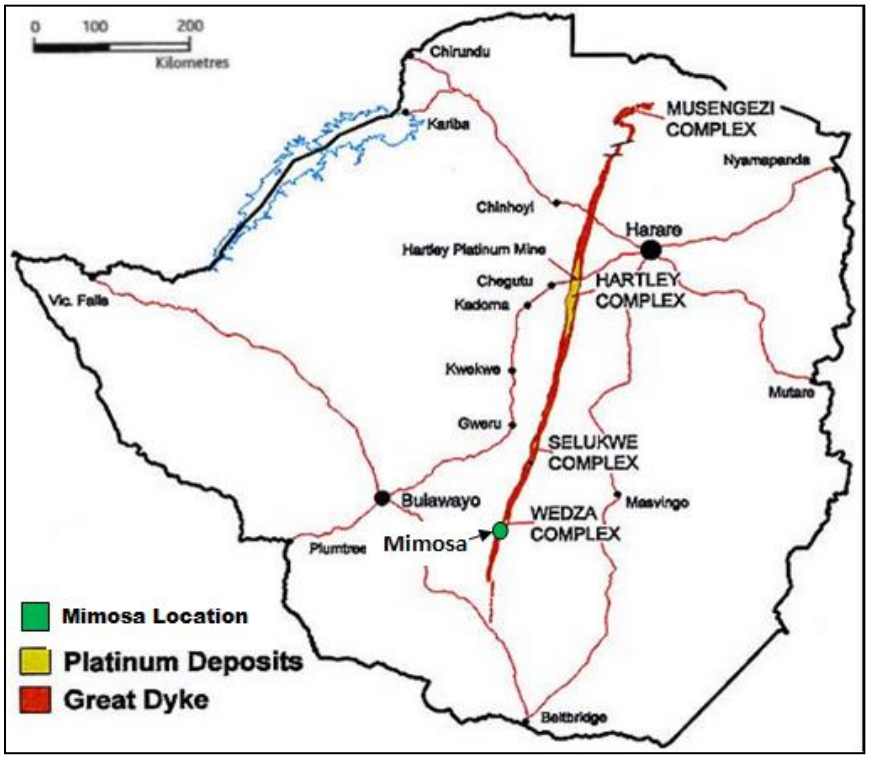


Figure 3: Geological map of the Great Dyke of Zimbabwe showing location of Mimosa mine (adapted from Implats, 2004).

2.4 Previous work on flotation of oxidised pgm ores

Although no commercial processing facility for oxidised PGM ores exists, a number of workers have conducted research aimed at improving recoveries of PGMs from oxidised PGM ores. Some of the research employs pre-treatment of the ores using techniques such as sulfidisation of the oxidized ores, acid pre-treatment, and use of various flotation reagent schemes to process the oxidised PGM ores. Other researchers have focused on improving PGE extractions from oxidised PGM ores by leaching methods. The review of these research efforts to process oxidised PGM ores is presented in the following sections.

2.4.1 Ore pre-treatment before flotation

Flotatibility of oxidized ores is believed to be impaired by the presence of base metal oxides which act as a passivating layer on the mineral surfaces. This makes the conventional reagents suites which are based on sulphide collectors unable to adsorb and make ore particles of the oxidized PGM ore hydrophobic (Mphela, 2010). Pre-treatment of oxidized PGM ore is conducted in an attempt to condition or dissolve the passivating layer from the mineral surfaces so that flotation reagents can access the 'fresh' sulphide mineral surface more effectively.

2.4.2 Sulfidisation and flotation

Sulfidisation is an aqueous process through which a non-sulfide mineral surface is converted to a sulfide-like surface. Sulfidisation involves the reaction of sulfidising agents such as sodium sulphide (Na_2S) or sodium hydrogen sulfide (NaHS) with the oxidised mineral surface. Sodium sulphide hydrolyses and dissociates in the pulp releasing hydroxide ions (OH^-), hydrosulfide ions (HS^-) and sulphide ions S^{2-} into solution as summarised by reactions 2 to 5.

$$Na_2S + 2H_2O \rightleftharpoons 2NaOH + H_2S \quad (3)$$

$$NaOH \rightleftharpoons Na^+ + OH^- \quad (4)$$

$$H_2S \rightleftharpoons H^+ + HS^- \quad (5)$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \quad (6)$$

One of the mechanisms suggested for sulfidisation is adsorption of produced hydrosulfide ions onto the oxidised mineral surface followed by formation of a sulfide surface through anionic exchange (Castro et al, 1974) .

Controlled Potential Sulfidisation (CPS) reduces the chances of excessive sulphide concentration in the pulp and is extensively employed in the flotation of base metal oxides like copper and lead oxidic ores (Jones & Woodcock, 1978; John, 1991). Examples of industrial CPS applications include recovery of oxidised digenite at Ok Tedi Concentrator (Orwe et al, 1998),

flotation of oxidised copper ores at the Nchanga Consolidated Copper Mines (Wills & Napier-Munn, 2006), flotation of bonite at Northparkes Mines (Freeman et al, 2000) and flotation of oxidised copper-cobalt ores at Gecamines in the Democratic Republic of Congo (Kongolo, et al., 2003).

Despite its extensive industrial application, the major challenge with CPS is the poor reproducibility of optimum sulphidisation conditions because of sensitivity to conditioning times, sulphidiser type and concentration (Soto & Laskowski, 1973). Consequently, various optimum suphidising potentials for processing of oxidized copper ores have been reported by a number of workers (Jones & Woodcock, 1978; Nagaraj & Gorken, 1991).

Newell and Bradshaw (2007) investigated the remediation of chemically and thermally oxidized Nkomati ore and oxidized pentlandite using the controlled potential sulfidisation. This technique involved addition of base metal ions (copper and iron) during sulfidisation to improve flotatibility of oxidized mineral pentlandite. The sulfidisation system consisted of a Radiometric PHM 290 pH-Stat Controller, the silver sulfide electrode, a magnetic valve and a burette containing the sulfide electrode. Optimum operating conditions in this study were determined as the sulfidisation potential of -650 mV and copper ion addition in the range of 10 – 100 g/t of ore. After sulfidisation the solution was decanted and replaced with a fresh solution of calcium ions with ionic strength of 10^{-2} Ca^{2+}. Flotatibility of heavily oxidized pentlandite was restored because 80% flotation recovery was achieved while unsulfidised ore was observed not to float at all. Hence it was suggested that CPS could be a viable technique of improving flotation recovery of PGMs from oxidized ores (Newell et al, 2006). The typical experimental flow diagram of sulfidisation followed by flotation of oxidised ore is depicted in Figure 4.

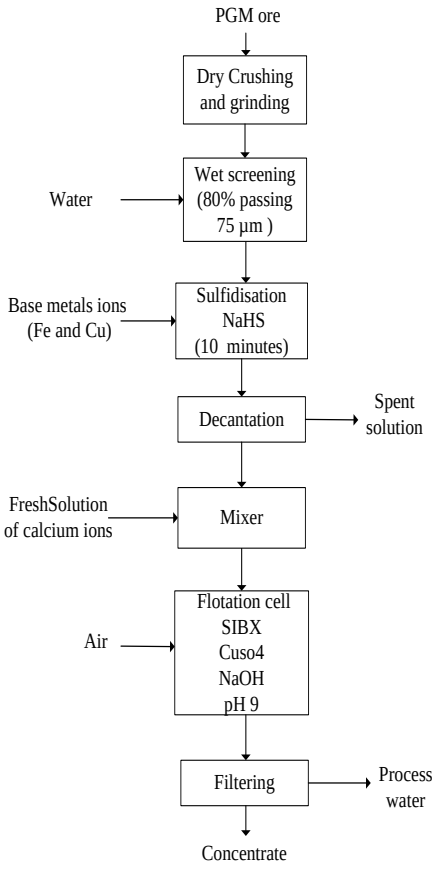


Figure 4 Experimental flow diagram of oxidized PGM ore potential processing through sulfidisation route, adapted from (Newell et al, 2007)).

2.4.3 Acid pre-treatment

Ramonotsi (2011) studied the efficacy of acid pre-treatment of oxidized PGM ore. In this work sulfuric acid (H_2SO_4) was used to pre-treat the oxidised ore from Pilanesburg Platinum Mines in a 4L Denver flotation machine made of stainless steel 316 while agitating the slurry with an impeller made of polyethylene. At the end of the leaching reaction filtration was used to separate the leach residue and spent acid. Then potassium hydroxide (KOH) pebbles were added to the leach residue to raise pH to 9 before flotation. Thereafter, conventional flotation reagents such as sodium isobutyl xanthate (SIBX) and Sendep depressant were added to the flotation cell to conduct batch flotation tests. Experimental results revealed that the acid pre-treatment of this weathered ore dissolved part of the passivating layer thereby increasing flotation recoveries by 20% when

compared to untreated ore. The recovery achieved from untreated ore was 50% while acid pre-treatment for 20 minutes increased the recovery to 70%.

The observations by Ramonotsi (2011) are consistent with the findings of the earlier study by Luszczkiewicz & Chmielewski (2008) on sulphuric acid pre-treatment of copper sulphide middlings in the flotation of carbonate ores. In this study the optimum pre-leaching of 70% of carbonates gangue improved copper flotation recovery and grades by 3% and 6% respectively. Industrial applications of the combined leaching/flotation process for the beneficiation of oxidised ores include the zinc-lead sulphide ore concentrator at Tara Mine in Ireland and Trzebionka Mine in Poland (Gorman, et al., 1976; Szolomicki, 1995).

Even though sulphuric acid pre-treatment showed some success, its highly corrosive nature would imply the need for specialized equipment constructed from stainless steel or other acid resistant materials. Additionally, a pre-wash or neutralization stage would be necessary because flotation collectors typically operate at higher pH values. Figure 5 shows the experimental flow diagram for oxidised PGM ore pre-treatment with sulphuric acid.

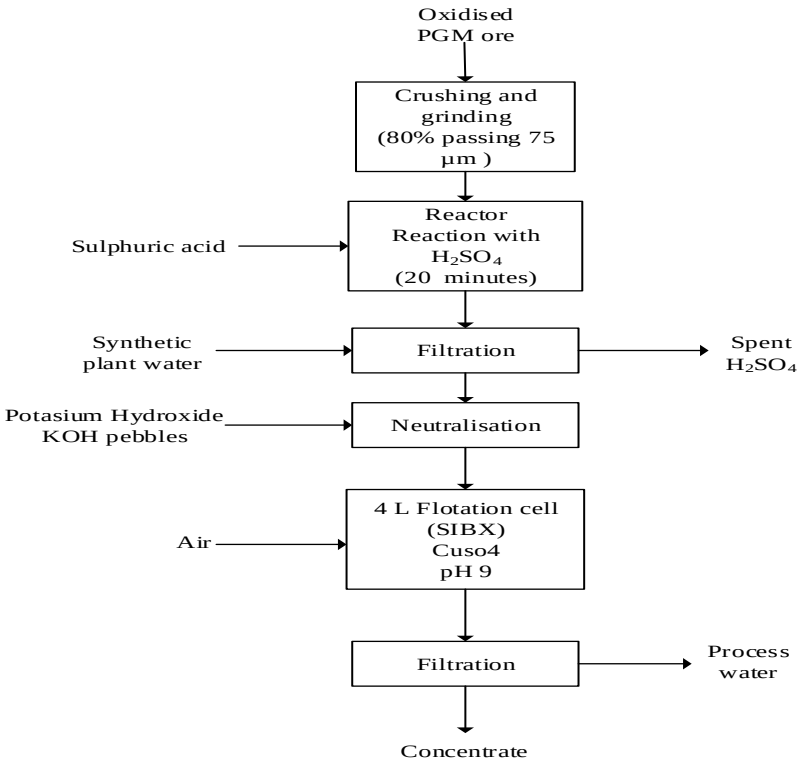


Figure 5: Experimental flow diagram for processing of oxidized PGM ore through pretreatment with sulphuric acid, adapted from (Ramonotsi, 2011).

Mild acidic pre-treatment can also be achieved by the use of carbonic acid as suggested by Mphela (2010). In this approach carbon dioxide (CO_2) gas is absorbed in water on the mineral surfaces to form carbonic acid which ionizes to digest the PGM alteration products on the surfaces of minerals like Iron hydroxyl groups. Then deprotonation of the absorbed bicarbonate follows as summarized by equations 7 - 10:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \quad (7)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad (8)$$

$$Fe\text{-}OH + HCO_3^- \rightleftharpoons Fe\text{-}OCO_2H + OH^- \quad (9)$$

$$Fe\text{-}OCO_2H + OH^- \rightleftharpoons Fe\text{-}CO_3^- + H_2O \quad (10)$$

In this study, 30 minutes of carbon dioxide pre-treatment improved the PGMs recovery from 40.6% to 50.4 %. Processing of oxidized PGM ores through CO_2 pretreatment is shown as a flow sheet in Figure 6.

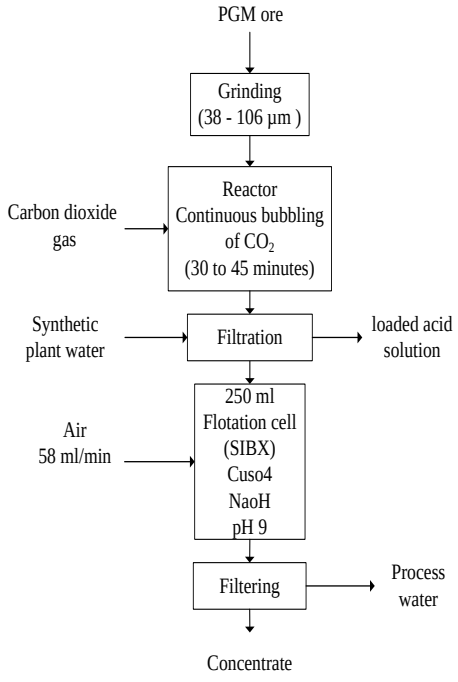


Figure 6: Experimental flow diagram of processing oxidized PGM ore through pre-treatment with carbon dioxide gas, adapted from (Mphela, 2010) .

2.4.4 Ammonia pre-treatment

In an effort to avoid the process equipment corrosion challenges associated with acid pretreatment, Musonda (2015) investigated the effect of ammonia leaching as a pre-treatment for processing of oxidised PGM ores from Pilanesburg Platinum Mines. However, this study showed that ammonia pre-treatment was not viable for remediation of the oxidized Pilanesburg Platinum Mine PGM ore because alteration phases (Fe oxides/hydroxides) were not leached from particle surfaces during the pre-treatment step and the improvement in the flotation recoveries of PGMs was only marginal. The proposed processing of oxidized PGM ore through ammonia pretreatment is shown as a flow sheet in Figure 7.

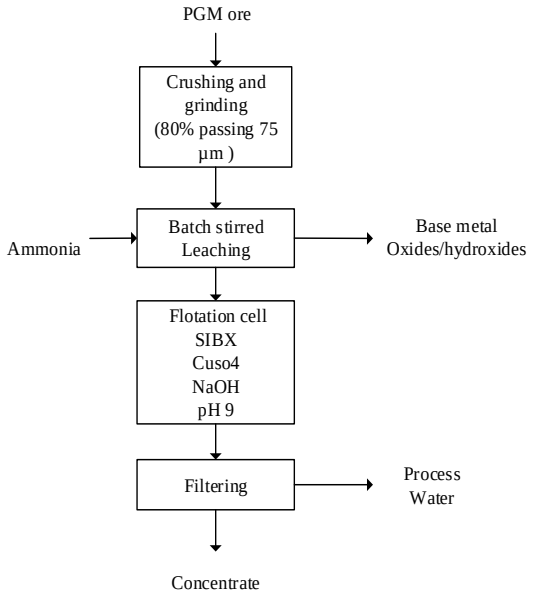


Figure 7: Experimental flow diagram for processing of oxidized PGM ore through ammonia pre-treatment, adapted from (Musonda, 2015).

2.4.5 Different flotation reagent schemes

2.4.6 Benefits of collector mixtures in flotation

The flotation efficiency of sulphide ores is often controlled by carefully designed collector schemes using mixtures of commonly used sulphydryl collectors (xanthates, dithiophosphates and dithiocarbamates). The performance benefits of employing collector mixtures scheme instead of single collector systems include reduced reagent dosages and improved recovery, grades and selectivity and have been proved in several flotation plants and test works (Bradshaw, et al., 1998; Pearse, 2005; Wiese et al, 2005; Kloppers et al, 2016). In particular, the South African platinum industry improved PGE recoveries and grades when it implemented a collector mixture of Cyanamid's 3477 (sodium di-isobutyl dithiophosphate) and SIBX in early 1970s (Lotter & Bradshaw, 2010).

Despite the extensive industrial application of xanthates as primary sulphide collectors, they have associated operational challenges such as limited selectivity and instability in acidic circuits. Acidic conditions are avoided by addition of lime to achieve an alkaline pH conducive for xanthates flotation, but this increases operation costs. The need to improve selectivity and reduce alkali consumption in flotation processes led to the development of xanthate derivatives such as xanthogen formates and thionocarbamates. Earlier flotation test works have proven xanthogen formates and thionocarbamates to have superior selectivity against gangue mineral pyrite (FeS) and stability in acidic conditions when compared to traditional xanthates collectors (Leppinen, et al., 1988; Ackerman, et al., 2000). Hence, the recently developed co-collectors based on xanthogen formates and thionocarbamates will be included in this study to investigation their efficacy on flotation of oxidized PGM ore.

The superior stability and selective power of xanthogen formate and thionocarbamate collectors are embedded in their structures depicted in Figure 8 and their adsorption mechanisms discussed below.

Figure 8: Chemical structures of (a) xanthogen formate and (b) isopropyl ethyl thiocarbamate (Ackerman, et al., 2000; Leppinen, et al., 1988)

It is generally agreed that xanthogen formates adsorb to mineral surfaces through chelation (Somasundaran & Nagaraj, 1984; Ackerman, et al., 2000). However, various adsorption mechanisms of IPETC on copper sulphide minerals have been proposed by workers who have studied the role of IPETC as a sulphide collector (Buckley, et al., 2014). Bogdanov et al (1976) proposed that thionocarbamate attached to a Cu metal film in anionic (deprotonated) form and by chemisorption in molecular (protonated) form onto the surface of chalcopyrite. Based on the molecular structure of thionocarbamates, Glembostskii (1977) argued that the electron density and steric hindrances dictated that chemisorption of the collector to the surfaces of Cu sulfides is more likely to involve the O rather than the N in addition to the S atom. On the other hand, Ackerman et al (1999) insisted that the N atom rather than O atom would be involved in chelate ring formation because collectors which achieved highest recoveries and selectivity against pyrite were those which contained N and S as functional groups for chelation. Additionally, Yuan and Zhong (2012) attributed the collecting power and superior selectivity to the formation of complexes when dithionocarbamates interact with copper cations. The dissolution-precipitation mechanisim has also been proposed for thionocarbamate adsorption onto sulphide minerals as an alternative to chemisorption (Yoon & Basilio, 1993).

2.4.7 Use of modified xanthate collectors

Bulatovic (2003) conducted research work to evaluate alternative reagent schemes for the flotation of platinum group minerals from various ores. For the chromium-rich, highly oxidised ore from Panton Sill deposit in Australia, poor recoveries were obtained using conventional

xanthate (SIBX) collector even after long flotation times and large quantities of collector dosages. Conventional xanthate collector achieved 68% Pt and 67% Pd recoveries while the use of modified xanthate (PM230) with dithiophosphate on oxidised Panton Sill ore improved recoveries of PGE to 79.3% Pt and 79.2% Pd respectively. PM230 is explained as a xanthate modified with a phosphate ester. Ramonotsi (2011) also observed improved flotation recoveries and selectivity benefits of using thionocarbamates and xanthogen formate mixture, TC6000 (supplied by Beijing Tecrich Development Co., Ltd) in flotation of oxidized PGM ore from Pilanesburg Platinum Mine. Hence, in this research the efficacy of xanthogen formate and IPETC mixtures as co-collector will also be investigated as a strategy to improve flotation of oxidized PGM ore from Mimosa Mine.

2.4.8 Use of hydroxamates co-collectors

Hydroxamates are chelating collectors that are largely used as oxide collectors because they selectively form complexes with base metals (Assis et al, 1996). Lee et al. (1998) conducted a study on practical aspects of oxide copper recovery with alkyl hydroxamates through flotation case studies of seven different ores. The study demonstrated the benefits of hydroxamates for recovery of copper oxides such as eliminating the need for sulphidisation and reducing xanthate and frother dosages. These results were validated by flotation test work on mixed copper oxide and sulphide ore from Minto Mine using potassium n-octyl hydroxamate (AM28). The AM28 co-collector successfully recovered oxide copper minerals (malachite and azurite) without adversely affecting the performance of the traditional copper sulphide collector (PAX) (Lee et al, 2009). On this basis, Becker et al. (2014) recently studied the use of AM28 in conjunction with conventional xanthate collector (SIBX) for recovery of PGMs from oxidised ore. This study involved the initial controlled potential sulfidisation of oxidised ore with NaHS and then using the hydroxamate. The results revealed that the use of hydroxamate, AM28 increased overall recovery of four elements (Pt, Pd, Rh and Au) from 27 to 39% at depressant (CMC) dosage of 750 g/t. However, in this case the authors attributed improved recoveries to increased frothiness and water recovery to the concentrate rather than selectivity of the hydroxamate.

Hydroxamates have thus far been limited to academic research because guidelines for their industrial applications have not yet been fully developed and because of the rigidity of the industry to change from the traditional sulfidisation-flotation method (Lee et al, 1998). The limited success

of hydroxamate co-collectors suggests the need for further research to improve their selectivity and to devise optimum collector suites before their industrial implementation. The flow diagram for flotation of oxidized PGM ore using hydroxamate co-collectors is illustrated in Figure 9. A similar processing route was followed in processing oxidised PGM ores by Bulatovic (2003). The only difference being the flotation collectors used.

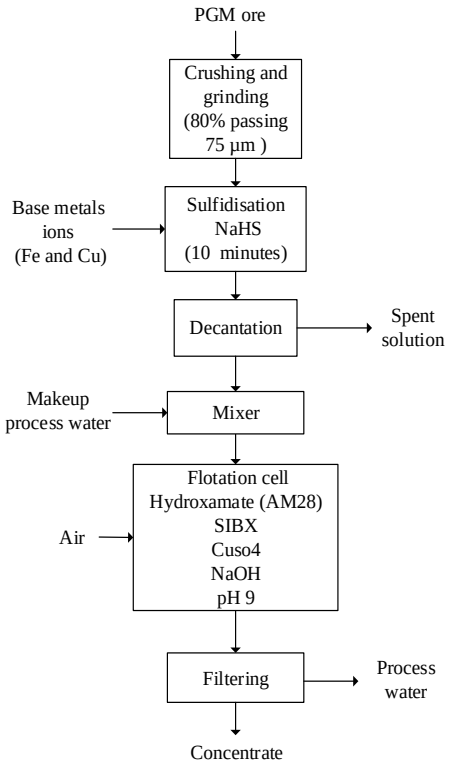


Figure 9: Experimental flow diagram for processing of oxidized PGM ore using CPS and hydroxamate co-collector, adapted from (Becker et al, 2014).

While there is concensus that collector mixtures provide significant performance benefits, there are contradicting opinions on whether the collectors in collector mixture act synergistically or play different but parallel roles that improve the flotation process. For instance, Mingione (1984) proposed that the improved recovery of PGMs using a 70% di-iso-butyl DTP/30% sodium iso-propyl xanthate (SIPX) was due to synergistic interaction between collectors. However, Corin et al (2012) in a study of the role of dithiophosphate as a collector using mixtures of sodium di-ethyl dithiophosphate and SIBX observed no evidence of synergistic interactions. The authors

attributed the improved metallurgical performance to different and parallel roles played by each collector.

2.5 Recovery of PGMs from oxidised ores by leaching

Limitations experienced in processing of weathered PGM ores by conventional flotation have motivated some researchers to evaluate alternative processing routes such as leaching to improve extractions of PGMs from oxidised ores. A brief theory of leaching techniques is presented in this section, followed by leaching circuits that have been explored for PGM extraction from oxidized ores.

2.5.1 Leaching techniques

Hydrometallurgical extraction of precious metals mainly consists of leaching of precious metals from ores by suitable lixiviants such as aqua regia and sodium cyanide solutions. The two main leaching techniques are percolation and agitation leaching (Devasia & Natarajan, 2004).

2.5.2 Percolation leaching

Percolation leaching involves the trickling of the lixiviant through a static ore bed. An example of percolation leaching is heap leaching which consists of piling crushed ore to a given height on a sloping impermeable bed. The heap is irrigated with a lixiviant which slowly flows down through the heap extracting valuable metals in the process. The loaded lixiviant is then directed along a sloping floor of the heap to a collection pond. Precious metals are recovered by solvent extraction and electro-winning processes before the leach solution is recycled to the top of the heap. Heap leaching is characterised by slow kinetics compared to agitated leaching because of generally larger ore particle size and slow rates of percolation of lixiviant (Fleming, 1992).

2.5.3 Agitation leaching

Agitation leaching involves agitation of finely ground ore particles in a lixiviant. The ore is crushed and milled to increase the liberation of valuable minerals and to increase the leaching reaction kinetics which depend on variables such as particle size, concentration of lixiviant, residence time, temperature and pressure (Osman, et al., 2013). Agitation leaching is conducted in air-agitated Pachuca tanks which are cylindrical vessels with a conical bottom and a central tube through which compressed air is passed to achieve the required slurry motion (Mehrotra & Shekhar, 2000). Alternatively mechanically stirred leaching tanks are used for agitated leaching.

2.5.4 Cyanide leaching

One possible processing technique for PGM recovery from oxidised ores is cyanidation process which has been proven to be effective for extraction of gold and silver by direct leaching of oxidised ores/concentrates (Prasad etal, 1991). Based on the success achieved in gold extraction by cyanidation, some studies have been conducted on cyanide leaching of PGM sulphide concentrates and promising recoveries were obtained (Mwase et al., 2014; Chen and Huang, 2006). However, very few studies exist on the application of cyanide leaching for extraction of PGE from weathered PGM ores.

The presence of oxidation products on mineral surfaces makes PGM ores to be resistant to the effective action of lixiviants such as cyanide solutions (i.e. they are refractory) (Green et al, 2004; vanwyk, 2014). Hence ore pre-treatment is necessary for removal of oxidation products and base metals (Cu and Ni sulphides) in order to limit consumption of reagent in the cyanide leaching step. The effect of oxidised PGM ore pre-treatment before cyanidation is discussed in the following studies.

2.5.5 Cyanide leaching of oxidized pgm ore

The efficiency of cyanidation for extraction of PGMs from run of mine (ROM) oxidised PGM ore was investigated by Musonda, (2015). In this study, base metal (Cu and Ni) extraction prior to cyanidation was carried out using ammonia leaching which is an extensively researched technique

for base metal extraction (Radmehr, et al., 2012). Ammonia leaching achieved poor base metal extractions (3% Ni and 55% Cu) from the oxidized Pilanesburg Platinum Mine ore compared to high base metal extractions (95% Cu and 60% Ni) that were achieved during column leaching of Platreef low-grade flotation concentrates (Muzawazi & Petersen, 2015). However, subsequent cyanidation for 40 days with 0.5M cyanide in a column aerated at 80 ml/min and at 40^0C yielded 3%, 40% and 73% total extraction of Ni, Pt and Pd respectively which is a significant improvement on the recoveries obtained by flotation means. The process is summarised in the flow diagram in Figure 10.

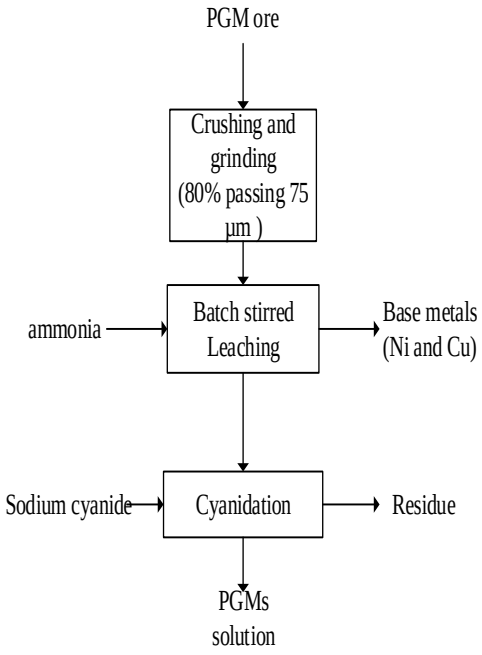


Figure 10: Experimental flow diagram for processing of oxide PGM ore through ammonia pretreatment and cyanidation, adapted from (Musonda, 2015).

2.5.6 Cyanide leaching of pgm ores with low sulphide content

McInnes et al (1994) investigated the extraction of platinum, palladium and gold by direct cyanide leaching of Coronation Hill PGM ore. This particular ore could not be upgraded by conventional metallurgical techniques such as flotation because it was composed of fine grained PGE minerals and had low sulphide mineral content. After the amalgamation with mercury for 2 hours to recover coarse gold, high temperature (100 – 125^0C) cyanide leaching was used to extract

80 % Pt and 90- 95% palladium (Bruckard et al., 1992). The simplified flow sheet for this process is shown in Figure 11.

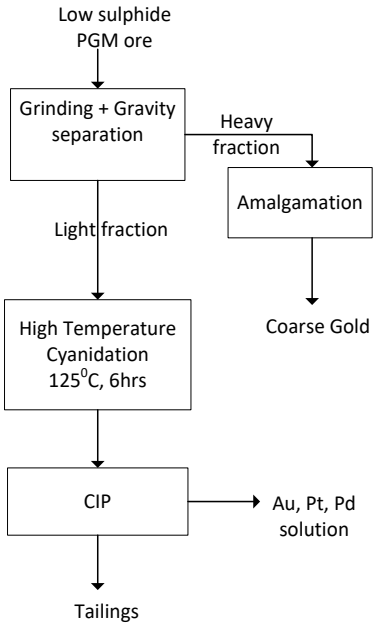


Figure 11: Experimental flow diagram for processing of low sulphide PGM ore through cyanidation, adapted from (Bruckard, et al., 1992).

2.5.7 Acid leaching of oxidised pgm ores

2.5.7.1 Hydrochloric acid leaching of oxidized ore

Acid leaching of oxidised PGM ore from the Hartley Mine in Zimbabwe was investigated by Becker and Wotruba (2008). Bulk leaching methods using hydrochloric acid at room temperature and pH 3 for 72 hours achieved maximum recoveries of 18.9 % Pt and 18.5% Pd. The use of sulphuric acid in the same study yielded lower recoveries of 11.1% Pt and 13.8% Pd. Process modifications such as using multistep leaching, increase in leaching time and further grinding of ore did not improve the recoveries obtained at ambient temperature significantly. However, high temperature leaching showed better recoveries as a maximum of 65% Pt recovery was achieved from leaching of flotation tailings using dilute HCl at 75^{0}C in 5 hours (Locmelis et al, 2009). To improve PGM extractions from oxidised ores at ambient temperatures a multistep leaching

technique involving hydrochloric acid and other novel lixiviants has to be implemented as outlined in the next section.

2.5.7.2 Multi-step hydrochloric acid and siderophore leaching of oxidized ore

The recovery of PGMs from oxidized ores through leaching was also explored using a multistep leaching technique involving acids and metal complexing agents (Kraemer et al, 2015). Mohwinkel and Bau (2012) studied the efficiency of using a multi-step leaching technique in their investigation of siderophore-enhanced extraction of platinum (Pt) from oxidized PGM ores of the Great Dyke. Experimental results showed considerably low Pt recoveries (less than 1 %) for untreated ore. However, a combination of 0.5M HCl pre-treatment followed by drying of a solid residue and buffered siderophore (Desferrioxamine B) leaching increased platinum recoveries from the Ngezi Open Pit Mine sample to a maximum of 78% which is a very encouraging improvement.

The same combined HCl pretreatment and siderophore leach only achieved low Pt recoveries of only 33% from the Hartley Open Pit sample, indicating that leaching conditions need to be adjusted depending on ore type (Kraemer et al, 2015). The multi-step acid leaching process is depicted in the flow diagram in Figure 12.

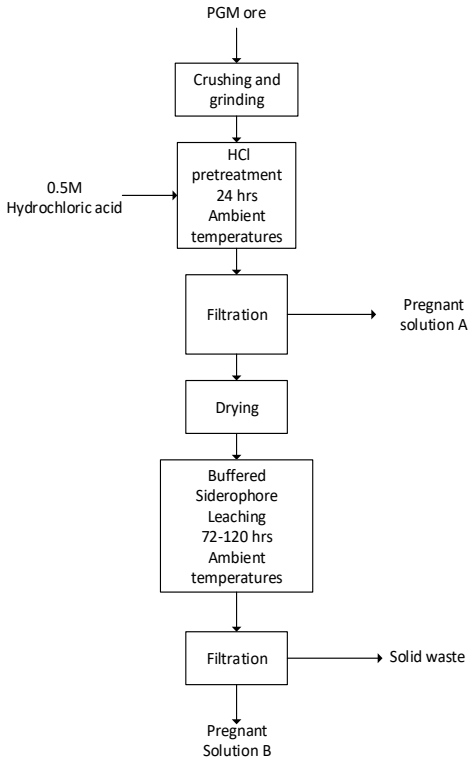


Figure 12: Experimental flow diagram for processing of oxidised PGM ore through a multi-step leaching approach, adapted from (Kraemer et al, 2015).

2.5.8 Bromide leaching of oxidized ore

The Minerals Laboratory (TML) of BHP Minerals proposed a novel leaching process in which substantial PGM recoveries from oxidised ores were achieved. Improved recoveries of 95% for gold, 85% for platinum and over 65% for rhodium were achieved when the oxidised ore from the Hartley ore was processed using the TLM process. This process involves roasting of the PGM ore followed by acidic bromine leaching of the oxidized PGM ore. In this process sulfuric acid is used for acidity control, bromide ions for the formation of PGM complexes and bromine for redox potential control (Duyvesteyn et al, 1994). The simplified flow diagram of the TLM process is shown in Figure 13.

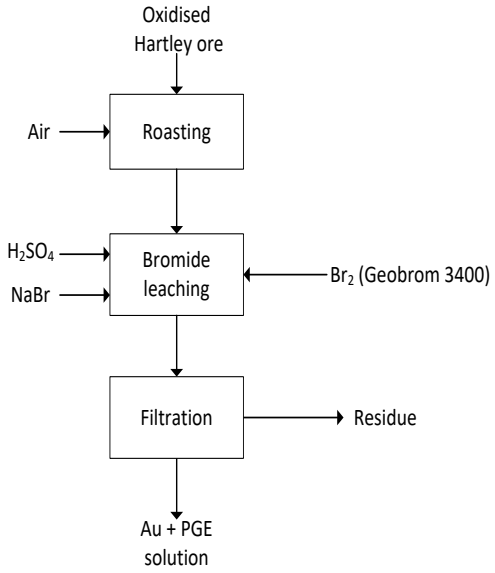


Figure 13: Flow diagram for a The Minerals Laboratory (TML) process.

Surprisingly, there are no successful reported studies of chloride leaching for oxidised PGM ores considering that PGM refining is entirely based on chloride leaching. However, leaching experiments conducted on a magnetite ore containing platinum, palladium and gold using concentrated chloride solutions and ozone gas injection as oxidizing agent resulted in >90% Pt, 70 % Pd and 50% Au extractions. These extractions were obtained after 3 hours of leaching at under atmospheric pressure at ambient temperatures and a pH 4. The workers observed that the magnetite mineral matrix was not attacked during the leaching process (Torres & Lapidus, 2016). The mineralogy of the magnetite ore used in this study might be different from that of southern African oxidized PGM ores, however both minerals consist of oxide matrix hence this leaching method might be worth exploring.

2.6 Cyanide leaching of pgm sulphide flotation concentrates

Other processes which may be adapted were conducted using PGM sulphide flotation concentrates as outlined in the following sections.

2.6.1 High pressure cyanide leaching of pgm ores

Chen and Huang, (2006) studied extraction of platinum group metals using 5 kg-scale batch experiments of 80 g/t Pt and Pd flotation concentrate in a 50L autoclave. Their investigation involved pressurised sulphuric acid pre-treatment of the ore to oxidise sulphides into sulfates and oxides, thereby exposing the targeted PGMs. The subsequent two stage high-temperature pressure cyanide leaching yielded 90 – 94 % Pt and 99% Pd. Based on these results, this approach was proposed as a promising technique for extraction of PGMs from Pt and Pd flotation concentrates and spent auto-catalysts.

2.6.2 High temperature cyanide leaching of PGM ores.

Platinum Australia Limited and Lonmin Plc also developed the Panton process for extraction of PGM from low-grade flotation concentrates. The concentrates were subjected to low temperature calcination followed by high temperature cyanidation to dissolve PGMs, gold and base metals. The Panton process recovered 90.8% Pt, 91.9% Pd, 94.4% Au, 69% Cu and 32% Ni from the Panton Sill flotation concentrates (Mpinga et al., 2015).

2.6.3 Multistep bioleaching and cyanide leaching of pgm ores

Another study on cyanide leaching of PGM concentrate was conducted by Mwase et al., (2012) using a low grade ore flotation concentrate. The investigation involved initial bioleaching of the ore using the proprietary GEOCOAT process at 65^0C to first extract base metals, followed by leaching with 0.15M sodium cyanide solution at 23^0C, atmospheric pressure and pH = 10. According to their results, 50% Pt extraction was achieved after 50 days of cyanide leaching. This process was proposed as a low-cost hydrometallurgical method for extraction of PGMs from low grade ores and concentrates.

However, bioleaching in this study achieved 52% copper extraction after 30 days as compared to nickel and cobalt extractions which were 95% and 85% respectively. The limited copper extraction has dire implications on the economics of the process because it leads to excessive

consumption of the cyanide solution. Hence, to successfully adapt this process to treatment of oxidised PGM ores higher copper extractions need to be achieved first.

2.7 PGM Leaching in aqua regia solutions

There is no documented research on recovery of PGMs from oxidised ores by aqua regia. However, several researchers have achieved considerable success in recovery of Pt and other PGMs from high grade sources such as spent catalysts. The dissolution of PGMs in aqua regia solutions is controlled by the formation of stable chloro-complexes under the high oxidation potential and pH of the solution in the presence of ionic species (Lide, 1995). The reaction between nitric acid and hydrochloric acid in aqua regia solution produces nascent chlorine (Cl_2) and nitrosyl chloride (NOCl) which provide the necessary high oxidation potential and the high chloride-ion concentration that acts as the complexing agent (Jha, et al., 2013). The dissolution of platinum in aqua regia solutions is summarised by reactions 11 to 16.

$$HNO_3 + 3HCl \leftrightarrow NOCl + Cl_2 + 2H_2O \quad 11$$

$$2NOCl \rightarrow 2NO + Cl_2 \quad 12$$

$$NOCl + H_2O \leftrightarrow HNO_2 + HCl \quad 12$$

$$3Pt + 18HCl + 4HNO_3 \leftrightarrow 3[PtCl6]^{2-} + 6H^+ + 4NO + 8H_2O \quad 13$$

$$3Pt + 4NO_3^- + 16H^+ \rightarrow 3Pt^{4+} + 4NO + 8H_2O \quad 14$$

$$Pt + 4NO_3^- + 8H^+ \rightarrow Pt^{4+} + 4NO_2 + H_2O \quad 15$$

Based on the proven efficiency of aqua regia to solubilize PGMs, aqua regia solution was included as part of the investigation to improve PGM recovery from the oxidized ore in this present work.

3. EXPERIMENTAL AND ANALYTICAL METHODS

3.1 Ore preparation

The oxidized PGM ore sample from Mimosa Mine in the Great Dyke, Zimbabwe was used in this study. The crushed PGM oxide ore sample was supplied at 70% passing 1 mm as depicted in Figure 14.

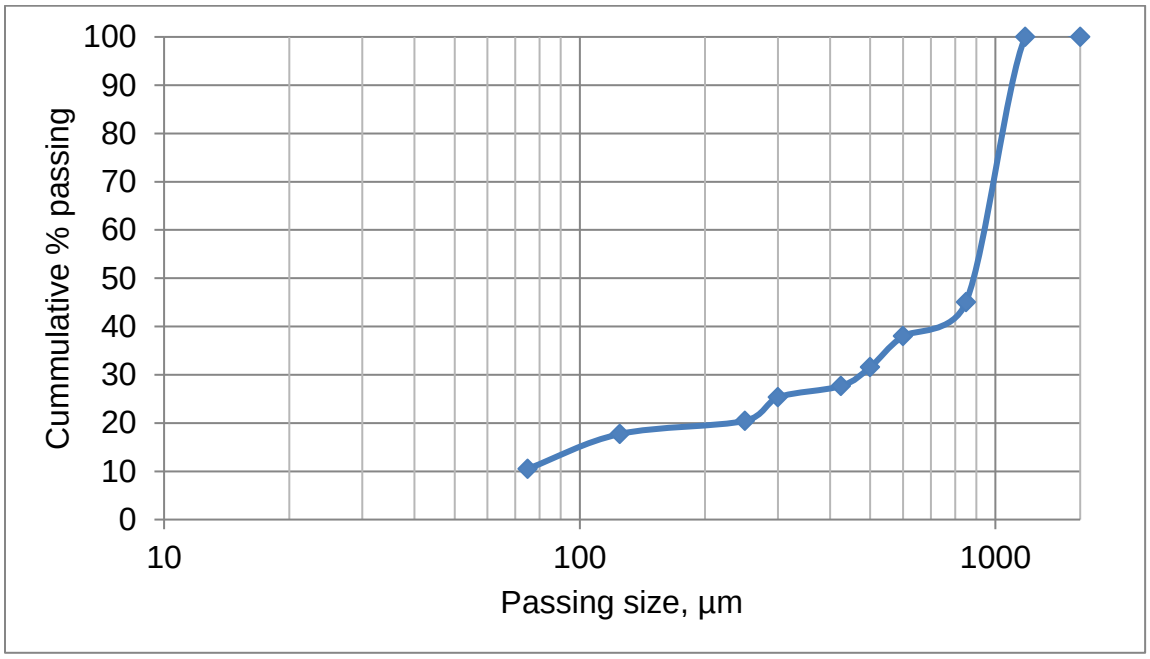


Figure 14: Particle size distribution of crushed oxidized ROM ore from Mimosa mine

The ore was crushed to 100%-1mm and, thereafter thoroughly blended and split by coning and quartering from which a representative 15kg aliquot was split and stored as a reference and backup sample. The remaining sample was rotary split into representative aliquots for metallurgical test work in the Minerals Processing laboratory at University of the Witwatersrand as summarised in Figure 15.

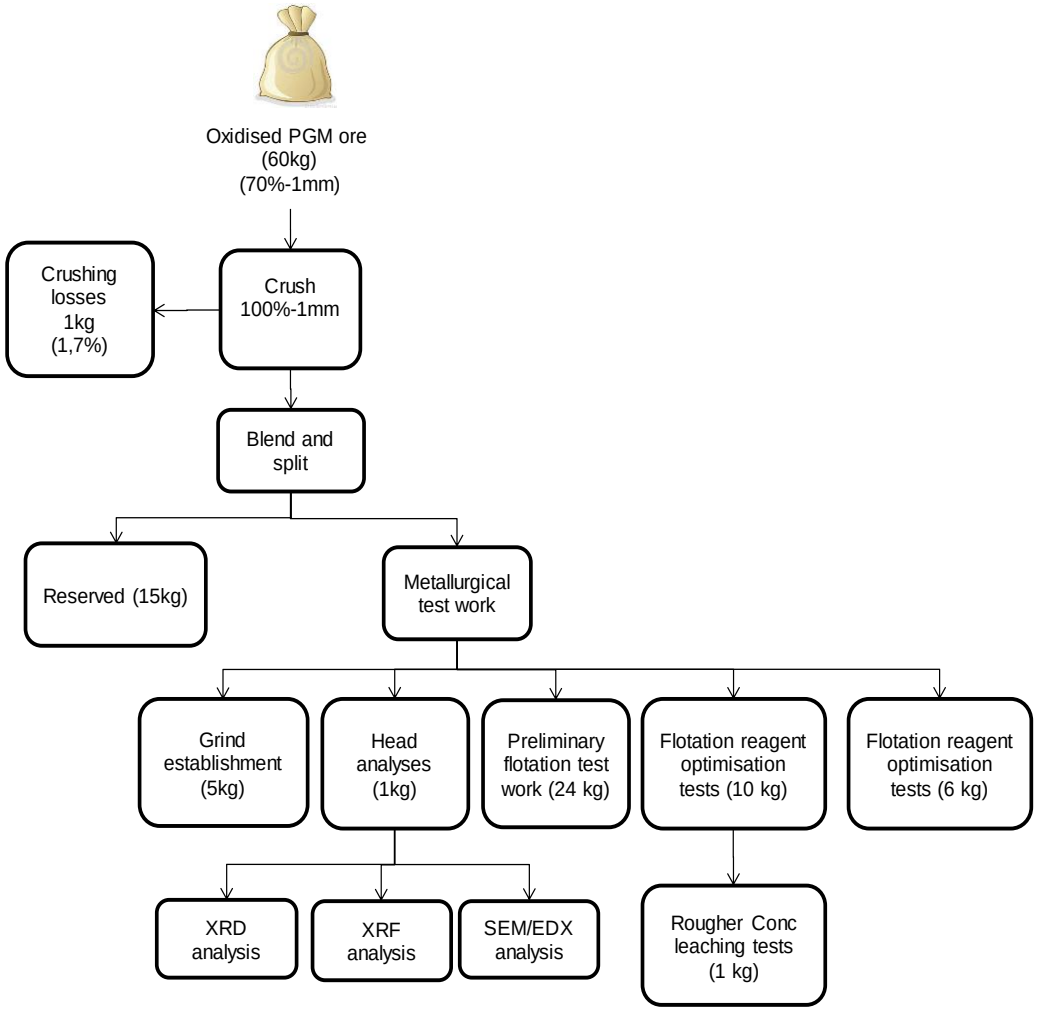


Figure 15 Schematic sample preparation procedure for the Mimosa oxidized PGM ore

3.2 Ore characterization

Approximately 300 g representative samples of the ROM oxidised PGM ore were split out from the bulk using the standard riffle and rotary splitter method and pulverized to ~90% -75 μm, in preparation for head analyses at Mintek. PGM analyses (in duplicate) were done by fire assaying, and lead collection with ICP-EOS Finish. X-ray diffraction (XRD) analysis was also carried out to establish the bulk mineralogical composition of the ore by identifying the major crystalline phases. The bulk mineralogical composition from XRD technique needed to be validated by elemental analysis because amorphous minerals were not detectable by XRD since it

can only identify crystalline particles (Dish, 1994). Hence additional pulverized samples were analysed using X-Ray Fluorescence (XRF) and EDX techniques to establish the elemental composition of the ore.

3.3 Flotation Test work

3.3.1 Process water preparation

The composition of typical process water at PGM concentrator plants was used as a guide for preparation of synthetic plant water used in this test work. Synthetic plant water was prepared using distilled water modified by addition of ionic salts to achieve the ionic strength typical of process water at PGM concentrator plants (Wiese, et al., 2005). The plant water was prepared in 20 litre batches following the recipe summarized in Table 2.

Table 2: Synthetic plant water recipe

Salt name	Quantity (g)
$MgSO_4.7H_2O$	12.30
$Mg(NO_3)_2.6H_2O$	2.14
$Ca(NO_3)_2.4H_2O$	4.72
$CaCl_2.2H_2O$	2.94
NaCl	4.12
Na_2CO_3	0.60

3.3.2 Batch flotation tests

Reagent scouting flotation test work was carried out to establish the flotation response of the oxidised PGM ore to various carefully and appropriately selected reagent suites. Rougher flotation tests were carried out on samples milled to 60%-75µm at a slurry density of 30% w/w solids in a Denver flotation cell. The slurry was agitated with a top driven variable speed impeller at 1200rpm

to keep the slurry homogeneous prior to reagent conditioning using the reagent scheme which is summarized in table 3. Flotation tests were performed following the standard flotation procedure which involved manually scraping off the froth every 15 seconds into collection trays to collect concentrates for 20 minutes of cumulative flotation time (Wiese, et al., 2005). The experimental setup for batch flotation tests is depicted in Figure 16.

Figure 16: Equipment set-up for batch flotation tests

The reagent scouting tests were conducted using bulk roughing to minimise outsourced ICP analysis costs in the preliminary stages by reducing the number of concentrate samples while ensuring that sufficient data was obtained to identify conditions that would be further investigated through kinetic rougher flotation. Both PGM recovery and grade were used as a metric for selecting a preferred reagent scheme and flotation conditions. The results obtained from the 3 reagent schemes at different conditions studied are summarised in Table 15 while the statistical analysis

results of the main effects and interaction effects of variables for the reagent testing flotation tests are illustrated in Figure 20 and Figure 21.

3.3.3 Flotation Reagents

The flotation reagents used in this study were supplied by ChemQuest (Pty) Ltd. The primary collector, Sodium Isobutyl Xanthate (SIBX) was supplied in powder form at a purity of 90%. Fresh solutions of SIBX collector were prepared daily to 1% wt by mixing 1 g of the powder with de-ionised water in a 100 ml volumetric flask. Then calculated volumes that would ensure the investigated collector dosages as indicated in tables 3-4 were measured with a syringe. Similarly, the depressant and activator solutions were prepared by dissolving the Depressants M98B granular powder and $CuSO_4.5H_2O$ crystals in de-ionised water respectively. The stock solution of 1% wt of a secondary collector was prepared by diluting 1ml of FLOMIN C5460 (a blend of dithiophosphate and IPETC) in a 100ml volumetric flask. A similar procedure was followed to prepare a stock solutions of co-collector FLOMIN C7133 (Xanthogen and IPETC blend) and hydroxamate oxide collector using AM810 solution supplied by Axis house. FLOMIN F200 which is a polyethylene glycol monobutyl ether mixture was added as the frother without any dilution. The reagent dosage sequence and conditioning times summarized in Table 3 were implemented.

Table 3: Summary of flotation reagent schemes studied

Flotation reagent schemes investigated				
Sequence of reagent dosages	Reagent name	Function	Typical reagent dosages (g/t)	Conditioning time (min)
1	Copper Sulphate	Activator	40-50	5
2	Sodium Isobutyl Xanthate (SIBX)	Primary collector	100-150	2
3	FLOMIN C7133 (Xanthogen + IPETC blend)	Secondary collector	30-50	2
	FLOMIN C5460 (Sodium Isobutyl Dithiophosphate + IPETC blend)	Secondary collector	30-50	2
	AM 810 (Hydroxamate collector)	Oxide co-collector	50-100	2
4	Depressant M98B	Depressant	50-100	3
5	FLOMIN F200	Frother	40-50	1

3.3.4 Design of experiments

A 2^3 full factorial design (three factors each, at two levels) was used to evaluate the importance and interactions of the primary collector (SIBX) dosage, secondary collector dosage and M98B depressant dosage for all three reagent suites investigated. The response variables of this study were the PGM rougher flotation recovery and rougher concentrate grade. In all cases, the tests required by the factorial design were executed randomly in order to correctly evaluate experimental errors. The matrix of three variables was varied at two levels (+1, −1) with the higher level of variable designed as'+' while the lower level was designed as '−'. Table 4 shows the values of the factors selected as higher and lower levels for the three reagent schemes studied during the reagent scouting phase.

Table 4: Summary of experimental conditions for reagent schemes investigated

Reagent scheme name	Variables	Reagent dosages (g/t)	
		Low	High
1	SIBX	100	150
	FLOMIN C5460 (DTP + IPETC)	30	50
	M98B depressant	50	100
2	SIBX	100	150
	FLOMIN C7133 (Xanthogen formate + IPETC)	30	50
	M98B depressant	50	100
3	SIBX	100	150
	AM 810 Hydroxamate	30	50
	M98B depressant	50	100

NB: The activator and frother dosages were maintained at 50 g/t during the flotation test work in this study.

This full factorial design resulted in eight batch flotation tests for each reagent scheme with all possible combinations of SIBX dosage (*A)*, secondary collector dosage (*B)* and depressant dosage (*C)*. PGM rougher flotation recovery and rougher concentrate grade were measured for each of these tests as shown in Table 12 to Table 14.

3.4 Leaching test work

3.4.1 Baseline PGM dissolution test work on ROM ore

PGM dissolution tests were carried out on representative aliquots of the oxidised PGM ROM ore samples milled to a 80%-75µm grind in order to establish the baseline performance of the various acid leaching conditions on PGM dissolution. The following conditions were tested during this stage of test work:

- ✓ Effect of acid type
- ✓ Effect of Solid/Liquid ratio
- ✓ Effect of leaching temperature
- ✓ Effect of leaching time

The leaching tests were conducted in a 500 ml flask agitated with a magnetic stirrer at the constant agitation of 500 rpm. The leaching temperatures were controlled by means of a heated oil bath. The condenser was used to maintain a constant solid/liquid ratio by minimising the lixiviant evaporative losses. The experimental set-up for leaching experiments is shown in Figure 17.

Figure 17: Experimental set-up for leaching experiments

3.4.2 Leaching reagents and conditions

The leaching conditions adopted for PGM dissolution from rom ore are presented in Table 5 to Table 8.

Table 5: Leaching conditions for lixiviant scouting test work.

Variable	Constant parameters					
Lixiviant type	Concentration	Leaching time (min)	Leaching temperature (^oC)	Solid/liquid ratio	Agitation rate (rpm)	Ore grind
HCl	2M	120	85	2 g/100 ml	500	80%- 75 um
HNO_3	2M					
H_2SO_4	2M					
Aqua regia	$1HNO_3$: 3HCl					

Table 6: Leaching conditions for investigation of effect of solid/liquid ratio on PGM recovery.

Variable	Constant parameters					
Solid/liquid ratio	Lixiviant ID	Lixiviant Concentration	Leaching time (min)	Leaching temperature (^oC)	Agitation rate (rpm)	Ore grind
2 g/100 ml	Aqua regia	$1HNO_3$: 3HCl	120	85	500	80%- 75 um
6 g/100 ml						
10 g/100 ml						

Table 7: Leaching conditions for investigation of effect of temperature on PGM recovery.

Variable	Constant parameters					
Leaching temperature (^oC)	Lixiviant ID	Lixiviant Concentration	Leaching time (min)	Solid/liquid ratio	Agitation rate (rpm)	Ore grind
50	Aqua regia	$1HNO_3$: 3HCl	120	2 g/100 ml	500	80%- 75 um
60						
70						
80						
85						

Table 8: Leaching conditions for investigation of effect of time on PGM recovery.

Variable	Constant parameters					
Leaching time (min)	Lixiviant ID	Lixiviant Concentration	Leaching temperature (^{0}C)	Solid/liquid ratio	Agitation rate (rpm)	Ore grind
15	Aqua regia	1HNO_3: 3HCl	85	2 g/100 ml	500	80%- 75 um
30						
60						
90						
120						

3.4.2 Leaching of flotation concentrate to upgrade residue

Experiments were conducted to leach the flotation concentrate that had the highest PGM recovery with sulphuric acid in order to target the base metals and further concentrate the PGMs in the residue. Leaching tests were conducted to establish:

i. the effect of lixiviant (H_2SO_4) concentration (tested at 3 levels of concentration of 2.0 M, 3.0 M and 4.0 M) and
ii. the effect of leaching temperature (also tested at 3 levels of 55^0C, 85^0C and 105^0C)

on the overall base metal dissolution achieved. In all cases the leach pulps were filtered and the leach solutions analysed for Cu, Ni and Fe by AAS.

The parameters that were maintained constant for these leaching tests are:

- ✓ Stirring rate (500 rpm)
- ✓ Solid/liquid ratio 2 g/100 ml
- ✓ Leaching time 2 hours

4. RESULTS

This chapter presents the results of the characterisation and laboratory test work done on the oxidised PGM ore. The chapter starts by presenting the characterisation findings which provided insights on the composition of the ore which was helpful in informing the decision on the possible processing routes of the ore material.

The second part of this chapter presents flotation test work results showing the response of the oxidised PGM ore to different reagent schemes. The statistical analysis of the flotation data leads to the identification of the best reagent suite, this analysis is then followed by flotation reagent optimisation based on the best reagent suite that is selected. The third part of this chapter presents the hydrometallurgical test work results from the leaching of the ROM ore to extract PGMs and base metal leaching from flotation concentrate to upgrade PGMs in the leach residue. The test work raw data and procedures are presented in the appendix.

4.1 Characterization

4.1.1 Mineralogy

The bulk mineralogical results obtained from XRD characterisation test work are summarised in Table 9 and further illustrated in Figure 18 while detailed results and methods used are outlined in section 8.1.3 in the appendix.

Table 9: Summary of XRD characterization results.

Phase name	Content(%)
Enstatite, ordered	0.00
chabazite high, calcium tecto-alumosilicate	21.82
iron diiron(III) oxide, magnetite HP, syn	33.07
Quartz low	45.10
Chromite	0.00
Magnesiochromite	0.00
Anorthite	0.00
iron diiron(III) 00-002-1228@oxide, magnetite HP, syn	0.00
Magnesiochromite	0.00
iron diiron(III) 00-002-1083@oxide, magnetite HP, syn	0.00
Anorthite	0.00
Total	**100**

NB: The XRD technique used could not quantify trace mineral phases with concentrations less than 1%.

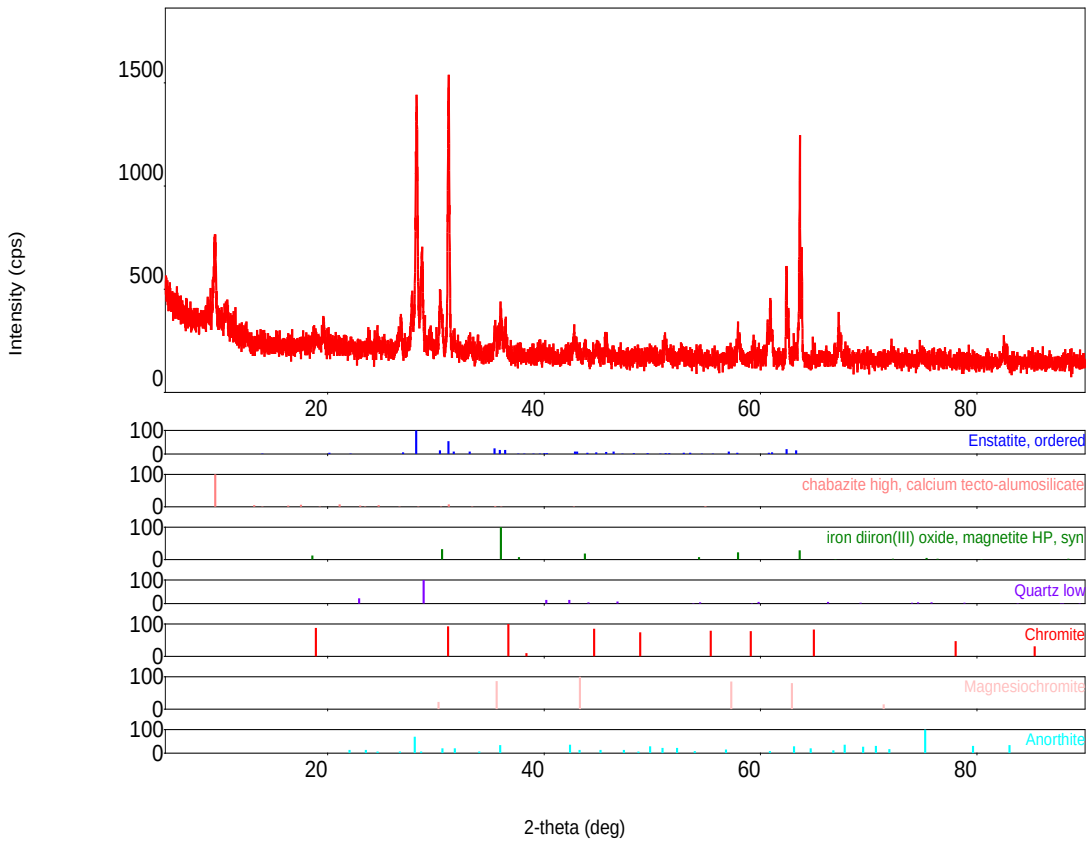


Figure 18: X-ray diffractograms of the Mimosa oxidized PGM ore feed sample

The XRD results indicated that the oxidised PGM ore feed sample was dominated by gangue silicate minerals such as chabazite, quartz and oxide mineral magnetite. The ore also contained trace quantities of pyroxenic enstatite and anorthite which belong to the plagioclase mineral series. Chromite and magnesiochromite were also identified as trace minerals in the ore. Although the alteration minerals such as iron oxyhydroxide (FeOOH) was not identified, the mineralogical characterisation test work confirmed that the Mimosa ore sample studied was a non-sulphide ore and hence could not be efficiently beneficiated by conventional xanthate flotation.

The elemental analysis determined by the XRF and EDX techniques are summarised in Table **10** and Figure 19. Detailed results of the XRF and EDX analyses are presented in Table 27 and Table 28 respectively in the appendix.

4.1.2 Detailed SEM/EDX elemental analysis results

Table 10: Summary of XRF and EDX elemental analysis on oxidized PGM ore.

Item No	Element ID	Analysis Technique	
		XRF (wt%)	EDX (wt%)
1	Na	0,54	0,49
2	Mg	18,10	11,75
3	Al	5,25	2,21
4	Si	32,00	19,16
5	P	0,03	-
6	S	0,64	0,49
7	Cl	0,04	-
8	K	0,41	-
9	Ca	7,12	2,07
10	Ti	0,50	-
11	V	0,11	-
12	Cr	7,97	-
13	Mn	0,42	-
14	Fe	25,90	6,91
15	Co	0,05	-
16	Ni	0,58	-
17	Cu	0,31	0,60
18	Zn	0,05	-
19	Sr	0,02	-
20	O	-	56,32
Totals		100	100

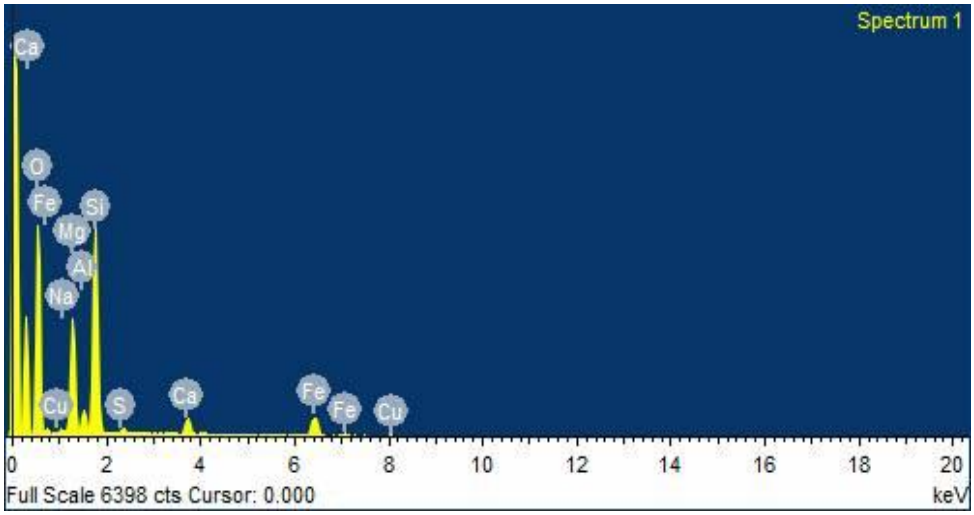


Figure 19: X-ray diffractograms of the Mimosa oxidized PGM ore feed sample (from EDX elemental analysis).

The results from the two elemental analyses methods confirmed that the ore is dominated by gangue silicates minerals as was established by the XRD analysis. The major element was determined by XRF and EDX as Silica at a concentration of 32.00% and 19.16% respectively. However, XRF and EDX also could not identify any PGE in the feed sample possibly because the PGM content in most ores is in the ppm range which is relatively far lower than the content of the other elements.

4.1.3 Head assay

The concentrations of PGMs in the oxidised ROM ore was determined by ICP-EOS and the results are presented in Table 11.

Table 11: PGM Head assay results for the Mimosa oxidised PGM ore sample

		Assay values			
Item	Description	Pt (ppm)	Pd (ppm)	Au(ppm)	3E (ppm)
1	Sample 1	1,45	0,85	0,09	2,39
2	Sample 2	1,38	0,84	0,09	2,31
Average		1,42	0,85	0,09	2,35

The average PGM assay value obtained for the Mimosa oxidised PGM ore was 2.35 g/t 3E (Pt, Pd and Au). This PGM grade and the elevated concentration of gangue minerals as indicated by the XRF and EDX analyses explains why the PGMs could not be picked up by the XRF and EDX. The absence of sulphides as indicated by the low concentration of the sulphur element explains the challenges encountered during the beneficiation of this PGM ore by conventional processes. Hence, non-conventional flotation reagent schemes were investigated in an attempt to improve the PGM rougher flotation recoveries from this ore sample.

4.2 Reagent scouting test work results

The PGM rougher flotation recovery and rougher concentrate grade results obtained using different reagent conditions are presented in Table 12 to Table 14 and further summarised in Table

15. Detailed results and experimental conditions are outlined in flotation test sheets in Table 31 to Table 33 in the appendix.

Table 12: Experimental design matrix and results for Pt, Pd and Au rougher flotation recovery and rougher concentrate grade – reagent scheme 1

Run number	Level			Experiment	Grade (g/t)				Recovery (%)			
	A	B_1	C	No.	Pt	Pd	Au	3E	Pt	Pd	Au	3E
1	-	-	-	2	10,70	4,24	0,45	15,39	47,0	31,2	31,1	40,7
2	+	-	-	7	22,30	9,47	0,48	32,25	59,9	31,9	20,3	48,3
3	-	+	-	4	22,80	8,25	0,53	31,58	66,1	40,1	24,2	55,1
4	+	+	-	8	6,29	10,50	0,24	17,03	52,5	45,2	31,5	49,1
5	-	-	+	1	19,60	7,56	0,49	27,65	39,1	27,4	15,4	34,0
6	+	-	+	3	23,15	7,09	0,90	31,14	43,8	30,0	26,8	38,2
7	-	+	+	5	31,70	3,23	0,82	35,75	55,7	30,9	22,7	45,5
8	+	+	+	6	23,20	5,16	0,57	28,93	46,7	25,5	18,0	37,9

Table 13: Experimental design matrix and results for Pt, Pd and Au rougher flotation recovery and rougher concentrate grade – reagent scheme 2

Run number	Level			Experiment	Grade (g/t)				Recovery (%)			
	A	B_2	C	No.	Pt	Pd	Au	3E	Pt	Pd	Au	3E
1	-	-	-	6	14,90	5,78	1,21	21,89	57,1	37,1	72,9	50,5
2	+	-	-	8	32,20	11,90	1,36	45,46	60,9	37,7	40,5	51,8
3	-	+	-	7	19,20	7,49	1,31	28,00	46,1	30,1	49,4	40,5
4	+	+	-	1	15,80	5,16	0,42	21,38	53,5	29,3	22,4	43,6
5	-	-	+	3	25,00	7,79	0,94	33,73	52,1	27,2	30,8	42,4
6	+	-	+	4	16,00	6,21	1,22	23,43	43,2	28,1	51,8	38,1
7	-	+	+	5	14,00	5,75	1,08	20,83	49,7	34,2	60,3	44,5
8	+	+	+	2	19,70	7,73	0,99	28,42	42,7	28,0	33,7	37,1

Table 14: Experimental design matrix and results for Pt, Pd and Au rougher flotation recovery and rougher concentrate grade – reagent scheme 3

Run number	Level			Experiment No.	Grade (g/t)				Recovery (%)			
	A	B_3	C		Pt	Pd	Au	3E	Pt	Pd	Au	3E
1	-	-	-	6	21,30	6,88	0,38	28,56	36,0	19,5	10,1	29,1
2	+	-	-	7	38,10	14,80	0,88	53,78	62,0	40,3	22,5	52,7
3	-	+	-	2	13,20	5,16	0,34	18,70	74,0	48,4	29,9	63,1
4	+	+	-	4	24,80	8,01	0,48	33,29	58,5	31,6	17,8	47,3
5	-	-	+	5	51,20	15,90	0,91	68,01	53,3	27,7	14,9	42,6
6	+	-	+	8	38,00	13,50	0,87	52,37	53,2	31,7	19,2	44,2
7	-	+	+	1	44,40	16,30	0,99	61,69	54,6	33,6	19,2	45,7
8	+	+	+	3	22,80	8,12	0,59	31,51	61,5	36,7	25,0	51,2

Reagents:

A = Primary collector dosage (SIBX)

B = Dithiophosphate & IPTEC (C5460) co-collector dosage (for reagent scheme 1),

= Xanthogen formate & IPTEC (C7133) co-collector dosage (for reagent scheme 2) and

= AM810 Hydroxamate oxide co-collector dosage (for reagent scheme 3)

C = M98B depressant dosage

Table 15: Summary of best PGM recoveries achieved during reagent scouting test work

Test conditions	Collector suite	Grade (g/t)				Recovery (%)			
		Pt	Pd	Au	3E	Pt	Pd	Au	3E
Reagent scheme 1	SIBX & DTP	22,80	8,25	0,53	31,58	66,1	40,1	24,2	55,1
Reagent scheme 2	SIBX & Xanthogen formate	32,20	11,90	1,36	45,46	60,9	37,7	40,5	51,8
Reagent scheme 3	SIBX & Hydroxamate	13,20	5,16	0,34	18,70	74,0	48,4	29,9	63,1

The best PGM flotation recovery was obtained using reagent scheme 3 test 2 conditions which comprised of 50g/t $CuSO_4$ (Copper sulphate), 150g/t SIBX, 30g/t AM810 Hydroxamate, 50g/t M98B Depressant and 50 g/t F200 Frother. Using these conditions, ~63% of the total platinum, palladium and gold (3E) was recovered into the rougher concentrate at a grade of 18.70 g/t. Further flotation test work of reagent optimisation was therefore carried out using reagent scheme 3. The

superior recoveries achieved with the AM810 Hydroxamate oxide co-collector confirmed the characterization results which indicated that the sample studied was non-sulphidic.

4.2.1 Statistical analysis for reagent scouting results

The statistical analysis was carried out using the platinum and palladium flotation recovery and grades results obtained using the 3 reagent schemes to establish the main effects and interaction effects of the reagent factors. The decision to use recoveries of Pt and Pd for statistical analysis was based on their relatively higher grades compared to Au grade as shown in Table 11. The statistical significance of the factors studied was judged using the half-normal probability plots of effects plots illustrated in Figure 20 and Figure 21 and the P-values from the Anova analysis. The sample calculations of the effect estimates are shown in appendix 8.3.3.

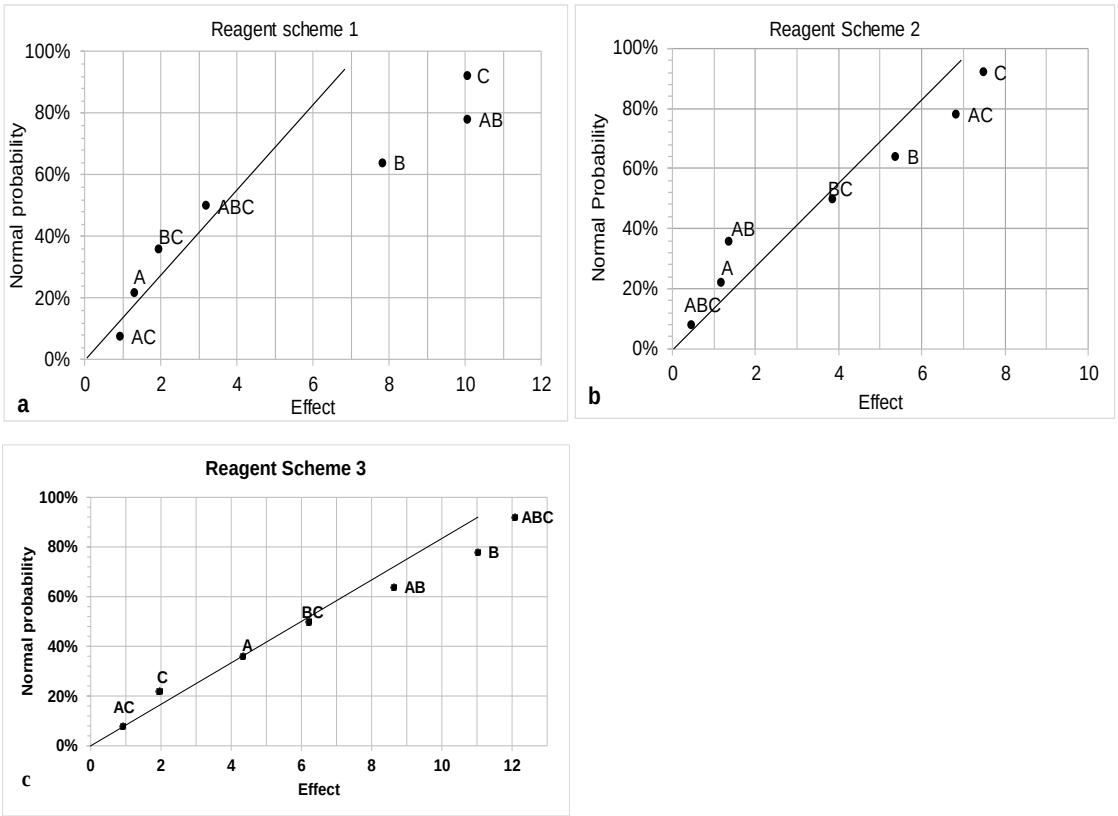


Figure 20: Half-normal probability plots for the platinum recovery models of the 3 reagent schemes investigated during preliminary phase.

The half –normal probability graphs plot the absolute values of the effect estimates against their cumulative normal probabilities. The straight line on the half-normal plots passes through the origin and should also pass close to the fiftieth percentile data value. The statistically insignificant effects lie near the straight line while the main effects lie far from the line (Myers, et al., 2009).

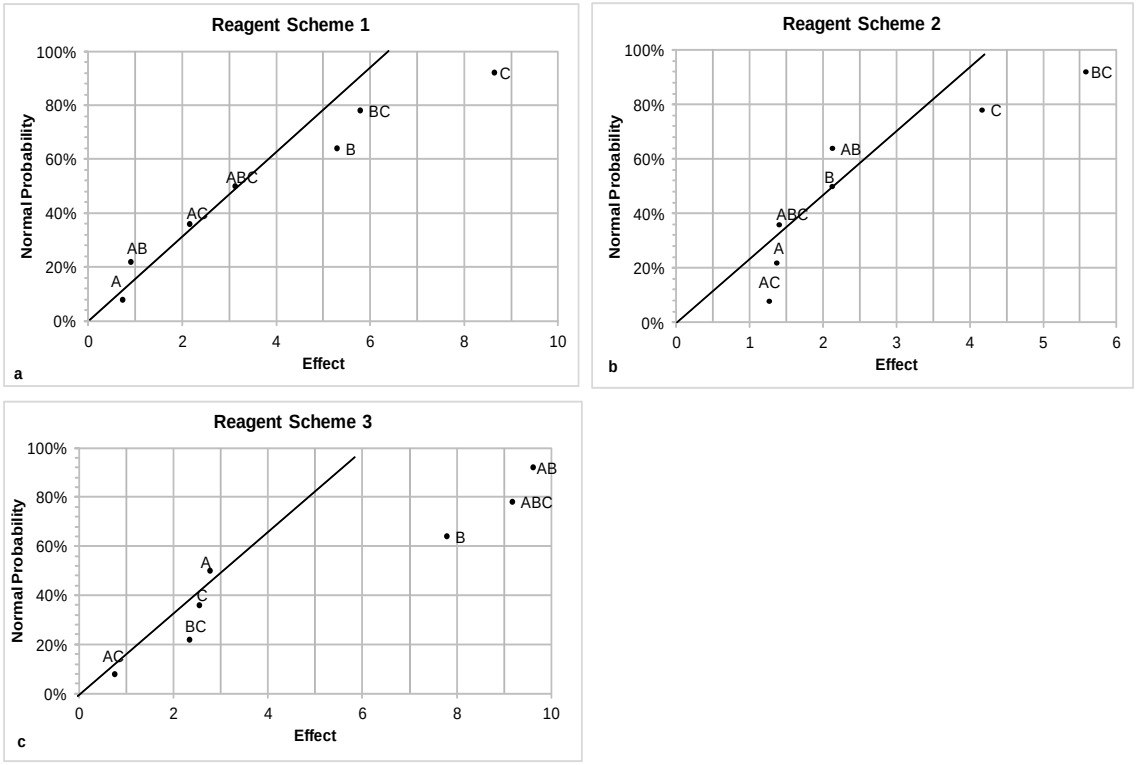


Figure 21: Half-normal probability plots for the palladium recovery models of the 3 reagent schemes investigated during preliminary phase.

The half-normal probability plots indicated that the effects of factor B (co-collectors dosage), factor C (depressant dosage), factor AB (interaction effect of SIBX and co-collectors) and factor BC (interaction effect of co-collectors and depressant) were significant on platinum and palladium recovery from oxidized PGM ore across the 3 reagent schemes studied. The effect of ABC also emerged as significant for the platinum and palladium recovery for reagent scheme 3.

4.2.2. Further analysis of best reagent scheme

The statistical significance of the factors were confirmed by the p-values from the analysis of variance that were less than 0.05 as shown in Table 16 and Table 17 (Anova results for scheme 3). It was concluded that factors B (AM810 dosage), AB (SIBX and AM810) interaction and ABC interaction effects were statistically significant on PGM flotation recovery at 95% confidence level.

Table 16: Analysis of variance for the platinum recovery model (Reagent scheme 3)

Source of Variation	Sum of Squares	Degrees of freedom	Mean Square	F_0	P-Value
B	242.86	1	242.86	15.65	5.49E-03
AB	148.42	1	148.42	9.56	1.75E-02
ABC	291.02	1	291.02	18.75	3.44E-03
BC	77.07	1	77.07	4.96	6.11E-02
Error	46.57	3	15.52		
Total	805.93	7	115.13		

Table 17: Analysis of variance for the palladium recovery model (Reagent scheme 3)

Source of Variation	Sum of Squares	Degrees of freedom	Mean Square	F_0	P-Value
B	121.24	1.00	121.24	11.98	1.05E-02
AB	184.80	1.00	184.80	18.26	3.69E-03
ABC	168.25	1.00	168.25	16.63	4.70E-03
Error	40.48	4.00	10.12		
Total	514.77	7.00	73.54		

The regression equations 17 and 18 used to predict the platinum and palladium recoveries were developed using the main and interactive effects coefficients.

$$Pt_{recovery} = 56.64 + 2.16A + 5.51B - 4.31AB - 3.11BC + 6.03ABC \quad (16)$$

$$Pd_{Recovery} = 33.69 + 3.90B - 4.81AB + 4.59ABC \quad (17)$$

The positive signs of the coefficients of main effects SIBX (A) and AM810 (B) in the Pt recovery equation suggested that platinum recovery may be improved by increasing dosages of SIBX (A) and AM810 (B). However, the interactions between SIBX and AM810 had to be considered when maximizing the response. The negative coefficient of the AB interactions in the regression equations implied that the interaction terms should be minimised to improve Pt and Pd recovery. Since the PGM ore studied was proved to be non-sulphide in section 4.1.1, it would be prudent to adopt higher dosages of AM810 and lower dosages of SIBX to reduce the AB interaction. The AB interaction plots shown in Figure 22 and Figure 23 also suggested that higher platinum recoveries were achieved when AM810 was high (positive) and SIBX was low (negative).

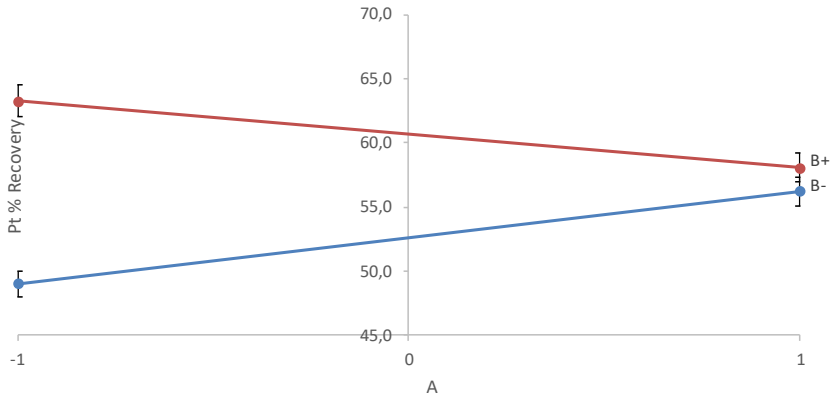


Figure 22: SIBX-AM810 interaction graph for Pt recovery

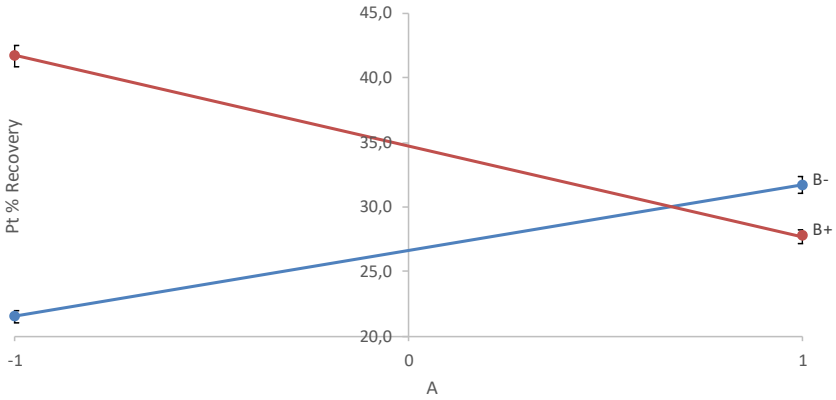


Figure 23: SIBX-AM810 interaction graph for Pd recovery

4.3 Reagent optimization test work results

Following the establishment of reagent scheme 3 as the best reagent scheme that recorded the highest recovery and grade of PGMs from the oxidised PGM ore, a campaign was carried to test the effectiveness of increasing AM810 dosages on PGM recoveries and not necessarily grade as rougher flotation is mainly recovery driven flotation stage. The dosage of AM810 was increased using step sizes of 10 g/t while maintaining the SIBX dosage constant at a low dosage of 100 g/t. The flotation conditions tested and results obtained for this stage of optimisation are presented in Table 18 and further illustrated in Figure 24.

Table 18: Flotation conditions tested during reagent optimisation test work

Experiment Number	SIBX dosage (g/t)	AM810 dosage (g/t)	PGM grade (g/t)				PGM recovery (%)			
			Pt	Pd	Au	3E	Pt	Pd	Au	3E
Rgnt. Opt. Exp 1	100	60	30,3	11,7	0,5	42,5	67,0	41,3	49,5	57,0
Rgnt. Opt. Exp 3	100	70	19,1	9,9	0,3	29,4	70,7	56,1	51,8	64,7
Rgnt. Opt. Exp 2	100	80	16,4	8,1	0,3	24,8	70,8	59,1	51,4	66,3
Rgnt. Opt. Exp 4	100	90	14,9	7,7	0,2	22,9	75,7	61,6	50,7	70,0

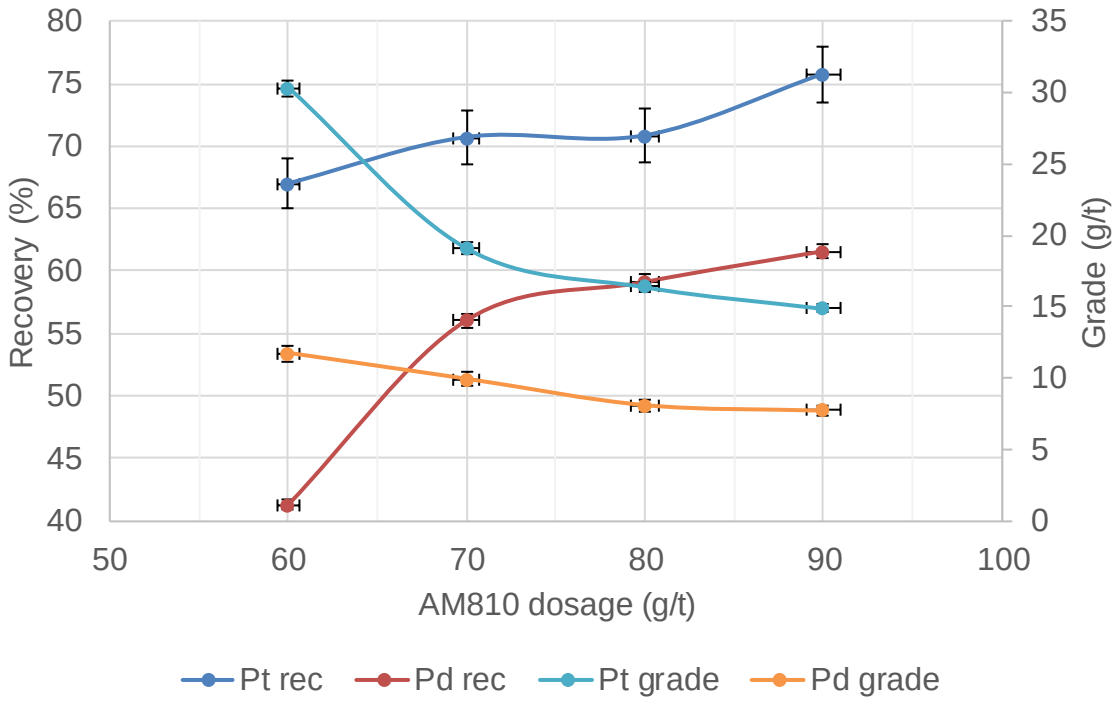


Figure 24: Flotation PGM recoveries and grades obtained at different AM810 dosages at constant SIBX dosage.

The oxidized PGM ore exhibited significant loss of grade for small increases in recovery when the co-collector dosage was increased. Since the focus of these optimisation tests was just to maximize PGM rougher recovery, further test work may investigate the upgrading the recovered concentrates by introducing cleaning stages.

Having established that the increase of co-collector dosage alone achieved limited improvement in PGM recoveries, the **steepest ascent method** (Myers, et al., 2009) was also used to search for the optimum operating conditions. The first step in using this method was to choose a step size in one of the process variables, which was significant. In this case variable B (AM810) was chosen and assigned a factor of 1.0.

$$\Delta B = +1.0 \rightarrow 10\ \mathrm{g/t}$$

Then the coefficients of the most significant factors in the regression equation for platinum recovery were used to determine the step size of A (SIBX) as follows;

$$\Delta A = \frac{b}{2*\lambda} = \frac{2.16}{5.51} = 0.39$$

Where: b is the coefficient of AB interaction and

λ is the coefficient of factor B in the platinum recovery regression equation

$$\Delta A = 0.39 \times \frac{150-100}{2} = 9.75\ g/t$$

Because the dosage of A (SIBX) should be low in order to maximise the recovery, the step size took a negative value, $\Delta A = -9.75\ g/t$ so the path of maximum recovery can be followed.

Table 19 presents the path of steepest ascent, experimental runs from (Base +Δ to Base +4Δ) were conducted in order to search for the maximum recovery. The dosage of the depressant (C) was kept at a constant low of 50 g/t in order to maximise mass pull in the rougher stage.

Table 19: Path of steepest ascent of PGM recovery

	Coded variables		Natural variables	
Point	A	B	SIBX (g/t)	AM810 (g/t)
Base (Starting point)	0	0	125	50
Increment Δ	-0.39	1.0	-9.75	10
Base +Δ	-0.39	1.0	115.25	60
Base +2Δ	-0.78	2.0	105.5	70
Base +3Δ	-1.17	3.0	95.75	80
Base +4Δ	-1.56	4.0	86	90

Table 20: Flotation conditions tested during reagent optimisation –steepest ascent method

Experiment Number	SIBX dosage (g/t)	AM810 dosage (g/t)	PGM grade (g/t)				PGM recovery (%)			
			Pt	Pd	Au	3E	Pt	Pd	Au	3E
Rgnt. Opt. Exp 5	115	50	14,7	7,0	0,2	21,9	71,6	54,5	50,2	64,8
Rgnt. Opt. Exp 6	105	60	19,0	9,7	0,3	29,0	72,1	58,9	52,3	66,8
Rgnt. Opt. Exp 7	96	70	17,3	8,4	0,3	26,0	73,3	59,2	52,6	67,8
Rgnt. Opt. Exp 8	86	80	17,9	9,4	0,3	27,6	78,5	69,3	52,3	74,7

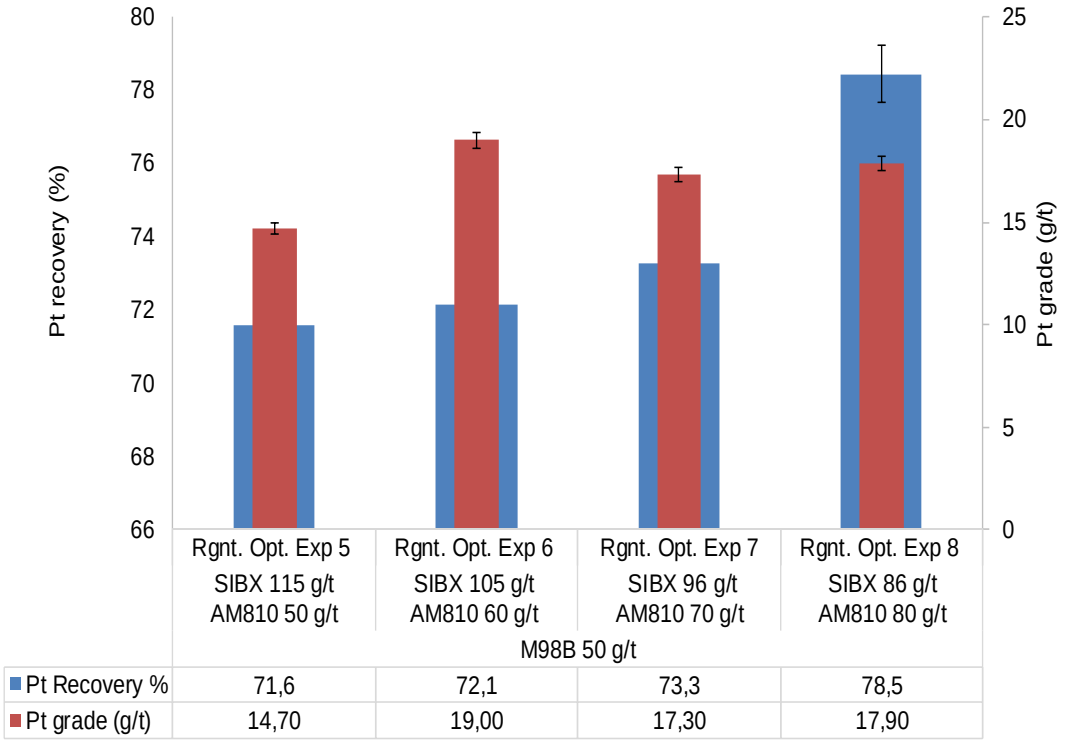


Figure 25: Steepest ascent method reagent optimisation platinum recovery and grade results

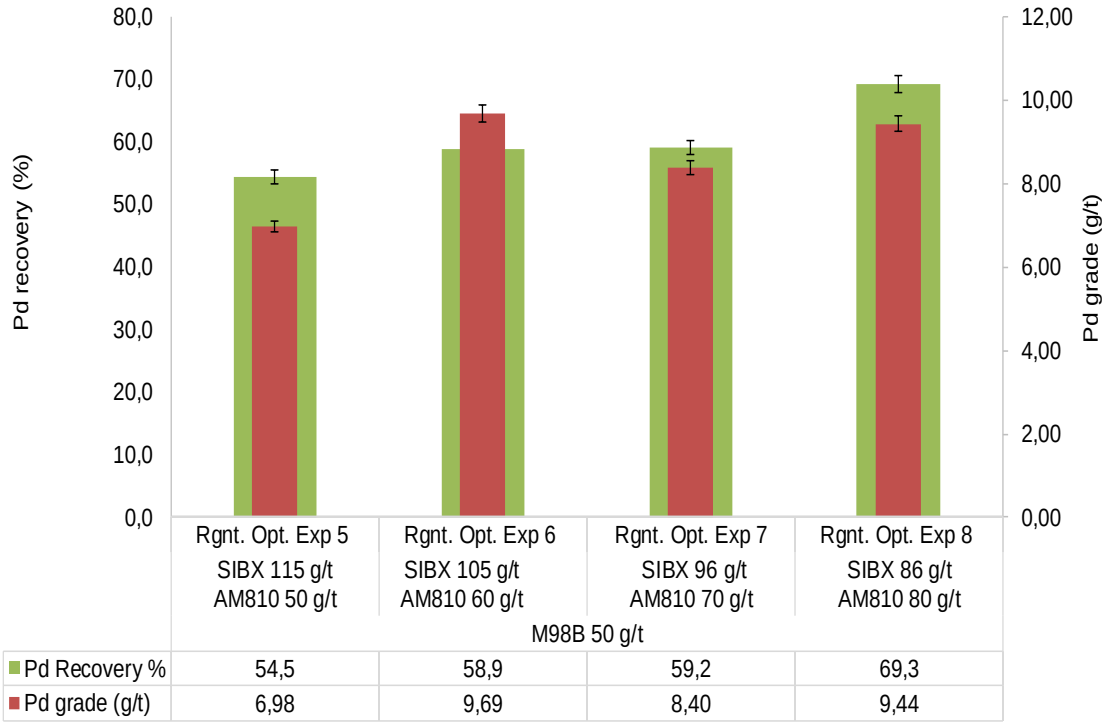


Figure 26: Steepest ascent method reagent optimisation palladium recovery and grade results

The PGM recovery and grade generally increased with decreasing SIBX dosage for the range investigated as predicted by the platinum regression equation. This observation suggests that the oxide co-collector AM810 was probably more selective when the interactions of the primary collector are minimised by lower dosages. Further experiments were conducted to leach the flotation concentrate that was produced at the highest PGM recovery using sulphuric acid in order to target the base metals and further enrich it in PGMs.

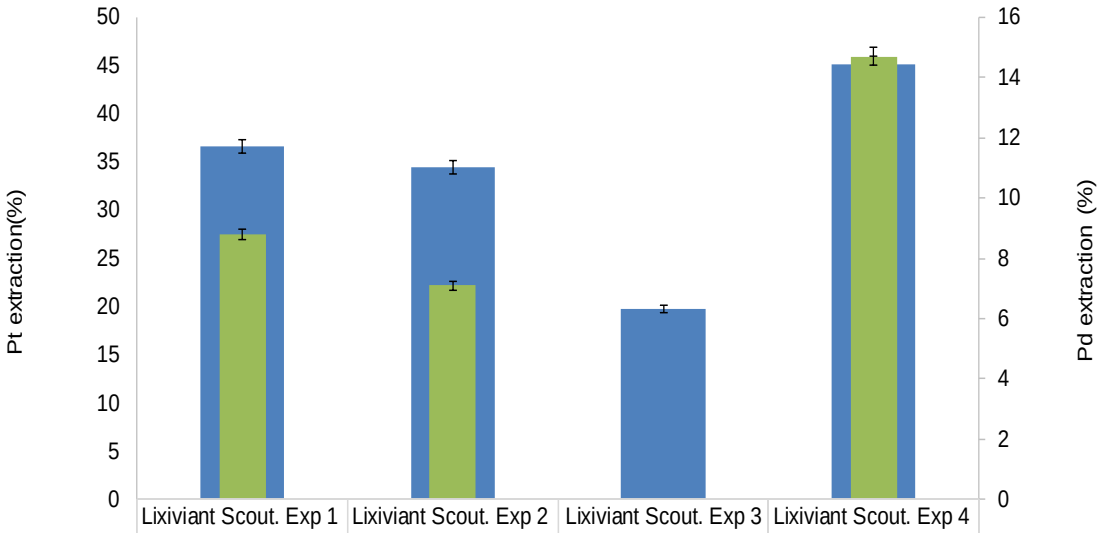
4.4 PGM dissolution from ROM ore test work results

4.4.1 Effect of acid type on PGM dissolution

The PGM dissolution test work was carried out on representative samples milled to 80%-75µm using 4 different acids to establish the best lixiviant system for extraction of PGMs from the ROM oxidised PGM ore. The acids investigated were Hydrochloric acid (HCl), Nitric acid (HNO_3), Sulphuric acid (H_2SO_4) and Aqua Regia. The results obtained are summarised in Table 21 and further illustrated in Figure 27.

Table 21: Summary of lixiviant scouting test work conditions and results

Experimental conditions		PGM recovery (%)	
Constant parameters	Lixiviant type	Pt	Pd
Solid/liquid ratio @ 2g/100ml, Leaching temperature @ 85^{o}C, Cumulative Leaching time 2 hrs	HCl	36,6	8,8
	HNO_3	34,5	7,1
	H_2SO_4	19,7	0,0
	Aqua Regia	45,1	14,7



	Lixiviant Scout. Exp 1 HCl	Lixiviant Scout. Exp 2 HNO3	Lixiviant Scout. Exp 3 H2SO4	Lixiviant Scout. Exp 4 Aqua Regia
Pt extraction (%)	36.6	34.5	19.7	45.1
Pd extraction (%)	8.8	7.1	0.0	14.7

Figure 27: Lixiviant scouting test work results

4.4.2 Effect of solid/liquid ratio on PGM dissolution

The effect of pulp density on PGM dissolution from ROM ore was investigated by varying solids/liquid ratios. The three conditions of pulp density tested were; 2, 6 and 10 g per 100 ml of aqua regia at a leaching temperature of 85^{o}C. The results obtained are shown in Table 22 and further illustrated in Figure 28.

Table 22: Test conditions and results for effect of solid-liquid ratio on PGM leaching recovery

Experimental conditions		PGM recovery (%)	
Constant parameters	Solid/liquid ratio	Pt	Pd
Lixiviant - Aqua Regia, Leaching temperature @ 85°C, Cumulative Leaching time 2 hrs	2 g/100 ml	45,4	14,7
	6 g/100 ml	34,0	9,8
	10 g/100 ml	17,6	4,7

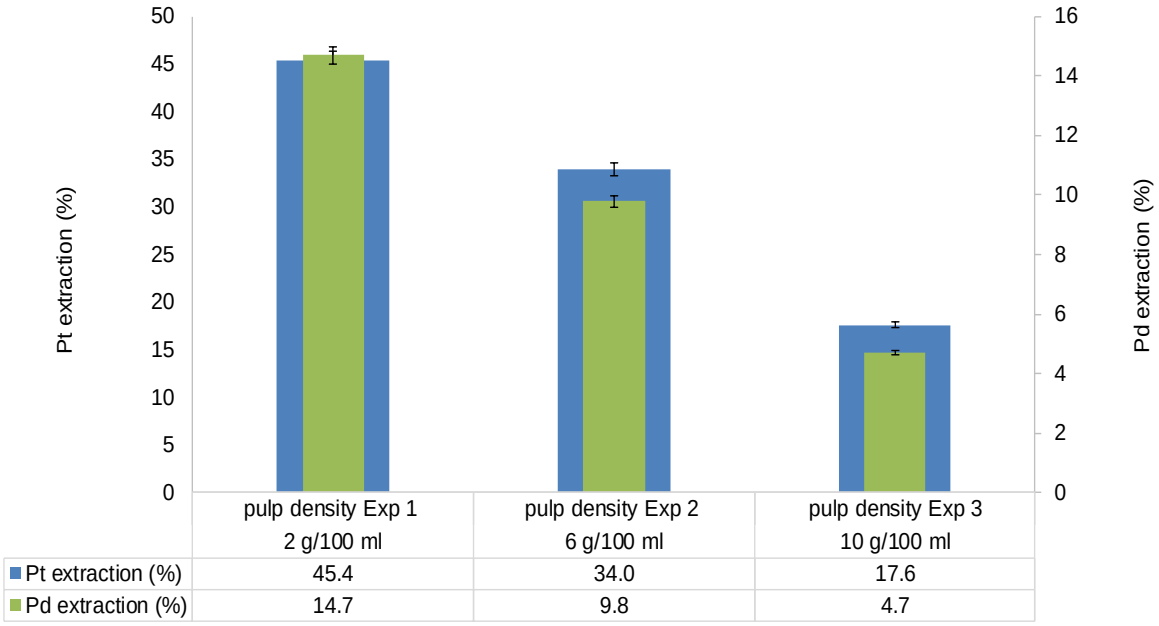


Figure 28: Effect of solid/liquid ratio on PGM recovery results

The results in Figure 28 show that pulp density had a significant effect on the leaching recoveries of Pt and Pd. High recoveries of Pt and Pd were achieved at low solids/liquid ratio probably because of the availability of more lixiviant (Hosseini, et al., 2017). The increase of solid/liquid ratio possibly caused premature consumption of the lixiviant by gangue minerals before leaching the targeted PGMs since the low grade ore was processed without prior upgrading at this stage of test work. Therefore solid/liquid ratio of 2 g/ 100 ml was used in subsequent dissolution tests.

4.4.3 Effect of leaching temperature on PGM dissolution

The effect of temperature on PGM dissolution from oxidised PGM ROM ore using aqua regia was investigated at five different temperatures ranging from 50ºC to 85ºC. The specific experimental conditions and results for these tests are presented in Table 23 and further illustrated in Figure 29.

Table 23: Experimental conditions and results for effect of temperature on leaching recovery

Experimental conditions		PGM recovery (%)	
Constant parameters	Leaching Temperature (^{O}C)	Pt	Pd
Lixiviant - Aqua Regia, Solid/liquid ratio @ 2g/100ml, Cumulative Leaching time 2 hrs	50	12,3	5,9
	60	16,9	9,0
	70	26,4	9,8
	80	44,0	13,2
	85	48,6	14,7

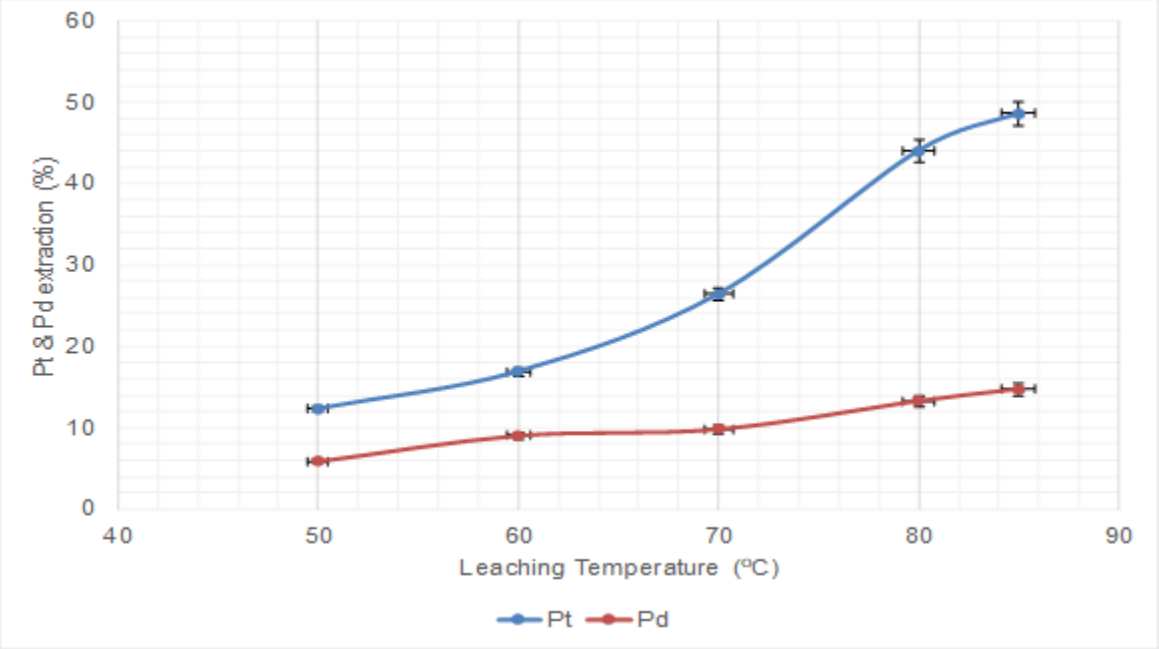


Figure 29: Effect of leaching temperature on PGM recovery results

4.4.4 Effect of Leaching time on overall PGM extraction

Following the establishment of the optimum temperature for PGM dissolution from ROM ore, a campaign was carried out to evaluate the impact of leaching time on overall PGM dissolution. The leaching time was varied from 15 minutes to 120 minutes while maintaining all the other parameters constant. The results obtained are summarised in Table 24 and further illustrated in Figure 30.

Table 24: Test conditions and results for effect of leaching time on PGM leaching recovery

Experimental conditions	PGM recovery (%)		
Constant parameters	Retention time (min)	Pt	Pd
Lixiviant - Aqua Regia, Solid/liquid ratio @ 2 g/100 ml, Leaching temperature @ 85°C,	15	23,5	4,7
	30	29,3	5,9
	60	36,1	18,8
	90	46,0	23,5
	120	48,1	24,5

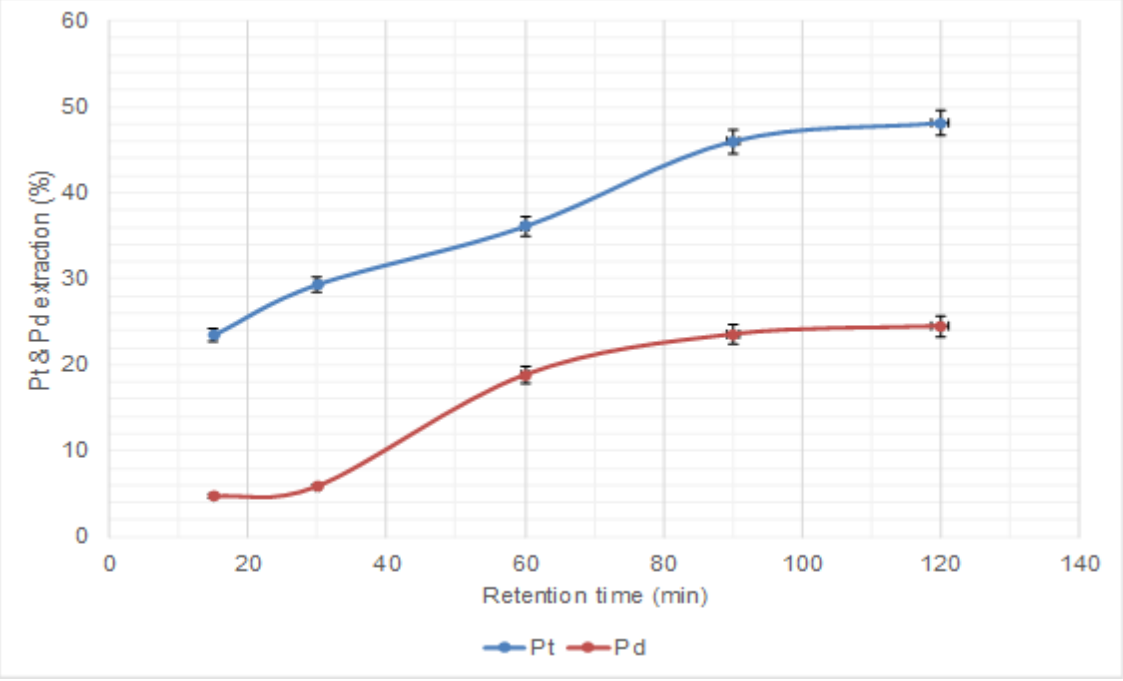


Figure 30: Effect of leaching time on PGM recovery results

4.4.5 Evaluation of leaching conditions on PGM recovery

The highest PGM dissolution from ROM ore was achieved using Aqua Regia at a lowest solid/liquid ratio of 2 g/100 ml. The overall PGM dissolution generally increased with leaching temperature and time for the conditions studied. These observations were consistent with literature (Baghalha, et al., 2009) because higher temperature improved the reactions kinetics while prolonged leaching times ensures that the leaching reactions reach equilibrium.

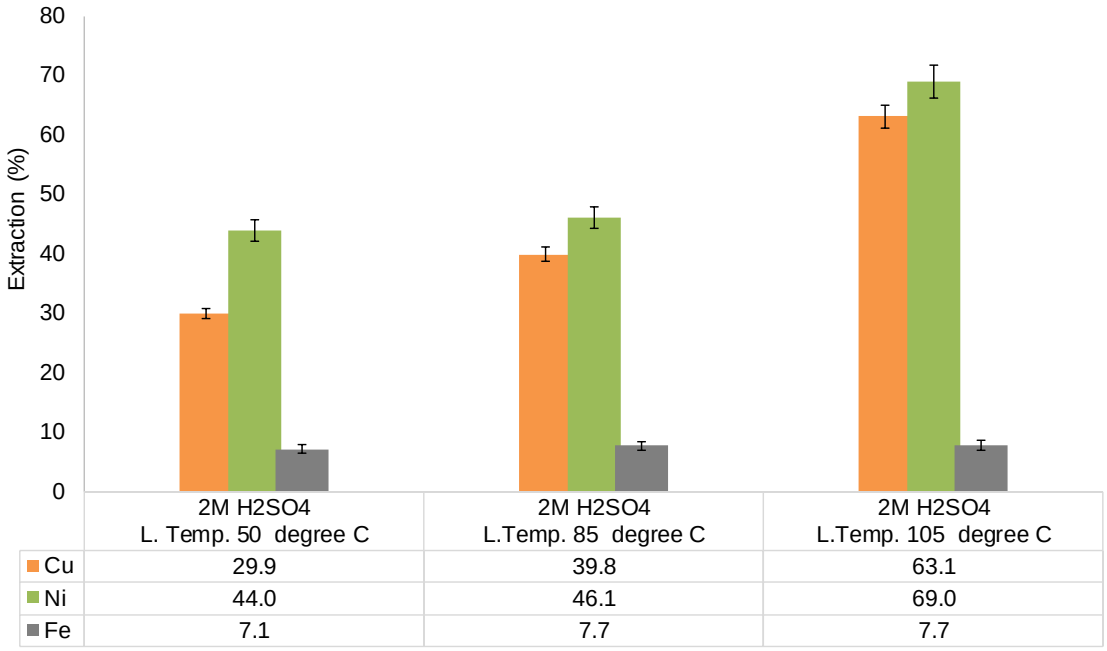
4.5 Base metal leaching tests on rougher PGM concentrates

Leaching of base metals (Copper, Nickel and Iron) with sulphuric acid was carried out to upgrade the low grade flotation concentrate. Sulphuric acid was chosen because it is an efficient lixiviant for base metals but does not solubilise PGMs. The dissolution of base metals in sulphuric acid proceeds as summarised by reaction 19 (Kumar, et al., 2010).

$$Me^{2+} + 2H_2SO_4 + 2H_2O_2 \rightarrow MeSO_4 + 2H_2SO_3 + 2H_2O \quad 18$$

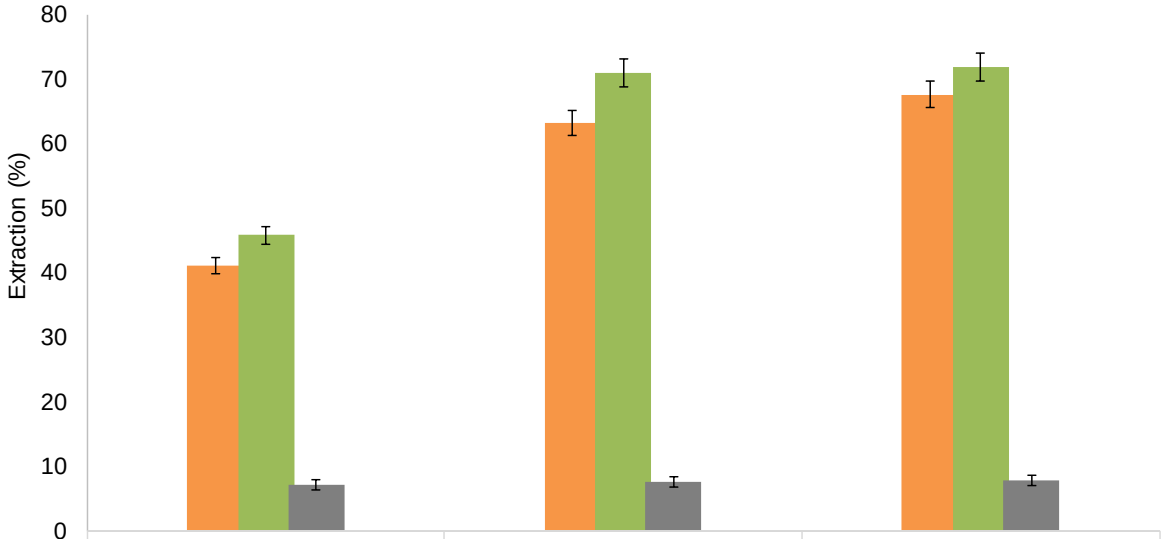
Where: Me = Cu, Ni, Fe

The results of base metal leaching tests on flotation concentrates are presented in Figure 31 to Figure 34.



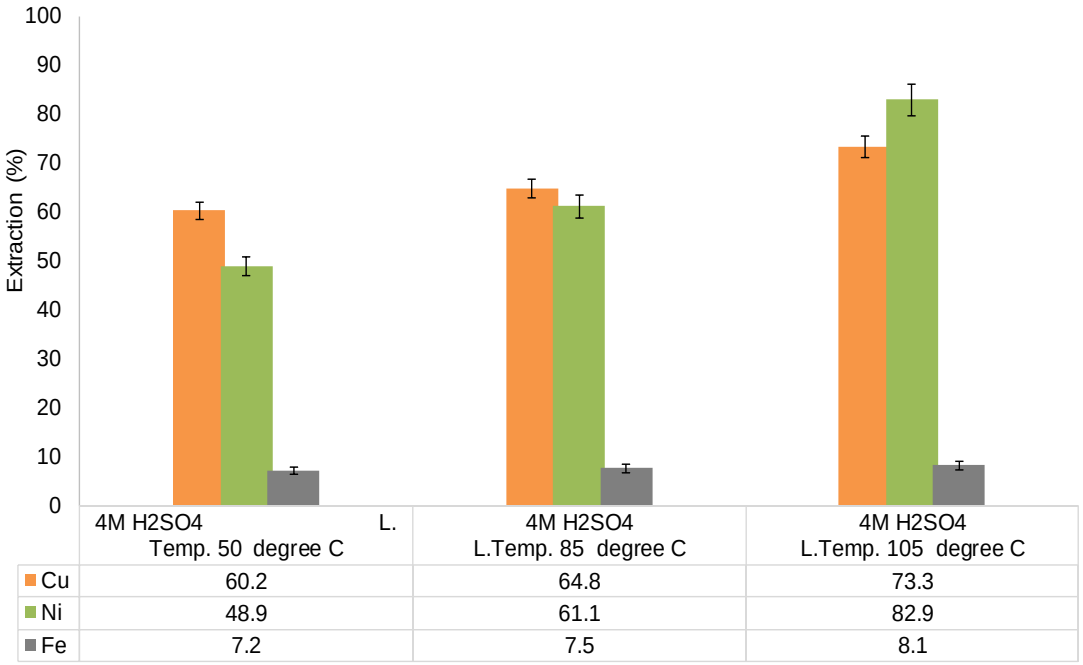
	2M H2SO4 L. Temp. 50 degree C	2M H2SO4 L.Temp. 85 degree C	2M H2SO4 L.Temp. 105 degree C
Cu	29.9	39.8	63.1
Ni	44.0	46.1	69.0
Fe	7.1	7.7	7.7

Figure 31: Effect of temperature on base metal leach recovery at 2M H_2SO_4 concentration.



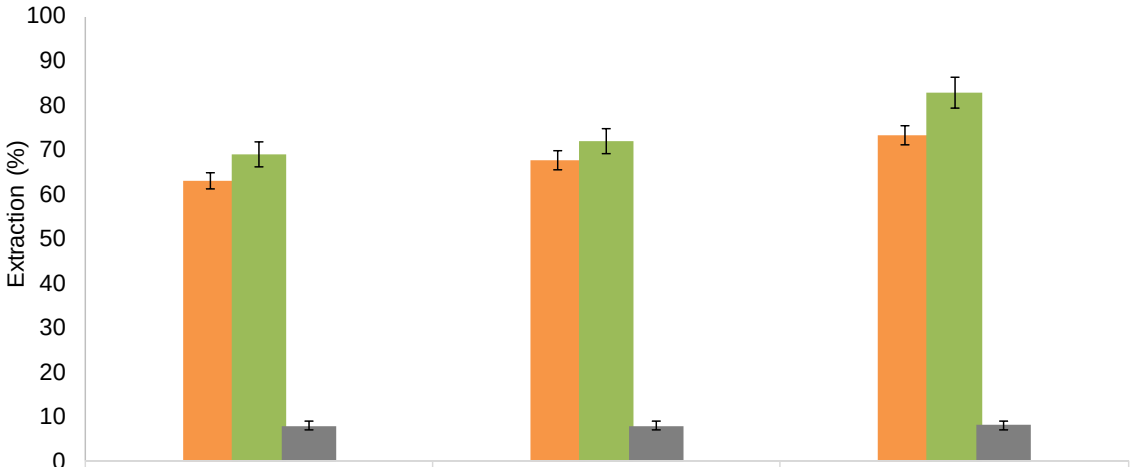
	3M H2SO4 L. Temp. 50 degree C	3M H2SO4 L.Temp. 85 degree C	3M H2SO4 L.Temp. 105 degree C
Cu	41.1	63.3	67.7
Ni	45.9	71.0	72.1
Fe	7.1	7.7	7.9

Figure 32: Effect of temperature on base metal leach recovery at 3M H_2SO_4 concentration.



	4M H2SO4 L. Temp. 50 degree C	4M H2SO4 L.Temp. 85 degree C	4M H2SO4 L.Temp. 105 degree C
Cu	60.2	64.8	73.3
Ni	48.9	61.1	82.9
Fe	7.2	7.5	8.1

Figure 33: Effect of temperature on base metal leach recovery at 4M H_2SO_4 concentration.



	2M H2SO4 L. Temp. 105 degree C	3M H2SO4 L.Temp. 105 degree C	4M H2SO4 L.Temp. 105 degree C
Cu	63.1	67.7	73.3
Ni	69.0	72.1	82.9
Fe	7.7	7.9	8.1

Figure 34: Effect of H_2SO_4 concentration on base metal leach recovery at 105 ^oC.

5. DISCUSSION

The purpose of this chapter is to discuss the test work results with regards to the key questions raised in section 1.6. The response of the PGM oxide ore to flotation and the flotation recoveries from the oxidised PGM ore will be discussed and related to the ore bulk mineralogy. The discussion will then evaluate the three reagent suites conducted in an attempt to improve rougher flotation recoveries from the oxidised Mimosa PGM ore. The hydrometallurgical recovery of PGMs from ROM ore will also be discussed and evaluated. The discussion will conclude with a discussion on leaching the rougher flotation concentrate to eliminate base metals and upgrade the concentrate further for downstream smelting or leaching process. A brief high level discussion on the comparative costs of the flotation and hydrometallurgical process routes will be done.

5.1 Ore mineralogy and effects on flotation recovery

The XRD test work results indicated that oxidised PGM ore studied was non-sulphide and contained significant concentrations of gangue silicate minerals such as chabazite, quartz and base metal oxide magnetite. The small concentrations of Cu and Ni as measured by XRF analysis suggested that the oxidised ore contained relatively low concentrations of base metal sulphide minerals. The XRD and XRF analysis results which showed very low sulphur content explained the poor flotation recoveries achieved when treating the oxidised PGM ore using the conventional sulphide collectors. The PGM mining operations normally target the flotation recovery of base metal sulphide minerals such as chalcopyrite, pentlandite and pyrrhotite because of their close association to the PGMs (Kloppers et al, 2016).

Research has indicated that during weathering, the iron-containing sulphide minerals such as pyrrhotite oxidises to form hydrophilic iron oxyhydroxides on the particle surfaces that reduce the flotation recoveries ((Buckley & Woods, 1984; Legrand, et al., 2005; Newell et al, 2006)). Magnetite was analysed as the most abundant base metal mineral present in the oxidised ore. Although magnetite is not the direct product of the weathering processes as explained by the work of (Holwell, et al., 2017), the decomposition of the iron oxyhydroxide according to reaction 19 probably resulted in the elevated magnetite content in the ore.

$$2\,FeO(OH) \rightarrow Fe_2O_3 + H_2O \qquad (19)$$

5.2 Evaluation of Reagent suites tested

5.2.1 Dithiophosphate and thionocarbamates co-collector (FLOMIN C5460)

The C5460 co-collector contained Dithiophosphate and dialkyl thionocarbamate 0-isopropyl-N-ethyl thionocarbamate (IPETC). The di-alkyl thionocarbamate collectors possess superior selectivity for copper sulphide minerals particularly against gangue iron sulphides (Leppinen, et al., 1988; Fairthone, et al., 1997). The C5460 co-collector generally exhibited poor PGM recovery because this particular ore is not a sulphide ore as shown by the characterisation test work results.

5.2.2 Xanthogen formate and thionocarbamates co-collector (C7133)

The C7133 co-collector containing xanthogen formate and thionocarbamates also achieved limited recoveries because xanthogen formates are only selective for base metal sulphides (Ackerman, et al., 2000) and not the oxidised/altered minerals which are contained in the ore sample studied. The efficiencies of both sulphide co-collectors (C5460 and C7133) would possibly be improved if sulfidisation was conducted before flotation as outlined by the work of (Newell et al, 2007).

5.2.3 Hydroxamates co-collectors

The hydroxamate co-collector AM810 achieved higher PGM recoveries and grades than the other two reagent suites tested. This is because unlike C5460 and C7133, hydroxamates are chelating collectors that are used as oxide collectors because they form complexes with all metals (Assis et al, 1996). The hydroxamate collectors have been proven to efficiently improve flotation recoveries of oxide sulphide mineral component from mixed copper sulphide/oxide blend without any adverse effect of the performance of primary sulphide collector (Lee et al, 2009).The superior PGM recoveries achieved with the AM810 hydroxamate validate the findings of the earlier research on oxidised PGM ore by (Ramonotsi, 2011) which indicated that hydroxamate AM28 co-

collector was efficient for PGM extraction. However, the low concentration grades imply poor selectivity of the hydroxamate collector and the need for complex cleaning stages to upgrade the rougher concentrates.

5.3 Evaluation of the hydrometallurgical test work

5.3.1 Direct leaching of ROM oxidised ore

The best PGM leaching recovery from ROM oxidised ore was achieved with aqua regia solution. The superior aqua regia leaching recoveries were achieved with aqua regia because PGMs form stable chloro-complexes under the high oxidation conditions provided by the reaction of HCl and HNO_3 (Lide, 1995). The benefit of hydrometallurgical PGM recovery is that a high grade leach solution that can be sent straight to the refinery is produced compared to the low grade flotation that still needs upgrading by cleaner flotation and energy intensive smelting process (Sefako, et al., 2017). However, the economics of leaching of the low grade ROM ore using aqua regia would be adversely affected by high lixiviant consumption because of the unselective nature of aqua regia. The leaching operating costs would also be high because low concentrations of the targeted PGMs in the ROM ore would lead to low leaching kinetics.

5.3.2 Base metal leaching from flotation concentrates.

5.3.2.1. Effect of leaching temperature on base metal recovery

The copper and nickel leaching recoveries generally improved with increasing leaching temperature. The observed increase of copper and nickel recoveries with increasing leaching temperature was consistent with the Arrhenius theory and the findings of the works of (Wen, et al., 2017; Hosseini, et al., 2017) which indicated that copper and nickel leaching kinetics in sulphuric acid improved at high temperatures.

5.3.2.2 Effect of lixiviant concentration on base metal recovery

The copper and nickel leaching recoveries depended on sulphuric acid concentration as shown in Figure 34. Increasing acid concentration from 2M to 4M increases the H^+ activity in solution which favours the dissolution of copper and nickel by shifting the equilibrium to the right according to Le chatelier's principle (Hosseini, et al., 2017). Therefore, the 4M H_2SO_4 concentration was selected as the best condition for upgrading of the low grade flotation concentrate in this study. The results indicated that leaching temperature had more effect of on copper and nickel recoveries than lixiviant concentration.

Despite the high concentrations of magnetite in the ore as indicated by the characterisation test work, poor leaching recoveries were achieved for iron at all conditions tested. This observation was consisted with the findings of (Liu, et al., 2009) which indicated that magnetite and other iron minerals exhibit low dissolution kinetics in sulphuric acid even at elevated temperatures and acid concentrations. The low Fe leaching extraction suggested that more intensive conditions such as high pressure process may need to be adopted for efficient extraction of Fe prior to subsequent PGM leaching (Mpinga, et al., 2015).

5.4 Cost benefit analysis

The high level economic evaluation of the flotation and the hydrometallurgical processing of ROM ore using aqua regia was carried out to establish the feasibility of each process. The following assumptions were made for economic evaluation calculations:

1. The cost of acquiring the oxidised PGM ore from stockpiles was assumed as ZAR 50/ tonne because no additional mining would be required.
2. The total revenues of PGMs in the flotation concentrate and leach liquor were discounted by 50% considering that further processing to produce pure metal would still be necessary in each case.
3. The reagent costs used in the economic model were based on quotations of bulk chemical suppliers in the mining industry.
4. The USD/ZAR exchange rate of 13.22 was used for calculations.
5. The PGMs prices sourced from Johnson Matthey were used for the cost analysis are shown in Table 25.

Table 25: Approximate selling prices of individual PGMs.

Description	Price/ounce	Price/ounce
Pt	USD 840,00	ZAR 11 104,80
Pd	USD 948,00	ZAR 12 532,56

The results of cost benefit analysis for both processing routes are presented in Table 26.

Table 26: Bill of materials for flotation and leaching routes.

Total Revenue/ton ore processed							
Description	Head assays	Flotation route			Leaching route		
		Recovery (%)	Mass (grams) produced/ton ore	Revenue	Recovery (%)	Mass (grams) produced/ton ore	Revenue
Pt	1,42	78,7	1,12	ZAR 438,00	48,6	0,69	ZAR 270,33
Pd	0,85	69,6	0,59	ZAR 261,50	14,7	0,12	ZAR 55,24
Totals				ZAR 699,50			ZAR 325,56
Discounted total revenue				**ZAR 349,75**			**ZAR 162,78**

Reagent costs								
Material ID	**Unit cost (ZAR/tonne)**	**Flotation route**		**Leaching route**				
		dosage (g/t)	Operating cost (ZAR/tonne ore)	solid/liquid ratio	Start up mass (kg)	Start up Cost (ZAR)	Top up mass (kg)	Operating cost (ZAR/tonne ore)
Cost of ore/ tonne	ZAR 50,00	-	ZAR 50,00	-				ZAR 50,00
SIBX collector	ZAR 21 819,61	150	ZAR 3,27					
AM810 hydroxamate co-collector	ZAR 117 658,00	80	ZAR 9,41					
Copper sulphate	ZAR 22 804,50	50	ZAR 1,14					
F200 frother	ZAR 30 000,00	50	ZAR 1,50					
HCl	ZAR 2 181,30	0		2 g/100 ml	44625,00	97340,51	44,625	ZAR 97,34
HNO_3	ZAR 6 107,64	0		2 g/100 ml	17500,00	106883,70	17,50	ZAR 106,88
Total costs			ZAR 65,33			204224,21		ZAR 254,22
Gross profit/loss			**ZAR 284,42**					**-ZAR 91,44**
Percentage gross profit/loss			81%					-56%

5.4.1 Cost analysis discussion

Flotation route was the profitable of the two processing routes with the excess of revenue over reagent costs of 81% while the leaching route showed a deficit of -56%. The hydrometallurgical processing of ROM ore using aqua regia at the pulp density tested was unprofitable because of excessive consumption of the non-selective lixiviant. This implied the need to investigate alternative lixiviants that can achieve superior PGM extractions at higher solids-liquid ratios to develop an efficient hydrometallurgical processing of these resources. Additionally, the implementation of highly corrosive aqua regia would result in undesirable infrastructural changes such as rubberization of tanks or use of stainless steel tanks that leads to both high capital and operating costs. The low PGM head grades of the weathered ore shown in section 3.2 would not be sufficient to support the exorbitant capital and operational costs associated with aqua regia leaching and would render the process impractical in industry. Although the profitability of the flotation route will also be reduced when other operating costs such as utilities and labour are considered, this high level economic evaluation indicated that more research effort must be directed towards optimising flotation as the first pre-concentration step as opposed to the purely hydrometallurgical processing.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This chapter presents the conclusions drawn and recommendations made based on the test work results obtained in this study.

The basis of the work presented in this thesis was the poor PGM recoveries achieved when processing oxidised PGM ores using the conventional flotation route. The aim of the research was to address the following key questions:

- ✓ Can the PGM flotation recovery from the oxidised PGM ore be improved by improving the flotation conditions,
- ✓ Can the hydrometallurgical processing of ROM oxidised ore be an alternative to the conventional flotation route? and
- ✓ Can the low grade flotation concentrate be upgraded by leaching base metals with sulphuric acid?

The three flotation reagent suites were investigated to address the first key question. The co-collectors tested were C5460 (Dithiophosphate and IPETC mixture), C7133 (Xanthogen formate and IPETC mixture) and AM810 Hydroxamate. The sulphide co-collectors (C5460 and C7133) could not improve the flotation PGM recoveries from the oxidised PGM ore in this study. These co-collectors could not enhance/impart hydrophobicity on PGM carrying minerals because weathering of the ore altered the sulphide minerals which are often associated with the targeted PGMs. The PGM recoveries using sulphide co-collector schemes could possibly be improved by sulphidisation before flotation because it has been proved to restore the flotatibility of oxidised minerals (Newell et al, 2007).

Superior flotation recoveries and grade were achieved by the AM810 hydroxamate co-collector. The efficiency of the hydroxamate is based on its ability to form complexes by chelation with metals (Assis et al, 1996). Since the oxidised PGM ore contained high concentrations of iron as

shown by the characterisation test work, it was deduced that recovery of iron oxide minerals by the hydroxamate collector resulted in improved PGM recoveries.

The flotation reagent optimisation results indicated that PGM recovery gradually improved with increasing AM810 dosage. As indicated in the literature (Lee et al, 2009), hydroxamates improve the oxide mineral recovery without adversely affecting the performance of the primary collectors. However, the results of this study indicated significant interactions between the primary collector SIBX and the hydroxamate co-collector especially at high SIBX dosages exists. The interactions between AM810 and SIBX showed that detailed mineralogy was important to establish factors influencing flotation performance in order to determine optimum collector dosages for the specific ore. The best flotation PGM recovery was obtained at reagent conditions comprising 86 g/t SIBX and 80 g/t AM810 collector system. Using these conditions, 74.7% of the total 3E was recovered in to the rougher concentrate at the grade of 27.6 g/t.

The series of leaching tests were conducted to address the second key question. The best PGM leaching recovery from ROM ore achieved using aqua regia solution was 48.6% Pt and 14.7 Pd. The low PGM leaching recoveries indicated that hydrometallurgical processing of ROM ore was not efficient because it would also be characterised by high reagent consumptions because of the unselective nature of aqua regia.

The results indicated that upgrading of the ROM ore by flotation using oxide hydroxamate co-collector as the first step was the most promising processing route. This is because this processing option would use the already existing infrastructure. Therefore more research efforts should be directed towards improving the selectivity and establishing optimum dosages of hydroxamate co-collectors in the PGM industry.

The results of this study have shown that hydrometallurgical processing of the low grade flotation concentrates would be a better option than leaching of ROM ore. The works of (Mwase, et al., 2012; Shaik & Petersen, 2017) have also shown that hydrometallurgical processing of low grade concentrates has the potential to be a more economical and environmentally sustainable than the conventional smelting route. However, the poor selectivity of the PGM lixiviants that have been

tested on low grade concentrates to date (aqua regia and sodium cyanide) dictate this processing route to involve a pre-leaching stage for base metals. Sulphuric acid leaching proved to be efficient for upgrading the low grade concentrate by extraction of copper and nickel. The low recoveries of iron by sulphuric acid would still result in high reagent consumptions in the downstream PGM leaching.

6.2 Recommendations

The following recommendations are made based on the results and conclusions:

- ✓ Additional mineralogical tests should be performed on the flotation tails to establish the nature of the minerals and PGMs that are not recovered into the concentrate. The other tests should be performed on the low grade concentrate to determine if the PGM phases recovered can be recovered by leaching.

- ✓ The scope of this study was limited to establishing the efficient processing route between non-conventional flotation reagent schemes and hydrometallurgical recovery of PGMs. The further investigation should focus on efficiently upgrading of the low grade concentrate recovered using the hydroxamate reagent scheme.

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8. APPENDIX

8.1 Detailed analytical results

8.1.1 Detailed XRF elemental analysis

Table 27: XRF analysis results for oxidized PGM ore

2017-3-27 10:23

SQX Calculation Result

Sample : PGMT
Application : EZS002MNV Model : Bulk
Date analyzed : 2017-3-23 13:05
Balance :
Matching library:
File : EZS2712

No.	Component	Result	Unit	Det.limit	El.line	Intensity	w/o normal
1	Na	0.543	mass%	0.02942	Na-KA	0.6027	0.3272
2	Mg	18.1	mass%	0.02305	Mg-KA	62.5293	10.8908
3	Al	5.25	mass%	0.00974	Al-KA	45.6443	3.1611
4	Si	32.0	mass%	0.01456	Si-KA	264.9398	19.2937
5	P	0.0254	mass%	0.00266	P -KA	0.3613	0.0153
6	S	0.640	mass%	0.00349	S -KA	7.9365	0.3859
7	Cl	0.0365	mass%	0.01225	Cl-KA	0.1015	0.0220
8	K	0.414	mass%	0.00498	K -KA	6.9024	0.2497
9	Ca	7.12	mass%	0.00831	Ca-KA	107.7247	4.2902
10	Ti	0.504	mass%	0.01562	Ti-KA	2.2638	0.3039
11	V	0.106	mass%	0.01329	V -KA	0.7807	0.0641
12	Cr	7.97	mass%	0.08523	Cr-KB1	16.7485	4.8039
13	Mn	0.424	mass%	0.01592	Mn-KA	6.4239	0.2554
14	Fe	25.9	mass%	0.01665	Fe-KA	445.4589	15.5930
15	Co	0.0505	mass%	0.01339	Co-KA	1.1574	0.0305
16	Ni	0.582	mass%	0.00884	Ni-KA	11.2537	0.3508
17	Cu	0.313	mass%	0.00790	Cu-KA	7.7089	0.1886
18	Zn	0.0458	mass%	0.00704	Zn-KA	1.4886	0.0276
19	Sr	0.0203	mass%	0.00461	Sr-KA	2.1665	0.0122

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8.1.2 Detailed SEM/EDX elemental analysis results

Table 28: EDX analysis results for oxidized PGM ore

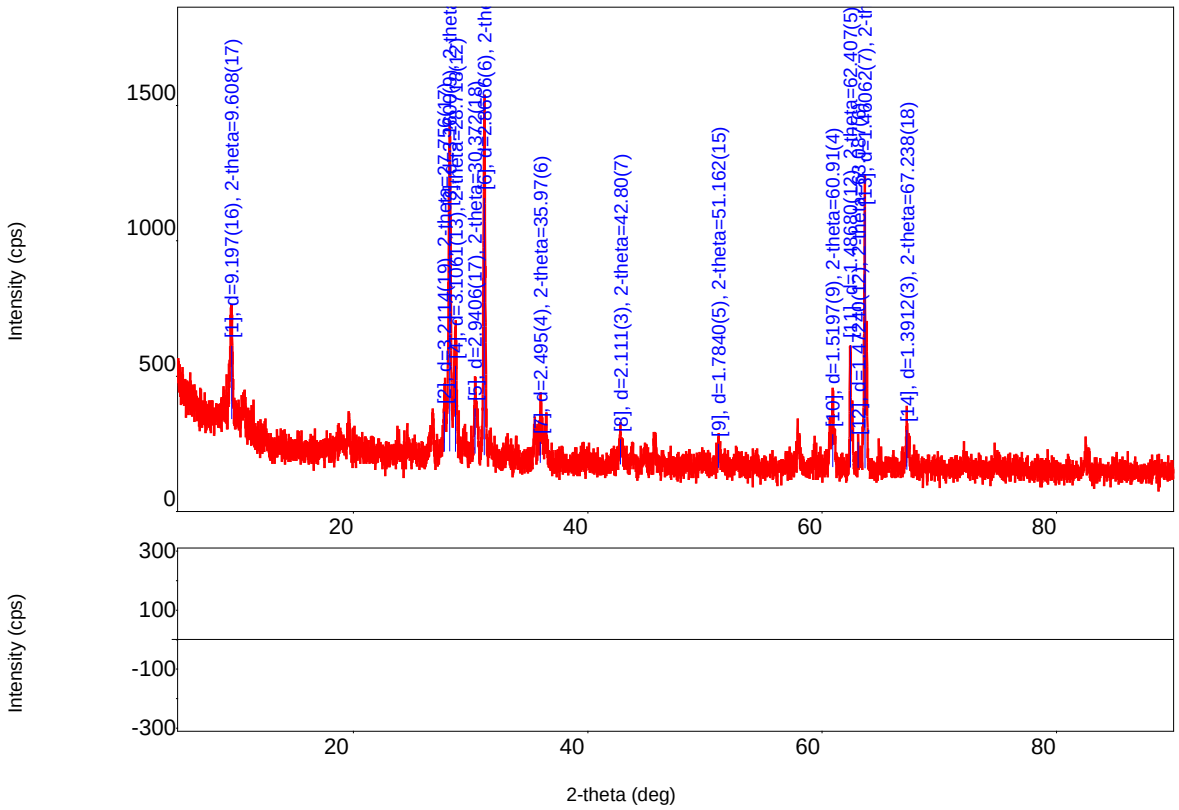
Element	Weight%	Atomic%
O K	56.32	70.56
Na K	0.49	0.42
Mg K	11.75	9.69
Al K	2.21	1.64
Si K	19.16	13.68
S K	0.49	0.31
Ca K	2.07	1.03
Fe K	6.91	2.48
Cu K	0.60	0.19
Totals	100	

8.1.3 Detailed XRD analysis results

General Information

Analysis date	2017/09/26 08:34:30 AM		
Sample name	PGM T	Measurement date	2017/03/24 07:22:08
File name	PGM T.raw	Operator	User
Comment	Full Chart		

Measurement profile



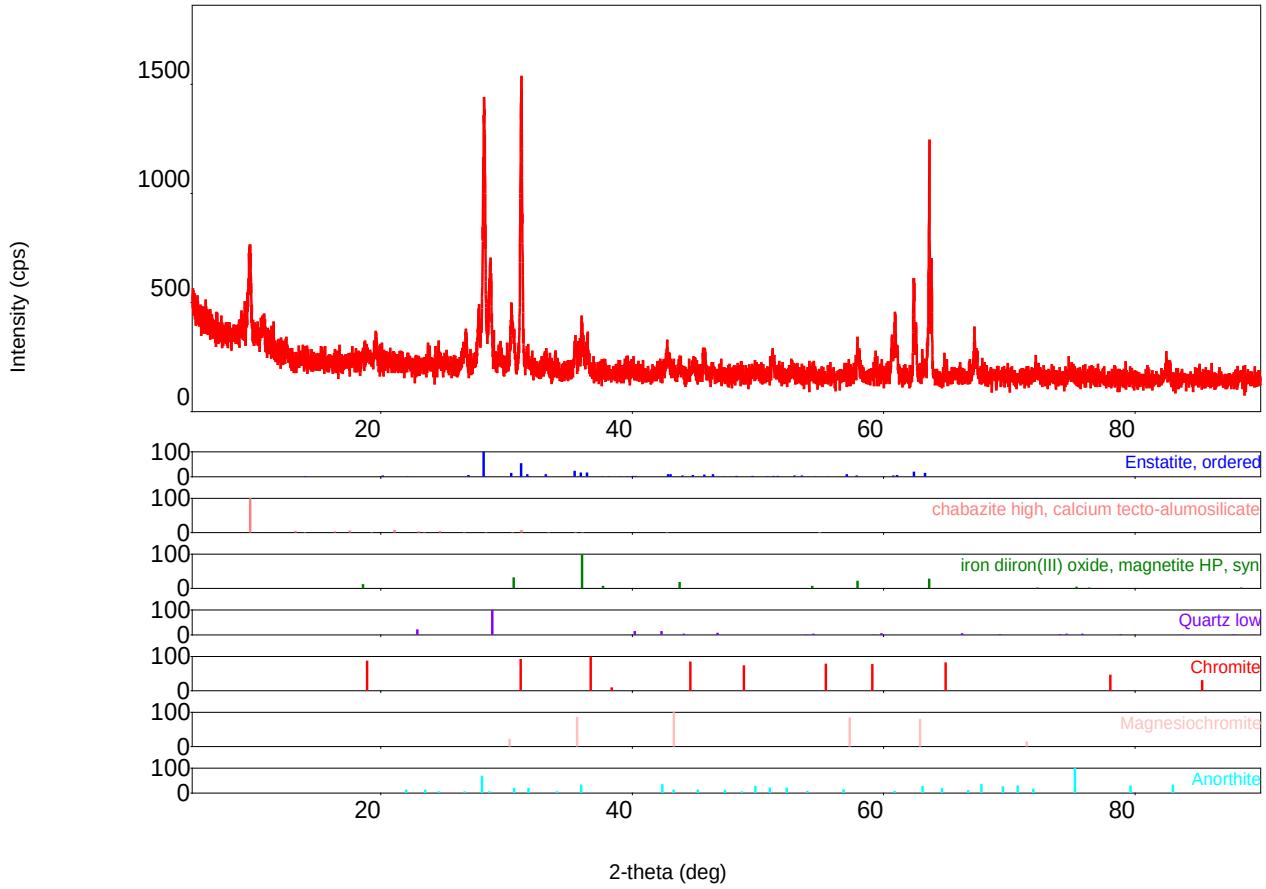
Measurement conditions

X-Ray	40 kV , 30 mA	Scan speed / Duration time	2.0000 deg./min.
Goniometer		Step width	0.0100 deg.
Attachment	-	Scan axis	2theta/theta
Filter	K-beta filter	Scan range	5.0000 - 90.0000 deg.
CBO selection slit	-	Incident slit	2/3deg.
Diffrected beam mono.		Length limiting slit	-
Detector	Scintillation counter	Receiving slit #1	Open
Scan mode	CONTINUOUS	Receiving slit #2	0.60mm

Qualitative analysis results

Phase name	Formula	Figure of merit	Phase reg. detail	DB card number
Enstatite, ordered	Mg Si O3	0.780	ICDD (PDF2010)	00-022-0714
chabazite high, calcium tecto-	Ca1.85 (Al3.7 Si8.3 O24)	0.961	ICDD (PDF2010)	01-085-1140
iron diiron(III) oxide, magnetite	Fe3 O4	0.791	ICDD (PDF2010)	01-071-6339
Quartz low	Si O2	1.859	ICDD (PDF2010)	01-070-2537
Chromite	Cr2 O3 · Fe O	1.949	ICDD (PDF2010)	00-002-1083
Magnesiochromite	Mg O · Cr2 O3	2.934	ICDD (PDF2010)	00-002-1228
Anorthite	Ca Al2 (Si O4)2	3.158	ICDD (PDF2010)	00-002-0523

Phase name	Formula	Space group	Phase reg. detail	DB card number
Enstatite, ordered	Mg Si O3	61 : Pbca	ICDD (PDF2010)	00-022-0714
chabazite high, calcium tecto-	Ca1.85 (Al3.7 Si8.3 O24)	166 : R-3m,hexagonal	ICDD (PDF2010)	01-085-1140
iron diiron(III) oxide, magnetite	Fe3 O4	227 : Fd-3m,choice-2	ICDD (PDF2010)	01-071-6339
Quartz low	Si O2	154 : P3221	ICDD (PDF2010)	01-070-2537
Chromite	Cr2 O3 · Fe O	227 : Fd-3m,choice-2	ICDD (PDF2010)	00-002-1083
Magnesiochromite	Mg O · Cr2 O3	227 : Fd-3m,choice-2	ICDD (PDF2010)	00-002-1228
Anorthite	Ca Al2 (Si O4)2	2 : C-1	ICDD (PDF2010)	00-002-0523



Peak list

No.	2-theta(deg)	d(ang.)	Height(cps)	FWHM(deg)	Int. I(cps deg)	Int. W(deg)	Size(ang.)
1	9.608(17)	9.197(16)	268(30)	0.225(18)	89(4)	0.33(5)	370(29)
2	27.756(17)	3.2114(19)	146(22)	0.11(2)	21(3)	0.14(4)	807(172)
3	28.217(9)	3.1600(9)	877(54)	0.171(7)	201(4)	0.229(19)	501(20)
4	28.718(12)	3.1061(13)	314(32)	0.205(15)	86(4)	0.27(4)	419(30)
5	30.372(18)	2.9406(17)	164(23)	0.254(16)	48(2)	0.29(6)	338(22)
6	31.175(7)	2.8666(6)	948(56)	0.154(4)	162(3)	0.171(14)	559(16)
7	35.97(6)	2.495(4)	76(16)	0.92(6)	74(6)	1.0(3)	95(6)
8	42.80(7)	2.111(3)	90(17)	0.18(12)	30(3)	0.33(10)	500(330)
9	51.162(15)	1.7840(5)	87(17)	0.13(2)	15.7(18)	0.18(6)	728(137)
10	60.91(4)	1.5197(9)	118(20)	0.39(3)	49(4)	0.42(10)	246(21)
11	62.407(5)	1.48680(12)	450(39)	0.106(4)	53(2)	0.118(15)	919(37)
12	63.087(6)	1.47240(12)	94(18)	0.025(19)	4.8(13)	0.05(2)	3909(3033)
13	63.655(3)	1.46062(7)	945(56)	0.098(3)	123(2)	0.130(10)	993(35)
14	67.238(18)	1.3912(3)	146(22)	0.13(3)	32(2)	0.22(5)	796(168)

Parameters used for WPPF

Profile parameters

WPPFProfileParameters.txt

Structure parameters

WPPFStructureParameters.txt

File name	Rwp	Rp	Re	S	Chi^2	Maximum shift/e.s.d.
PGM T	0	0	0	0	0	0

Lattice constants

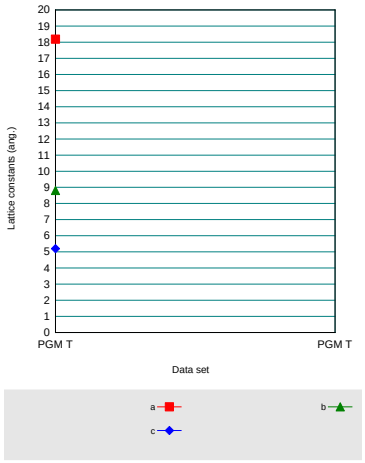
Angular correction

	No correction
	Use external standard
	Use internal standard

Analysis results

File name	a(A)	b(A)	c(A)	alpha(deg)	beta(deg)	gamma(deg)
PGM T	18.186451	8.805975	5.196478	90.000000	90.000000	90.000000
PGM T	13.367121	13.367121	15.141049	90.000000	90.000000	120.000000
PGM T	8.263897	8.263897	8.263897	90.000000	90.000000	90.000000
PGM T	4.480150	4.480150	5.107415	90.000000	90.000000	120.000000
PGM T	8.114974	8.114974	8.114974	90.000000	90.000000	90.000000
PGM T	8.348114	8.348114	8.348114	90.000000	90.000000	90.000000
PGM T	8.158045	12.868049	14.070392	93.220001	115.930000	91.199997
PGM T	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000

Phase name	a(A)	b(A)	c(A)	alpha(deg)	beta(deg)	gamma(deg)
Enstatite, ordered	18.186451	8.805975	5.196478	90.000000	90.000000	90.000000
chabazite high, calcium	13.367121	13.367121	15.141049	90.000000	90.000000	120.000000
iron diiron(III) oxide,	8.263897	8.263897	8.263897	90.000000	90.000000	90.000000
Quartz low	4.480150	4.480150	5.107415	90.000000	90.000000	120.000000
Chromite	8.114974	8.114974	8.114974	90.000000	90.000000	90.000000
Magnesiochromite	8.348114	8.348114	8.348114	90.000000	90.000000	90.000000
Anorthite	8.158045	12.868049	14.070392	93.220001	115.930000	91.199997
Unknown	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000	0.000000e+000



Crystallinity

File name	Crystallinity (%)

CrystallinityGraph.emf

Williamson-Hall method

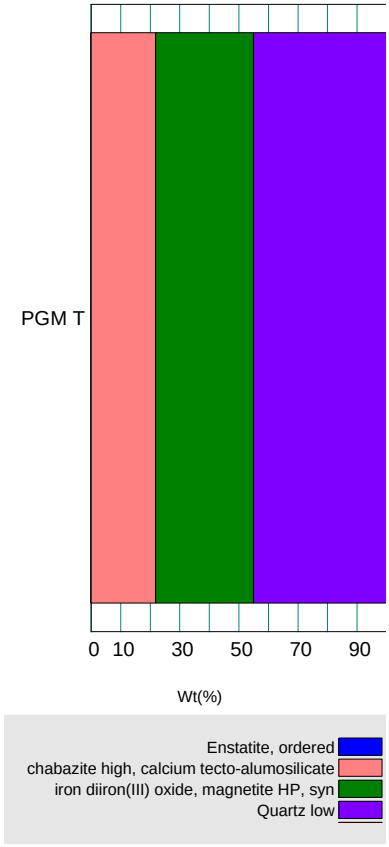
File name	Crystallite size(A)	Strain (%)
PGM T	534.27(7)	0.0451(14)
PGM T	412.62(16)	0.042(8)
PGM T	534.2(5)	0.037(10)
PGM T	337.76(2)	0.0817(9)
PGM T	418.54(2)	0.0659(7)
PGM T	229.71(18)	0.08(2)
PGM T	391.63(5)	0.0615(19)

Phase name	Crystallite size(A)	Strain (%)
Enstatite, ordered	534.27(7)	0.0451(14)
chabazite high, calcium tecto-alumosilicate	412.62(16)	0.042(8)
iron diiron(III) oxide, magnetite HP, syn	534.2(5)	0.037(10)
Quartz low	337.76(2)	0.0817(9)
Chromite	418.54(2)	0.0659(7)
Magnesiochromite	229.71(18)	0.08(2)
Anorthite	391.63(5)	0.0615(19)

CSSGraph.emf

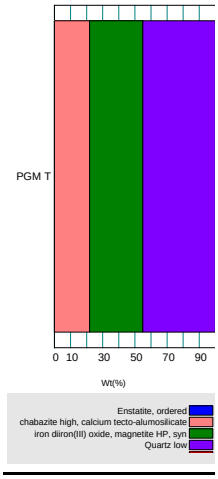
Quantitative analysis results (RIR)

Phase name	Content(%)
Enstatite, ordered	0.000000e+000
chabazite high, calcium tecto-alumosilicate	21.823546
iron diiron(III) oxide, magnetite HP, syn	33.070953
Quartz low	45.105501
Chromite	0.000000e+000
Magnesiochromite	0.000000e+000
Anorthite	0.000000e+000
Unknown	0.000000e+000
iron diiron(III) 00-002-1228@oxide, magnetite HP, syn	
Magnesiochromite	
iron diiron(III) 00-002-1083@oxide, magnetite HP, syn	
Chromite	
Magnesiochromite	
Anorthite	



Quantitative analysis results (WPPF)

Calibration data



QCGraph.emf

Quantitative analysis results (External Standard method)

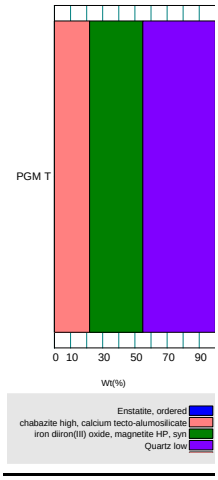
Calibration data

QACalibration.emf

QCGraph.emf

Quantitative analysis results (internal standard method)

Calibration Data



QCGraph.emf

Stress

Stress constants

Analytical conditions

Analysis results

StressGraph.emf

8.2 Design of experiments matrix

Table 29: Factorial experimental design for preliminary flotation experiments (Nanthakumar and Kelebek, 2007)

Experimental run	SIBX	Secondary collector DTP	Depressant M98B
1	Low	Low	Low
2	Low	Low	High
3	Low	High	Low
4	Low	High	High
5	High	Low	Low
6	High	Low	High
7	High	High	Low
8	High	High	High

8.3 Detailed flotation results

8.3.1 Sample calculation for reagent dosage volumes:

$$\text{Reagent dosage (ml)} = \frac{\text{amount to float (g)} \ \text{x required dosage} \left(\frac{\text{g}}{\text{t}}\right) \ \text{x} \ \frac{1\text{t}}{1000000\text{g}}}{\text{Reagent strength} \left(\frac{\text{g}}{\text{ml}}\right)}$$

Table 30: Calculated flotation reagent dosage volumes

Reagent name	Dosage (g/t)	Dosage volume (ml of 1%wt solution)
CuSO4	50	5.8
SIBX	100	11.6
M98B	100	11.6
Hydroxamate	100	5.8
Dithiophosphate	30	2.4
Frother	50	5.8
Xanthogen formate	30	2.4

8.3.2 Detailed reagent scouting flotation results

Table 31: Reagent scheme 1 Rougher tests results

Wits: Oxidised Mimosa Mine ore processing -FLOTATION TEST SHEET										
PROJECT:	**Oxidised Mimosa Mine ore flotation**									
Procedure:	Rougher rate tests									
Operating conditions										
Grind:	60% - 75µm									
Feed:	1.16kg in a 3 L flotation cell									
Make up water	Distilled water modified by addition of ionic salts									
pH:	9									
Reagent Conditions										
Reagent Scheme 1										
Purpose: PGM recovery/grade investigation using SIBX and DTP collector suite										
Test number	**Reagent name**	**Level**	**Dosage (g/t)**	**conditioning time (min)**	**Recovery (%)**			**grade (g/t)**		
					Pt	**Pd**	**3E**	**Pt**	**Pd**	**3E**
1	SIBX DTP (C5460) M98B	low low high	100 30 100	2 2 3	39,1	27,4	38,8	19,60	8,19	32,28
2	SIBX DTP (C5460) M98B	low low low	100 30 50	2 2 3	47,0	31,2	45,1	10,70	4,24	17,05
3	SIBX DTP (C5460) M98B	high low high	150 30 100	2 2 3	43,8	30,0	42,7	23,15	9,47	37,52
4	SIBX DTP (C5460) M98B	low high low	100 50 50	2 2 3	66,1	40,1	55,1	22,80	8,25	31,58
5	SIBX DTP (C5460) M98B	low high high	100 50 100	2 2 3	55,7	30,9	45,5	31,70	10,50	43,02
6	SIBX DTP (C5460) M98B	high high high	150 50 100	2 2 3	46,7	25,5	37,9	23,20	7,56	31,33
7	SIBX DTP (C5460) M98B	high low high	150 30 100	2 2 3	59,9	31,9	48,3	22,30	7,09	29,87
8	SIBX DTP (C5460) M98B	high high low	150 50 50	2 2 3	52,5	45,2	54,6	6,29	3,23	10,86
	$CuSO_4$	constant	50	5	Activator and Frother dosages were constant for all tests					
	F200	constant	50	1						

Table 32: Reagent scheme 2 Rougher tests results

Wits: Oxidised Mimosa Mine ore processing -FLOTATION TEST SHEET

PROJECT: **Oxidised Mimosa Mine ore flotation**
Procedure: Rougher rate tests

Operating conditions

Grind: 60% - 75µm
Feed: 1.16kg in a 3 L flotation cell
Make up water Distilled water modified by addition of ionic salts
pH: 9

Reagent Conditions

Reagent Scheme 2
Purpose: PGM recovery/grade investigation using SIBX and Xanthogen formate collector suite

Test number	Reagent name	Level	Dosage (g/t)	conditioning time (min)	Recovery (%)			grade (g/t)		
					Pt	Pd	3E	Pt	Pd	3E
1	SIBX	low	100	2	53,5	29,3	43,6	15,80	5,16	21,38
	C7133	low	30	2						
	M98B	low	50	3						
2	SIBX	high	150	2	42,7	28,0	37,1	19,70	7,73	28,42
	C7133	low	30	2						
	M98B	low	50	3						
3	SIBX	low	100	2	52,1	27,2	42,4	25,00	7,79	33,73
	C7133	high	50	2						
	M98B	low	50	3						
4	SIBX	high	150	2	43,2	28,1	39,1	16,00	6,21	24,03
	C7133	high	50	2						
	M98B	low	50	3						
5	SIBX	low	100	2	49,7	34,2	46,7	14,00	5,75	21,83
	C7133	low	30	2						
	M98B	high	100	3						
6	SIBX	high	150	2	57,1	37,1	50,5	14,90	5,78	21,89
	C7133	low	30	2						
	M98B	high	100	3						
7	SIBX	low	100	2	46,1	30,1	40,8	19,20	7,49	28,20
	C7133	high	50	2						
	M98B	high	100	3						
8	SIBX	high	150	2	60,9	37,7	51,8	32,20	11,90	45,46
	C7133	high	50	2						
	M98B	high	100	3						
	$CuSO_4$	constant	50	5	Activator and Frother dosages were constant for all tests					
	F200	constant	50	1						

Table 33: Reagent scheme 3 Rougher tests results

Wits: Oxidised Mimosa Mine ore processing -FLOTATION TEST SHEET										
PROJECT:	**Oxidised Mimosa Mine ore flotation**									
Procedure:	Rougher rate tests									
	Operating conditions									
Grind:	60% - 75µm									
Feed:	1.16kg in a 3 L flotation cell									
Make up water	Distilled water modified by addition of ionic salts									
pH:	9									
	Reagent Conditions									
Reagent Scheme 3										
Purpose: PGM recovery/grade investigation using SIBX and AM810 Hydroxamate collector suite										
Test number	**Reagent name**	**Level**	**Dosage (g/t)**	**conditioning time (min)**	**Recovery (%)**			**grade (g/t)**		
					Pt	**Pd**	**3E**	**Pt**	**Pd**	**3E**
1	SIBX Hydroxamate (AM810) M98B	low low low	100 30 50	2 2 3	54,6	33,6	45,7	44,40	16,30	61,69
2	SIBX Hydroxamate (AM810) M98B	high low low	150 30 50	2 2 3	74,0	48,4	63,1	13,20	5,16	18,70
3	SIBX Hydroxamate (AM810) M98B	low high low	100 50 50	2 2 3	61,5	36,7	52,6	22,80	8,12	32,41
4	SIBX Hydroxamate (AM810) M98B	high high low	150 50 50	2 2 3	58,5	31,6	47,3	24,80	8,01	33,29
5	SIBX Hydroxamate (AM810) M98B	low low high	100 30 100	2 2 3	53,3	27,7	42,6	51,20	15,90	68,01
6	SIBX Hydroxamate (AM810) M98B	high low high	150 30 100	2 2 3	36,0	19,5	29,1	21,30	6,88	28,56
7	SIBX Hydroxamate (AM810) M98B	low high high	100 50 100	2 2 3	62,0	40,3	52,7	38,10	14,80	53,78
8	SIBX Hydroxamate (AM810) M98B	high high high	150 50 100	2 2 3	53,2	31,7	44,2	38,00	13,50	52,37
	$CuSO_4$ F200	constant constant	50 50	5 1	Activator and Frother dosages were constant for all tests					

8.3.3 Sample calculations for statistical analysis

Figure 35 shows the possible experimental combinations of the 3 factor 2 level design used for flotation reagent scouting test work.

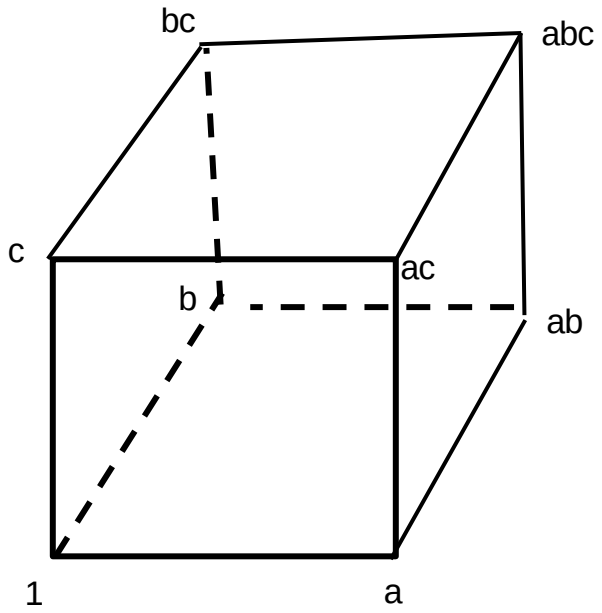


Figure 35: Geometric representation of eight combinations for 2^3 factorial experimental design.

Derivations of factor estimates equations

The high levels of any factor in the 2^3 factorial design were denoted by the corresponding lowercase letter while the low levels were denoted by the absence of the letters. The equations for factor effects were derived as the difference between the averages of high levels and low levels of each factor. For instance, The A effect was calculated as:

$A = \bar{y}_{A+} - \bar{y}_{A-}$

$$A = \frac{a + ab + ac + abc}{4n} - \frac{1 + b + c + bc}{4n}$$

$$A = \frac{1}{4n}\ [a + ab + ac + abc - 1 - b - c - bc] \quad 20$$

Where: n denotes the number of replicates for the particular treatment combination (Myers, et al., 2009).

Similarly, the effects of B and C as well as the two factor and three factor interaction effects (AB, AC, BC and ABC) are shown in equations 21-26.

$$B = \frac{1}{4n}\ [b + ab + bc + abc - 1 - a - c - ac] \quad 21$$

$$C = \frac{1}{4n}\ [c + ac + bc + abc - 1 - a - b - ab] \quad 22$$

$$AB = \frac{1}{4n}\ [abc + ab + c + 1 - bc - b - ac - a] \quad 23$$

$$AC = \frac{1}{4n}\ [1 - a + b - ab - c + ac - bc + abc] \quad 24$$

$$BC = \frac{1}{4n}\ [1 + a - b - ab - c - ac + bc + abc] \quad 25$$

$$ABC = \frac{1}{4n}\ [abc - bc - ac + c - ab + b + a - 1] \quad 26$$

Sum of squares and mean square calculations

The sum of squares for the 2^3 factorial experimental design are calculated by:

$$SSi = \frac{(contrast)2}{8n} \quad 27$$

Where contrasts are equal to the bracketed terms in equations 20 – 26, i.e.:

$$contrast(A) = [a + ab + ac + abc - 1 - b - c - bc]$$

$$contrast(B) = [b + ab + bc + abc - 1 - a - c - ac]$$

$$contrast\ (C) = [c + ac + bc + abc - 1 - a - b - ab]\ ,\ \text{etc.}$$

And

The mean squares were determined by the equation 28.

$$MSi = \frac{(SSi)2}{degrees\ of\ freedom} \quad 28$$

Where 7 degrees of freedom exist for the 2^3 experimental design adopted in this study.

The effect estimates calculated using equations 20 to 26 are shown in

Table 34 to Table 39.

Table 34: Factor effects calculations for Pt recovery in the 2^3 design for reagent scheme 1.

Runs	Main Effects			*Interaction Effects*				Pt recovery
	SIBX (A)	AM810 (B)	M98B (C)	AB	AC	BC	ABC	
1	-1	-1	-1	1	1	1	-1	47.03
2	1	-1	-1	-1	-1	1	1	59.86
3	-1	1	-1	-1	1	-1	1	66.12
4	1	1	-1	1	-1	-1	-1	52.53
5	-1	-1	1	1	-1	-1	1	39.13
6	1	-1	1	-1	1	-1	-1	43.79
7	-1	1	1	-1	-1	1	-1	55.74
8	1	1	1	1	1	1	1	46.66
Effects estimates (%)	-1.29	7.81	-10.05	-10.04	-0.91	1.93	3.17	
Sum of squares	3.35	12.19	20.22	20.17	1.67	7.43	20.11	

Table 35: Factor effects calculations for Pd recovery in the 2^3 design for reagent scheme 1.

Runs	Main Effects			*Interaction Effects*				Pd
	SIBX (A)	AM810 (B)	M98B (C)	AB	AC	BC	ABC	recovery
1	-1	-1	-1	1	1	1	-1	31.21
2	1	-1	-1	-1	-1	1	1	31.87
3	-1	1	-1	-1	1	-1	1	40.06
4	1	1	-1	1	-1	-1	-1	45.17
5	-1	-1	1	1	-1	-1	1	27.38
6	1	-1	1	-1	1	-1	-1	29.98
7	-1	1	1	-1	-1	1	-1	30.92
8	1	1	1	1	1	1	1	25.46
Effects estimates (%)	0.73	5.29	-8.64	-0.90	-2.16	-5.79	-3.12	
Sum of squares	1.06	56.01	14.94	1.64	9.29	66.96	19.52	

Table 36: Factor effects calculations for Pt recovery in the 2^3 design for reagent scheme 2.

Runs	Main Effects			*Interaction Effects*				Pt
	SIBX (A)	AM810 (B)	M98B (C)	AB	AC	BC	ABC	recovery
1	-1	-1	-1	1	1	1	-1	57.09
2	1	-1	-1	-1	-1	1	1	60.93
3	-1	1	-1	-1	1	-1	1	46.09
4	1	1	-1	1	-1	-1	-1	53.54
5	-1	-1	1	1	-1	-1	1	52.14
6	1	-1	1	-1	1	-1	-1	43.23
7	-1	1	1	-1	-1	1	-1	49.71
8	1	1	1	1	1	1	1	42.65
Effects estimates (%)	-1.17	-5.35	-7.48	1.36	-6.81	3.85	-0.44	
Sum of squares	2.72	57.23	11.19	3.73	92.84	29.61	0.39	

Table 37: Factor effects calculations for Pd recovery in the 2^3 design for reagent scheme 2.

Runs	Main Effects			*Interaction Effects*				Pd
	SIBX (A)	AM810 (B)	M98B (C)	AB	AC	BC	ABC	recovery
1	-1	-1	-1	1	1	1	-1	37.08
2	1	-1	-1	-1	-1	1	1	37.71
3	-1	1	-1	-1	1	-1	1	30.11
4	1	1	-1	1	-1	-1	-1	29.28
5	-1	-1	1	1	-1	-1	1	27.20
6	1	-1	1	-1	1	-1	-1	28.10
7	-1	1	1	-1	-1	1	-1	34.19
8	1	1	1	1	1	1	1	28.03
Effects estimates (%)	-1.37	-2.12	-4.17	-2.13	-1.27	5.58	-1.40	
Sum of squares	3.74	9.02	34.70	9.04	3.20	62.27	3.93	

Table 38: Factor effects calculations for Pt recovery in the 2^3 design for reagent scheme 3.

Runs	Main Effects			Interaction Effects				Pt
	SIBX (A)	AM810 (B)	M98B (C)	AB	AC	BC	ABC	Recovery
1	-1	-1	-1	1	1	1	-1	36.05
2	1	-1	-1	-1	-1	1	1	61.95
3	-1	1	-1	-1	1	-1	1	73.95
4	1	1	-1	1	-1	-1	-1	58.50
5	-1	-1	1	1	-1	-1	1	53.28
6	1	-1	1	-1	1	-1	-1	53.25
7	-1	1	1	-1	-1	1	-1	54.64
8	1	1	1	1	1	1	1	61.51
Effects estimates (%)	4.32	11.02	-1.95	-8.61	-0.90	-6.21	12.06	
Sum of squares	37.36	24.29	7.57	14.84	1.63	77.07	29.10	

Table 39: Factor effects calculations for Pd recovery in the 2^3 design for reagent scheme 3.

Runs	Main Effects			*Interaction Effects*				Pd
	SIBX (A)	AM810 (B)	M98B (C)	AB	AC	BC	ABC	recovery
1	-1	-1	-1	1	1	1	-1	19.50
2	1	-1	-1	-1	-1	1	1	40.30
3	-1	1	-1	-1	1	-1	1	48.41
4	1	1	-1	1	-1	-1	-1	31.64
5	-1	-1	1	1	-1	-1	1	27.71
6	1	-1	1	-1	1	-1	-1	31.68
7	-1	1	1	-1	-1	1	-1	33.59
8	1	1	1	1	1	1	1	36.68
Effects estimates (%)	2.77	7.79	-2.55	-9.61	0.76	-2.34	9.17	
Sum of squares	15.38	12.12	12.99	18.48	1.15	10.96	16.83	

Half normal probability plots calculations

Half normal probability plots which are easier to interpret for experimental designs with few effect estimates such as the 2^3 were developed through ranking absolute values of effect estimates in ascending order and implementing equation 29.

$$Gringorten\ positioning = (i - 0.44)/(n + 0.12) \quad 29$$

The half normal probability plots for recoveries of platinum and palladium using each of the three flotation reagent schemes is shown in Table 40 to Table 45.

Table 40: Half normal probability calculations for flotation Pt recovery using reagent scheme 1.

Effect name	Estimate	i	(i-0.44)/(n+0.12)
AC	0,91	1	7,9%
A	1,29	2	21,9%
BC	1,93	3	36,0%
ABC	3,17	4	50,0%
B	7,81	5	64,0%
AB	10,04	6	78,1%
C	10,05	7	92,1%
	n	7	

Table 41: Half normal probability calculations for flotation Pd recovery using reagent scheme 1.

Effect name	Estimate	i	(i-0.44)/(n+0.12)
A	0,73	1	7,9%
AB	0,90	2	21,9%
AC	2,16	3	36,0%
ABC	3,12	4	50,0%
B	5,29	5	64,0%
BC	5,79	6	78,1%
C	8,64	7	92,1%
	n	7	

Table 42: Half normal probability calculations for flotation Pt recovery using reagent scheme 2.

Effect name	Estimate	i	(i-0.44)/(n+0.12)
ABC	0,44	1	7,9%
A	1,17	2	21,9%
AB	1,36	3	36,0%
BC	3,85	4	50,0%
B	5,35	5	64,0%
AC	6,81	6	78,1%
C	7,48	7	92,1%
	n	7	

Table 43: Half normal probability calculations for flotation Pd recovery using reagent scheme 2.

Effect name	Estimate	i	(i-0.44)/(n+0.12)
AC	1,27	1	7,9%
A	1,37	2	21,9%
ABC	1,40	3	36,0%
B	2,12	4	50,0%
AB	2,13	5	64,0%
C	4,17	6	78,1%
BC	5,58	7	92,1%
	n	7	

Table 44: Half normal probability calculations for flotation Pt recovery using reagent scheme 3.

Effect name	Estimate	i	(i-0.44)/(n+0.12)
AC	0,90	1	7,9%
C	1,95	2	21,9%
A	4,32	3	36,0%
BC	6,21	4	50,0%
AB	8,61	5	64,0%
B	11,02	6	78,1%
ABC	12,06	7	92,1%
	n	7	

Table 45: Half normal probability calculations for flotation Pd recovery using reagent scheme 3.

Effect name	Estimate	i	(i-0.44)/(n+0.12)
AC	0,76	1	7,9%
BC	2,34	2	21,9%
C	2,55	3	36,0%
A	2,77	4	50,0%
B	7,79	5	64,0%
ABC	9,17	6	78,1%
AB	9,61	7	92,1%
	n	7	