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A STUDY OF THE FLOTATION BEHAVIOUR OF Pt AND Pd TELLURIDES AND ARSENIDES

By

Shamudulu Shamaila

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NOMENCLATURE

$(Fe,Ni)_9S_8$	**Pentlandite**
$(PtAs_2)$	**Sperrylite**
$(PdPt(BiTe)_2)$	**Merenskyite**
$(PtPd(BiTe)_2)$	**Moncheite**
Au	**Gold**
As	**Arsenic**
Ca	**Calcium**
$Ca(NO_3)_2.4H_2O$	**Calcium nitrate tetra hydrate**
Ca^{2+}	**Calcium ion**
$CaCl_2.2H_2O$	**Calcium chloride dihydrate**
Cl^-	**Chloride ion**
CO_3^{2-}	**Carbonate ion**
Cu	**Copper**
Mg	**Magnesium**
$Mg(NO_3)_2.6H_2O$	**Magnesium nitrate hexahydrate**
Mg^{2+}	**Magnesium ion**
$MgSO_4.7H_2O$	**Magnesium sulphate heptahydrate**
n	**Number of particles**
Na^+	**Sodium ion**
Na_2CO_3	**Sodium carbonate**
NaCl	**Sodium chloride**
Ni	**Nickel**
NO_2^-	**Nitrite ion**
NO_3^-	**Nitrate ion**
Pd	**Palladium**
Pt	**Platinum**
Rh	**Rhodium**
S	**Sulphur**
SO_4^{2-}	**Sulphate ion**
Te	**Tellurium**

LIST OF ABBREVIATIONS

AR	Anglo Research
BFP	Barren Feldspathic Pyroxenite
BMS	Base metal sulphides
BSE	Back Scattered Electron
CMC	Carboxymethylcellulose
DS	Degree of substitution
DTC	Dithiocarbamate
DTP	Dithiophosphate
EDS	Energy Dispersive Spectrometer
EDX	Energy Dispersive X-ray
EPMA	Electron Probe Micro Analysis
ICP	Inductive Coupled Plasma
ICP-MS	Inductive Coupled Plasma Mass Spectrometry
JKMRC	Julius Kruttschnitt Minerals Research Centre
LG	Lower group
MG	Middle group
MLA	Mineral Liberation Analyser/Analysis
PGE	Platinum group elements
PGM	Platinum group minerals
PPL	Potgietersrus Platinum Mine Limited
QemSCAN	Quantitative Evaluation of Minerals by Scanning Electron Microscopy.
SEM	Scanning electron microscope
SG	Specific gravity
SIBX	Sodium isobutyl xanthate
ToF SIMS	Time of Flight Secondary Ion Mass Spectroscopy
UG	Upper group
XPS	X-ray Photelectron Spectroscopy
XRD	X-ray diffraction

SYNOPSIS

The Platreef situated in the Limpopo province of South Africa constitutes a significant source of PGEs produced in the world. Of the various PGE bearing minerals in the Platreef, PGE tellurides are the most abundant, occurring in excess of 30% in terms of PGM relative abundance, followed by PGE arsenides at 21%. As is well known, flotation is a key process in the upgrading and recovery of such minerals from the mined ores. The flotation response of these minerals can therefore have a significant bearing on the economics of the ore processing. It has been previously hypothesised that PGE tellurides exhibit significantly different flotation behaviour compared to PGE arsenides and thus the main focus of the present study has been to investigate this hypothesis and by so doing develop a better understanding of the flotation behaviour of these minerals.

Carrying out this objective included comparing the flotation responses of these minerals in natural ores as well as in synthesised ores. The use of synthetic ores in this case was necessitated by the need to carry out some of the experiments on specially designed ores with controllable contents of specific minerals. Using naturally occurring PGMs for this purpose is impractical due to the tremendous difficulty in isolating sufficient quantities of the minerals in their natural state from PGM ores. The author is aware of related studies, but of a fundamental nature, currently being undertaken elsewhere in which PGM surface chemistry and its effect on flotation is being carried out using synthetic PGMs. Therefore, the other question being addressed in the present study is whether these synthetic minerals adequately simulate the behaviour of naturally occurring PGMs in a flotation circuit and what the relative flotation responses are of these PGMs.

Results obtained from continuous flotation testwork carried out on a Platreef ore sample using a Flexi-Float mini-pilot plant showed that there were indeed significant differences in the flotation responses of naturally occurring PGE tellurides and arsenides, with the former yielding better recoveries, higher flotation rate constants and upgrade ratios.

There are many factors which could explain the observed differences in the flotation responses of these minerals. These include sizes of the particles associated with these minerals, their associations with other minerals, their liberation characteristics and surface chemical effects. This necessitated flotation comparison testwork in which such possible differences could be controlled. It was decided to compare synthetic forms of these minerals which were synthesised to resemble fully liberated minerals of a close size range. The question of whether the synthetic minerals could be used to simulate the flotation behaviour of their natural equivalents had to be addressed before such an application could be made. This was carried out by comparing Pt and Pd batch flotation recoveries from naturally occurring ores from both the Platreef and Merensky reefs with the recoveries achieved when these ores were blended to various levels with synthetic sperrylite ($PtAs_2$), moncheite ($PtPd(BiTe)_2$) and merenskyite ($PdPt(BiTe)_2$). It was found in these tests that the synthetic minerals behaved in a manner similar to that of the naturally occurring ores and thus that they could be used to carry out further fundamental investigations aimed at identifying the reasons for the better flotation behaviour of the tellurides compared to the arsenides. The synthetic minerals used in these tests all had fully liberated mineral grains of a similar and relatively narrow size distribution. It was found that the synthetic Pt tellurides had greater flotation rate constants, upgrade ratios and recoveries compared to the synthetic Pt arsenides. These findings were consistent with those observed of naturally occurring PGMs from the Flexi-Float testwork. And thus confirmed the fact that PGE tellurides and arsenides exhibit significantly different flotation behaviour and that the recoveries of the former were better than in the case of the arsenides.

Mineral liberation analysis (MLA) carried out on samples taken down the bank of the Flexi-Float showed that despite being poorer floating, PGE arsenides were better liberated in the feed compared to PGE tellurides. It was also found that particles associated with the former were slightly finer than those associated with the latter. PGE tellurides in the feed were found to have a significantly higher association with base metal sulphides whereas PGE arsenides had a higher association with silicates. These differences could not however account for the differences in flotation behaviour since the synthetic samples were fully liberated and had very similar particle size distributions. Preliminary investigations into the possibility that a different reagent regime could improve the recoveries of arsenides did not produce results which indicated that this was possible.

In conclusion it has been shown in this study that tellurides float more readily than arsenides although significant recoveries of the latter are achievable. It has also been shown that the relatively poor performance of arsenides compared to tellurides cannot be explained in terms of their particle size nor their degree of liberation and hence it is deduced that it is possibly a result of differences in the surface chemical interaction between the different minerals and the thiol collectors traditionally used in the recovery of minerals on a PGM flotation plant. Some proposals are presented to explain the differences observed.

CHAPTER 1

Introduction and Literature review

The world's exploitable platinum group elements (PGEs) resources are virtually all associated with layered intrusions such as the Bushveld Complex in South Africa (Viljoen and Schürmann, 1998). Anglo Platinum, the largest platinum producer in the world, mines nearly all of its PGM ores from the Bushveld Complex spanning 250km x 450km revealed as outcrops in the North Western, Limpopo and Mpumalanga provinces of South Africa. The Bushveld Complex, Figure 1.1, is subdivided into three sections namely, the Western Bushveld, Eastern Bushveld and Northern Bushveld all in which Anglo Platinum has mining interests. The Western and Eastern Bushveld can be more accurately described in terms of the northwestern and southwestern lobes separated for most part by the Pilanesberg Alkaline Complex and the somewhat analogous northeastern and southeastern lobes, transected by the Steelpoort fault (Viljoen and Schürmann, 1998).

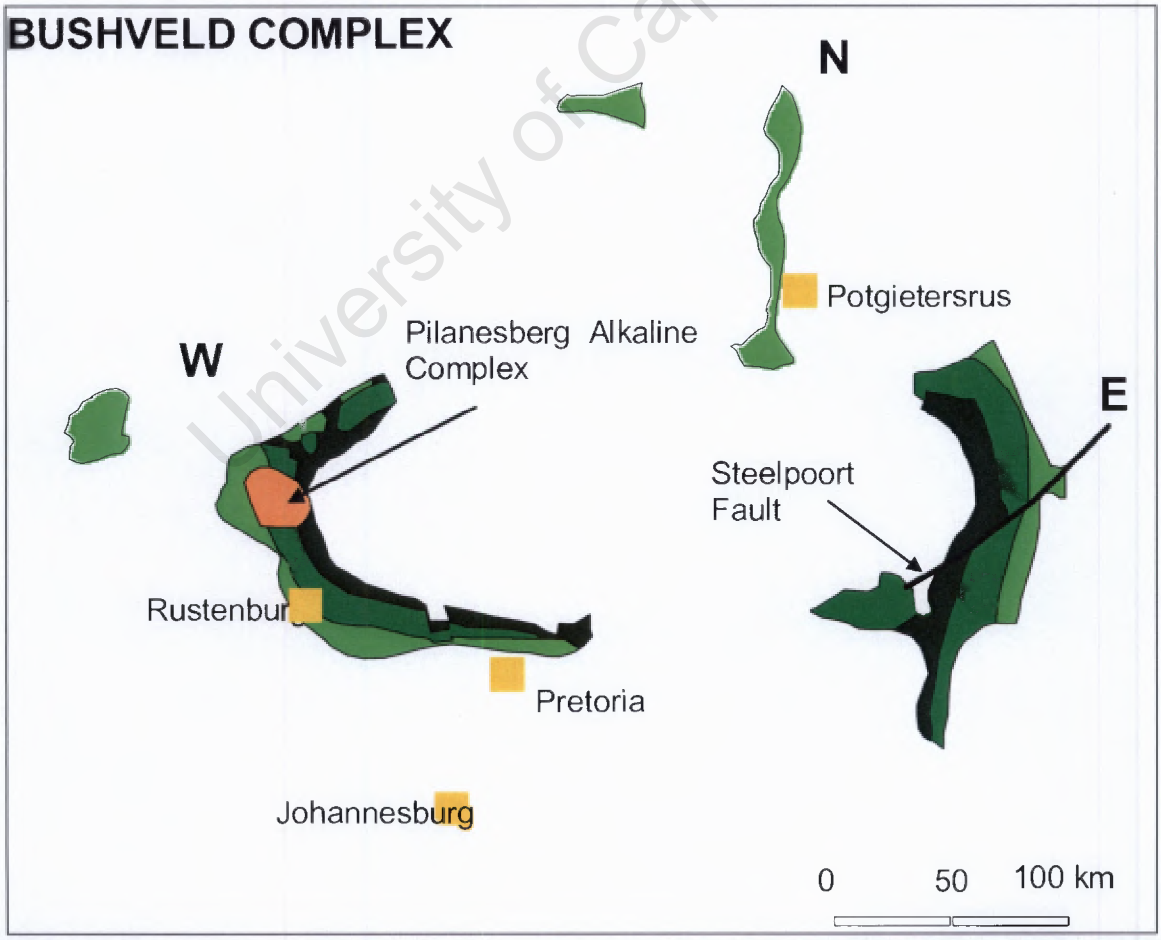


Figure 1.1: A map showing the Bushveld Complex outcrops. (Modified after Vermaak, 1995)

1.1 Bushveld complex

The Bushveld Complex has a stratigraphy that can be divided into five zones known as the Marginal, Lower, Critical, Main and Upper Zones from the base upwards, see Figure 1.2. The Marginal Zone comprising of generally finer grained rocks is highly variable in thickness and may be completely absent in some areas and contains no known economic mineralisation (Viljoen and Schürmann, 1998). The overlaying Lower Zone shows well defined small layers of cumulus chromite within pyroxenite and olivine-rich rocks. This marks the commencement of the Critical Zone which hosts all the chromitite layers of the Bushveld Complex, of which up to 25 have been identified. The first set of chromitite layers within pyroxenites of the lower Critical Zone have been termed the Lower Group (LG) chromitite layers. Seven main LG layers are generally present though this number varies from place to place. Two further layers at the top of the pyroxenite (the MG or Middle Group layers 1 and 2) mark the top of the pyroxenite dominated lower Critical Zone. From this point upwards, plagioclase becomes a cumulus phase and noritic rocks predominate. The MG3 and MG4 Chromitite Layers occur at the base of the Upper Critical Zone. Two more groups of chromitite layers occur in the upper section of the Upper Critical Zone and these are the Upper Group Chromitite Layers, the UG1 overlain by the UG2. The UG2 which averages less than 1m in thickness is of considerable importance because it contains economic concentrations of PGEs. Amongst the uppermost cycles of the Critical zone is the Merensky reef, a PGE bearing pyroxenitic and pegmatoidal feldspathic assemblage, with associated thin chromitite layers that rarely exceeds 1m in thickness.

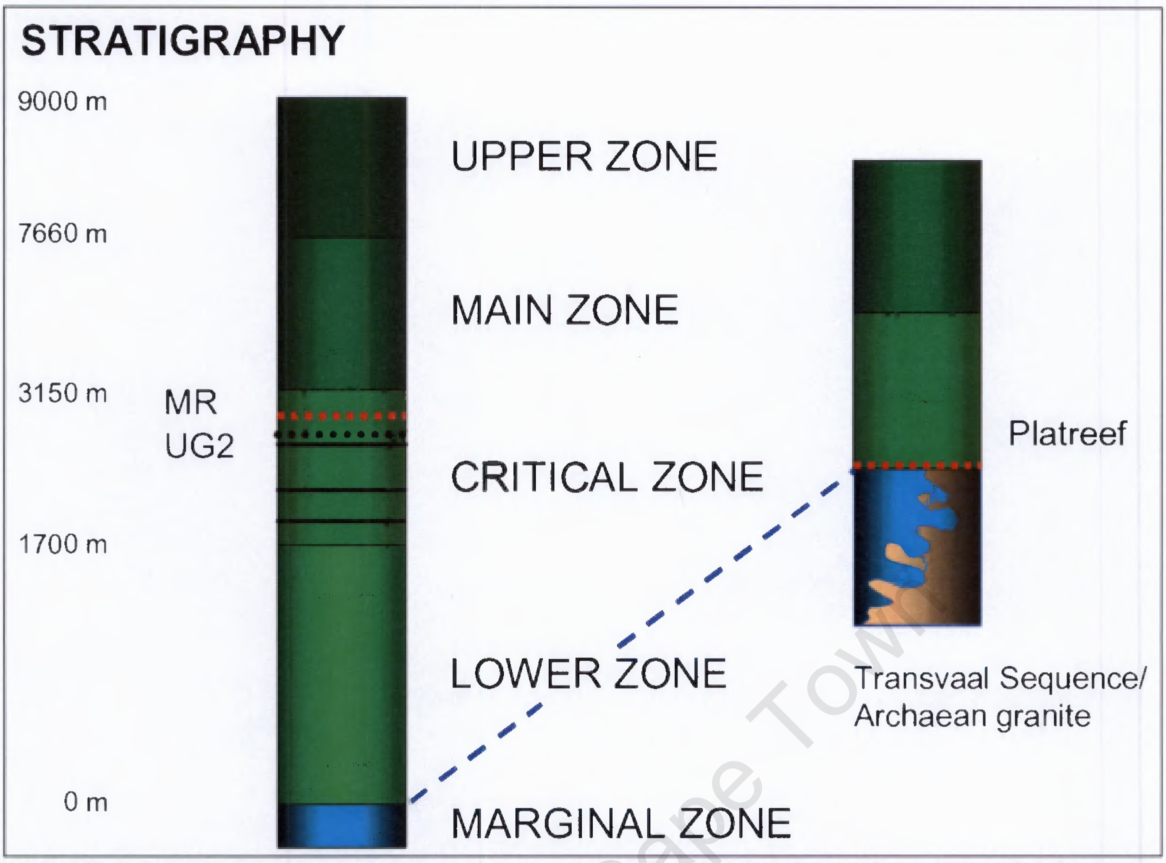


Figure 1.2: Generalised stratigraphic column of the Bushveld Complex. (Modified after Schouwstra, 2000)

1.1.1 Merensky reef

The Merensky reef can be described as largely feldspathic pyroxenite which is under and overlain by thin (5 to 15mm) layers of chromite concentrations (Schouwstra, 2000). The total thickness of this package is generally known to be less than 30cm and occurring at a depth of 5km. The rock-forming silicate minerals of the Merensky reef consist predominantly of orthopyroxene (~60%), plagioclase feldspar (~20%), pyroxene (~15%), phlogopite (~5%) and occasional olivine. Secondary minerals such as talc, serpentine, chlorite and magnetite have wide spread occurrence.

The pegmatoidal feldspathic pyroxenite of the Merensky reef in the Rustenburg facies normally contains between 3 and 10% base metal sulphides dominated by pyrrhotite, pentlandite, chalcopyrite and pyrite with minor sulpharsenides, galena and sphalerite (Viljoen and Schürmann, 1998). The major platinum group minerals are cooperite (PtS), braggite [(Pt,Pd)NiS], sperrylite ($PtAs_2$) and PGE tellurides and alloys, although in certain areas minerals such as laurite (RuS_2) can be abundant. An average distribution of PGM for the

Rustenburg facies is: PGE sulphides 36%, PGE tellurides 32%, Ru phases 15%, PGE alloys 7%, PGE arsenides 7% and Au/Ag phases 3%.

1.1.2 UG2 reef

The UG2 chromitite layer main seam is known to vary in thickness from 70cm to 150cm.The UG2 consists predominantly of chromite (60-90%) with lesser silicate minerals (5-30% pyroxene and 1-10% plagioclase feldspar). Other minerals in minor concentrations can include the silicates: phlogopite and biotite, the oxides: ilminite and rutile and magnetite, and base metal sulphides. Secondary minerals include quartz, serpentine, chlorite and talc. The major base metal sulphides constitute chalcopyrite, pentlandite and pyrrhotite and occur almost entirely within the interstitial silicate and only very rarely enclosed within the chromite particles.

The PGMs present are Pt-Pd sulphides (35%), laurite (30%), Pt-Fe alloy (21%), Rh sulphides (11%) and palladium alloys (3%). Most of the PGMs occur in association with the base metals and silicates. It is only the mineral laurite which exhibits a preferred association with the chromite grains (Viljoen and Schürmann, 1998).

1.1.3 Platreef

The Platreef which is the reef type on which this study is focused is hosted in the Northern Bushveld which is situated in the northern part of South Africa in the Limpopo Province. The Lower and the Critical zones of the Bushveld are poorly developed. Where the Bushveld rocks are in contact with the floor rocks (i.e. Archaen granite and sediments of the Transvaal Sequence), a unique type of mineralization has developed (Figure 1.2). This reef (known as the Platreef) consist of a complex assemblage of pyroxenites, serpentinites and calc-silicates. The different nature of these rocks (as opposed to normal Merensky reef) is the result of the hot Bushveld magma reacting with lime-rich floor rocks (Schouwstra, 2000). It can be sub divided into three major pyroxenitic units based on texture and mode. The thickness of each unit is variable, with some units being totally absent in places. The upper pyroxenite, termed the 'C' reef is usually barren of PGE mineralisation whilst the underlying pyroxenite unit, termed the 'B'reef, contains fair to good grades of disseminated BMS mineralisation. The lowest pyroxenitic phase called the 'A' reef comprises of a highly feldspathic unit which has marked heterogeneous texture and grain size. It contains disseminated mineralisation and, commonly, some fairly large blebs of composite BMS (Viljoen and Schürmann, 1998). The

Platreef has largely been described as the local equivalent of the Merensky Reef (Cabri, 2002). The most common base metal sulphides of the Platreef, in order of decreasing abundance are, pyrrhotite, pentlandite and chalcopyrite. The distribution of PGMs in the Platreef tends to be erratic. Constituting about 30% of the PGMs and by far the most important class are the Pt/Pd tellurides. The three other important classes in order of decreasing abundance are the PGE arsenides (21%) and alloys (26%). The PGE sulphide content appears to be highly variable, Viljoen and Schürmann (1998) report as high as 19% whereas Armitage et al. (2002) point to the absence of PGE sulphides as a characteristic feature distinguishing the Platreef from other Bushveld PGE reefs. Platinum group mineral (PGM) assemblages in the Platreef at Sandsloot area, the source of the samples used in this study, in a variety of lithologies reveal a complex multi-stage mineralisation history. During crystallisation of the Platreef pyroxenites, platinum group elements (PGE) and base-metal sulphides (BMS) were distributed throughout the interstitial liquid forming a telluride-dominant assemblage devoid of PGE sulphides (Holwell, 2006). The tellurides and arsenides are predominantly enclosed in silicate gangue, although generally in close proximity to the principle BMS. A total of 62% by volume of platinoid minerals are associated with silicate gangue and 38% by volume with BMS.

To summarise, distribution of mineralisation in the Platreef is variable, but has a strong tendency to be richer at the top of the 'B' reef (where a chromitite seam may be present) and decreases downward. In this respect it bears a general similarity to the normal Merensky reef. The 'A' reef, in general, has lower values than the 'B' reef and may be barren in places where the 'B' reef contains good values. The 'C' reef is invariably barren of mineralisation (Viljoen and Schürmann, 1998).

1.2 PGM beneficiation-froth flotation

The production of final PGE commodities from the mined ores involves various processes and these include valuable mineral concentrating, smelting and refining. This study particularly focuses on valuable mineral concentration in which the predominant unit process employed is froth flotation. This process for which the main objective is to economically maximise valuable mineral recovery and grades to the concentrate exploits differences in the hydrophobicity of minerals in pulp to achieve selective mineral separation. Concentrators are typically challenged to maximise on achieving this objective. Flotation research has in the past focused on sulphide minerals and BMS in particular (O'Connor, 2005). However, in recent times there has been increased interest in the recovery of PGMs. It is therefore important to maximise technical understanding of the behaviour of these minerals in froth flotation, a production stage in which substantial gains or losses can be incurred.

Platreef ores are treated at the PPL concentrator in Mokopane, formally Potgietersrus, in the Limpopo province. As PPL accounts for about 8% of Anglo Platinum's platinum production, subsequently making it a substantial source of company revenue, it is imperative that efforts are made to maximise PGE recoveries at PPL.

Flotation tests in this study have been carried out using bench scale tests as well as a Flexi-Float which is similar to a mini pilot plant. Bench scale tests, mini pilot plants and indeed pilot plants are all important tools in mineral processing providing information at various levels of accuracy for predicting the behaviour of ores ahead of production, testing proposed plant changes or in the design stage of a new concentrator. Andrade et al. (2004) writes that in the early stages of a project inexpensive bench-scale testwork may be sufficient. However, the results provided are somewhat limited due to the difficulty in accurately predicting the effects of recirculating middling streams and/or gradual changes in the solution chemistry. As the project progresses it becomes necessary to perform tests in continuous circuits. Those tests often performed in conventional pilot plant circuits, provide the detailed engineering data required to develop a final process flow sheet and to size equipment. The pilot plants are however expensive to set-up and operate and are only viable for major, well-advanced projects. In the past locked cycle tests have bridged the gap between bench scale tests and pilot plants in providing ore behaviour information from exploration phase to the feasibility and construction phase. In more recent times mini pilot plants have replaced locked cycle tests as they are a relatively inexpensive configuration better suited for simulating continuous flotation as on a full circuit. The inherent advantages of mini pilot plants over conventional piloting include smaller sample size, reduced time to steady state and ability to perform variability analysis among others (Fragomeni et al., 2006)

1.3 PGM flotation reagents

Amongst the most widely used reagents for PGM flotation in South Africa are xanthates as primary collectors, dithiophosphates (DTP) as secondary collectors and combinations of alcohols and poly glycol ethers as frothers. Guar gum and carboxymethylcellulose (CMC) are used as depressants whereas some operations include copper sulphate as an activator (Wiese, 2005; Wills, 1992; Wesseldijk et al., 1999; Vos et al., 2006). It is for this reason that such reagents have been used during flotation tests in this study. Dithiocarbamates are another group of secondary collectors which even though not commonly used in South African PGM operations have been included in the current study.

1.3.1 Primary collectors

Xanthates are anionic thiol collectors with a molecular structure as shown in Figure 1.3 where R is a hydrocarbon group and M^+ is a metallic cation.

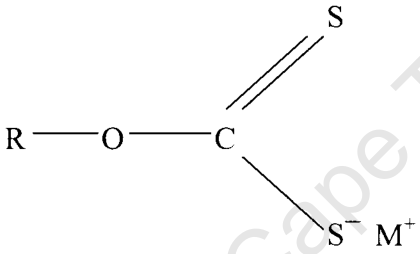


Figure 1.3: Xanthate

The reaction of sulphide minerals with xanthates has been well documented, (Wills, 1992). The steps of this reaction in alkaline solution have been illustrated below.

$2MS + 2O_2 + H_2O \rightarrow MS_2O_3 + M(OH)_2$ 1.1

$MS_2O_3 + 2ROCS_2^- \rightarrow M(ROCS_2)_2 + S_2O_3^{2-}$ 1.2

The insoluble metal xanthate formed $[M(ROCS_2)_2]$ renders the mineral surface hydrophobic due to the hydrophobicity of the non- polar section of the xanthate molecule.

Considering that the effect of reagents on PGE arsenide flotation is investigated in this study, the investigation on the interaction of ethyl xanthate with Pd-Bi-Te by Vermaak (2004) is of great interest. In the said investigation, Vermaak (2004) addresses a problem of reported high proportions of Pt-Pd-Bi-Te, in excess of 70%, in the liberated PGMs' distribution in the tailings of Mimosa mine. The Mimosa platinum deposit in the Great Dyke of Zimbabwe is said to have mineralogy very similar to that of the Platreef. In this investigation (Vermaak, 2004) it is concluded, by using electrochemical and Raman spectroscopy, that xanthate retains its molecular integrity when adsorbed on the surface of Pd-Bi-Te and that dixanthogens are also present on the mineral surface following anodic polarisation. It is therefore concluded that the poor flotation recovery of the Pd-Bi-Te minerals from flotation feeds cannot be attributed to the lack of interaction of the collector with the surface. Particle size was instead suggested to have contributed to the poor flotation response because the liberated PGM grain sizes were usually less than 4µm which were said to be too small for favourable flotation.

Yekeler and Yekeler (2005) compare the stabilities of As(III) xanthates and dixanthogens and show that the magnitudes of the interaction energies for their formation increase when the oxygen atom in $C_2H_5OCS^-_2$ is replaced by the sulphur atom to form $C_2H_5SCS^-_2$. This suggests that As(III) xanthate is more likely to form than dixanthogens.

1.3.2 Secondary collectors

Phillip (1984) reports the use of dialkyl and diaryl dithiophosphates as flotation reagents dating back to 1926 which was just a year after the discovery of xanthates. The molecular structure of a dithiophosphate is shown in Figure 1.4.

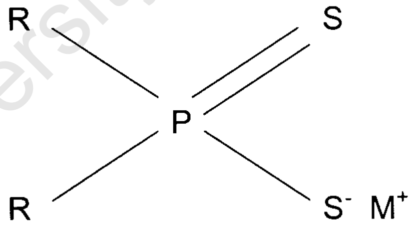


Figure 1.4: Dialkyl dithiophosphate

Dithiophosphates and xanthates belong to a broad range of thiol collectors and as a result have very similar applications as collectors for base-metal ores and ores containing precious metals. As it is widely held that dithiophosphates are relatively weaker collectors, their most successful usage has been in conjunction with other collector types to enhance the collecting properties of both. Xanthate is amongst the most widely used collector in conjunction with dithiophosphates resulting in reduced total coll.ector consumption and/or improved metallurgical results (Phillip, 1984).

Dithiocarbamates, with a molecular structure given in Figure 1.5, are secondary collectors with similar properties to xanthates. They are however more expensive (Wills, 1992).

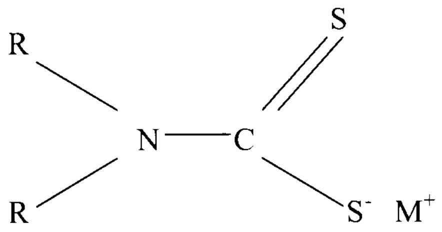


Figure 1.5: Dialkyl dithiocarbamate

Literature reviews on dithiocarbamates revealed the scarcity of research on these reagents in relation to PGM flotation. Bradshaw and O'Connor (1994) demonstrated the synergistic effects by way of improved pyrite recoveries and grades on blending dithiocarbamates especially in small proportions with other collectors viz. other dithiocarbamates, xanthate, sodium mercaptobenzothiazole and dithiophosphate. O'Connor et al. (1990) report the improvement of separation of arsenopyrite from aged arsenopyrite/pyrite ore when copper sulphate and a dithiocarbamate were added in the second stage following a first addition of dithiophosphate at pH 11.

1.3.3 Frothers

Collectors render the mineral surface hydrophobic and thereafter bubble attachment has to follow for flotation to occur. The stability of bubble attachment, especially at the pulp surface, depends to a considerable extent on the efficiency of the frother (Wills, 1992). Frothers are characterised in terms of their ability to reduce bubble size and to increase foam stability (Melo, 2006). It has been demonstrated in recent research that the first-order flotation constant is linearly related to S_b, the bubble surface area flux, which is in turn inversely related to the bubble size (Melo, 2006; Gorain et al., 1997). The size of bubbles is mainly determined by frothers which operate by preventing bubbles from coalescence (Melo, 2006).

1.3.4 Activator – copper sulphate

Copper sulphate is commonly used as an activator in PGM concentrator plants in South Africa. However, a literature search reveals that this use is widely based on the activation of BMS which in the Merensky and UG2 reefs are known to be substantially associated with PGMs (Miller, 2005; Wiese, 2006). On the other hand, there is hardly any literature on the role of copper sulphate as an activator in the flotation of PGMs of the Platreef, the reef type of primary interest in this study, in which there is very little BMS-PGM association. Wiese (2006) describes the classical understanding of the activation process in which copper ions are added to the system initially to allow the adsorption of copper ions on the surface of the sulphide minerals. Addition of collector which reacts with the copper ions at the surface renders the mineral hydrophobic. The postulated reaction steps (Fuerstenau, 1982; Wesseldijk et al., 1999) are given below,

$$Cu^{2+} + 2X^{-} \rightarrow CuX_2 \qquad 1.3$$

followed by rapid decomposition

$$2CuX_2 \rightarrow 2CuX + X_2 \qquad 1.4$$

Miller (2005) highlights the difficulty of recovering of PGMs associated with pyrrhotite under conventional flotation conditions (open to air and pH 9.0). Pyrrhotite is easily oxidized to ferric hydroxide/oxide creating a hydrophilic state which is resistant to copper activation leading to PGM losses during flotation. Seke (2005) showed that sphalerite and galena recoveries increased following activation with Cu(II) ions.

One of the disadvantages of copper activation is the inadvertent activation of gangue minerals such as feldspar (Malysiak, 2002; Shackleton, 2003) and talc at pH 9 resulting into concentrate grade dilution. This is of particular importance to the occurrence of talc rims on pyroxene and chromite (Gottlieb and Adair, 1991; Becker et al., 2006) which can exacerbate concentrate dilution by flotation of these composite particles.

1.3.5 Depressants

Depressants are used in most South African PGM concentrators to improve the grade of the final concentrate by depressing naturally floatable gangue. The most commonly used depressants are guar gum and carboxymethlycellulose (CMC) which are all essentially long chain polysaccharides (Mackenzie, 1980). Figures 1.6 and 1.7 show the monomeric structures of guar gum and CMC respectively.

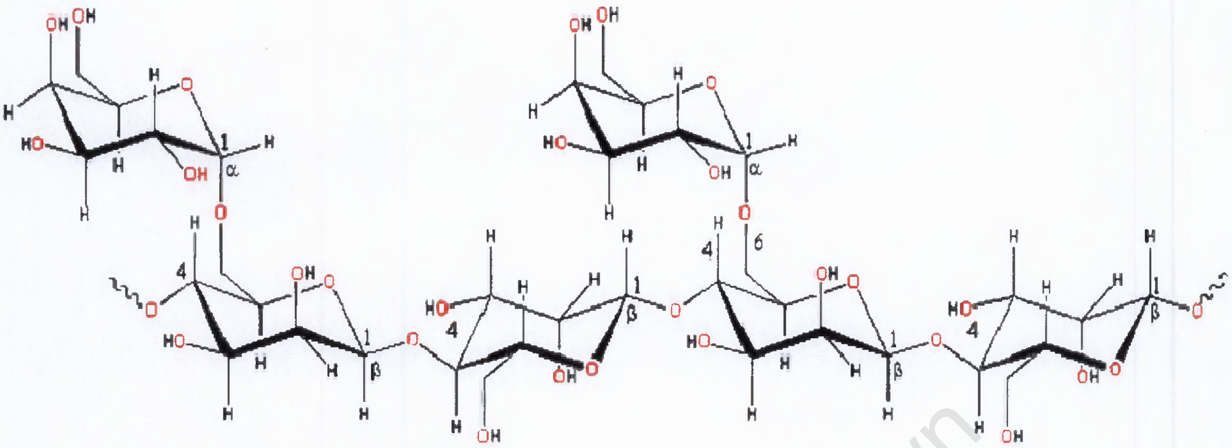


Figure 1.6: The monomeric structure of guar gum

For CMCs, a parameter called the degree of substitution (DS) gives an indication of the extent of substitution of carboxymethyl groups for OH groups per glucose unit. The maximum DS is 3 although it will normally fall in the range of 0.4 to 1.4. Substitution increases the water solubility of the polysaccharide and also decreases the viscosity (for the same molecular weight).

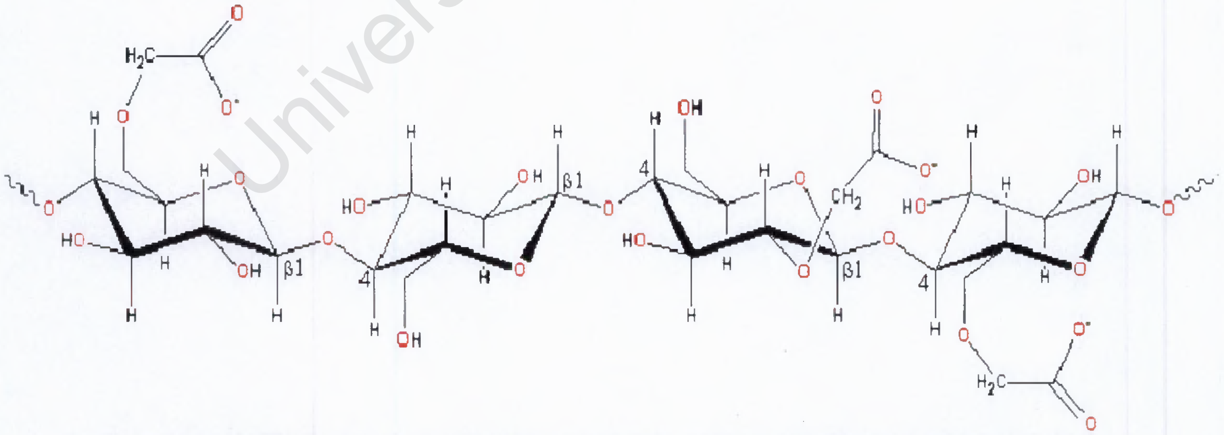


Figure 1.7: The monomeric structure of sodium carboxymethylcellulose.

The use of these depressants is mainly targeted at the depression of talc, a layer silicate with a unit structure of $Mg_3(Si_2O_5)_2(OH)_2$, which is a significant constituent of the gangue in the platinum-bearing ore bodies of South Africa (Shortridge et al., 2000; Wang et al., 2005). Talc has a high degree of floatability (Steenberg and Harris, 1984; Fuerstenau et al., 1988; Morris, 1996; Rath, 1997) and as such it is difficult to separate from valuable minerals during flotation (Shortridge et al., 2000). Wang et al. (2005) reports that hydrogen bonding is one of the main driving forces for guar adsorption on talc.

Guar gum has been found to be more effective depressants compared to CMCs at ionic strength of 10^{-3} M KNO_3 (Shortridge et al., 2000). The depression of talc by guar gum has also been found to increase with increase in the guar molecular weight whereas that by CMCs has been found to be insensitive to the CMC molecular weight (Shortridge et al., 2000). Beattie (2005) in a study of the depression of talc by a range of polymers showed that the adsorption of the polymers was not affected by the presence of the collector and vice versa.

A search of published literature reveals the absence of any investigations on the comparison of flotation behaviour of Platreef PGM phases. In fact despite finding some remotely related literature (Penberthy et al., 2000) it is observed that there is a scarcity of information on PGE telluride and arsenide flotation. This scarcity is also alluded to in a study of the selective flotation of pyrite and gold tellurides (Yan and Hariyasa, 1997).

1.4 Relative floatability of UG2 PGMs

An investigation into the behaviour of PGMs in UG2 during milling and flotation (Penberthy et al., 2000) revealed that at a grind of 80% -75µm, more than 50% of the PGM grains in the investigated sample were liberated from the ore matrix. PGM grain sizes were found to be usually very small, mostly smaller than 10µm diameter. The grain size, mineral type and mode of occurrence of the PGMs were found to be important factors in determining their flotation responses. The PGMs associated with base metal sulphides were found to be a faster floating species compared to liberated PGM grains which despite their small size reported to flotation concentrates albeit at a slower rate. The coarser grained liberated PGMs were found to preferentially report to the fast floating concentrates. Of the various liberated PGM phases, sulphides in general, except for laurite, were found to be faster floating than the non sulphides. PGMs locked in gangue or in base metal sulphides associated with gangue tended to report to the tailings and slow floating concentrates depending on the degree of liberation. A challenge encountered in this work which is common to the current study was collecting statistically sufficient data on PGM mineralogy due to their relatively low concentrations as well as due to their very small grain sizes.

1.5 Synthetic minerals

The availability of natural cooperite, vysotskite, sperrylite, palladoarsenide, moncheite and merenskyite is limited due to the low content and small grain size of the Pt and Pd sulphide, arsenide and telluride minerals found in the ore body and hence the only realistic way to study the flotation behaviour of these minerals is to synthesise the mineral and to assume that the synthetic sample generally reflects the behaviour of the naturally occurring mineral. At the very least if all the minerals are synthesised in a similar manner the relative effects of various parameters on their behaviour will be valid.

There are a few papers describing the synthesis of the PGE arsenide, telluride and sulphide minerals with the aim of studying them mineralogically. The focus of these papers are on the identification, structures, properties and phase relationships of the minerals, viz. Greoneveld Meijer (1955) reported on the synthesis, structures and properties of platinum metal tellurides. The paper describes the synthesis by dry and wet fusion methods and characterisation of the minerals using x-ray and optical methods. Merkle and Verryn (1999) discuss the results obtained on experimental investigations in a dry system PtS-PdS-NiS at 1100°C. Synthetic cooperite, braggite and vysotskite phases were observed at various temperatures profiles. Pikl et al. (1999) and Merkle et al. (1999) described Raman spectroscopic identification of synthetic braggite, comparing the results obtained for braggite to cooperite and vysotskite, respectively.

It is important to know whether the synthetically prepared mineral behaves in a similar manner to that found in nature. This is not always possible to test due to size and distribution of these minerals in the ore. A few studies have been carried out comparing synthetic and naturally occurring minerals.

Cabri et al. (1975) reported on a study where natural specimens of palladoarsenide and sperrylite were compared to synthetically prepared ones. It was reported that the natural minerals were more difficult to characterise due to their diffraction patterns being generally weaker compared to those of the synthetically prepared material. The natural palladoarsenide, however, was equivalent to the low-temperature polymorph of the synthetic Pd_2As originally defined by Bergizov et al. (1974).

In another study, Forssberg and Jonsson (1981) carried out experiments that have shown that relatively large amounts of heavy metal ions can adsorb on both synthetic and natural pyrrhotite in an acidic pH. The possible cause is the presence of iron vacancies in the crystal lattice, as indicated by the chemical formula of pyrrhotite, $Fe_{1-x}S$. The vacancies can be filled by metal ions of suitable size. Pyrrhotite releases fairly large quantities of Fe^{2+} and Fe^{3+} ions under oxidising conditions. This can adversely affect the adsorption of heavy metals. Synthetic samples showed a higher specific adsorption, probably due to pores, which give them a higher adsorption rate.

The surface characteristics and flotation behaviour of PGE tellurides and arsenides have been studied at a fundamental level using synthetic minerals (Shackleton et al., 2006). These studies were carried out on synthetic sperrylite ($PtAs_2$), palladoarsenides (Pd_2As), moncheite ($PtPd(BiTe)_2$ and $PtTe_2$) and merenskyite ($PdPt(BiTe)_2$ and $PdTe_2$). The minerals used were generally synthesised by thermally treating stoichiometric measurements of their respective constituent elements in evacuated and sealed silica tubes. X-ray diffraction (XRD) analyses were performed to quantify the mineral phases as well as to determine the crystal structure of the synthesised minerals and to compare with those found in nature. Microflotation, Zeta potential determinations, ToF-SIMS analysis (time of flight secondary ion mass spectrometry) and X-ray photoelectron spectroscopy (XPS) were used for the surface and flotation behaviour characterisation. Microflotation used for the determination of flotation response essentially measured the hydrophobicity of the minerals after various treatment whereas Zeta potential studies were used to study the adsorption characteristics of various reagent combinations by measuring mineral surface charge. ToF-SIMS analysis was used to determine in relative terms the occurrence of atomic/molecular species on the surface of the minerals.

During the experiments carried out, the effect of SIBX, $CuSO_4$ and a combination of these reagents on the mineral surface alterations were investigated over pH ranging from 6 to 10. Zeta potential determinations for all the synthetic PGMs generally showed that the addition of $CuSO_4$ resulted as expected in a positive shift in the zeta potentials compared to the measured potentials without any reagent. This shift was attributed to the electrostatic adsorption of the positive Cu(II) ion species for tests conducted at below pH7 whereas for tests carried out at higher pH it was attributed to the adsorption of $Cu(OH)^+$ colloids. On addition of SIBX a negative shift in the zeta potential was observed indicating the presence of X^- ions on the mineral surfaces. Relative percentage copper and xanthate ion surface coverage was analysed using the ToF-SIMS and the results confirm the adsorption of $CuSO_4$, SIBX and $CuSO_4$ + SIBX on the synthetic PGMs surfaces.

Results of microflotation tests carried out on sperrylite and moncheite without any reagents showed that these synthetic PGMs have low natural floatabilities. By way of example, sperrylite produced recoveries ranging from 1% to 7% whereas moncheite recoveries ranged from 18% to 49%. When SIBX was used as a collector the recovery of sperrylite increased to as high as 69% whereas that of moncheite increased to above 99%. The tests carried out with the addition of $CuSO_4$ followed by xanthate generally produced a reduction in the recoveries of the synthetic PGMs. The recovery of sperrylite dropped from 74% to 69% whereas that of moncheite dropped from >99% to as low as 41%. A relatively lower reduction in recovery was observed in the case of Merenskyite, dropping from >90% down to 87%.

Oxidation tests were carried out on the synthetic moncheite and merenskyite samples (Shackleton et al., 2006) and it was observed that oxidation of these mineral negatively affected the flotation performance of the bismuth-rich samples but not the Pt and Pd telluride samples.

In a study investigating the separation of gold tellurides from pyrite by selective flotation (Yan and Hariyasa, 1996), microflotation was carried out on hand picked samples from a high grade telluride ore. Of course this approach of hand picking samples from an ore is impractical when the targeted samples are discrete PGM phases due to their microscopic nature and hence the use of synthetic PGMs as is the case in the current investigation. This view is supported by Vermaak (2004) as it is stated that despite most fundamental flotation work being carried out on natural mineral samples in a state as pure as possible, this is not an option for PGMs due to their small size and scarcity and hence the need for these minerals to be synthetically prepared.

Literature also shows the earlier use of synthetic minerals for the purpose of fundamental studies on gold minerals (Padmanaban and Lawson, 1990). In this case synthetic calaverite ($AuTe_2$) is used to investigate the leaching characteristics of its natural equivalent. In an extension of this work, (Zhenya and Lawson, 1994) carried out similar studies on synthetic sylvanite ($AuAgTe_4$).

1.6 Mineralogical analysis using SEM

Some of the flotation feeds and products in this study were subjected to mineralogical analysis which was carried out at the Mineralogy department at AR-Germiston. The analysis was conducted by electron beam technique using an MLA (Mineral Liberation Analyser) FEI QUANTA 600. This is an automated multi-sample measurement instrument with interactive data processing. It is a Scanning Electron Microscope (SEM) integrated to an energy dispersive X-ray system (EDX) (Figure 1.8).

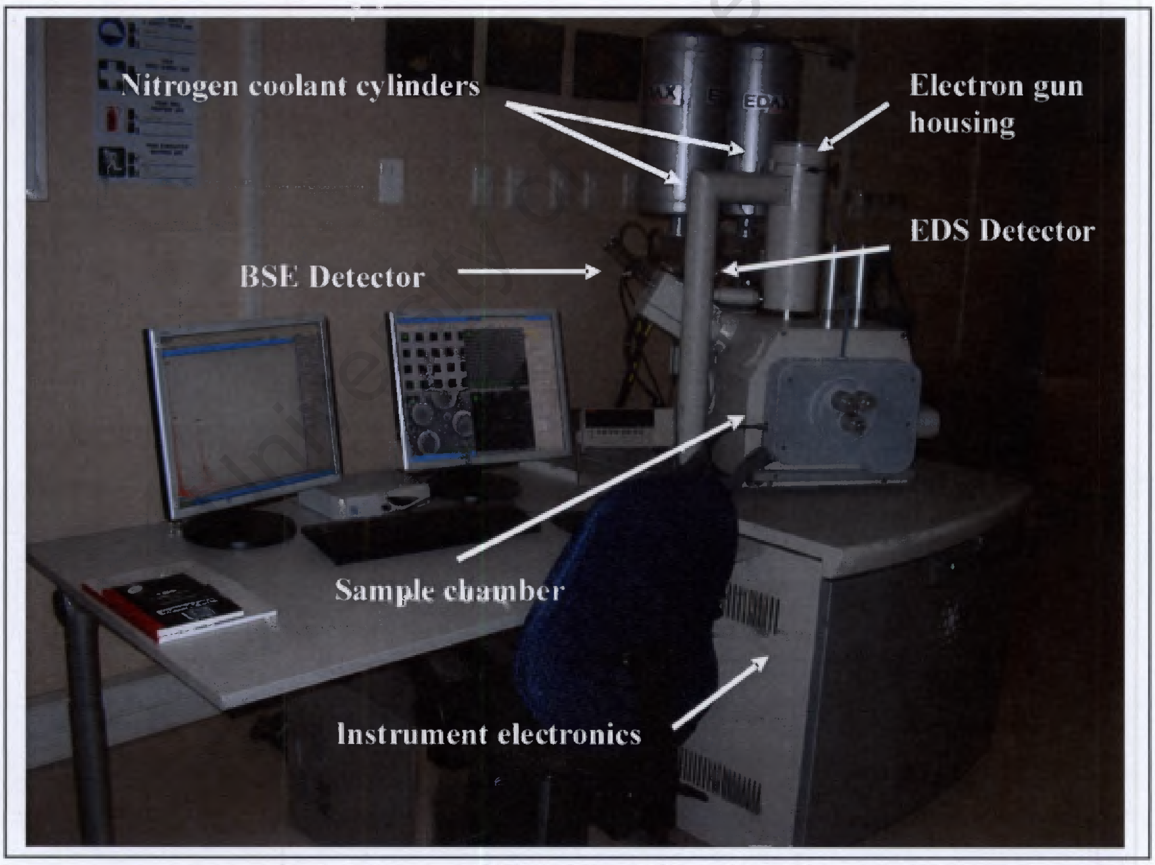


Figure 1.8: A photograph of the MLA (FEI QUANTA 600) used for mineralogy in this study.

Scanning electron microscopy (SEM) incorporates secondary electron, backscattered electron and energy dispersive x-ray detectors (Walker and LeCheminant, 1989; Petruk, 2000). The scanning electron microscope is a powerful instrument which permits the observation and characterisation of organic and inorganic materials and surfaces on such local scale. In this instrument, the area to be examined or the microvolume to be analysed, is irradiated with a finely focused electron beam, which may be static or swept in a raster across the surface of the specimen (Goldenstein et al., 1981). The type of signals produced when the electron beam impinges on a specimen surface include secondary electrons, back scattered electrons, Auger electrons, characteristic X-rays and photons of various energies. These signals are obtained from specific emission volumes within the sample and can be used to examine many characteristics of the sample (composition, surface topography, crystallography, etc.). In the SEM, the signals of greatest interest are the secondary and backscattered electrons, since these vary as a result of differences in surface topography as the electron beam is swept across the specimen. In addition to these two signals, in the case of the MLA, energy dispersive X-rays are critical for obtaining qualitative and quantitative compositional information from regions of a specimen as small as a few micrometers in diameter. Walker and LeCheminant (1989) state that secondary electrons are used to characterise surface topography, whereas the backscattered electrons distinguish regions of differing average atomic number. Chemical composition is characterised by X-ray analysis. Whereas much of the secondary electron signal originates from the surface of a sample, the back scattered electrons are excited from areas deeper in the sample. Backscattered electrons are more representative of the chemical nature of the material by presenting to the viewer an image wherein the contrast is solely dependent on average atomic number differences. It is assumed that the depth of penetration of the beam is in the order of 4-5μm. Multi-element X-ray mapping is used to complement backscattered electron imaging in analysing heterogeneous mineralogical samples which present difficulties in detecting and isolating features with poorly defined grain boundaries.

Goldenstein et al. (1981) report great similarity between the SEM and another instrument, the electron probe microanalyser (EPMA). The functioning of the EPMA also closely resembles that of an MLA in that its primary usefulness is that compositional information, using characteristic X-ray lines with a spatial resolution of the order of 1 μm can be obtained from a sample. In a manner also similar to the MLA, the EPMA is capable of obtaining X-ray scanning pictures. The X-ray pictures show the elemental distribution in the area of interest.

1.7 Mineral Liberation Analysis (MLA)

The importance of mineral liberation analysis for applied mineralogy and metallurgical processing has been well documented (Gu, 1997 and 2003; Jones, 1987; Petruk, 2000; King, 1993; Xiao 2004). The data obtained from this analysis constitute part of fundamental parameters used in plant design and optimisation. The mineral liberation analyser (MLA) developed by Julius Kruttschnitt Mineral Research Centre (JKMRC) runs on a FEI QUANTA 600 detector. This instrument uses the Mineral Liberation software package and sample preparation techniques developed by JKMRC. The software offers automated multiple-sample measurement, interactive and batch processing, and user controlled presentation of mineral liberation data. The complete system offers fast and accurate quantitative liberation assessment of samples from mineral processing streams with results presented in an accessible and easily understood form.

Particles are presented to the microscope dispersed in a specially made resin mould. The sample is mixed with an epoxy filler in a 30mm circular mould and allowed to set. The surface is ground and polished using diamond media. Emphasis is placed on the representativity of the sample as 3g sample aliquots are used per mould. The polished sections are loaded into a chamber of the electron microscope using a holder containing up to 14 samples, see Figure 1.9.

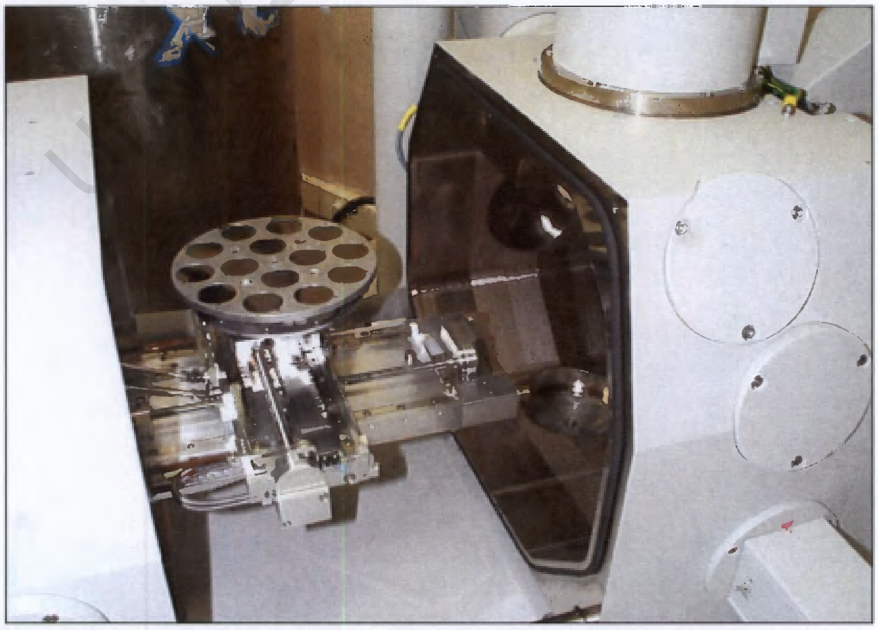


Figure 1.9: An open MLA sample chamber showing the sample holder.

Figure 1.10 shows the finely focused electron beam impinging upon the surface of a mineral particle. X-rays and back scattered electrons (BSE) are amongst the most important signals emitted from the surface.

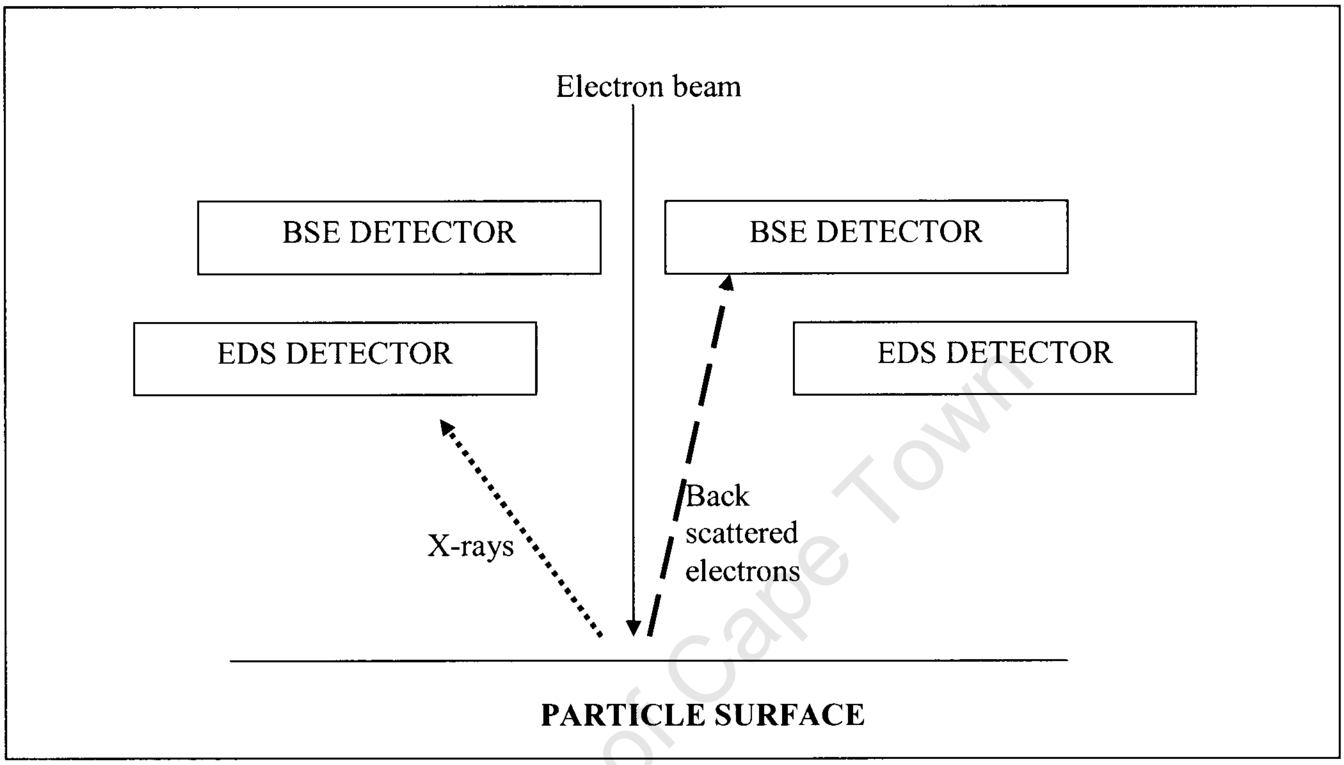


Figure 1.10: Electron beam and specimen interaction

Samples are measured following one of two procedures. In the fast measurement procedure, a series of back scattered electron (BSE) images are acquired for each sample and are processed off-line. The fast measurement procedure can be applied to samples in which all the minerals of interest can be distinguished by their BSE intensity alone. This applies to some sulphide mineral assemblages. Gu (2004) reports that the two distinct advantages of BSE signal are having a high spatial resolution (<0.1µm) and high speed acquisition (10000 points per second). Figure 1.11 shows an example of a BSE image in which the particles are shown in a black background due to the very low intensity of the BSE signal from the organic resin material. Other particles, or areas within particles, are displayed at a varying level of brightness according to the average atomic number of the mineral phase at those points.

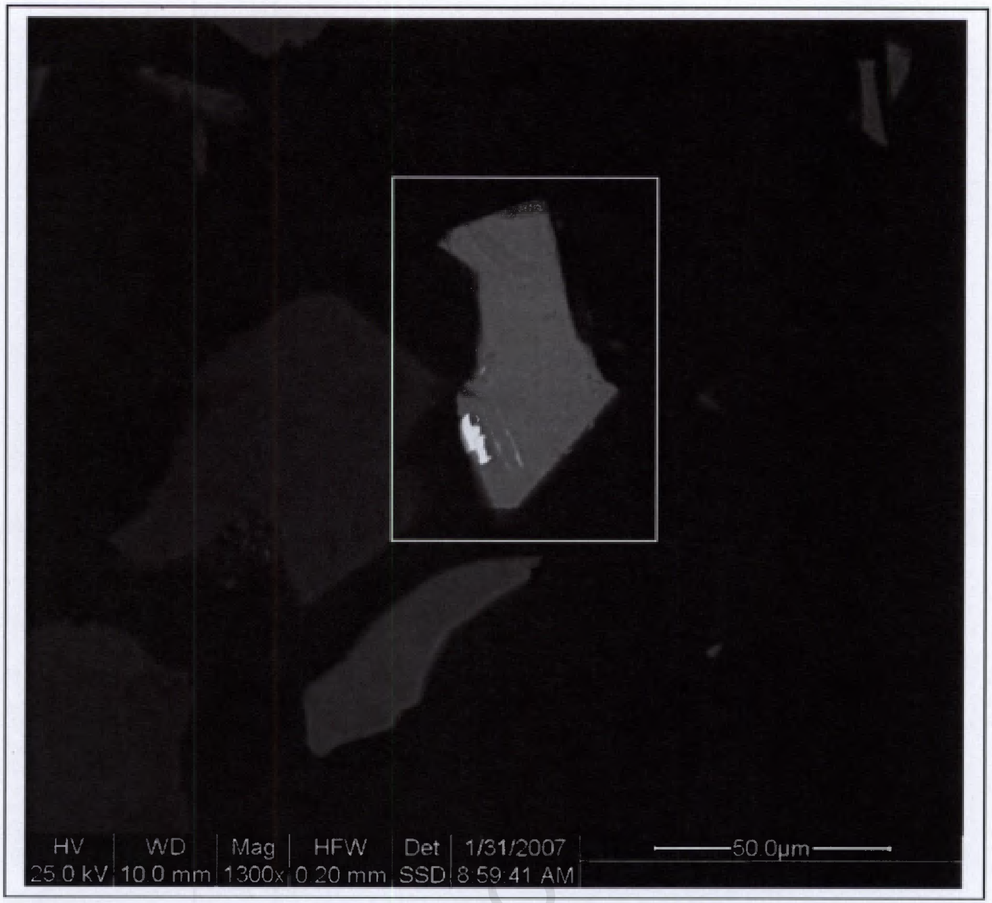


Figure 1.11: BSE image taken on the MLA (FEI QUANTA 600). Note the boxed particle with a conspicuously brighter spot which is characteristic of PGMs.

In the detailed procedure, on-line automated X-ray is selectively applied to mineral phases that can not be positively identified by BSE gray level. Then off-line data processing makes use of information from both BSE images and X-ray spectra for mineral identification purposes. Gu (2004) also reports that X-ray acquisition is very slow at 100 points per second and at a lower resolution of 1-5 µm. However, as earlier stated X-ray data is acquired only for the particular mineral types that are observed with overlapping BSE intensity range. A rare-phase search technique allows for millions of particles in a mould to be searched in a few hours. Figure 1.12 shows an image of the boxed particle from Figure 1.11 with mineral phases identified using EDS information.

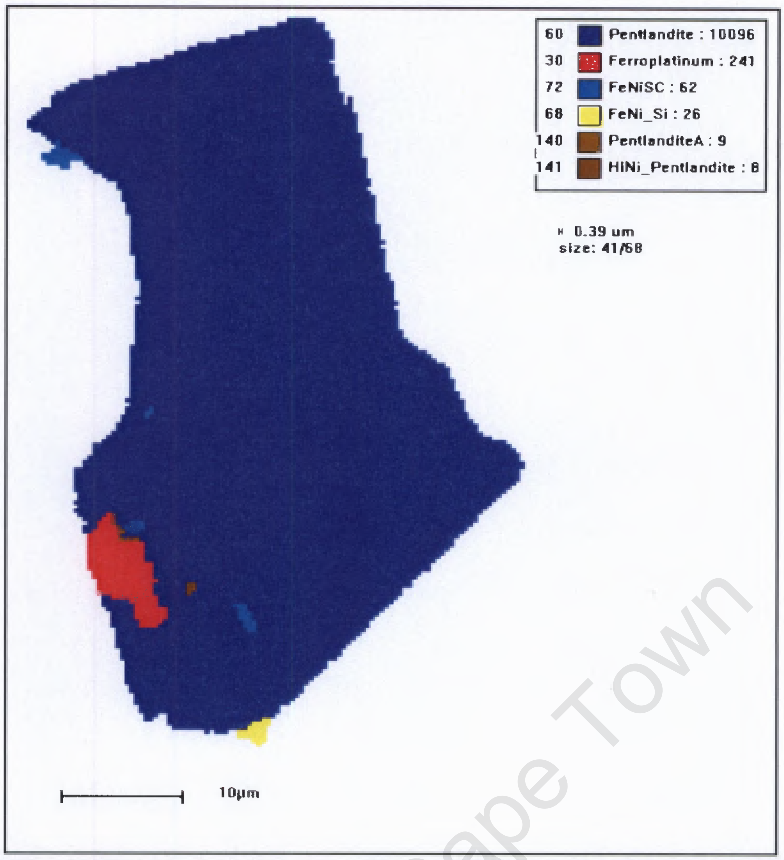


Figure 1.12: An image of the boxed particle from Figure 1.11 with its various mineral phases identified using EDS information.

The MLA retains coordinates of particles in images allowing for these particles to be examined individually and characterised by EDS and photographed. The chemical composition at specific points of the particle can be obtained and scrutinised as illustrated in Figure 1.13.

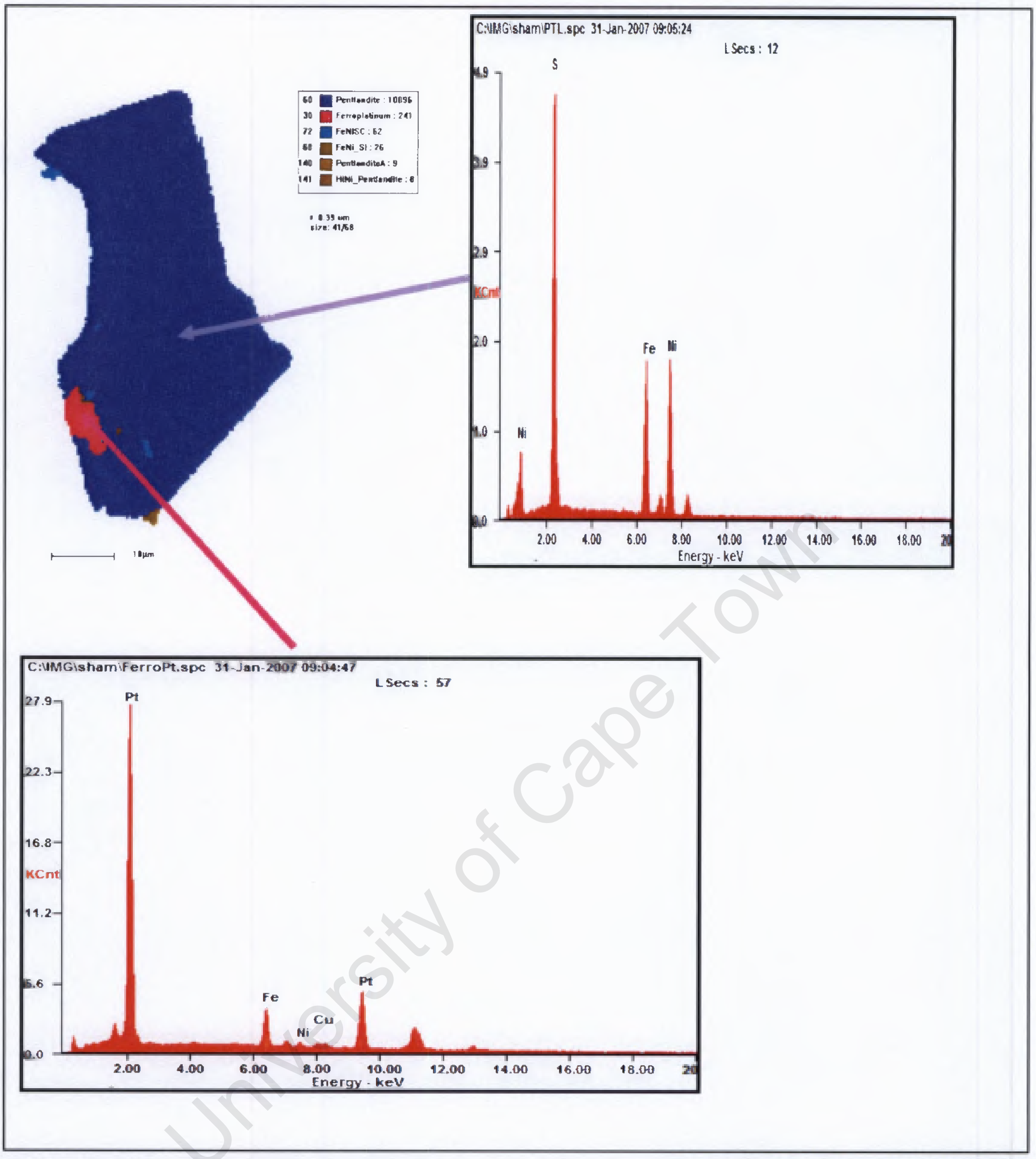


Figure 1.13: Energy dispersive spectra at the indicated points of the particle from Figure 1.12.

The image analysis process can be carried out interactively or automatically with previously saved parameters, using state- of- the art image processing algorithms. Image processing follows the following sequence of tasks, all embodied in the MLA software package,

1. Particle extraction: identification of each likely particle by discrimination against the background.
2. Particle de-agglomeration: identification of the particles which are actually two separate particles that are touching each other in mounted specimen

3. Mineral grain segmentation: identification of mineral phases within each particle and creation of coloured mineral maps.
4. Data extraction: creation of a standard database table containing all the information needed to present the results.

The extent of mineral liberation is dependant on area proportion of the mineral of interest in the host particle as seen in an image.

The results file will contain,

1. Colour image maps of every particle used in the analysis as given in Figure 1.12
2. A viewing program enabling single frame images, searching and sorting of particles according to minerals present and combining minerals into groups such as Platinum tellurides.
3. The data base of quantitative results and a presentation program that can create tables and graphs modal, liberation and association data.
4. The presentation program will allow comparison of measurements made on different size fractions for one stream sample, and of the same size fraction for a number of samples of the same stream, or any other combination of results obtained at different times.

CHAPTER 2

Objectives of the research

The objective of the research was to investigate the flotation behaviour of PGE tellurides and arsenides present in the Platreef with a view to improving the flotation of these species. In addition, investigations were carried out to determine the flotation behaviour of ore samples spiked with synthetic PGE tellurides and arsenides. This was done in order to see whether such synthetic minerals can adequately represent the behaviour of their natural equivalent. This is important if any conclusions are to be made regarding any application using such synthetic minerals.

The key questions addressed in this research are:

- Do PGE tellurides and arsenides exhibit significantly different flotation behaviour and if so how can this be addressed so as to increase the flotation response of the poorer floating species?
- In order to address this question it was also necessary to establish if synthetic PGE tellurides and arsenides could be used to simulate flotation of the naturally occurring PGE tellurides and arsenides?

Hypothesis

In addressing these objectives it is hypothesised that:

1. Synthetic PGE tellurides and arsenides can be used to simulate the flotation behaviour of their natural equivalents.
2. PGE tellurides and arsenides present in the Platreef exhibit significantly different flotation responses as a result of their different surface characteristics and not their associations, size or extent of liberation.

CHAPTER 3

Experimental methods

The experiments conducted included the comparison of the flotation behaviour of Platreef PGE tellurides and arsenides by way of tellurium and arsenic chemical analysis down the bank of a small scale continuous flotation circuit (Flexi-Float). Mineralogical examination of the Flexi-Float feed, concentrates and tailings was also carried out. In addition, batch flotation tests were carried out aimed at establishing the applicability of synthetic PGMs in simulating the flotation response of naturally occurring PGMs. Batch flotation tests and synthetic PGMs were also used in studying the relative floatabilities of PGE tellurides and arsenides as well as PGE arsenide's response to various reagent regimes.

3.1 Ore samples

3.1.1 Platreef ore

For tests requiring Platreef ore, a pyroxenite Run of Mine ore sample from PPL North Pit A-reef (Anglo Platinum Research Centre-ARC sample ID. OD597) was used. This sample was received at ARC from PPL on 06/10/02 and was crushed to –12.5mm using a jaw crusher. A rotary splitter was used to blend and split the sample which was then stored away in bulk bags. Representative aliquots of the ore were cone crushed to –3mm and split into 2kg aliquots for batch flotation tests.

Mineralogical examination was carried out on a sample of this ore milled to 60% -75µm by the Mineralogical Department at Anglo Research-Germiston using an MLA (Mineral Liberation Analyser) FEI QUANTA 600 and a QemSCAN LEO 1450. The bulk modal mineralogy results showed a composition of 70.7% pyroxene, 15.2% feldspar, 5.8% altered silicates, 2.9% base metal sulphides (BMS) and 5.4% of other minerals with PGMs occurring in trace amounts (less than 10ppm). The BMS distribution was 42.6% pentlandite, 31.9% pyrrhotite and 24% chalcopyrite. These results also showed a PGM relative abundance of 62.6% tellurides, 9.0% arsenides, 4.8% sulphides, 8.6% ferroplatinum and 10.4% PGE alloys.

3.1.2 Waterval Merensky Ore

A Merensky ore sample from Waterval Merensky concentrator was sourced for the purpose of batch flotation tests work. The objective for carrying out this testwork was to provide an alternative natural environment apart from Platreef ore against which to evaluate the flotation response of synthetic PGMs.

A mineralogical examination (similar to that described for the Platreef ore above) was carried out on this sample. The bulk modal mineralogy results showed a composition of 51.8% pyroxene, 35.6% feldspar, 2.6% altered silicates, 1.3% base metal sulphides (BMS), 5.8% chromite and 2.9% of other minerals with PGMs occurring in trace amounts (less than 10ppm). The BMS consisted of 39.5% pentlandite, 39.0% pyrrhotite and 19.6% chalcopyrite. These results also showed a PGM relative abundance of 26.6% tellurides, 1.3% arsenides, 24.8% sulphides, 23.8% ferroplatinum and 17.4% PGE alloys.

3.1.3 Feldspathic pyroxenite

Samples of hanging wall and foot wall feldspathic pyroxene barren in PGMs were supplied by the Mineralogical Department at Anglo Research-Germiston). These samples, from various Bushveld Complex reef types, were sourced from left over portions of sampled exploration drill cores. The feldspathic pyroxenite was required for batch flotation tests aimed at investigating the flotation response of synthetic PGMs in a natural environment in the absence of naturally occurring PGMs. The samples of feldspathic pyroxenite as received were crushed to -3mm, blended and split into 2kg aliquots for flotation. The blending of the feldspathic pyroxenite from various reefs was necessitated by the limited amounts available from any particular reef against the amounts required for the testwork. Bulk modal mineralogy carried out on this sample showed that it consisted of 57.8% pyroxene, 38.5% feldspar, 1.9% chromitite, 1.1% alteration minerals, 0.1% BMS and 0.6% other minerals (barren of PGMs).

3.1.4 Synthetic minerals and ores.

3.1.4.1 Natural ore spiking

Aliquots of the naturally occurring ores, Platreef, Merensky and barren feldspathic pyroxenite were spiked to varying degrees with synthetic minerals to generate the “synthetic ores”. The synthetic minerals used included sperrylite ($PtAs_2$), moncheite ($PtPd(BiTe)_2$), merenskyite ($PdPt(BiTe)_2$) and pentlandite ((FeNi)S). The synthetic PGMs grain size, -38µm, was chosen to resemble that of the fully liberated naturally occurring PGE telluride and arsenide grains in the Platreef when wet milled to 60% -75µm using a bench scale rod mill. Similarly, synthetic pentlandite grain size,+38µm -106µm, was also chosen to resemble typical base metal grain size in the Platreef when wet milled to 60% -75µm using a bench scale rod mill. The synthetic minerals were synthesised at Anglo Research-Germiston using an in house technique.

3.1.5 Preparation of synthetic minerals

Sperrylite was prepared by weighing stoichiometric amounts of the pure elements (platinum sponge and arsenic powder) into a silica tube which was evacuated overnight, sealed and thermally treated. Platinum sponge was obtained from Anglo Platinum Precious Metal Refinery and arsenic was supplied by Alfa Aesar at > 99.9% purity.

The thermal treatment involved heating the ampoule to 800°C for 6 hours followed by cooling to ambient temperature. This product was further treated by grinding the material to a fine powder and transferring to a silica tube, which was evacuated overnight and sealed. The ampoule was again thermally treated by heating to 800°C and keeping at that temperature for 1 week followed by cooling to ambient temperature. From Table 3.1 showing EDS and XRD results for the sperrylite it can be seen that there where some impurities produced in the form of Pt specks and quartz from the ampoule (Shackleton et al., 2006).

Sample	**EXPECTED**		**IDENTIFIED**		
	Phase	**Composition**	**Phase**	**Proportion (%)**	**EDS Results**
SP1	Sperrylite	56.6% Pt 43.4% As	Sperrylite	93.5	55.9% Pt, 44.1% As
			Pt specks	4.5	99.8% Pt. 0.2% As
			Quartz	2.0	-

Table 3.1: Energy Dispersive Spectroscopy (EDS) and XRD results for sperrylite.

Synthesis of Moncheite (PtPd(BiTe)$_2$)

Moncheite was prepared by weighing stoichiometric amounts of the pure elements (platinum and palladium sponge and bismuth and tellurium powder) into a silica tube which was evacuated overnight, sealed and thermally treated. The thermal treatment involved heating the ampoule to 1150°C, holding at that temperature for 15 minutes, then switching off the furnace and allowing cooling naturally to ambient temperature. This product was further treated, due to in-homogeneity, by grinding the material to a fine powder and transferring to a silica tube, which was evacuated overnight and sealed. The ampoule was thermally treated by heating to 1150°C and then cooling to 480°C, keeping at that temperature for 4 weeks then switching off the furnace and allowing cooling naturally to ambient temperature. Table 3.2 shows the various phases produced and their relative proportions (Shackleton et al., 2006).

Sample	EXPECTED		IDENTIFIED		
	Phase	Composition	Phase	Formula	Proportion (%)
NS 142	Moncheite PtPd(BiTe)$_2$	18.9% Bi 41.3% Te 0.14% Pd 39.6% Pt	Moncheite	$Pt_{0.95}Pd_{0.05}Te_{0.09}Bi_{1.10}$	86.9
			Platinum Telluride	$Pt_{12}Te_{18}$	12.3
			Bismuth Tellurium Oxide	$Bi_{32}Te_{32}O_{112}$	0.8

Table 3.2: Energy Dispersive Spectroscopy (EDS) and XRD results for moncheite.

Synthesis of Merenskyite (PdPt(BiTe)$_2$ and PdTe$_2$)

Merenskyite, NS143, was prepared by weighing stoichiometric amounts of the pure material (platinum and palladium sponge and bismuth and tellurium powder) into a silica tube which was evacuated overnight, sealed and thermally treated. The thermal treatment involved heating the ampoule to 800°C, holding at that temperature for 30 minutes, and then subjected to a controlled linear slow cooling to 350°C over 60 hours then switching off the furnace and allowing cooling naturally to ambient temperature. Table 3.3 shows the various phases produced and their relative proportions (Shackleton et al., 2006).

Sample	EXPECTED		IDENTIFIED		
	Phase	Composition	Phase	Formula	Proportion (%)
NS 143	Merenskyite PdPt(BiTe)$_2$	11.9% Bi 58.5% Te 25.5% Pd 4.07% Pt	Merenskyite	$Pt_{0.10}Pd_{0.90}Te_{1.80}Bi_{0.20}$	97.1
			Tsumoite	$Bi_{6.00}Te_{6.00}$	1.7
			Michenerite	$Pd_{4.00}Bi_{4.00}Te_{4.00}$	1.2

Table 3.3: Energy Dispersive Spectroscopy (EDS) and XRD results for Merenskyite.

All synthetic PGMs in storage were kept under argon gas to minimise mineral surface oxidation.

3.2 Reagents

The following are some of the reagents of commercial grade that were used for the flotation campaigns. These reagents were used in various combinations according to the requirements of a test, (cf. Appendix A).

Reagent type	Reagent name	Supplier
Primary collector	SIBX (Sodium Iso Butyl Xanthate)	Senmin
Secondary collectors	Senkol 3 (dithiophosphate)	Senmin
	Senkol 5 (dithiophosphate)	Senmin
	S-8474 Promoter (dithiocarbamate)	CYTEC
	S-9887 Promoter (mixture of thionocarbamates)	CYTEC
Activator	Copper sulphate	AnalaR
Frother	Betafroth (polypropylene glycol monomethyl ether)	Betachem
Depressants	Guar colloids 369	Pelichem
	KU9(Guar)	GM Associates

Table 3.4: A compilation of the reagents used for the various flotation tests.

3.3 Synthetic water composition

Synthetic water with a composition similar to Amandelbult process water was used in all the batch flotation tests. This water had a key ion composition of Ca^{2+} 80ppm, Mg^{2+} 80ppm, Na^+ 135ppm, Cl^- 270ppm, SO_4^{2-} 250ppm, NO_3^- 135ppm, NO_2^- 40ppm, CO_3^{2-} 40ppm, TDS 1030ppm. The synthesised water was used in order to minimise the possible effect of water compositional change on the test results. This water was made by adding to distilled water a suite of inorganic compounds in predetermined concentrations, (cf. Table 3.5). The choice of synthesised water, in this case Amandelbult process water, was based on the knowledge that the contained ions are typically present in most other PGM plant process waters in South Africa. The water was used at its natural pH following synthesis.

Chemical compound	Formula	Mass(g) per liter	Mol/dm^3
Calcium chloride	$CaCl_2.2H_2O$	0.147	0.001
Calcium nitrate	$Ca(NO_3)_2.4H_2O$	0.236	0.001
Magnesium sulphate	$MgSO_4.7H_2O$	0.615	0.0025
Magnesium nitrate	$Mg(NO_3)_2.6H_2O$	0.107	0.0004
Sodium chloride	NaCl	0.356	0.0061
Sodium carbonate	Na_2CO_3	0.058	0.0005

Table 3.5: Synthetic water composition.

3.4 Batch flotation

3.4.1 Natural ores

Platreef, Waterval Merensky and Barren feldspathic pyroxenite

The batch flotation of any of these ores was carried out by first wet batch rod milling a 2kg aliquot of the ore at 66% solids and to a final grind of 60% passing 75µm. The mill product was then floated using a D12 Denver bench flotation machine in a 4.5 liter cell at an adjusted density of 33% solids. Synthetic water was used for all water requirements from milling through to flotation. Different flotation procedures were followed for each ore type (cf. Appendix A). During each flotation test, five separate concentrate samples were collected with whatever remained in the flotation cell constituting the tailings. Head samples were generated by milling an aliquot of the ore as per the earlier described milling procedure.

3.4.2 Synthetic ores.

A Sartorious (MC5) micro balance capable of weighing down to 0.0001mg was used to weigh out the required minute masses of the synthetic minerals (cf. Appendix B). Synthetic ores were made by spiking any of the natural ores in a flotation cell with the weighed out amounts of synthetic minerals and conditioning for 30 minutes prior to flotation in the procedure described above. There were no head samples for tests carried out on spiked samples and so the head assays had to be calculated, see Appendix C.

3.4.3 Sample preparation and analyses

Feed, concentrates and tailing samples were filtered and dried in an oven at temperatures less than 50°C. The concentrates and aliquots of the heads and tailings were submitted for Pt, Pd, Au, Cu and Ni analysis. Rh analysis was requested for the heads and tailings samples. The analysis for Pt, Pd and Au was carried out by the silver collection whereas Cu and Ni content was determined by ICP after complete fusion with sodium peroxide.

3.5 Flexi-Float

3.5.1 General description

The Flexi-Float is a laboratory scale multi-cell continuous flotation unit. It consists of a bank of eight 7.3litre perspex cells arranged in series. Each cell is equipped with an agitator which is coupled via v-belts to a variable speed drive. Each cell in the bank is supplied with an independent variable air supply. The feed to the Flexi-Float was generated by wet milling a minus 12.5mm ore sample in a 2m length X 1m diameter laboratory ball mill. The ball mill was run in closed circuit with a classifying screen with the undersize as final slurry product. The product was transferred with buckets to a holding tank which also served for slurry density adjustment. The slurry was fed to the Flexi-Float at a controlled feed rate via two reagent conditioning tanks by using a variable speed peristaltic pump. Reagents were fed to the conditioning tanks at controlled rates by using pulsating pumps. Figure 3.1 below shows a general roughing circuit, though additional cells are available which presents the option to set up various circuit configurations.

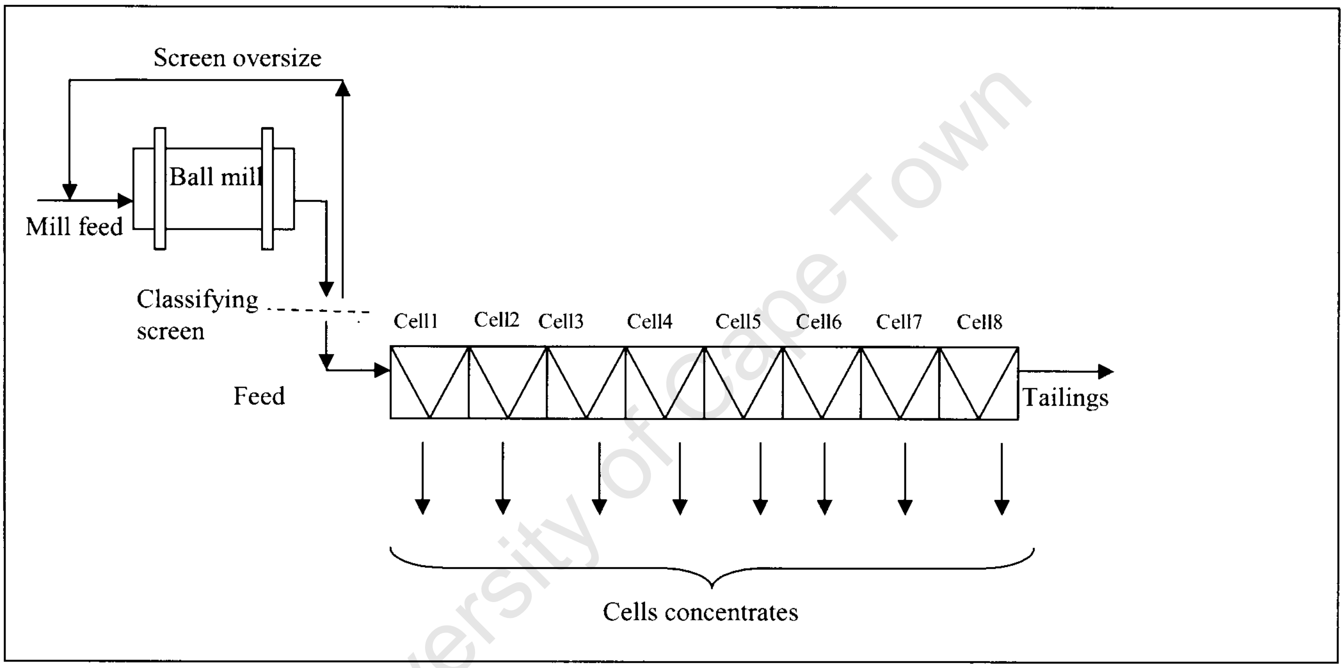


Figure 3.1: A schematic diagram incorporating milling and classification ahead of a Flexi-Float roughing circuit.

3.5.2 Testwork parameters

Feed for the Flexi-Float was drawn from the –12.5mm OD597 Platreef bulk ore sample which was fed to the ball mill and wet milled at 50% solids to a final grind of 80% passing 75µm. The mill product density was adjusted to 33% solids prior to feeding to the rougher bank of eight cells of the Flexi-Float at a rate of 33kg/hr. The feed was fed via two reagent conditioning tanks in series ahead of the flotation bank. SIBX and Senkol 3, a dithiophosphate, were added to the first tank followed by Guar colloids 369 depressant and betafroth to the second tank. At a solids SG of 3.1 and a slurry SG of 1.3 the slurry flowrate was 77l/hr. A total bank volume of 58.4l being fed at this flowrate gives an overall calculated mean residence time of 45 minutes.

Having introduced air and commenced flotation the bank was controlled at steady state for an hour before sampling commenced.

3.5.3 Sampling

Sampling was conducted in two configurations (Figure 3.2), in both configurations feed and tailings were sampled and the only difference was in concentrate sampling. In the first configuration three sets of concentrates were sampled i.e. Conc 1 consisting of concentrate from the cell 1, Conc 2-3 which was a combination of concentrates from cells 2 and 3 and lastly Conc 4-8 constituting of concentrates from cells 4, 5, 6 ,7 and 8. In the second configuration each of the eight cells' concentrates were sampled separately.

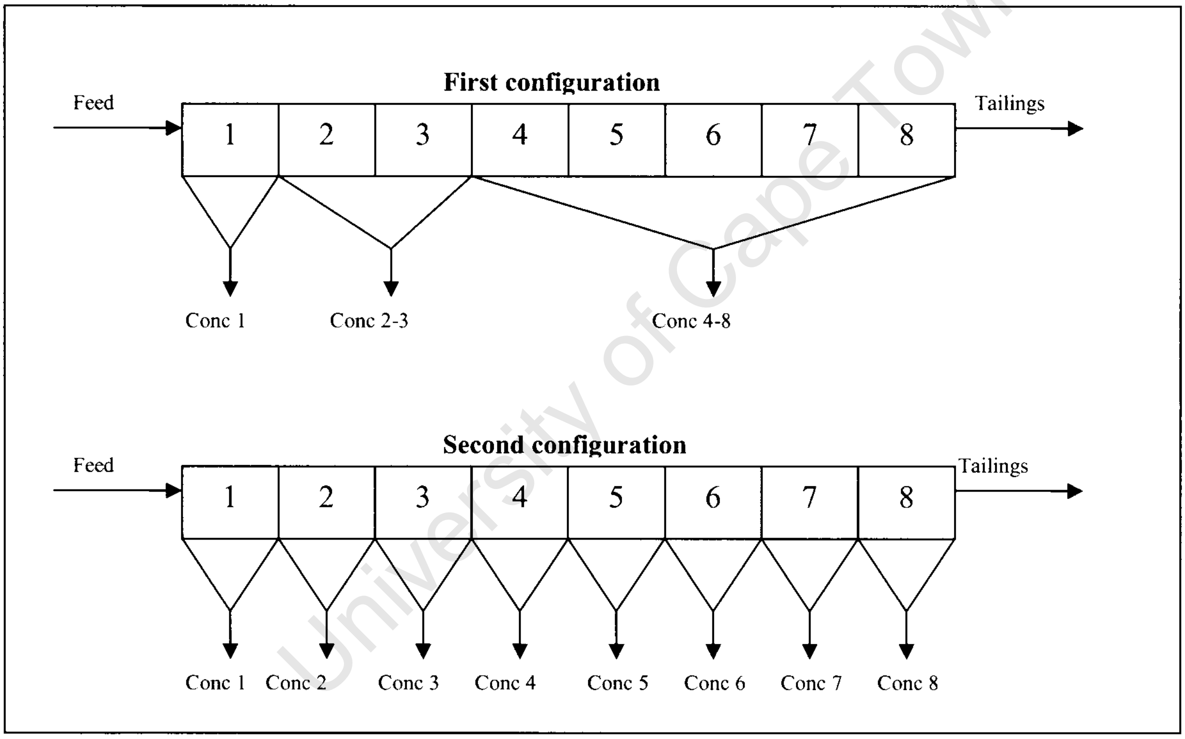


Figure 3.2: Schematics showing the sampled streams for the two Flexi-Float configurations.

Sampling in the first configuration was carried out over a period of 1 hour and immediately thereafter sampling in the second configuration was carried out over 45min. In each configuration the feed was sampled for 15seconds in intervals of 15min to minimise disturbances on the flotation. The rest of the samples were collected continuously in their entirety over the period of sampling.

3.5.4 Sample preparation and analyses

All the collected samples were filtered and then dried in an oven at temperatures not exceeding 50^{O}C. The dried samples were weighed and the masses recorded.

3.5.4.1 Chemical analysis

Aliquots of all the samples from the Flexi-Float were submitted for analyses for Pt, Pd, Au, Cu, Ni, Te and As. The analysis for Pt, Pd and Au was carried out by the silver collection method whereas Cu and Ni contents were determined by ICP after complete fusion with sodium peroxide. As and Te were analysed by microwave dissolution, standard addition followed by ICP-MS (HR).

3.5.4.2 Mineral liberation analysis (MLA).

Mineral Liberation Analysis (MLA) was the chosen technique for Flexi-Float down the bank mineralogical characterisation. From the MLA results, various mineralogical classifications were deduced and these included PGM distribution, PGM species size distributions, PGM species liberation and PGM species association. The standard practice at Anglo Research requires a minimum of 100 PGM grains to carry out a statistically sound characterisation in any of these mineralogical classifications. This practice was therefore also adopted for this study and by way of example, to generate a particle size distribution of particles associated with PGM tellurides in a sample, at least 100 such particles were required to be analysed by MLA in that sample.

The mineralogical analysis was carried out at the Mineralogy department at Anglo Research-Germiston. The analysis was conducted by electron beam technique using an MLA (Mineral Liberation Analyser) FEI QUANTA 600. This is an automated multi-sample measurement instrument with interactive data processing. It is a Scanning Electron Microscope (SEM) integrated to an energy dispersive X-ray system (EDX). Specially prepared polished sections of the samples are prepared and loaded in the MLA. Upon running the MLA a Back Scattered Electron (BSE) image is generated which is used to differentiate minerals that have sufficiently different BSE brightness. Subsequent X-ray spectra collected at centroid positions in various BSE zones can then be used to confirm the chemistry of the phase and hence characterise the mineral.

Taking into consideration the limited available MLA instrument time coupled with the earlier mentioned statistical requirements it was decided that mineralogical characterisation of the ore down the Flexi-Float bank could only be completed in the proposed duration of the study if only configuration 1 was considered. MLA work was therefore only carried out on the Flexi-Float configuration 1 streams which amounted to only five compared to ten for configuration 2.

CHAPTER 4

Results

All recoveries and grades are reported in values obtained by normalising the absolute values with respect to the highest values of recovery and grade obtained in the study respectively.

4.1 Simulating the flotation behaviour of natural PGMs using synthetic PGMs

The results in this section are from tests carried out to investigate whether synthetic PGMs can be used to simulate the flotation responses of naturally occurring PGMs.

4.1.1 Platreef ore spiked with a blend of synthetic PGMs.

The following are results from batch flotation tests carried out on a Platreef ore spiked with a blend of synthetic moncheite, merenskyite and sperrylite (cf. Appendix B) . The term 'Natural' in this section will be used to refer to the unaltered Platreef ore sample.

Table 4.1 shows the PGE, Au and base metals head grades of the head samples. It can be seen that Pt and Pd head grades increased significantly above those of the natural ore following spiking with synthetic PGMs and the increments continued to increase progressively with increased levels of spiking.

	Test	**Pt:Pd ratio**	**(g/t)**				**(%)**	
			Pt	**Pd**	**Au**	**3E**	**Cu**	**Ni**
1	Natural	1.20	2.80	2.32	0.32	5.47	0.18	0.38
2	Natural-No collector	1.19	2.80	2.36	0.32	5.65	0.19	0.37
3	Spiked (Level 1)	1.18	3.60	3.05	0.29	6.99	0.18	0.37
4	Spiked (Level 2)	1.10	4.10	3.71	0.31	8.16	0.18	0.39
5	Spiked (Level 3)	1.06	5.26	4.98	0.37	10.63	0.18	0.38
6	Spiked (Level 3)-No collector	0.98	4.92	5.00	0.31	10.43	0.18	0.34
7	Spiked (Level 4)	1.05	6.49	6.19	0.33	13.03	0.18	0.38

Table 4.1: Normalised head grades for the Platreef ore spiked with various amounts of a blend of synthetic moncheite, merenskyite and sperrylite. Note that the head grades for natural samples were determined by chemical analysis whereas those of spiked samples were the calculated values (cf. Appendix C). The spiking levels refer to the relative amounts of a specific blend of synthetic PGMs added to the natural ore in incremental order, Level 1< Level 2< Level 3< Level 4.

Table 4.2 shows the final recoveries and grades obtained. It can be seen that tests conducted without collector whether spiked or not had relatively very poor recoveries and grades. On the other hand, the rest of the tests carried out with the addition of collector showed marked recovery improvement for both natural and spiked samples. This result shows that both natural and synthetic PGMs are not naturally hydrophobic but that collector is required to impart hydrophobicity in order to achieve significant final recoveries.

	Test	Mass Pull (%)	Pt Rec. (%)	Pt Grade (g/t)	Pd Rec. (%)	Pd Grade (g/t)
1	Natural	11.96	91.3	20.62	90.9	17.08
2	Natural-No collector	11.58	11.4	2.65	15.2	2.99
3	Spiked(Level 1)	9.82	86.9	31.16	89.4	26.82
4	Spiked(Level 2)	10.06	94.6	37.29	96.1	34.32
5	Spiked (Level 3)	10.01	94.8	48.19	97.4	46.91
6	Spiked (Level 3)-No collector	8.37	8.9	5.05	27.1	15.70
7	Spiked (Level 4)	10.03	95.2	59.56	98.2	58.53

Table 4.2: Normalised Pt and Pd ultimate recoveries and grades for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

The grade-recovery graphs (Figures 4.1 and 4.2), show that the Pt and Pd flotation responses generally followed the order of the level of spiking. The cumulated grades at each stage are higher with increased spiking and this is probably due to higher head grades. It can also be seen that the natural sample and that spiked to level 1 produced very similar flotation responses. Better flotation responses were achieved with increased level of spiking.

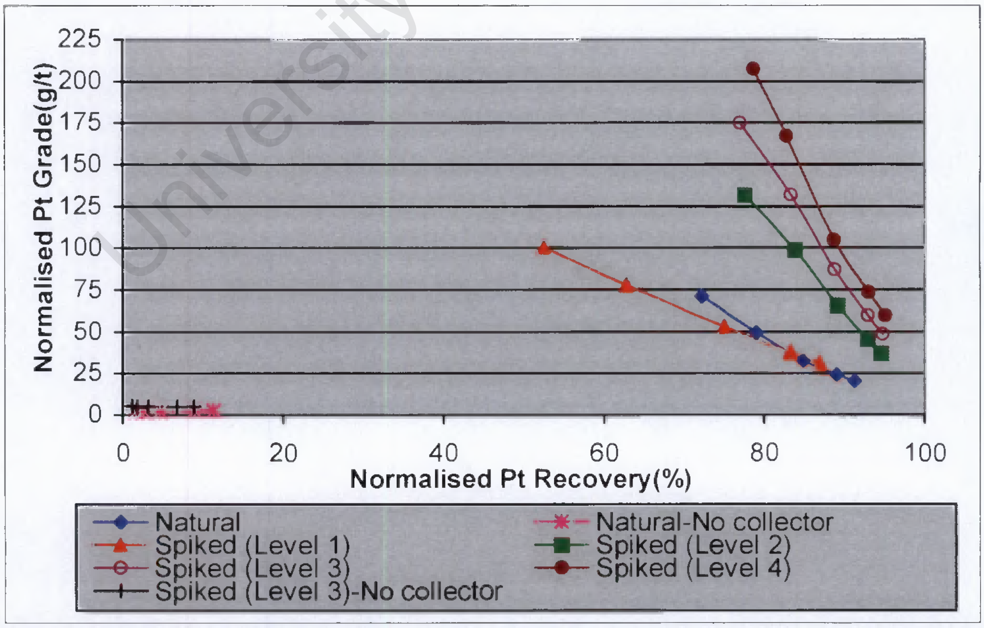


Figure 4.1: Normalised Pt grades versus Normalised Pt recoveries for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

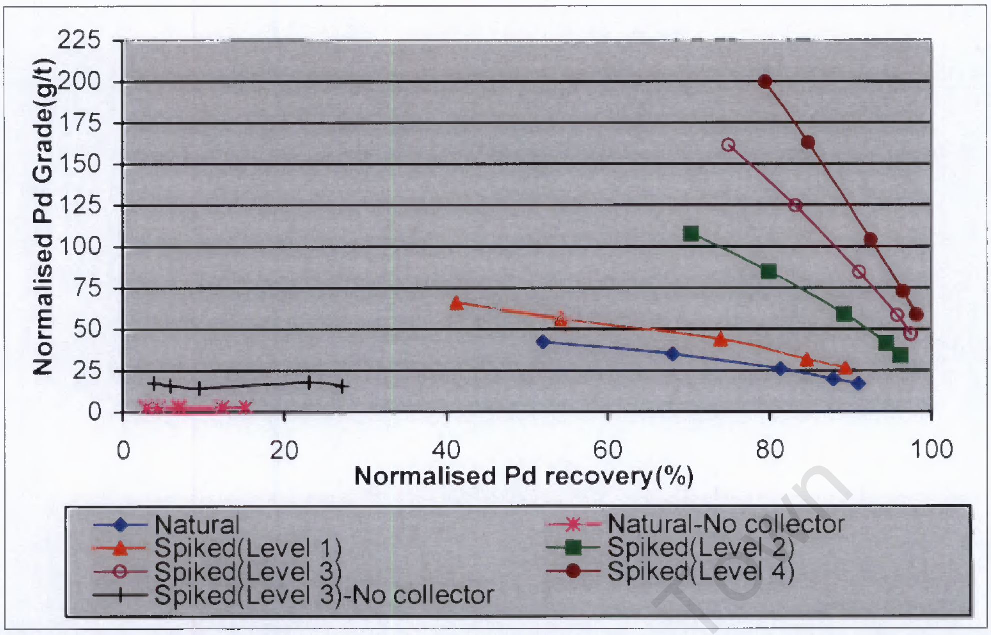


Figure 4.2: Normalised Pd grades versus Normalised Pd recoveries for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

To take into account differences in head grades in comparing these results, Pt and Pd upgrade ratio-recovery curves are plotted in Figures 4.3 and 4.4 respectively. The upgrade ratio is the ratio of the cumulative concentrate grade at any stage relative to the calculated feed grade (cf. Appendix C). It can be seen that all the spiked samples except for (Level 1) had similar upgrade ratios for both Pt and Pd which were higher than those of the natural ore in the early stages of flotation. It is uncertain why the Pt response of Level1 deviated from the observed trend. It can however be seen that the ultimate upgrade ratios for all tests were comparable. Overall it can be said that comparing tests that were carried out with and without collector, natural and synthetic PGMs produced similar responses.

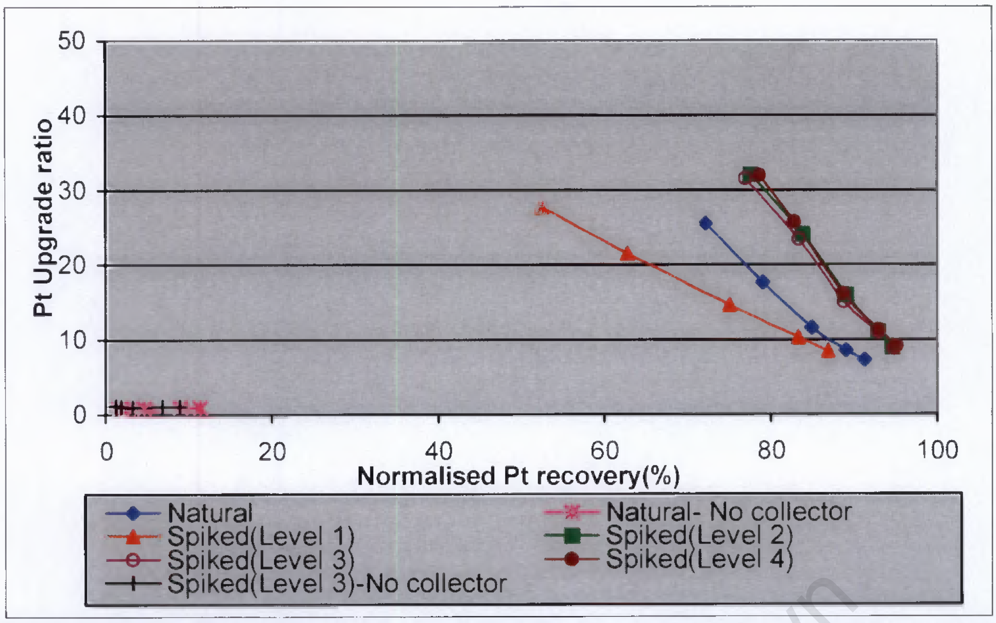


Figure 4.3: Pt Upgrade ratios versus Normalised Pt recoveries for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

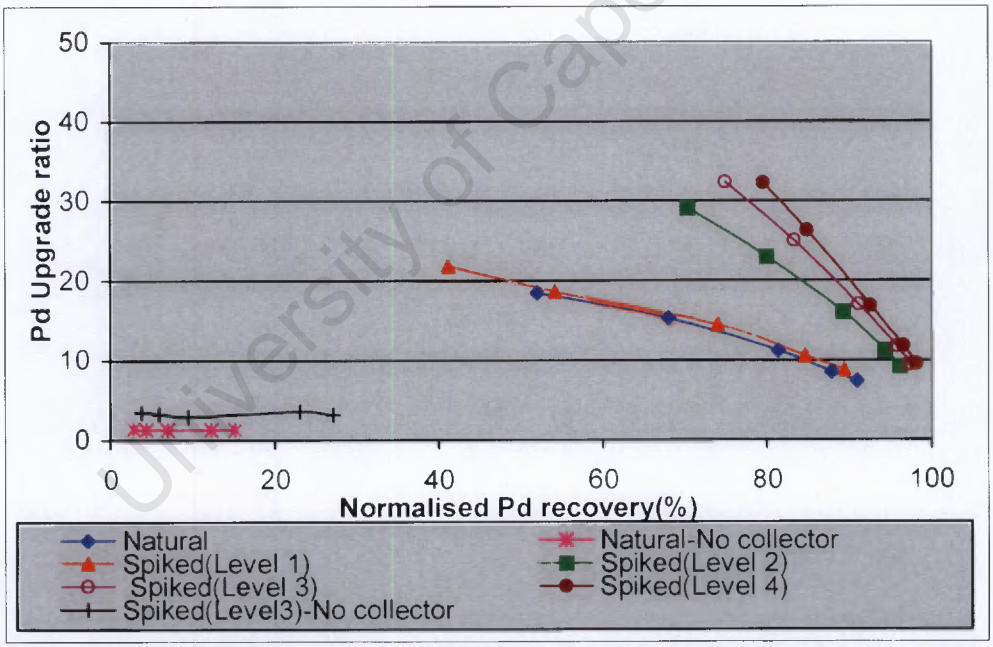


Figure 4.4: Pd Upgrade ratios versus Normalised Pd recoveries for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

Table 4.3 shows Pt and Pd flotation rate constants determined using the Klimpel model (Mishra and Klimpel, 1987; Klimpel, 1980) as shown in equation 4.1.

$$Rec = Rec_{\infty}[(1-(1/kt))(1-e^{-kt})] \qquad 4.1$$

Where,

Rec = recovery determined from assays

Rec_{∞}= equilibrium recovery after long flotation time

k= flotation rate constant

t= flotation time

Rec_{∞} and k are model parameters which were determined by numerical methods. It can be seen from the results in Table 4.3 that tests carried out with collector, spiked or not, produced greater rates compared to those carried out without collector. This is also illustrated in Figures 4.5 and 4.6 in which Pt and Pd recoveries are plotted as functions of time, respectively. It is also noteworthy in each test that the rates of flotation of the Pt minerals were significantly greater than those of Pd minerals although the final recoveries were comparable.

TEST	**Pt**			**Pd**		
	k (min^{-1})	**Rec_{∞} (%)**	**R^2**	**k (min^{-1})**	**Rec_{∞} (%)**	**R^2**
Natural	2.30	90.6	0.95	0.94	92.7	0.99
Natural-No collector	0.06	22.0	0.99	0.09	23.2	0.99
Spiked (Level 1)	1.01	86.8	0.96	0.58	92.5	0.98
Spiked (Level 2)	2.68	94.1	0.96	1.69	96.4	0.97
Spiked (Level 3)	2.56	94.2	0.95	2.01	97.4	0.97
Spiked (Level 3)-No collector	0.04	19.8	0.99	0.04	62.7	0.97
Spiked (Level 4)	2.78	94.0	0.90	2.45	97.7	0.94

Table 4.3: Pt and Pd flotation rate constants for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

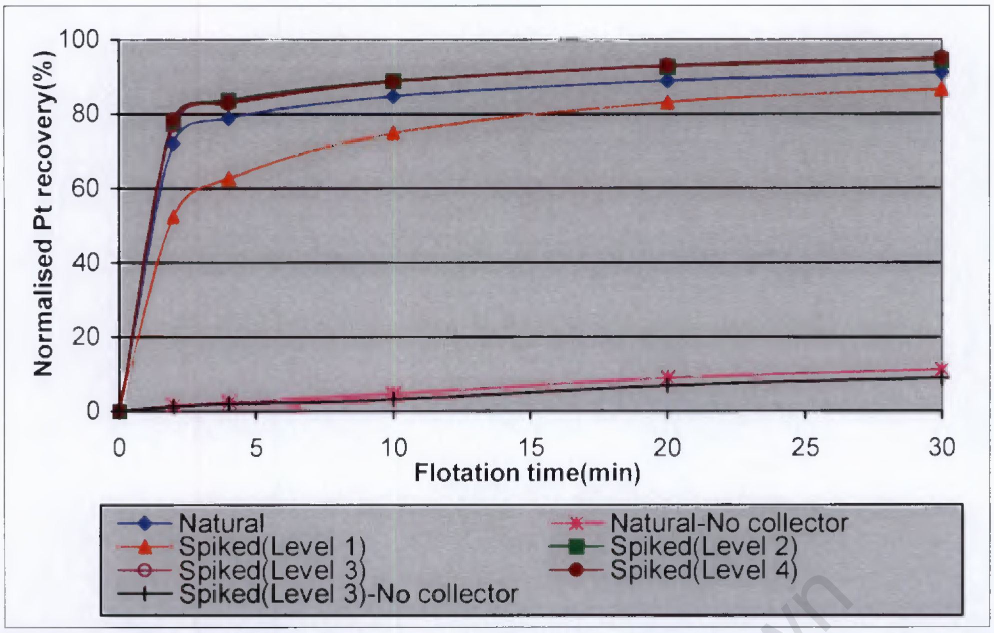


Figure 4.5: Pt Normalised recoveries versus Flotation time for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

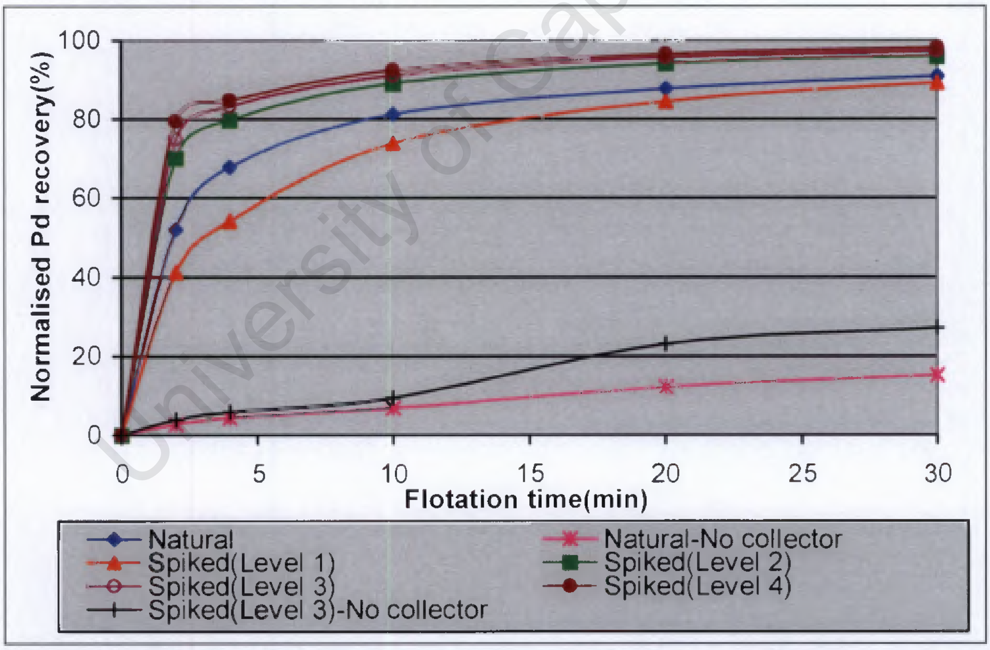


Figure 4.6: Pd Normalised recoveries versus Flotation time for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

It is important to note that since Pt and Pd recoveries were of similar orders of magnitude for natural and spiked samples, this indicated that the extra Pt and Pd from the spiking was being recovered to the concentrates in a manner similar to the naturally occurring Pt and Pd. The results achieved thus far show that synthetic PGMs can be used to simulate in general the flotation behaviour of the naturally occurring PGMs in the Platreef ore. Appendix D presents the results for Cu, Ni and Au grades versus recoveries.

4.1.2 Merensky ore spiked with a blend of synthetic PGMs.

Table 4.4 shows the head grades for the Merensky ore as well as the same ore spiked with a blend of synthetic PGMs (cf. Appendix B). The term 'Natural' in this section will be used to refer to the unaltered Merensky ore sample.

The Pt and Pd head grades increased significantly above those of the natural ore following spiking with synthetic PGMs and the increments continued to increase progressively with increased levels of spiking.

	Test	**Pt:Pd ratio**	**(g/t)**				**(%)**	
			Pt	**Pd**	**Au**	**3E**	**Cu**	**Ni**
1	Natural	2.09	3.28	1.57	0.26	5.13	0.09	0.15
2	Natural-No collector	2.15	2.81	1.30	0.24	4.50	0.08	0.15
3	Spiked (Level 1)	1.79	4.38	2.45	0.40	7.25	0.09	0.15
4	Spiked (Level 2)	1.53	4.73	3.10	0.30	8.17	0.10	0.15
5	Spiked (Level 3)	1.37	6.50	4.73	0.28	11.54	0.09	0.15
6	Spiked (Level 3)-No collector	1.26	5.41	4.28	0.26	10.09	0.09	0.16
7	Spiked (Level 4)	1.23	7.83	6.36	0.28	14.48	0.09	0.14

Table 4.4: Normalised head grades for the spiked Merensky samples. Note that as opposed to assayed grades for natural samples, those for all spiked samples are calculated head grades (cf. Appendix C). The spiking levels refer to the relative amounts of a specific blend of synthetic PGMs added to the natural ore in the incremental order, Level 1< Level 2< Level 3< Level 4.

Table 4.5 shows the final recoveries and grades achieved. It can be seen that tests conducted without collector irrespective of whether spiked or not, had relatively very poor final recoveries and grades. This illustrates that the natural PGMs in the Merensky ore, as well as synthetic PGMs used in spiking, are not inherently floatable.

	Test	Mass Pull (%)	Pt Rec. (%)	Pt Grade (g/t)	Pd Rec. (%)	Pd Grade (g/t)
1	Natural	7.88	95.1	38.34	94.3	18.24
2	Natural-No collector	7.63	19.2	6.84	22.5	3.73
3	Spiked (Level 1)	8.46	96.1	48.11	97.3	27.27
4	Spiked (Level 2)	7.56	94.5	57.32	97.9	38.89
5	Spiked (Level 3)	6.66	92.7	87.50	99.1	68.14
6	Spiked (Level 3)-No collector	6.95	13.5	10.16	48.0	28.66
7	Spiked (Level 4)	7.18	94.7	100.00	100.0	85.70

Table 4.5: Normalised Pt and Pd final recoveries and grades for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

The Pt flotation responses in Figure 4.7 show that the concentrate grades achieved generally increased with increased spiking for points of equivalent recovery. Level 1 spiking grades were marginally higher than was observed in the case of level 2 spiking. The final Pt recoveries were all very similar. The concentrate grades in the case of Pd (Figure 4.8) followed the order of level of spiking. The final Pd recoveries were however also quite similar.

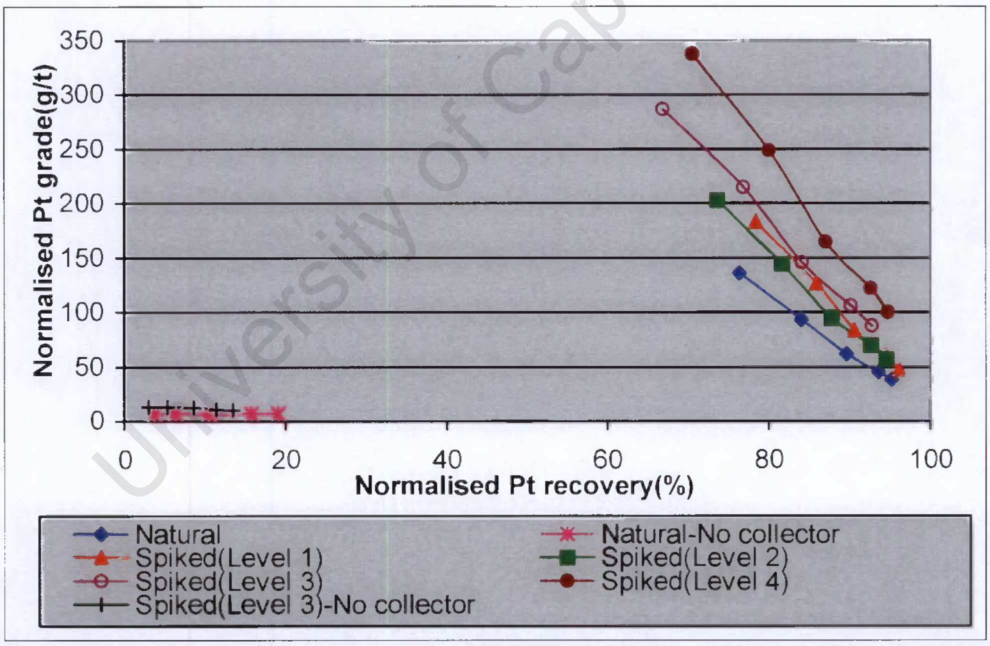


Figure 4.7: Normalised Pt grades versus Normalised Pt recoveries for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

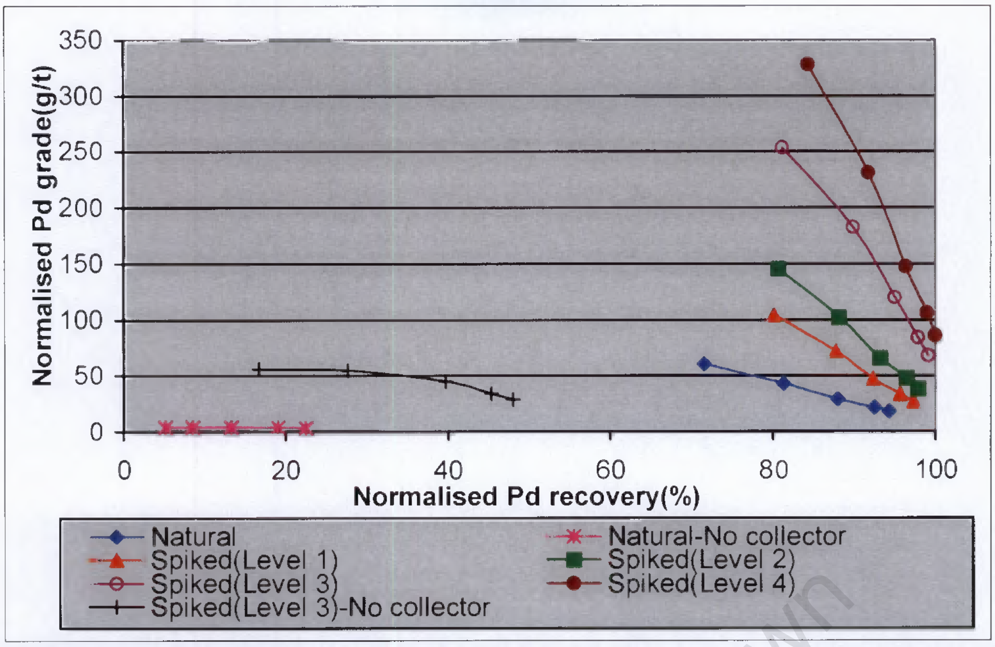


Figure 4.8: Normalised Pd grades versus Normalised Pd recoveries for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

The Pt and Pd upgrade ratio versus recovery curves (Figures 4.9 and 4.10 respectively), show that samples treated with collector produced similar final upgrade ratios even though there were distinct differences in the upgrading of Pd in the earlier stages of flotation.

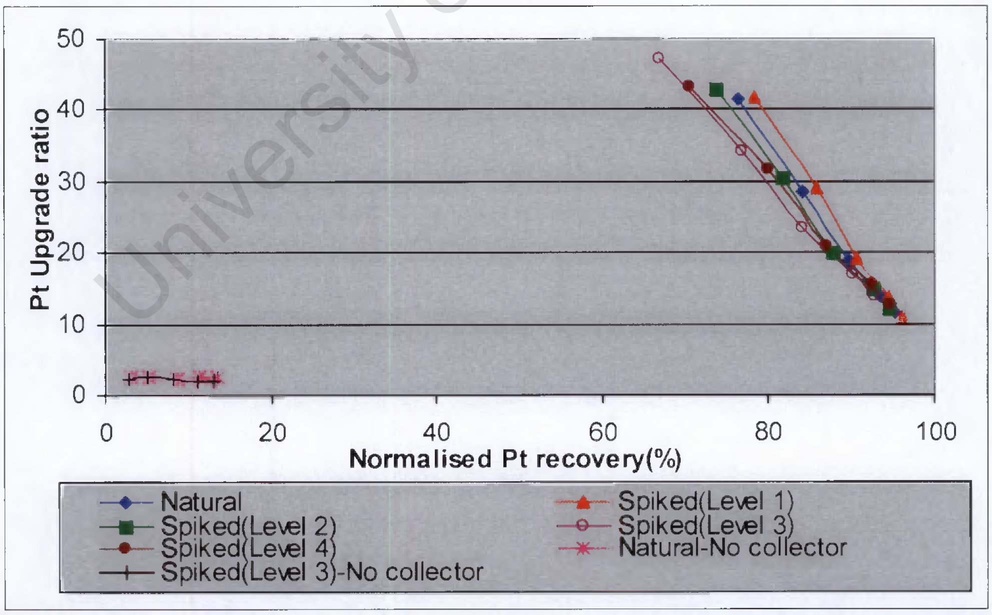


Figure 4.9: Pt Upgrade ratios versus Normalised Pt recoveries for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

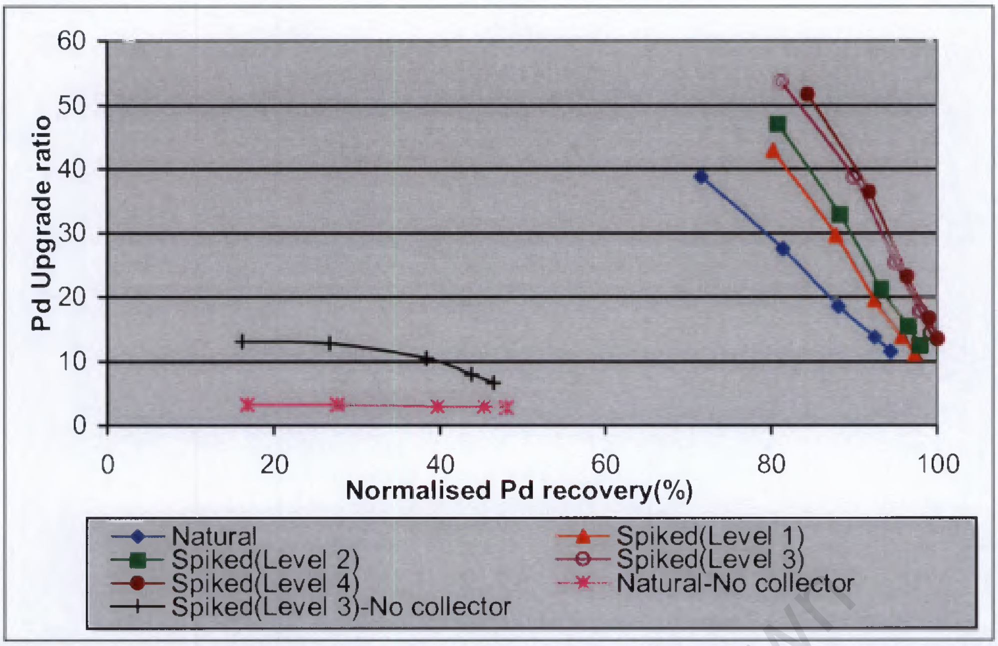


Figure 4.10: Pd Upgrade ratios versus Normalised Pd recoveries for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

The flotation rate constants determined from the Klimpel model (Table 4.6) show that tests carried out with collector produced much better flotation behaviour going by their higher flotation rate constants compared to the tests carried out without collector. This is also illustrated in Figures 4.11 and 4.12 in which Pt and Pd recoveries are plotted as functions of time.

TEST	**Pt**			**Pd**		
	k (min^{-1})	**Rec.$_\infty$ (%)**	**R^2**	**k (min^{-1})**	**Rec.$_\infty$ (%)**	**R^2**
Natural	2.41	95.0	0.97	1.95	94.5	0.98
Natural-No collector	0.14	24.7	0.99	0.18	26.9	0.99
Spiked (Level 1)	2.62	95.9	0.97	2.75	97.2	0.98
Spiked (Level 2)	2.14	94.1	0.96	2.74	97.9	0.98
Spiked (Level 3)	1.67	92.2	0.96	2.64	99.6	0.99
Spiked (Level 3)-No collector	0.20	15.6	0.99	0.43	51.6	1.00
Spiked (Level 4)	1.83	94.4	0.97	3.05	100	0.99

Table 4.6: Pt and Pd flotation rate constants for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

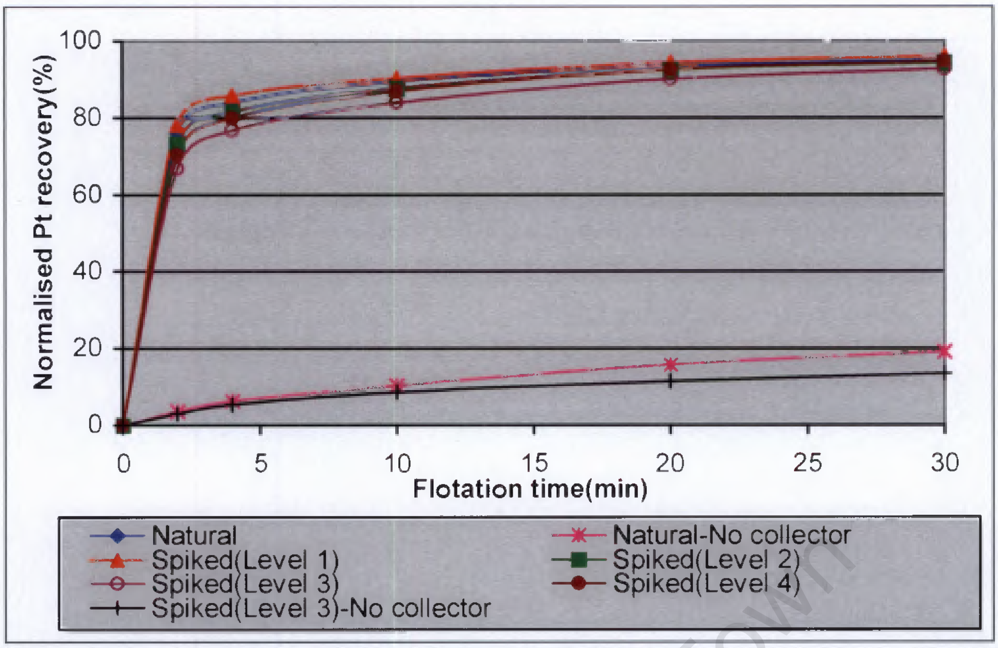


Figure 4.11: Pt Recovery versus Flotation time for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

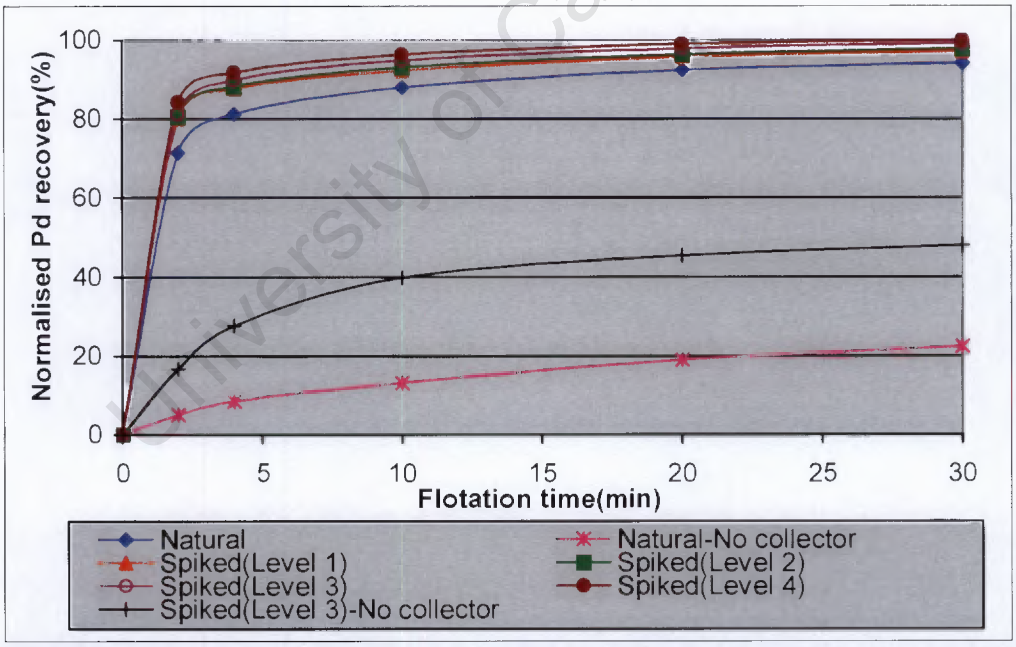


Figure 4.12: Pd Recovery versus Flotation time for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

It is important to note that since Pt and Pd recoveries were of similar orders of magnitude for natural and spiked samples, this indicated that the extra Pt and Pd from the spiking was being recovered to the concentrates in a manner similar to the naturally occurring Pt and Pd. The results achieved thus far show that synthetic PGMs can be used to simulate in general the flotation behaviour of the naturally occurring PGMs in the Merensky reef ore. Appendix E presents the results for Cu, Ni and Au grades versus recoveries.

4.2 A comparison of Flexi-Float configurations

The Flexi-Float was run in two configurations as given in Figure 3.2 for reasons that are discussed in detail in chapter 5. In this section, a comparison of the two Flexi-Float configurations are compared using Pt and Pd assay results.

		(g/t)					(%)	
		Pt	**Pd**	**Au**	**As**	**Te**	**Cu**	**Ni**
Configuration 1	**Assayed**	1.76	2.51	0.28	0.76	0.70	0.17	0.42
	Calc.	1.42	2.37	0.24	0.99	0.92	0.18	0.42
	Accountability (%)	81	94	86	130	132	106	101
Configuration 2	**Assayed**	1.62	2.55	0.28	0.81	0.98	0.17	0.43
	Calc.	1.46	2.37	0.26	1.06	0.98	0.14	0.41
	Accountability(%)	90	93	94	130	100	80	95

Table 4.7: Normalised assayed and calculated Platreef head grades from the two Flexi-Float configurations.

Table 4.7 shows Pt and Pd head grades and accountabilities. The accountability can be used as an error indicator as it is a percentage ratio of the calculated grades to the assayed grades. It can be seen that the accountabilities were in the range 80% to 132% with generally better accountabilities in configuration 2.

Table 4.8 shows the final recoveries and grades achieved in the two configurations. It can be seen that the final Pt and Pd recoveries for both configurations were similar, all lying in the range of 83% to 86%. The mass pulls for the two configurations were also quite similar.

	Mass Pull	Pt		Pd		As		Te	
	(%)	Rec.	Grade	Rec.	Grade	Rec.	Grade	Rec.	Grade
		(%)	(g/t)	(%)	(g/t)	(%)	(g/t)	(%)	(g/t)
Configuration 1	11.97	86.1	9.89	87.2	15.39	54.8	2.68	82.6	3.14
Configuration 2	12.28	86.7	12.87	88.2	20.77	52.8	4.73	89.9	7.48

Table 4.8: Pt, Pd, As and Te normalised final grades and recoveries from the Flexi-Float running on Platreef ore.

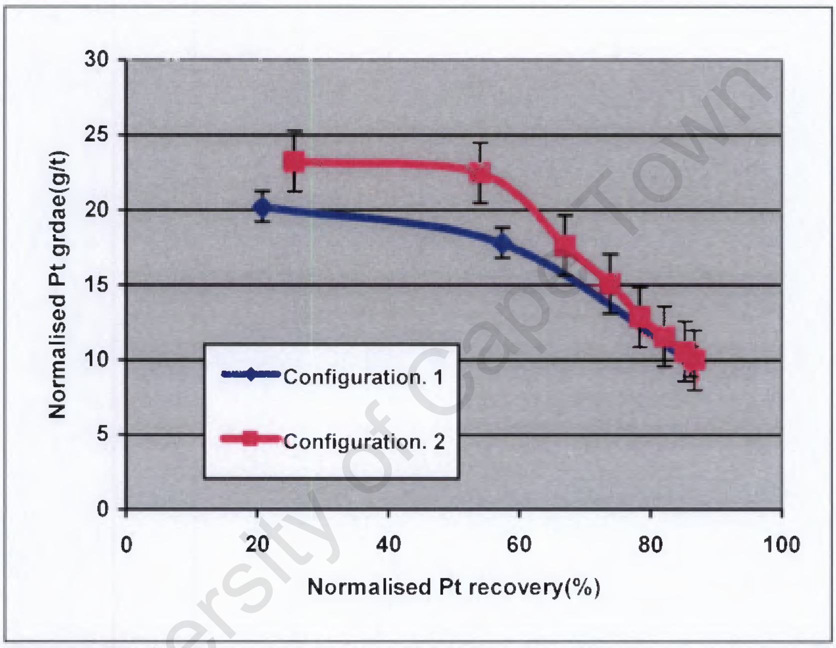


Figure 4.13: Normalised Pt grades versus Normalised Pt recoveries down the bank of the Flexi-Float for the two configurations investigated using Platreef ore.

Figure 4.13 shows the cumulative Pt grade versus the cumulative Pt recovery for each configuration plotted with 95% confidence limits. The Pt flotation response profile for Configuration 1 consists of three points representing cumulative grades and recoveries of the three concentrates sampled as illustrated in Figure 3.2. The Pt flotation response of Configuration 2 on the other hand is represented by eight cumulated points as eight concentrates were sampled (Figure 3.2). This comparison shows that despite configuration 2 producing slightly higher Pt grades in the early stages, the final grades and recoveries were similar for the two configurations. The similarity of shapes of the curves was sufficient to validate the use of only configuration 1, as will be seen in subsequent sections, for mineralogical flotation characterisation down the Flex-Float bank.

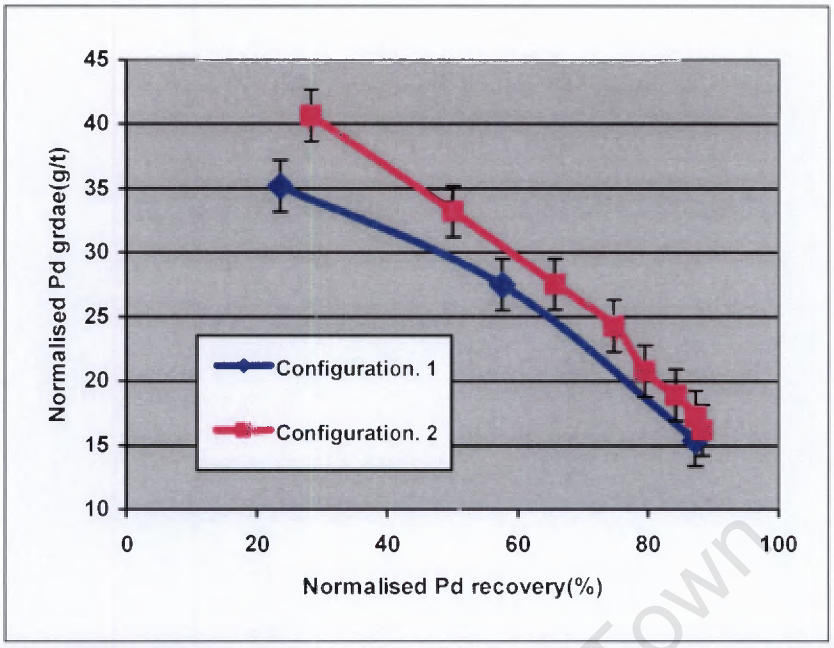


Figure 4.14: Normalised Pd grades versus Normalised Pd recoveries down the bank of the Flexi-Float for the two configurations investigated using Platreef ore.

Figure 4.14 shows the cumulative Pd grade versus the cumulative Pd recovery for each configuration plotted with 95% confidence limits. The Pd flotation response profile for Configuration 1 consists of three points representing cumulative grades and recoveries of the three concentrates sampled (Figure 3.2). The Pd flotation response of Configuration 2 on the other hand is represented by eight cumulated points since eight concentrates were sampled (Figure 3.2). This comparison shows that despite configuration 2 producing slightly higher Pt grades in the early stages, the final grades and recoveries were similar for the two configurations. The similarity of shapes of the curves validated the use of only configuration 1, as will be seen in subsequent sections, for mineralogical flotation characterisation down the Flex-Float bank. This validation is further supported by the similarity of the curves in Figures 4.15 and 4.16 in which Pt and Pd recoveries are plotted as functions of time.

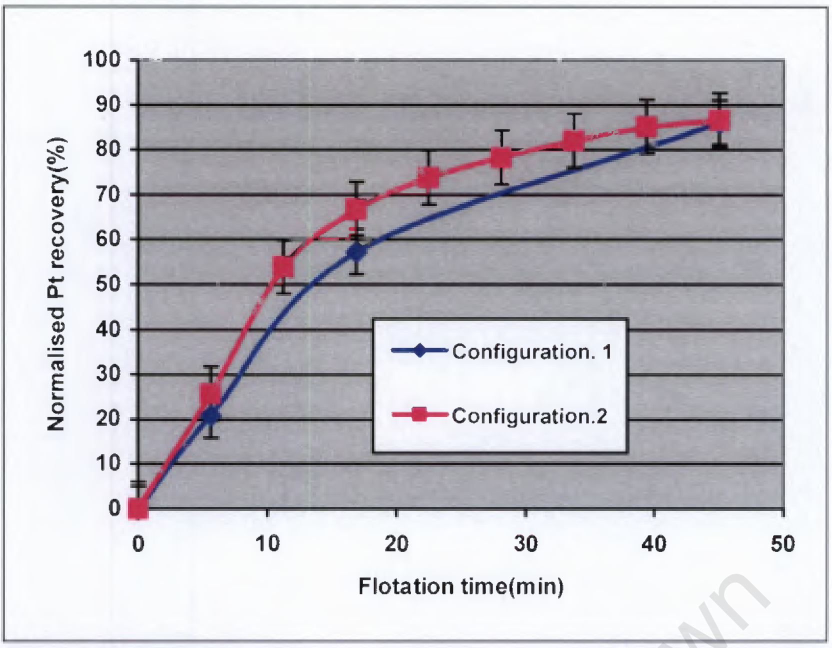


Figure 4.15: Normalised Pt recovery versus Flotation time down the bank of the Flexi-Float for the two configurations investigated using Platreef ore.

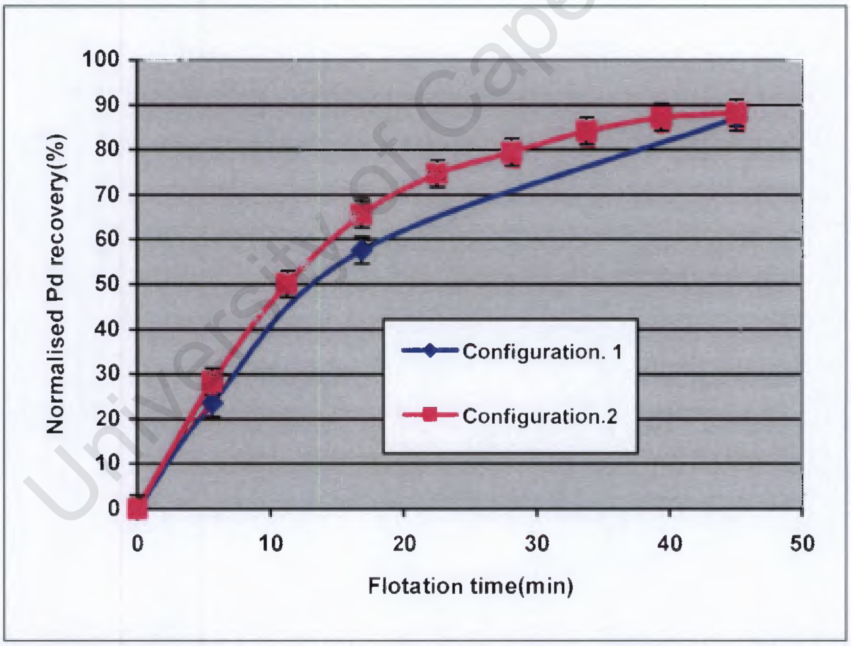


Figure 4.16: Normalised Pd recovery versus Flotation Time down the bank of the Flexi-Float for the two configurations investigated using Platreef ore.

4.3 Comparing the flotation responses of PGE tellurides Vs PGE arsenides

Various tests were carried out to characterise and compare the flotation responses of PGE tellurides and PGE arsenides. Amongst the tests conducted, some compared the naturally occurring forms of these PGMs and in others synthetic equivalent PGMs were compared. The results from these tests are reported in this section.

4.3.1 Down the Flexi-Float bank

The flotation responses of naturally occurring PGE tellurides and PGE arsenides in the Platreef ore were characterised in both configurations of the Flexi-Float test earlier referred to in section 4.2. The behaviour of the PGE tellurides and PGE arsenides down the bank was traced by analysing for Te and As respectively.

Figure 4.17 compares the flotation responses of PGE tellurides and arsenides. It can be seen that tellurides produce significantly better flotation responses compared to arsenides, viz. final recoveries of more than 30% points better than those of PGE arsenides.

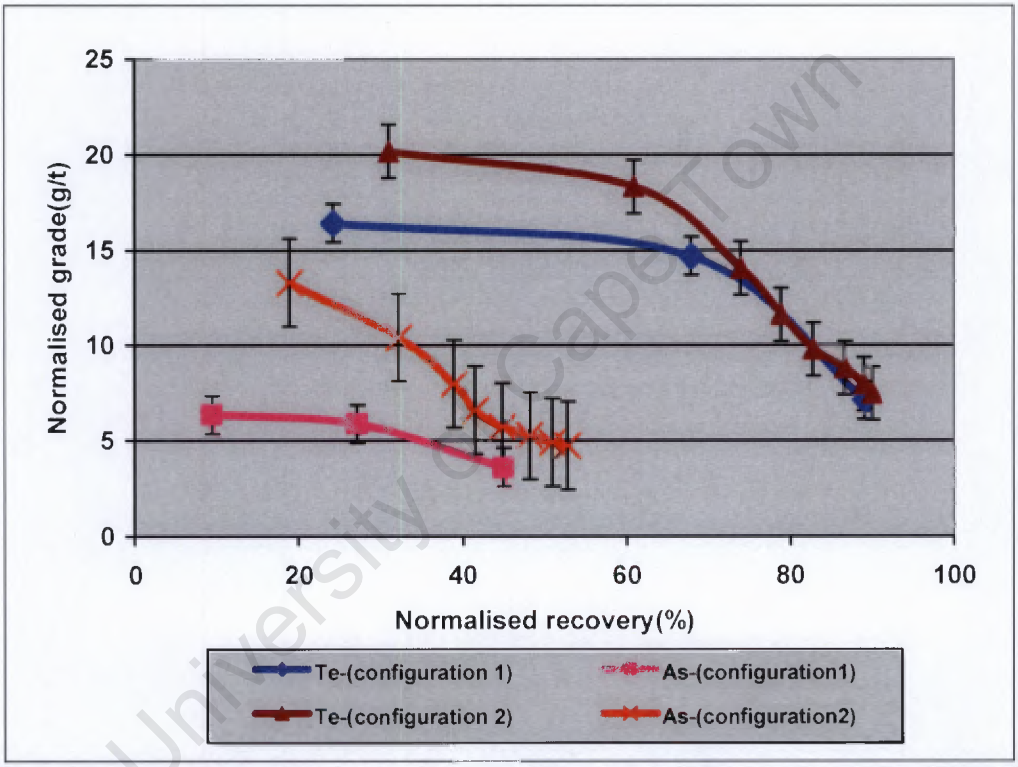


Figure 4.17: Te and As Normalised grades Vs Normalised Te and As recoveries for Platreef ore down the bank of the Flexi-Float for both configurations. As tellurium and arsenic are mainly associated with PGMs in this particular Platreef sample in the form of tellurides and arsenides respectively, their flotation responses as seen in this graph can be taken to reflect the flotation response of PGE tellurides and arsenides.

In order to eliminate the effect of differences in head grades in the flotation response comparison, Te & As upgrade ratios are plotted versus their respective recoveries as given in Figure 4.18. This graph shows that tellurides had initial recoveries in excess of 20% with initial upgrade ratios exceeding 15 compared to those of arsenides at less than 20% and less than 12 respectively. Over almost the entire flotation period tellurides had about double the upgrading ratios of arsenides at equivalent recoveries.

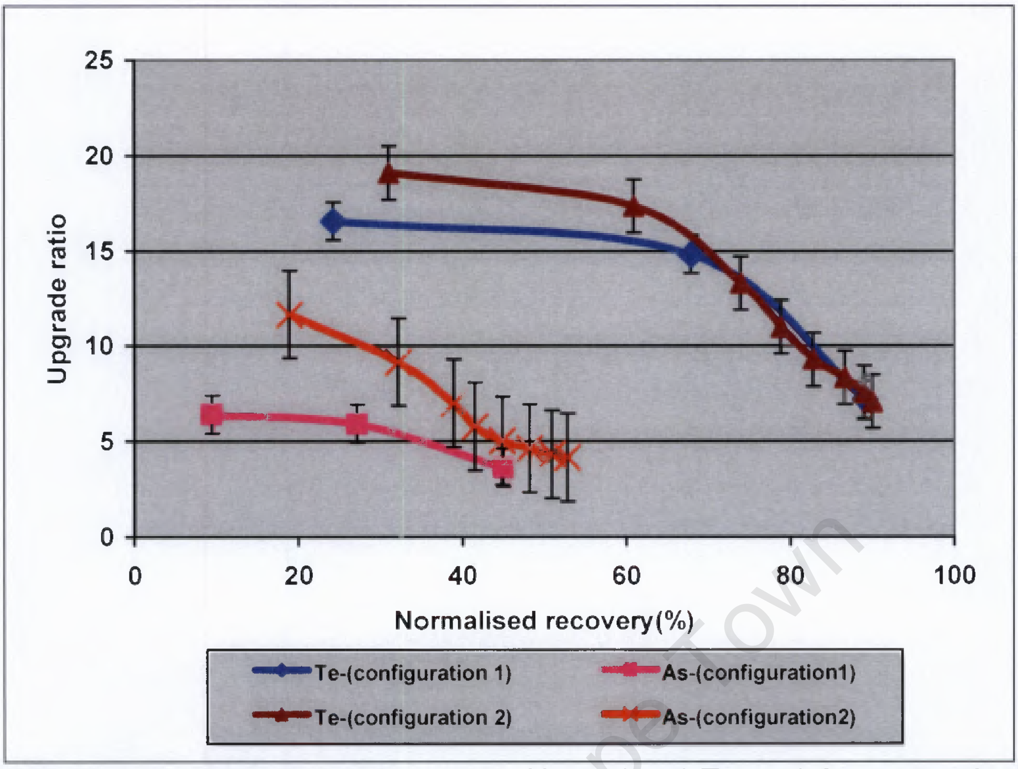


Figure 4.18: Te and As Upgrade ratios versus Normalised Te and As recoveries for Platreef ore down the bank of the Flexi-Float. As tellurium and arsenic in this particular sample have been found to be associated with only PGMs in the form of tellurides and arsenides respectively, their flotation responses as seen in this graph can be taken to reflect the flotation responses of PGE tellurides and arsenides respectively.

PGE tellurides and arsenides flotation rate constants presented in Table 4.9 were determined using the perfectly mixed model (Runge et al., 2003) as shown in equation 4.2.

$$Rec = [kt/(1+kt)] \qquad 4.2$$

Where,

Rec = recovery determine from assays

k= flotation rate constant

t= flotation time

k is a model parameter which was determined by numerical methods. The results show that tellurides had higher rate constants in both configurations and consequently better flotation response. This is further illustrated in Figure 4.19 in which tellurides and arsenides recoveries are plotted as functions of time (residence time down the bank).

TEST	Tellurides		Arsenides	
	k (min^{-1})	R^2	k (min^{-1})	R^2
Configuration 1	0.09	0.99	0.02	0.99
Configuration 2	0.11	0.98	0.03	0.97

Table 4.9: PGE tellurides and arsenides flotation rate constants determined using the perfectly mixed models for the two Flexi-Float configurations running on Platreef ore.

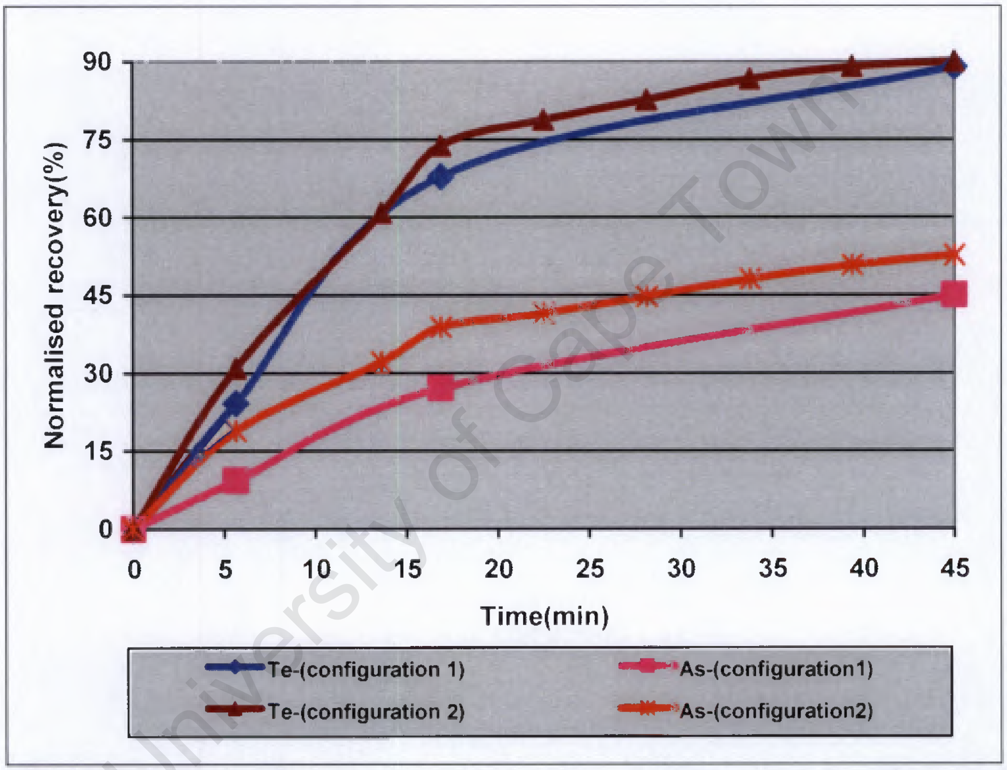


Figure 4.19: Te and As Normalised recoveries versus Flotation time for Platreef ore down the bank of the Flexi-Float. As tellurium and arsenic in this particular sample have been found to be associated with only PGMs in the form of tellurides and arsenides respectively, their flotation responses as seen in this graph can be taken to reflect the flotation response of PGE tellurides and arsenides.

4.3.2 Batch flotation of Platreef ore spiked with synthetic PGMs.

This section presents results from testwork aimed at comparing the flotation responses of synthetic moncheite (Pt telluride) and sperrylite (Pt arsenide) spiked in separate samples of a Platreef ore. It should be noted that in this case individual minerals are being added as opposed to a blend. These tests were carried out on the basis of having previously established (section 4.1) that synthetic PGMs adequately simulate the flotation response of naturally occurring PGMs in the Platreef ore. The testwork was carried out by conducting batch flotation tests on Platreef ore samples that had been separately spiked with equal amounts of synthetic moncheite and sperrylite. The head grades for these tests are given in Table 4.10.

	Test	Pt:Pd ratio	(g/t)				(%)	
			Pt	Pd	Au	3E	Cu	Ni
1	Natural Platreef	1.12	2.66	2.37	0.36	5.39	0.19	0.39
2	With sperrylite (Pt arsenide)	2.12	5.38	2.54	0.37	8.29	0.22	0.39
3	With moncheite (Pt telluride)	1.80	4.58	2.55	0.44	7.58	0.22	0.39

Table 4.10: Normalised head grades of Platreef ore separately spiked with equal amounts of synthetic sperrylite and moncheite.

The sample spiked with sperrylite had a slightly higher Pt head grade as was expected on the basis of the higher stoichiometric Pt content in sperrylite compared to moncheite. The Pt and Pd final grades and recoveries (Table 4.11) show that natural Platreef ore and that enriched with synthetic moncheite produced similar Pt recoveries, viz. around 83%. The sample enriched with the synthetic sperrylite however produced a much poorer Pt recovery at 68%. The Pd recoveries were all quite comparable for the three tests, ranging between 74% and 79% since no extra Pd was added in this case.

	Test	Mass Pull (%)	Pt Rec. (%)	Pt Grade (g/t)	Pd Rec. (%)	Pd Grade (g/t)
1	Natural Platreef	5.67	82.9	37.63	73.9	29.87
2	With sperrylite	5.42	68.2	65.47	79.1	35.90
3	With moncheite	5.04	82.9	73.05	77.1	37.67

Table 4.11: Pt and Pd normalised ultimate concentrate grades and normalised recoveries from the test in which Platreef ore was separately spiked with equal amounts of synthetic sperrylite and moncheite.

Figure 4.20 shows that the Pt final recovery remained unaffected when natural Platreef ore was spiked with synthetic moncheite but reduced when spiked with sperrylite. It can also be seen that the sample spiked with moncheite produced a better flotation response compared to that of the sample spiked with sperrylite. Figure 4.21 shows that the Pd final recoveries of the Platreef remain unaffected when spiked with either moncheite or sperrylite. It is interesting to note the upgrade ratio differences in the early stages which progressively reduce to comparable final results.

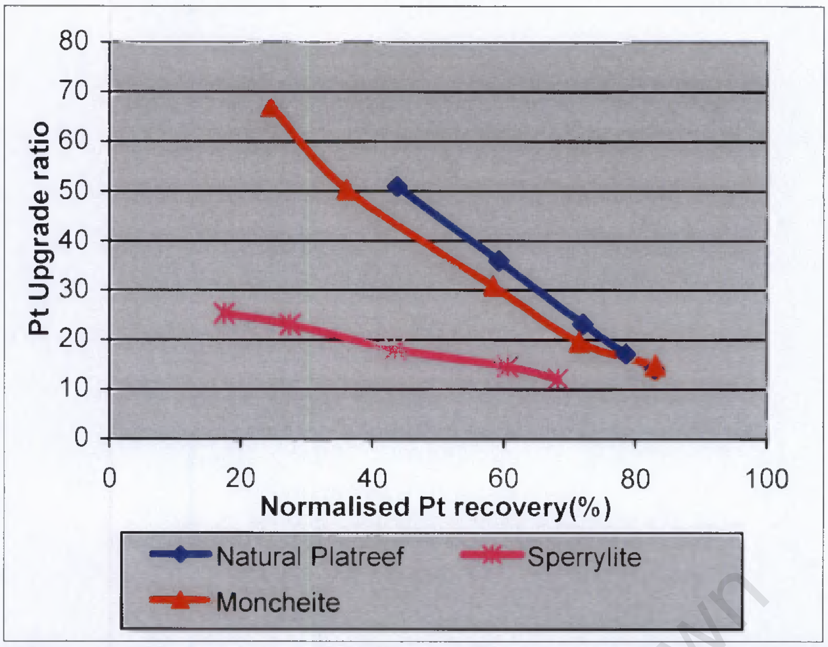


Figure 4.20: Pt Upgrade ratios versus Normalised Pt recovery for flotation tests carried out on Platreef ore as well as the same ore separately spiked with synthetic moncheite and sperrylite.

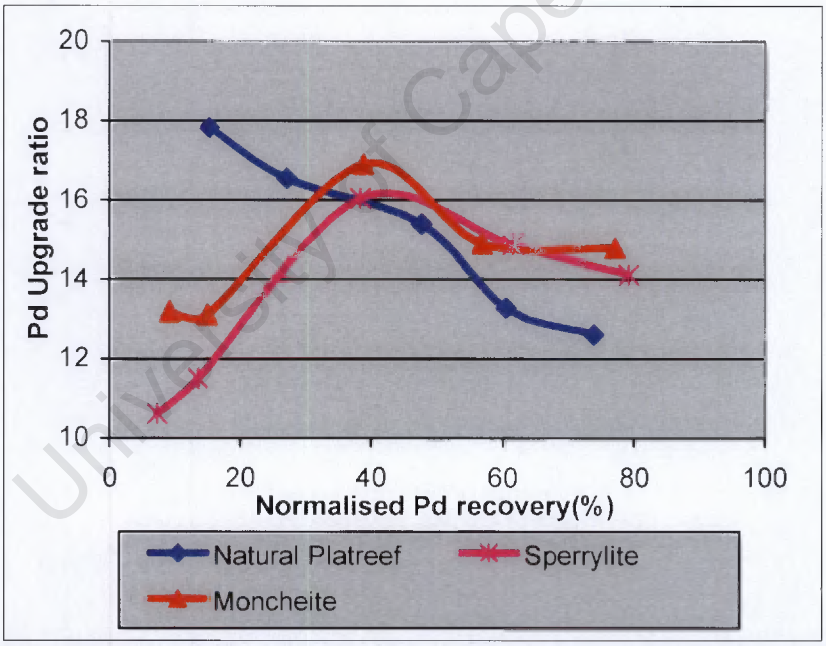


Figure 4.21: Pd Upgrade ratio versus Normalised Pd recovery for flotation tests carried out on Platreef ore as well as the same ore separately spiked with synthetic moncheite and sperrylite.

Looking at Pt recoveries as functions of time (Figure 4.22), it can be seen that despite the lower recoveries in the early stages for the sample spiked with moncheite compared to the natural sample, their final recoveries were the same. The recovery from the sample spiked with arsenide was consistently lowest throughout the entire flotation period.

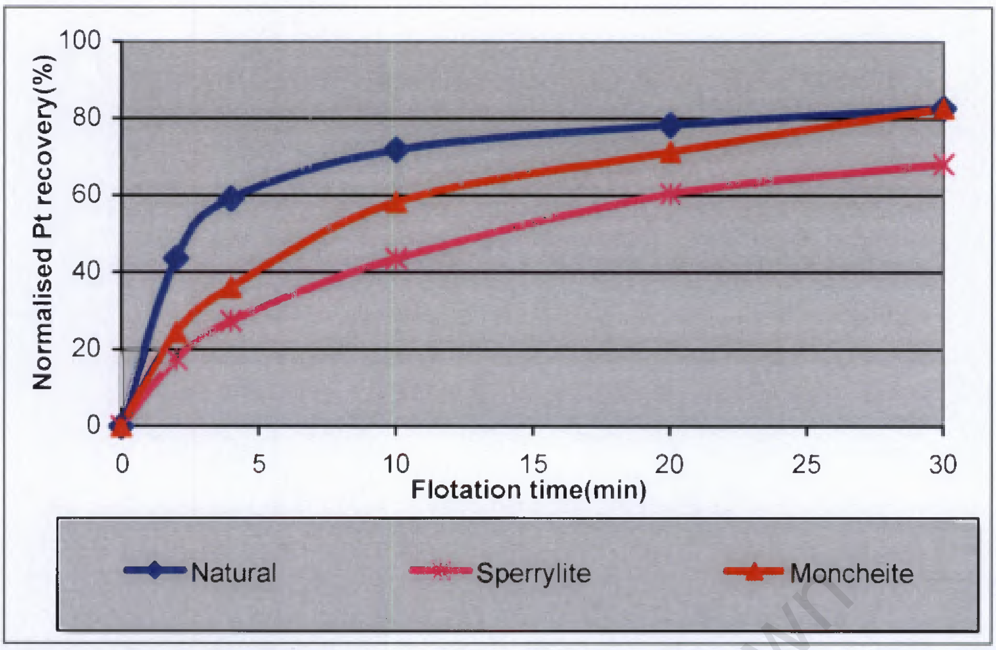


Figure 4.22: Normalised Pt Recovery versus Flotation time flotation tests carried out on Platreef ore as well as the same ore separately spiked with synthetic moncheite and sperrylite.

4.3.3 Barren feldspathic pyroxenite ore spiked with synthetic minerals.

The aim of this test was to compare the flotation of synthetic PGE telluride and PGE arsenides in a natural ore environment barren of naturally occurring PGMs and BMS. The flotation response of these minerals as well as in combination with synthetic base metal sulphide was also tested. Table 4.12 shows the Pt head grades for the various tests carried out.

	Ore	Description	Pt Head (g/t)
1	BFP	Barren feldspathic pyroxenite	0.07
2	Te	BFP spiked with synthetic $Pt(Te\ Bi)_2$	13.78
3	As	BFP spiked with synthetic $PtAs_2$	15.26
4	Te-As	BFP spiked with synthetic $Pt(Te\ Bi)_2$ and $PtAs_2$	27.26
5	Te-As-S	BFP spiked with synthetic $Pt(Te\ Bi)_2$,$PtAs_2$ and NiFeS	28.01

Table 4.12: Normalised Pt head grades for barren feldspathic pyroxenite ore (BFP) as well as the same ore spiked with various synthetic minerals (cf.Table B2 in Appendix B).

The amounts of moncheite and sperrylite added to samples 2 and 3 respectively, were chosen to achieve similar Pt head grades in these two samples. The amounts of moncheite and sperrylite used to prepare samples 4 and 5 were those amounts of each of these mineral types added to sample 2 and 3. Hence the Pt grades in samples 4 and 5 were double those of samples 2 and 3.

This test provided an opportunity to compare flotation responses of Pt telluride and Pt arsenide under very similar conditions eliminating possible differences in various aspects such as particle size, liberation or head grades.

Table 4.13 and Figure 4.23 show that the test in which barren feldspathic pyroxenite (BFP) was spiked with moncheite ($Pt(TeBi)_2$) produced the highest recovery whereas that spiked with sperrylite ($PtAs_2$) produced the lowest Pt recovery. The highest grades were produced by the test in which BFP was spiked with a combination of moncheite, sperrylite and pentlandite (Te-As-S) followed by that spiked with moncheite and sperrylite (Te-As). It should however be noted that the Pt head grades in these two tests (Te-As & Te-As-S) with higher concentrate grades were as high as double the Pt head grades in any of the other two tests.

	Test	**Mass Pull (%)**	**Pt Rec. (%)**	**Pt Grade (g/t)**
	BFP	-	-	-
2	Te	2.25	92.5	548.7
3	As	1.97	67.3	503.8
4	Te-As	2.07	77.3	986.7
5	Te-As-S	1.73	79.3	1241.9

Table 4.13: Normalised Pt ultimate concentrate grades and normalised Pt recoveries for the tests carried out by spiking Barren feldspathic pyroxenite with various synthetic minerals.

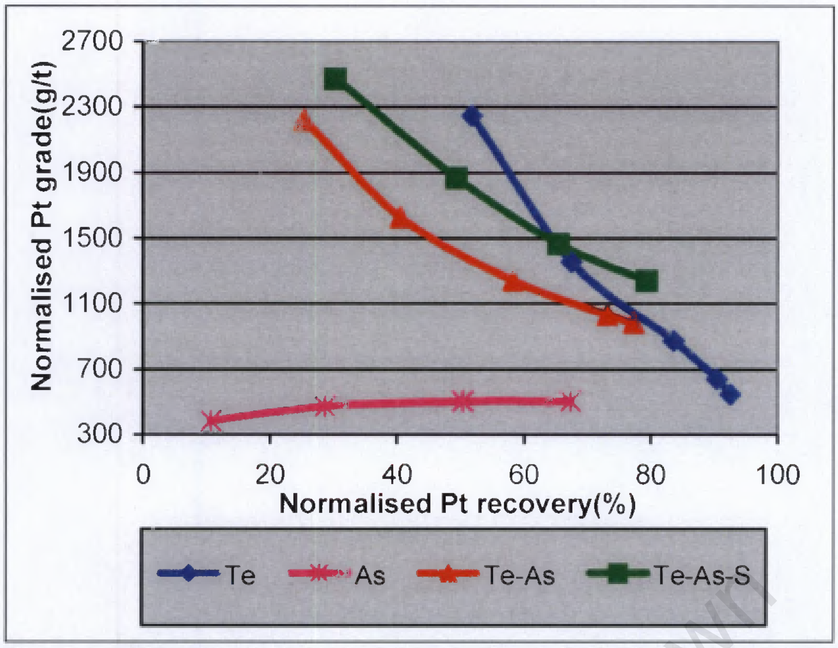


Figure 4.23: Normalised Pt grades versus Normalised Pt recoveries for flotation tests carried out on barren feldspathic pyroxenite ore spiked with various combinations of synthetic moncheite, sperrylite and pentlandite.

To eliminate the effect of head grade differences in making comparisons, Pt upgrade ratio was plotted against recovery (Figure 4.24). From this it can be seen that moncheite produced the best flotation response with sperrylite producing the worst with hardly any differential upgrading from one flotation stage to the next for the latter. It can also be seen that a combination of moncheite and sperrylite (Te-As) produces an intermediate response which is slightly enhanced on addition of pentlandite (Te-As-S).

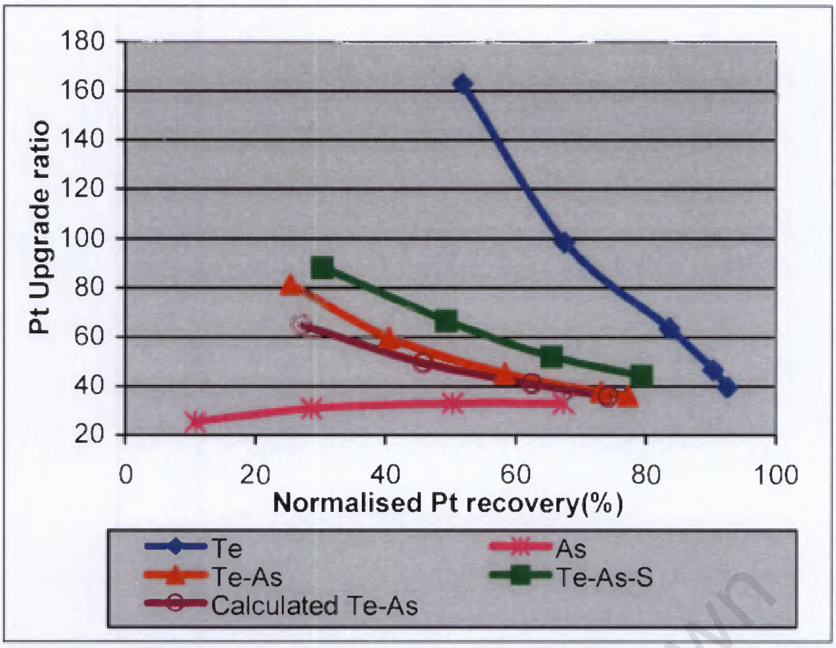


Figure 4.24: Pt Upgrade ratios versus Normalised Pt recoveries for flotation tests carried out on barren feldspathic ore spiked with various combinations of synthetic moncheite, sperrylite and pentlandite.

The Pt flotation rate constants determined from the Klimpel model (Table 4.14) show that Pt tellurides have the highest rate constant and consequently the best flotation response. Pt arsenides had the lowest rate constant whereas that of a combination of tellurides and arsenides was intermediate. Addition of a base metal sulphide to the combination slightly improved the flotation response. This however only occurred towards the end of the flotation period as can be seen from Figure 4.25 in which Pt recoveries are plotted against flotation time.

TEST	**Pt**		
	k (min^{-1})	**Rec.$_\infty$ (%)**	**R^2**
Te	0.88	95.3	0.96
As	0.21	88.1	0.99
Te-As	0.36	84.2	0.96
Te-As-S	0.48	86.6	0.97

Table 4.14: Pt flotation rate constants determined from the Klimpel model for flotation tests carried out on barren feldspathic ore spiked with various combinations of synthetic moncheite, sperrylite and pentlandite.

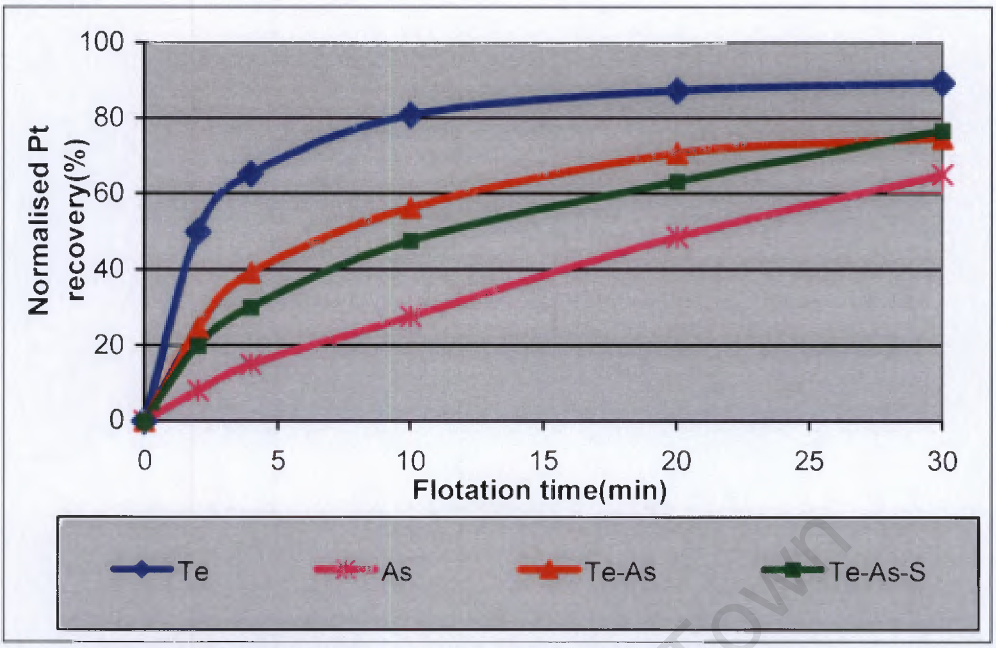


Figure 4.25: Normailised Pt recoveries versus Flotation time for flotation tests carried out on barren feldspathic ore spiked with various combinations of synthetic moncheite, sperrylite and pentlandite.

4.4 Platreef ore mineralogy down the Flexi-Float bank

Having established from section 4.3 that PGE tellurides produce better flotation response compared to PGE arsenides it was necessary to start investigating why this is so. Amongst the many factors that are known to affect the flotation response of minerals, those investigated in this study included mineralogy, reagent regimes and mineral surface chemistry. The results presented in this section are from mineralogical examinations carried out down the bank of the Flexi-Float in configuration 1 and running on Platreef ore as earlier described in section 4.2. The objective in this section is to mineralogically compare PGE tellurides and PGE arsenides in the various streams of the Flexi-Float in order to see if mineralogy contributes to the observed differences in the flotation responses of these PGMs.

4.4.1 PGM grain statistics

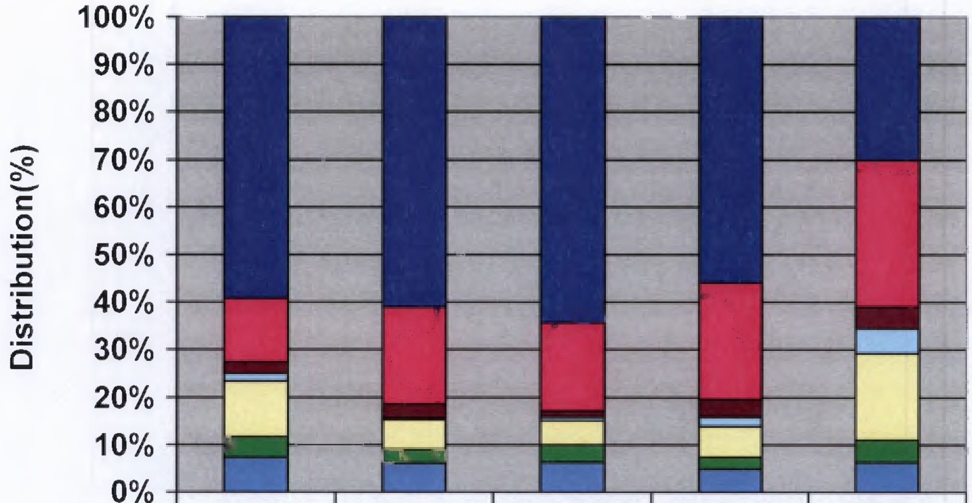
Table 4.11 shows that the total PGM grains analysed in all the Flexi-Float streams far exceeded the statistically required minimum of 100 grains for any collective PGM mineralogical classification. This means that sufficient grains were analysed to complete a mineralogical classification such as PGM distribution down the bank of the Flexi-Float. In addition to such a classification, cardinal to this study is the comparison of mineralogical characterisation down the bank of the separate PGM species. In this regard only PGE tellurides and arsenides had sufficient particles analysed to enable such a comparison down the bank. As will be seen in later sections, only PGE tellurides and arsenides will be compared down the bank in terms of their associated particles' size distribution, liberation as well as in terms of their associations.

	Feed	**Conc 1**	**Conc 2-3**	**Conc 4-8**	**Tailings**
PGE telluride	421	534	523	473	302
PGE arsenides	116	108	125	115	113
PGE sulphides	29	63	50	28	44
Ferroplatinum	16	11	12	14	26
PGE alloy	118	108	88	65	93
PGE sulpharsenides	54	65	82	41	35
Gold	47	93	56	53	107
Total	**801**	**982**	**936**	**789**	**720**

Table 4.15: Numbers(n) of PGM particles mineralogically analysed using the MLA on the various samples from the Flexi-Float run on Platreef ore in configuration 1.

4.4.2 PGM distribution

From the PGM distribution results shown in Figure 4.26 it can be seen that PGE telluride are the most abundant PGM in all the Flexi-Float streams followed by PGE arsenides. It can also be seen that the largest notable changes in the distribution in the feed compared to the tailings are those of PGE tellurides and arsenides. The distribution of PGE tellurides in the tailings is half that in the feed whereas that of the arsenides more than doubled in the tailings compared to the feed. This can be taken to be a qualitative indication that PGE tellurides in the Platreef ore had relatively better flotation response or recoveries compared to PGE arsenides.

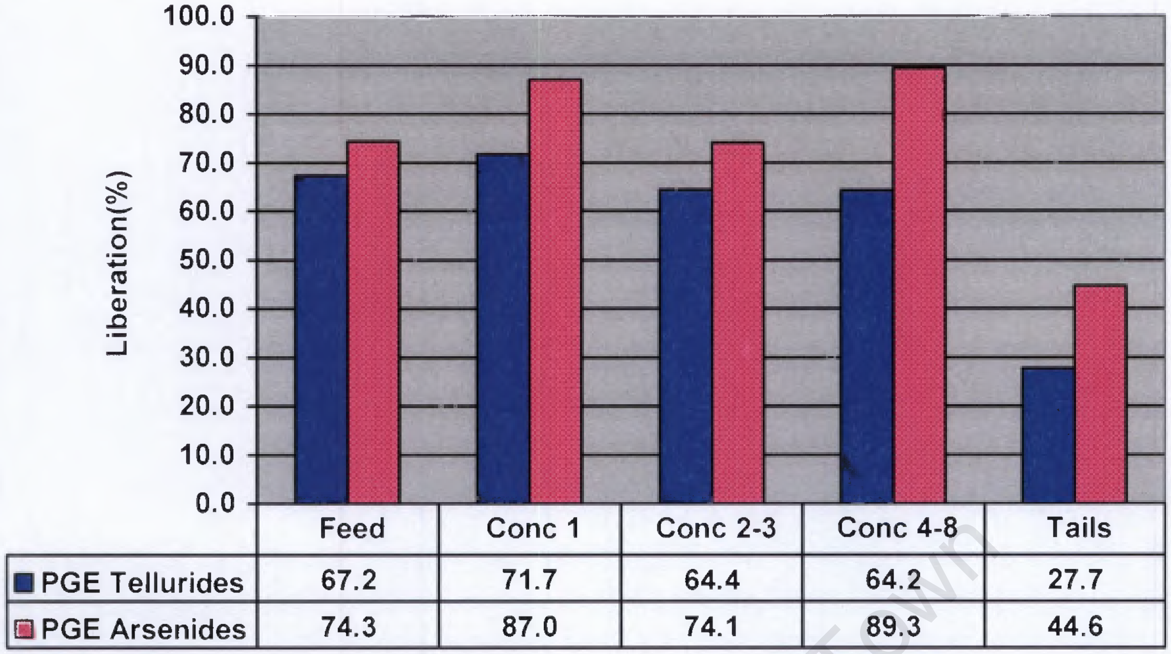


	Feed	Conc 1	Conc 2-3	Conc 4-8	Tails
■ PGE_tellurides	59.2	61.0	64.2	55.9	30.2
■ PGE_arsenides	13.3	20.5	18.8	24.6	30.9
■ PGE_sulphides	2.6	2.8	1.2	3.8	4.5
■ Ferroplatinum	1.6	0.5	0.8	1.9	5.2
■ PGE_alloys	11.7	6.3	5.0	6.5	18.3
■ PGE_sulpharsenides	4.3	2.9	3.7	2.4	4.7
■ Gold	7.3	6.0	6.3	5.0	6.3

Figure 4.26: PGM distribution in the various streams of configuration 1 of the Flexi-Float run on Platreef ore.

4.4.3 Liberation

The PGM liberation results in Figure 4.27 show that PGE tellurides in the feed are far better liberated compared to those in the tailings. This is probably due to a preferential recovery of liberated PGE tellurides to the concentrates thereby depleting the final tailings of this class of PGE tellurides. This is evident from the notably higher levels of liberated PGE tellurides in the concentrates compared to the tailings. A similar observation holds for PGE arsenides which are also better liberated in the feed compared to the tailings. It is also worth noting that the PGE arsenides are better liberated in all the streams of the Flexi-Float compared to PGE tellurides in corresponding streams.

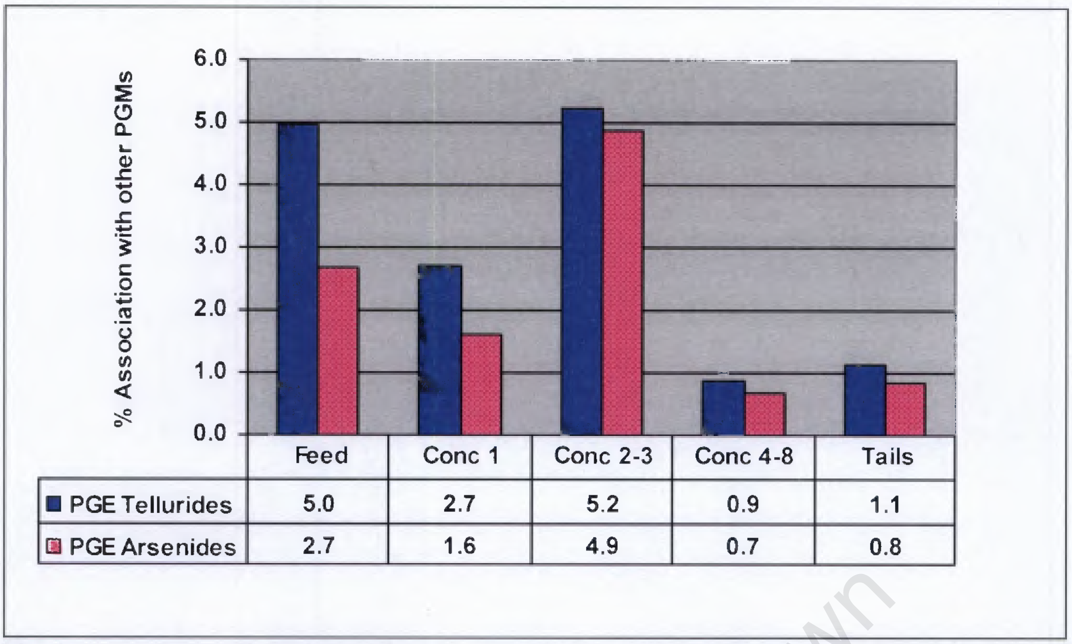


	Feed	Conc 1	Conc 2-3	Conc 4-8	Tails
■ PGE Tellurides	67.2	71.7	64.4	64.2	27.7
■ PGE Arsenides	74.3	87.0	74.1	89.3	44.6

Figure 4.27: Liberation results for PGE telluride and arsenides in the various flotation streams of configuration 1 of the Flexi-Float run on Platreef ore.

4.4.4 Association

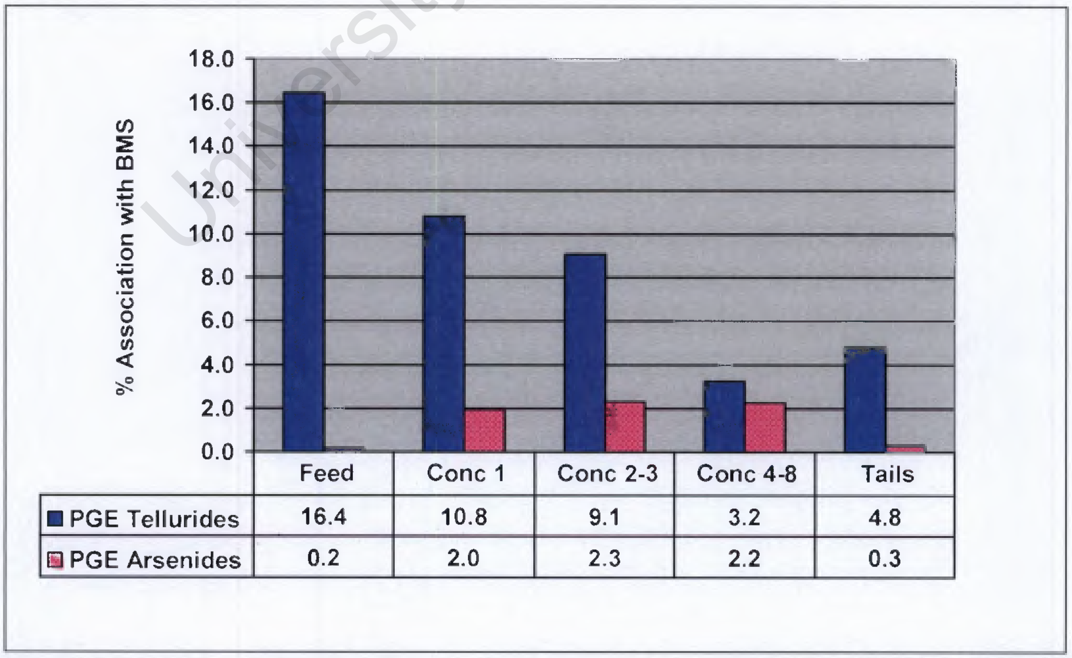
Figure 4.28 shows the association of PGE tellurides and arsenides with other PGM species, it should be pointed out that in the case of PGE tellurides, other PGM species includes PGE arsenides and vice versa. The results show that both PGE tellurides and arsenides have relatively low association with other PGM species in all streams of the Flexi-Float when compared to those liberated as earlier seen. However, within this generally low association, the association of PGE tellurides with other PGMs in the feed was double compared to that of PGE arsenides. In the rest of the Flexi-Float streams the PGE telluride association remains higher than that of PGE arsenides albeit at a reduced difference.



	Feed	Conc 1	Conc 2-3	Conc 4-8	Tails
■ PGE Tellurides	5.0	2.7	5.2	0.9	1.1
▨ PGE Arsenides	2.7	1.6	4.9	0.7	0.8

Figure 4.28: Association of PGE telluride and arsenides with other PGM types in the various flotation streams of configuration 1 of the Flexi-Float run on Platreef ore.

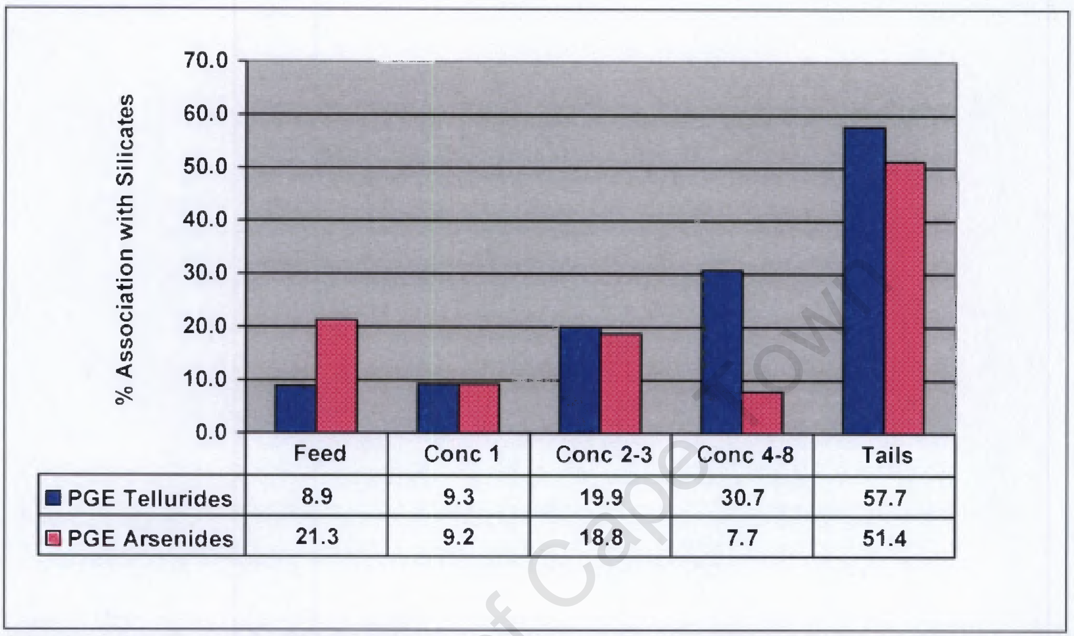
Figure 4.29 shows the association of PGE tellurides and arsenides with base metal sulphides. The results show that the PGE tellurides are substantially associated with BMS and this being most evident in the feed. The PGE arsenides in comparison are a lot less associated with the BMS and more so in the feed.



	Feed	Conc 1	Conc 2-3	Conc 4-8	Tails
■ PGE Tellurides	16.4	10.8	9.1	3.2	4.8
▨ PGE Arsenides	0.2	2.0	2.3	2.2	0.3

Figure 4.29: Association of PGE telluride and arsenides with base metal sulphides (BMS) in the various flotation streams of configuration 1 of the Flexi-Float run on Platreef ore.

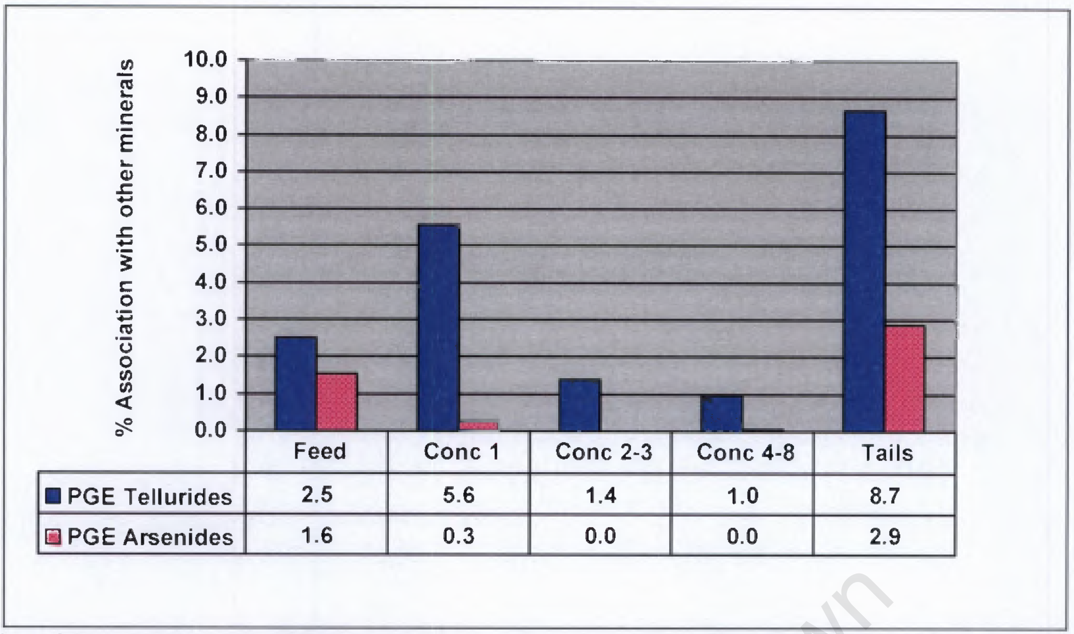
Figure 4.30 shows the association to silicates of PGE tellurides and PGE arsenides and the results show that as would be expected both these PGM types in the tailings are highly associated , in excess of 50%, with silicates. It is also interesting to note that PGE arsenides in the feed, in excess of 20%, are substantially associated with silicates which is more than double compared to PGE tellurides.



	Feed	Conc 1	Conc 2-3	Conc 4-8	Tails
■ PGE Tellurides	8.9	9.3	19.9	30.7	57.7
■ PGE Arsenides	21.3	9.2	18.8	7.7	51.4

Figure 4.30: Association of PGE telluride and arsenides with silicates in the various flotation streams of configuration 1 of the Flexi-Float run on Platreef ore.

Figure 4.31 shows the association of PGE tellurides and arsenides with the rest of the other minerals such as oxides which have not been included in the earlier reported associations. It can be seen that this class of association at less than 3% in the feed for both PGE tellurides and arsenides constitutes only a small proportion. However, this association for PGE tellurides in the tailings rises to significant levels which is in excess of 8%. In summary with respect to the tellurides in the feed, Figures 4.27 to 4.31 show that 67.2% were liberated, 5.0% were associated with other PGMs, 16.4% were associated with BMS, 8.9% associated with silicates with the balance of 2.5% being associated with other types of minerals. The same analysis can be applied to tellurides or arsenides in any chosen stream of the Flexi-Float.



	Feed	Conc 1	Conc 2-3	Conc 4-8	Tails
■ PGE Tellurides	2.5	5.6	1.4	1.0	8.7
▨ PGE Arsenides	1.6	0.3	0.0	0.0	2.9

Figure 4.31: Association of PGE telluride and arsenides with silicates in the various flotation streams of configuration 1 of the Flexi-Float run on Platreef ore.

4.4.5 Particle size distribution

Particle size distribution results are presented in this section for particles associated with PGE tellurides and PGE arsenides. These will include by way of illustration particles such as that seen in Figure 4.32 which is a fully liberated grain of PdTeBi/PdSb. Also included will be particles such as that in Figure 4.33 which constitutes a grain of PtTeBi associated with a grain of chalcopyrite.

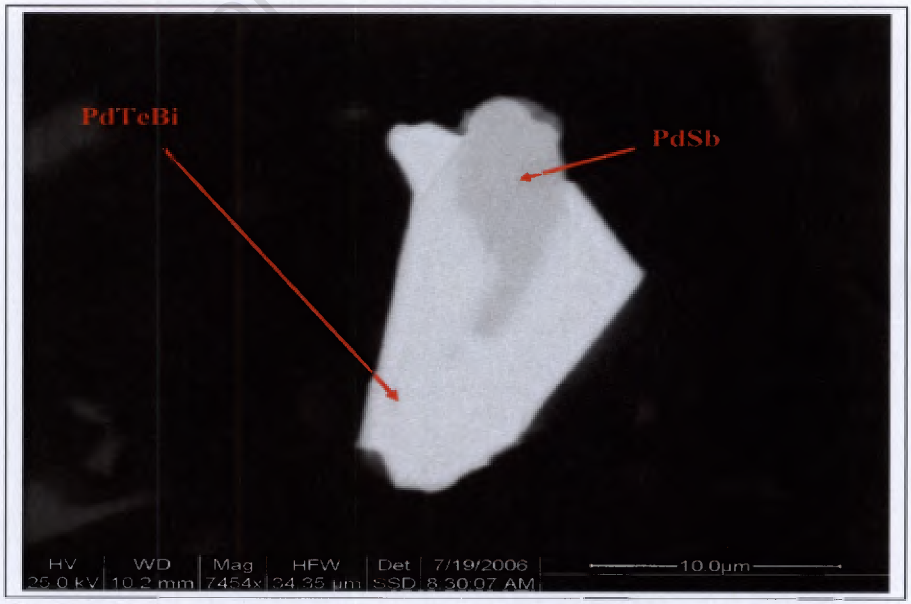


Figure 4.32: Back scattered electron image of a PdTeBi/PdSb grain in the feed to configuration 1 of the Flexi-Float run on Platreef ore.

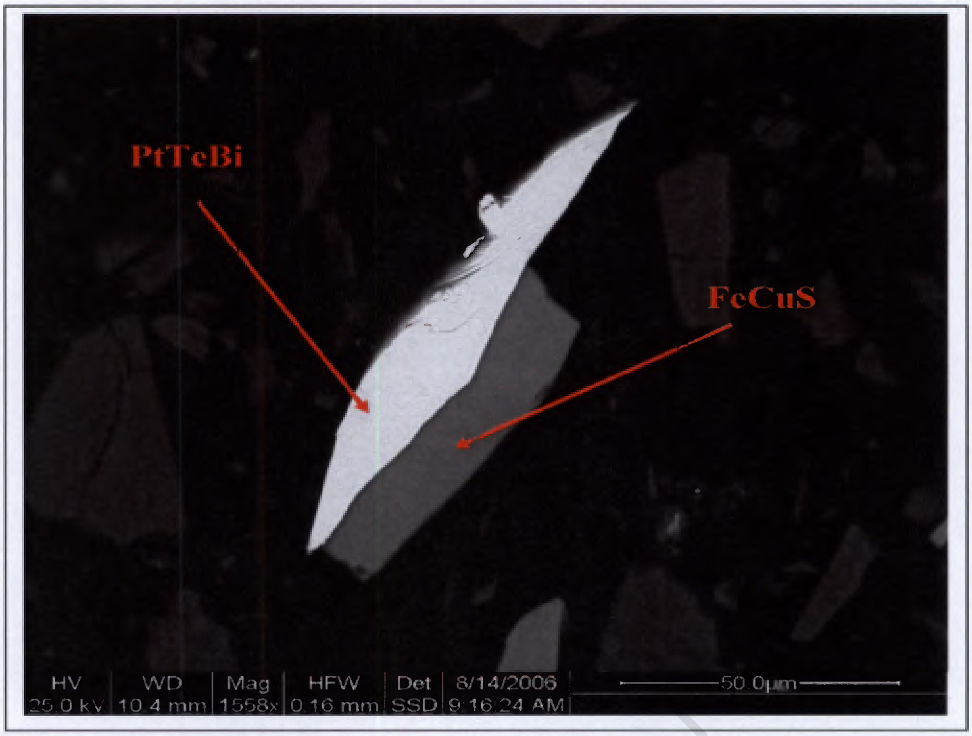


Figure 4.33: Back scattered electron image of a PtTeBi grain associated with chalcopyrite in the feed to configuration 1 of the Flexi-Float run on Platreef ore.

Figure 4.34 shows that particles associated with PGE tellurides in the feed were slightly coarser than those associated with PGE arsenides. The PGE telluride associated particles had a top size of 250µm whereas those associated with PGE arsenides had top size of 125µm. Their size distributions are however quite similar in the lower size fractions.

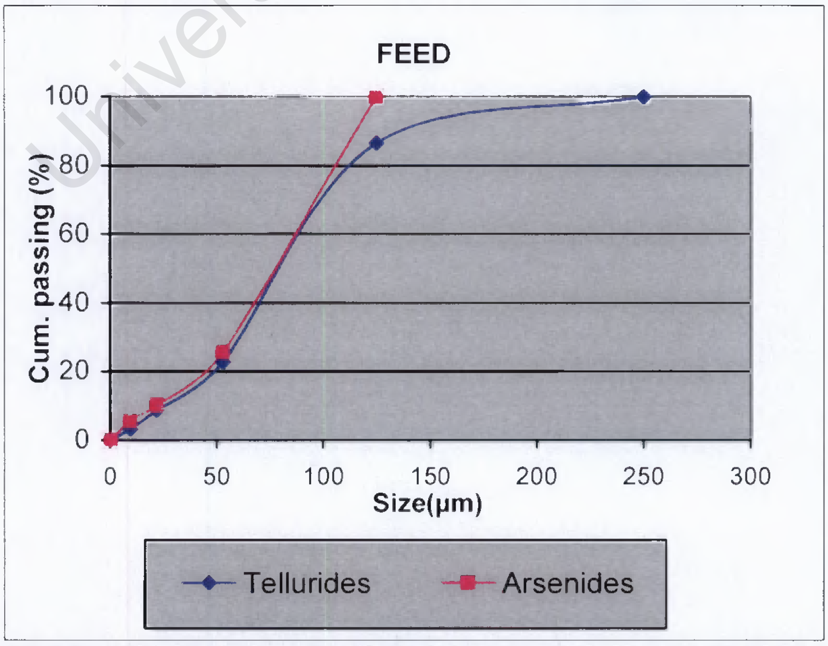


Figure 4.34: Size distribution (% cum. Passing) of particles associated with PGE tellurides and PGE arsenides in the Platreef feed from configuration 1 of the Flexi-Float.

The curves in Figure 4.35 show that particles associated with PGE arsenides that were recovered to Conc 1 had a top size of 50µm and were finer than the corresponding particles associated with PGE tellurides which had a top size of 125µm.

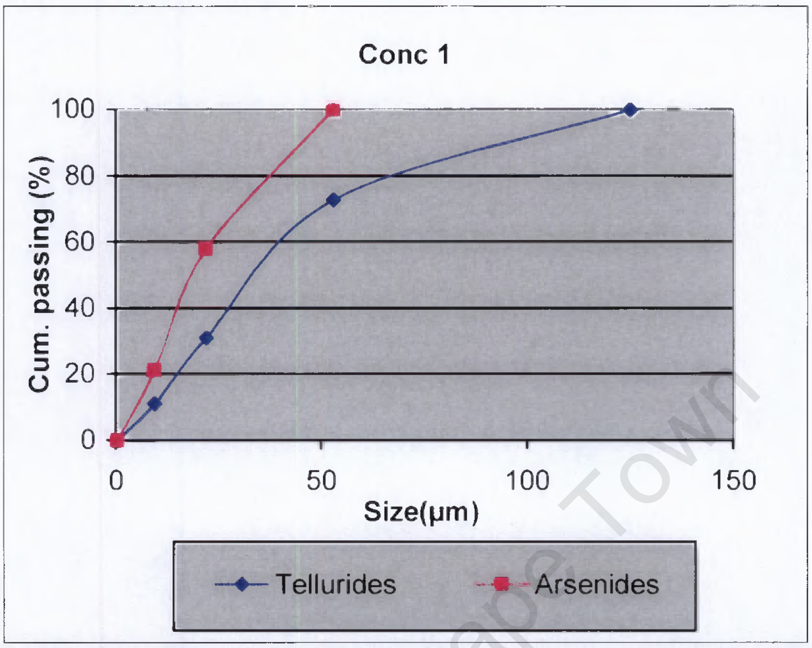


Figure 4.35: Size distribution (% cum. Passing) of particles associated with PGE tellurides and PGE arsenides in the Platreef Conc1 from configuration 1 of the Flexi-Float.

The size distribution trends in Conc 2-3 and Conc 4-8 as seen in Figures 4.36 and 4.37 respectively, are similar to those earlier seen in the feed whereby particles associated with PGE arsenides have a top size of 125µm and are slightly finer than corresponding particles associated with tellurides with a top size of 250µm.

Figure 4.38 shows that in the Flexi-Float tailings also similar to the feed, particles associated with PGE arsenides had a top size of 125µm and were a lot finer compared to particles associated with PGE tellurides with a top size of 250µm.

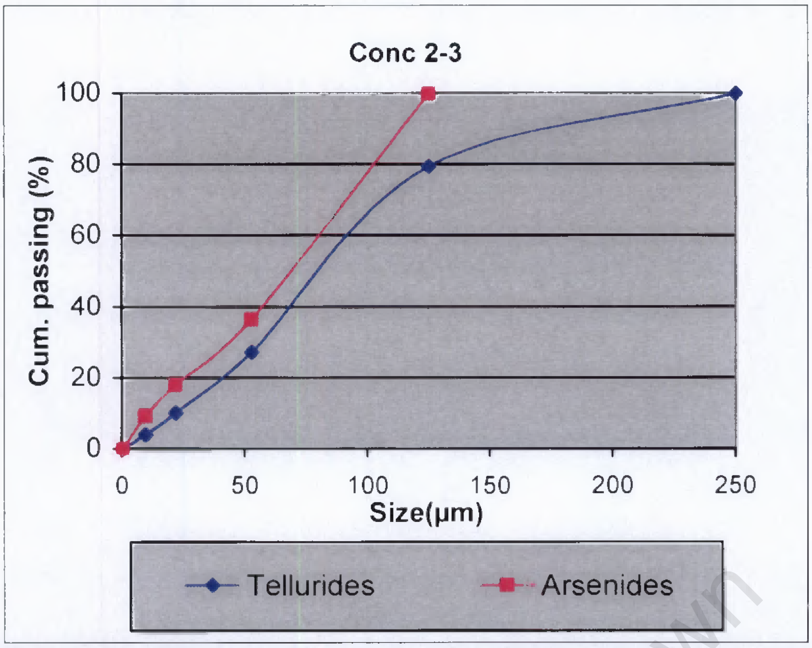


Figure 4.36: Size distribution (% cum. Passing) of particles associated with PGE tellurides and PGE arsenides in the Platreef Conc 2-3 from configuration 1 of the Flexi-Float.

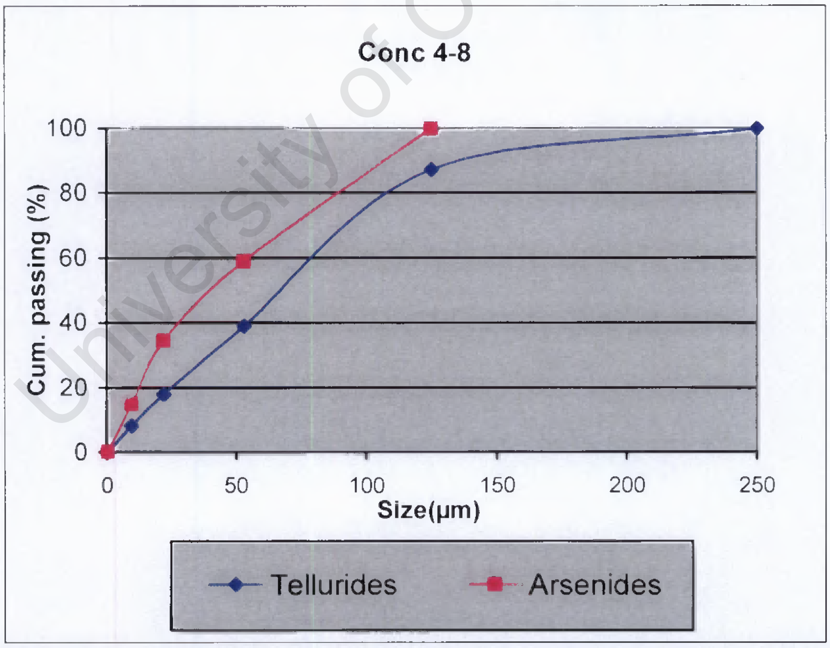


Figure 4.37: Size distribution (% cum. Passing) of particles associated with PGE tellurides and PGE arsenides in the Platreef Conc 4-8 from configuration 1 of the Flexi-Float.

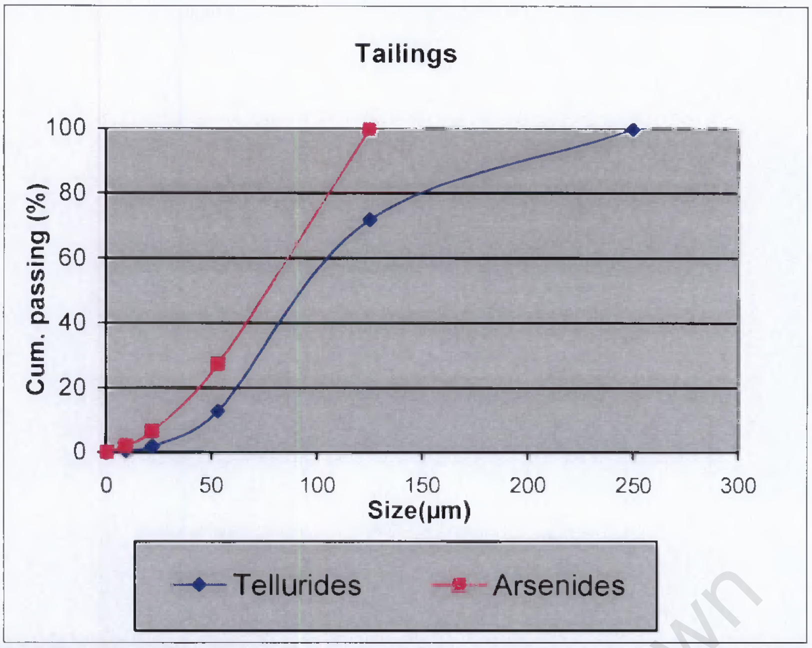


Figure 4.38: Size distribution (% cum. Passing) of particles associated with PGE tellurides and PGE arsenides in the Platreef tailings from configuration 1 of the Flexi-Float.

From Table 4.16 showing the p80 profiles down the bank of the Flexi-Float it can be seen that there was a preferential recovery of finer particles associated with both PGE tellurides and arsenides to Conc 1 compared to Conc 2-3 and Conc 4-8. In the feed, particles associated with PGE tellurides and those associated with PGE arsenides had p80s of 107µm and 97µm, respectively and these reduce in Conc1 to 65µm and 32µm respectively. Further down the bank in Conc 2-3 and Conc 4-8 their p80s increase and range from 90µm to 125µm. The PGE tellurides in the tailings at a p80 of 150µm were coarser than the PGE arsenides at a p80 of 105µm.

	p80(µm)				
	Feed	**Conc1**	**Conc2-3**	**Conc4-8**	**Tailing**
PGE tellurides	107	65	125	107	150
PGE arsenides	97	32	102	90	105

Table 4.16: Down the bank p80s of particles associated with PGE tellurides and PGE arsenides form configuration 1 of the Flexi-Float run on Platreef ore.

4.5 Reagent trials

The following results are for tests carried out to investigate the effect of various reagent suites on the flotation response of sperrylite. In all these tests SIBX is used as a primary collector and then a dithiophosphate and dithiocarbamates are compared as secondary collectors. Copper sulphate is also investigated as activator.

The results from Figure 4.39 show that in the early stages of flotation the best Pt concentrate grades were achieved with a combination of SIBX and S-9887. However, the Pt concentrate grade ultimately achieved by this test, though still amongst the best, was quite similar to those achieved by using SIBX on its own as well as that achieved with a combination of SIBX and Senkol 3.

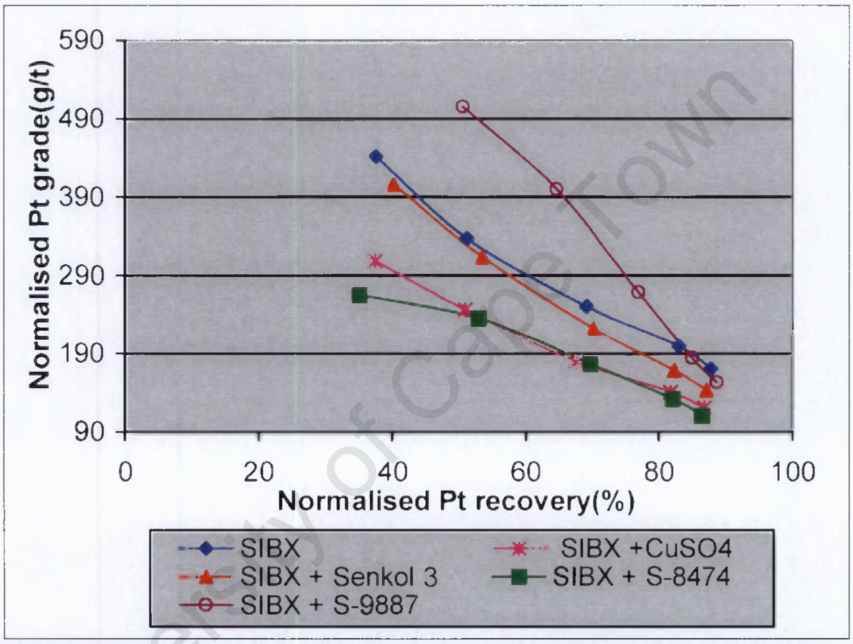


Figure 4.39: Normalised Pt grades versus Normalised Pt recoveries for the tests carried out on barren feldsphatic pyroxenite spiked with synthetic sperrylite aimed at investigating the flotation response of the sperrylite to various reagent suites.
SIBX – sodium isobutyl xanthate; Senkol 3- dithiophosphate; S-8474 –dithiocarbamate; S-9887- a mixture of thionocarbamates.

The Pt flotation rate constants determined from the klimpel model (Table 4.17) show that a combination of SIBX and S-9887 produced the highest rate constant and therefore supposedly the best flotation response. However, plotting Pt recoveries as a function of time (Figure 4.40) shows this to be significant only in the early stages of flotation as very similar final recoveries were achieved for all reagent suites.

TEST	Pt		
	k (min^{-1})	Rec.$_\infty$ (%)	R^2
SIBX	0.51	91.3	0.98
SIBX + $CuSO_4$	0.52	89.8	0.97
SIBX + Senkol 3	0.59	89.4	0.97
SIBX + S8474	0.51	90.5	0.99
SIBX + S9887	0.93	89.5	0.98

Table 4.17: Pt flotation rate constants determined from the Klimpel model for the tests carried out on barren feldspathic pyroxenite spiked with synthetic sperrylite aimed at investigating the flotation response of the sperrylite to various reagent suites.

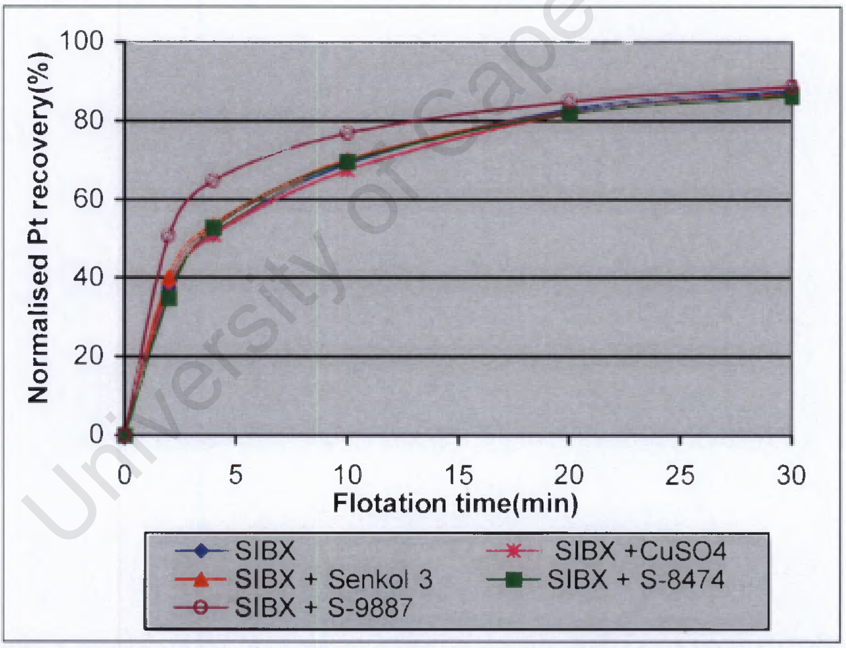


Figure 4.40: Pt response curves for the tests carried out on barren feldspathic pyroxenite spiked with synthetic sperrylite aimed at investigating the flotation response of the sperrylite to various reagent suites.

CHAPTER 5

Discussion

The hypothesis that PGE tellurides and PGE arsenides exhibit different flotation behaviours has been investigated in this study. In carrying out this investigation the flotation responses of PGE tellurides and PGE arsenides in a Platreef ore have been compared. Having factually established which one of these minerals is better floating, the challenge was to start investigating what factors significantly account for the observed differences in flotation responses of these minerals. The many factors which could account for the observed differences in the flotation responses of these minerals had to be investigated, viz. sizes of the particles associated with these minerals, their associations with other minerals, their liberation characteristics and surface chemistry. This necessitated flotation comparison testwork in which such possible differences could be controlled. It was decided to compare synthetic forms of these minerals which were synthesised to resemble fully liberated minerals of a close size range. As a result an additional hypothesis had to be investigated in this study and this was whether synthetic minerals adequately simulate the behaviour of naturally occurring PGMs in a flotation circuit and what the relative flotation responses are of these PGMs. All the flotation tests were carried out at natural pH which in this case fell in the range of 8 to 9.

Simulating the flotation behaviour of natural PGMs using synthetic PGMs

In comparing the flotation response of natural PGMs and synthetic PGMs in a natural ore environment, batch flotation responses of a Platreef ore and Merensky reef ore spiked with synthetic minerals were investigated. The blend of synthetic PGMs used for spiking consisted of a combination of moncheite, merenskyite and sperrylite in similar proportions in which they naturally occur in the Platreef ore sample used. The four incremental spiking levels referred to in section 4.1 were incremental amounts of the said blend of synthetic minerals carefully chosen to increase the content of each of the constituent mineral in the Platreef ore by 30%, 50%, 100% and 150%. The Merensky ore despite having a different mineralogy was spiked with the exact mass amounts of the blend for each level of spiking as for the Platreef ore. Spiking the synthetic PGMs into the natural ores was aimed at subjecting the synthetic PGMs to a pulp environment as complex as natural PGMs are exposed to during flotation. Having an indistinguishable mixture of natural and synthetic PGMs in the spiked ore, a mechanism had to be devised to distinguish the flotation response of the synthetic PGMs from that of the natural

PGMs. Since there currently is no readily applicable technique for obtaining mineral assays, the flotation responses of the minerals was traced by the flotation response of their associate elements and in this particular case Pt and Pd. It should be noted however that not all the Pd in the Bushveld complex is necessarily from PGMs as some has been reported to occur in solid solution with pentlandite (Ballhaus, 2000; McDonald et al., 2005; Holwell et al., 2004).

The flotation results achieved from natural ore samples without any synthetic PGMs spiking gave the base line case of the flotation responses of the naturally occurring Pt and/or Pd associated minerals. That obtained from the spiked ores gave the flotation response of combined natural and synthetic PGMs bearing Pt and Pd. Therefore any deviations from the baseline case would be attributed to the synthetic PGMs and if significant would be taken as a significant difference in flotation response compared to natural PGMs. The absence of significant deviation would obviously then indicate similarity in flotation responses. The extent of spiking with synthetic PGMs included levels that more than doubled the Pt and Pd head grades of the natural ores (cf. Tables 4.1 and 4.4) to ensure that the contribution of the synthetic PGMs to the flotation response would be notable. The reported head grades for the spiked ores were calculated from flotation products (cf. Appendix C) due to there not being sufficient amounts of synthetic PGMs required to generate spiked head samples for chemical assaying. It is important to note that the synthetic PGMs were in the size range 100% -38µm and, having been synthesised from pure elements (cf. section 3.1.5), resembled only a fraction of the mineralogical diversity of the naturally occurring PGMs in the ores (cf. section 4.4). As attempting to reproduce this diversity is clearly virtually impossible, it should be appreciated that the natural ore and the spiked ores will have slightly different mineralogy.

The results from this testwork (cf. section 4.1) show that flotation without collector, of natural ores or those spiked with synthetic PGMs, produced very poor Pt and Pd recoveries and grades. On the other hand, the rest of the tests carried out with the addition of collector showed marked recovery improvement for both natural and spiked samples. The Pt and Pd ultimate recoveries increased in excess of 50% points following the addition of collector. The results also showed that tests carried out with collector produced better flotation response as they had higher flotation rate constants. These observations were made for tests conducted on Platreef ore as well as on Merensky ore and showed that both natural and synthetic PGMs are not naturally hydrophobic but that collector is required to impart hydrophobicity for favourable flotation to take place.

The Pt and Pd flotation responses generally followed the order of spiking for both Platreef and Merensky ores. From the series of concentrates collected the cumulative grades at each stage were higher for higher levels of spiking. This was most likely due to the higher Pt and Pd head grades at the higher levels of spiking. To take into account these differences in head grades in making these comparisons, the results are considered in terms of Pt and Pd upgrade ratios versus their respective recoveries, the upgrade ratio in this case being simply the ratio of the concentrate grade relative to the head grade (cf. Appendix C).

In the case of the tests carried out on the Platreef ore the results show the Pt upgrade ratios (cf. Figure 4.3) at all stages of flotation were very close for all tests carried out with collector. A similar observation was made for the tests carried out without collector although the upgrade ratios were lower. In the case of collector being present, the upgrade ratios in the first stage were ±30 with the final upgrade ratios being ±9. In the absence of collector the upgrade ratios for all the stages of flotation were about 1 which virtually means that there was no upgrading. For the samples floated with collector, the Pd upgrade ratios of the natural ore were very similar to those of the lowest level of spiking (level1) at all stages of flotation. For these two samples the Pd upgrade ratio at the start of flotation was ±20 which was lower compared to ±32 achieved at higher levels of spiking. However, ultimately the Pd upgrade ratios (cf. Figure 4.4) achieved were all very close falling in the region of ±9. For all samples floated without collector, spiked and natural, the Pd upgrade ratios were much lower throughout all the stages as they fell in the range 1 to 4. The Pt and Pd flotation rate constants for the tests carried out with collector ranged from 0.58min^{-1} to 2.78min^{-1} which were much higher than those from the collectorless tests ranging from 0.04min^{-1} to 0.09min^{-1}. The flotation rates of natural and synthetic PGMs were greatly improved by the addition of collector. These results demonstrated the similarities in flotation responses between natural and synthetic PGMs. Amongst the samples floated with collector, Pt and Pd flotation rates were lowest for the sample with the lowest spiking level followed by the natural ore. The Pt and Pd flotation rates for the rest of the samples were very close and slightly higher. All the samples floated with collector achieved ultimate Pt and Pd recoveries ranging from 85% to 90% whereas none of those floated without collector exceeded 25%.

In the case of the tests carried out on the Merensky ore the results show the Pt upgrade ratios (cf. Figure 4.9) at all stages of flotation were very close for all tests carried out with collector. A similar observation was made amongst the tests carried out without collector however at relatively lower upgrade ratios. In the case of the former, the upgrade ratios in the first stage were ±45 with the final upgrade ratios being ±12. In the case of the latter the upgrade ratios for all the stages of flotation were around 2. On the other hand Pd upgrade ratios (cf. Figure 4.10) for samples floated with collector varied quite broadly in the early stages of flotation ranging from 38 to 52 but were ultimately very close at ±12. The Pd upgrade ratios for the samples floated without collector were much lower in the initial stages of flotation with the highest being 13. In the absence of collector, even though the concentration of Pd was much higher in the case of the spiked sample relative to the natural ore they were both much lower compared to those of samples floated with collector. The Pt and Pd flotation rate constants for the tests carried out with collector ranged from 1.67min^{-1} to 3.05min^{-1} which were much higher than those from the collectorless tests ranging from 0.14min^{-1} to 0.43min^{-1}. The flotation rates of natural and synthetic PGMs increased significantly on addition of collector. These results demonstrated the similarities in flotation responses of natural and synthetic PGMs. The Pt results for the natural ore and the spiked samples were almost indistinguishable throughout the various flotation stages. All the samples floated with collector achieved ultimate Pt recoveries of ±90% whereas those floated without collector only achieved as high as ±20%. Pd recoveries of the natural ore sample floated with collector were slightly lower at all stages of flotation compared to those of the spiked samples floated with collector. Their Pd ultimate recoveries ranged from 91% to 97% which are relatively close in comparison to that of the spiked sample floated without collector which was 46.5% or indeed compared to the natural ore sample floated without collector with an ultimate recovery of 21.8%.

Overall, these results showed that the synthetic PGMs investigated responded to reagents in a manner similar to naturally occurring PGMs. Their flotation responses in terms of grade/upgrade ratios and recovery relationships were quite similar based on the observed trends. These findings therefore show that it is acceptable to use the synthetic PGMs to investigate the flotation behaviour of naturally occurring PGMs.

Comparing the flotation responses of PGE tellurides vs. PGE arsenides

It was hypothesised in this research that PGE tellurides and arsenides present in the Platreef exhibit significantly different flotation responses as a result of the different mineralogical compositions. Various tests were carried out to characterise and compare the flotation responses of PGE tellurides and PGE arsenides. Amongst the tests conducted, some compared the naturally occurring forms of these PGMs and in others synthetic equivalent PGMs were compared. The naturally occurring forms of these PGMs in a Platreef ore were compared down the bank of the Flexi-Float mini-plant. In addition, having established the applicability of synthetic PGMs for simulation of natural PGMs the flotation response trends of synthetic moncheite (Pt telluride) and synthetic sperrylite (Pt arsenide) were investigated.

Natural PGE tellurides vs. natural PGE arsenides

For a comparison of the natural forms of these minerals down the Flexi-Float bank, a method had to be devised to separately trace the minerals in the absence of a readily available mineral assaying technique. Back calculating mineral assays from assays of their readily analysable constituents such as Pt and/or Pd is a possible technique only if the stoichiometry of the minerals involved are definite. This technique is easily applicable to Platreef PGE arsenides since this is essentially sperrylite with a molecular formula of $PtAs_2$. PGE tellurides compositions on the other hand vary considerably and are typically in association with bismuth (Kingston 1966., Harney et al. 1990., Cabri et al. 1976). Figure 5.1 shows an example of a ternary diagram for a Pd-Te-Bi system, which shows the variation in composition. The solid black triangles represent particles that are depleted in tellurium and bismuth and enriched in palladium.

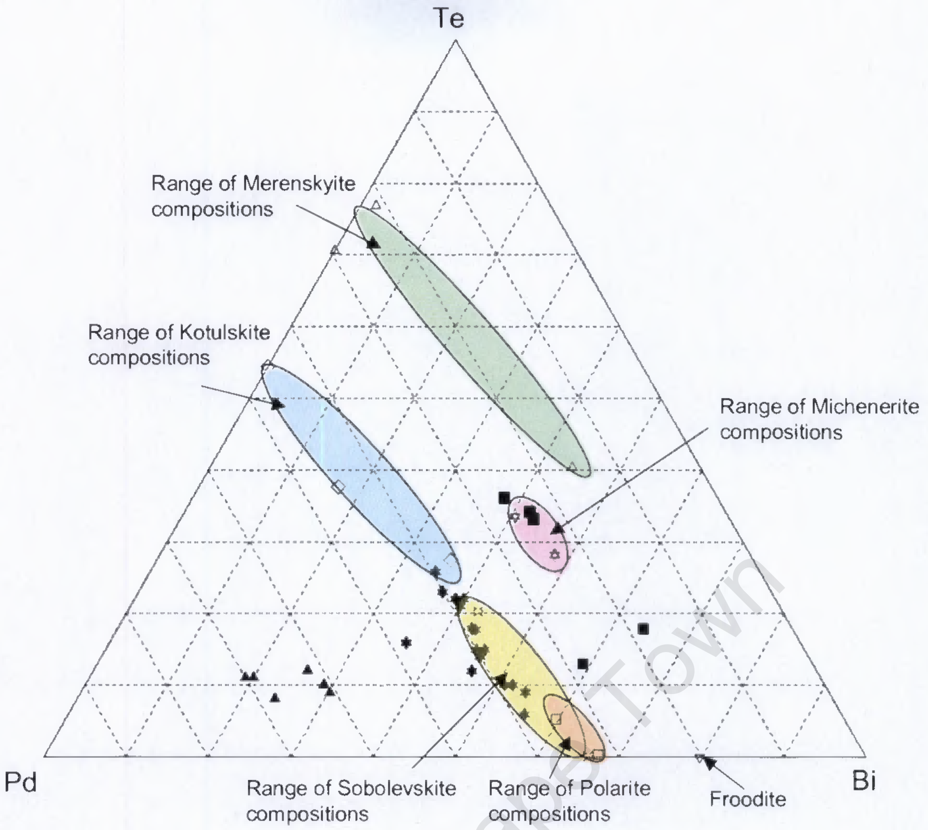


Figure 5.1: Pd-Bi-Te ternary diagram highlighting the variation in composition of PdBiTe particles (black symbols). The known naturally occurring PdBi-tellurides are Michenerite (PdBiTe), Kotulskite (PdTe), Merenskyite ($PdTe_2$), Sobolevskite (Pd(TeSb)Bi), Polarite (Pd(PbTe)Bi), and Froodite ($PdBi_2$). The compositional ranges (normalised in terms of the three components only) of these mineral compositions are shown by the coloured areas [(Cabri, 2002) and modified (Hey and Malysiak, 2004)].

Mineralogical analysis of the particular Platreef ore sample used in the investigation showed that the elements tellurium and arsenic occur separately and only in the form of PGE tellurides and arsenides respectively. It should be mentioned that in the literature, Viljoen and Schürmann (1998) report the presence of base metal tellurides such as gersdorffite in certain areas of the Platreef. However, bulk modal mineralogy of the Platreef sample for this investigation did not reveal any such mineral. It is for these reasons that in this investigation, the flotation responses of tellurium and arsenic as derived from chemical analysis of these elements in the Flexi-Float streams were confidently taken to infer the flotation responses of PGE tellurides and PGE arsenides respectively.

The results in section 4.3.1 showed that from the start of flotation to the end, tellurides showed better flotation response compared to arsenides. In the two Flexi-Float configurations, PGE tellurides had flotation rate constants in the range of 0.09min^{-1} to 0.11min^{-1} compared to those of arsenides ranging from 0.02min^{-1} to 0.03min^{-1}. In Configuration 1, tellurides had an initial recovery of 24.2% with an upgrade ratio of 16.6 compared to those of arsenides at 9.4% and 6.4 respectively. Over almost the entire flotation period tellurides produced almost double the upgrade ratios of arsenides for points of equivalent recovery. Tellurides produced a much higher final recovery of 89.9% compared to that of arsenides at 45.0%.

In Configuration 2, tellurides had an initial recovery of 31.0% with an upgrade ratio of 19.1 compared to those of arsenides at 18.9% and 11.7 respectively. Over the entire flotation period tellurides had a higher upgrade ratio compared to arsenides for points of equivalent recovery. Tellurides produced a much higher ultimate recovery of 89.9% compared to that of arsenides at 52.8%.

From these results it was concluded that naturally occurring PGE tellurides float more readily than naturally occurring PGE arsenides.

Synthetic PGE tellurides vs. synthetic PGE arsenides

The following discussion is based on batch flotation testwork aimed at comparing the flotation responses of synthetic moncheite (Pt telluride) and synthetic sperrylite (Pt arsenide) spiked in separate samples of a Platreef ore. In an approach similar to that earlier discussed, the flotation response of these PGMs was traced by way of Pt chemical analysis. On spiking the Platreef ore, equal amounts of synthetic moncheite and sperrylite were used and in each case this amount raised the Pt content to almost double that present in the natural Platreef ore.

The results for this testwork in section 4.3.2 show that natural Platreef ore and that spiked with synthetic moncheite produced similar Pt recoveries which were ultimately around 83%. It can also be seen that the sample spiked with the synthetic sperrylite produced much poorer Pt ultimate recovery at 68%. The Pd head grades of the spiked samples were quite similar to that of the natural ore sample as was expected since sperrylite did not contain any Pd and that in moncheite was only 0.13%. Therefore the Pd flotation response for all three tests reflects the behaviour of naturally occurring Pd minerals. It is however interesting to note that the Pd upgrading characteristics of the spiked samples was lower in the early stages compared to that of the natural sample. This suggests some interaction between synthetic minerals and natural minerals in the pulp which caused the Pd minerals to be less floatable in the early flotation stages for the spiked sample.

The experimental design of these tests demonstrates some of the benefits of using synthetic PGMs to investigate PGM flotation. A collective group of PGMs such as PGE tellurides has been unbundled and a specific constituent of the group, in this particular case Pt tellurides, has been investigated and compared against Pt arsenide. In a similar fashion, though not done in this study, Pd tellurides could be compared against Pt arsenides. This type of experimental design would be nearly impossible to achieve using the natural ores.

In another test similar to that discussed above, the flotation response of synthetic moncheite was compared to that of synthetic sperrylite by spiking these PGMs into barren feldspathic pyroxenite. This provided ore samples containing exclusively synthetic PGMs but with a gangue mineralogy very similar to that of the natural Platreef ore. This approach also provides the opportunity to custom design ores for experiments and also the ability to eliminate what in natural ores are uncontrollable variables such as mineralogy. For example, in additional tests the effect of base metals on the flotation response of the PGMs was tested by spiking synthetic pentlandite in addition to the synthetic PGMs.

The results in section 4.3.3 showed that moncheite produced the best flotation response with a final recovery of 92.5%. On the other hand sperrylite with a final recovery of 67.3% produced the poorest flotation response with hardly any differential upgrading from one stage to the next. It can also be seen that a combination of moncheite and sperrylite (Te-As) produces an intermediate response which is slightly enhanced on the addition of pentlandite (Te-As-S). This may be due to inadvertent activation of moncheite and/or sperrylite by nickel.

In summary these results have shown that the flotation behaviour of the naturally occurring PGMs and the synthetic PGMs are similar. They also show clearly that PGE tellurides float more readily than PGE arsenides.

Factors affecting PGE tellurides and PGE arsenides flotation

Having established that PGE tellurides are better floating compared to PGE arsenides the challenge was to investigate what factors account for this observation. It is hoped that findings from these investigations can be applied to develop means of improving the PGM recoveries. Some of the factors affecting flotation that have been investigated in this study include mineralogy, surface chemistry and reagents.

Mineralogy

The results presented in this section are from mineralogical examinations carried out down the bank of the Flexi-Float in configuration 1 and using Platreef ore. In characterising the Flexi-Float the concentrates down the bank were batched into fast floating (Conc1), medium floating (Conc2-3) and slow floating (Conc4-8). This was as opposed to analysing the concentrates from each of the eight cells separately due to limited MLA instrument time (cf. section 4.2 for a comparison of the two Flexi-Float configurations).

The results in section 4.4 show that PGE tellurides are the most abundant PGM species in the feed and concentrates of the Flexi-Float streams followed by PGE arsenides. PGE tellurides abundance in the feed was 59.2% which reduced to 30.2% in the tailings. On the other hand PGE arsenides had an abundance of 13.3% in the feed which increased to 30.9% in the tailings. The large difference in the abundances of these minerals in the feed can not account for the observed differences in their flotation rates as this was eliminated in the earlier tests in which flotation responses of synthetic ores containing similar amounts of Pt telluride and Pt arsenides were compared.

The results in section 4.4.3 show that PGE arsenides are better liberated in all the streams of the Flexi-Float compared to PGE tellurides in corresponding streams. By way of example, 67.2% of PGE tellurides in the feed were liberated compared to PGE arsenides which were 74.3% liberated. As is well known, better liberation should imply better mineral surface exposure for reagent adsorption and consequently enhanced flotation response. Vermaak (2005) reports higher PGM recoveries (86.5%) in the -45μm fraction compared to the recovery of 59% from the +45-75μm fraction of Mimosa Mine ore in Zimbabwe. Insufficient liberation is then highlighted as a possible cause for poor recoveries in the coarser fractions. However, in the current study although the PGE arsenides are better liberated they were nevertheless found to yield lower recoveries and slower flotation rate constants than the PGE tellurides.

Flotation behaviour can also be affected by the association of minerals with other species. The association of PGE tellurides and PGE arsenides with other minerals was investigated and it can be seen that over 16% of the former are associated with base metal sulphides in the feed which is quite significant compared to less than 1% for the latter. On the other hand, PGE arsenides have a high association with silicates which is in excess of 20% compared to below 10% for PGE tellurides. This may lead to the suggestion that it is through the association of tellurides with base metal sulphides and of arsenides with silicates that the PGE tellurides show higher recoveries than the arsenides. However, this possibility was eliminated in the previously discussed tests carried out using synthetic ores in which the flotation responses of synthetic Pt telluride was compared to that of Pt arsenides. These pure synthetic minerals were free of association with any other minerals and yet Pt telluride was better floating.

Recoveries are well known to be influenced by particle size effects and hence size distributions of particles associated with PGE tellurides and PGE arsenides were compared in the various Flex-Float streams. Particles associated with the minerals rather than mineral grains are being considered in this case as this is what can impact on flotation response. Grain size distribution can however be found in the Appendix E. Extensive studies of the influence of particle size on flotation have been made (Dobby and Finch, 1987; Wills, 1992). A model was proposed by Dobby and Finch (1987) in which particle collection is considered to occur by particle collision followed by the particle sliding over the bubble surface. The collection efficiency E_K given in equation 5.1 is directly proportional to collision efficiency and the attachment efficiency.

$$E_K = E_c . E_A \qquad 5.1$$

where,

E_c = collision efficiency defined as the rate at which particles collide with the bubble divided by the rate at which particles flow across the projected area of the bubble.

E_A = attachment efficiency defined as the fraction of all colliding particles that reside on the bubble for a time greater than the induction time t_i. It is assumed that after collision a particle slides over the bubble and attachment occurs when an intervening liquid film thins and raptures. The induction time is thus the time required for the film to rapture after which attachment is considered to have occurred.

Collection efficiency is directly proportional to the flotation rate constant (Jameson et al., 1977). In Figure 5.2, Dobby and Finch (1987) show the relationship of collection efficiency and flotation rate constant with particle size.

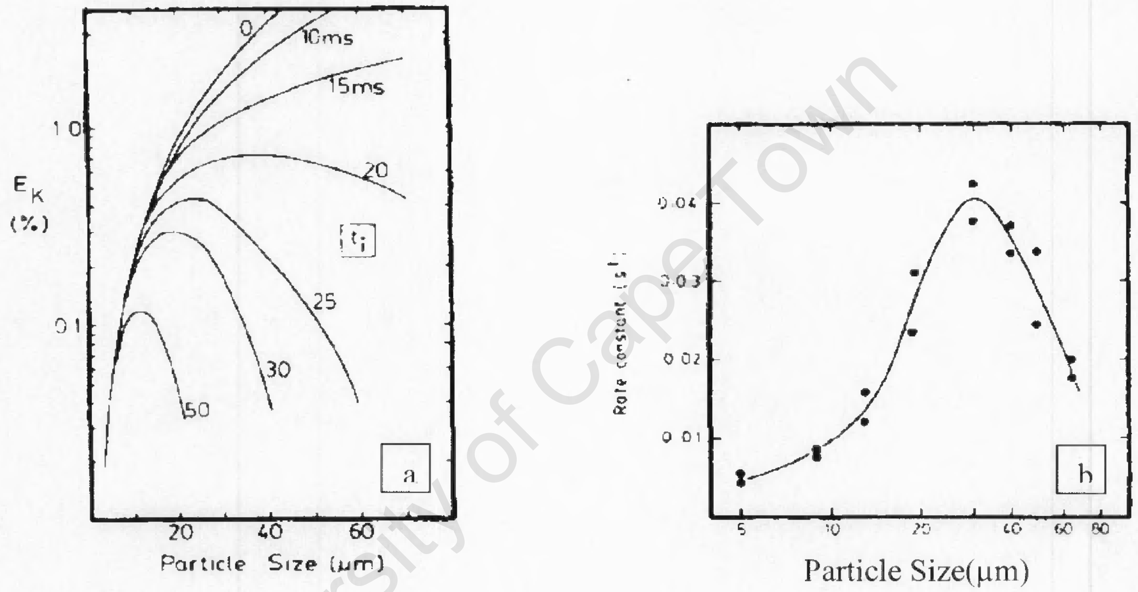


Figure 5.2: (a) Collection efficiency versus particle size and induction time. (b) Rate constant versus particle size for galena flotation. Courtesy (Dobby, 1987).

Figure 5.2 clearly illustrates the impact of particle size on flotation and that small particles sizes result in low recoveries and rate constants. The results in section 4.4.5 show that particles associated with Pt arsenide were slightly finer than those associated with Pt telluride in all of the flexi-float streams. In the feed, particles associated with PGE tellurides and those associated with PGE arsenides had p80s of 107μm and 97μm, respectively and these reduce in Conc1 to 65μm and 32μm respectively. Further down the bank in Conc 2-3 and Conc 4-8 their p80s increase and range from 90µm to 125µm. The PGE tellurides in the tailings at a p80 of 150µm were coarser than the PGE arsenides at a p80 of 105µm.

However, differences in size distributions were eliminated as a possible cause for the observed differences in the flotation responses of these two minerals. This was evident from the better flotation response achieved by Pt telluride in the previously discussed comparative flotation tests carried out on barren feldspathic pyroxenite spiked with synthetic PGMs. The synthetic PGMs used in these tests were all -38µm fractions which were generated by identical methods of crushing and screening of the respective synthetic PGM head samples. Therefore any possible mineral size differences in the head samples to these tests should have been eliminated.

Overall it can be said that factors such as liberation and particle size could not explain the observed differences in the flotation responses of PGE tellurides and PGE arsenides. Given that the relatively poor flotation of arsenides compared to tellurides is not related to liberation, association or size effects, it can be inferred that this may be due to a poorer degree of interaction between the arsenides and the thiol collectors compared to the interaction of the tellurides with these same reagents. It is beyond the scope of this study to explain whether or not this is a reasonable hypothesis. It may be however worth noting the following oxidation potentials:

$Pt + H_2O \rightarrow PtOH^+ + H^+ + 2e$	-1.200volts
$Te + 2H_2O \rightarrow TeO_2 + 4H^+ + 4e$	-0.593volts
$2As + 3H_2O \rightarrow As_2O_3 + 6H+ + 6e$	-0.234volts

This sequence appears to indicate that arsenic may be more prone to oxidation than tellurium. This could contribute to the poor reagent/mineral interaction for arsenides compared to tellurides. This is further reinforced by the fact that thiol collectors readily render Pt hydrophobic. It is thus possible that there is a relationship between the oxidation potentials of the minerals and the extent to which they interact with the thiol collector and that this could explain the relative floatabilities of the tellurides and arsenides.

Reagent suites

An investigation into the effect of various reagent suites on the ultimate recovery of Pt arsenide was carried out using barren feldspathic pyroxenite spiked with synthetic Pt arsenide. In all the tests conducted, SIBX was used as a primary collector and then a dithiophosphate and two dithiocarbamates were compared as secondary collectors. The effect of copper as an activator was also investigated. The choice of reagents used was amongst the most commonly used in PGM flotation (Bulatovic, 2003). The results in section 4.5 showed that the ultimate recoveries achieved by changing the reagent suites were very similar without any of them enhancing the recovery of Pt arsenide. The flotation reagents tested were typical of the most common types used in the PGM industry.

Mineral surface chemistry

The possibility that differences in the flotation behaviour of PGE tellurides and PGE arsenides are a result of differences in their liberation or particle size have been eliminated. A simple test of varying reagent regimes did not yield any indication of improving this poor flotation response. Clearly there is an opportunity for further investigations into the possibility that other reagent types may be more useful in rendering arsenides hydrophobic but this was beyond the scope of the present investigation.

CHAPTER 6

Conclusions

The Platreef situated in the Limpopo province of South Africa constitutes a significant source of PGEs produced in the world. Of the various PGE bearing minerals in the Platreef, PGE tellurides are the most abundant occurring in excess of 30% in terms of PGM relative abundance followed by PGE arsenides at 21%. As is well known, flotation is a key process in the upgrading and recovery of such minerals from the mined ores. The flotation response of these minerals can therefore have a significant bearing on the economics of the ore processing. This research has aimed at exploring the hypothesis that PGE tellurides exhibit significantly different flotation behaviour compared to PGE arsenides and then trying to explain any differences observed in terms of the properties of these minerals. In this way it is hoped that this will result in a better understanding of the flotation behaviour of these PGMs and overall increased recoveries in the plant situation.

The flotation response of naturally occurring PGE tellurides and arsenides were compared using two configurations of the Flexi-Float mini-plant running on naturally occurring Platreef ore. In both configurations PGE tellurides produced higher flotation rate constants in the range of 0.09min^{-1} to 0.11min^{-1} compared to those of arsenides (0.02min^{-1} to 0.03min^{-1}). In Configuration 1, tellurides produced an initial recovery of 24.2% with an upgrade ratio of 16.6 compared to those of arsenides at 9.4% and 6.4 respectively. Over almost the entire flotation period tellurides produced almost double the upgrade ratio of arsenides for points of equivalent recovery. Tellurides produced a much higher final recovery of 89.9% compared to that of arsenides at 45.0%. In configuration 2, tellurides also produced a much higher ultimate recovery of 89.9% compared to that of arsenides at 52.8%. These findings showed clearly that naturally occurring PGE tellurides and PGE arsenides exhibit significantly different flotation behaviour and that tellurides are more amenable to flotation.

The question of whether synthetic minerals could adequately address the flotation behaviour of their natural equivalents had to be addressed before they could be used to carry out further investigations on the flotation of these minerals. Synthetic minerals were proposed to be used given the great difficulty of accessing sufficient quantities of the natural tellurides and arsenides. This study was carried out by comparing Pt and Pd batch flotation recoveries from naturally occurring ores (Platreef and a Merensky reef) with the recoveries obtained when these ores were spiked to various levels with a blend of synthetic sperrylite ($PtAs_2$), moncheite ($PtPd(BiTe)_2$) and merenskyite ($PdPt(BiTe)_2$). The hydrophobicities of the natural and synthetic minerals were tested by conducting batch flotation tests in the absence of collector. The flotation results achieved under these conditions were then compared to those achieved in the presence of collector.

In the absence of collector, the Platreef ore produced final Pt and Pd recoveries of 11.4% and 15.2% respectively whereas those for Merensky reef were 19.2% and 22.5% respectively. The Pt and Pd flotation rate constants for the Platreef ore were $0.06min^{-1}$ and $0.09min^{-1}$ respectively whereas those of the Merensky ore were $0.14min^{-1}$ and $0.18min^{-1}$ respectively. The flotation tests carried out under similar conditions but in which Platreef was spiked with the synthetic PGMs produced final Pt and Pd recoveries of 8.37% and 27.1% respectively. The Pt and Pd flotation rate constants achieved in this test were both $0.04min^{-1}$. Under the same conditions the spiked Merensky sample produced final Pt and Pd recoveries of 13.5% and 48.0% respectively with Pt and Pd flotation rate constants being $0.20min^{-1}$ and $0.43min^{-1}$ respectively.

In the presence of collector, there were significant increases in the Pt and Pd recoveries and their respective rate constants for all the scenarios, viz. flotation of natural ores and natural ores spiked with synthetic samples. In every case, the Pt and Pd recoveries increased to values in excess of 85.0% with the flotation rate constants increasing to values which were at least more than five times those achieved in the absence of collector.

The flotation results achieved from natural ore samples without any synthetic PGMs spiking gave the base line case of the flotation responses of the naturally occurring Pt and/or Pd associated minerals. Those obtained from the spiked ores gave the flotation responses of combined natural and synthetic PGMs bearing Pt and Pd. Since the flotation response parameters compared i.e. recoveries and rate constants in the two scenarios (with and without collector) increased by similar orders of magnitude for natural and spiked samples, it was concluded that the synthetic PGMs were responding to flotation in a manner similar to the natural PGMs. The results also showed, as expected, that both natural and synthetic PGMs are not sufficiently naturally hydrophobic but require collector to impart the levels of hydrophobicity required to produce significant recoveries. These results confirmed that the synthetic PGMs behaved essentially in the same way as the natural ores in flotation and that it was appropriate to use them to evaluate in greater detail the behaviour of tellurides and arsenides in general.

The flotation responses of synthetic moncheite (Pt telluride) and synthetic sperrylite (Pt arsenide) were compared by carrying out flotation tests on samples of a Platreef ore separately spiked with equal amounts these minerals. In an approach similar to that described above, the flotation responses of these PGMs were traced by way of total Pt (from natural and synthetic PGMs) chemical analysis. The results achieved with the spiked ore were also compared to those achieved with a natural Platreef ore.

The natural Platreef ore and that spiked with synthetic moncheite produced similar Pt recoveries which were ultimately around 83%. The sample spiked with the synthetic sperrylite produced much poorer Pt final recovery at 68%. In another test, the flotation response of synthetic moncheite was compared to that of synthetic sperrylite by spiking these PGMs into barren feldspathic pyroxenite. This provided synthesised ores containing exclusively synthetic PGMs but with gangue typical of the natural Platreef ore. In this test the moncheite produced a final recovery of 92.5% with a flotation rate constant of 0.88min^{-1}. On the other hand, the sperrylite produced a much lower final recovery of 67.3% with a flotation rate constant of 0.21min^{-1}. It was concluded from the results from these two tests that synthetic moncheite, a PGE telluride, has better flotation response than synthetic sperrylite, a PGE arsenide. This finding was consistent with that observed in the case of the naturally occurring equivalents as previously mentioned. It was thus demonstrated that PGE tellurides and arsenides exhibit significantly different flotation behaviour. It is worth noting that the synthetic PGMs compared in the above mentioned testwork was all pure and all of a close size range which was 100% -38µm. This was an important component of the experimental design as association of the minerals and their particle size differences were eliminated as possible causes of the observed differences in the flotation behaviours of these minerals.

The mineralogy of the natural Platreef PGE tellurides and arsenides from the earlier discussed Flexi-Float testwork was scrutinised. The results showed that the PGE tellurides were the most abundant PGM species in the feed and concentrates of the Flexi-Float streams followed by

PGE arsenides. PGE tellurides abundance in the feed was 59.2% which reduced to 30.2% in the tailings. On the other hand PGE arsenides had an abundance of 13.3% in the feed which increased to 30.9% in the tailings. The large difference in the abundances of these minerals in the feed could not account for the observed differences in their flotation rates as this was eliminated in the previously discussed tests in which flotation responses of synthetic ores containing similar amounts of Pt telluride and Pt arsenides were compared.

Moreover the PGE arsenides were better liberated in all the streams of the Flexi-Float compared to PGE tellurides. By way of example, 67.2% of PGE tellurides in the feed were liberated compared to 74.3% for the PGE arsenides. Ideally better liberation usually implies higher recoveries but in this case, despite their better liberation, PGE arsenides were poorer floating compared PGE tellurides.

The association of PGE tellurides and PGE arsenides with other minerals was investigated It was shown that about over 16% of the former are associated with base metal sulphides in the feed which is quite significant compared to less than 1% for the arsenides. PGE arsenides, however, had a high association with silicates (in excess of 20%) compared to below 10% for PGE tellurides. It is obvious that it would be appropriate to infer that the better recovery of tellurides is due to their association with sulphides and that the relatively poor recovery of arsenides is because of their association with silicates. However, this possibility was eliminated in the tests carried out using synthetic ores in which the flotation responses of synthetic Pt telluride was compared to that of Pt arsenides. These pure synthetic minerals were free of association with any other minerals and yet the tellurides were still better floating.

Recoveries can be influenced by particle size effects. In the present study particles associated with PGE tellurides and arsenides in the feed had p80s of 107μm and 97μm respectively, and these reduced in Concentrate 1 to 65μm and 32μm respectively. Further down the bank in Concentrate 2-3 and Concentrate 4-8 their p80s increase to between 90μm and 125μm. The tellurides in the tailings at a p80 of 150μm were coarser than the arsenides at a p80 of 105μm. However, differences in size distributions did not appear to explain the observed differences in the flotation responses of these two minerals. This was evident from the better flotation response achieved by Pt telluride in the flotation tests carried out on barren feldspathic pyroxenite spiked with synthetic PGMs. In those studies the synthetic PGMs used were all -

38µm fractions which were generated by identical methods of crushing and screening of the respective synthetic PGM head samples.

In summary, liberation, association and particle size effects could not account for the differences observed in the recoveries of tellurides as opposed to arsenides. Therefore it can only be speculated that the reason for the different flotation behaviours must be due in some way to the different manner in which the reagents interact with the surfaces of these minerals. A preliminary investigation into the effects of different reagents was carried out using SIBX as a primary collector and then a dithiophosphate and two dithiocarbamates as secondary collectors, respectively. The effect of copper as an activator was also investigated. The results from these tests showed that there were no significant differences in the final Pt recoveries achieved for all the reagent suites tested.

In conclusion it has been shown in this study that tellurides float more readily than arsenides although significant recoveries of the latter are achievable. It has also been shown that the relatively poor performance of arsenides compared to tellurides cannot be explained in terms of their particle size nor their degree of liberation and hence it is deduced that it is possibly a result of differences in the surface chemical interaction between the different minerals and the thiol collectors traditionally used in the recovery of minerals on a PGM flotation plant. The solid state properties of arsenides and tellurides are the focus of significant research in the semi-conductor industry and it may be interesting to explore the possibility that those surface properties may be able to offer an explanation of these differences.

REFERENCES

1. Andrade, V.L.L., Santos, N.A., and Goncalves, K.L.C. (2004). How to obtain continuous flotation test data on drill-core samples using a Mini Pilot Plant. *Mining Engineering*, pp. 39-43.
2. Armitage, P.E.B., McDonald, I., Edwards, S.J., and Manby, G.M. (2002). Platinum-group element mineralisation in the Platreef and calc-silicate footwall at Sandsloot, Potgietersrus district, South Africa. *Transactions of the Institution of Mining and Metallurgy*, Section B: Applied Earth Science, vol. 111, (Jan. /April), pp. B36-B45.
3. Ballhaus, C., and Sylvester, P. (2000). Noble metal enrichment processes in the Merensky reef, Bushveld Complex. *Journal of Petrology*, vol. 41, no. 4, pp. 545-561.
4. Beattie, D.A., Huynh, L., Kaggwa, G.B.N., Ralston, J. (2005). The effect of polysaccharide and polyacrylamides on the depression of talc and flotation of sulphide minerals. *Minerals Engineering*, vol. 19, no. 6-8, (May-July). pp. 598-608.
5. Becker, M., Harris, P.J., Wiese, J., and Bradshaw, D. (2006). The use of quantitative mineralogy data to interpret the behaviour of gangue minerals in the flotation of Merensky Reef ores. *Presented at Automated Mineralogy*, (July).
6. Bergizov, V.D., Meshchankina, V.I., and Dubankina, L.S. (1974). Palladoarsenide, Pd_2As, a new natural palladium arsenide from copper-nickel ores of the Oktybar deposits. *Zapiski Vesesoyuznoe Mineralogicheskoe Obshchestvo*, vol. 103, pp. 104-107.
7. Bradshaw, D.J., and O'Connor, C.T. (1994). The flotation of pyrite using mixtures of dithiocarbamates and other thiol collectors. *Minerals Engineering,* vol. 7, no. 5-6, (May-June), pp. 681-690.
8. Bulatovic, S. (2003). Evaluation of alternative reagent schemes for the flotation of platinum group minerals from various ores. *Minerals Engineering,* vol. 16, pp. 931-939.
9. Cabri, L. J., Laflamme, J.H.G., Stewart, J.M., Rowland, J.F., and Chen, T.T. (1975). New data on some palladium arsenides and antimonides. *Canadian Mineralogist*, vol. 13, pp. 321 – 335.
10. Cabri, L.J. (2002). The geology, geochemistry, mineralogy and minerals of platinum-group elements. CIM Special volume 54, *Canadian Institute of Mining, Metallurgy and Petroleum.*

11. Cabri, L.J., and Laflamme, J.H.G. (1976). Mineralogy of the platinum –group elements from some copper nickel deposits of the Sudbury area, Ontario. *Economic Geology and the bulletin of the Society of Economic Geologists*, vol. 71, no. 7, (Nov.), pp. 1159-1195.

12. Dobby, S.G., and Finch. J.A. (1987). Particle size dependence in flotation derived from a fundamental model of the capture process. *International Journal of Mineral Processing,* vol. 21, pp. 241-260.

13. Forssberg, K.S.E., and Jonsson, H. (1981). Absorption of heavy metal ions on pyrrhotite. *Scandinavian Journal of Metallurgy*, vol. 10, pp. 225-230.

14. Fragomeni, D., Hoffman, M., Kelly, A., Yu, S., and Lotter, N.O. (2006). Flotation mini pilot plant experience at Falconbridge limited. *MPMSC Conference,* Sudbury, pp. 329.

15. Fuerstenau, D.W. (1982). Activation and flotation of sulphide minerals. Principles of Flotation, King, R.P. (ed.), *South African Institute of Mining and Metallurgy*, Johannesburg, pp. 188-198.

16. Fuerstenau, M.C., Lopez-valdivisieo, A., and Fuerstenau, D.W. (1988). Role of hydrolysed cations in the natural hydrophobicity of talc. *International Journal of Mineral Processing*, vol. 23, pp. 161.

17. Goldstein, J.I., Newbury, D.E., Echlin, P., Joy, D.C., Fiori. C., and Lifshin. E. (1981). Scanning electron microscopy and x-ray microanalysis. *Plenum Press, New York and London,* pp. 1.

18. Gorain, B.K., Franzidis, J.P., and Manlapig, E.V. (1997). Studies on impeller type, impeller speed and air flow rate in industrial scale flotation cell. Part 4: Effect of surface area bubble flux on flotation performance. *Minerals Engineering*, vol. 10, no. 4, pp. 367-379.

19. Gottlieb, P., Adair, I. (1991). Quantification of talc rimming chromites in Bushveld ores using Qem*SEM. *International Congress on Applied Mineralogy*, vol. 1, paper 18, pp. 11.

20. Greoneveld Meijer, W.O.J. (1955). Synthesis, structures and properties of platinum metal tellurides. *The American Mineralogist*, vol. 40, no. 7-8, pp. 646-657.

21. Gu, Y. (2003). Automated scanning electron microscope based mineral liberation analysis- An introduction to JKMRC/FEI Mineral Liberation Analyser, *Journal of Minerals and Materials Characterisation and Engineering*, vol.2, no.1, pp. 33-41.

22. Gu, Y. (2004). Rapid mineral liberation analysis with X-Ray and BSE Image processing, *Applied Mineralogy*, Pecchio et al. (eds.), icam-BR. Sao Paulo, pp. 110-122.

23. Gu, Y., and Napier-Munn T. (1997). JK/Philips Mineral Liberation Analyser- An introduction. *Minerals Processing Conference.* Cape Town, SA. pp. 2.

24. Harney, D.M.W., and Merkle, R.K.W. (1990). Pt-Pd minerals from the upper zone of the eastern Bushveld Complex, South Africa. *Canadian Mineralogist*, vol. 28, no. pt 3, (Sep.), pp. 619.

25. Holwell, D.A., McDonald, I., and Armitage, P.E.B. (2004). Platinum-group mineral assemblages in the Platreef at Sandsloot Mine, Limpopo Province, South Africa. *Geoscience Africa*, University of the Witwatersrand, (12-16 July), abstract.

26. Holwell, D.A., McDonald, I., and Armitage, P.E.B. (2006). Platinum-group mineral assemblages in the Platreef at the Sandsloot Mine, northern Bushveld Complex, South Africa. *Mineralogical Magazine*, vol. 70, no. 1, (February), pp. 83-101.

27. Jameson, G.J., Nam, S., and Moo Young, M. (1977). Physical factors affecting recovery rates in flotation. *Minerals Science Engineering*, vol. 9, no.3, pp.103-118.

28. Jones, M.P. (1987). Applied mineralogy: A quantitative approach. London, pp. 27.

29. King, R.P. (1993). Basic image analysis for mineralogy. *ICAM'93 Demonstration Workshop Manual*, pp. 119-193.

30. Kingston, G.A. (1966). The occurrence of platinoid bismuthotellurides in the Merensky reef at Rustenburg platinum mine in the Western Bushveld. *Mineralogical Magazine.*, vol. 35, pp. 815-834.

31. Klimpel, R.R. (1980). Selection of chemical reagents for flotation. *Mineral Processing Plant Design,* Mular, A.R., and Bhappu, R.B. (eds.), New York: AIME, pp. 907-934.

32. Mackenzie, J.M. (1980). Guar based reagents. *McGraw-Hill, Journal of Mineral Engineering,* (October).

33. Malysiak, V., O'Connor, C.T., Ralston, J., Gerson, A.R., Coetzer, L.P., and Bradshaw, D.J. (2002). Pentlandite-feldspar interaction and its effect on separation by flotation. *International Journal Minerals Processing*, vol.66, pp. 89-106.

34. McDonald, I., Holwell, D.A., and Armitage, P.E.B. (2005). Geochemistry and mineralogy of the Platreef and "Critical Zone" of the northern lobe of the Bushveld Complex, South Africa: Implications for Bushveld stratigraphy and the development of PGE mineralisation. *Mineralium Deposita.* Vol. 40, pp. 526-549.

35. Melo, F., and Laskowski, J.S. (2006). Fundamental properties of flotation frothers and their effect on flotation. *Minerals Engineering*, vol. 19, pp. 766-773.

36. Merkle, R.K.W., Pikl, R., Verryn, S.M.C., and De Waal, D. (1999). Raman spectra of synthetic 'braggite' (Pt,Pd,Ni)S. *Mineralogical Magazine*, vol. 63, no. 3, pp. 363-367.

37. Miller, J.D., Li, J., Davidtz, J.C., and Vos, F. (2005). A review of pyrrhotite flotation chemistry in the processing of PGM ores. *Minerals Engineering*, vol. 18, pp. 855-865.

38. Mishra, S.K., and Klimpel, R.R. (1987). Fine coal processing. *Noyes Publications*, pp. 92-95.

39. Morris, G.E. (1996). The adsorption characteristics of polymeric depressants at the talc water interface. PhD thesis, School of Chemical Technology, Faculty of Applied Science and Technology, University of South Australia, Adelaide, Australia.

40. O'Connor, C.T. (2005). Contributions to an improved understanding of the flotation process. A D. Eng thesis, The University of Stellenbosch, pp. iii-iv.

41. O'Connor, C.T., Bradshaw, D.J., and Upton, A.E. (1990). The use of dithiophosphates and dithiocarbamates for the flotation of arsenopyrite. *Minerals Engineering*, vol. 3, no. 5, pp. 447-459.

42. O'Connor, C.T., Malysiak, V., and Shackleton, N.J. (2005). The interaction of xanthates and amines with pyroxene activated by copper and nickel. *Minerals Engineering*, vol.19, Issues 6-8, pp. 799-806.

43. Padmanaban, V., and Lawson, F. (1991). Metallurgical properties of synthetic calaverite. *The Australian Institute of Mining and Metallurgy proceedings*, vol. 296, no. 1, pp. 31-937.

44. Penberthy, C. J., Oosthuyze, E. J., and Merkle, R. K. (2000). The recovery of platinum-group elements from the UG-2 chromitite, Bushveld Complex: A mineralogical perspective. *Mineralogy and Petrology*, vol. 68, pp. 213-222.

45. Petruk, W. (2000). Applied mineralogy in the mining industry. Amsterdam; New York, Elsevier Science BV.

46. Petruk, W. (2000). Applied mineralogy in the mining industry. Ottawa, Ontario, Canada. pp1-45

47. Phillip, A. M. (1984). Use of dialkyl and diaryl dithiophosphate promoters as mineral flotation agents. *Reagents in the minerals industry conference, Rome*.

48. Rath, R.K., Subramanian, S., and Lawskowski, J.S. (1997). Adsorption of dextrin and guar gum onto talc. A comparative study. Langmuir 13, pp. 6260.

49. Runge, K.C., Franzidis, J.P., Manlapig, E.V., and Harris, M.C. (2003). Structuring a flotation model for robust prediction circuit performance. *Proceedings:* XXII International Mineral Processing Congress. Cape Town, pp. 973-984.

50. Schouwstra, R.P., Kinloch, E.D., and Lee, C.A. (2000). A short geology review of the Bushveld Complex. *Platinum Metals Review*, vol.44, pp. 33-39.

51. Seke, M.D. (2005). Optimisation of the selective flotation of galena and sphalerite at Rosh Pinah Mine. PhD thesis, the Faculty of Engineering, Built Environment and Information Technology, University of Pretoria, pp. iii.

52. Shackleton, N.J. (2003). The role of complexing agents in the flotation of pentlandite-pyroxene mixtures. M. Sc. thesis, Faculty of Engineering and the Built Environment, University of Cape Town.

53. Shackleton, N.J., Malysiak, V., and O'Connor, C.T. (2006). Surface characterisation and flotation behaviour of platinum and palladium arsenides. *International Journal of Minerals Processing.* (Submitted for Publication).

54. Shackleton, N.J., Malysiak, V., and O'Connor, C.T. (2006). Surface characterisation and flotation behaviour of platinum and palladium tellurides. *International Journal of Mineral Processing.* (Submitted for Publication).

55. Shortridge, P.G., Harris, P.J., Bradshaw, D.J., and Koopal, L.K. (2000). The effect of chemical composition and molecular weight of polysaccharide depressants on the flotation of talc. *International Journal of Mineral Processing*, vol. 59, pp. 215-224.

56. Steenberg, E., and Harris, P.J. (1984). Adsorption of carboxymethylcellulose, guar gum and starch onto talc, sulphides, oxides and salt-type minerals. *South African Journal of Chemical Engineering*, vol. 37, pp. 85.

57. Vermaak, C.F. (1995). The platinum-group metals, A global perspective. pp 4.

58. Vermaak, M.K.G. (2005). Fundamentals of the flotation behaviour of palladium bismuth tellurides. PhD thesis, University of Pretoria, pp.12.

59. Vermaak, M.K.G., Pistorious, P.C., and Venter., J.A. (2004). Electrochemical and Raman spectroscopic studies of the interaction of ethyl xanthate with Pd-Bi-Te. Department of Materials Science and Metallurgical Engineering. University of Pretoria, Pretoria 0002, South Africa, *Minerals Engineering,* vol. 18, no. 6, pp. 575-584.

60. Viljeon, M.J., and Schurmann, L.W. (1998). Platinum-group metals. The mineral resources of South Africa - Sixth edition. Wilson, M.G.C., and Anhaeusser, C.R. (eds.), pp. 532-568.

61. Vos, C.F., Davidtz, J.C., and Miller, J.D. (2006). Trithiocarbonates for PGM flotation. *International Platinum Conference 'Platinum Surges Ahead' South African Institute of Mining and Metallurgy*, pp. 169.

62. Walker, D. A., and LeCheminant, G. M. (1989). An integrated image and x-ray analysis system. Short course on image analysis applied to mineral and earth sciences, Ottawa, Petruk, W. (ed.), (May), *Mineralogical Association of Canada*, pp. 43-55.

63. Wang, J., Somasundaran, P., and Nagaraj, D.R. (2005). Adsorption mechanism of guar gum at solid-liquid interfaces. *Minerals Engineering*, vol.18, pp. 77-81.

64. Wang, X.H., Jiang, C.L. Xuan, D., and Forssberg, E. (1992). An electrochemical study of selective separation of Cu (II) activated pyrite and arsenopyrite. *Electrochemistry Society proceedings.*, vol. 92-117, pp. 235-258.

65. Wesseldijk, Q.I., Reuter, M.A., Bradshaw, D.J., and Harris, P.J. (1999). The flotation behaviour of chromite with respect to the beneficiation of UG2 ore. *Minerals Engineering*, vol. 12 no. 10, pp. 1177-1184.

66. Wiese, J., Harris, P., and Bradshaw, P. (2005). Investigation of the role and interactions of a dithiophosphate collector in the flotation of sulphides from the Merensky reef. *Minerals Engineering*, vol. 18, no. 18, pp. 791-800.

67. Wiese, J., Harris, P., and Bradshaw, P. (2005). The influence of the reagent suite on the flotation of ores from Merensky reef. *Minerals Engineering*, vol. 18, no. 2, pp. 189-198.

68. Wiese, J.G., Becker, M., Bradshaw, D.J., Harris, P.J. (2006). Interpreting the role of reagents in the flotation of platinum bearing Merensky ores. *International Platinum Conference 'Platinum Surges Ahead'*, The South African Institute of Mining and Metallurgy. pp.175-180.

69. Wills, B.A. (1992). Mineral Processing Technology, 5th edition. Pergamon Press, Oxford, New York, Seoul, Tokyo, pp. 495-521.

70. Xiao, Z., and Laplante, A.R. (2004). Characterising and recovering the platinum group minerals-a review. *Minerals Engineering*, vol. 17, pp. 961-979.

71. Yan, D.S., and Hariyasa (1997). Selective flotation of pyrite and gold tellurides. *Minerals Engineering*, vol. 10, no. 3, pp. 327-337.

72. Yekeler, M., and Yekeler, H. (2005). Molecular modeling study on the relative stabilities of the flotation products for arsenic-containing minerals: dixanthogens and arsenic(III)

xanthates. *Journal of Colloids and Interface Science*, vol. 284, no. 2, (April), pp. 694-697.

73. Zhengya Lu and Lawson, F. (1994). Metallurgical properties of synthetic sylvanites. *The Australian Institute of Mining and Metallurgy proceedings,* vol. 295, no. 2, pp. 89-93.

APPENDICES

APPENDIX A: Flotation procedures

	Time (min)	Solids (%)	pH	Reagent consumption(g/t)			
				SIBX	Senkol3	Guar 389	B-Froth.
Milling	60% -75µm	66	Nat.				
Conditioning	2	32		60	15		
Conditioning	2					100	30
Float-RC1	2						
Float-RC2	2						
Float-RC3	6						
Conditioning	2			30	30		
Conditioning	2					20	15
Float-RC4	10						
Float-RC5	10						

Table A 1: Batch flotation procedure for Platreef ore

	Time (min)	Solids (%)	pH	Syn. PGMs	Reagent consumption(g/t)			
					SIBX	Senkol3	Guar 369	B-Froth.
Milling	60% -75µm	66	Nat.					
Conditioning	30	32		PGMs				
Conditioning	2				60	15		
Conditioning	2						100	30
Float-RC1	2							
Float-RC2	2							
Float-RC3	6							
Conditioning	2				30	30		
Conditioning	2						20	15
Float-RC4	10							
Float-RC5	10							

Table A 2: Batch flotation procedure for Platreef ore spiked with synthetic PGMs

	Time	Solids	pH	Reagent consumption(g/t)			
	(min)	(%)		SIBX	Senkol5	KU9	B-Froth.
Milling	60% -75µm	66	Natural				
Conditioning	2	32		60	15		
Conditioning	2					100	30
Float-RC1	2						
Float-RC2	2						
Float-RC3	6						
Conditioning	2			30	30		
Conditioning	2					20	15
Float-RC4	10						
Float-RC5	10						

Table A 3: Batch flotation procedure for Merensky ore.

	Time	Solids	pH	Syn. PGMs	Reagent consumption(g/t)			
	(min)	(%)			SIBX	Senkol5	KU9	B-Froth.
Milling	60% -75µm	66	Nat.					
Conditioning	30	32		PGMs				
Conditioning	2				60	15		
Conditioning	2						100	30
Float-RC1	2							
Float-RC2	2							
Float-RC3	6							
Conditioning	2				30	30		
Conditioning	2						20	15
Float-RC4	10							
Float-RC5	10							

Table A 4: Batch flotation procedure for Merensky ore or Barren Feldspathic Pyroxenite spiked with synthetic PGMs

	Time	Solids	pH	Syn. PGMs	Reagent consumption(g/t)		
	(min)	(%)			SIBX	Guar 369	B-Froth.
Milling	60% -75µm	66	Nat.				
Conditioning	30	32		PGMs			
Conditioning	2				60		
Conditioning	2					100	30
Float-RC1	2						
Float-RC2	2						
Float-RC3	6						
Conditioning	2				30		
Conditioning	2					20	15
Float-RC4	10						
Float-RC5	10						

Table A 5: Batch flotation procedure for the reagents trial test carried out on Barren Feldspathic Pyroxenite spiked with synthetic Pt arsenide using only SIBX as a collector.

	Time	Solids	pH	Syn. PGMs	Reagent consumption(g/t)			
	(min)	(%)			$CuSO_4$	SIBX	Guar 369	B-Froth.
Milling	60% -75µm	66	Nat.					
Conditioning	30	32		Spiked				
Conditioning	2				30			
Conditioning	2					60		
Conditioning	2						100	30
Float-RC1	2							
Float-RC2	2							
Float-RC3	6							
Conditioning	2					30		
Conditioning	2						20	15
Float-RC4	10							
Float-RC5	10							

Table A 6: Batch flotation procedure for the reagents trial test carried out on Barren Feldspathic Pyroxenite spiked with synthetic Pt arsenide using only SIBX as a collector and copper sulphate activator.

	Time	Solids	pH	Syn. PGMs	Reagent consumption(g/t)			
	(min)	(%)			SIBX	DTC or DTP	Guar 369	B-Froth.
Milling	60% -75µm	66	Nat.					
Conditioning	30	32		Spiked				
Conditioning	2				60	15		
Conditioning	2						100	30
Float-RC1	2							
Float-RC2	2							
Float-RC3	6							
Conditioning	2				30	30		
Conditioning	2						20	15
Float-RC4	10							
Float-RC5	10							

Table A 7: Batch flotation procedure for the reagents trial tests carried out on Barren Feldspathic Pyroxenite spiked with synthetic Pt arsenide using SIBX as a primary collector and any of the DTCs or DTP as a secondary collector.

APPENDIX B: Compositions of blends of synthetic minerals

PGM Type	**Mass amount spiked into 2kg aliquote of ore**			
	Level1 (mg)	**Level2 (mg)**	**Level3 (mg)**	**Level4 (mg)**
Moncheite	1.3	2.1	4.3	6.4
Merenskyite	6.4	10.6	21.2	31.8
Sperrylite	1.5	2.5	4.9	7.4

Table B 1: Mass amounts of synthetic PGMs spiked into Platreef or Merensky ore.

Test	**Mass amount spiked into 2kg aliquote of ore**		
	Moncheite (mg)	**Merenskyite (mg)**	**Pentlandite (g)**
Te	75	-	-
As	-	53	-
Te-As	75	53	-
Te-As-S	75	53	6

Table B 2: Mass amounts of synthetic minerals spiked into Barren Feldspathic Pyroxenite

APPENDIX C: Equations

Equation C 1: Calculated head grade

$$h_i = \frac{Tt_i + \sum_{m=1}^{m=j} C_m c_{im}}{T + \sum_{m=1}^{m=j} C_m} \qquad \text{Equation C 1}$$

Where,

h = head grade
T= tailings mass
t= tailing assay
C= concentrate mass
c= concentrate assay
m=number for a stage concentrate
i= any element being considered e.g. Pt, Pd, Cu etc
j= total number of stage concentrates being collected.

Equation C 2: Upgrade ratio

$$r_i = \frac{g_{im}}{h_i} \qquad \text{Equation C 2}$$

Where,

r= upgrade ratio
g= cumulated grade up to the m^{th} *concentrate.*

APPENDIX D: BMS and Au Grade-Recovery curves for spiked Platreef ores

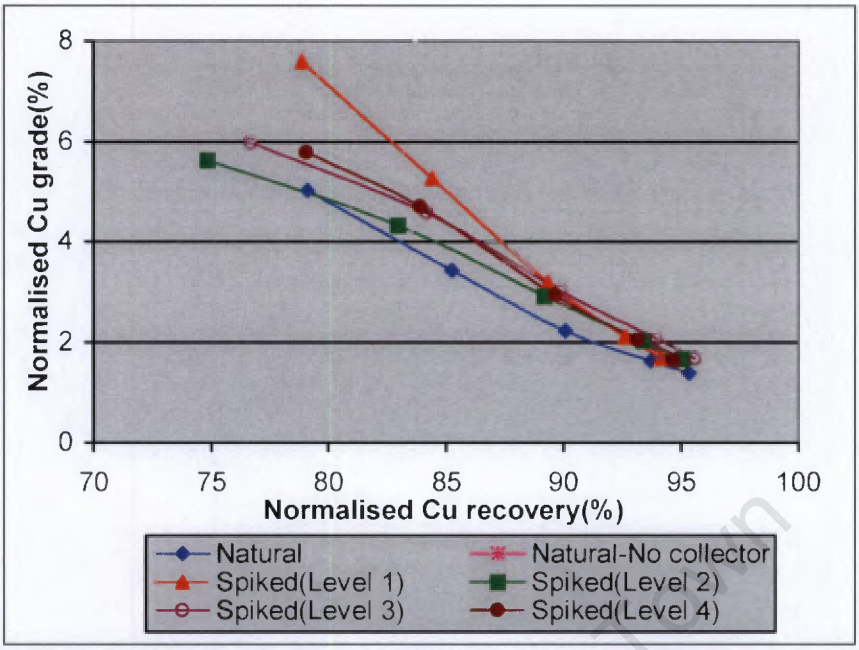


Figure D 1: Normalised Cu grade Vs Normalised Cu recovery for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

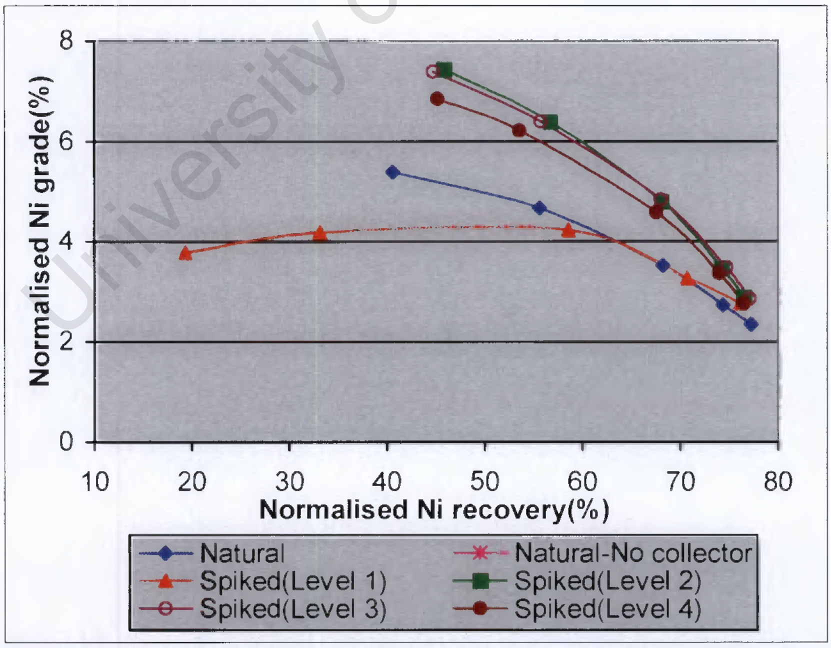


Figure D 2: Normalised Ni grade Vs Normalised Ni recovery for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

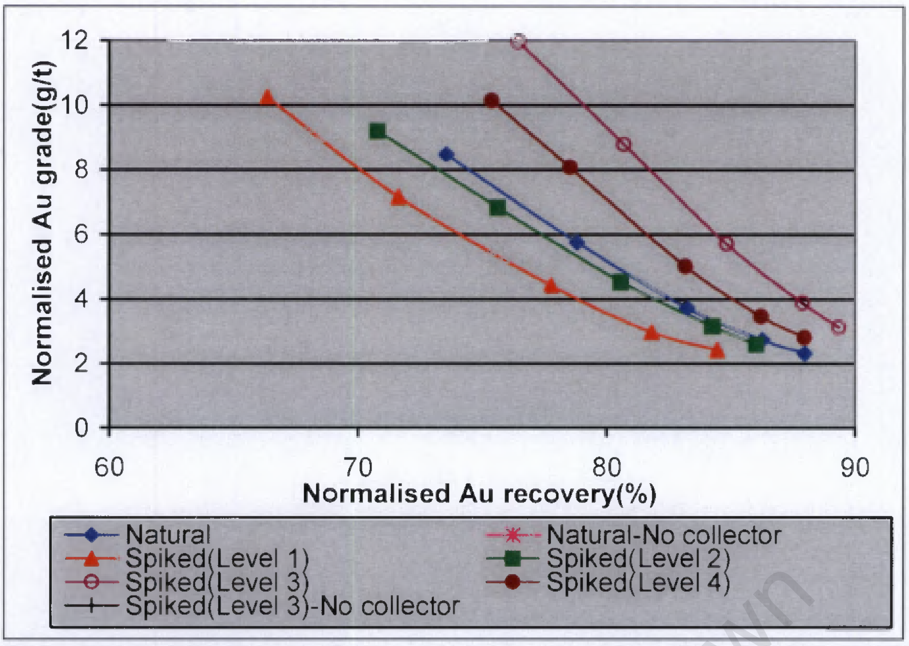


Figure D 3 :Normalised Au grade Vs Normalised Au recovery for flotation tests carried out on Platreef ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

APPENDIX E: BMS and Au Grade-Recovery curves for spiked Merensky reef ores

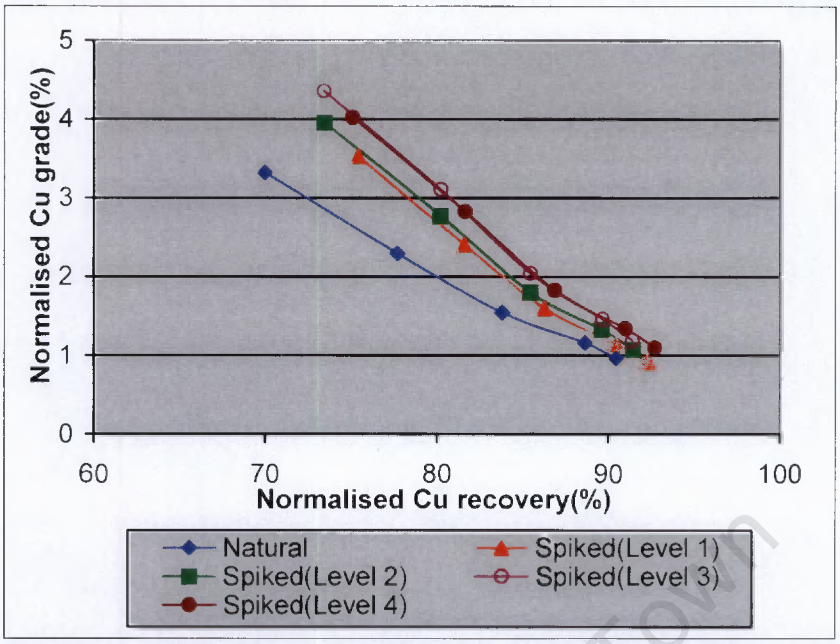


Figure E 1: Normalised Cu grade Vs Normalised Cu recovery for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

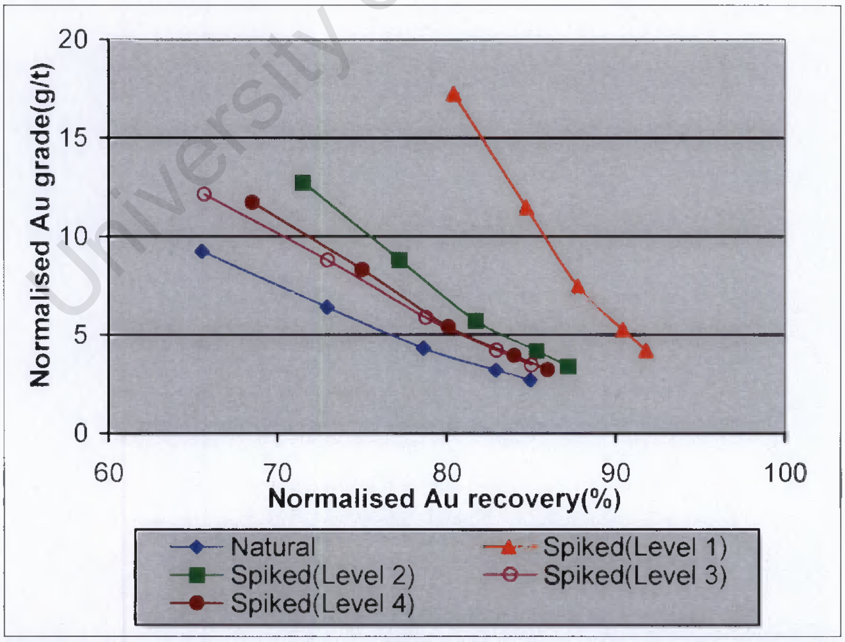


Figure E 2: Normalised Au grade Vs Normailsed Au recovery for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

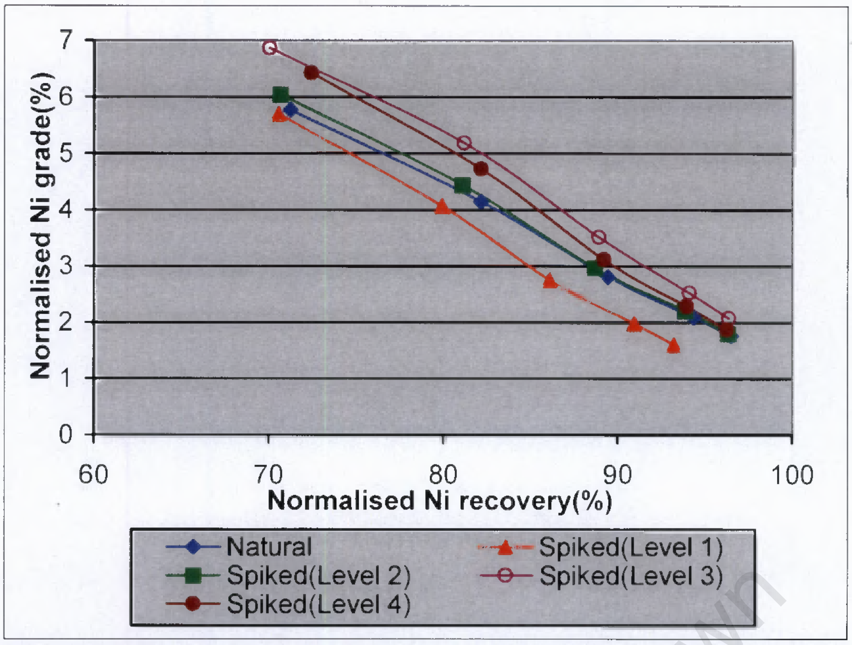


Figure E 3: Normalised Ni Grade Vs Normalised Ni recovery for flotation tests carried out on Merensky ore as well as the same ore spiked to various levels with a fixed blend of synthetic moncheite, merenskyite and sperrylite.

APPENDIX F: Platreef PGE telluride and arsenide grain sizes down the Flexi-Float bank

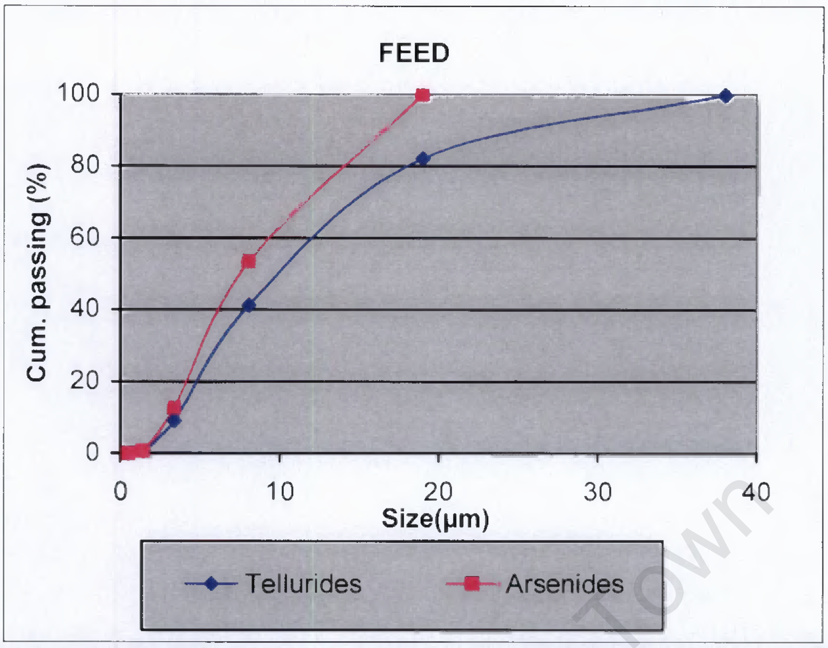


Figure F 1: Grain size distribution (% cum. Passing) of PGE tellurides and PGE arsenides in the Platreef feed from configuration 1 of the Flexi-Float.

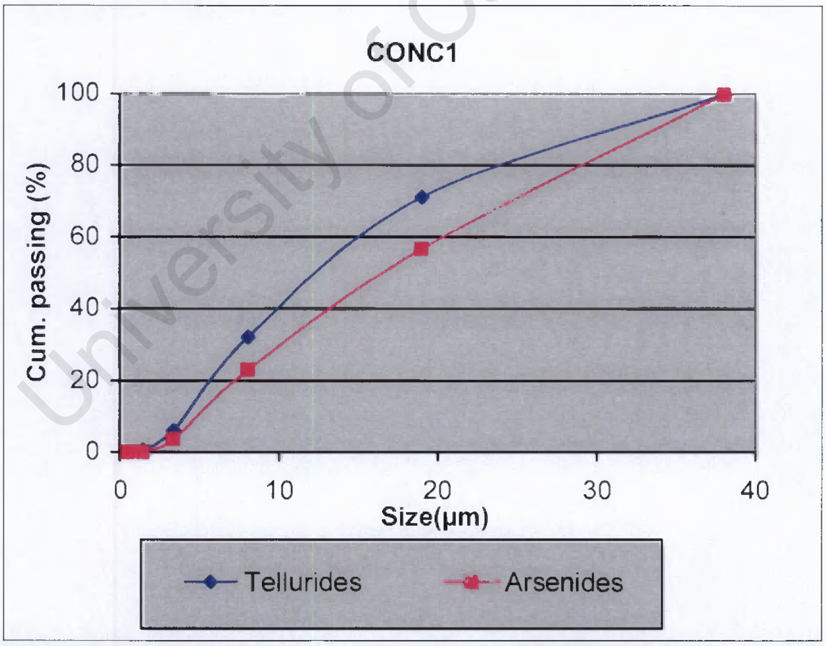


Figure F 2: Grain size distribution (% cum. Passing) of PGE tellurides and PGE arsenides in the Platreef Conc1 from configuration 1 of the Flexi-Float.

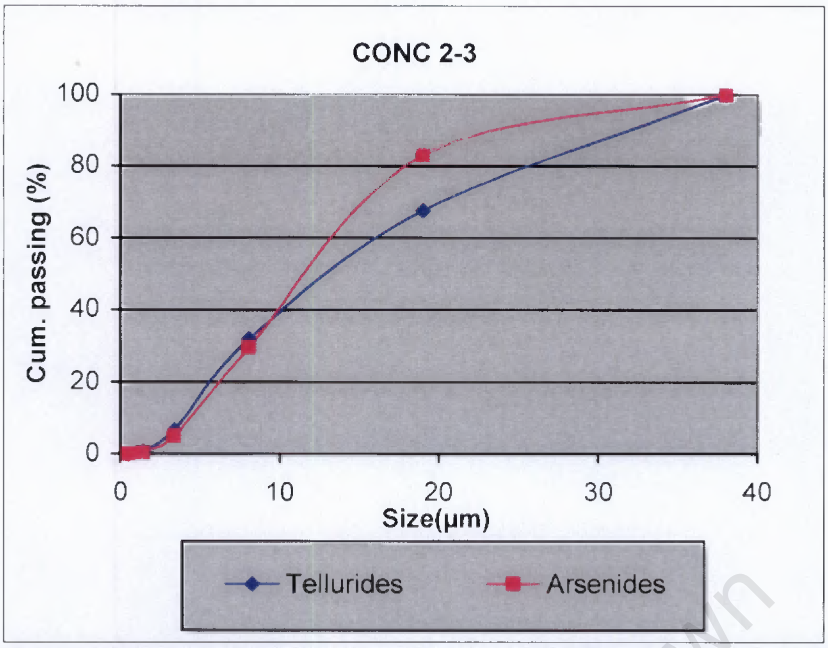


Figure F 3: Grain size distribution (% cum. Passing) of PGE tellurides and PGE arsenides in the Platreef Conc2-3 from configuration 1 of the Flexi-Float.

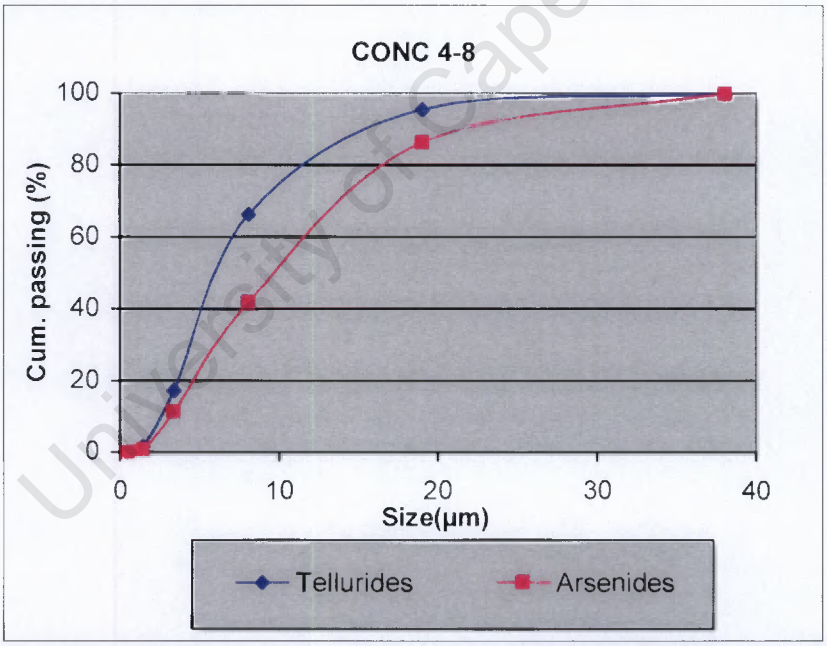


Figure F 4: Grain size distribution (% cum. Passing) of PGE tellurides and PGE arsenides in the Platreef Conc4-8 from configuration 1 of the Flexi-Float.

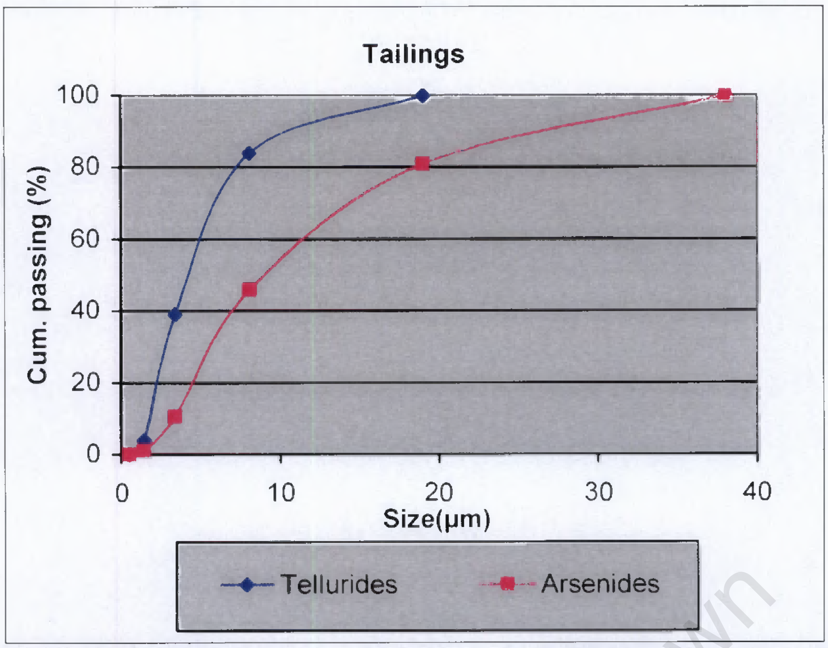


Figure F 5: Grain size distribution (% cum. Passing) of PGE tellurides and PGE arsenides in the Platreef tailings from configuration 1 of the Flexi-Float.