Investigating the role of pulp chemistry on the floatability of the Cu-Ni Sulfide ore

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Declaration

I declare that this thesis has not been submitted prior to this for any degree at this university or any other institution.

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SYNOPSIS

Sulfide minerals are a major source of metals. However, sulfide minerals, such as pyrite and pyrrhotite (Po), are few of the most abundant minerals, yet economically insignificant. Their existence with other sulfide minerals leads to an inefficient separation process as well as environmental problems, such as acid mine drainage during mining, processing and SO_2 emissions during smelting process. A part of the present study is focused on understanding the behavior of Po which leads to its undesired flotation and difficulties in its separation from Pentlandite (Pn).

In this study, the Magotteaux Mill® system was used in order to control the grinding pulp conditions, consequently surface properties of the minerals, which in turn affect the flotation behaviors. The Magotteaux Mill® allows for the simultaneous monitoring of electrochemical parameters; Eh, DO, pH and temperature during grinding. However, it is worth to mention here that the Magotteaux mill was purposely designed for testing different types of grinding media and generating plant conditions at a laboratory scale. Most of the studies in the past using Magotteaux Mill® were performed for this purpose only. This study is unique in this sense that a single grinding media (21 % Cr) has been used to test different grinding and flotation conditions in order to obtain the optimum floatability of the valuable minerals. However, it was not used in its “as it is” state for the present purpose. The mill has been modified to allow for the addition of reagent during the grinding stage, where first liberated surface generated was allowed to oxidize. The procedure developed in the current study exploits the slower oxidation of Pn in compared to Po to enhance the separation efficiency.

The current study had shown that adjustment of the surface properties of the minerals at grinding stage of is essential for the enhanced flotation of the valuable minerals. The properties of the surface layer at grinding stage dominate their surfaces characteristics in flotation, and manipulations of the pulp chemistry through reagent addition at later stage produces only marginal difference on their floatability. Further, it has been established from this study that the addition of xanthate at grinding stage is beneficial for the separation of the Pn from Po (which is susceptible for the rapid oxidation compared to the xanthate adsorption). However, wherever Po is a valuable mineral, the addition of xanthate in the flotation cell is recommended.

The batch flotation of the ore milled in the absence of oxygen (DO-0) and flotation with air has been used as an initial benchmark for comparison. The results come out to be very interesting and there was approximately 10% increase in the Pn recovery, when the ore was ground at a DO concentration of 0 ppm in comparison to no gas control at grinding stage. It becomes clear from this study that the presence of oxygen is critical to the consumption of xanthate and the absence of oxygen at various stages of grinding and flotation (Sparging with N_2 and floating with N_2) is detrimental for the recoveries of the valuable minerals. It can be also concluded from this study that initial xanthate consumption may takes place through the week physical adsorption and some of the xanthate get consumed in the absence of oxygen but it may not be making the mineral surface hydrophobic, and resulted in a poor recovery (Test-6). Another noteworthy observation of the current study is the apparent reversibility of xanthate consumption when the ore was ground at a DO concentration of 0 ppm and sparged with N_2 after slurry transfer. Further, surface analysis of the minerals at various stages is required to completely understand this behavior.

The flotation response of sulphide minerals is dependent on their oxidation characteristics, specifically what kind of layer that dominates their surfaces and how stable it is in the dynamic conditions of flotation slurries. In the case of Pn and Po, presence of iron oxide/hydroxides is always a dominant factor, although accumulation of activating metals ions, such as nickel and copper, on their surfaces are also critical as shown by XPS, IR spectroscopy, TOF-SIMS and surface extraction studies by many researchers. A greater extent of oxidation, as experienced by samples ground at DO concentration 6.5 showed a clear correlation with the high values of redox and DO concentration. Oxidation in sulphide flotation systems at grinding stage causes a reduction in grade and recoveries of the Pn and Po.

Kelsall unmodified kinetic model has been used for the analysis of the batch flotation test results. The analysis of the results showed that at a DO concentration of 1 ppm in the presence of X^- in the mill, the Pn surface was relatively unoxidized, while the Po surface is heavily oxidized which was confirmed by only marginal increase in the slow floating fraction of Pn and significant increase in the slow floating fraction of Po. The analysis result may have significant implications for fundamental study of the flotation, where sophisticated and expensive surface analysis techniques are being used for the study of mineral surface oxidation.

There are many proposals that a flotation system can be controlled by controlling the Eh value. However, the present study had shown that althouh the pulp potential measurement at grinding stage at a DO concentration of 1 ppm and pH-11 with no gas control were more or less similar but the variations in the recovery of the Pn between the two cases were entirely different. This confirms that Eh measurement can be used as a diagnostic tool for the process control in plant practice but it is also important to consider the means of Eh control.

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Note: In the result section, for all the figures test numbers are given followed by the test conditions. For e.g. test number 1 was conducted at a DO concentration of 0 ppm and is given by 1: DO-0.

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LIST OF ABBREVIATION

Å	Angstrom
BMZ	Basal Mineralized Zone
BMS	Base Metal Sulfide
Ca	Calcium
Ca^{2+}	Calcium ions
$Ca(NO_3)_2.4H_2O$	Calcium nitrate 4-hydrate
$CaCl_2$	Calcium chloride
C1	First concentrate
C2	Second concentrate
C3	Third concentrate
C4	Fourth concentrate
^0C	Degrees centigrade
CMR	Centre for Minerals Research
CSIRO	Commonwealth Scientific and Industrial Research Organisation
Cp	Chalcopyrite
DO	Dissolved oxygen
DS	Degree of substitution
g/t	grams per ton
g/mol	grams per mol
IR	Infra Red
L/min	Litres per minute

Mg	Magnesium
$MgSO_4.7H_2O$	Magnesium sulfate heptahydrate
$Mg(NO_3)_2.6H_2O$	Magnesium nitrate
MnO_2	Manganese dioxide
MLA	Mineral Liberation Analyser
MS	Metal Sulfides
MMZ	Main Mineralized zone
mm	Millimetres
m/v	Mass by volume
m^2/g	Square metres per gram
NaCl	Sodium chloride
Na_2CO_3	Sodium carbonate
NFG	Naturally floatable gangue
nm	Nanometres
ORP	Oxidation reduction potential
PAX	Potassium amyl xanthate
PCMZ	Chromititic Peridotite Mineralised Zone
PGM	Platinum group mineral
PGE	Platinum group element
PLC	Programmable logic control
Pn	Pentlandite
Po	Pyrrhotite
PSD	Particle size distribution

PID	Proportional integral and derivative
PandID	Piping and Instrumentation diagram
QEMSCAN	Quantitative Evaluation of Minerals using Scanning Electron Microscopy
ROM	Run of Mine
rpm	Revolutions per minute
SAX	Sodium Amyl Xanthate
SCADA	Supervisory Control and Discrete Access
SCE	Standard Calomel Electrode
SHE	Standard Hydrogen Electrode
SI	Selectivity Index
SIBX	Sodium Isobutyl Xanthate
TDS	Total Dissolved Solids
ToF-SIMS	Time of Flight Secondary Ion Mass Spectrometry
UCT	University of Cape Town
µm	Micron
X^-	Xanthate ions
X_2	Dixanthogen
XRF	X-ray Fluorescence

1 INTRODUCTION

1.1 Background

The process of froth flotation can be defined as the levitation/ elevation of the particles heavier than water by means of small quantities of the surfactant (Rao and Leja, 2004). The process utilizes the differences in the surface-chemical properties of the minerals to be separated. Sulphide ores are commonly exploited for their valuable components through the froth flotation. Thiol collectors are commonly used in sulfide flotation in order to enhance the differences in the surface properties of the valuable minerals and gangue minerals. The most commonly used thiol collectors are xanthates, which are alkali metal (e.g. Na^+, K^+) salts of monoalkyl esters of dithiocarbonic acid (e.g. Potassium Ethyl Xanthate: CH_3CH_2COSSK) (Harris, Ackerman and Aplan, 1988).

Despite the fact that the reduction of oxygen constitutes one half of the process of collector adsorption on the sulfide minerals, it has received only limited attention. The present study focuses on the influence of pulp oxygen content on the separation of pentlandite (Pn) and pyrrhotite (Po) contained in Nkomati ore.

Pn is the chief source of nickel worldwide and most often associated with Po (Buckley and Woods, 1991). Po is usually rejected to the flotation tailings as a waste product. However, the importance of Po flotation is evident in processing Platinum Group of Minerals (PGM) ores from the Bushveld complex in South Africa. A major difficulty in processing the Nkomati ore or in general Cu-Ni sulfide ores is the separation of Pn from Po. Maximum Po rejection is sought to obtain both a high grade Ni concentrate and to reduce the SO_2 emission at smelting stage.

Pn and Po are both very reactive to oxygen and exposure to atmospheric oxygen (during grinding) may result in the formation of ferric-oxy hydroxide (FeOOH) on both mineral surfaces. This may result in a similar behaviour during flotation and would make it difficult to separate these minerals by flotation. However, the current study aims to exploit the differences in the rest potentials of these minerals in order to separate them effectively. The grinding environment in the current study was adjusted such that deposition of the iron hydroxide could be directed towards the unwanted mineral i.e. Po and collector adsorption towards the valuable minerals i.e. Pn for the enhanced separation of Pn from Po.

Po is a metallic conductor having higher conductivity and lower rest potential than Pn (a semiconductor) i.e. free electrons are radically available on the Po surface. As soon as it comes into contact with the oxygen (reducing agent), it donates its free electrons and as a result hydroxide or oxyhydroxide species form in the presence of water on the surface which immediately react with the Fe present in the crystal lattice of Po and a thin monolayer of FeOOH is able to form on the surface. Pn is a semiconductor having a higher rest potential and lower conductivity than Po, depending upon the impurities it may be either a p-type or an n-type semiconductor. If it is assumed that it is n-type semiconductor its conductivity should always be less than Po i.e. the availability of free electrons is lower in compared to Po hence it is apparent that the FeOOH overlayer formation is more rapid on Po than on Pn in limited pulp Dissolved Oxygen (DO) concentrations.

If oxygen is present in a sufficient amount in the system as in the case of the grinding and classification circuit both Pn and Po are uniformly covered by a thin FeOOH overlayer, and hence their interaction with collectors should be similar. It is probable that the separation of these two minerals by flotation is inefficient unless either they are exposed to the flotation agents prior to oxidation, or their FeOOH overlayer is removed in some way. If collectors are added during the milling stage at a controlled DO level, the freshly generated fracture surfaces can be protected from the immediate exposure of oxidation and rather expose them to xanthate adsorption. The slower oxidation of Pn is obviously used to enhance its flotation, and it is hoped that the relative rates of oxidation/alteration of these two minerals combined with controlled pulp DO level can be utilized to enhance the flotation behaviour of the Pn.

This project investigates the relationship between xanthate adsorption at different pulp chemistry conditions in the mill and flotation cell and the subsequent effect on the flotation performance of the Nkomati ore. The main objectives of the project are to establish the optimum grinding and flotation conditions for the increased selectivity of Pn recovery and to conduct a xanthate adsorption study in different grinding and flotation environments.

In order to control the oxygen level and pulp potential, Magotteaux Mill® has been used. The Magotteaux Mill is a comminution device that allows for the measurement of insitu pulp chemistry. The mill enables the measurement and control of pH, dissolved oxygen (DO), oxygen reducing potential (Eh) and temperature during the grinding process. This specially designed mill allows for a detailed investigation of the effect of pulp chemical conditions in the mill during grinding on flotation efficiency.

The batch flotation of ore milled under normal atmospheric conditions and using air as the flotation gas would be considered as the initial benchmark/baseline for comparison. This test work focuses on the effects of varying DO concentration during grinding, changing the point of xanthate addition, varying sparging and flotation gases as well as adjusting the pH during grinding to determine the effects that these factors will have on the subsequent batch flotation recoveries and grades of the valuable minerals.

In last part of the tests work, some of the tests were conducted under no gas control at different pH conditions in order to compare and validate the effect of DO control on the recovery of the valuable minerals. It was hypothesized in these tests that this may results in a decrease in the recovery of the valuable mineral because of the effect of media corrosion and FeOOH formation and its deposition onto the mineral surface.

In the past studies have been conducted to study the effect of grinding media, DO, xanthate adsorption, flotation gases and pH separately. Further, most of the studies done in the past have observed the effect of these parameters in single mineral systems and it has been established by many researchers that when minerals are combined, as in an ore, they behave differently from the individual minerals. This study is unique in the sense that the DO concentration was measured and controlled in the grinding stage as well as in the flotation stage and focuses on a complex massive sulfide Cu-Ni ore.

1.2 Scope of work

Monitoring of the pulp chemistry in the mill will be achieved using the Magotteaux Mill® and flotation performance will be evaluated using the standard UCT batch flotation procedure. Xanthate adsorption studies will be carried out using UV spectroscopy at various DO levels and residual xanthate remaining in the solution will be monitored at different stages of the process. Flotation conditions will be varied using N_2 and air as sparging and flotation gases. All of the test work will be conducted using a 21 % chrome grinding media.

1.3 Objectives

The current study aims to investigate the effect of the pulp chemistry on the grinding environment and the subsequent flotation efficiency of the valuable minerals from an Nkomati ore. Specifically it will investigate the effect of oxygen content in the mill during grinding as well as in the flotation cell and the effect this will have on xanthate adsorption and the flotation selectivity of Pn.

2 LITERATURE REVIEW

2.1 Nkomati Mine

In 1970, a magnetic ore deposit on the Uitkomst farm in the Waterval-Boven district was discovered by the Anglo American Corporation (AAC) scientist, Dr Louis Coetzee. In 1975, the first assessment study was conducted and the results indicated a large tonnage low-grade open-pit resource of nickel and copper on the farm. Some preliminary geological and geophysical work to investigate the nickel potential on the adjoining farm, Slaaihoek was carried out by Anglovaal's Eastern Transvaal Consolidated (ETC) gold mine in late 1975. During that time, ETC had bought the mineral rights on Slaaihoek for its gold potential. The Ni resources in this region did not get further attention until 1987. In 1987, previous data on the Uitkomst was reviewed by AAC and this led to a feasibility study conducted between 1989 and 1991. Although the results of the study were not viable to motivate the development of a mining operation, in 1989 ETC drilled its first boreholes on Slaaihoek. A bulk sample of 21,300 tons obtained by the sinking of the Nico vertical shaft was evaluated in a pilot-scale concentrator (Walker, 1997). In March 1996 the development of the MSB mine had been given environmental approval and by January 1997 Nkomati started production.

Since 1997, mining was concentrated within the massive sulfide body (MSB) located beneath the basal gabbro in the Uitkomst complex, which was expected to be a sufficient reserve, to sustain the production up to 2006-07(Walker, 1997). In addition to these reserves, there was also expected to be about a million tons of high-grade and 7-million tons of low-grade nickel ore in the immediate vicinity of the current infrastructure (Bowers and Smit, 2008). Currently mining is focused on exploiting the more disseminated ores located in the Main Mineralized zones (Becker, 2009).

2.1.1 General Geology

Nkomati, a picturesque valley surrounded by a pine forest was first discovered by Dr P. Wagner in 1929. Nkomati is South Africa's first primary Nickel mine (Walker, 1997) in the Uitkomst complex, is situated between Waterval-Boven, Badplaas and Nelspruit in the Mpumalanga Province of South Africa as shown in Figure 2.1. It is approximately 300km east of Johannesburg. The complex is a long linear body, which is roughly boat-shaped in cross-section consisting of a series of lithological units of gabbros, harzburgites and pyroxenenites that form a keel or trough-like feature at the base (Becker, 2009; Gauert, 2001). The base and top of the body are concordant with the Transvaal sediments which dip at about 4^0 to the northwest. Due to erosion, the lowermost units of the complex are exposed on Vaalkop, while successively higher units are exposed to the west on Uitkomst and Slaaihoek. The complex dips below the escarpment at Slaaihoek where drilling has indicated at least a further 4km of down dip extent (Wolmarans and Morgan, 2009).

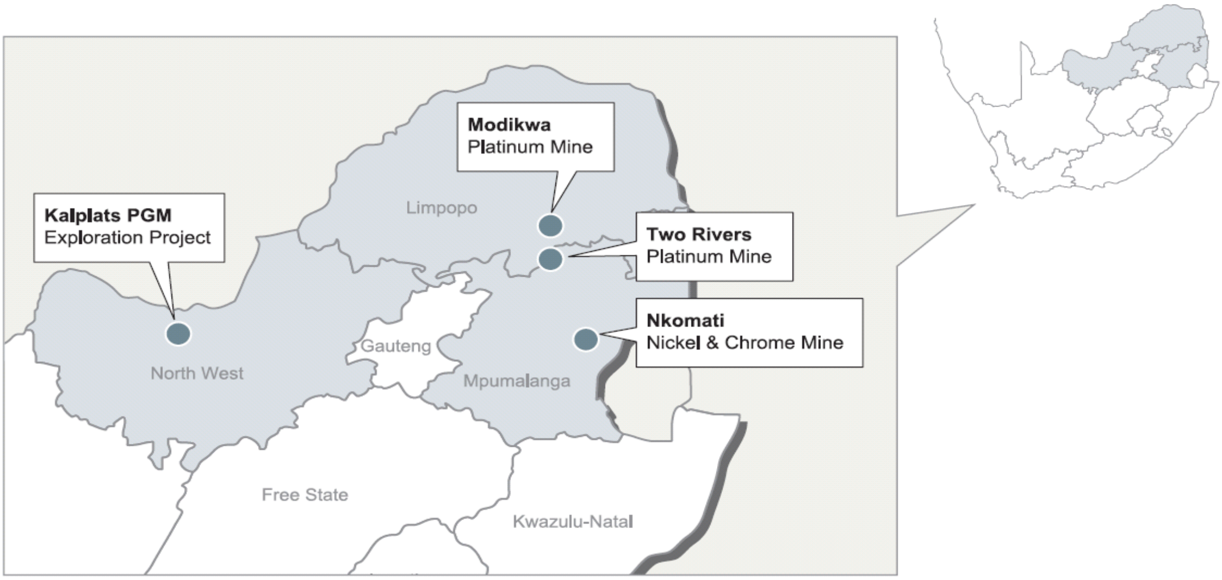


Figure 2.1: Nkomati general geology (Slater, 2006)

2.1.2 Nkomati Mineralogy

Nickel, copper, cobalt and Platinum Group Minerals (PGM) sulfide mineralization in the Uitkomst complex occurs in a variety of textural types that include disseminated sulfides, net textured sulfides, local concentrations of sulfides, and as a massive sulfide ore (Bradford and others, 1998; Gauert, 2001). Four zones of Ni-Cu-Co-PGM sulfide mineralization formed within the early Bushveld age (2 billion years ago) Uitkomst Complex is a layered, mafic-ultramafic body, intruded into the basal sediments of the Transvaal sequence (Wolmarans and Morgan, 2009). The complex outcrops for about 9km on the farms Vaalkop, Slaaihoek and Uitkomst in a broad valley in the Mpumalanga escarpment region. The four zones of sulfide mineralization comprise the following (Wolmarans and Morgan, 2009):

- The Main Mineralised Zone (MMZ) – The MMZ continues over about 8 km having a range of pristine to transformed, hybrid mafic-ultramafic rocks with small to very large quartzite and dolomite xenoliths, hosted by the Lower Pyroxenite Unit (LrPXT).

- The Chromititic Peridotite Mineralised Zone (PCMZ) - PCMZ having lower grade than MMZ, is hosted by the talcose and highly altered Chromititic Peridotite Unit (PCR).
- The Massive Sulfide Body (MSB) - The ore reserves in this zone, as on July 1, 1999, were 1.2-million tons at a nickel grade of 2.73%.
- Basal Mineralized Zone (BMZ) - BMZ in the Basal Gabbro (GAB) is more copper-rich and higher grade than the adjoining mineralization of the MMZ.

Pyrrhotite (Po), pentlandite (Pn), chalcopyrite (Cp) and pyrite are the prevailing sulfide minerals in decreasing order of profusion and small inclusions of cobaltite, gersdorffite, tucekite, galena, digenite, mackinawite, stibiopalladinite, millerite, arsenopyrite and gold were also observed within the other sulfides, where there are indications of alteration of the primary minerals (Wolmarans and Morgan, 2009). Magnetite, ilmenite and chromite are the common oxide minerals. Enrichment of the platinum group of element (PGE) also occurs as discrete platinum-palladium tellurides (merenskyite, michenerites, testibiopalladite) or as the arsenides (sperrylite) (Theart and de Nooy, 2001).

2.1.3 Brief Description of the processing plant

In 2005, laboratory test work was performed in order to develop a process route for treating the PCMZ ore. The results from laboratory scale test work on the PCMZ ore motivated Nkomati to move forward to a pilot plant campaign. In June 2006, the pilot plant campaign was started for both base metal as well as chromite recovery. The objective of this campaign was to use the breakage and selection parameters generated by the tests to estimate ball charges, mill power draws and circulating loads to compare two distinct milling options to produce required mill product of 80% passing 75μm. Three flotation circuits were also tested during the pilot plant commissioning. The circuit shown in the Figure 2.2 was later accepted because of its high efficiency and performance over the other two.

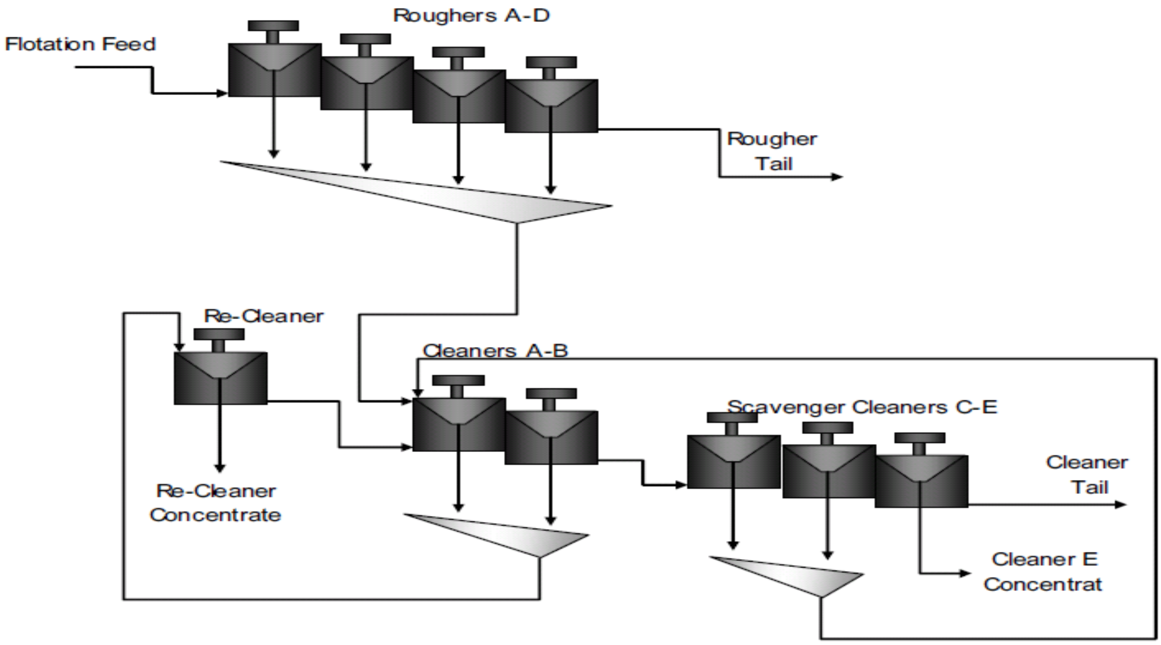


Figure 2.2: Nkomati PCMZ ore processing flow sheet (Wolmarans and Morgan, 2009)

This circuit was further investigated by making minor adjustments to optimize the reagent suite and adapted for the ore beneficiation. Present operating circuit details were unavailable in the literature but, based on the mineralogy as discussed in section 2.1.2, it could be established that it would be the modified version of the above flotation circuit, which is in present practice.

2.2 Mineral Processing

Generally unit operations in the mineral processing industry are broadly subdivided into four distinct operations: Liberation, Separation, Dewatering, and Disposal (Figure 2.3). Liberation, namely the release of the valuable minerals from their waste gangue minerals is accomplished by *comminution*, which involves crushing, and most often grinding, to such an extent that the valuable minerals could be released from the gangue minerals at the coarsest possible particle size (Wills et al, 2006). Lambert acknowledged that liberation of the valuable minerals, from the gangue minerals, without grinding the gangue mineral is the greatest technological challenge for comminution research around the world (Lambert, 2010).

Based on the mineralogy of the ore, various separation or concentration techniques such as optical sorting, gravity concentration, magnetic concentration, high-tension separation or froth flotation can be utilized to concentrate the valuable minerals from the gangue minerals.

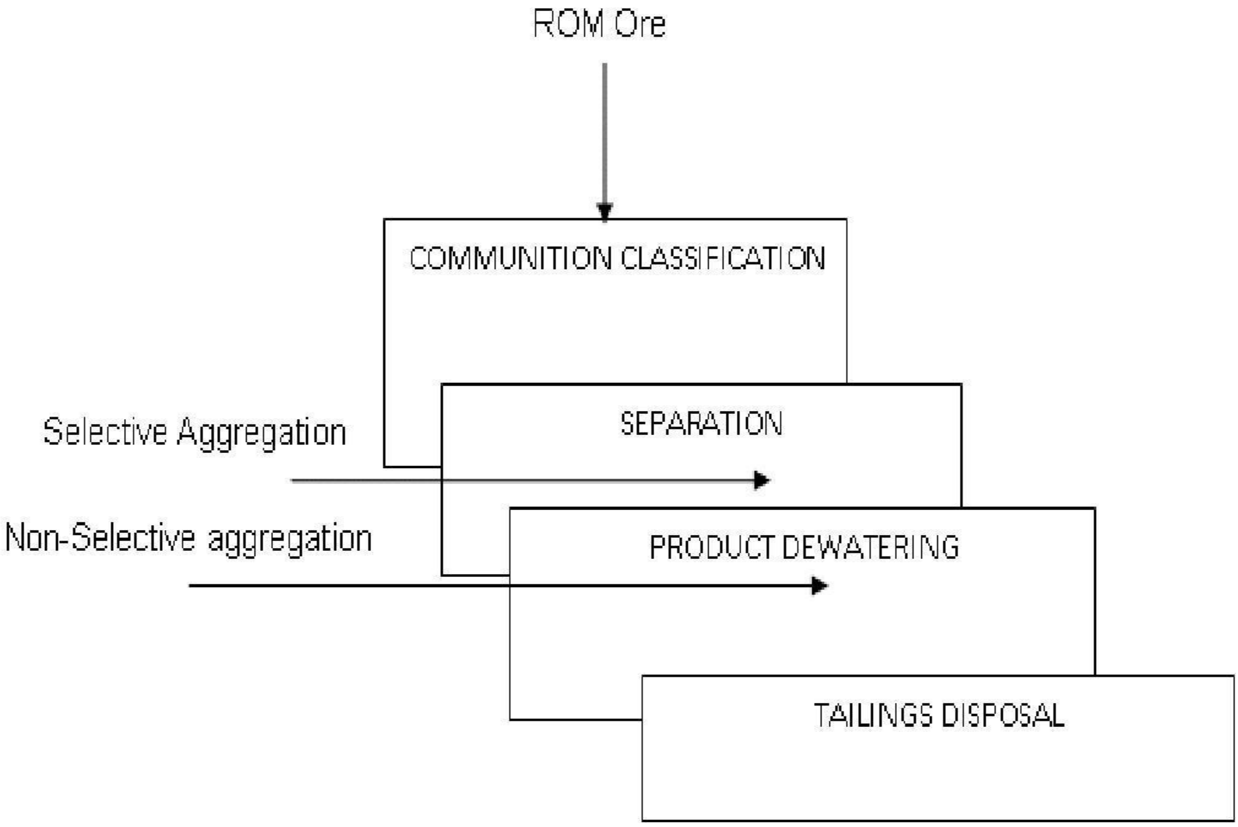


Figure 2.3: Mineral processing flow sheet (Laskowski, 2005)

2.3 Froth Flotation

Froth flotation, discovered in the mid 18th century, has become the single most important process in the recovery of metal sulfides in the minerals industry (Fuerstenau, 1976)). It is the only immense beneficiation process, which is used to treat approximately two billion tonnes of ore annually (Pearse, 2005). This process utilizes the differences in surface properties between the valuable and gangue minerals in order to separate them.

(Laskowski, 2005) expressed froth flotation as a carrier process in which air bubbles drag the hydrophobic minerals to the froth phase to be recovered to the concentrate and leave the hydrophilic minerals into the pulp phase which can then report to the tailings. In other words, by controlling the surface properties of the minerals in the pulp, the desired minerals can be separated from the gangue. So, the primary requirement for the successful recovery of the valuable minerals by froth flotation is that the surfaces must be rendered hydrophobic, thus the valuable minerals are lifted by an air bubble through the pulp phase and enter the froth, from where they can be collected to the concentrate. Thus, the unwanted gangue remains in the pulp and passes out of the cell in the tailings.

A large number of physical and chemical variables influence the flotation process.(Klimpel, 1984) divided these major variables into three main groups as shown in Figure 2.4. The primary focus of this research is on the chemical aspects of flotation.

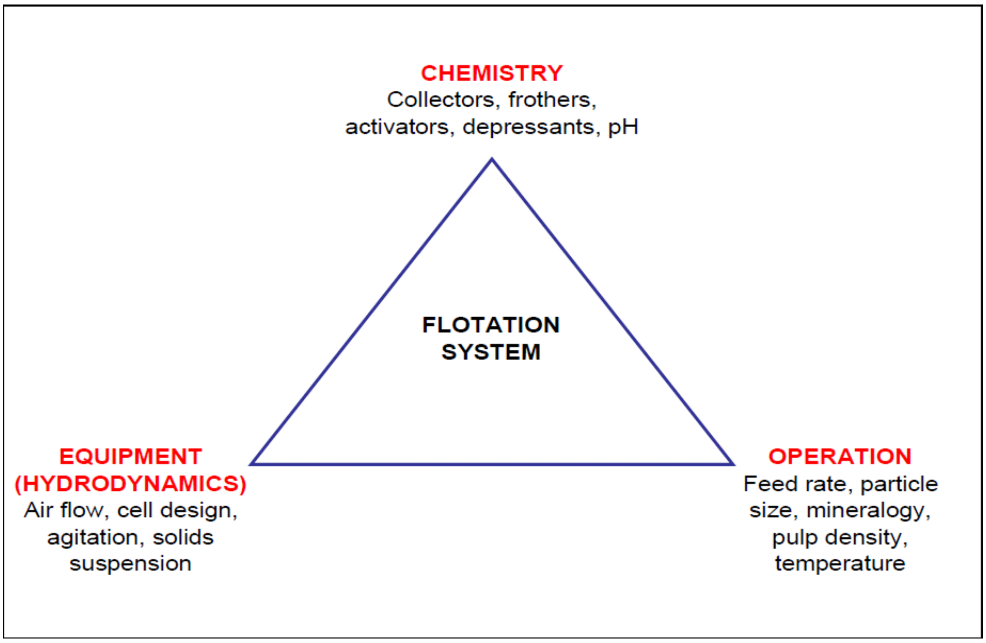


Figure 2.4: Summary of the variables in the flotation system (Klimpel, 1984).

2.4 Collectors in sulfide mineral flotation

Collectors are organic compounds (ionizing or non-ionizing), which render selected minerals water-repellent, or hydrophobic by adsorption of ions or molecules onto the mineral surface. Collector adsorption reduces the hydrated layer stability of valuable minerals and allowing for the attachment of the particle to a bubble on contact. Ionizing collectors are classed in accordance with the type of ion, anion or cation that produces the water-repellent effect in water (Wills et al,, 2006). Sulphydryl (thiol collectors) are anionic collectors in which the polar group contains bivalent sulphur (thio compounds) are reported to be the most powerful, selective and commonly used collectors in the minerals industry (Avotins et al, 1994) Commonly used collectors are the xanthate series, in the form of the sodium or potassium salts of a xanthic acid, and in this work sodium isobutyl xanthate (SIBX) was used for all flotation tests. The structure of SIBX is shown in Figure 2.5.

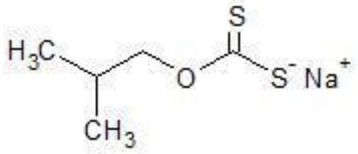


Figure 2.5: Chemical structure of Sodium Isobutyl Xanthate (King, 1982)

According to (Laskowski, 2005) the most widely used thiol collectors, xanthate, accounts for 65% of the anionic collectors utilized in the flotation of sulfide ores. The surface activity of the collectors at the minerals surface leading to the formation of hydrophobic film follows chemical or electrochemical interactions were remain in controversy for many years. The detailed mechanism of collector interactions with mineral will be discussed in the following section.

2.5 Mineral-Collector Interaction theory

Most flotation research in the early 1900's was devoted to understanding the concept of mineral-collector interactions and hydrophobic surface generation. Although the use of xanthate as a collector started in 1924-1925 (Gaudin and Fuerstenau, 1976; Sutherland and Wark, 1955), the detailed studies of the mechanisms of collector adsorption onto sulfide minerals only commenced in the late 1950's. Different theories have been proposed by different researchers, but most of them remained in controversy until the 1960's. Ian Wark quoted the honorary lecture of Maurice Fuerstenau in his book according to whom, "flotation was the happy hunting ground of the theorist, and there were almost as many ‘theories of flotation’ as there were writers on the subject.”(Sutherland and Wark, 1955).

Four different theories on the mechanism of the collector adsorption in flotation have been advanced:

- Chemical reaction theory
- Ion exchange theory
- Neutral molecule adsorption theory
- Electrochemical theory (Mixed Potential Theory)

2.5.1 Chemical reaction theory of collector adsorption

(Taggart and Behre, 1945) proposed the theory of collector mineral interaction through “chemical reaction”. These researchers had defined the collector as a reagent having the right structure that can produce a salt of low solubility by interaction with the mineral (Sutherland and Wark, 1955). They hypothesized that when a mineral interacts with a collector the reaction product is a metal-collector salt which has a lower solubility and renders the mineral surface hydrophobic. This theory was not accepted, as the major difficulty with this theory was that there are many other collectors (non xanthate or sulphur-containing) which do not form insoluble compounds with the mineral components, and further quantitative study has shown that the solubility product as derived from adsorption measurements differs from the solubility product as determined stoichiometrically.

2.5.2 The ion exchange theory (Ion Adsorption theory)

In the early stage of flotation, the hydrophobic character of the surface covered with xanthate species was judged by contact angle measurement. It was assumed that xanthate would form a chemisorbed uniform monolayer on the mineral surface, from the fact that a constant value of contact angle was obtained for all concentrations exceeding the critical concentration. However, using autoradiography, Plaskin and Bessonov clearly established that a non-uniform, patchlike distribution of adsorbed xanthate is created on the mineral surface (Plaksin and Bessonov, 1957; Rao and Leja, 2004). Sutherland and Wark believed that the interaction of a thiol collector with a mineral surface should be considered as *adsorption* i.e. collector is loosely held by weak attraction to the surface of the mineral which is non permanent and much weaker than *absorption* (Sutherland and Wark, 1955). Their mechanism was based on the adsorption measurements, which showed an exchange of xanthate ion for an equivalent amount of anionic species (sulfoxy ions like sulphate or thiosulphate) from the mineral surface (Sutherland and Wark, 1955). Further experimental proof for an ion exchange mechanism is provided by thermo-chemical measurements on the interaction between the sulfide mineral and collector. In the late 1950's, Plaskin and coworker had also established the necessity of oxygen for the flotation of sulfide minerals with thiol collectors(Plaksin and Bessonov, 1957) and based on their findings Gaudin concurred with Sutherland and Wark's explanation of simple ions adsorption phenomena (Gaudin and Fuerstenau, 1976) and proposed the mineral collector interaction as chemisorption, in which interaction between a collector and a mineral surface is strong, as opposed to physisorption, which is characterized by a weak Van der Waals forces.

2.5.3 Neutral molecule adsorption theory

Cook and coworkers pointed out that adsorption of collector ions would lead to the surface of the mineral being highly charged which would not be the case for hydrophobicity (Cook and Nixon, 1950; Cook and Wadsworth, 1957). (Cook and Nixon, 1950) hypothesize the adsorption of a non-ionic collector species (xanthic acid) and explained their results regarding xanthate adsorption isotherms, contact angle on polished sulfides, and flotation (Rao and Leja, 2004). The driving force behind the theory of non-ionic adsorbate was that adsorption of the neutral molecules was not inhibited by the excess charge in the electrical double layer. However, this theory was also rejected due to the instability and very short life of xanthic acid (Rao, 1971).

2.5.4 Electrochemical theory (Mixed Potential Theory)

(Salamy and Nixon, 1954) considered another view of neutral surface generation and (Nixon, 1957) suggested an alternate mechanism "in which, due to the semiconducting nature of sulfide minerals, the troublesome electrons are removed by reaction with oxygen". Based on their xanthate adsorption experiments on mercury, (Salamy and Nixon, 1953; Salamy and Nixon, 1954) revealed the necessity of oxygen for the sulfide mineral to float with xanthate collector. Salamy and Nixon's model of neutral surface generation was also supported by (Plaksin and Bessonov, 1957). (Nixon, 1957) reconciled the theory of collector adsorption and specified different anodic reactions of electron transfer from collector to mineral to explain the different theories. However, the cathodic reaction was assumed to be the reduction of oxygen for all theories.

At Cathode:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (2.1)$$

At Anode:

$$X^- \rightarrow X_{ads} + e^- \qquad \text{(Wark's Adsorption Model)} \quad (2.2)$$

$$MS + 2X^- + 4H_2O \rightarrow MX_2 + SO_4^{2-} + 8H^+ + 8e^- \qquad \text{(Taggart's Adsorption Model)} \quad (2.3)$$

In addition, Nixon recognized a third anodic oxidation of the thiol collector to its dithiolate at the mineral surface, which has chemisorbed the collector or reacted to form a metal collector compound, as given by reaction (2.4) (Nixon, 1957).

$$2X^- \rightarrow X_2 + 2e^- \qquad (2.4)$$

Overall reaction (Redox reaction):

$$MS + 2X^- + 2O_2 \rightarrow MX_2 + SO_4^{2-} \qquad (2.5)$$

$$2X^- + \tfrac{1}{2} O_2 + H_2O \rightarrow X_2 + 2OH^- \qquad (2.6)$$

This theory had been supported by many investigators (Fuerstenau, 1976; Hu, 2009; Janetski, Woodburn and Woods, 1977; Rand and Woods, 1984; Richardson et al, 1994).

In order for the overall redox reaction (anodic oxidation of xanthate and cathodic reduction of oxygen) to proceed at a finite rate, there must be a potential between the mineral and the solution. This potential is known as the mixed potential and this term is extensively used for flotation systems.

The role of oxygen reduction in xanthate adsorption has kept the xanthate adsorption mechanism in controversy even after the 1960's (King, 1982). In the 1970's and 80's further electrochemical studies were conducted in order to investigate the electrochemical aspects of the flotation system (Chander and Fuerstenau, 1974; Kowal and Pomianowski, 1973; Woods, 1971). To consider the flotation system from this aspect in detail, it is essential to understand the various technical terms and principles of electrochemical measurements used in defining the electrochemistry of a flotation system.

2.6 Electrochemical Potential and their implementation

The electrochemical potential (E) and the redox potential are used as general terms in electrochemical measurement. They do not imply any particular condition for the system being studied except that a measurement is taken. However, the rest potential (E^r), standard potential (E^0), and oxidation reduction potential (ORP or Eh) refers that measurements that are taken, when the system is at equilibrium (Rao and Leja, 2004).

For the standard state (P = 1 atm, T= 298^0K), the measured potential is the standard potential of the reaction (E^0). Eh implies that the potential expressed was measured with respect to standard hydrogen electrode (Natarajan and Iwasaki, 1972). Under dynamic conditions in a complex system, such as those encountered in flotation, the electrochemical potential is expressed as a mixed potential as it involves several charge transfer reactions (Rao and Leja, 2004).

When the measurement refers to ions in the system, it is termed the solution potential. When it refers to the solid phase in contact with ions it is referred as the galvanic potential. If the state of the system (temperature, pressure and activity of ions) is known, the measured potential can be correlated to the thermodynamic properties of the reaction occurring within the system. By means of this, many researchers (Becker, 2009; Bozkurt et al, 1998; Buswell et al,, 1998; Chander and Fuerstenau, 1974; Ekmekci and Demirel, 1997; Gardner and Woods, 1979b; Harris and Finkelstein, 1975b; Rand and Woods, 1984; Woods et al, 1989; Woods et al, 1994; Woods, 2003) have used linear potential sweep voltammetry (lpsv) with sulfide mineral electrodes to interpret the reaction product in single mineral as well as mixed mineral systems. One obvious difficulty with the application of thermodynamic data to a mixed mineral system is that it does not take into account the rates of the processes. A process may proceed in the mixed mineral system because it has the greatest rate rather than the most favorable equilibrium potential.

The potential measured in a mineral slurry or pulp is termed the pulp potential Ep (Jones, 1991). It is measured by the use of a noble metal electrode such as Pt and gold in combination with a standard reference electrode, usually a saturated calomel or Ag/AgCl electrode. The value with reference to Standard Hydrogen Electrode (SHE) is calculated by adding the value of the standard redox potential of the reference electrode used.

2.6.1 Principal of Electrode potential Measurement

(Natarajan and Iwasaki, 1972) conducted a fundamental study of Eh measurements in a hydrometallurgical system. They stated that when an electrode is dipped into an aqueous solution, the thermal energy of the ions would cause its continuous interaction with the electrode surface. However, only those ions which possess sufficient energy were able to overcome the energy barrier (activation energy) and transfer the electrons to electrode surface as shown in Figure 2.6.

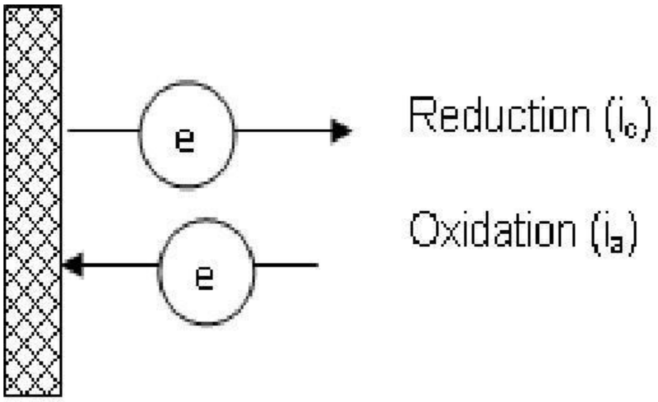


Figure 2.6: Electrochemical free energy profiles for a metal (electrode)-solution interface.
(Natarajan and Iwasaki, 1972)

At equilibrium, this oxidation and reduction phenomena may result in two equal and opposite currents anodic and cathodic (i_a and i_c), the magnitude of which is defined as the exchange current density (i_0). When i_a and i_c are plotted in the Tafel plot (Logarithmic current Vs Potential), they each represent a reversible half cell reaction. The intersection of the two lines corresponding to i_a and i_c on the tafel plot gives the equilibrium potential E_0 defined by the Nernst equation and exchange current density.

2.6.2 Rest Potential

When a sulfide mineral is immersed in water, it can form an electrode. When this is connected to a second electrode via a voltammeter as shown in Figure 2.7 a potential can be recorded. This potential is believed to results from the following reaction at the mineral-water interface.

$$MS + H2O \rightarrow M(H_2O)^{2+} + S^{-} + e \qquad (2.7)$$

This reaction is known as an oxidation, de-electronation, or anodic reaction. The electrons released are accepted by the second electrode in a reduction, electronation or cathodic reaction. The potential measured is termed the rest potential (Er). The mineral electrode is more correctly known as the working electrode. A common reference electrode is the standard calomel electrode (SCE) in which case the reduction is given by:

$$Hg_2Cl_2 + 2e \rightarrow 2Hg + 2Cl^- \qquad (2.8)$$

Rest potential values for e.g. pyrite measured at pH 4 with reference to the different electrodes, are given as:

0.39 V vs. SCE

0.44 V vs. Ag/AgCl and

0.66 V vs. SHE

Thus to convert SCE to SHE 0.27 V is added to the SCE value and to convert from Ag/AgCl to SHE 0.22 V is added to the Ag/AgCl value The absolute values of the potentials are not as important as their relative values. The experimental set-up as shown in Figure 2.7 can be used to determine the effect on the potential of a system on changing a variable such as pH, collector addition, aeration etc.

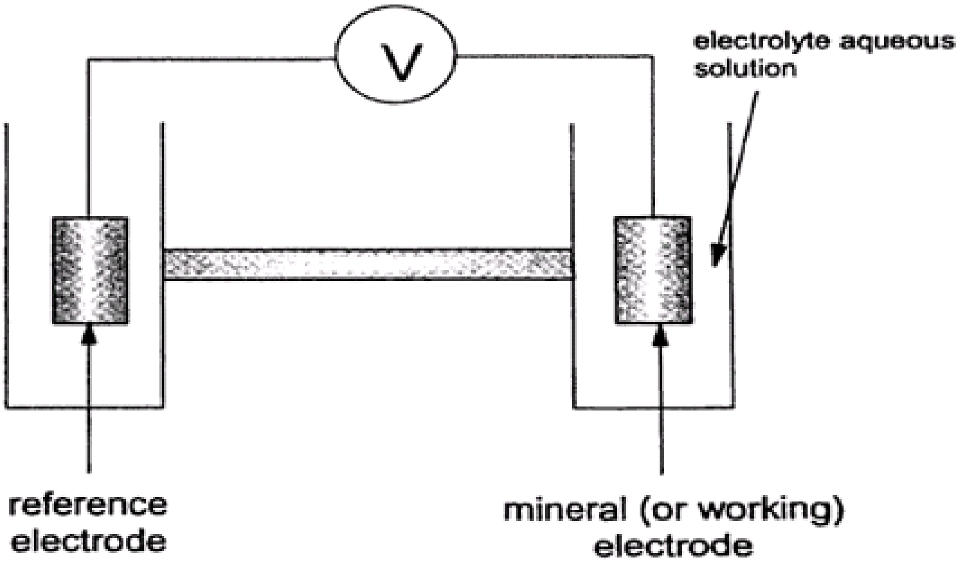


Figure 2.7: Schematic Representation of the experimental set up to measure the rest potentials at a mineral surface (Rao and Leja, 2004)

Electrochemical characterization of sulfide minerals can be done by measurement of their rest potentials. Rest potentials of some minerals are given in Table 2.1. The higher the rest potential, the nobler (less susceptible to oxidation) the mineral and the least active it is in a thermodynamic sense. Pyrite has the highest rest potential when compared to other minerals in a mixed sulfide minerals system as shown in Table 2.1, the surface of the other given sulfide minerals will act as anodic relative to pyrite and can therefore be oxidized.

Table 2.1: Rest potential of certain sulfide minerals at pH 4 (Majima and Takeda, 1969)

Mineral	Rest Potential (V vs. SHE)
Pyrite	0.66
Marcasite	0.63
Chalcopyrite	0.56
Sphalerite	0.45
Covelite	0.42
Bornite	0.40
Galena	0.28
Argentite	0.12
Stibnite	0.11

The rest potential assumes that only one reaction is occurring and the reduction and oxidation reaction is at equilibrium, however under real conditions this is rarely the case (Rao and Leja, 2004). If oxygen is assumed to be present within the system, it is quite feasible that, on one part of the mineral surface, the oxidation reaction is occurring while at another the reduction of oxygen is occurring as shown in the Figure 2.8, although in such a case the measured potential is termed the rest potential, the redox condition in the solution is determined by the mixed potential. When considering complex systems, such as flotation, it is very difficult to interpret the mixed potential, as there are several minerals and reagents reacting simultaneously.

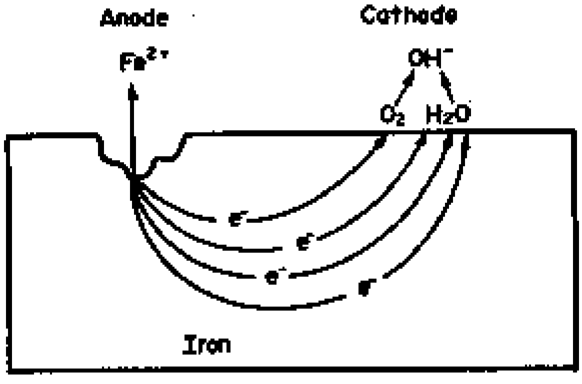


Figure 2.8: Electrochemical cell set up between anodic and cathodic sites on an iron surface undergoing corrosion (Anon, 2010)

2.6.3 Mixed Potential

A mixed potential arises when there are two (or more) redox couples present in the system and they are not in equilibrium, i.e.

$$E^0_{Red1/Ox1} + (0.059/n_1) \log [Ox_1] / [Red_1] \neq E^0_{Red2/Ox2} + (0.059/n_2) \log [Ox_2] / [Red_2]$$

Thus, the redox condition in the solution is not characterized by a unique Eh value, but rather it is represented by two potentials, i.e., those of the two redox couples present as shown in Figure 2.9. When an indicator electrode is introduced into the solution, its electrons can be exchanged in between two separate redox couples and the measured potential will reach a value, lying between the reversible couple where the anodic and cathodic components of the process proceed at equal and opposite rates and is termed the mixed potential of the system.

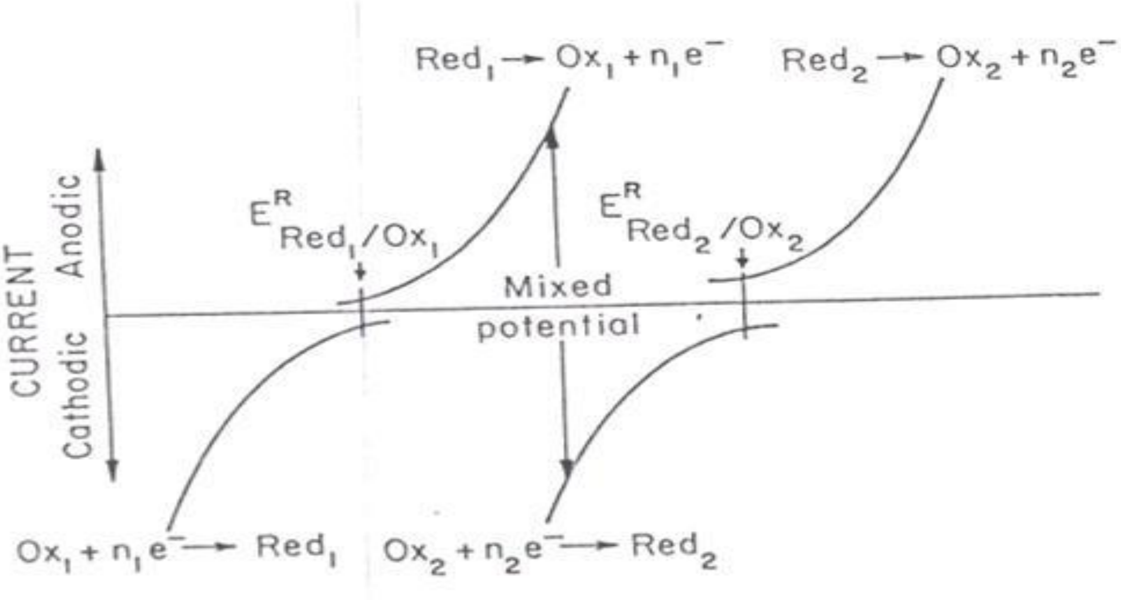


Figure 2.9: Schematic representation of a mixed potential system (Rand and Woods, 1984)

Mixed potential in a system can be different for different indicator electrodes because the rate of an electrode reaction (i.e. electron transfer to electrode) is dependent on the nature of the electrode surface.

2.6.4 Type of Electrode

Natarajan and Iwasaki (1984) mentioned that to measure the electrode potential of a system, it is critical to choose the electrodes according to the conditions and objectives of the test, otherwise the observed potential may not be that of a redox potential but simply an electrode response. In order to measure the oxidation reduction potential of the pulp three types of electrodes are commonly used in the mineral industry (Chander, 2003).

- Metal electrodes
- Ion selective electrodes
- Mineral electrodes

2.6.4.1 *Metal Electrodes*

Generally platinum is used as the electrode material in Eh measurements although gold, carbon, iridium are also cited in the literature (Glasstone, 1942). In noble metal electrodes, the potential is measured with reference to the calomel (Hg/Hg_2Cl_2) or silver/silver chloride (Ag/AgCl) electrode and reported on a hydrogen scale. Noble metal electrodes are generally believed to be inert and act only as reservoirs for electron transfer but in practice an oxide coating is often formed on the electrode surface, unless special precautions are taken to avoid its exposure to air. While measuring the electrode potential of an aqueous Po suspension (Natarajan and Iwasaki, 1972) observed that, when sufficient oxygen is present in the system and all the dissolved species from Po get oxidized, the electrode responded to the oxygen concentration in the pulp and the Eh measured by the platinum electrode followed the relation:

$$Eh = Ea - 0.059\ pH$$

Where, Ea is 0.85 V in an oxygenated acid solution and 0.95 V in an oxygenated alkaline solution. The difference in the Ea values is as a consequence of the platinum which corresponds to the Pt/Pt-O reaction in acid solutions and $Pt/Pt\ (OH)_2$ in alkaline solutions.

(Rand and Woods, 1984) investigated the effect of oxygen on the response of the Pt electrode for a range of Fe^{2+}/Fe^{3+} ratios present in the solution. In the absence of oxygen, the Eh value was determined by the ratio of Fe^{2+}/Fe^{3+} but not by the total concentration of the iron, as expected by the Nernst equation.

$$xOxid + mH^+ + ne^- = yRed + zH_2O \qquad (2.9)$$

$$Eh = Eh^0 - 0.059\ (m/n)\ pH + (0.059/n) \log [Oxid]^x / [Red]^y \qquad \text{at } 25^0C$$

However, in the presence of oxygen, the measured Eh was affected by the total iron concentration as shown in Figure 2.10. It can be seen from this figure that, at low iron concentrations, DO in solution overcome the presence of the iron species.

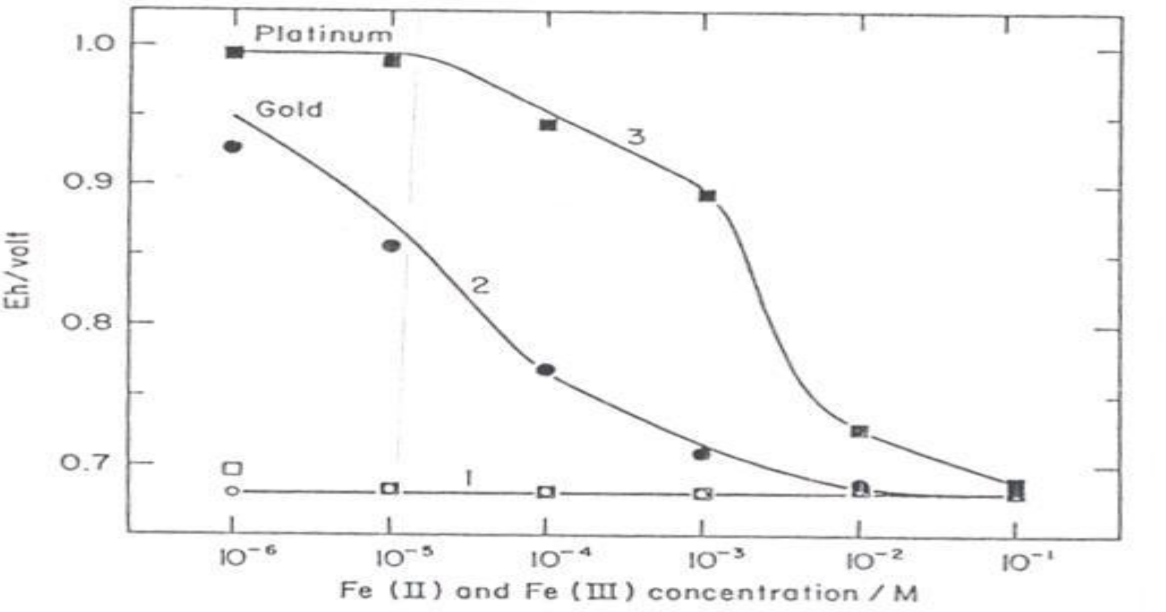


Figure 2.10: Variation of the electrode potential with iron ions, Fe2+ and Fe3+, of equal concentration in 1M H2SO4, in the presence (2 and 3) and absence (1) of oxygen (Rand and Woods, 1984)

(Gebhardt, 1988) also studied the effect of oxygen on the response of platinum electrodes. Their experimental results implied that platinum is much more sensitive to oxygen and the measured electrode potential of platinum should vary with DO content of the solution. Based on this, Chander strongly recommended the use of platinum as an Eh electrode when the oxygen content in the pulp is an important species to be monitored (Chander, 2003). However, when it comes to correlating and understanding the flotation behavior of a complex sulfide ore with respect to the electrode potential measured with a Pt electrode care should be taken, as it is measuring the potential of the mineral-solution interface rather than the platinum electrode potential that controls the electrochemical reaction occurring at the mineral surface (Buswell and Nicol, 2002).

(Rand and Woods, 1984) made a comparison of Au with Pt as the Eh electrode in a solution containing Fe^{2+} and Fe^{3+} ions as shown in Figure 2.10, and found that Au is much more sensitive to oxygen concentration in solution than Pt. (Chander, 1991) in a similar experiment, found that at a low hydrosulfide ion concentration, the kinetic response of the Pt was slow as compared to the Au although the measured electrode potentials were in reverse order (Zhou and Chander, 1989; Zhou and Chander, 1991). The higher electrode potential of the Pt electrode as observed was explained by its higher affinity for oxygen (Rao et al, 1963).

(Kuopanportti et al, 2000) measured the electrode potential of a chalcopyrite-pyrite mixture with an Au electrode in the absence and presence of xanthate ions at various DO concentrations. Their experimental results showed that, in the absence of oxygen, the electrode potential is higher before xanthate addition. However, at a saturated oxygen concentration, the effect of oxygen and xanthate on the potential is additive and the addition of xanthate results in a decrease in the potential of mixture. This phenomenon can be explained by the 'mixed-potential' theory (Chander and Fuerstenau, 1974; Chander and Fuerstenau, 1983; Rand and Woods, 1984).

2.6.4.2 Ion Selective Electrode

An ion selective electrode (ISE) is defined as an electro-analytical sensor with a membrane whose potential indicates the activity of ions (oxidizing or reducing) to be determined in a solution (Koryta, 1986). The membranes of the sulfide ISEs consist of pressed synthetic metal sulfide (generally silver sulfide) that usually has negligible electron conductivity. The measurement of the sulfide electrode potential is made relative to saturated calomel electrode (Jones and Woodcock, 1978). These electrodes had been tested in the control of the sulfidization process of the oxidized ores (Jones and Woodcock, 1978; Jones and Woodcock, 1979). The advantage of such an electrode is its quick response even at low ion concentration and the results are highly reproducible (Jones and Woodcock, 1979). Chander had found that the potential varies with the free sulfide ion concentrations in the solution and follow the Nernst equation (Chander, 1991).

2.6.4.3 Mineral Electrode

The redox potential established at the mineral/ solution interface (Electrical double layer) is one of the most important parameters for sulfide mineral flotation. Therefore, the use of mineral being floated as the Eh electrode is a common trend in the laboratories. (Finch and Labonté, 1989) tested chalcopyrite, pyrite, and galena electrodes for monitoring in sulfide flotation circuits. (Heimala et al, 1988) studied different mineral electrode response in the flotation plant as well in the laboratory and established that the mineral electrode mixed-potential value correlates directly with the rate of main electrochemical reactions for the mineral being studied. They confirmed that from a floatability or surface chemistry point of view the measured values of mineral electrodes correlate directly with the oxidation state of the mineral if no inert passive phases are formed on the surface of the electrode. The potentials exhibited by the mineral electrodes were related to the flotation response. For example, under reducing grinding conditions, the flotation recoveries increased with the potential in the presence or absence of collectors. The investigators also tested gold and black platinum electrodes for the sake of comparison. They observed that the potential response of the gold electrode was similar to that of natural mineral electrodes under certain conditions. It was suggested that the use of several mineral electrodes in flotation process may provide additional information about the system. For example, when cyanide ion was introduced as NaCN, Cp exhibited a potential lower than that of galena. The difference in the potential might suggest the preferential adsorption of cyanide ion onto Cp surface. This could be the reason behind the Cu–Pb separation using cyanide. Their studies indicated that the potential sensed by black platinum was not related to mineral floatability. A flotation control system developed in Outokumpu, Oy, Finland (Heimala et al, 1988; Heimala and Saari, 1992), is a typical example, in which mineral electrodes are used to monitor the behavior of minerals in the flotation circuits. (Heimala and Saari, 1992) claimed a significant improvement in the recovery of various minerals when the reagent control in this system is based on Eh measurements.

2.6.5 Application of Electrode Potential Measurement in Industry

Electrochemical studies of flotation have shown that the recovery of the valuable mineral is a function of the potential across the mineral/pulp interface (King, 1982). Since its first use in Australian flotation plants in 1971, many researchers across the world have explored the possibility of using potential (Eh) measurements. After two decades, (Ralston, 1991) reviewed the research into Eh measurements and found that Eh could be used as a diagnostic parameter in the plant or the laboratory to monitor the subsequent flotation behavior. However, the most significant effort to industrialize Eh control on the flotation plant was done by Outokumpu (Woods, 2003). Outokumpu introduced Outokumpu potential controlled flotation (OK-PCF) monitoring and first implemented it at Hitura nickel mines in 1984.(Ruonal et al, 1997) reported that since the replacement of pH with Eh control, the recovery of Ni was improved by 2 % and hence the profitability increased by 10-20%.

The central South university of Technology in Changsha, China has conducted electrochemical studies in the laboratory to develop their Original Potential Control Flotation (OPCF) technology. These researchers have successfully implemented OPCF technology on Pb-Zn plants. The benefits incurred due to OPCF are improved grade and recovery of the product, simplified flow sheet and lower operating and maintenance costs (Hu, 2009).

2.7 Electrochemistry of Milling/ Grinding

Sulfide minerals are semiconductors and show varying degrees of electrical and magnetic properties as shown in **Error! Not a valid bookmark self-reference.**. Electrical conductivity of sulfide minerals leads to electron transfer between a sulfide mineral and other sulfide minerals and/or grinding media during the milling process. Interactions between the sulfide minerals and/or grinding media are termed galvanic interactions. The role of a sulfide mineral (to be an anode or cathode in a galvanic cell) is demonstrated by its electrochemical reactivity which in turn depends on the rest potential of the mineral.

Table 2.2: Electrical and magnetic properties of common sulfide minerals (Abramov and Avdohin, 1998)

Mineral	Chemical Formula	Electrical properties	Magnetic properties
Sphalerite	ZnS	Weak Semiconductor	Diamagnetic
Galena	PbS	Semiconductor	Diamagnetic
Cp	$CuFeS_2$	Semiconductor	Paramagnetic
Po	$Fe_{(1-x)}S$	Metallic Conductor	
Pyrite	FeS_2	Semiconductor	Diamagnetic
Pn	$(Ni,Fe)_9S_8$	Semiconductor	Paramagnetic

2.7.1 Galvanic interaction between Mineral/Mineral systems

If during the grinding phase, two sulfide minerals do not touch each other, each would oxidized at a rate determined by their rest potential. However, when sulfide minerals come into contact with one another, a galvanic cell is formed and the mineral with the higher rest potential draws electrons from the one with lower rest potential as shown in Figure 2.11. If oxygen is assumed to be present in the system, the cathodic reduction reaction can be represented by the reduction of oxygen (reaction 2.1) at the mineral surface with the higher rest potential while the anodic oxidation of the sulfide mineral with a lower rest potential is generally given by reactions 2.10 - 2.12 in the absence of collector and by reactions 2.13 - 2.14 in the presence of collector. As a consequence, the rate of oxidation or xanthate adsorption on the surface of the mineral with the lower rest potential is accelerated at the expense of the mineral with the higher rest potential.

Oxidation of the Sulfide mineral:

$$MS \rightarrow M^{2+} + S^0 + 2e \qquad (2.10)$$

$$MS + 2H_2O \rightarrow M(OH)_2 + S^0 + 2H^+ + 2e \qquad (2.11)$$

$xS^0 + yH_2O \rightarrow SxOy^{2-} + 2yH^+ + (2y-2)e$ (2.12)

Metal/ Collector Salt formation:

$MS + X^- \rightarrow MX + S^0 + e$ (2.13)

$MS + 2X^- \rightarrow MX_2 + S^0 + 2e$ (2.14)

Based on the mixed potential models (Bozkurt et al, 1998; Rand and Woods, 1984) the galvanic interaction between two minerals having different rest potentials can be illustrated by Figure 2.9. In this figure, the rest potential of the second redox couple is considerably higher than that of the first and acts as the cathode in the galvanic interaction. It draws electrons from the first redox couple. Reduction of oxygen is the common reduction reaction for both minerals. However, since the mixed potential of the system is higher than the $Er^0_{Red1/Ox1}$ couple and lower than the $Er^0_{Red2/Ox2}$ couple, the first redox couple (Red1/Ox1) will oxidized and reduction of oxygen would takes place on the second redox couple (Red2/Ox2).

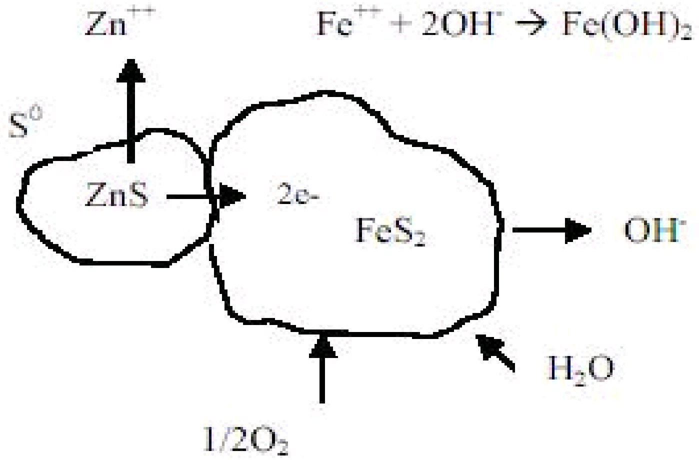


Figure 2.11: Model of galvanic interaction between sphalerite and pyrite (Anon, 2010)

Several researchers (Bozkurt et al, 1998; Junior et al, 2006; Rao and Finch, 1991; Rao and Finch, 1988; Urbano et al, 2008) had investigated the effect of the galvanic interaction on the flotation of sulfide minerals and reported the following observations as noteworthy:

- The rate of dissolution (oxidation) of the sulfide mineral depends upon the difference in the rest potentials of the two sulfide minerals.
- Density and viscosity of the slurry affects the rate of dissolution.
- Galvanic interactions are stronger in locked particles, e.g. middlings, than the liberated particles.

- Oxidation products on minerals which are generally metal hydroxide/ oxyhydroxide species may hinder the collector adsorption.
- Oxygen is the most important species for the galvanic interactions to occur.
- The effect of galvanic interactions on the mixed mineral system has been studied by many researchers; (Gebhardt, 1988) on chalcocite and pyrite, (Ekmekci and Demirel, 1997) on Cp and pyrite, (Bozkurt et al, 1998) on Po and Pn, (Junior et al, 2006) and (Urbano et al, 2008) on arsenopyrite and pyrite. In general, they found that the flotation response of the mixture did not follow the behavior predicted from the measurement of the individual minerals. This was attributed to the galvanic interactions between the two minerals which can be explained by the mixed potential model.

2.7.2 Galvanic interaction between Mineral/Grinding Media system

Grinding is essential for the liberation of the sulfide minerals from the gangue material, and in order to achieve effective liberation, steel grinding media (rods or balls) are generally used. Galvanic interactions between the grinding media and different minerals have various effects on the flotation process. Galvanic interactions between grinding media and sulfide minerals had been studied by many researchers (Adam et al, 1984; Huang et al, 2006; Yelloji Rao and Natarajan, 1988; Yelloji Rao and Natarajan, 1989; Yelloji Rao and Natarajan, 1990) and it was established that steel grinding media are able to behave as a cathodic site for oxygen reduction during the grinding while the mineral will act as an anode. The mechanism of galvanic interactions between a single sulfide mineral and mild steel media is illustrated in Figure 2.12.

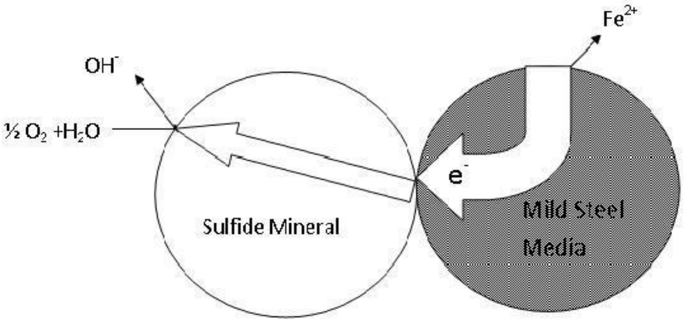


Figure 2.12: Model of galvanic interaction between mild steel media and sulfide Mineral
(Ekmekçi, 2009)

As a result of galvanic interactions, the media will corrode at an accelerated rate and add further electrons into the system which may lead to the oxygen reduction reaction at the mineral-water interface, and result in the formation of hydroxyl ions. These hydroxyl ions interact with the dissolved iron ions from the milling media to form hydroxide species which may later precipitate at the mineral surface.

$$\frac{1}{2} O_2 + H_2O + 2e \rightarrow 2OH^- \text{ (Cathodic reaction)} \qquad \text{(See 2.1)}$$

$$Fe \rightarrow Fe^{2+} + 2e \text{ (Anodic reaction)} \qquad (2.15)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \text{ (Precipitation)} \qquad (2.16)$$

Due to galvanic interactions between the grinding media themselves, an electrochemical cell is formed between the abraded (anode) and non-abraded (cathode) surface as shown in Figure 2.13. The electrons are able to flow from the abraded site to the non-abraded site due to the difference in the electrochemical potentials between these two sites, and this result in galvanic corrosion.

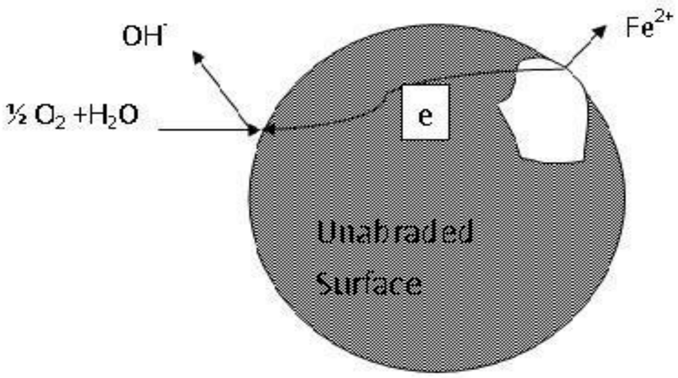


Figure 2.13: The galvanic interaction within the mild steel media (Ekmekçi, 2009)

2.7.3 Galvanic interaction between Mineral/Mineral/Grinding media system

In the case of grinding of a real ore, it is not single minerals or binary particles which interact with either the media or one another, but rather a polymineral system which interact by random contacts of the particles and grinding media. As a result multi-electrode galvanic cells are formed in the case of a complex sulfide ores. (Pozzo and Iwasaki, 1989) studied the electrochemical model of galvanic interactions in systems consisting of two sulfide minerals and grinding media. The model of (Pozzo and Iwasaki, 1989) is shown in

Figure 2.14.

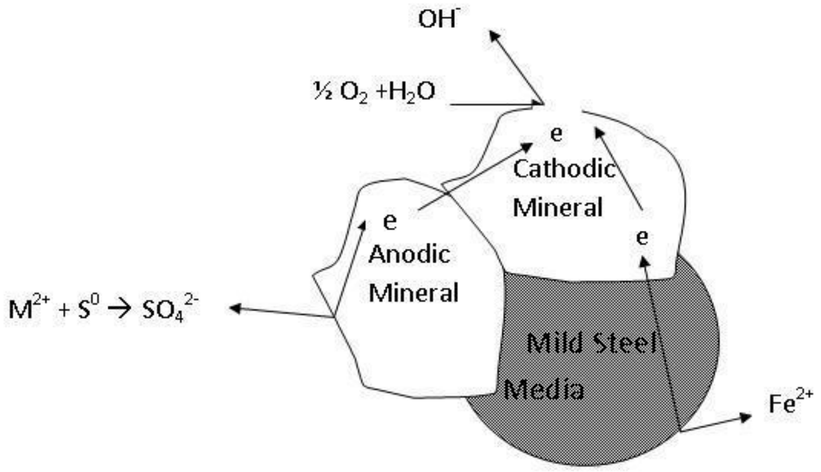


Figure 2.14: Model of galvanic interaction within the mild steel media (Pozzo and Iwasaki, 1989)

Although many of the researchers mentioned in Section 2.7.2 have investigated the effect of galvanic interactions on the floatability of the different mineral and media combinations, the most significant work in this area comes from (Yelloji Rao and Natarajan, 1988; Yelloji Rao and Natarajan, 1989). These researchers investigated the effect of galvanic interaction on the floatability of Cp, galena and sphalerite under various combinations and came to the conclusion that owing to the difference in open circuit potential or rest potential of the various sulfide minerals, the flotation recovery of the cathodic mineral (noble mineral having the higher rest potential) is significantly lowered, while the floatability of anodic mineral (active mineral having the lower rest potential) is only slightly decreased.

Stronger galvanic interactions occur in the presence of the steel grinding media, and owing to the large difference in the open circuit potential between the minerals and the media, the floatability of all the minerals is adversely affected, while the active mineral is less affected than the noble mineral.

- The floatability of a sulfide mineral is significantly reduced after contact with grinding media, owing to the deposition of iron oxy-hydroxide species at the mineral surface. However, after the addition of a relatively noble mineral, the effect is found to occur mostly on the noble mineral and the floatability of the active mineral is increased.
- The presence of oxygen enhances the deleterious effect owing to galvanic interactions.
- Galvanic interactions between the minerals and the media do not affect the microstructure of the grinding media.

2.8 Characterization of the grinding environment:

The conditions under which grinding occurs have a marked effect on the pulp potential of the slurry which in turn affects the flotation response of the sulfide minerals. The standard operating practice is the use of grinding media which gives the correct grind while minimizing the cost. The chemistry is then adjusted by reagent addition and/ or aeration at the flotation stage. Reagent addition and aeration can cost as much as the media itself, and yet the role the media plays in reducing or eliminating these extra costs is seldom addressed. (Cullinan et al, 1999) conducted a fundamental study to examine the effect of grinding media with differing ferrous content on the flotation performance of galena within the lead circuit of the lead/zinc concentrator at Mount Isa Mines. Their study showed that, changing the grinding media from a high carbon steel to a high chromium alloy resulted in a significant increase in the maximum recovery as well as the flotation rate constant of the galena fine (-5 µm). (Johnson, 2002) found that the corrosion products, as a result of galvanic interaction, of the grinding media (e.g. FeOOH) invariably precipitated on to the surfaces of the sulfide minerals thereby affecting their floatability.

In laboratory-scale tests, the comminution of ores is normally carried out in standard stainless steel batch mills. However, it is generally known that in most cases batch grinding and continuous grinding result in very different products. In view of this, whenever laboratory grinding employs a procedure different from that used on the production scale, an accurate prediction for the production-scale product cannot be gained. Thus the need for a lab mill which can mimic plant conditions has been evident for a long time.

2.8.1 Magotteaux Mill Development

In 1991 Outokumpu made an effort to imitate their plant conditions at a laboratory scale, as a result the continuous classifying laboratory mill as shown in Figure 2.15 was developed in 1994. Several nickel, copper, oxides, and industrial mineral ore types were tested on this new continuous classifying mill and the results showed that this mill offers much greater scope for research into the chemistry control during grinding than a batch mill (e.g. pH, redox potential, and grain size distribution of the milled product).

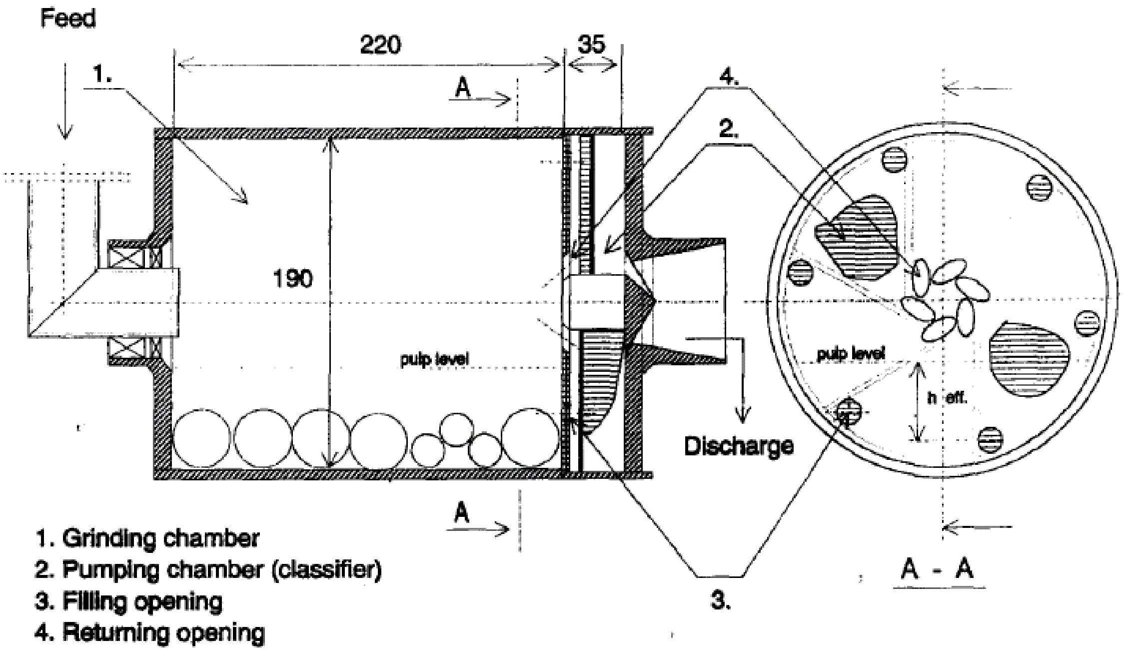


Figure 2.15: Cross-sectional view of the continuous classifying grinding mill (Hintikka et al, 1996)

In 1995 Yuan and coworkers tried to test the influence of the DO concentration during grinding on the Cu/ Fe sulfide separation. In order to control the grinding environment (Yuan et al, 1996) drilled a small hole at each end of the body of a mild steel mill and continuously purged the mill with different gases from one of the ends and they termed the mill an air-sparged mild steel mill. Magotteaux took one step further in order to control and mimic the grinding environment and developed a special mill, known as the Magotteaux mill (Greet et al, 2004). The Magotteaux Mill allows for the quantifying of in situ grinding conditions so that an accurate prediction for the production-scale product can be made from laboratory grinding tests. The objectives of developing such a Mill were:

- To quantify the galvanic interactions between different grinding media types on different sulfide minerals based on their electrochemical characterization during grinding.
- To control the surface properties of sulfide minerals during grinding where fresh mineral surfaces are being generated.
- To improve the floatability of sulfide minerals with respect to the grinding conditions produced by different types of grinding media and purging gases.
- To mimic plant conditions in the laboratory, in order to make proper comparison with plant.

The Magotteaux Mill offers a similar control panel and operating procedure as used in plant practice. Details of the Magotteaux Mill and its control philosophy are discussed in Section 3.5.2.

2.8.2 Grinding Media effect

(Rey and Formanek, 1960) investigated the effect of grinding media on the flotation of a Pb-Zn ore and reported that the sphalerite showed natural floatability when ground in a porcelain mill with ceramic grinding media, however, it had no more natural floatability after grinding in a steel mill in alkaline pulp. This was an influential paper, despite no follow up to their work until the early 1970’s (Martin et al, 1991). In the early 1970’s Bruce reported that grinding in the absence of steel media, resulted in the loss of selectivity between copper, lead and zinc minerals. However, (Thornton, 1973) reported that steel grinding media resulted in a decrease in the floatability of galena. (Huang and Grano, 2005) used the Magotteaux Mill to quantify the galvanic interaction between different grinding media; forged steel, 15 % Cr, 21 % Cr and 30 % Cr, and arsenopyrite. They found that the high chrome media had a significantly weaker galvanic interaction with arsenopyrite, producing much less hydrophilic, oxidized iron species in the mill discharge than the forged steel medium and increasing the DO concentration in the mill. In a similar test with pyrite (Huang and Grano, 2006) noted that the galvanic current increased with the DO concentration, which in turn lowered the floatability.

The more electrochemically active the grinding media and the longer the period of interaction with the minerals, the less floatable the cathodic sulfide minerals were. (Adam et al, 1984; Peng et al,, 2003; Vathsala and Natarajan, 1989; Yelloji Rao and Natarajan, 1988; Yelloji Rao and Natarajan, 1989; Yuan et al, 1996). Many researchers have studied the effect of galvanic interactions on the floatability of various minerals such as galena (Cullinan et al,, 1999; Peng et al,, 2003; Rey and Formanek, 1960), pyrite (Huang and Grano, 2005; Peng et al,, 2003; Pozzo and Iwasaki, 1989), Po (Adam et al, 1984; Bozkurt et al, 1998; Nakazawa and Iwasaki, 1986; Pozzo and Iwasaki, 1989), sphalerite (Vathsala and Natarajan, 1989; Yelloji Rao and Natarajan, 1989), and Cp (Peng et al, 2003; Yelloji Rao and Natarajan, 1988; Yuan et al, 1996). These researchers showed that the galvanic interactions between conductive grinding media and semi-conductive sulfide minerals not only promotes the corrosion rate of steel grinding media, but also deteriorates the floatability of the ground sulfide minerals.

A less electrochemically active steel media, such as stainless steel and high chrome media may give better grades and/or higher recoveries of sulfide minerals (Cullinan et al, 1999; Grano, 2009; Greet et al, 2004; Greet, 2008).

2.8.3 Gas purging effect

Many researchers (Adam et al, 1984; Pecina-Trevino et al, 2003; Peng et al, 2003; Rao and Finch, 1988; Yelloji Rao and Natarajan, 1990) have proposed that the oxygen reduction rate has a significant effect on the floatability of sulfide minerals. The reduction of oxygen during galvanic interactions produces hydroxyl ions through reaction 2.1. These hydroxyl ions forms metal hydroxides at the mineral surfaces and render the surfaces hydrophilic, which in turn hinders xanthate adsorption onto the minerals. Nitrogen purging during grinding is considered to be able to weaken the galvanic interactions (Rao and Finch, 1988) and this has been verified by measuring the galvanic current (Yelloji Rao and Natarajan, 1988; Yelloji Rao and Natarajan, 1989), as well as the oxidized iron species in the slurry by EDTA extraction (Peng et al, 2003). An increase in DO concentration during grinding, however, enhances galvanic interactions and increases the iron hydroxide species at the mineral surface (Adam et al, 1984; Natarajan and Iwasaki, 1984; Peng et al, 2003). The oxidized iron species may inhibit the interaction of the sulfide minerals with xanthates (Wang et al, 1989). Therefore, oxygen purging during grinding may impair the floatability of a sulfide mineral (Peng et al, 2003).

2.9 Electrochemical behavior of Pn and Po

Pn is the principle source of nickel (Becker, 2009; Buckley and Woods, 1991). It often occurs in association with Po. In the case of Ni processing operations, Po is rejected to the flotation tailings as a waste product (Becker, 2009; Bozkurt et al, 1998; Khan and Kelebek, 2004). The separation efficiency of Pn from Po in a conventional circuit is generally very poor owing to the similarity of the surface chemistry behaviors of both sulfide minerals (Buckley and Woods, 1985; Buckley and Woods, 1985; Buckley and Woods, 1991; Legrand et al, 2005a; Legrand et al, 2005b; Ruonal et al, 1997). However, some researchers have reported that electrochemical potential control during flotation resulted in an improved performance of the nickel concentrates (Kelebek and Nanthakumar, 2007; Khan and Kelebek, 2004; Rantapuska and Heimala, 1990). Therefore understanding the mechanism and factors influencing the floatability of these minerals is of importance in determining and predicting their flotation behavior.

2.9.1 Natural or collectorless floatability of Po

In 1933 (Ravitz and Porter, 1933) first reported the collectorless floatability of high-purity galena (Ekmekci and Demirel, 1997). Since then several studies have been conducted to determine the natural floatability of the sulfide minerals. (Hodgson and Agar, 1984) observed the natural floatability of Po in acidic solution for short conditioning times and at low oxidation potential of 0-200 mV (SHE). Although the major products reported in their experiments were $Fe(OH)_3$ and S^0 which formed at the mineral surface, their postulation for the natural hydrophobicity was the stable intermediate surface state, $Fe(OH)S_2$. However, (Hamilton and Woods, 1981) pointed out that the collectorless flotation of Po is as a result of the elemental sulphur formation at the mineral surface since sulphur is strongly hydrophobic and may remain stable for a long time, even in alkaline solutions. Although the identity of the hydrophobic species responsible for the collectorless flotation of individual sulfide minerals is still debatable, sulphur-based compounds, i.e. elemental sulphur, sulphur-enriched metal-deficient sulfide or a metal polysulfide are the most acceptable species responsible for the collectorless flotation of sulfide minerals (Buckley and Woods, 1985; Ekmekci and Demirel, 1997; Hamilton and Woods, 1981; Heyes and Trahar, 1984; Hu, 2009).

Po surfaces get oxidized rapidly upon exposure to air and extensive oxidation during long conditioning time leads to poor floatability (Hodgson and Agar, 1984; Hodgson and Agar, 1989). If the oxidation time is long enough, which also results in a higher pulp potential, the hydrophilic Fe^{3+} hydroxide (Buckley and Woods, 1985; Heyes and Trahar, 1984; Legrand et al, 2005b; Legrand et al, 1997) formed at the mineral surface would reduce its natural floatability (Nanthakumar and Kelebek, 2007). The potential at which Po shows its natural floatability sometimes differs from one publication to the next, not only owing to differences in measurement conditions but owing to the differences in the mineralogy (Becker, 2009). Hu (2009) simplified the situation and defined the Eh-pH region in which different minerals exhibit collectorless floatability. They considered the 50 % recovery of the mineral in consideration as the baseline to define the limit of the Eh-pH range. The upper and lower potential point is defined as the potential in which the mineral recovery was greater than 50 %. These researchers found that the collectorless floatability of Po is in the range of 0.25 V to 0.35 V at pH 8.8. From their floatability Eh-pH diagram, they concluded that under acidic conditions Po exhibits collectorless floatability over a wide potential range.

2.9.2 Natural or collectorless floatability of Pn

Heiskanen et al, (1991) conducted collectorless flotation studies on three lean nickel sulfide ores, from Outokumpu Finnmines Oy (Enonkoski (0.31% Ni and 0.14% Cu), Vammala (0.9% Ni and 0.45% Cu) and Hitura (0.32% Ni and 0.11% Cu)). They revealed that the natural floatability of all sulfides was good under acidic pH conditions, when the samples were ground in a common steel-lined ball mill. However, the natural floatability was good over a much wider pH-range when the sample was ground in a ceramic mill using ceramic balls, however Pn did not float well above neutral pH in both cases. In 1991 Buckley and Woods conducted XPS and voltammetric studies in which they found that iron is preferentially removed from the Pn on exposure to oxygen forming an oxide layer, leaving a metal deficient sulfide. Thus, the self-induced flotation of Pn is due to the formation of metal deficient, sulphur rich surfaces. However, one obvious difficulty with this model lies in the fact that there is an associated formation of FeOOH (Buckley and Woods, 1991; Legrand et al, 2005b; Vaughan, 1989) that is expected to be hydrophilic. So, the natural floatability of the mineral is only possible, if the oxide is removed in the turbulence (Buckley and Woods, 1991) within the flotation cell, however the surface product formed is a chemical product and it may not be possibly to be removed physically. The second possibility is that the surface species might form in patches and during bubble particle collision, bubbles come into contact with the metal deficient sulphur rich region of the mineral. It was found that Pn and Po were both very reactive to oxygen and self induced flotation occurs only at low potentials or oxygen deficient environments. (Healy and Trahar, 1989) reported that Pn showed self induced flotation (50% recovery in first min) at an Eh value of -0.15 V.

2.9.3 Oxidation of Po

A better understanding of the reactivity and oxidation of Po is needed for improved mineral processing and to prevent the production of acid mine drainage (AMD) from iron sulfide mine waste, which is a major environmental problem. In the early stage of flotation, the oxidation products on the mineral surface were determined through chemical extractive methods and the identity of the oxidation product has remained in controversy. However, advancement in surface analysis technology has led to some consensus on a progressive enrichment of the surface with respect to sulphur when Po is oxidized.(Hamilton and Woods, 1981) studied the electrochemical oxidation of Po at pH 4.6, 9.2 and 13.0 using linear potential sweep voltammetry (lsmv). Their results indicated that sulphur is the main product formed on the surface but sulphate is also present in significant quantities in alkaline solution.

However, under alkaline conditions the oxidation of Po is strongly repressed owing to the formation of a passive ferric oxide/hydroxide surface. In 1985, Buckley and Woods studied the oxidation of Po by air using XPS and proposed the diffusion of iron from the outermost layers of the solid lattice to form a Fe^{3+} hydroxyl-oxide or hydrated oxide at the air/solid interface, via a Fe^{2+} oxidation. In the same year these researchers studied the effect of H_2O_2 solution on the oxidation of Po and reported the presence of elemental sulphur as well as sulphate as the oxidation product (Buckley and Woods, 1985). In 1988 (Buckley et al, 1988), further studied Po oxidation using voltammetry and XPS and found that the initial oxidation products for Po oxidation include metal-deficient sulfides rather than elemental sulphur. (Jones and Smart, 1992) noticed an additional tetragonal Fe_2S_3 species as a reaction product along with the presence of sulphate, Fe^{3+} oxide/hydroxides and iron deficient sulfide species.

2.9.4 Oxidation of Pn

It is well established in the literature that the floatability of sulfide minerals is depressed by excessive oxidation (Malysiak et al, 2002) and oxidation products onto the mineral surface inhibit the collector adsorption. The understanding of the first 20-50 Å of the surface oxidation/alteration of the mineral could be extremely valuable for understanding the floatability of the minerals. (Vaughan, 1989) studied the effect of oxidation on synthetic Pn in a range of inorganic oxidants and found that after oxidation the Pn surface shrinks and Ni enriched violarite forms at the subsurface. The immediate oxidized surface, of approximately 10 Å thickness, indicated a range of iron oxides and hydroxides (Fe_3O_4, Fe_2O_3 and FeOOH, with possible $Fe_{1-x}O$ and $Fe(OH)_3$), nickel oxide (NiO), and iron sulphates ($FeSO_4$, $Fe_2(SO_4)_3$). Although (Vaughan, 1989) did not find any indication of the presence of $NiSO_4$ in their Ni spectra however he had reported that there is evidence in the literature for the presence of $NiSO_4$. In 1991, Buckley and Woods indicated the presence of $NiSO_4$ in their study of the surface alteration of natural Pn (Buckley and Woods, 1991). In 2005, Legrand studied the detailed mechanism of the surface oxidation/alteration of Pn and found that the first stage of reaction is characterized by formation of violarite and FeOOH on Pn (Legrand et al, 2005b). With continued oxidation, this assemblage yields NiSO4, FeOOH and violarite, which are eventually converted to $Ni(OH)_2$. Finally, after the violarite is consumed, the $NiSO_4$ and FeOOH combination occurs as the thermodynamically stable assemblage.

2.9.5 Po Xanthate adsorption

The available literature describing the mechanism of xanthate adsorption is limited for Po and more so for Pn. (Allison et al, 1972) analysed the product of xanthate formed on various sulfide minerals and found dixanthogen to be the principle product on Po. In 1989 (Hodgson and Agar, 1989) conducted electrochemical studies using cyclic voltammetry and proposed that the xanthate-mineral interaction is not a direct chemisorption onto the surface of Po, as this would result in a cathodic shift in the voltammetric peak after xanthate adsorption, however, an anodic shift in the reduction peak was observed (Hodgson and Agar, 1989). (Hodgson and Agar, 1989) postulated that the Po surface was being rendered hydrophobic by the dixanthogen, which was later supported by other researchers (Bozkurt et al, 1998). However, dixanthogen was formed as part of a mixed potential reaction involving the normal Po oxidation process. Unlike chemisorption no electron transfer is considered to arise through the initial adsorption of xanthate onto the mineral surface, the collector being adsorbed through coulombic attraction with the cationic Fe^{3+} site generated through oxidation of the mineral surface. The following sequence of reaction was proposed for the formation of dixanthogen onto the Po surface.

$$FeS + 2H_2O = Fe(OH)[S]^+ + 2H^+ + 2e^- \qquad (2.17)$$

$$Fe(OH)[S]^+ + X^- = Fe(OH)[S][X] \qquad (2.18)$$

As no additional peak was detected on the voltammogram which could be ascribed to dixanthogen, dixanthogen formation was considered to take place adjacent to the oxidized Po surface and physiosorbed via the alkyl group of the Fe(OH)[S][X] complex.

$$Fe(OH)[S][X] + X^- = Fe(OH)[S][X_2] + e^- \qquad (2.19)$$

These oxidation (or anodic) reactions are coupled with the common cathodic reaction, oxygen reduction (reaction-2.1) to the hydroxide ion. Evidently dixanthogen is the species which conferred the hydrophobicity onto the surface of Po and oxygen was required to promote the bubble contact. It was also reported that dixanthogen did not form on Po when air was replaced by nitrogen, which confirms the important role of oxygen in the adsorption of xanthate (Hodgson and Agar, 1989; Rao and Finch, 1991).

2.9.6 Pn Xanthate adsorption

Electrochemical investigations (Hodgson and Agar, 1989) suggested that the xanthate interaction which infers hydrophobicity onto the Pn surface is a two step process:

1. Chemisorption (xanthate ions adsorb probably at Ni site) - inducing hydrophobicity
2. Dixanthogen formation within the double layer.

Unlike Po, the formation of dixanthogen was considered to originate from the chemisorbed xanthate on the Pn surface, according to the equilibria:

$$Ni + X^- \rightarrow NiX + e^- \qquad (2.20)$$

$$NiX + X^- \rightarrow Ni(X)_2 \rightarrow NiX_2 + e^- \qquad (2.21)$$

2.9.7 Collector adsorption on Po and Pn in Mixture

(Bozkurt et al, 1998) investigated the interaction of SIBX with a Pn-Po mixture and found that dixanthogen adsorption on Pn was increased as compared to a Pn only sample, while in the case of Po, the situation was reversed. (Ralston, 1991) used data from (Fuerstenau and Sabacky, 1981; Guy and Trahar, 1984; Hayes and Ralston, 1988) to rank sulfide minerals according to their natural floatability and correlated them with their rest potentials. The general descending hydrophobicity order was as follows: Chalcopyrite > Galena > Pyrrhotite > Pentlandite > Covellite > Bornite > Chalcocite > Sphalerite > Pyrite > Arsenopyrite. (Ralston, 1991) observed that, except for Cp, the collectorless floatability of sulfide minerals decreased with increasing rest potentials. However, (Bozkurt et al, 1998) found that in the presence of xanthate, the order of rest potential or open circuit potential gets reversed and also a lowering of the open circuit potential was registered for Pn over Po. This indicates that xanthate uptake onto Pn is preferential, which was also confirmed by the spectroscopic studies of (Bozkurt et al, 1998). These researchers explained the preferential xanthate adsorption on Pn through the mixed potential theory and stated that in the mixed potential of the mixed mineral system, the anodic reaction (oxidation of xanthate to dixanthogen) occurred preferentially on the Pn and the cathodic reaction (reduction of oxygen to hydroxyl ion) occurred on the Po as shown in Figure 2.16. Their explanation takes into account that the rest potential of Po is higher than Pn in the presence of xanthate which also supports the different chemical pathway proposed by (Hodgson and Agar, 1989) for Pn and Po xanthate adsorption. Their results showed that in the Pn-Po mixture the floatability of Pn could be enhanced at the expense of Po and this is the usual approach to Pn/Po separation, namely to float Pn while depressing Po. Although they had specified the role of oxygen in their paper they did not monitor the oxygen concentration in their tests. The reason for the reversibility in their experiments may be due to oxygen deficiency in the system as noticed by (Kelebek, 1993) in a case study of the Strathcona mill flotation. Kelebek noticed that the ease of individual mineral floatability under normal aeration conditions is Cp> Pn> Po which changes to Pn> Cp> Po in an oxygen deficient system.

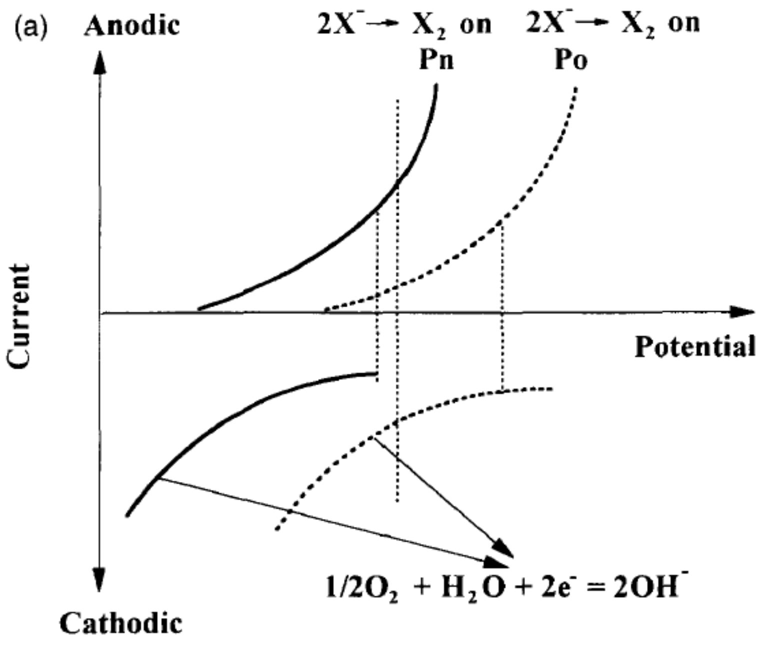


Figure 2.16: Mixed potential model of xanthate adsorption on Pn and Po mixture (Bozkurt et al, 1998)

In 2005, (Legrand et al, 2005a) studied the oxidation/alteration of massive coexisting Pn and Po in aqueous solution at pH 9.3, using potassium amyl xanthate (KAX) at varying solution oxygen concentrations. Their results showed that in the presence of fine Pn/Po, the oxidation of Pn and Po decreases, suggesting that the powder scavenges oxygen owing to the large surface area, and that the oxidation of Pn is more sensitive to oxygen concentration than the oxidation of Po. When the oxygen concentration is decreased drastically to <0.01 ppm (by Argon purging), in the presence of KAX, both minerals show less FeOOH than the unreacted sample, which implies that the mineral surfaces are being cleaned under these conditions. Such surface cleaning has been seen at low oxygen concentrations with the addition of KAX to Po (Rao and Finch, 1991) and other sulfide surfaces (Buckley et al, 2003; Fairthorne et al, 1997; Zachwieja et al, 1989) although the mechanism, for this cleaning, is not well understood (Fairthorne et al, 1997). However the postulation for surface cleaning as hypothesised by most of researchers might be due to thermodynamic instability of the FeOOH film, at low oxygen concentrations. At low oxygen concentration FeOOH might well dissolve or the AX^- will adsorb and reduce the Fe^{3+} to Fe^{2+} (Bozkurt et al, 1998) and destabilize the oxide even more. Rao and Finch indicated that at low oxygen concentrations in a nitrogen atmosphere, dixanthogen would not form on Po surfaces (Rao and Finch, 1991). In oxygen deficient system AX^- should chemisorb to the mineral surfaces or the AX^- anion could exchange with the OH^- groups in the oxide giving Fe and Ni AX complexes in solution

(Fornasiero et al, 1995). Legrand et al, (2005a) noted that the degree of oxidation of both mineral surfaces increased with an increase in the oxygen solution concentration but even at low oxygen concentration, the Po surface get heavily oxidized, while the Pn surface remains largely unoxidized. These results strongly indicate that the flotation separation of Pn and Po could be enhanced at low oxygen concentrations.

2.10 Summary and objective of study

Sulfides are unstable and very reactive in air. Throughout the mining process the sulfides come into contact with air and as a consequence oxygen begins playing its role through the weathering of the sulfides (Sato, 1960). During storage and transport the minerals also get oxidized and thus affect the surface properties of the ore. Throughout this oxidation process, the reduction of oxygen is the most important cathodic reaction.

As soon as the ore enters the grinding circuit, galvanic interactions between mineral/mineral (Bozkurt et al, 1998) and mineral/media come into existence (Iwasaki et al, 1988). Oxygen reduction is again the key reduction reaction in galvanic interactions. Moving into the flotation circuit, xanthate adsorption and dixanthogen formation proceeds through the catalytic activity of the mineral present for the oxygen reduction.

A number of researchers (Biegler et al, 1975; Janetski et al, 1977; Majima and Takeda, 1969; Majima, 1969; Tolun and Kitchener, 1963; Tolun and Kitchener, 1964) have found that the presence of oxygen is essential for electrochemical reactions to occur on sulfide mineral surfaces. Based on the electrochemical theory, the reduction of oxygen affects the oxidation of; sulfide minerals, mineral/mineral and mineral/media galvanic interaction as well as the mineral/collector interactions. However, the mineral/collector interactions have pronounced influence on the flotation behavior of sulfide minerals (Buckley and Woods, 1991; Buckley and Woods, 1997; Hamilton and Woods, 1986; Harris and Finkelstein, 1975a; Woods et al,, 1992; Woods et al, 1994)

In sulfide minerals, sulphur occurs in its lowest oxidation state of -2. This can be oxidized to the higher oxidation states of; 0, +2, +4 and +6 depending upon the activity of the oxygen in the system and the rate of oxidation (Rao, 1971). Oxidation is primarily important for the fines due to their large surface area. Fine particles generated during mining, transportation and stockpiling activities are generally very high grade, soft materials and prone to oxidation. (Kelebek and Nanthakumar, 2007) investigated the impact of oxidation on the flotation of a complex Cu-Ni massive sulfide ore. The objective of this study was to determine the correlation between the oxidation time before and after grinding and the flotation performance. The results showed that oxidation before and after grinding produce an inferior quality Pn grade-recovery. However, in the case of oxidation after grinding Pn recovery losses were up to 25 % compared to a maximum of 3.5 % recovery loss in the case of oxidation before grinding. The reason for the smaller influence on the recovery of the oxidized sample before grinding could be due to the sample surfaces, which were sufficiently oxidized prior to the experiment. However, in the case of oxidation after grinding, the freshly liberated surface generated during grinding was allowed to oxidize thereby resulting in a significant change in the recovery. Although the ground slurries in the second approach (oxidation after grinding) were filtered and the filtrate was stored in the freezer to avoid differences in the experimental conditions, they did not find any clear correlation with the length of time and the extent of oxidation after grinding. The reason for this may be the difference in the amount of water used, which might change from case to case thereby resulting in the availability of the oxygen being different in each case.

(Kelebek et al, 1996) suggested that there is a stronger correlation between the oxidation of the surface after grinding and its influence on the grade and recovery of the Pn. Surface Analysis studies by (Legrand et al, 2005b) suggested that the separation of Pn from Po minerals via flotation is inefficient unless either they are exposed to the flotation reagents prior to oxidation, or their FeOOH overlayer is removed in some way. This might be the reason why, collectors are added during the milling stage, thus allowing them to immediately react upon the exposure of the fracture surfaces. Therefore, the study of oxygen control during the grinding stage might be an efficient means to avail better grades and recoveries of Pn. However, there appears to be very little published work which could quantify the significant effect of oxygen on flotation considering oxidation, xanthate adsorption and galvanic interaction simultaneously. The scarcity of literature might be due to the non-availability of such a system, where oxygen can be controlled at the same time when fresh mineral surfaces are being generated and reagent can be added simultaneously. The Magotteaux mill offers the opportunity to understand the combined system and possibly develop an efficient process for the improved grade and recovery of Pn.

2.11 Key Questions

Based upon the literature review, the following key questions have been formulated for this study:

- What would be the optimum oxygen level for enhanced selectivity?
- Which is the preferential xanthate adsorbing mineral, Cp, Pn or Po, at different DO concentrations?
- Will N_2 sparging clean the oxygenated surfaces and enhance the selectivity?
- What would be the preferred reaction; oxidation or xanthate adsorption?
- Will grinding and floating with N_2 further enhance the selectivity of Pn?
- Will Air sparging decrease the selectivity?
- Where is the preferred xanthate addition point for enhanced selectivity, Mill or Cell?
- Can oxidation overcome xanthate adsorption or vice versa?
- How does pH affect the selectivity at different DO concentrations?
- What would be impact on the valuable mineral recovery if Eh is controlled?

2.12 Hypothesis

Hypothesis-1

Lower DO concentrations in the mill, in the presence of flotation reagent (xanthate), will improve the efficiency of the subsequent flotation of sulfide minerals due to the selective adsorption of xanthate and reduced formation of iron oxides/hydroxides on the surfaces of the sulfide minerals.

Hypothesis-2

Lower DO concentrations in the mill will enhance the selectivity of Pn over Po because of the reduced formation of the FeOOH layer onto the surface of Pn. The extent of oxidation of Po in the presence of air is higher due to the presence of high spin Fe compared to low spin Fe present in Pn. The High spin Fe allows for very fast diffusion in structural vacancies of Po and covers the mineral with a thin FeOOH overlayer

Hypothesis-3

The separation of Pn from Po by flotation could be made efficient either by exposing it to xanthate adsorption prior to oxidation, or by removing the FeOOH overlayer by deoxygenating the slurry to make it available for xanthate adsorption because Pn and Po are both very reactive to oxygen and once they are uniformly covered by a thin FeOOH overlayer, their interaction with xanthate should be similar.

3 MATERIALS AND EXPERIMENTAL METHODS

3.1 Introduction

It has established in Chapter-2 that the literature indicates that oxygen control at various stages of grinding and flotation may result in an improvement in grade and recovery of Pn and Po from a sulfide ore because of controlled oxidation and reduced FeOOH formation on to the mineral surface. In order to test this hypothesis, it was necessary to have a system, where oxygen content, reagent addition at the same time fresh mineral surface generation, can be measured and controlled.

The Magotteaux mill was chosen for this purpose as it fulfills the basic requirements of the tests i.e. pulp chemistry control at the time of fresh unoxidized surface generation at grinding stage. Since, the Magotteaux mill was purposely designed for testing different grinding media and generating plant conditions at a laboratory scale, it cannot be used in its “as it is” state for the study of xanthate adsorption measurement. The modifications made to the Magotteaux mill to make it appropriate for this test work is detailed in this chapter. The difficulties and challenges encountered during application and modification made to the Magotteaux mill will be discussed in this chapter.

Operating the Magotteaux mill and understanding the principle of operation in itself is a challenging task. The operating principles and procedure relevant to this project have been described in this chapter. However, the detailed operating procedure can found in the relevant operating manuals (E.J.B., 2009). This chapter also describes the detailed experimental methods which have been derived on combining the available laboratory grinding and flotation procedures used by the Centre for Minerals Research (CMR) at University of Cape Town (UCT) as well as those used by Magotteaux. Some of the diagnostic tests along with the main tests were performed during the study to verify the unforeseen results obtained during the xanthate adsorption measurement, were also discussed in this chapter. Analytical techniques, which had been extensively used to accomplish the objective of the study is also described in this chapter. The error associated with these procedures and any inconsistency or deviations from the standard techniques are also described.

3.2 Ore

Three drums of ore samples, weighing approximately 500 kg each were obtained from three separate locations of the Main Mineralised Zone (MMZ) of the Lower Pyroxenite Unit (LrPXT) of Uitkomst Complex (Nkomati), South Africa.

Preparation of the samples was carried out in the CMR at the UCT. The entire sample was spread out onto plastic sheeting in a closed room for drying. It was noted after 24 hours that the sample was ready to start the sample preparation activities. The samples were blended and the screened with a 4mm screen. The -4 mm size fraction was collected and stored in an air tight container. The +4 mm size was further screened with an 8mm screen. The +8mm portion was crushed to 100% passing 6mm using double toggle Jaw crusher. The crushed product was further screened through a 4 mm screen. The -4 mm product was then blended with the stored samples. The remaining +4 mm portion was then crushed in a cone crusher in CMR lab to 100% passing 4 mm. The Cone crusher product was blended with -4 mm stored sample. The entire sample were transferred onto a plastic sheet and blended thoroughly, weighed out in a number of 20 kg portions. These portions were riffled and split into representative 2 kg portions using a rotary sample splitter manufactured by Dickie and Stockler (Wiese, 2009)

The mean reconstituted feed values for copper, nickel and sulphur for the ores are shown in Table 3.1.

Table 3.1: Avg. Feed assay values for the Cu, Ni and Sulphur

Copper, wt %	Nickel, wt %	Sulfur, wt %
0.36	0.67	5.67

3.2.1 Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN)

The feed samples below 150 µm (+106, +75, +53, +25, +10, -10 µm) were, depending upon the quantity of the sample, first split in a rotary splitter and then in a micro-splitter to obtain the required quantity of the representative sample. While splitting in the micro-splitter, samples were collected in three different plastic containers for each size fraction. In the first container approximately 7 to 8 g of sample were collected. These samples were further split into two and micronized to 90 % passing 20 µm. 3.5 g of each size fraction were separately sent to UCT as well as M/s Mintek analytical lab for independent ICP-OES analysis of the sample. In the second container approximately 0.95 g to 1.05 g samples were submitted for QEMSCAN analysis. The third parts of the samples were kept for further analysis if needed.

3.2.1.1 *Data Validation*

Figure 3.1 shows the comparison of the chemical analysis from ICP-OES and the QEMSCAN analysis of the feed sample. The graph shows a good correlation between the major elements from the chemical assay and QEMSCAN data, especially Al, Ca and Si. Iron values show a slight underestimate for the chemical analysis while QEMSCAN slightly overestimated the values. Similarly with the Mg values; QEMSCAN slightly underestimated the values while chemical assays slightly overestimated the values.

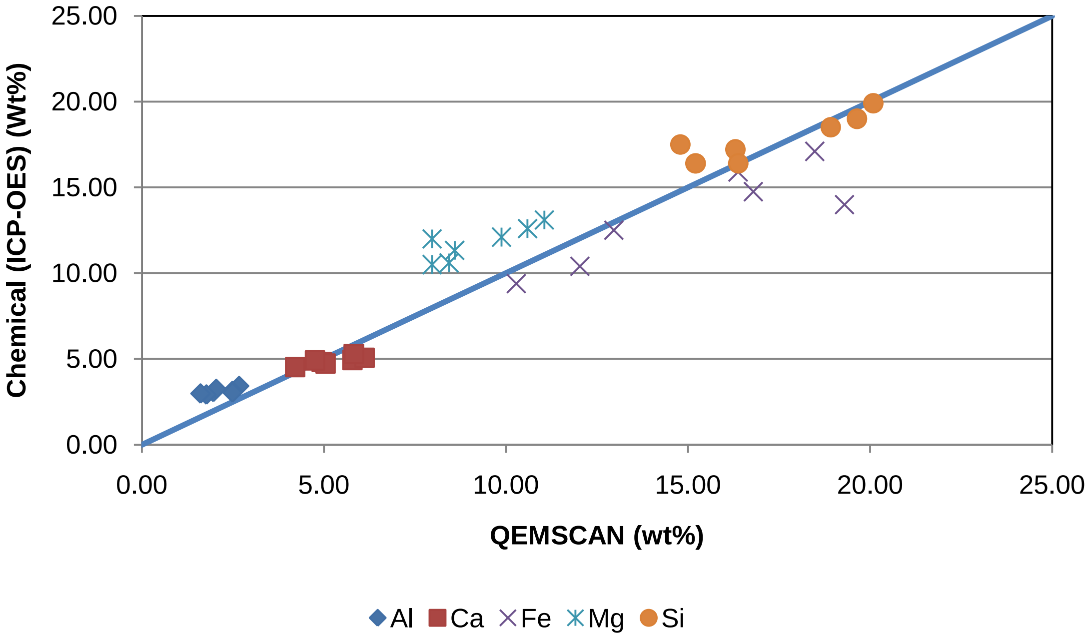


Figure 3.1: Graph showing the correlation between the chemical assay and the QEMSCAN assay for the major elements present in the feed sample. The line indicates 1:1 relation

Considering the sulfide elements; Cu, Ni and S show a very good correlation between the chemical analysis and QEMSCAN analysis of the feed sample (Figure 3.2). Cu and Ni values shows an excellent correlation with the two analysis, however, sulphur values shows one obvious abnormality circled in red.

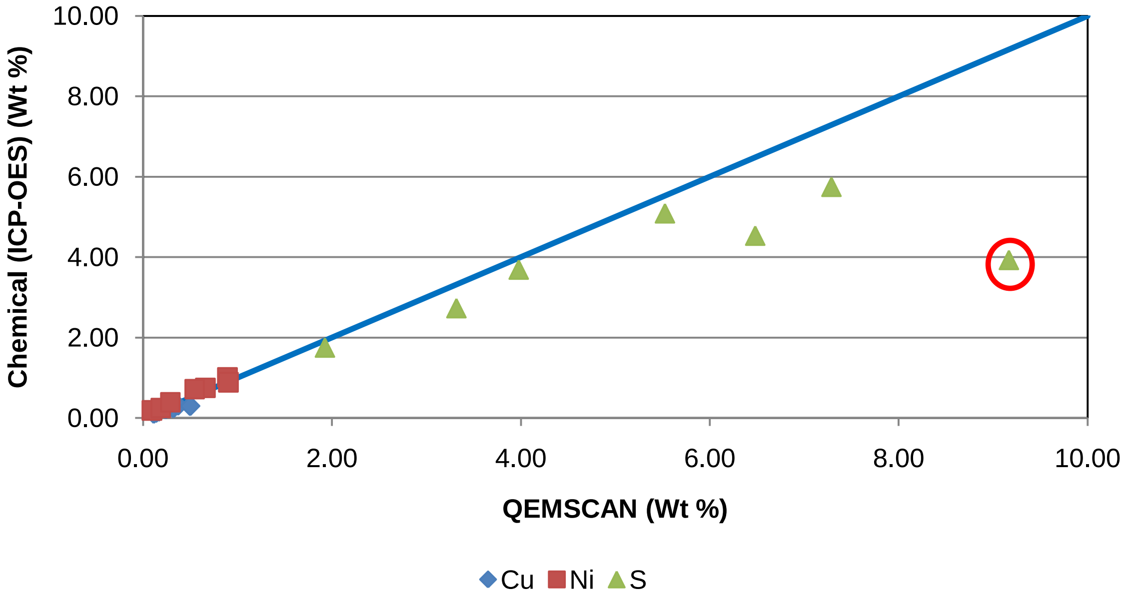


Figure 3.2: Graph showing the correlation between the chemical assay and the QEMSCAN assay for trace elements Cu, Ni and S, with a solid blue line demarcating a 1:1 relationship and a red circled point with an inconsistent value.

3.2.1.2 Analysis Method

Two methods were used in the QEMSCAN analysis of the samples. The first one was the Bulk Mineralogy Analysis (BMA). Figure 3.3 shows a section of the BMA analysis of the feed sample. This is a linear analysis method. Each color in the figure represents a different mineral.

Figure 3.3: Images showing a section of BMA analysis. Each color represents a different mineral.

The second method was the Specific Mineral Search (SMS) which identifies each mineral present in the grains analysed (Figure 3.4).

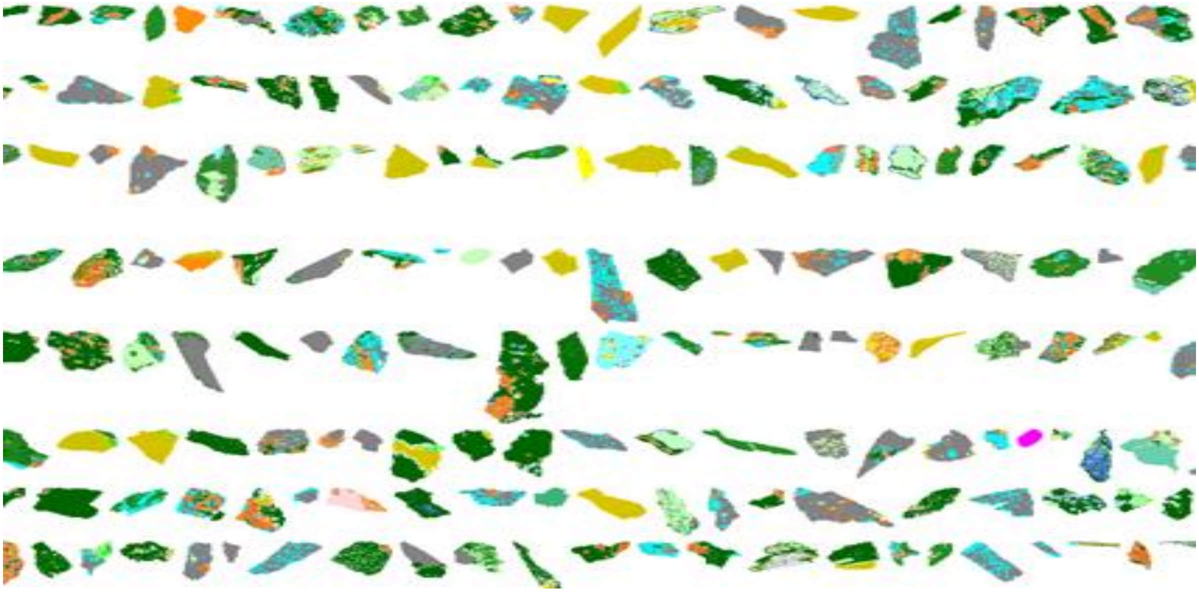


Figure 3.4: Image showing SMS analysis of various particles grains. Each color represents a different mineral with visible associations

3.2.1.3 Mineralogical Characterization

A modal analysis of the feed sample of the ore was conducted using QEMSCAN at UCT. The system acquires energy dispersive X-ray spectra and back scattered electron image information to identify minerals (Gottlieb et al, 2000). Gangue minerals and BMS present in the ore are shown in Table 3.2. All BMS are mainly associated with the major gangue minerals clinopyroxene and tremolite. In the ore sample there was some association between Po and both Cp and Pn. However, there was very little association between Cp and Pn. The modal BMS composition for different size fractions are shown in Table 3.3.

Table 3.2: Modal composition: sulfide and gangue minerals present in the ore samples as determined by QEMSCAN

Minerals	Size Fractions						Combined
	-1000/+106	-106/+75	-75/+53	-53/+25	-25/+10	-10	
Pentlandite	0.01	0.04	0.09	0.43	0.65	0.67	1.88
Chalcopyrite	0.01	0.03	0.05	0.18	0.27	0.37	0.91
Pyrrhotite	0.08	0.44	0.80	2.71	3.25	2.91	10.20
Pyrite	0.03	0.09	0.17	0.46	0.51	1.64	2.90
Other sulfides	0.00	0.00	0.00	0.01	0.00	0.02	0.03
Olivine	0.20	0.45	0.78	1.46	1.02	0.70	4.60
Orthopyroxene	0.24	0.41	0.60	1.00	0.58	0.44	3.28
Clinopyroxene	0.72	2.06	2.96	5.68	4.10	2.90	18.42
Serpentine	0.24	0.84	1.11	2.43	1.99	1.77	8.39
Talc	0.16	0.41	0.53	1.21	1.31	1.97	5.59
Chlorite	0.15	0.40	0.58	1.26	1.47	1.90	5.76
Tremolite	0.23	0.51	0.83	2.00	2.83	3.84	10.23
Plagioclase	0.13	0.33	0.58	1.23	1.03	0.93	4.23
Epidote	0.02	0.06	0.09	0.20	0.17	0.13	0.67
K-Feldspar	0.01	0.03	0.05	0.11	0.08	0.06	0.35
Biotite/Phlogopite	0.14	0.36	0.47	0.82	0.64	0.52	2.94
Calcite	0.02	0.06	0.11	0.29	0.40	0.44	1.32
Quartz	0.07	0.21	0.40	0.99	0.73	0.49	2.91
Chromite	0.10	0.20	0.53	3.25	2.73	2.32	9.12
Other	0.16	0.37	0.68	1.54	1.63	1.90	6.27
Total							100.00

Table 3.3: Modal composition of Base Metal Sulfide (BMS) present in the ore samples as determined by QEMSCAN

Minerals	Size Fractions						Combined
	-1000/+106	-106/+75	-75/+53	-53/+25	-25/+10	-10	
Pentlandite	5.68	6.39	8.33	11.28	13.86	11.91	11.82
Chalcopyrite	6.43	4.54	4.65	4.80	5.69	6.66	5.71
Pyrrhotite	65.01	73.80	71.53	71.78	69.58	52.10	64.21
Pyrite	22.88	15.27	15.48	12.14	10.87	29.34	18.26
Total							100.00

3.3 Water

Synthetic plant water was used in all grinding and batch flotation tests conducted in this study (Wiese, 2009). The ions present in the synthetic plant water are shown in Table 3.4. In CMR laboratory distilled water was modified by the addition of various chemical salts to achieve specific total dissolved solids content. The water was prepared in batches of 40 L (see Appendix).

Table 3.4: The concentration of ions present in the synthetic plant water used in all batch flotation tests.

Ion	Ca^{2+}	Mg^{2+}	Na^{+}	Cl^{-}	SO_4^{2-}	NO^{3-}	NO_2^{-}	CO_3^{2-}	TDS
Concentration (ppm)	80	70	153	287	240	176	-	17	1023

3.4 Flotation reagents

Initial test work was started with the reagent suites available in the literature and UCT experience with Nkomati ore. This included primary collectors, secondary collector, depressant and the frother. However, along with the oxygen control the and above mentioned variables it was found difficult to interpret the flotation data. In order to make proper interpretation of the test results some of the variables had been removed from the reagents suites, and SIBX was decided to be added into mill. However, due to similarity between DOW 200 and XP 200, XP 200 was used a frother in this test work. Condition time for the frother was chosen as per standard UCT batch flotation procedure. The literature published (Kelebek, 1993) on the floatability of Pn and Po showed that pH 9.2 is ideal for effective separation of Pn. So, initial work was started with the flotation at natural pH. The final reagent suite used for this test-work is shown in Table 3.5.

Table 3.5: Reagent suites used in this study

Reagent	Dosage (g/t)	Conditioning time (min)
SIBX	20	Milling
DOW 200	20	1

3.4.1 Collectors

In all batch flotation tests to evaluate the influence of grinding environment on the flotation performance of the ores, SIBX was only used as a collector with a purity of 90%. The collector was added at a dosage of 20 g/t. 1% solutions of the xanthate collector was prepared fresh each day using distilled water. All xanthate collectors used in this study have a purity of close to 90% and were supplied by Senmin.

3.4.2 Frother

The frother used in all the batch flotation tests was DOW 200 supplied by Betachem having specific gravity 0.973. The frother dosage was kept constant at 20 g/t in all tests.

3.4.3 Depressant

The depressant used in the confirmatory batch flotation tests was Guar KU-49 supplied by Senmin. The depressant dosage was kept constant at 100 g/t in the test.

3.4.4 The pH Modifier

Acid used in the acid wash batch flotation tests was 32% HCl supplied by Betachem. However, lime was used as a pH modifier in all the cases wherever is necessary, except in case of acid wash test, where NaOH was used to bring pH up. Lime, being cheap, is very widely used to regulate pulp alkalinity, and is used in the form of milk of lime in the present study. A suspension of calcium hydroxide particles in a saturated aqueous solution was used at the beginning. Lime or soda ash is often added to the slurry prior to flotation to precipitate heavy metal ions from solution.

3.5 Magotteaux Mill®

The Magotteaux Mill was developed by Magotteaux Australia (Pty) Ltd. as a way of testing the effect of grinding media on subsequent flotation performance. In order to prove that certain grinding media would change the metallurgical performance on real plants, the mill had to be able to mimic real plant conditions.

The Magotteaux Mill allows for the measurement of the chemistry of the pulp in situ. Within the mill, there are two chambers separated by a separating plate. The grinding chamber holds the grinding media, ore, water and reagents and the measuring chamber contains the pulp chemistry probes. The probes allow the measurement of the pH, Eh, DO and temperature in the mill during grinding. DO and Eh are controlled by adding gases to the grinding chamber. The pH can be controlled during milling by addition of lime solution through a lime dosing pump. The temperature is controlled by the heating coil in the walls of the mill. Figure 3.5 gives a schematic of the milling system.

The separating plate has circular openings covered by 400 µm sieves, allowing movement of the pulp liquid between the two chambers. A peristaltic pump continually pumps slurry from the measuring chamber back to the grinding chamber to ensure that the slurry in the measuring chamber is always fresh. There is a ring of slots around the steel tube of the separating plate as shown in Figure 3.13, to release the excess pressure of the grinding chamber, in the case of sieve blockage.

When, the ore is of high clay content, there may be build up of ore on the mesh. The clay may coat the mesh on the ports and stop the flow of slurry and gas from the grinding chamber to the measuring chamber. As a result pressure builds up on the grinding chamber. Sometimes the ring slots on the separating plate would not be sufficient to reduce the pressure build up and in this case, the high pressure in the grinding chamber can blow the slurry return line off and discharge line slides down. In this case, it would be recommended to replace the mesh with the higher size (Greet, 2010).

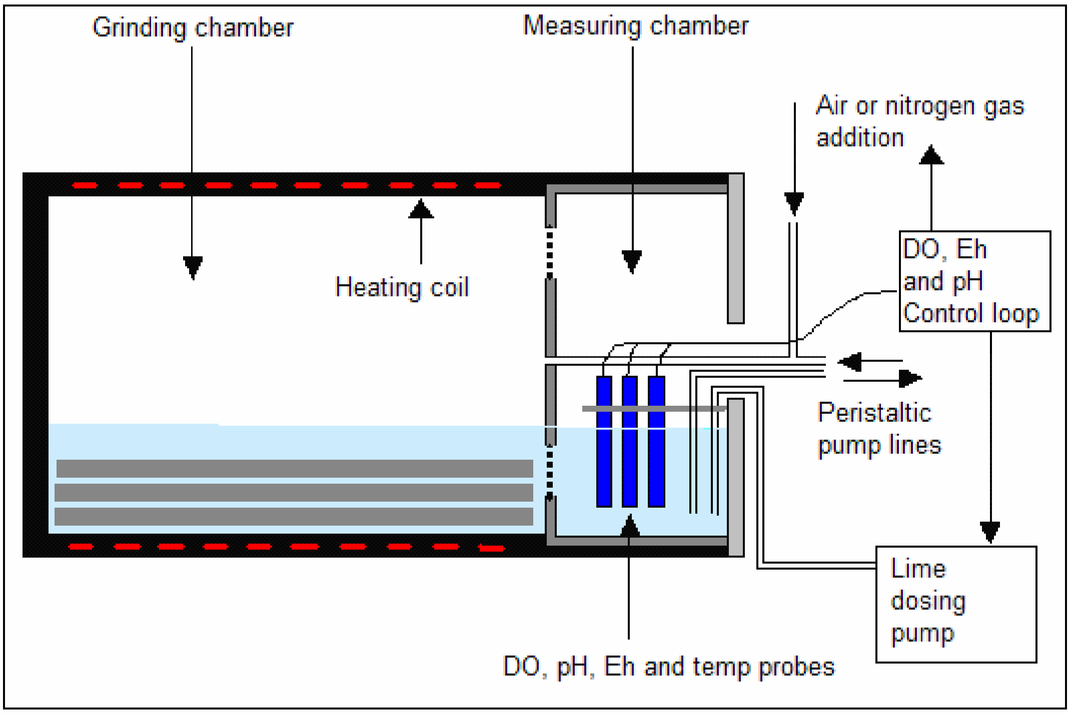


Figure 3.5: Schematic of the Magotteaux Mill (Magotteaux Mill® user manual)

The mill is controlled using a Compact Logix 1769-L35E programmable logic control (PLC) logic solver. The PLC receives both hardwired signals from existing and/or upgraded equipment and ASCII strings via a serial communication link from the TPS analytical instrument mounted to the mill assembly (E.J.B., 2009). The mill can operate in four modes named as local manual operation, local automatic operation, remote manual operation and remote automatic operation as per requirement and availability of instruments. However, throughout this study, the mill was operated in the remote automatic mode. This mode allows the user to operate the mill using an automatic batch control strategy, where input parameters such as control set points, times, and/or batch formulation data is entered and used to execute consistent batch sequences. In this mode the mill operates through the supervisory control and data acquisition (SCADA) system user interfaces available on a laptop. The communication type used between the mill PLC panel and the Experion PKS Server is wireless 802.11g at approximately 54 MB as shown in Figure 3.6. Although the wireless communications should be effective over 15 to 25 meters from mill panel without disruption, it is the best to provide a clear line of sight between the mill PLC panel and the Industrial laptop.

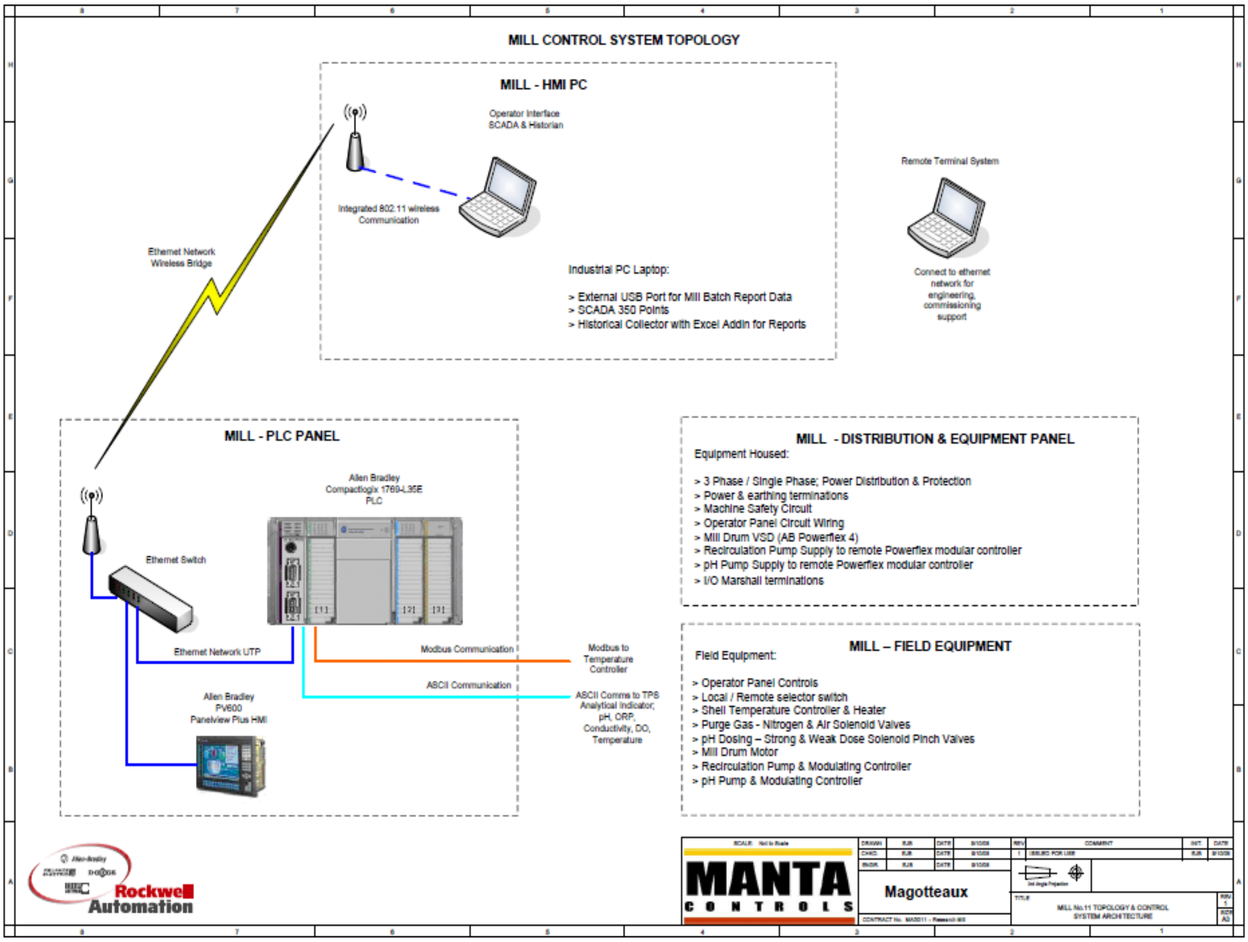


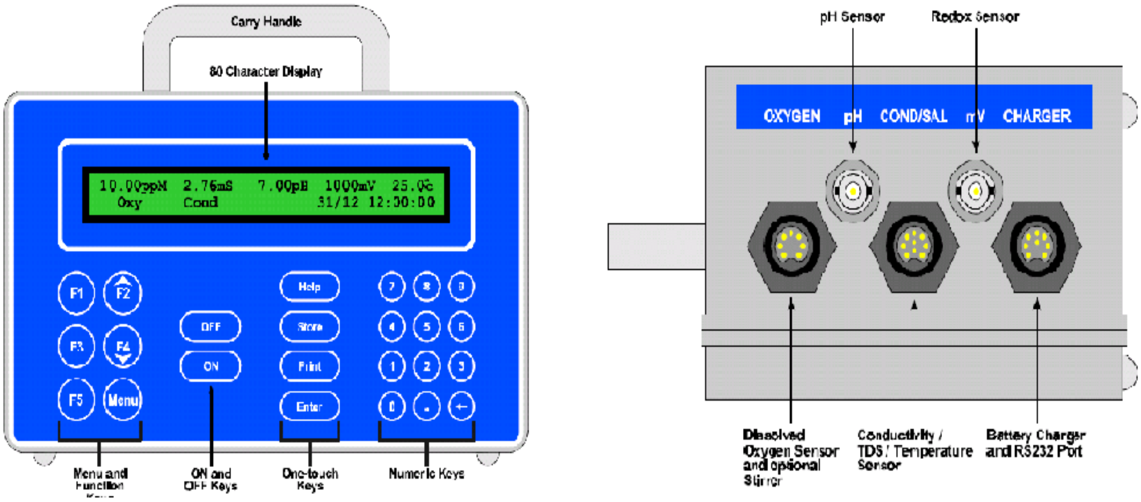
Figure 3.6: Schematic of the Communication link of the Magotteaux Mill panel to the SCADA (Magotteaux Mill® general drawing)

3.5.1 TPS Logger (90 FL-MV) and Probe

The 90 FL-MV TPS logger is used in the Magotteaux mill in order to monitor the conductivity, DO, total dissolved solid (TDS), pH, oxidation reduction potential (ORP) and temperature as shown in the Figure 3.7 (A). The data can be stored during the experiments in the memory of the TPS logger itself and could be later transferred to PC for further analysis. Due to limited memory of the TPS logger only 1808 readings can be logged into it. However, the Win-TPS software, which is acting as a gateway between the TPS and personal computer (PC), offers to log onto more data directly on to a PC. This software package (Win-TPS) handles the communication protocols for TPS instruments fitted with an RS232 port as shown in the

[A] [B]

Figure 3.7 (B). It is designed to quickly and easily download the vital data and even manage some of the instrument's functions. This software along with the Experion PKS server (Honeywell) might have been utilized in the development of the Magotteaux Mill control panel.



[A] [B]

Figure 3.7: Schematic of the 90 FLMV TPS logger (90 FLMV manual)

3.5.1.1 Dissolved oxygen Probe

The Clark oxygen electrode (Clark et al, 1953) is a device used for measuring oxygen activity in a liquid. It consists of a gold cathode and a silver/silver chloride anode, placed in potassium chloride electrolyte solution. The electrolyte solution is kept in contact with the gold electrode by a 0.001 inch PTFE (Teflon) membrane. The operating principle of the Clark oxygen electrode relies on the diffusion of oxygen through the membrane into a constant environment of potassium chloride electrolyte. The thickness of the membrane should always be kept the same because the change in the thickness will change the temperature compensation of the membrane permeability. A polarizing voltage of about 800 mV is applied between the two electrodes. The polarizing voltage causes the reduction of diffusing oxygen (through membrane) at the gold electrode.

$O_2 + 2H^+ + 2e = H_2O_2$

This reduction process will produce a current through the oxygen electrode. This current would be a linear measure of partial pressure of oxygen, assuming sufficient liquid flow conditions (a few cm/sec is sufficient) across the probe. The flow across the probe is required to minimize the formation of an unstirred layer next to the membrane. In the case of the Magotteaux mill, this has been achieved by the recirculation pump which is continuously recirculating the slurry from the measuring chamber to the grinding chamber. A load resistor (thermistor) situated in the electrode itself, converts this current into a voltage proportional to oxygen partial pressure. The thermistor provided within the body of the electrode gives an accurate temperature compensation for the temperature/permeability effect of the membrane, over a range of about 5 to 45 ^{0}C. A separate sensor is also built into the tip of the probe to achieve the solubility effect. Detail calibration, storage and maintenance procedure for the DO probe can be obtained from the 90 FLMV manuals (MS, 2001).

3.5.1.2 Eh or ORP Probe

A platinum electrode is used for the Eh or ORP measurement in the 90 FLMV TPS logger. It consists of a Pt cathode and silver/silver chloride anode, placed in potassium chloride electrolyte solution. The detailed operating principles and types of Eh or ORP electrode used in the mineral industries have been discussed in Chapter-2.

The Eh or ORP probe used in 90 FLMV the TPS logger is factory calibrated. There is no user-calibration facility for this electrode. However, different cleaning techniques applicable to get optimum performance are available in literature (Natarajan, 1992).

3.5.1.3 The pH Probe

The pH electrode consists of a pH sensing membrane and a reference electrode in the single body. The sensing membrane is a round or spear shaped bulb at the tip of electrode, constructed from an especially composed glass which senses the hydrogen ion concentration. This glass is typically composed of alkali metal ions. The alkali metal ions of the glass and the hydrogen ions in solution undergo an ion exchange reaction, which results into the varying potential. However, the potential of the reference portion, which is produced by the internal element in contact with the reference fill solution, always remains constant. In summary the measuring electrode delivers a varying voltage and the reference electrode delivers a constant voltage. This produces an overall potential difference that changes with the pH of the solution. An “ideal” pH electrode produces 0 mV output at 7.00 pH. As the pH goes up, an “ideal” pH electrode produces –59.16mV/pH unit at 25 ^{0}C and as the pH goes down, an “ideal” pH electrode produces +59.16mV/pH unit. The details of the calibration, storage and maintenance procedure for the pH probe can be obtained from the 90 FLMV manuals (MS, 2001).

3.5.1.4 Temperature probe

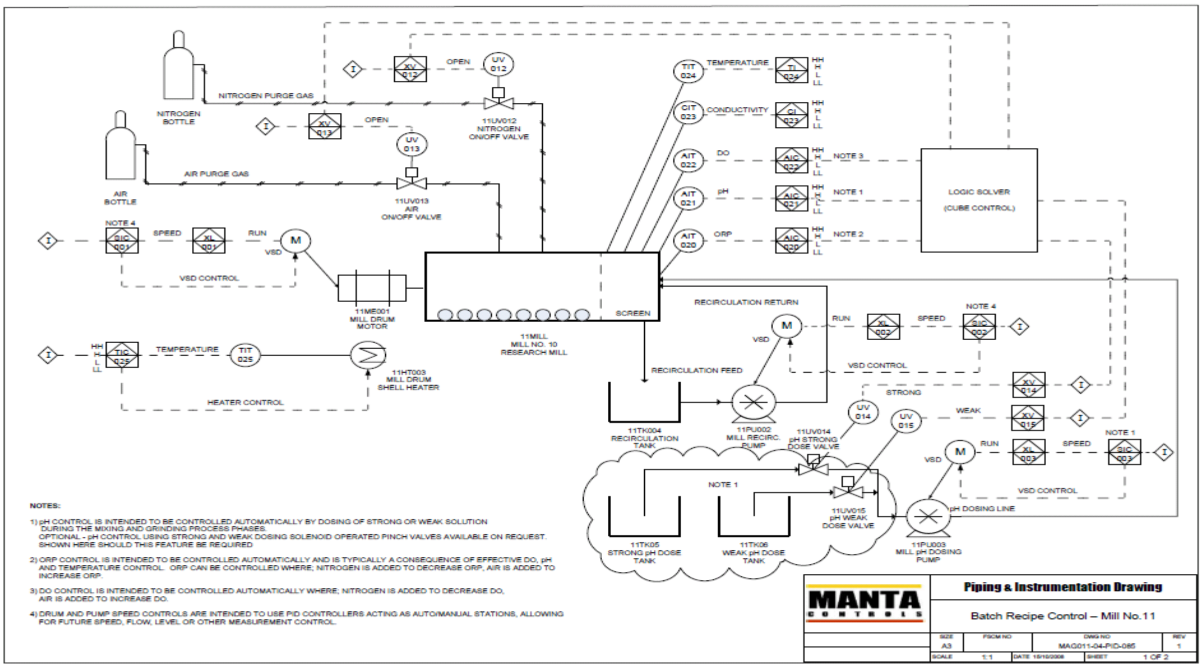
A temperature probe (thermocouple) consists of two wires, each made of a different homogeneous metal or alloy. The wires are joined at one end to form a measuring junction. This measuring junction is exposed to the fluid or medium being measured. The other end of the wires is terminated at the 90 FLMV TPS logger, where they form a reference junction. When the two junctions are at different temperatures, current will flow through the circuit. The potential difference due to current flow is measured to determine the temperature of the measuring junction. This probe must be calibrated first, before attempting pH or DO calibration and measurements.

3.5.2 Control Philosophy of Magotteaux Mill®

Magotteaux mill operated under remote automatic control as discussed earlier can be operated in two modes, namely calibration mode and grinding mode. As a consequence air and nitrogen valve (solenoid) would operate automatically to achieve the DO set point in a particular time interval. After the completion of the test in calibration mode, this file or valve actions can be stored in calibration index. The same test conditions can be obtained by operating the mill in the grinding mode for the duplicate test. In the grinding mode, there is no need to formulate the recipe of the test. The system would automatically take the recipe stored in the calibration index.

In the calibration mode, there are four stages of mill operation namely conditioning, mixing, grinding, and discharge preparation. In the conditioning phase mill remains stationary but the recirculation pump and gas purging available for use. The targeted DO set point chosen for a specific test is generally obtained in this phase. However, it was experienced that the significant change in the DO values were materialize in the next phase i.e. mixing. In the mixing phase, the mill was allowed to rotate very slowly (generally 10 rpm), so that the water ore and reagents could be properly mixed before the grinding stage. If the required set points of the DO values are not achieved in the previous phase, the valves action would be continued in this phase as well. This phase generally lasts in 2 to 3 min. Once, the mixing phase is completed, the mill enters into the grinding phase. In the grinding phase the mill operates at the established speed set point for a fixed time derived from the grinding curve conducted separately. The next phases of operation i.e. discharge preparation which is much relevant to mimic the real plants conditions at the lab scale, and is not considered for this study.

Detail control loops and the 'piping and instrumentation diagram' (P & ID) of the Magotteaux mill are shown in the Figure 3.8. The control action of the gas purging valves, drum speed, lime dosing pump and recirculation pump speed is governed by 'proportional integral and derivative' (PID) control. The "PID control" is the method of feedback control that uses PID controller as the main tool. The basic structure of conventional feedback control systems is shown in Figure 3.9, where, the process is the object to be controlled.



NOTES:

1) pH CONTROL IS INTENDED TO BE CONTROLLED AUTOMATICALLY BY DOSING OF STRONG OR WEAK SOLUTION DURING THE MIXING AND GRINDING PROCESS PHASES.
OPTIONAL - pH CONTROL USING STRONG AND WEAK DOSING SOLENOID OPERATED PINCH VALVES AVAILABLE ON REQUEST. SHOWN HERE SHOULD THIS FEATURE BE REQUIRED

2) ORP CONTROL IS INTENDED TO BE CONTROLLED AUTOMATICALLY AND IS TYPICALLY A CONSEQUENCE OF EFFECTIVE DO, pH AND TEMPERATURE CONTROL. ORP CAN BE CONTROLLED WHERE; NITROGEN IS ADDED TO DECREASE ORP, AIR IS ADDED TO INCREASE ORP.

3) DO CONTROL IS INTENDED TO BE CONTROLLED AUTOMATICALLY WHERE; NITROGEN IS ADDED TO DECREASE DO, AIR IS ADDED TO INCREASE DO.

4) DRUM AND PUMP SPEED CONTROLS ARE INTENDED TO USE PID CONTROLLERS ACTING AS AUTO/MANUAL STATIONS, ALLOWING FOR FUTURE SPEED, FLOW, LEVEL OR OTHER MEASUREMENT CONTROL.

Figure 3.8: Schematic of the Magotteaux Mill P & ID showing control loop (Magotteaux Mill® General drawing)

The purpose of control is to make the process variable y follow the set-point value r. To achieve this purpose, the manipulated variable u is changed at the command of the controller. As an example in the Magotteaux mill control, consider the DO concentration is the object to be controlled to a desired DO value by gas purging. The process variable y is the DO concentration of the slurry, the set-point value r is the desired DO value to be obtained and the manipulated variable u is the action of the gas (N_2/ air) purging valve. The "disturbance" is any factor, other than the manipulated variable, that influences the process variable. The error (e) from the set point is defined by $e = r - y$. The compensator $C(s)$ is the computational rule that determines the manipulated variable u based on its input data, which is the error e in the case of Figure 3.9. When the error is positive the manipulated variable (u) would direct the command for opening the air purging valve otherwise the N_2 purging.

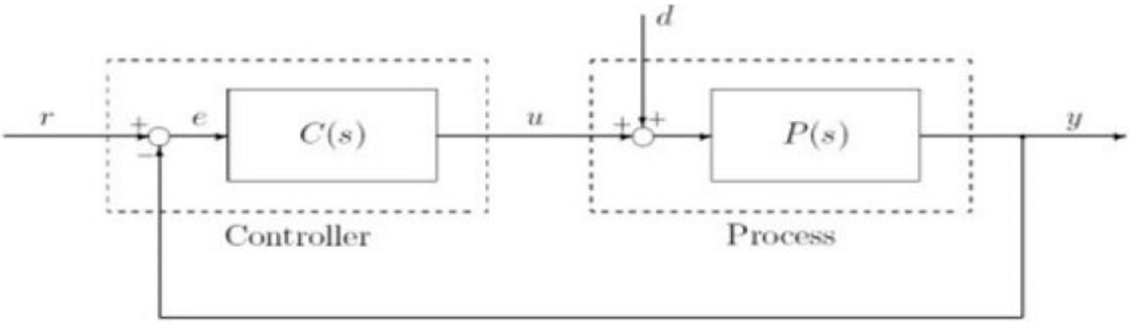


Figure 3.9: Conventional feedback control system (Araki, M.)

The PID controller can be understood as a controller that takes the present, the past, and the future of the error into consideration to derive the action. The P element is proportional to the error at the instant t, which is the “present” error (difference between the target value and present value at an instant t). I element is proportional to the *integral* of the error up to the instant t, which can be interpreted as the accumulation of the “past” error. D element is proportional to the *derivative* of the error at the instant t, which can be interpreted as the prediction of the “future” error.

3.5.3 Operational Issues

The Magotteaux mill is one of the best instruments for the fundamental study of the grinding system. The Magotteaux mill is a device that not only allows one to conduct electrochemical measurements but also to control the pulp chemistry during grinding (Greet et. al, 2004). However, some limitations observed during this study are discussed in this section. The operational issues developed during the test work are also included in this section.

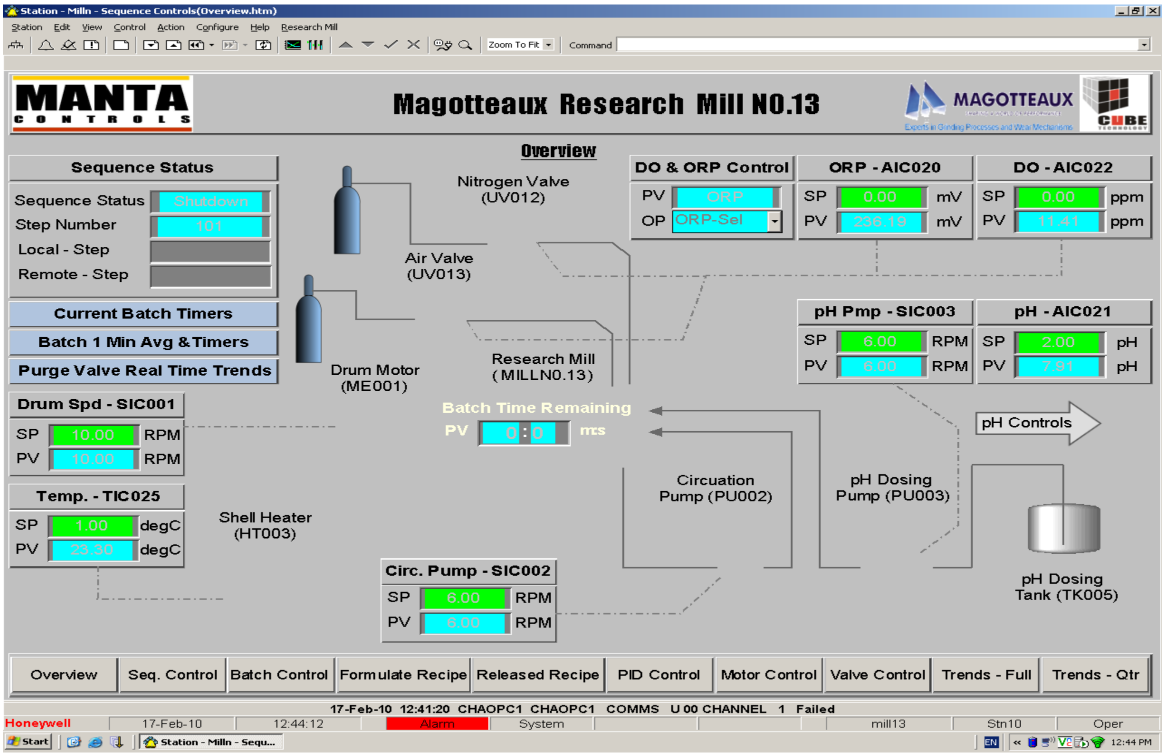
Initial test work was started with the intention of developing a system to achieve the collectorless floatability of a sulfide ore through varying the Eh-pH conditions in the pulp. However, during the test work it was observed that the higher Eh values cannot be achieved through air purging alone. It was thus hypothesized that purging pure oxygen during the grinding may result into the higher Eh values. However, after careful discussion it was established that in excess of oxygen, species that can oxidize would get oxidized too quickly, adding electrons to the slurry and lowering the Eh. Further, using oxygen will promote oxidation reactions, which may in turn alter the collectorless floatability of the minerals. The effect of Eh may be masked by the effect of oxidation.

3.5.3.1 *Channel and Controller failure*

A channel is a physical communications link, such as a network cable, between the server and one or more controllers. If a channel fails, a communication gap may occur between the server and PLC and a continuous system alarm would start blinking on SCADA. As a result, the SCADA would become blank as shown in Figure 3.10, and no further command can be executed to the mill from the SCADA. The status of each communication channel, as well as its type can be displayed by the following commands. View / System Status/ Channels.

More information about a channel status can be obtained from the channel's detail display as shown in Figure 3.11. This shows error statistics and barometer values. The current barometric value for a healthy channel should be always less than the marginal limit.

The information about the controller attached to a particular channel can be obtained by clicking the controller’s button.



Sequence Status
Sequence Status: Shutdown
Step Number: 101
Local - Step:
Remote - Step:

Drum Spd - SIC001
SP 10.00 RPM
PV 10.00 RPM

Temp. - TIC025
SP 1.00 degC
PV 23.30 degC

Circ. Pump - SIC002
SP 6.00 RPM
PV 6.00 RPM

Batch Time Remaining
PV 0:0 m:s

DO & ORP Control
PV ORP
OP ORP-Sel

ORP - AIC020
SP 0.00 mV
PV 236.19 mV

DO - AIC022
SP 0.00 ppm
PV 11.41 ppm

pH Pmp - SIC003
SP 6.00 RPM
PV 6.00 RPM

pH - AIC021
SP 2.00 pH
PV 7.91 pH

17-Feb-10 12:41:20 CHAOPC1 CHAOPC1 COMMS U 00 CHANNEL 1 Failed

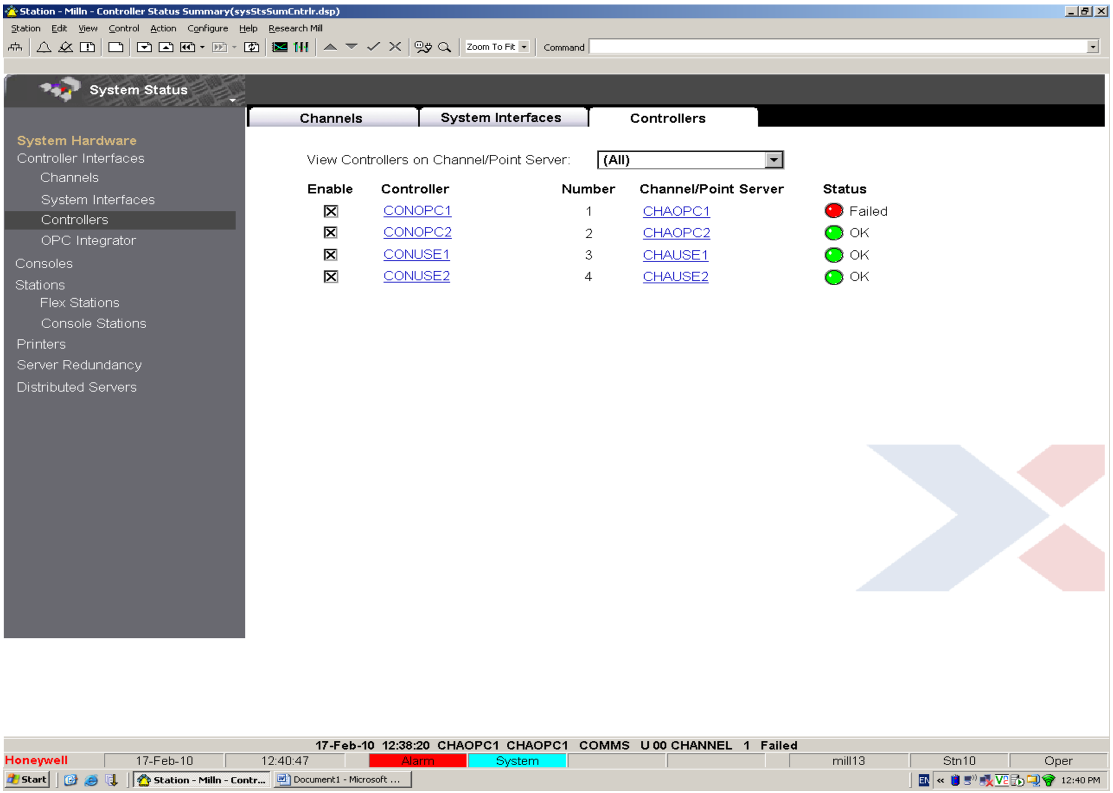
Honeywell | 17-Feb-10 | 12:44:12 | Alarm | System | | | mill13 | Stn10 | Oper

Figure 3.10: Magotteaux Mill SCADA showing consequences of channel and controller failure

It was one of the most rigorous problems observed during this test work. The entire process from identifying the cause to remedy the issues took several weeks and it had been discussed here one by one.

At first glance, it was observed that during the time of channel and controller failure, the industrial laptop was also detecting the UCT wireless network. So, it was assumed that the UCT wireless may be intervening or prevailing over the mill panel wireless. As a result proper communication between the mill panel and the server was not getting established to execute the command from the SCADA. Although, the UCT wireless connection was completely disconnected after the event the problem was still persisting. It was decided to change the wireless connection between the mill panel and industrial laptop with hardwire. Before changing the connection, the entire devices on the mill was pinged from industrial laptop, the wireless signal strength of the mill was checked and found to be well. This reason was completely discarded.

The next possibility was the communication (*Communication* refers to serial or TCP/IP communication between the controller module and the PC-based HMI SCADA software) failure between server and SCADA. In industrial process control, generally server and SCADA are kept in separate systems (PC) but in case of Magotteaux mill, Honeywell OPC server and SCADA are in the same system. So, it was suspected that some software or communicating device in the industrial laptop was corrupted as a result of the communication gap established between server and SCADA.



View Controllers on Channel/Point Server: (All)

Enable	Controller	Number	Channel/Point Server	Status
☒	CONOPC1	1	CHAOPC1	🟥 Failed
☒	CONOPC2	2	CHAOPC2	🟩 OK
☒	CONUSE1	3	CHAUSE1	🟩 OK
☒	CONUSE2	4	CHAUSE2	🟩 OK

17-Feb-10 12:38:20 CHAOPC1 CHAOPC1 COMMS U 00 CHANNEL 1 Failed

Figure 3.11: Magotteaux Mill SCADA showing details of the channel and controller failure

After meticulous study of the manuals, drawings and discussion with UCT and Magotteaux experts, the OPC servers were started manually through My Computer/Manage/Service and application/ Services/ OPC Enum. Although the system starts working well thereafter but the reason was not identified. The problem was communicated to the MANTA control system, the developer of the Magotteaux control system. At the same time the starting mode for the OPC server was changed from manual starting mode to automatic starting mode so that whenever the laptop would start, the server would automatically get started. MANTA controls had given further instruction to enable and configure the remote desktop for administration in Windows Server 2003, so that they can figure out and rectify the problem through the remote access server, from Australia. The method to configure the remote desktop as instructed by MANTA is as follows: Start/ Control Panel/ System.

Click the Remote tab, click to select the Allow users to connect remotely to your computer check box, and then click OK.

Select Start/ control panel/ Network Connections/ Local Area Connection.

Select Properties.

Record the existing IP Address and subnet mask.

Select the “Obtain an IP address automatically” option.

Select OK and exit the setup.

Connect the laptop to your existing Internet connection using a straight through cable.

Try going online to a web page for example www.google.com to check whether the connection is active.

The laptop was configured for remote access to the MANTA controls. No irregularity in the system was identified and MANTA concluded that, if there were any irregularities in the system, it had already been rectified. MANTA controls had recommended one additional step in the starting of the industrial laptop i.e. checking of free ping before start-up of mill station.

3.5.3.2 Coarser particles transfer from grinding chamber to measuring chamber

Grinding product size is often considered as an important parameter when comparing the plant performance with the laboratory mill. However, in the case of grinding with the Magotteaux mill, grinding feed size is also one of the important factors. Extensive research with the mill led Magotteaux to establish that a finer feed is best for the operation of mill (Greet, 2010). A coarser feed size not only resulted in the blockage of the recirculation line and tubing damage but also resulted in the critical size build up.

When, the ore has higher percentage of quartz as in the case of Nkomati ore, this will impact the breakage rate and result in increased grinding time. Further, if balls were used as a grinding media, it resulted in random breakage. This results in a buildup of a critical size, which is then manifested by blocking the pump line and therefore blocking the flow of slurry and gas into the mill. In the worst case the slurry started entering into gas line instead of returning back to the grinding chamber.

During the course of initial experimental work, it was observed that the rubber tube piping across the recirculation pump was frequently getting damaged, although it was Masterflex tubing which is supposed to be having longer life than silicon tubing. It was suspected that, due to the lack of lubrication across the peristaltic pump bearing, the tubing accumulated over the bearing and got damaged.

Later, it was noticed in the transparent piping that sometimes the recirculation line was chocked up during the grinding phase of mill operation, although the recirculation pump operates at the same speed, the slurry stops pumping. The reason for chocking up was not quite clear until the Masterflex tube was replaced with the transparent silicon tube. After replacement, it was observed that due to the difference in pipe diameter, the particles accumulated at the junction of silicon tubing and polyethylene low density (PELD) pipeline near the recirculation pump and as a consequence slurry flow completely stops even though the pump is operating.

In full time air-purging and full time N_2 purging experiments, the situation reaches its extreme. As soon as the mixing and conditioning stages were complete and the system enters into the grinding stage, after 3 to 5 minutes, the joint split and resulted in the spilling of the slurry into the lab. When the joint was clamped, first the joint started expanding but later the slurry started going back into the gas line and started accumulating until splattering occurred at the joint of the gas line. Once these joints were also clamped, the silicon tubing of the gas line started expanding. The expanding gas line confirmed the blocking up of the recirculation line (Grant, 2010). However, the system was cleaned properly at the end of each grind, until clear water started coming through the system. So, the probability of line blocking was completely discarded. The problem was analyzed from various aspects of the Magotteaux mill operation and it is discussed here in sequence.

The problem arises during full time air/N_2 purging experiments. It was presumed that due to full time gas purging, the grinding chamber's pressure kept on increasing due to the clogging of the mesh and slots of the separating plate (Greet, 2010). This may restrict the gas and slurry flow from the measuring to the grinding chamber, resulting in blown off joints. This reason was also discarded as the Nkomati ore used in this study did not contain the clay material which may block the mesh and slots.

Finally, the high pressure (4 bar) of the purging gas as compared to the head of the peristaltic pump was also analyzed. In the Magotteaux mill, the high pressure gas line and slurry line meet at a 90 ^{0} T-joint (gas enters from the top) and goes together with the recirculating slurry into the grinding chamber. Due to the high pressure of the purging gas, it may block the slurry flow and preferentially pass through the common discharge line. All possibilities to avoid the situation were explored and it was concluded that it can be avoided in two ways; first, to replace the 90 ^{0} T-joint with a 45 ^{0} joint and second, to create two separate lines for slurry and gas. Due to unavailability of the 45 ^{0} joint, it was decided to create two separate lines for the gas and slurry flow. However, M/s Magotteaux had never experienced a problem with the common line for the slurry and gas during operation. Before separating the line into two, water tests were carried out in manual mode of the mill. In these tests, the peristaltic pump was operated with and without gases and discharge head was monitored. It was found that gas flow is helpful for the slurry/water flow and it resulted in an increase in head flow. This prospect was also discarded. At this point each section of the piping and fitting was disconnected and cleaned again with high pressure water. Some particles come out of it had made it clear that the problem was due to the ore which trapped into the middle of pipe or at the joint (and not visible) as shown in the figure. It will allow the water to flow through, but when slurry starts coming, other particle also starts accumulating at that point and results into the blockage of the line. As the PELD pipe and associated fittings are colored it would not be visible. At this point complete piping was replaced with transparent piping wherever transparent pipes were available and noted that some of the coarser particles were often stuck in the middle of the pipes or fittings, during the tests of full time gas purging.

Although the problem was resolved, the size of the particles raised some question about the operation of the mill, such as, how do the coarser particles get into the piping and tubing?

These coarser particles may be entering either through the measuring chamber or through the grinding chamber but the probability of getting particles through the measuring chamber is higher as compared to the latter. It was hypothesized that the coarser particles from the grinding chamber may be coming to the measuring chamber through the slots of the separating plate as shown in the Figure 3.13 and then along the slurry recirculation flow and being trapped in the piping. As the sizes of the slots are big enough, the system allows some of the coarser particles through this path while reducing the pressure inside the grinding chamber. However, when grinding starts these particles along with other fine particles start coming through the recirculation line. If the particle at some point attains a position as shown in Figure 3.12, it may block the line, consequently to reduce the pressure slurry start exiting through the undesired path.

Figure 3.12: Magotteaux Mill piping and fittings showing the blockage of slurry line

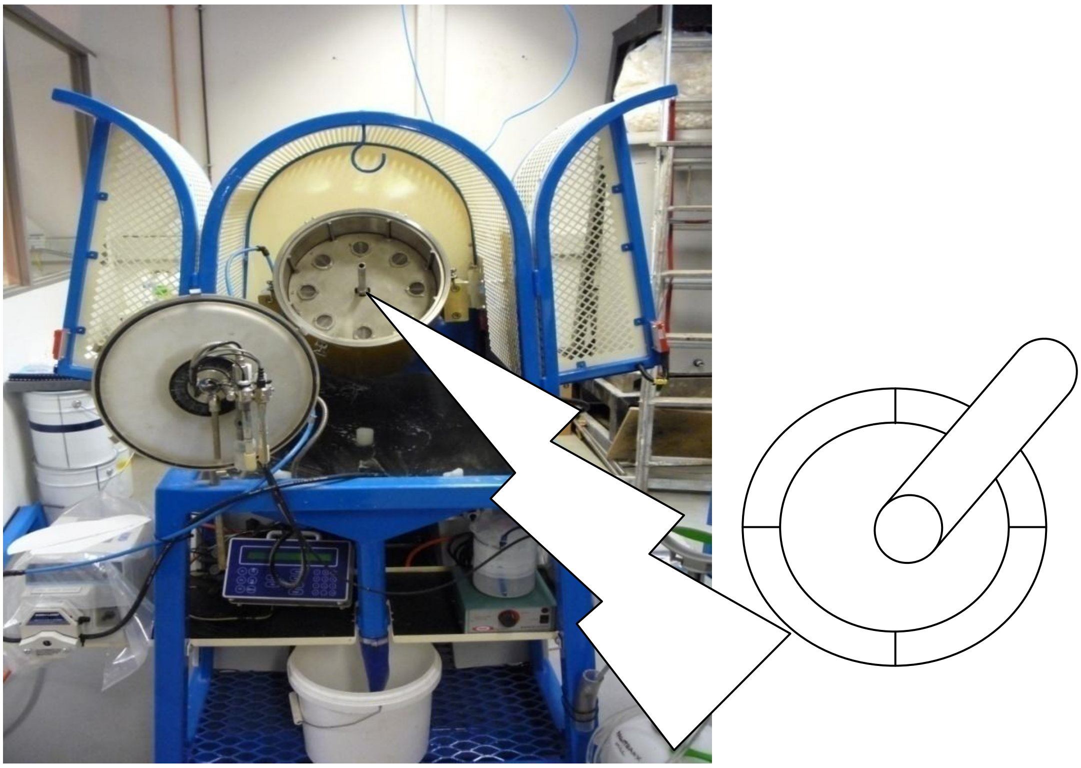


Figure 3.13: Magotteaux Mill, showing the slots around the separating plate

This issue was completely resolved either by using a smaller feed size, preferably 100 % passing 2 mm (Greet, 2010) or restricting the coarser particles from entering the measuring chamber. Changing the feed size at this stage of the test-work would have been a very cumbersome and frustrating job. So, the second approach was adopted and the details and difficulty of this are discussed in section 3.5.4.

3.5.3.3 The pH control through lime dosing pump

One of the important features of the Magotteaux mill is its pH control competency within the band width of 0.05 pH units. The required pH set point is achieved through PID controller of a lime dosing pump. The PID controller manoeuvres the speed as well as the mode of operation (start-stop) of the lime dosing pump. It is recommended to use a 1 % lime solution due to the probability of chocking of the lime dosing line at higher concentrations. However, if the required pH is high enough, the added volume of 1 % lime solution may alter the grinding pulp density and consequently the grind size. It may also result in an increase in the volume of the slurry which cannot be fed to the flotation cell.

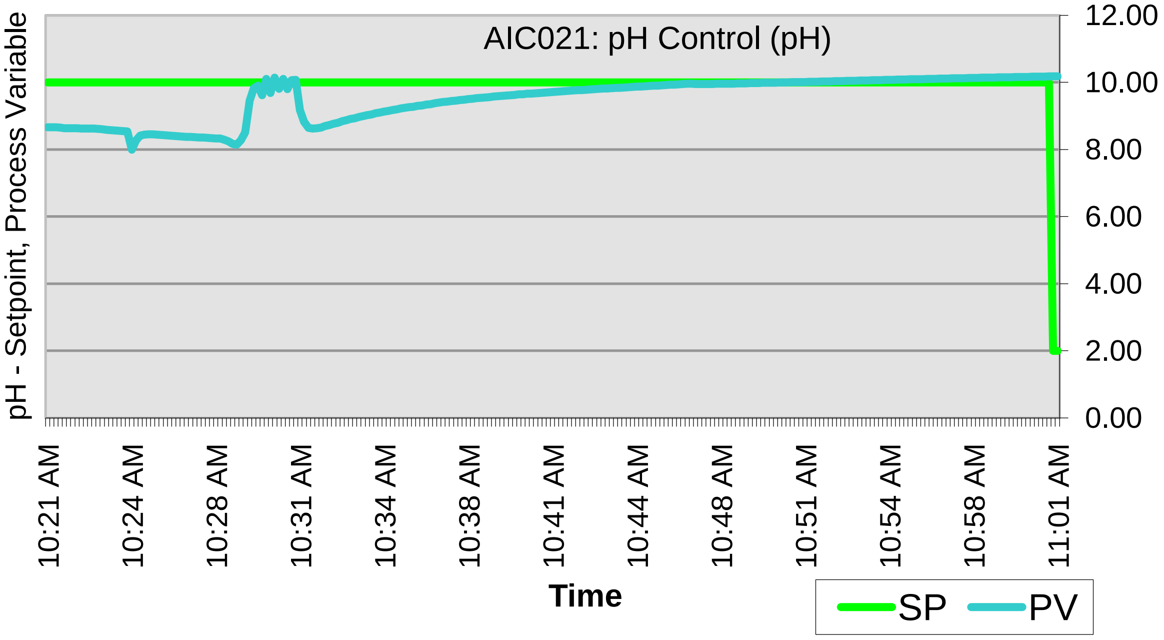


Figure 3.14: Magotteaux Mill, showing the irregularity in pH control due to direct lime addition onto the probe

Another difficulty with the lime dosing line is that it is adding lime into the measuring chamber. As a result, the pH in measuring chamber and grinding chamber may be different initially but, due to continuous recirculation of the slurry it will ultimately turn out to be similar in both chambers. However, if the recirculation line gets chocked in the middle of experimentation, the pH in the measuring chamber remains higher than that in the grinding chamber, and at the end of the experiment the required pH would not have been achieved. Further, if the lime dosing line acquires a position such that, it will start adding lime directly onto the pH probe, the pH jumps immediately to a higher value although the actual set points have not been achieved as shown in Figure 3.14. In order to avoid the aforesaid irregularity in pH control, in this study, lime was added directly to the grinding chamber along with the ore and water as needed at the beginning of the test.

3.5.3.4 DO control during grinding stage.

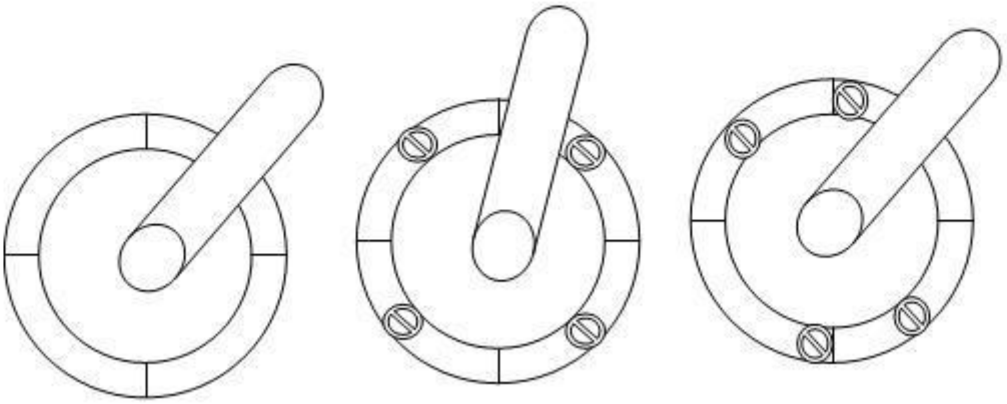
As discussed in section 3.5.1, the flow of the slurry across DO probe is essential for the accurate measurement and control of the DO and ORP. It also shows the significance of recirculation pump into the system. It was observed during the experiments that when the recirculation line gets chocked, the DO value gets stabilize. This may results into different DO values in grinding chamber and measuring chamber. It turns out be a disaster when, the sample is to be taken during grinding for the UV analysis. If, the situation arises before the xanthate injection into the system, operating the pump in opposite direction for 30 sec to 1 min may solve the problem. However, if xanthate is injected into the system, the test had been repeated. So, all the precautionary measure had been taken during this study to avoid the choking of recirculation line, which would have been discussed in the section 3.5.4

3.5.4 Modifications in Magotteaux Mill

As explained in section 3.5, the Magotteaux mill was specifically designed for the comparison of different grinding media and to mimic plant conditions in the laboratory. Extensive research has proven that 21 % Cr grinding media may give optimum plant performance when compared to other grinding media types (forged steel and 15% Cr). The objective set for this study was to use 21 % Cr grinding media and manipulate the grinding environment to improve the flotation performance. In order to make better use of the system some modifications have been made to the piping system as well as in the separating plate which is discussed in this section.

3.5.4.1 Partial blocking of separating plate

The feed size used for this study, as discussed in section 3.2, was 100 % passing 4mm. Further, Nkomati MMZ ore is also one of the hardest ores available in South Africa (Volmarans and Morgan, 2009). Even after grinding it to 80 % passing 75 µm, approximately 7 % of the +1 mm size fraction remained in the grinding product. This may behave as a critical mass during grinding and get transferred to the measuring chamber through the slots at the middle of the separating plate as shown in Figure 3.15 (A). When, it comes in contact with the rubber tube and PELD pipe during recirculation, it might be resulting in the damage of the tube or the blocking of the slurry flow. In order to restrict the coarse particle transfer from the grinding to the measuring chamber, it was initially planned to put sieves in the slots. However, after discussion with the M/s Magotteaux, it was clear that the slots had been left intentionally large to reduce the pressure inside the grinding chamber, while dealing with clay material. M/s Magotteaux had recommended using 100% passing 2mm feed size and assures that it will solve almost 90% operation problem (Greet, 2010). This hypothesis was tested and after the test, it becomes clear that reducing the feed size or slots size would definitely solve the problem.



[A] [B] [C]

Figure 3.15: Magotteaux Mill separating plate, showing the slots around the separating plate

All the possibilities for reducing the slot size were explored first owing to cumbersome sample preparation work that would be required to change the feed size. The slot sizes were reduced from 15 mm to equal 5 mm by placing 5 mm nuts and bolts as shown in Figure 3.15 (B) inside the slots. Although, this reduced the coarse particle transfer to the measuring chamber it also reduced the rate of slurry transfer. As the flow rate of the pump became higher when compared to the rate of transfer from the grinding to the measuring chamber. This resulted in a lower slurry concentration in the measuring chamber and consequently errors in the readings of DO, ORP and Eh values. The alternative positions of the nuts and bolts as shown in the Figure 3.15 (C) were also tested so that sufficient slurry flow could be maintained.

3.5.4.2 Replacement of the separating plate sieve

It was observed during the tests that the 90 FLMV TPS logger was showing some inconsistent readings in the middle of some experiments. The mill was stopped during these experiments and the slurry level was verified in the measuring chamber through the transparent probe plate (Figure 3.13). It was observed that although the alternative positions of the nuts and bolts were able to control the coarse particle transfer it is also restricted the slurry flow. The problem was now to maintain the required slurry level in the measuring chamber. This could be done in two different ways, either by reducing the speed of peristaltic pump or by increasing the flow rate of the slurry from the grinding chamber. However, reducing the pump speed also decreased the pump head thus the second approach was preferred.

Initially 50 % of the 400 µm sieves on the separating plate were replaced with a 900 µm sieve size to increase the slurry flow rate from the grinding chamber. In this test it was found that relative size distribution of +400 µm particles is quite high, which may not be good for the probes. Only 25 % of the 400 µm sieves on the separating plate were replaced with 900 µm sieve size. It was found that the mill started functioning well and the additional advantage of this system was that a relatively coarse feed size can be used effectively.

3.5.4.3 Establishing reagent insertion and sample collection point

This test work was started with the objective of establishing the DO concentration required in the slurry for the complete consumption of the xanthate present into the system. It was hypothesized that the DO control would affect the selectivity of Pn and Po by preferential xanthate adsorption. The test work was commenced by placing the xanthate, ore and water into the mill simultaneously at the beginning of the experiment. The DO concentration was brought down to zero during the conditioning and mixing phases after which it was controlled in the grinding phase to remain at the required set point. But, in these tests, it was possible that some of the xanthate had already been able to react during the conditioning and mixing phases. The precision of the results would be doubtful.

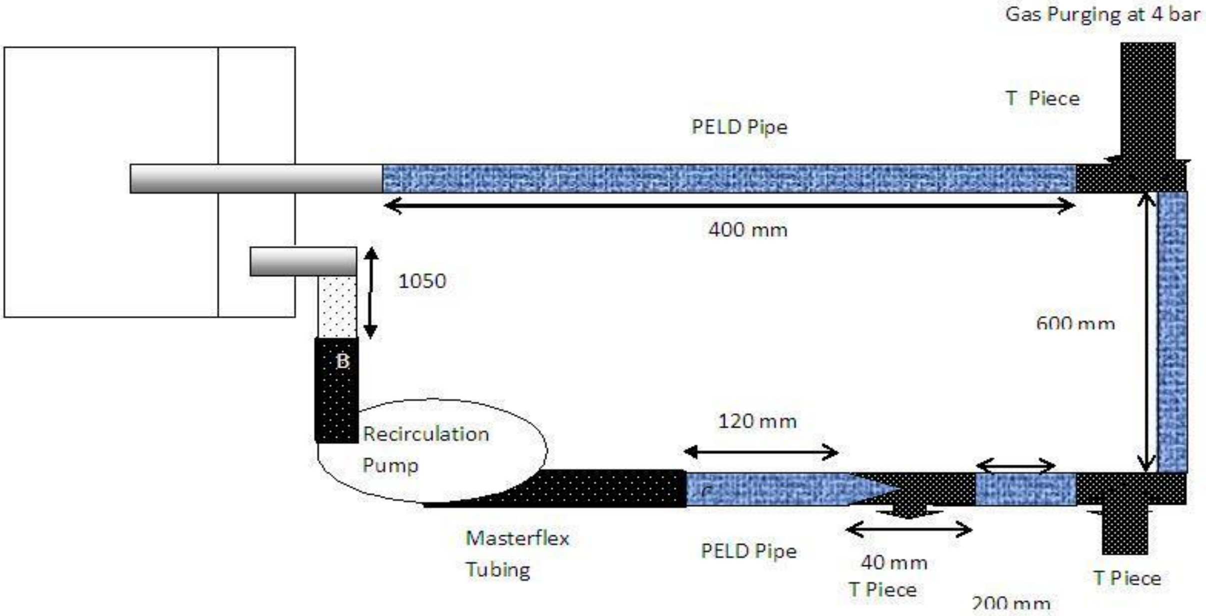


Figure 3.16: Modified Magotteaux mill recirculation line piping

In order to test such a hypothesis, it was necessary to first make the system oxygen free before inserting the xanthate and then controlling the DO concentration afterwards. This was done by placing a T-piece into the PELD pipe line after the Masterflex tubing as shown in Figure 3.16. The third discharge point of the T-piece was blocked with a rubber cap. The rubber cap would allow for reagent insertion via needle throughout the mill operation.

As the amount of xanthate remaining in the solution is an important measurement in determining the xanthate consumption at different time intervals during grinding, it became necessary to locate a sampling point from where sample could be collected for UV analysis of remaining xanthate at different time intervals during grinding,. Initially, the Masterflex tubing and PELD pipe joint was used to collect the sample but this incurred spillage as well as slurry loss. Another T-piece was inserted into the pipe line for sample collection as shown in Figure 3.16. This point was placed behind the xanthate insertion point so that the possibility of xanthate accumulation at the junction would be avoided. However, placing two joints may generate a head loss in the line which in turn may again result into blockage of the recirculation line. So, the Masterflex tubing was replaced with silicon tubing, the flow rate was checked and the pump was calibrated to achieve the same flow rate as with the Masterflex tubing.

3.6 Grinding Curve

A grinding curve was established for 21 % Cr grinding media. This was achieved by milling the ore at a fixed time for varying speeds and comparing the particle size distribution (PSD) obtained. The target size of the grinding was 80 % passing 75 µm. The procedure was as follows:

- The mill was charged with 20 kg of grinding media, 2 kg sample of Nkomati ore and 1.5 L of water
- The mill was closed and moved to the horizontal position for grinding
- The grind was completed at 3 different time interval while keeping the speed fixed, with fresh ore samples. Three mins of mixing time at 10 rpm precedes the main grind in order to mimic later experimental procedure. The grinding times and speeds tested are shown in Table 3.6.
- After grinding, the mill pulp was filtered and dried in the oven overnight before being split in a rotary splitter.
- A split sample of between 150 and 250 g of ore was then wet screened. The screen sizes used in wet screening were: 53, 38 and 25 µm. The screened samples were dried overnight and weighed to obtain the size classes -25, +25, +38 and +53 µm.
- The +53 µm size class was then dry screened to obtain a full PSD. The dry screens used were: 1000, 850, 600, 425, 212, 150, 106, 75, 53, 38 and 25 µm.
- Once the grinding time was established for the fixed speed (60 rpm), grinding size distribution was obtained up to (-) 10 µm in a separate grinding test.

Table 3.6: Grinding curve test

Media	Mill speeds tested (rpm)	Grind time (mins)		
21% Chrome	60	25	35	45

3.7 Batch flotation

The Nkomati MMZ ore was first time used for study at UCT and as discussed earlier the numbers of variables were reduced and validated techniques were developed. The standard batch flotation techniques of UCT were combined along with the reagent suites as described in the section 3.5.4.2 and this procedure is followed throughout the study unless and otherwise specified.

The procedure used for all feed samples was the same in all details. Sodium isobutyl xanthate, used as a collector was received from Senmin Ltd. Dow froth 200 (from Dow Chemical) was used as frother. Both reagents were technical grade and were used in their 'as received' form, which, in each case, was adjusted to a dilute solution of 0.1 wt-percent. After grinding the slurry to 80% passing 75 µm, the sample was transferred into a 5 L Magotteaux flotation cell. The impeller speed was kept at 1200 rpm. For all the tests, collector and frother dosages were the same at 20 g/t respectively. The choice of these conditions is based on the M/s Senmin report. Flotation was continued for 20 min. A total of four concentrates were collected for a detailed definition of separation curves.

3.7.1 Magotteaux Float cell

The milled slurry was floated in a 5 L Magotteaux Float cell as shown in Figure 3.17. It has a bottom driven stainless steel impeller which allow the entire surface of the froth to be scraped with a paddle/scrapper at a constant depth and a constant time interval. The impeller is fitted with a variable speed drive mechanism and its speed can be controlled between the ranges of 0 to 2100 rpm. The impeller speed was kept constant at 1200 rpm for all tests. An additional advantage of the bottom driven cell was observed while performing the N_2/air sparging tests. In these tests, it facilitated the complete coverage of the top of the cell with a Polytetrafluoroethylene (PTFE) plastic plate minimizing air intrusion from the atmosphere to the pulp. The sides of the flotation cell are perspex which facilitated pulp level control. The air supply to the flotation cell can be regulated to a required set point between 0 and 20 L/min. Magotteaux recommended maintaining an air flow rate of 10 L/min. The float cell incorporates the use of DO, Eh, pH and temperature measurement during flotation via ports at the rear of the cell in which probes can be fitted. The data can be directly logged into the PC from the associated TPS logger with the help of Win-TPS software package as discussed in section 3.5.1.

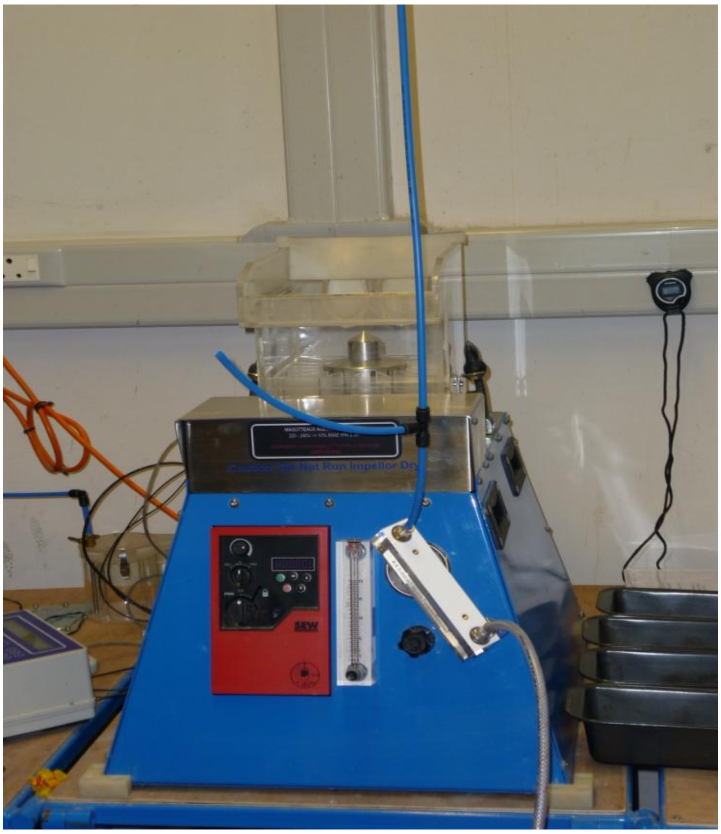


Figure 3.17: The Magotteaux bottom driven 5 L flotation cell.

3.7.2 Standard Batch flotation procedure

The mill and probes were cleaned after grinding with pressurized water (synthetic plant water) to control the wash water. The slurry was transferred into a bucket which was placed below as shown in Figure 3.13. The bucket was marked at 4.5 L water capacity so that the quantity of wash water can be controlled. In order to get reproducibility in the results, the time of slurry transfer after grinding were also kept constant for 30 min so that in the entire test work slurry would come in contact with the atmosphere for fixed time. The slurry was decanted and water was collected in a beaker. The decanted slurry was screened on top of the Magotteaux float cell with 1 mm screen so as to protect impeller from damage. The decanted water was used to wash the bucket, screen and pulp level control.

The required amount of frother was added and this was conditioned for 1 min. At this stage the air was turned on and the froth was allowed to develop. The froth height was kept constant at 2 cm throughout the flotation test. Four concentrates were collected at 2, 6, 12 and 20 min of flotation time by scraping the froth into a collecting pan every 15 seconds. A feed sample was taken before and two tailings samples after each test. Water recoveries were measured for each test. Feeds, concentrates and tails were filtered, dried and weighed before analysis. All tests were conducted in duplicate. Table 3.7 shows a summary of the flotation procedure used in this study.

Table 3.7: Summary of the batch flotation procedure used in this study

Action	Time (mins)
Milling	As determined by milling curve
Collector	Added to mill once required DO concentration achieved
Frother	0
Air turned on and froth allowed to develop	1
C1	3
C2	7
C3	13
C4	21

3.8 Electrochemical Controlled Grinding and Flotation

All experiments were carried out in duplicate. Synthetic plant water was used during both the grinding and flotation tests. Pulp chemistry was controlled by the Magotteaux Mill. Each grind consisted of three stages (conditioning: 10 min; mixing: 3 min; and grinding: 30 min) as described in the control philosophy of the mill. The baseline (No gas control or DO-5.5) grind gave our first flotation comparison point. No pulp parameters were controlled in this case and natural conditions of the pulp were monitored.

The experimental details have been categorized into four sections. Experimental conditions are summarized at the beginning of each section and the detailed procedure is explained afterwards. The results generated from the first section enabled the questions for the following sections and in this way the various sections were developed. In section 3.8.1, only grinding conditions were controlled and the flotation was performed according to the standard batch flotation procedure. In section 0, the extreme conditions of Pn recovery were chosen and tests were performed with varying flotation gases and condition times. In section 0, tests were performed in order to differentiate whether the difference in the grade and recovery of the Pn is due to oxygen control or due to xanthate addition into the mill. Finally, in section 3.8.4, the tests were done so as to prove the hypothesis that Eh management through DO control is the main factor influencing the Pn recovery and whether the Eh can be controlled through pH control would the recovery for both Pn as well as Po drop.

3.8.1 Dissolved oxygen controlled Grinding

The objective of these tests was to establish the amount of oxygen (DO concentration) required for complete consumption of the xanthate into the mill, so that no xanthate would remain available to react during and after slurry transfer. Grinding was performed at different concentration of oxygen control as shown in Table 3.8. The Eh and pH during grinding was monitored and the Eh-pH and DO concentration were monitored and controlled in these tests. These experiments were performed with the 21% Cr media.

Table 3.8: Summary of the batch flotation tests performed in section 3.8.1

Test. No.	Test Condition/ Name
1.	DO-0 (Full time N_2 Purging)
2.	DO-1 (1 ppm Dissolved oxygen control)
3.	DO-6.5 (Full time air purging)
4.	DO-3 (3 ppm Dissolved oxygen control)

Once the required DO set point of dissolved oxygen was achieved and the mill enters into the mixing phase, xanthate was inserted into the system through the xanthate insertion point as described in section 3.5.4.3. After the mixing phase was complete and the system entered the grinding phase, fresh surfaces start being generated and xanthate was expected to be consumed. As soon as the system enters the grinding phase a sample was collected to establish the rate of xanthate consumption. The maximum number of samples taken should be kept to less than four so that any inconsistencies in the flotation data due to the loss of slurry sample were avoided. The samples were kept in air-tight containers to avoid any air contact and were analyzed within four hours for the measurement of remaining xanthate during grinding.

3.8.2 Varying flotation conditions at DO concentration of 0 and 6.5 ppm

In the previous section, air was used as the flotation gas and no gas conditioning was incorporated. In this section tests were performed by varying the grinding conditions at the two extremes i.e. air sparging (DO-6.5) throughout the entire grinding process and nitrogen purging (DO-0) throughout the entire grinding process. Xanthate was inserted after the completion of the grinding conditioning phase. These conditions were selected because Pn recovery was maximum in one case (DO-0) and minimum in another (DO-6.5) as established in section 3.8.1. Samples were collected for the analysis of remaining xanthate at five points throughout the test; (1) during grinding, (2) after grinding, (3) after slurry transfer, (4) after Nitrogen sparging and (5) after flotation when the grinding is performed at DO-0. Analysis of residual xanthate was not conducted on the tests under full time air purging as it has previously been established that xanthate is consumed in less than 5 mins after grinding begins.

Table 3.9: Summary of the batch flotation tests performed in section 3.8.2

Test No.	Test Conditions/ Name		
	Grinding Conditions	Flotation Condition	
		Gas Sparging	Time of Sparging
5.	DO-0 (Full time N_2 Purging)	Air	30 min
6.	DO-0 (Full time N_2 Purging)	N_2	30 min
7.	DO-6.5 (Full time air purging)	N_2	30 min
8.	DO-0 (Full time N_2 Purging)	N_2	60 min

In order that the effect of oxygen is minimised during flotation for the tests conducted in the nitrogen sparging tests, the flotation cell top as well as lip were covered with a PTFE plate, to minimize atmospheric air contact with the slurry. The electrochemical parameters after nitrogen or air sparging were monitored, using a VSI multi probe. The data stored in the Multi-probe was transferred to a PC through the Eco-watch software system. The slurry obtained from the 60 min N_2 sparging test was not floated but samples were collected after 30 min and 60 min for residual xanthate measurement. The residual xanthate data shows no difference in the xanthate concentration after 30 min and 60 min measurement hence was assumed that it would not make any further difference on the floatability of the minerals.

3.8.3 Varying xanthate addition points at DO concentration of 0 and 6.5 ppm

The objective of these tests was to identify the effect of xanthate over oxygen on floatability of Pn and Po. Whenever xanthate is added to the mill the same procedure as mentioned in Section 3.8.1 was followed. However, in the cases when xanthate addition was added to the flotation cell, two minutes conditioning time was given for xanthate adsorption in the cell. Frother was added after xanthate conditioning and 1 min conditioning time was allowed. The standard UCT batch flotation procedure was followed. The summary of these tests is given in Table 3.10.

Table 3.10: Summary of the batch flotation tests performed in section 3.8.3

Test. No.	Test Condition/ Name		
	Grinding Conditions	Xanthate addition point	Conditioning time
1.	DO-0 (Full time N_2 Purging)	Mill	-
3.	DO-6.5 (Full time air purging)	Mill	-
9.	DO-0 (Full time N_2 Purging)	Cell	2 Mins
10.	DO-6.5 (Full time air purging)	Cell	2 Mins

3.8.4 Varying Eh through pH control

The objective of this section was to monitor the Eh by varying pH and observe the net effect on the grade and recovery of the sulfide minerals. The pH of the pulp was varied only from pH 9 to 11 by using lime in the milling stage. This pH range was chosen because generally sulfide flotation operates in plants in alkaline pH rather than acidic. The summary of these tests is given in Table 3.11. Due to irregularity of the pH control through the lime dosing pump as previously explained in section 3.5.3.3, the quantity of lime required was determined by performing dummy tests using the lime dosing pump. The determined amount of lime was then added to the grinding chamber at the beginning of each test. In order to determine the quantity of the lime addition following procedures were followed.

The weight of the empty lime dosing pot along with the magnetic stirrer was noted.

The balance was reset to zero and 20 g lime was added along with synthetic plant water to make up 1000 g, giving a 2 % lime solution

On completion of the test the lime pot was weighed along with the stirrer and the remaining 2 % lime solution.

The final weight was subtracted from the initial weight to find out the weight of the 2 % lime solution required to raise the pH to the chosen level.

The weight of lime required to raise the pH was calculated and thereafter added directly to the grinding chamber at the beginning of further experiments.

It was found that to raise the pH from 9 to 10 the amount of lime added should be 16 g and from 9 to 11 it should be 32 g (see appendix).

Table 3.11: Summary of the batch flotation tests performed in section 3.8.4

Test No.	Test Condition/ Name
1.	pH-9.2 and DO-0 (Full time N2 Purging)
11.	pH-10 and DO-0 (Full time N2 Purging)
12.	pH-11 and DO-0 (Full time N2 Purging)
13.	pH-9.2 (Baseline/No gas Control)
14	pH-10 (No gas Control)
15.	pH-11 (No gas Control)

Xanthate was added to the mill on completion of the mixing phase. In all cases xanthate was added to the mill once the required DO concentration had been achieved. Xanthate concentrations were checked after grinding and flotation.

3.8.5 Confirmatory tests:

Certain confirmatory tests were performed in order to validate unexpected results. The summary of the tests work performed in this category is shown in the Table 3.12.

Table 3.12: Summary of the diagnostic tests performed in the study

Sl. No.	Test Condition/ Name	DO	pH
1.	Water test-1	1	9.0-9.5
2.	Water test-2	0	9.0- 9.2
3.	Lime test (32 gm lime)	0	9.2 and 11
4.	Acid Wash test	6.5	9.0- 9.2
5.	Depressant test	6.5	9.0- 9.2

3.8.5.1 Water tests

The objective of performing these tests was to validate the significance of the sulfide ore in the xanthate adsorption reaction. It is well established in the literature that the floatability of Pn, Po and Cp is due to anodic oxidation of xanthate into dixanthogen. Oxygen drives this reaction. It initially seems that this is a two phase reaction but in actuality it is a three phase reaction with sulfide minerals acting as catalysts for the reaction. In order to confirm this hypothesis, tests were conducted using water, xanthate and grinding media, i.e. ore-less tests. oxygen was controlled at 1 ppm DO and the mill was operated at 10 rpm for 30 min. Samples were taken during the milling for analysis of remaining xanthate in the solution at different grinding intervals. Similar tests were performed at 0 ppm DO to determine whether there was any difference in the remaining xanthate under the different conditions.

3.8.5.2 Lime Test

It was observed during the pH control test that the remaining xanthate in solution increases at pH 11 as compared to the DO-0 test at pH 9 as noted in section 3.8.4. It was hypothesized that some species present in the ore reacts at the lower pH and requires no oxygen. However, at a higher pH these species are not available to react and as a result the remaining xanthate at the end of the test had increased. In order to test the hypothesis, grinding was performed at a DO of 0 ppm in the presence of ore and a sample was taken at the end of grinding for the analysis of remaining xanthate. At the end of grind, 32 g of lime was added through the recirculation pump into the grinding chamber so that pH increased to 11. The mill was again allowed to rotate at a speed of 10 rpm in order to mix the lime. The DO concentration was further brought down to zero by Nitrogen purging and samples were taken after 5 min and analyzed for the remaining xanthate.

3.8.5.3 Acid Wash test

It was observed from section 0 that the oxidation control of the ore resulted in an improved recovery of Pn and Po which may be due to the prevention of FeOOH layer formation on the mineral surfaces (Legrand et al, 2005a). It was hypothesized that, if the FeOOH layer can be removed from these mineral surfaces, they would perform in the same way as the ore ground at a DO of 0 ppm. In order to test this hypothesis, an experiment was conducted with the ore ground at a DO concentration of 6.5 ppm. The slurry was transferred to the float cell and the impeller was started. The pH of the slurry was dropped to between 2 and 3 by continuous addition of 32 % pure HCl. This was maintained for 30 min and it was assumed that after 30 min the surface of the minerals would be cleaned of the FeOOH layer created from the milling. The acid consumed in maintaining the pH between 2 and 3 for 30 min was approximately 100 ml. After 30 min 5 M NaOH solutions was added to return the pH to 9.2. The NaOH consumed was approximately 80 ml. Once the pH stabilized at 9.2, xanthate was added and allowed to condition for 2 min. Frother was then added allowed to condition for 1 min. The standard UCT batch flotation procedure was followed. Concentrate sample were filtered, dried, weighed and sent for assay analysis.

3.8.5.4 Depressant test

Another confirmatory test was performed in order to test the hypothesis that oxidation control of the ore results in an improved recovery of Pn and Po owing to the prevention of FeOOH layer formation on the mineral surfaces. In this test depressant, in the form of modified guar gum (KU-49), was added to the float cell after grinding under full time air purging (DO-6.5). It was hypothesized that since guar has free hydrogen ions addition of this depressant may remove the oxide or hydroxide species from the surface of the minerals, thereby cleaning the surface and enhancing the floatability.

3.9 Determination of xanthate in solution

In order to determine xanthate in solution, a small amount of pulp was drawn during the grinding as well as batch flotation tests as specified previously. The pulp was centrifuged at 50 rpm for 5 min to remove the solid material using a Hettich EBA 20 centrifuge. The solutions were further filtered using KC-745 filter paper in order to avoid any solid particle interference with the light path of the Ultra-Violet spectrophotometer.

The clear solutions were dispensed into precision quartz cuvettes with a 3.5 ml capacity and a light path of 10 mm. The solutions were read using an Ultrospec Ultra Violet spectrophotometer with respect to synthetic plant water at 270, 300 and 330 nm.

The UV region of electromagnetic spectrum is considered to be in the region of 200 to 400 nm and their corresponding energies in the region of 36 to 17 KJ/ mol. UV absorbance measurement is based on the measurement of the absorbance of radiation in the solution. Absorbance $A = \log P_0/P = abc$, where P_0 is the radiant power of the transmitted light, P radiant power of the transmitted radiation after the light has passed through the absorbing solution. c is the concentration of the absorbing molecules, b distance traversed (thickness of the optical cell containing the solution) and ‘a’ is a constant called absorptivity or extinction coefficient. If ‘c’ is in g/L and ‘b’ in cm, ‘a’ has the unit liter/g.cm. This relationship is called Beer-Lambert law.

3.10 Analysis of flotation performance

All feeds, concentrates and tailings samples were analyzed in dry powder form. The samples were split into 15 to 20 gm., in order to get the representative sample for the concentrate. Copper and total nickel analysis of all samples was done using a Bruker S4 Explorer XRF Spectrophotometer. Sulphur analysis was carried out using a LECO DR 423 sulphur analyzer.

The results obtained for chemical assays are used to calculate grade and recovery in order to show the percentage of available mineral recovered as well as purity. A kinetic analysis of the various flotation tests of nickel–copper sulfide samples was presented. Different kinetic models available in the literature such as Klimpell, Agar, and Kelsall have been used to analyze the data. However it has been found that the analysis of Kelsall Model is more informative for this type of system. It is not only giving the information about the slow and fast floating component of the valuable minerals but also it give the information about the affinity of different minerals towards the oxidation. In order to avoid the confusion only the analysis of Kelsall kinetic model has been shown I the thesis. The same model has been used to estimate the flotation rate constant and slow floating fraction of Cp, Pn and Po at various tests conditions. Kelsall unmodified two-component equation (Kelsall, 1961) used in the analysis of the data is as follows:

$$R = [(1-Ø)(1-e(-k_f t)] + Ø[1-e(-k_s t)]$$

where Ø is the slow floating fraction, R is the per cent recovery at time t, k_f is the fast floating rate constant (min^{-1}), k_s is the slow floating rate constant (min^{-1}) and t is the time (min).

Po vs. Pn recovery curves were also plotted at various tests conditions to define the selectivity of the Pn over Po. The variation of Eh with respect to pulp DO concentration and mineral recovery were also drawn in order to compare the combined impact of the tests conditions on mineral recoveries. Mineral assays are reported as copper and nickel and not as Cp and Pn. However, sulphur data were used to calculate the amount of unaccounted sulphur and reported as Po. Copper recoveries in this work are equivalent to Cp recoveries. Nickel recoveries are equivalent to Pn recoveries with assumption that total nickel is associated Pn and not with the gangue present in these ores which is also confirmed by the QEMSCAN and XRD analysis of feed data. The Po recovery is reported as unaccounted sulphur recovery based on the assumption that pyrite is in negligible amount compared to Po in the ore. This assumption is validated by the XRD as well as QEMSCAN analysis of the feed sample. Detail calculation of Po is attached in Appendix-1.

4 RESULTS

4.1 Introduction

The aim of this work was to evaluate the effect of pulp DO concentration on xanthate adsorption and oxidation of a complex Cu-Ni sulfide ore and consequently its effect on the mineral floatability. The detailed procedure for batch flotation tests and the reagent suite used are described in Chapter-3.

This chapter is divided into seven sections. Section 4.2 describes the results obtained in generating the milling curve. Section 4.3 shows the reproducibility of the flotation tests conducted.

The following sections show the results of the tests carried out in this study. Section 4.4 compares the flotation performance of Nkomati ore at different concentrations of DO in the grinding stage. The results from Section 4.4 lay the foundation for the sections that follow. The conditions chosen for Section **Error! Reference source not found.** were those which gave the maximum and minimum Pn recoveries as found in Section 4.4. This section explores the effect of using different sparging gases prior to flotation. In section 4.6 the xanthate addition points were varied at the conditions of maximum and minimum Pn recoveries in order to compare the effect of oxidation on xanthate adsorption. Section 4.7 describes the effect of Eh variation, achieved by varying pH, on the grades and recoveries of the valuable minerals. Each section starts by showing the grinding and flotation conditions and later the mass and water recovery, grade and recovery of Cp, Pn and Po, xanthate adsorption data and finally the kinetics of the flotation were analyzed using the Kelsall model. Some confirmatory test work was also done in order to verify some of the ambiguous results from the main test work. These results are included in Appendix-1. The confirmatory tests were not performed in duplicate except for the depressant tests.

It is to be noted here that the scales chosen for the figures was kept consistent throughout the chapter. The scale was chosen such that the maximum and minimum recovery of the Cu, Ni and Po can be represented with consistency.

4.2 Milling Curve

In order to get a uniform PSD for all grinds, a grinding curve was determined for the ore being investigated. Figure 4.1 shows the cumulative weight percentage passing 75 µm of the ground product obtained at different grinding times. This grinding curve as shown in Figure 4.1 was developed in order to obtain the grinding time needed to obtain a PSD of 80 % passing 75 µm. The time to obtain this specific grind size was 30 min.

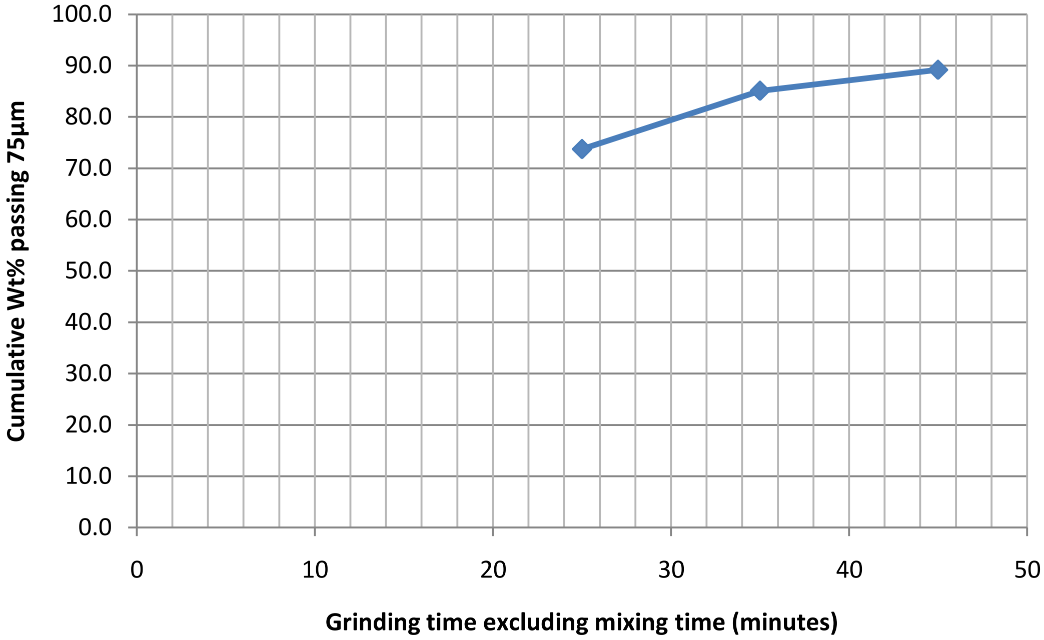


Figure 4.1: Grinding curve obtained at 60 rpm for different grinding times

Figure 4.2 shows the cumulative weight % passing different particle sizes of the ore ground at 60 rpm mill speed and for 30 min grinding time. This graph shows that after grinding the ore under these conditions, the product had a d_{80} of 75 µm. However, it also contains approximately 7 % of the +1 mm size fraction. The +1 mm fraction was screened out before the start of each test in order to avoid impeller damage.

Table 4.1 shows the size by size analysis of the feed sample obtained from the ICP-OES analysis performed at Mintek. It can be seen from the table that the Cu, Ni and Fe values were much higher in the lower size range.

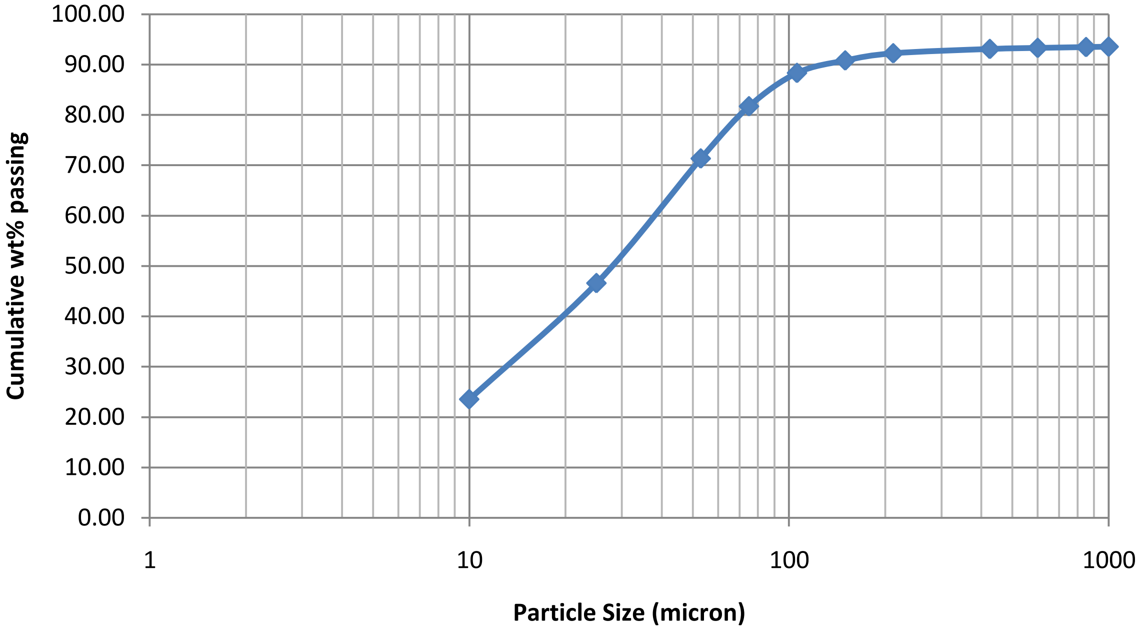


Figure 4.2: Particle size distribution of the ore ground with 21% chrome grinding media

Table 4.1: Size by size ICP-OES analysis of the feed sample

Size	Fe %	Ni %	Cu %
-150+106	9.39	0.19	0.11
-106+75	10.4	0.25	0.13
-75+53	12.5	0.39	0.16
-53+25	15.9	0.72	0.22
-25+10	17.1	1.01	0.31
-10	14.0	0.89	0.30
Total	14.75	0.75	0.25

4.3 Reproducibility

Reproducibility is the closeness of agreement between two independent results obtained with the same method on identical test materials but at a different time. Reproducibility of a flotation test depends on several factors but one of the most important is the froth stability. In each of the test conditions all precautionary measures were taken to generate reproducible data. Figure 4.3 to Figure 4.7 show recovery time plots for different parameters (mass, water recovery and Cu, Ni and Po recovery) evaluated in this study.

As per the UCT standard batch flotation procedure used in this study the standard error in water recovery should not exceed 10 to 12.5% of the total water recovered. However, for the mass, the standard error should not exceed 5% of the total mass recovered. In all of the tests conducted in this study, the absolute differences between two single test results on identical material obtained under the specified conditions lie within the 5 % limit.

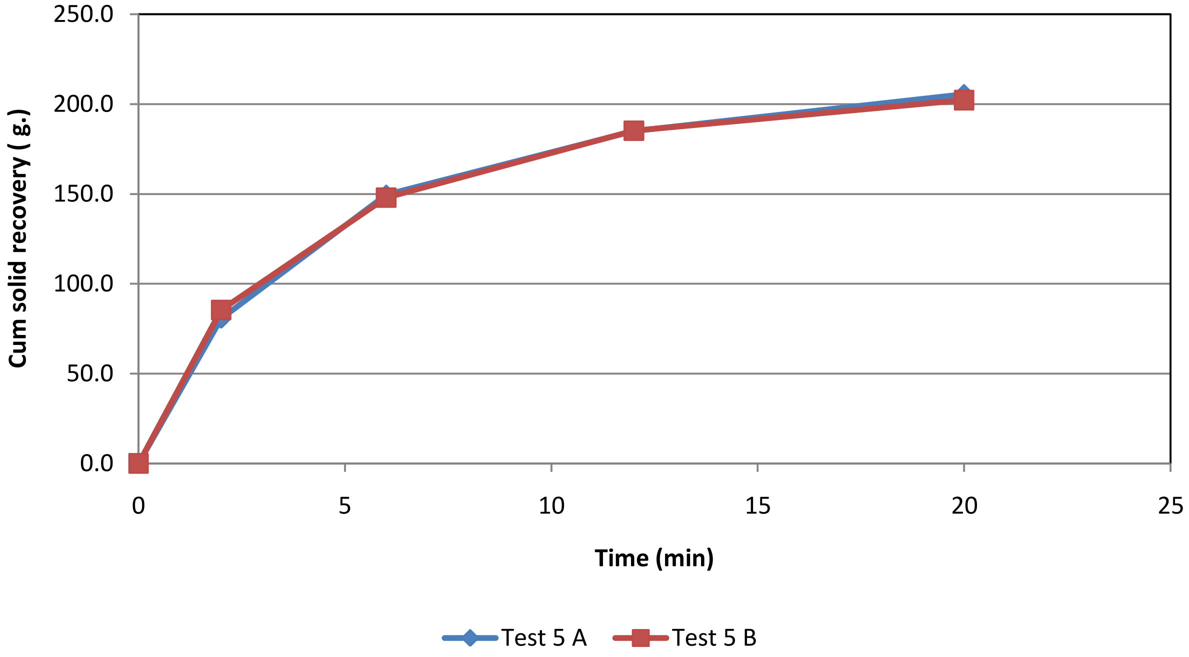


Figure 4.3: Average cumulative mass recovery vs. time at DO-0 after 30 min of air sparging and flotation with air

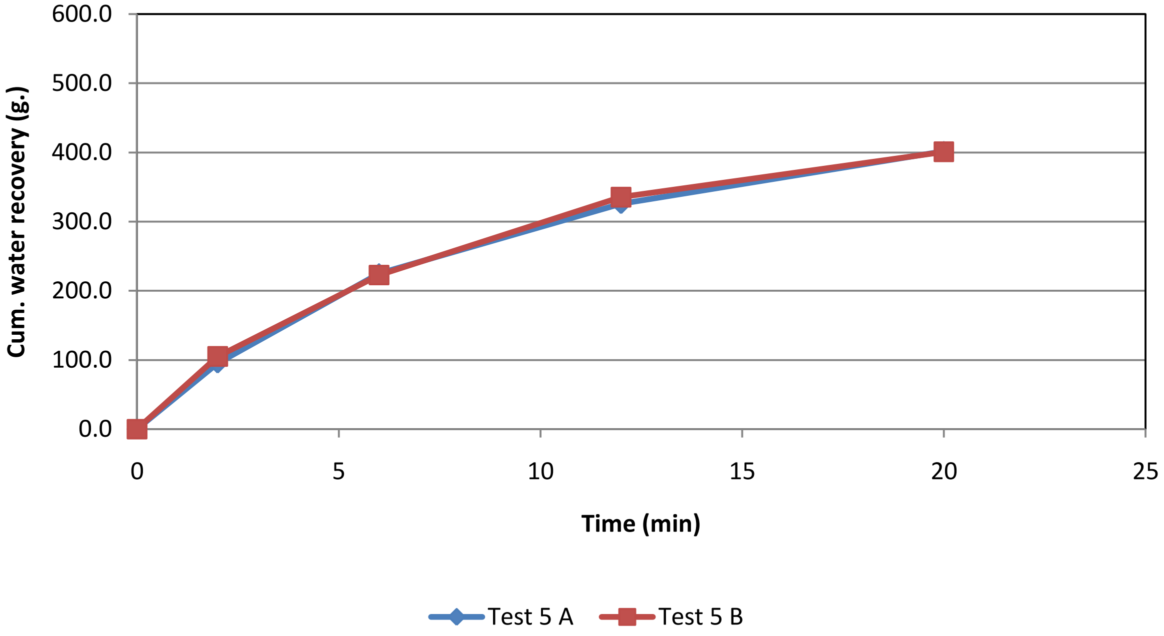


Figure 4.4: Average cumulative water recovery vs. time at DO-0 after 30 min of air sparging and floating with air

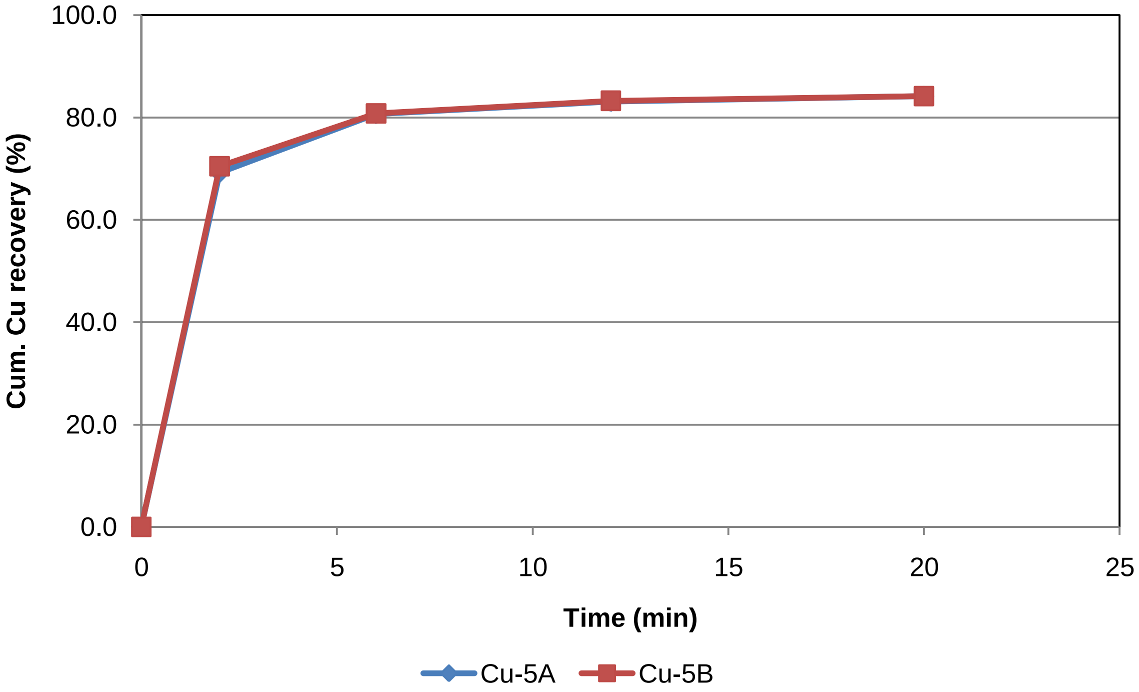


Figure 4.5: Average cumulative Cu recovery vs. time at DO-0 after 30 min of air sparging and floating with air

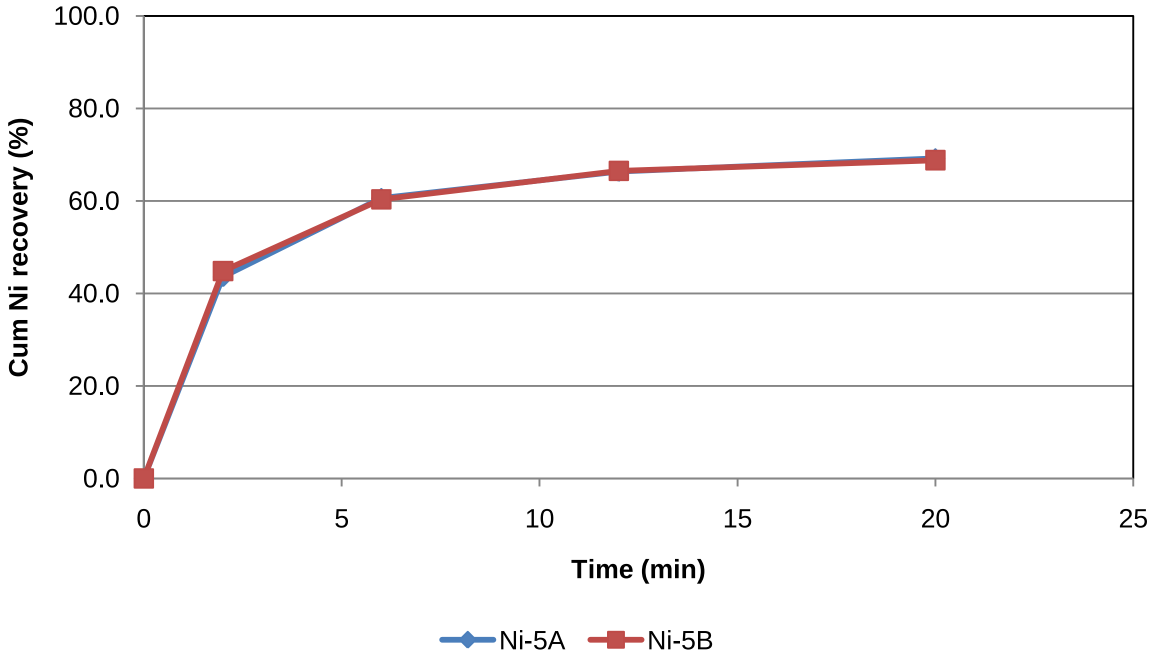


Figure 4.6: Average cumulative Ni recovery vs. time at DO-0 after 30 min of air sparging and flotation with air

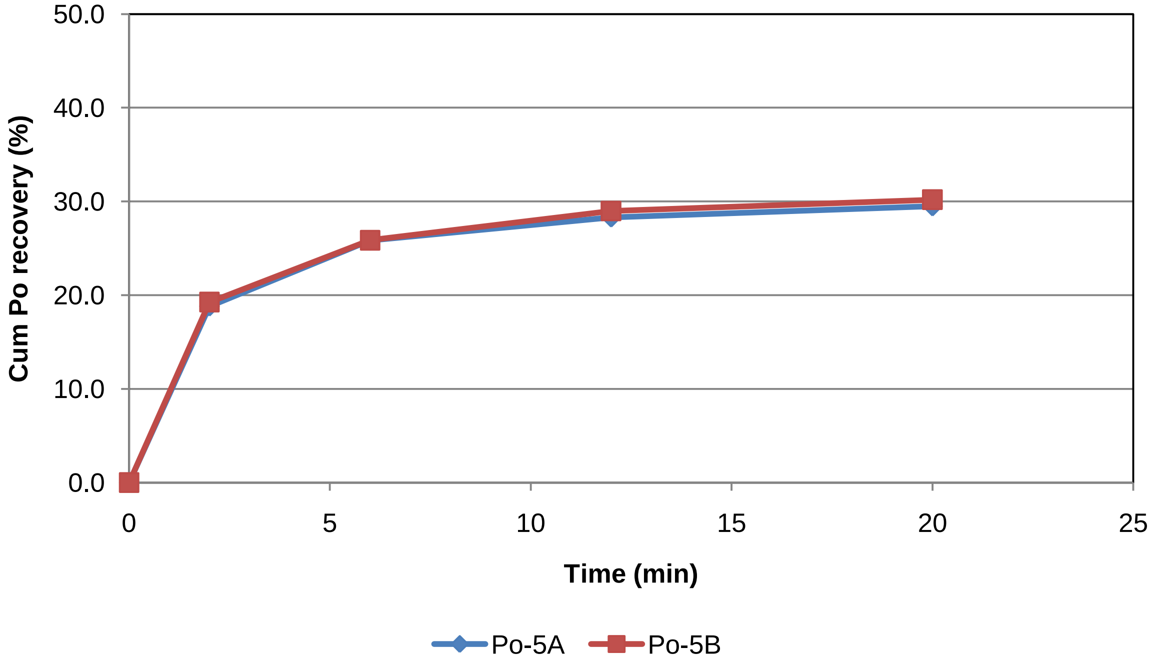


Figure 4.7: Average cumulative Po recovery vs. time at DO-0 after 30 min of air sparging and flotation with air

4.4 Effect of Dissolved oxygen on flotation

The pulp chemical readings recorded from the Magotteaux Mill® discharge for the test conditions in this section are shown in Table 2.1. As described in Chapter 3, a platinum electrode was used for pulp potential measurements in the Magotteaux mill. A Ag/AgCl electrode was used as a reference electrode for the pulp potential measurements. This data indicated that changing the DO concentration from a reducing environment in which oxygen was totally excluded (Test-1) to an oxidizing environment (Test-4) produced an increase in the Eh value from -180 mV to 240 mV (SHE). The change in grinding environment from a DO concentration of 0 ppm (Test-1) to a DO concentration of 1 ppm (Test-2) resulted in an increase in the Eh value to about 320 mV. After Test-2 the increases were much smaller as the DO concentration increased from 1 to values up to 6.5. The pulp potential specified in Table 2.1 has been reported with respect to SHE (by adding 220 mV as discussed in Section 2.6.2). It is to be noted here that the test name represents the set points given for the DO control and DO concentration represents the variation of the DO concentration found during grinding. The Eh, pH and DO profiles recorded during grinding are attached in Appendix-1. There were only marginal differences in pH recorded with the change in DO values. However, in the case of a DO concentration of 0 ppm, a slightly higher pH value (±0.15) was recorded. Although test work was conducted at DO-3, it was found that all the xanthate was consumed within the first five minutes, which was similar to the DO-1 Test-2, flotation was conducted at this DO-1 and therefore flotation was not carried out for the DO-3 Test-4.

Table 4.2: Pulp chemistry details for Test-1, -2, -3, and -4

Test. No.	Test Name	Test Conditions	DO conc.	Eh mV (SHE)	pH
1.	DO-0	Full time N_2 Purging	0	-160 to -180 mV	9.2-9.3
2.	DO-1	1 ppm oxygen concentration	0.5 to 1.5	170 to 145 mV	9.0-9.2
3.	DO-6.5	Full time air purging	6.0 to 6.5	230 to 245 mV	9.0-9.2
4.	DO-3	3 ppm oxygen concentration	2.5 to 3.5	210 to 220 mV	9.0-9.2

4.4.1 Recovery-time data

Figure 4.8 shows the results obtained for the mass recovered during the tests conducted at different DO concentrations in the mill. It can be seen that, the amount of mass recovered after 2 min of flotation for all test conditions were similar. However, at the end of 20 min of flotation there was a substantial difference in the overall mass recovery between the test at DO concentration of 0 ppm (Test-1) and the other test conditions.

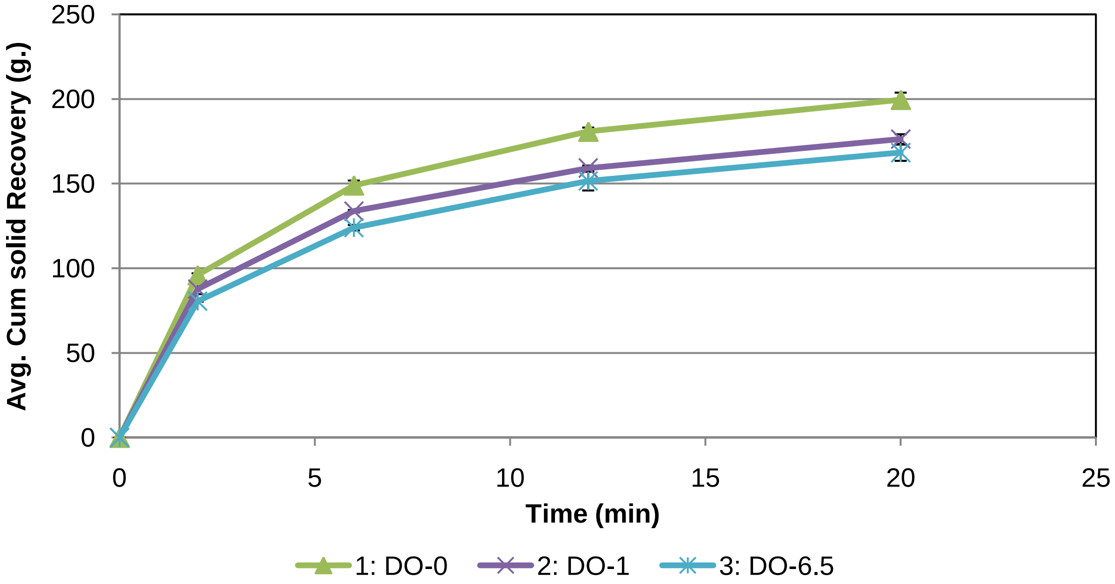


Figure 4.8: Average cumulative mass recovery vs. time plot at different DO concentrations

**** Test number 1 was conducted at DO concentration of 0 ppm and is given by 1: DO-0, similarly rest of the notations.**

Figure 4.9 shows the results obtained for the water recovered during the tests conducted at different DO concentrations. It can be seen that, on changing the grinding DO concentration, no significant difference in the overall water recovery was found.

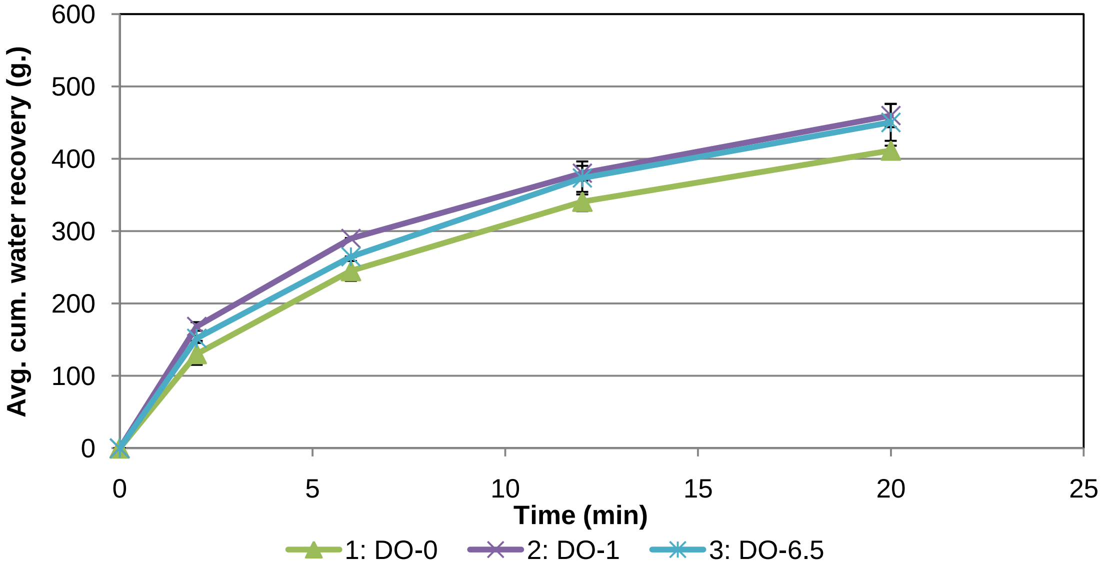


Figure 4.9: Average cumulative water recovery vs. time plot at different DO concentrations

Figure 4.10 shows the cumulative Cu recovery–time performance of the ore ground at different DO concentrations. It can be seen that there were virtually no differences in the floatability of Cu. All test conditions produced slightly higher Cu recoveries than the inert environment grinding (DO-0) test. The cumulative recoveries at the end of 20 min of flotation for all test conditions fell into similar ranges. It can also be seen that the initial recovery of the Cu in the DO-0 test was slightly lower compared to the other test conditions. However, there were only marginal differences in the overall recoveries for all tests.

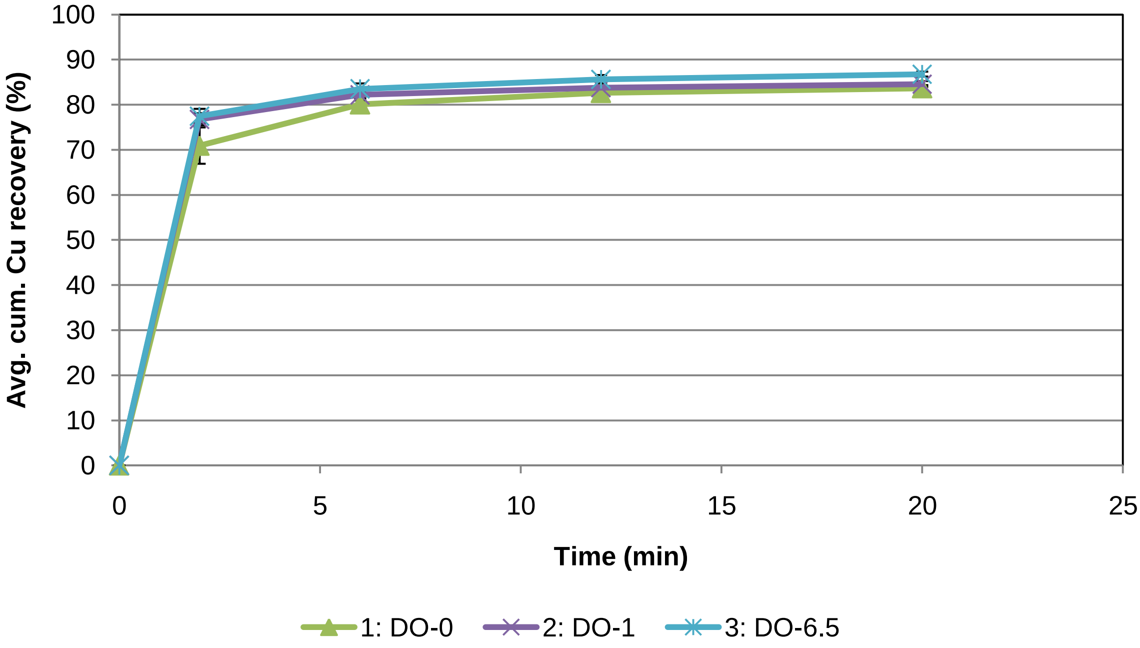


Figure 4.10: Average cumulative Cu recovery vs. time plot at different DO concentrations

Figure 4.11 shows the cumulative Ni recovery as a function of time for the ore ground at different DO concentrations. It can be seen that there was significant variation in the Ni recovery of the samples, Ni recovery increased as DO decreased. The Ni recovery from the inert grinding (DO-0) test was higher than the Ni recovery for the oxidizing test conditions. The cumulative Ni recovery after 2 min of flotation time for DO-0 (Test-1) was 50.9 % and the recoveries for DO control Test-2 and -3 were 42.4 % and 31.0 % respectively. These differences were sustained until the end of the flotation test. There is also an approximate correlation between DO concentration during the grinding and the rate of flotation as observed in Ni flotation.

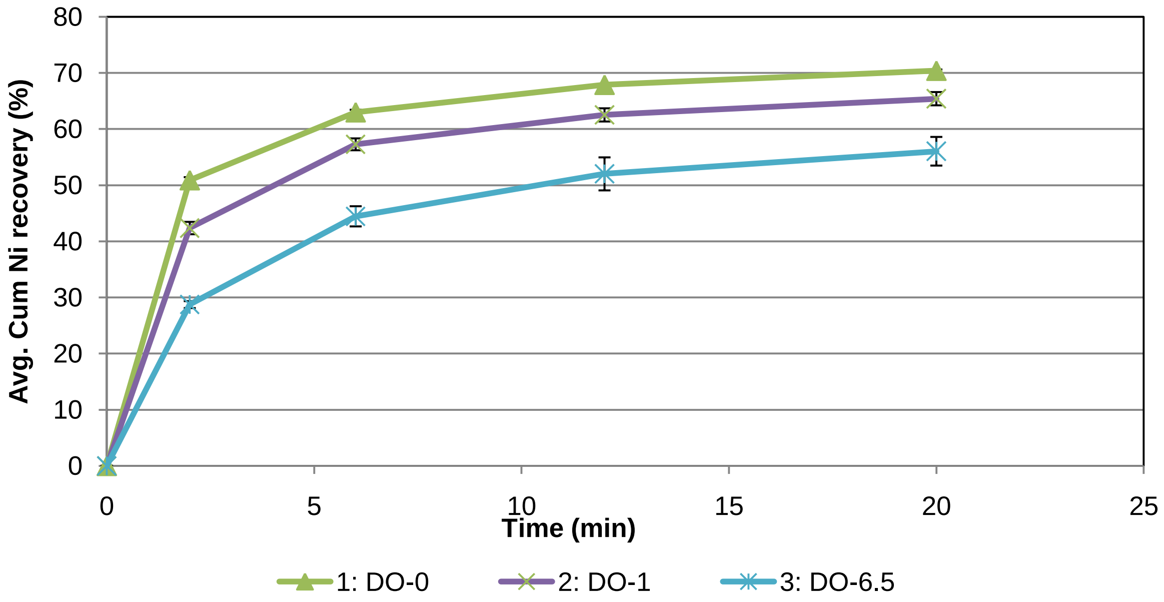


Figure 4.11: Average cumulative Ni recovery vs. time plot at different DO concentrations

Figure 4.12 shows the cumulative Po recovery–time plot of the ore ground at different DO concentrations. It can be seen that there are notable variations in the floatability of Po. Po recoveries also follow the same trend as was the case with Ni. The cumulative Po recovery at the end of 2 min of flotation for the inert environment test (DO-0) was 25.6 % and the recoveries for the DO control Test-2 and -3 were 7.7 % and 5.8 % respectively. There also seems to be a correlation between DO concentration during the grinding and the rate of flotation as observed in Ni flotation.

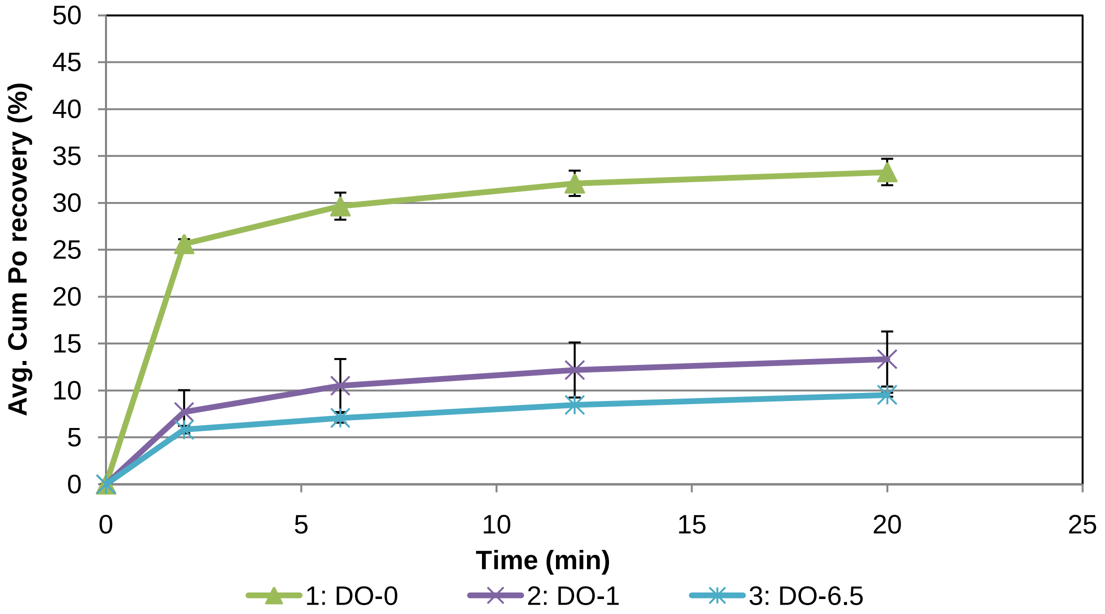


Figure 4.12: Average cumulative Po recovery vs. time plot at different DO concentrations

4.4.2 Solid-Water recovery data

The final mass of solid and water recoveries obtained from the flotation using the different DO conditions are shown in Figure 4.13. It can be seen from Figure 4.13, that there was a substantial increase in the mass of solid recovered in the flotation of the ore ground at a DO concentration of 0 ppm than with the rest of the test conditions. However, there were only marginal differences in the water recoveries recorded for both other test conditions (DO-1 and 6.5).

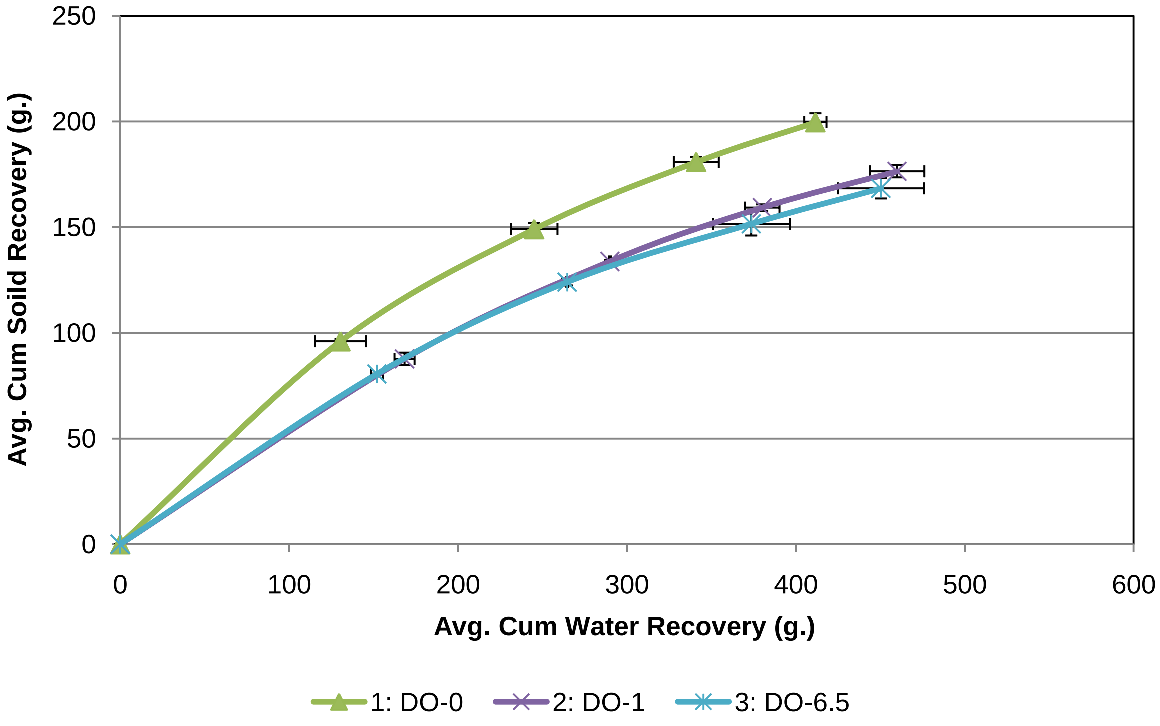


Figure 4.13: Average cumulative solid-water recovery graphs at different DO concentrations of the pulp during grinding

4.4.3 Grade-recovery data

Figure 4.14 shows the cumulative Cu grade–recovery performance of the ore ground at different DO concentrations. It can be seen that the grade vs. recovery curves for three out of four test conditions fall into a similar grouping with the data points within a close range of each other. However, in the case of Test-1, the grade and recovery of Cu was lowest. The concentrate grade and recovery was highest in case of Test-3. The cumulative Cu recovery for DO-0 test was 83.7 % and the recoveries for oxygen control tests (numbered 2 and 3) were 84.6% and 86.8 % respectively. The overall Cu recoveries for the different test were in a very close range. There was almost no difference in the recoveries of the Cu by varying the

DO concentration apart from the DO concentration of 0 ppm. However, a significant variation in the grade of Cu was recorded.

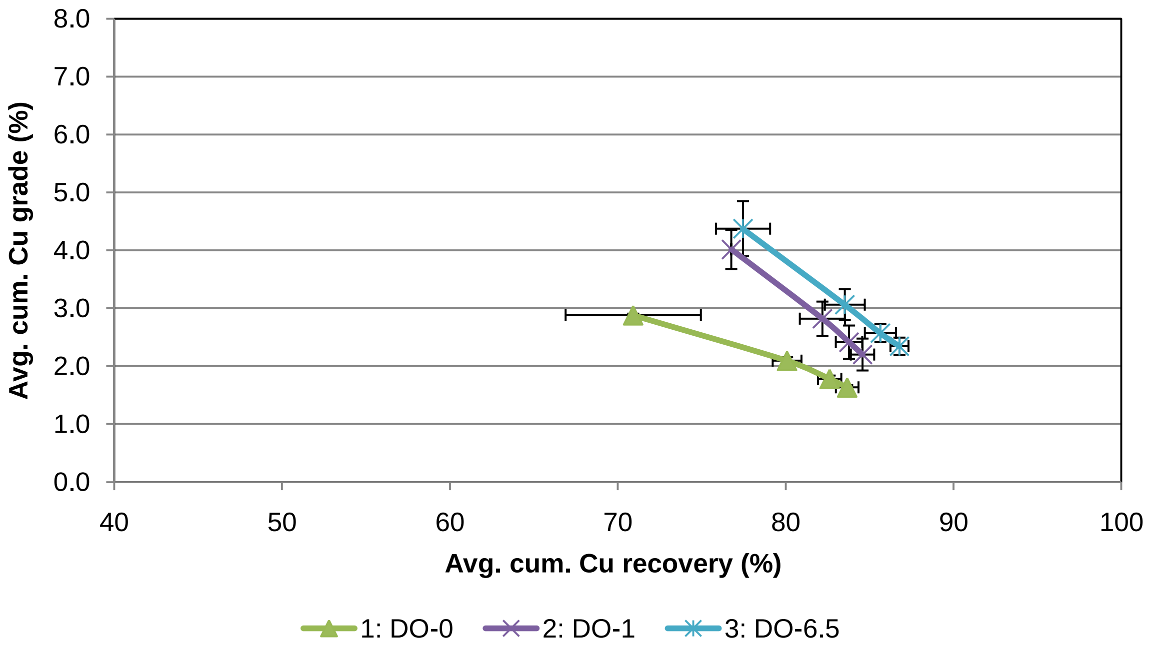


Figure 4.14: Average cumulative Cu grade-recovery graphs at different DO concentrations of the pulp during grinding

Figure 4.15 shows the cumulative Ni grade–recovery performance of the ore ground at different pulp DO concentrations. In all cases, a higher DO concentration during grinding caused a significant deterioration in the performance in comparison with the DO-0 Test-1. Although the variation in the recovery of the Ni was inverse with respect to DO concentration i.e. Ni recovery increased as the DO was decreased but no systematic change in final grade with pulp DO concentration was observed. In the case of lower DO concentrations (Test-1 and Test-2), initial grade was quite high. However, as the flotation progresses the concentrate grade drops relatively fast. A significant loss of Ni recovery was noted for all the tests compared to Test-1. The cumulative Ni recovery for Test-1 was 70.4 % and the recoveries for DO control Test-2 and -3 were 65.4 % and 56.1 % respectively. There was a direct correlation between these values and the pulp DO concentration. The overall Ni recoveries of the oxidized samples were considerably lower than the recovery that was obtained from the DO-0 test.

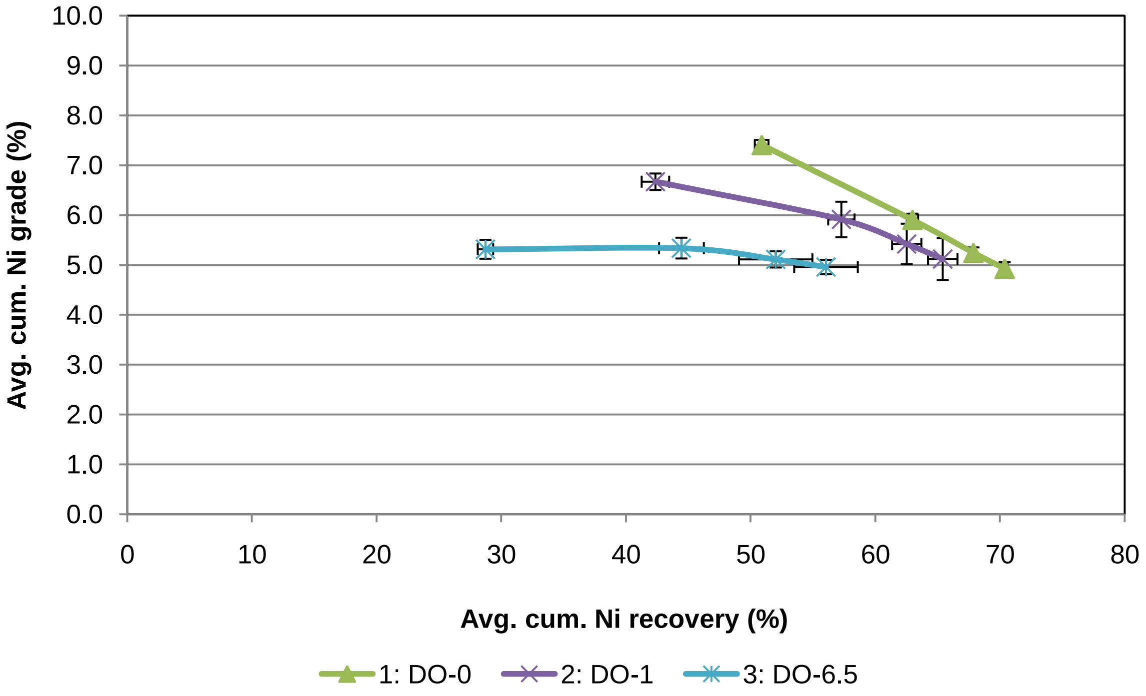


Figure 4.15: Average cumulative Ni grade-recovery graphs at different DO concentrations of the pulp during grinding

Figure 4.16 shows the cumulative Po grade–recovery performance of the ore ground at different pulp DO concentrations. As can be seen, the presence of oxygen during the grinding stage produced extremely poor grade–recovery curves compared to the absence of oxygen (DO-0) Test-1. In the absence of oxygen, initially a significant increase in grade was observed but the concentrate grade declined steadily with the progress of flotation. The cumulative Po recovery for the DO-0 Test-1 was 33.3 % and the recoveries for oxygen control Test-2 and -3 were 13.4 % and 9.5 % respectively. However the grade variation was 15.7 %, 6.7 % and 4.6 % for Test-1, -2 and -3 respectively. Although in the majority of the cases, the recovery of the Po varies in a narrow range it decreased with the increase of pulp DO concentration. The overall Po grade-recovery results for cases where DO>0 were consistently lower than the grade-recovery that was obtained from the DO-0 Test-1.

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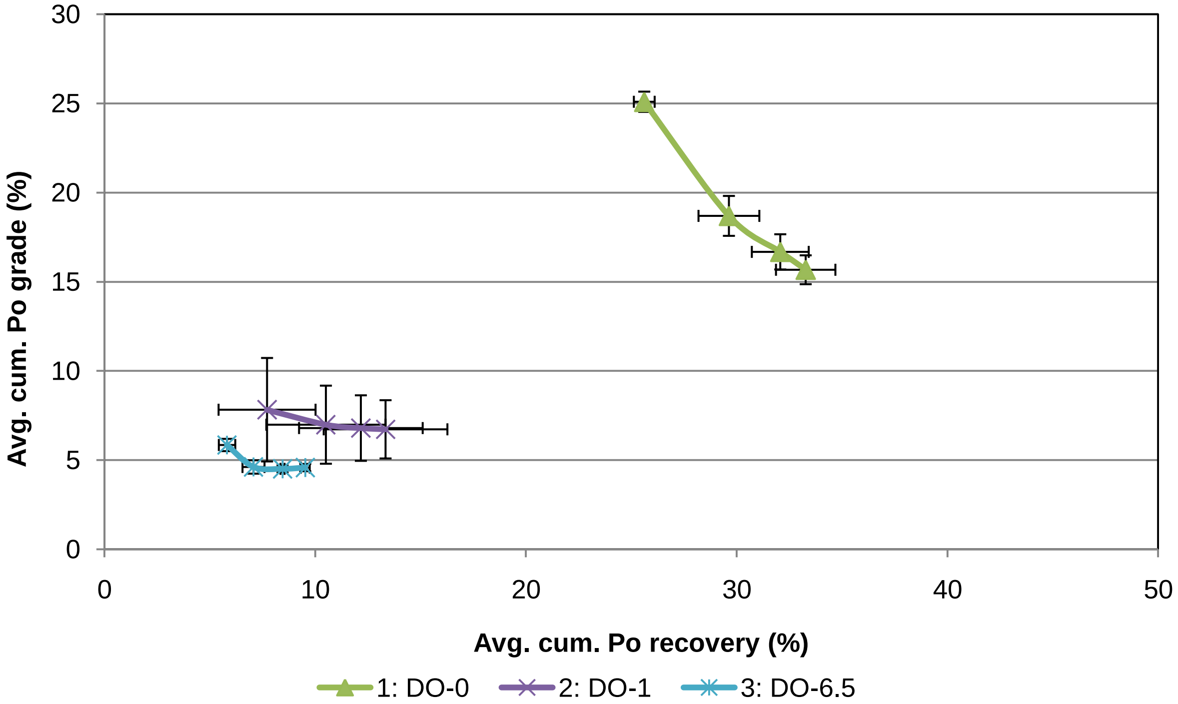

Figure 4.16: Average cumulative Po grade-recovery graph at different DO concentrations of the pulp during grinding

The effect of oxygen control during the grinding stage is shown in Figure 4.17. As can be seen, the mixed potentials of the system were anodic in the presence of oxygen. However, in the absence of oxygen it was highly cathodic. There was only a relatively small change in the mixed potential observed for the tests, where DO>0 ppm. In the absence of oxygen the mixed potential of the system was significantly negative. It can be seen that the Cu recovery was more or less independent of Eh or pulp DO concentration during the grinding stage. However, the presence of oxygen during the grinding stage had a considerable impact on the recovery of Ni as well as the mixed potential of the system. The variation in the recovery of the Ni was consistent with the variation of pulp DO concentration or Eh. The change in Po recovery with pulp DO concentration, while controlling the DO concentration >0 ppm was not significant and both the cases they fell in a narrow range. It is also noted that the Po recovery decreased significantly in the presence of oxygen during grinding.

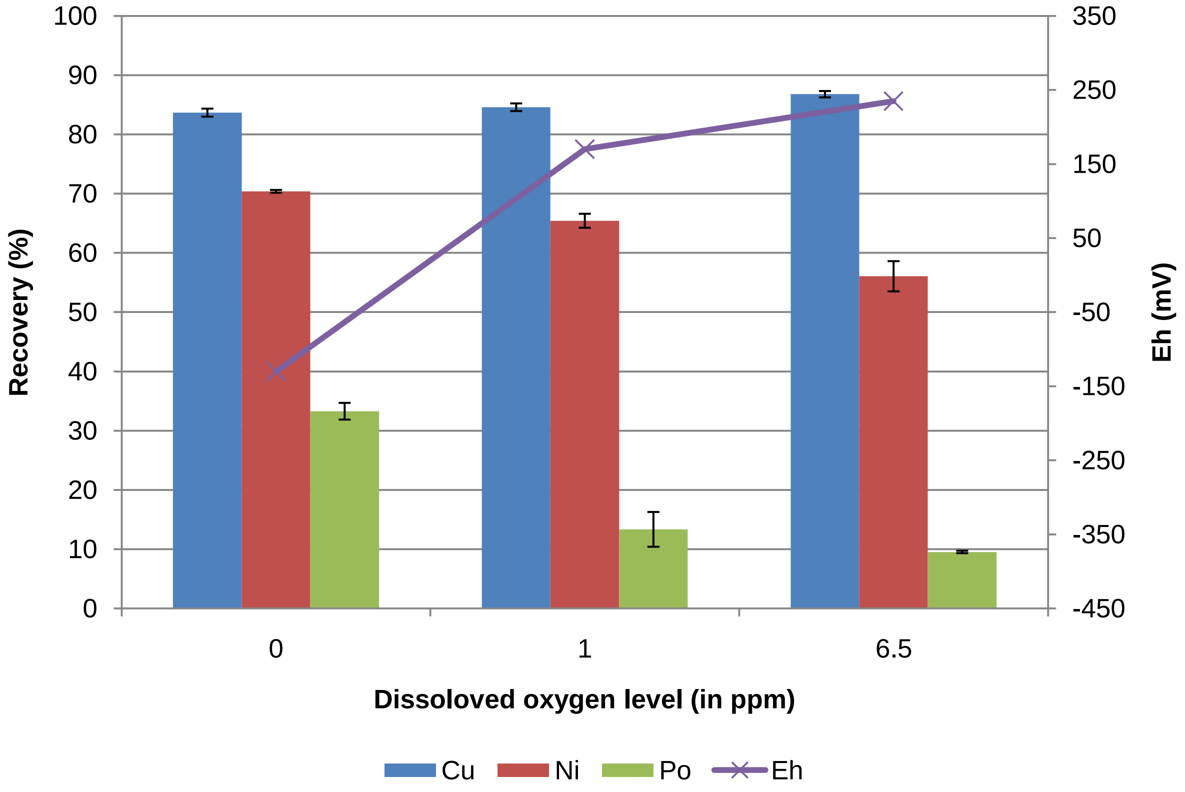

Figure 4.17: Variation of the floated mineral with respect to Eh by controlling the DO concentration during grinding

4.4.4 Kinetic analysis of flotation data

Table 4.3 shows the results obtained in the kinetic analysis of the flotation results obtained conducted at different DO concentrations. The Kelsall first order kinetic model was used for this analysis. It can be seen that the rate constant for the slow floating component of the ore was about 2 orders of magnitude lower when compared to the fast floating component and remains unchanged through the set of tests. However, the rate constant for the fast floating component of the ore, k_f, changes due to the change of the grinding conditions. The chalcopyrite was always the fastest floating mineral. The rate of flotation of the fast floating Pn was not much different to that of the Po. The most significant differences were seen in the fraction of the slow floating components (Øs) of the different minerals in the different grinding environments. The slow floating fractions of the Cp remained unchanged through the course of changing the grinding environment (Øs =0.17-0.21). However, the changes in the grinding environment resulted in a significant change in the slow floating fraction of the Pn (Øs =0.40-0.57) and even more so for Po (Øs =0.72-0.94).

Table 4.3: Kinetic analysis of batch flotation test results based on Kelsall model

Test Number	Cp			Pn			Po		
	ks	kf	Øs	ks	kf	Øs	ks	kf	Øs
Test-1	0.01±0.00	1.11±0.35	0.21±0.01	0.02±0.00	0.86±0.01	0.40±0.00	0.00±0.00	1.07±0.33	0.72±0.02
Test-2	0.01±0.00	1.41±0.06	0.17±0.01	0.01±0.00	0.68±0.01	0.45±0.01	0.00+0.00	0.71±0.04	0.90±0.03
Test-3	0.01±0.00	1.38±0.03	0.18±0.02	0.01±0.00	0.50±0.04	0.57±0.03	0.00+0.00	1.09±0.03	0.94±0.01

4.4.5 Xanthate adsorption results

Figure 4.18, shows the UV absorbance at 301 nm (the characteristic absorption wavelength of xanthate) as a function of the time at which the sample was taken from the mill or after transfer to the flotation cell. The sample taken after 5 minutes was after the commencement of the grinding. It can be seen from the figure that while grinding the pulp at DO-0 (Test-1), all of the xanthate remained unconsumed and did not absorb or react during the process of grinding. However, all of the xanthate was consumed after transferring the slurry from the mill to the cell (60 min. sample). When, the ore was ground at controlled DO concentrations as shown in Figure 4.18, DO-1 (Test-2) and DO-3 (Test-4), all of the xanthate was consumed within 5 minutes of the start of grinding.

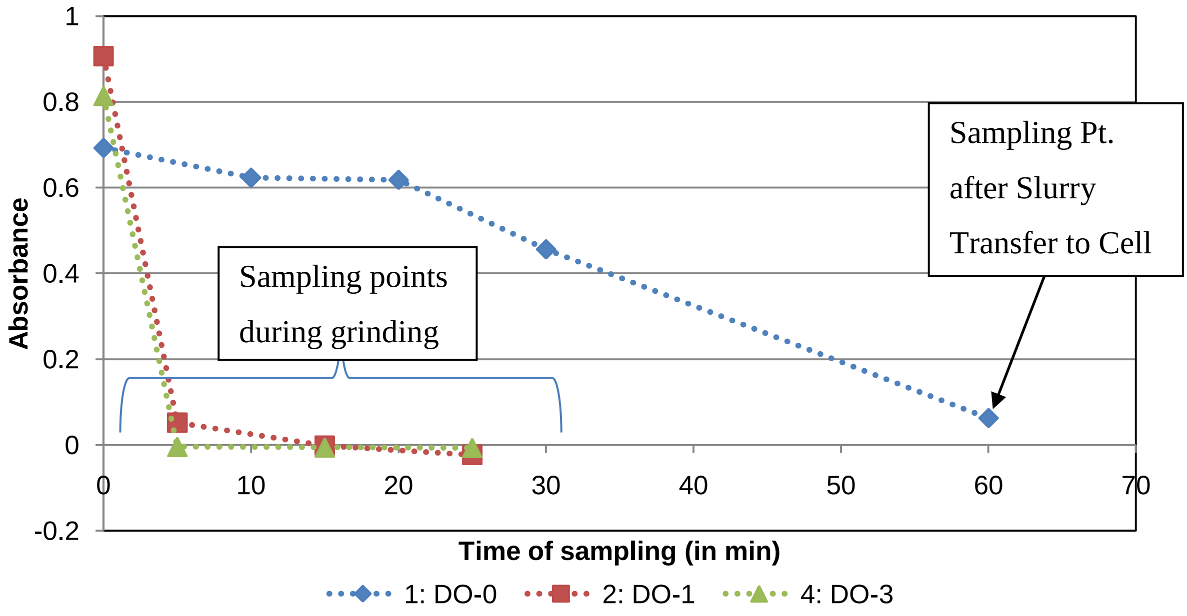

Figure 4.18: Residual concentration of xanthate remaining in the solution at different time intervals during grinding at different DO concentrations

4.5 The effect of sparging gas on flotation

In all the tests of the last section, compressed air was used as the flotation gas and no additional conditioning time was incorporated except for the 1 minute for frother conditioning. In this section tests were performed by varying the grinding conditions at the two extremes of DO i.e. continuous air purging (DO-6.5) and continuous N_2 purging (DO-0). Table 4.4 shows the pulp chemical readings recorded for the Magotteaux Mill discharge under the specified test conditions. The Eh, pH and DO profiles recorded during grinding are attached in Appendix-1. It should be noted that an additional conditioning time of 30 min was incorporated into these tests, in order to compare the effect of oxidation/inert environment on xanthate adsorption.

Table 4.4: Pulp Chemistry details for Test-5, -6, -7 and -8

Test No.	Test Name	Test conditions			
		Flotation condition		Grinding conditions	
		Sparging gas and time		Eh mV (SHE)	pH
5.	DO-0 and air sparging	Air	30 min	-160 to -180 mV	9.2-9.35
6.	DO-0 and N_2 sparging	N_2	30 min	-160 to -180 mV	9.2-9.35
7.	DO-6.5 and N_2 sparging	N_2	30 min	230 to 245 mV	9.2-9.35
8.	DO-6.5 and N_2 sparging	N_2	60 min	-160 to -180 mV	9.2-9.35

4.5.1 Varying flotation conditions at DO concentration of 0 ppm

Maximum Ni recovery recorded in Section 4.4 was in Test-1 (DO-0 in the mill and floating with air, no sparging). In the tests presented in this sub-section the grinding conditions were the same (DO-0) but the flotation conditions were varied (Test-5 and -6). Various pulp chemistry parameters were recorded at different stages of flotation as well, starting from slurry transfer to the completion of the flotation. These results are shown in

Table 4.5. It can be seen from the Table that the Eh value of the slurry became less cathodic after transfer as compared to the mill discharge. However, after 30 min of N_2 sparging, the Eh value dropped significantly (~ -125 mV) and again became more cathodic. The slurry was floated with N_2 which resulted in a positive shift in the Eh values. There was no significant change in the DO and pH values recorded during the various stages of flotation.

Table 4.5: Pulp chemistry conditions at different stages of flotation in Test-6

DO-0 during grinding and 30 min N_2 sparging before flotation with N_2			
Stages of flotation	Eh mV (SHE)	pH	DO
Pulp chemistry after slurry transfer	-24 to -34	9.0 to 9.2	0.50 to 0.30
Pulp chemistry after N_2 sparging	-125 to -130	9.20	0.30 to .20
Pulp chemistry after flotation with N_2	-68 to -08	9.20	0.3 to 0.8

4.5.1.1 Recovery time data

Figure 4.19 shows the cumulative solid recovery vs. time plot while grinding the ore at DO-0. It can be seen that the initial solid of the concentrate was higher in the case of Test-6 however; by the fourth concentrate the overall solid of the floated mineral was significantly lower than the other two test conditions. The amount of solid recovered at the end of 20 min of flotation was the same in the case of Test-1 and Test-5 which was higher than the Test-6.

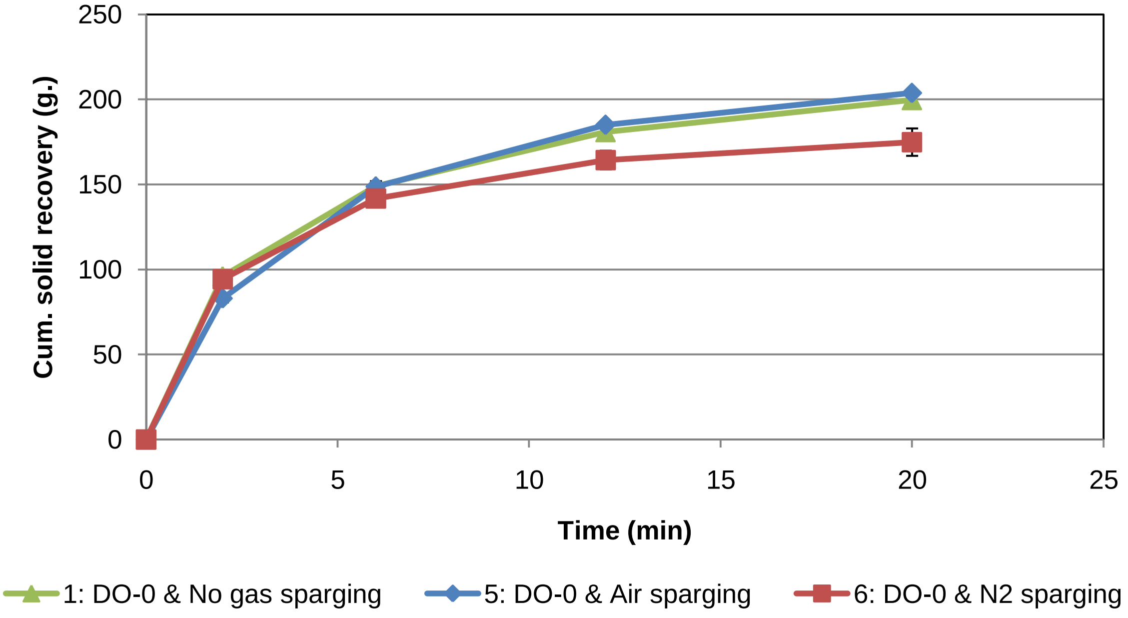

Figure 4.19: Avg. cum. solid recovery vs. time plot at DO-0 and varying sparging gas

Figure 4.20 shows the cumulative water recovery vs. time plot for the different flotation conditions while grinding the ore at DO-0. It can be seen that the water recovery follows the opposite trend to that which was observed in the solid recovery vs. time plot. There were initial differences in the water recoveries among the three tests conditions. However the overall water recovery was similar for Test-1 and Test-5 at the end of the tests. The amount of water recovered at the end of 20 min of flotation was slightly more in the case of Test-6 as compared to the other two test conditions (Test-1 and Test-5).

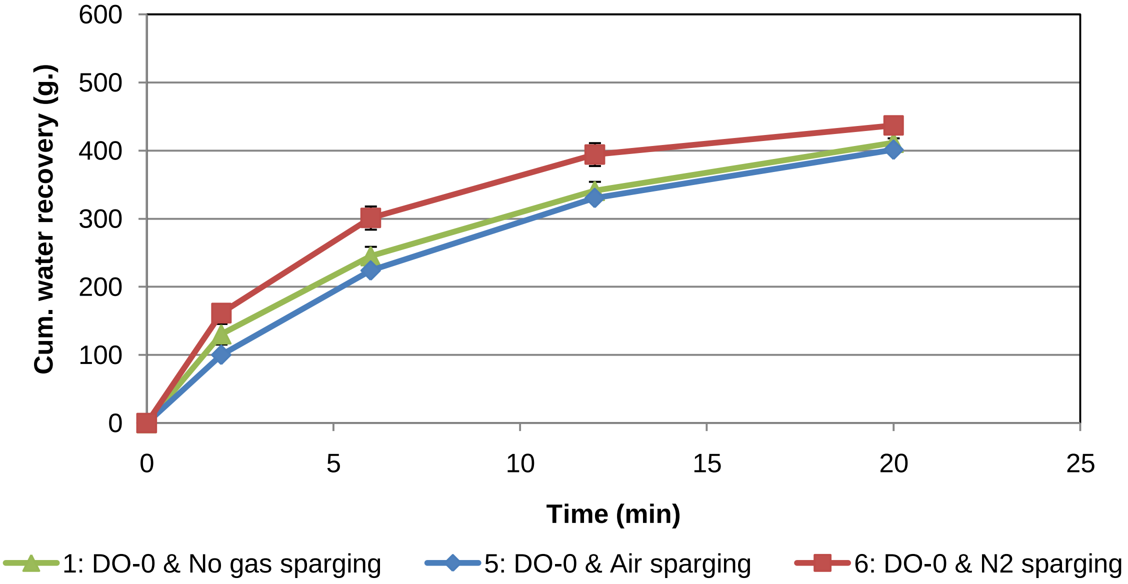

Figure 4.20: Average cumulative water recovery vs. time plot at DO-0 and varying sparging gas

Figure 4.21 shows the variation in the cumulative Cu recovery vs. time for the ore ground at DO-0 while varying the flotation conditions. It can be seen that N_2 sparging (Test-6) resulted in a significant decrease in the initial recovery as well as overall recovery of Cu. However, air sparging (Test-5) or no gas sparging (Test-1) did not result in any significant differences in the Cu recovery. Initially the differences in the recoveries between the two cases as discussed in the grade recovery curve of Cu (after 2 min of flotation) was less than 25 %, however, at the end of the tests the differences in the recoveries became more the 30 %. There seems to be a direct relationship between the floatability of Cu and the oxygen concentration of the pulp.

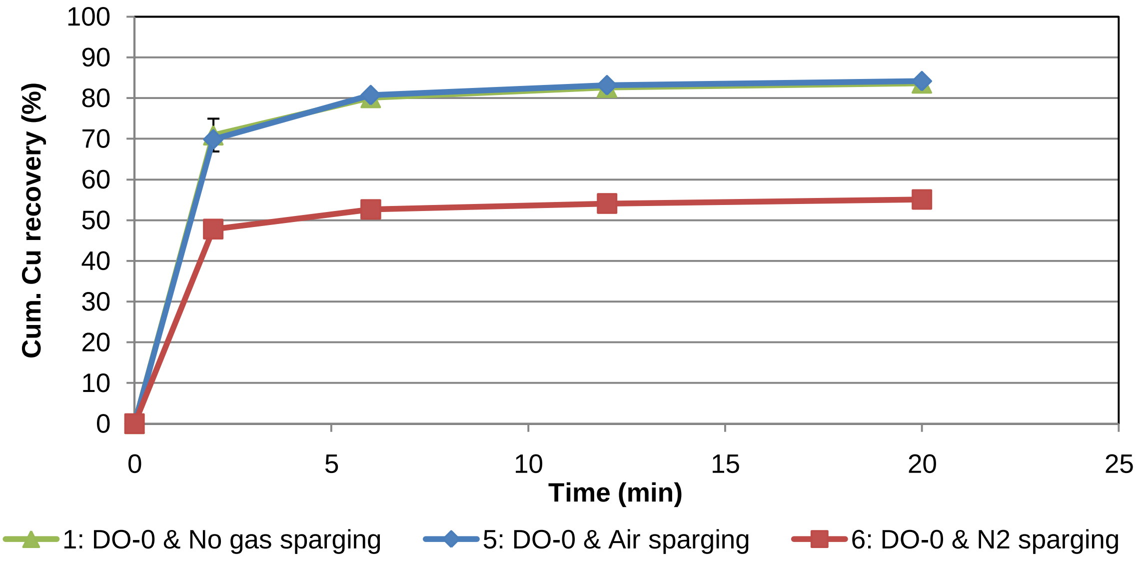

Figure 4.21: Average cumulative Cu recovery vs. time plot at DO-0 and varying sparging gas

Figure 4.22 shows the variation in the cumulative Ni recovery vs. time for the ore ground at DO=0 while varying the flotation conditions. It can be seen that the initial rate of flotation for the Ni followed the order; Test-1, Test-5, Test-6. However, at the end of 20 min of flotation the overall recovery of Test-1 and Test-5 became almost the same. The total recovery of the Ni was lowest in Test-6.

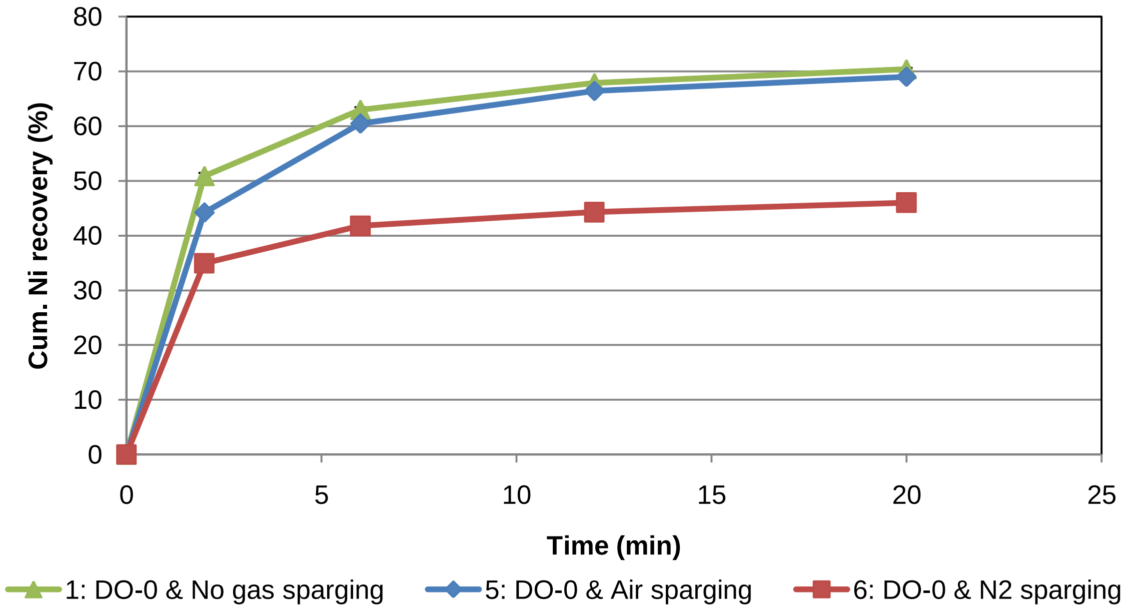

Figure 4.22: Average cumulative Ni recovery vs. time plot at DO-0 and varying sparging gas

Figure 4.23 shows the variation of the cumulative Po recovery time plot for the ore ground at DO= 0 ppm while varying flotation conditions. It can be seen from the Figure 4.23 that the gas sparging had a detrimental effect on the initial as well as the overall recovery of the Po. The effect was more prominent with the N_2 sparging compared to the air sparging. There appeared to be a relation between the recovery of the Po and the gas sparging conditions.

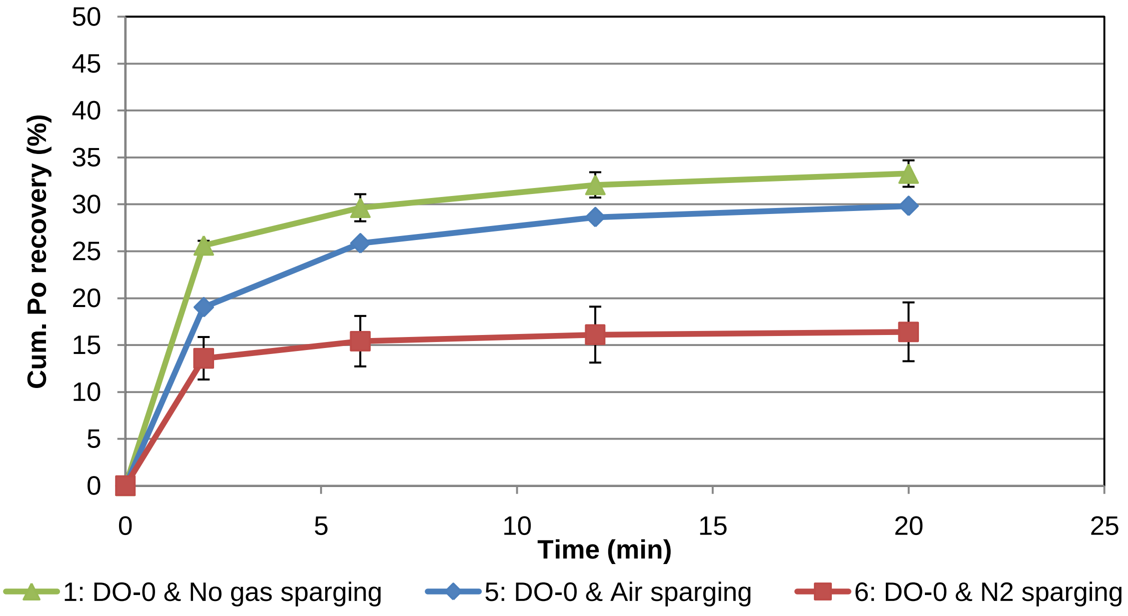

Figure 4.23: Average cumulative Po recovery vs. time plot at DO-0 and varying sparging gas

4.5.1.2 Solid-Water recovery data

The final solid and water recoveries for the different test conditions are shown in Figure 4.24. The amount of solid recovered in Test-1 and Test-6 were higher as compared to Test-5. However, the differences in the water recoveries were only marginal under all test conditions. Initial solid and water recoveries were higher for Test-6 compared to Test-1 or Test-5 but at the end of flotation the order of the solid recovery was reversed.

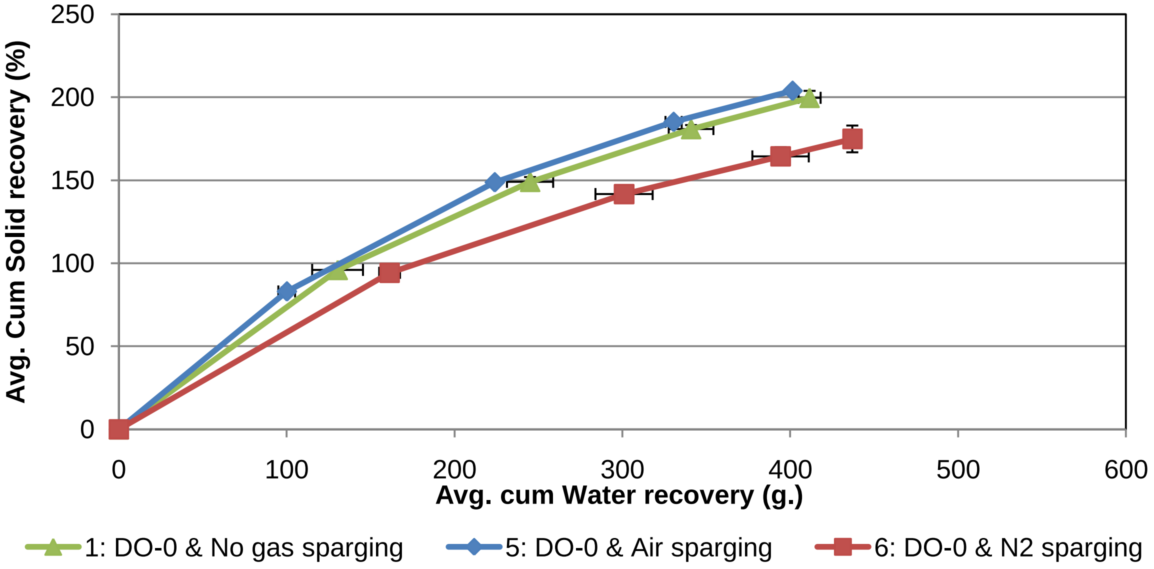

Figure 4.24: Average cumulative solid-water recovery graph at DO-0 and varying sparging gas

4.5.1.3 Grade-recovery data

Figure 4.25 shows the effect of various flotation conditions on the grade-recovery of Cu. It is noted that air sparging did not affect the flotation performance of the Cu and the grade–recovery curves for Test-1 and Test-5 were in the same range. However, N_2 sparging (Test-6) resulted in a lower grade and recovery of Cu. The difference in the recoveries between the two ranges was approximately 20 % after the first concentrate and after the completion of the flotation test, these differences increased and the overall difference in the recovery became more than 30 %. However, the differences in the grade became marginal towards the end of the tests 1.63 % for Test-1, 1.54 % for Test-5 and 1.19 % for Test- 6.

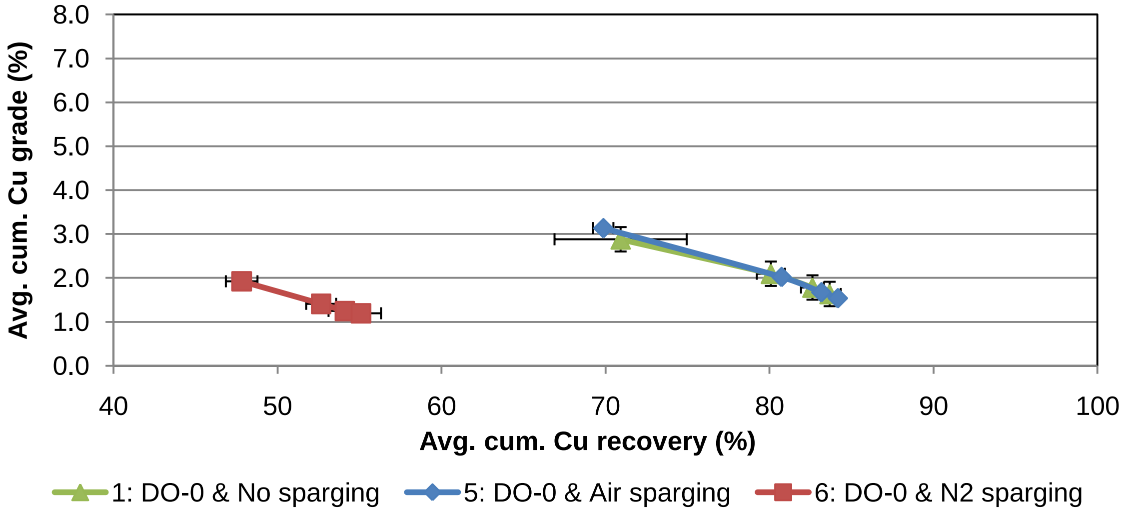

Figure 4.25: Average cumulative Cu grade-recovery graph at DO-0 and varying sparging gas

Figure 4.26 shows the grade-recovery of Ni under varying flotation conditions. In all cases, gas sparging whether it was N_2 (Test-6) or air (Test-5), resulted in significant deterioration in the performance as compared to no gas sparging (Test-1). Initial trends showed that the recovery was higher at the beginning of Test-1, followed by Test-5 and lowest in Test-6. However, as flotation progresses, the grade–recovery curves for Test-1 and Test-5 were fall in the same category by the end of flotation. Air sparging did not have much influence on the grade-recovery of the Ni. However, N_2 sparging resulted in a significant decrease in the grades as well recoveries.

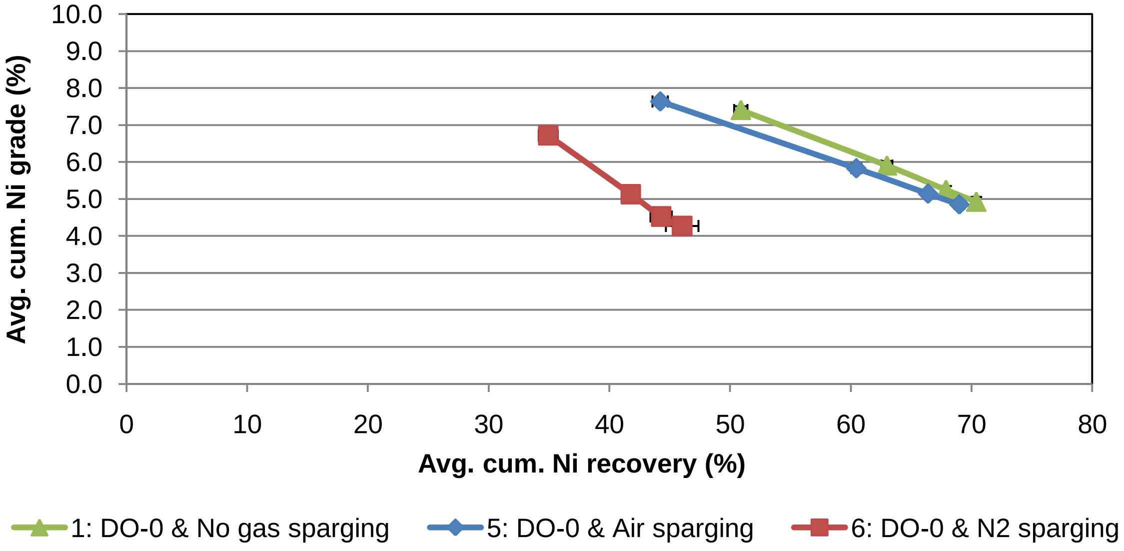

Figure 4.26: Average cumulative Ni grade-recovery graph at DO-0 and varying flotation conditions

Figure 4.27 shows the effect of various flotation conditions on the grade-recovery of Po. It can be seen from this figure that gas sparging caused a significant decrease in the initial as well as overall recovery of the Po. Initial recovery of the Po followed a similar trend as Ni. Maximum recovery of the Po was obtained in the case of no gas sparging. Air sparging caused a decrease in the overall recovery of Po. However, in the case of N_2 sparging, the effect was much more significant and resulted in a further decrease in the overall recovery. Initial as well as final grades of Po with air sparging and no gas sparging were in the same range but were higher than the N_2 sparging condition.

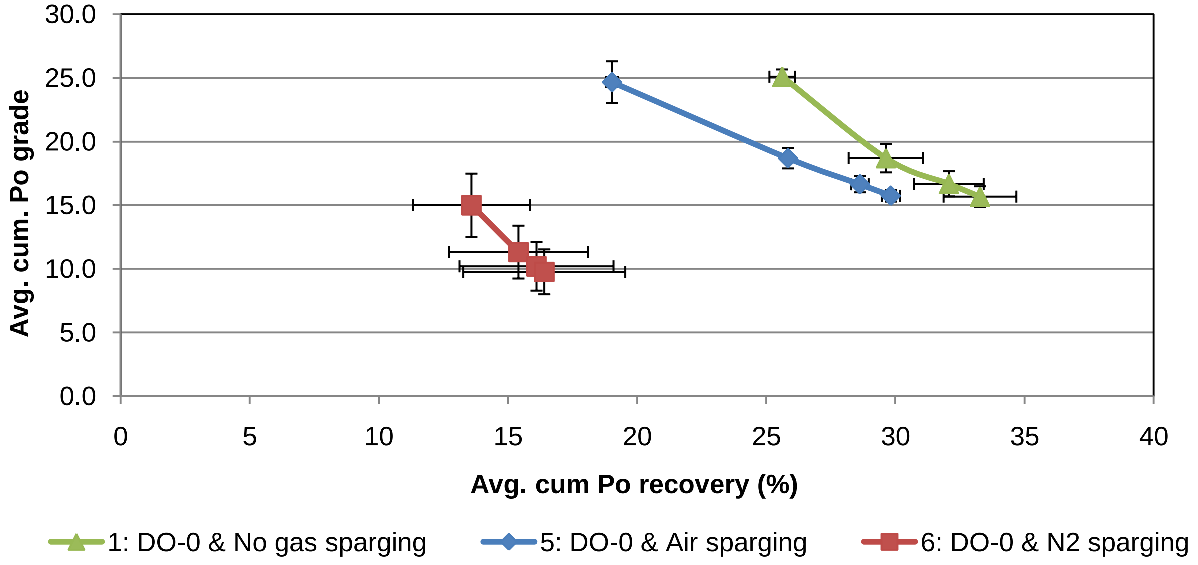

Figure 4.27: Average cumulative Po grade-recovery graph at DO-0 and varying flotation condition

4.5.1.4 Kinetic analysis of flotation data

Kinetic Analysis of flotation results Table 4.6 shows the kinetic analysis results for the tests conducted at a DO = 0 ppm while changing flotation conditions. It can be seen that the fraction of the slow floating component (Øs) increased in the case of Cu, in Test-6. However, in the case of Test-1 and Test-5, there was no change in the fraction of the slow floating component. The rate constant for the slow floating component of the ore was almost 2 orders of magnitude lower compared to the fast floating component for all minerals. However, the rate constant for the fast floating component of the ore changed at the different flotation conditions. In all cases the fast floating rate constant (kf) was highest for Test-6 conditions.

Table 4.6: Kinetic analysis of batch flotation test results based on Kelsall model

Test Number	Cp			Pn			Po		
	ks	kf	Øs	ks	kf	Øs	ks	kf	Øs
Test-1	0.01±0.00	1.11±0.35	0.21±0.01	0.02±0.00	0.86±0.01	0.40±0.00	0.00±0.00	1.07±0.33	0.72±0.02
Test-5	0.01±0.00	1.02±0.03	0.20±0.03	0.02±0.00	0.66±0.02	0.41±0.00	0.00+0.00	0.66±0.02	0.75±0.00
Test-6	0.00±0.00	1.24±0.03	0.48±0.01	0.01±0.00	0.93±0.03	0.59±0.02	0.00+0.00	1.10±0.02	0.85±0.03

4.5.2 Varying flotation conditions at DO concentration of 6.5 ppm

Minimum Ni recovery recorded in Section 4.4 was found in the case of Test-4 while floating the pulp with air as a sparging gas. In order to determine the effect of varying the flotation conditions, the grinding conditions were kept similar while the pulp was sparged with N_2 prior to flotation and the sparging gas during flotation was N_2. These test conditions were chosen keeping in mind that N_2 sparging may affect the xanthate adsorption (Rao and Finch 1991) or may clean the oxidized surface through reduced galvanic interactions (Bozkurt and Finch 1998) and enhance the floatability. Various pulp chemistry parameters were recorded at different stages during flotation; from the slurry transfer stage to the completion of flotation as shown in Table 4.7. It can be seen from the Table 4.4 and Table 4.7 that, the Eh value of the slurry becomes more anodic after slurry transfer. However, after 30 min of N_2 sparging, the Eh value was hardly affected. Floating with N_2 did not have much influence on the Eh value. There was a significant decrease in the DO level after N_2 sparging but floating with the N_2 did not produce any further change in the DO value.

Table 4.7: Pulp chemistry conditions at different stages of flotation in Test-7

DO-6.5 during grinding and 30 min N_2 sparging before flotation with N_2			
Stages of flotation	Eh mV (SHE)	pH	DO
Pulp chemistry after slurry transfer	205 to 215	9.0 to 9.2	7.0 to 7.2
Pulp chemistry after N_2 sparging	205 to 210	9.2	0.5 to 0.3
Pulp chemistry after flotation	205 to 210	9.2	0.2 to 0.3

4.5.2.1 Recovery time data

Figure 4.28 and Figure 4.29 show the cumulative solid recovery-time and water recovery-time plot obtained under the specified test conditions. The amount of solid and water recovered in both the cases were similar. Solid and water recovery after 2 min and at the end of flotation met at the same point.

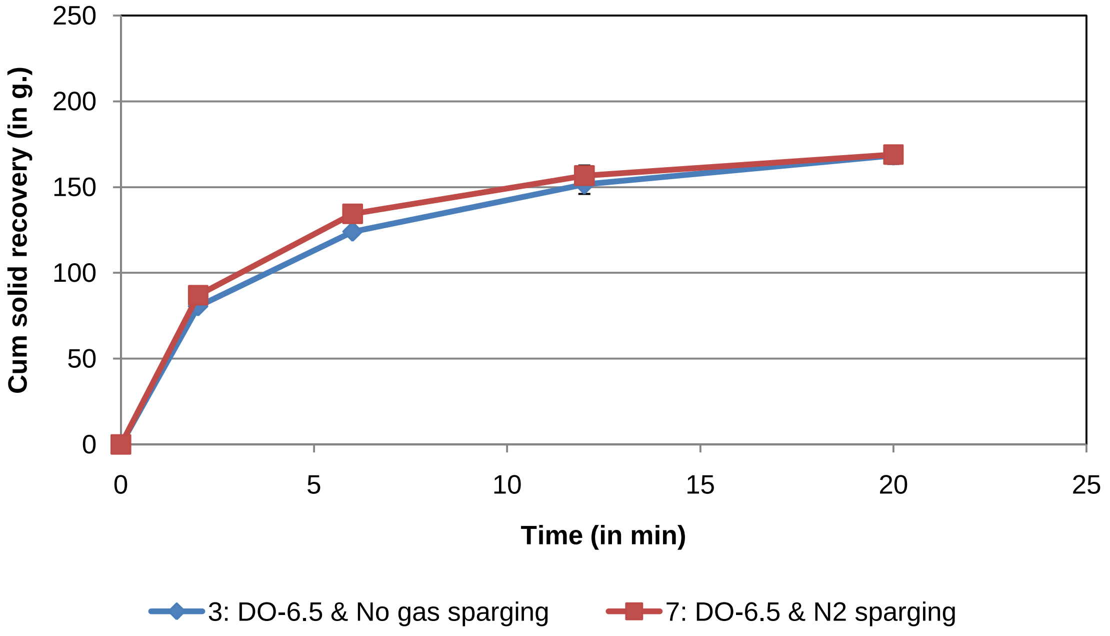

Figure 4.28: Avg. cum. solid recovery vs. time plot at DO-6.5 and varying flotation condition

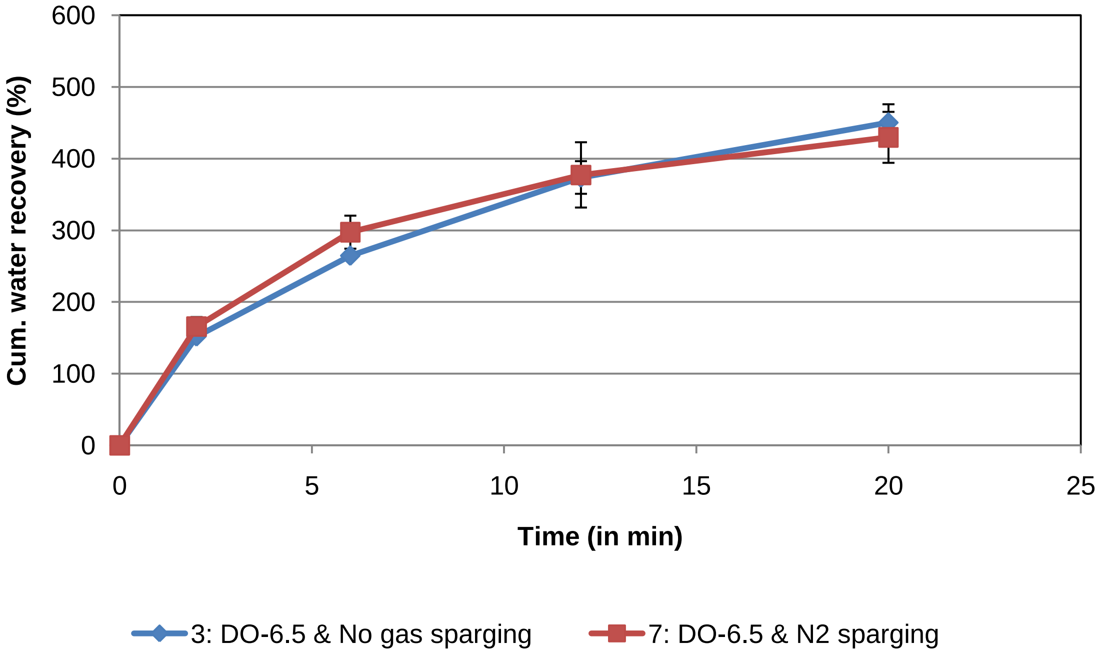

Figure 4.29: Avg. cum. water recovery vs. time plot at DO-6.5 and varying flotation condition

Figure 4.30 shows the cumulative Cu recovery–time plot obtained under the specified test conditions. It can be seen that there was virtually no difference in the floatability of Cu in the two different test conditions. The cumulative recovery values for both of the test conditions were almost identical.

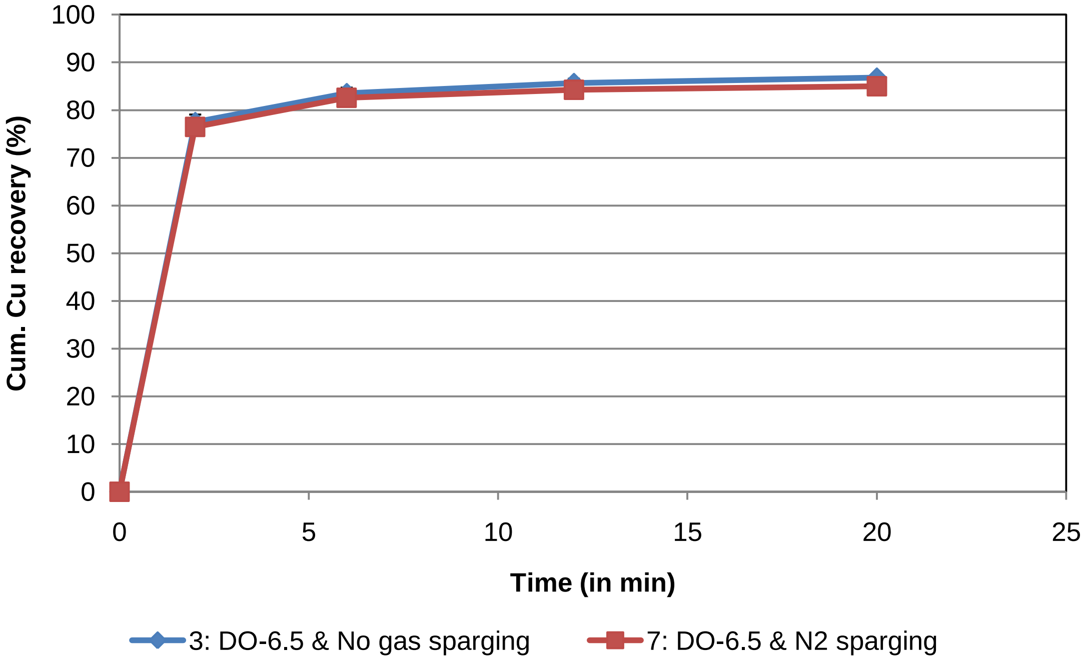

Figure 4.30: Avg. cum. Cu recovery vs. time plot at DO-6.5 and varying flotation condition

Figure 4.31 shows the cumulative Ni recovery as a function of time under the specified test conditions. It can be seen that the initial rates of flotation for Ni in both of the cases were similar. However, as the flotation progressed the difference in the recoveries became more significant. At the end of 20 min of flotation time the overall recovery differences between the two test conditions was more than 10 %.

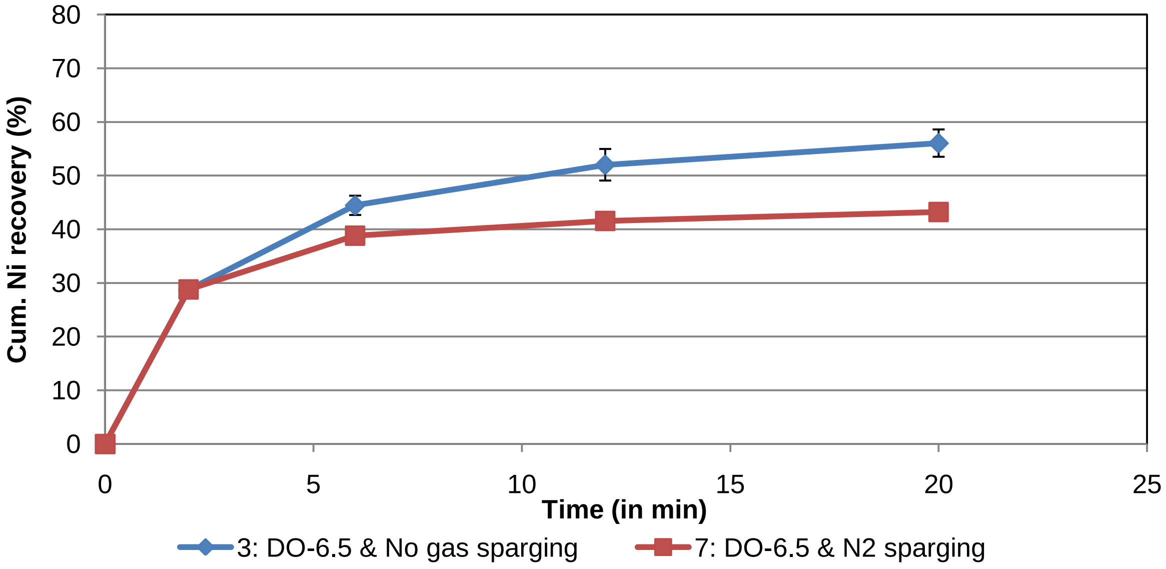

Figure 4.31: Avg. cum. Ni recovery vs. time plot at DO-6.5 and varying flotation condition

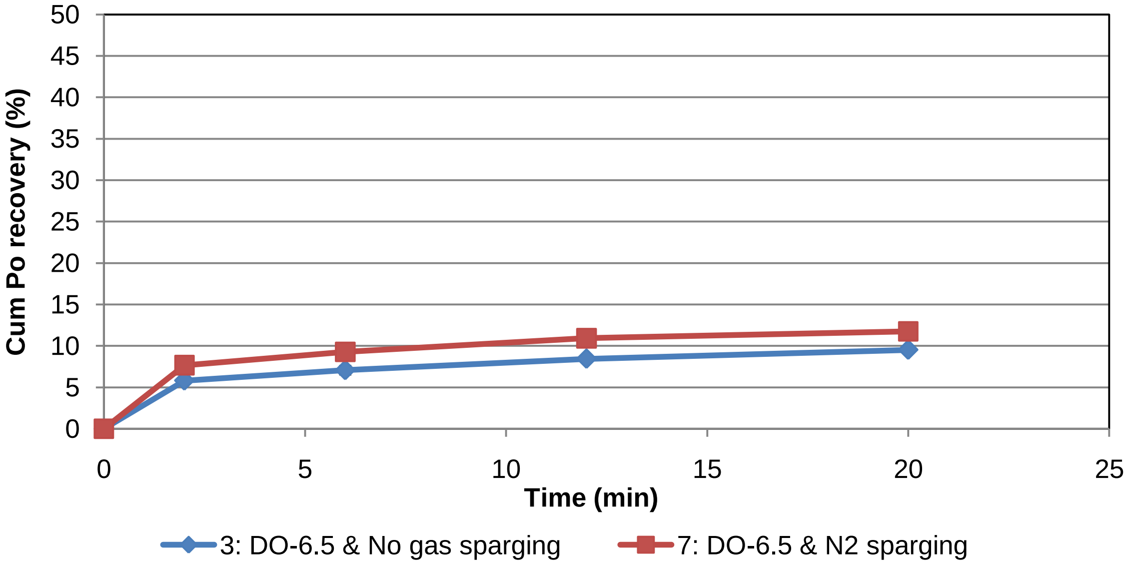

Figure 4.32 shows the cumulative Po recovery–time obtained under the specified test conditions. It can be seen that the floatability of Po was similar in both of the test conditions. The cumulative recovery values were also similar for both of the test conditions.

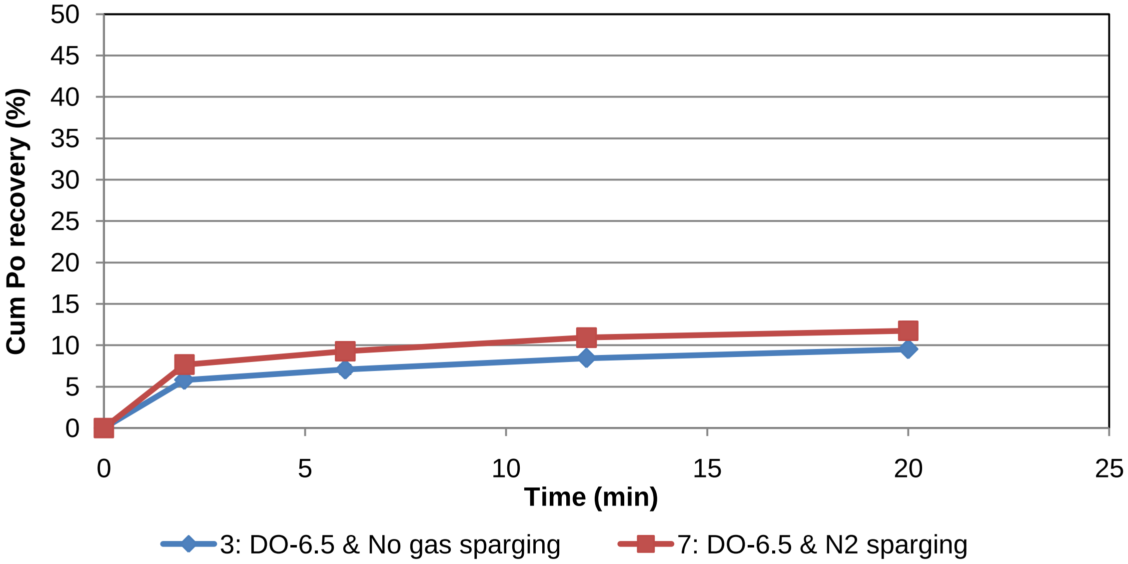

Figure 4.32: Avg. cum. Po recovery vs. time plot at DO-6.5 and varying flotation condition

4.5.2.2 Solid-water recovery results

Figure 4.33 shows the results obtained for the final solid and water recovered for the tests under the specified flotation conditions. The amount of solid and water recovered in both of the cases having only a marginal difference.

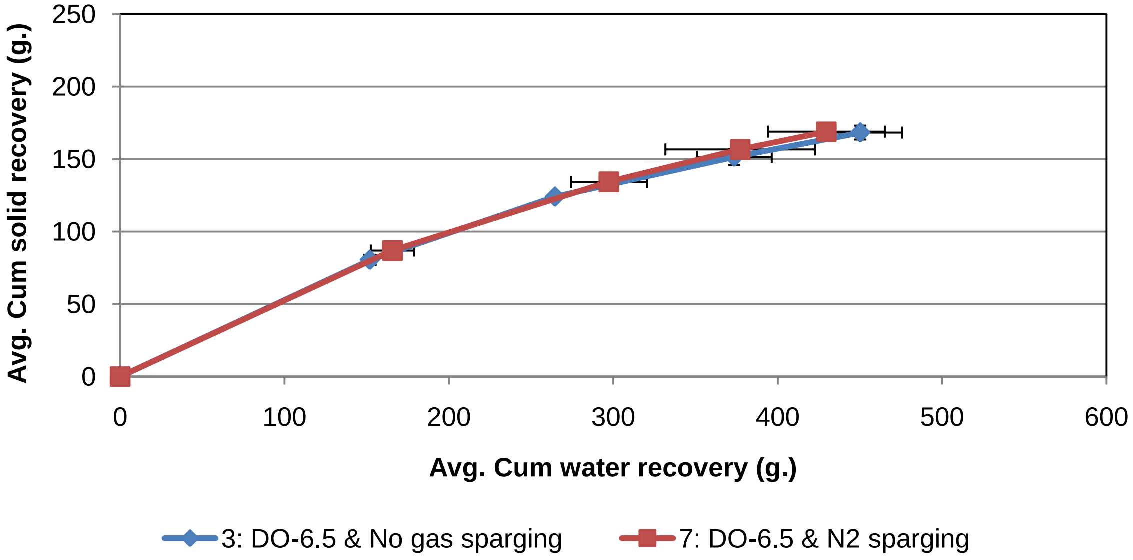

Figure 4.33: Average cumulative solid-water recovery graph at DO-6.5 and varying flotation condition

4.5.2.3 Grade recovery results

Figure 4.34 shows the cumulative Cu grade–recovery performance under the specified tests conditions. The overall Cu recoveries of the two tests conditions varied in a narrow range. There was almost no difference in the grades and recoveries of the Cu from varying the flotation conditions.

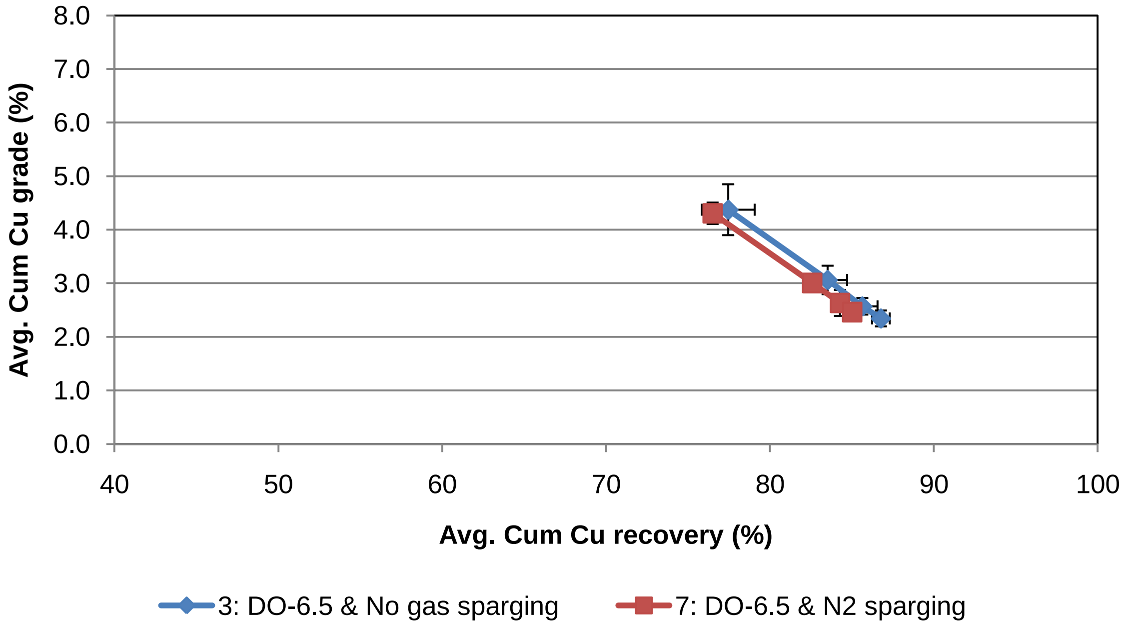

Figure 4.34: Average cumulative Cu grade-recovery graph at DO-6.5 and varying flotation condition

Figure 4.35 shows the cumulative Ni grade–recovery performance under the specified tests conditions. It can be seen that N_2 sparging caused a significant deterioration in the overall grade-recovery of the Ni. Initial recovery in both the tests conditions were similar however, the recovery gradually decreases in the case of N_2 sparging, with the progress of flotation. At the end of flotation, more than 10 % difference in the recovery between the two tests was observed.

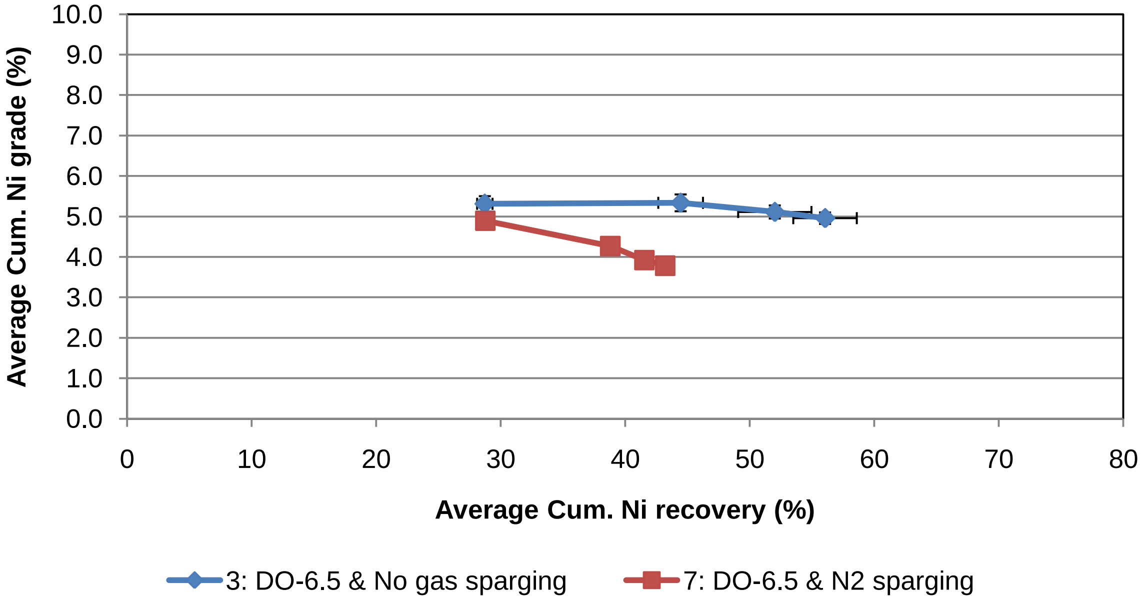

Figure 4.35: Average cumulative Ni grade-recovery graph at DO-6.5 and varying flotation condition

Figure 4.36 shows the cumulative Po grade–recovery performance under the specified tests conditions. As can be seen, in the case of Po, N_2 sparging (Test-7) resulted in an improvement in the performance compared to the no gas sparging (Test-3) condition. Initial as well as the overall grade-recovery of the Po showed only marginal difference in both of the test conditions.

Test	Cp	Pn	Po

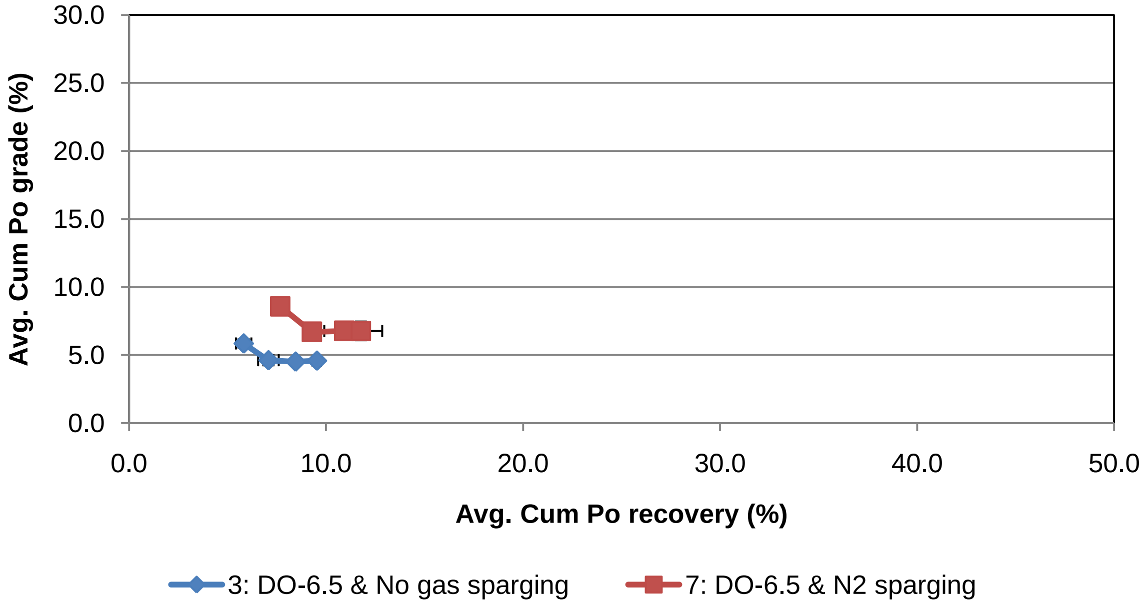

Figure 4.36: Average cumulative Po grade-recovery graph at DO-6.5 and varying flotation condition

Kinetic analysis of flotation results emains consistent in both cases.

Table 4.8 shows the results of the kinetic analysis of the tests conducted at DO concentration of 6.5 ppm while changing the flotation conditions. It can be seen that the fraction of slow floating component (Øs) increased slightly for Pn while floating with the N_2. However, in the case of Po the difference in the slow floating component was only marginal, when it was floated with N_2. In the case of Cu, the flotation behaviour remains consistent in both cases.

Table 4.8: Kinetic analysis of batch flotation test results based on Kelsall model

	ks	kf	Øs	ks	kf	Øs	ks	kf	Øs
Test-3	0.01±0.00	1.38±0.03	0.18±0.02	0.01±0.00	0.50±0.04	0.57±0.03	0.00+0.00	1.09±0.03	0.94±0.01
Test-7	0.01±0.00	1.34±0.02	0.18±0.00	0.00±0.00	0.68±0.02	0.62±0.00	0.00+0.00	0.99±0.05	0.92±0.00

4.5.3 Xanthate adsorption results

Figure 4.37 shows the UV absorbance at the characteristic absorption wavelength of xanthate (301nm) after different grinding and flotation conditions. The absorbance is a direct measure of the amount of soluble xanthate remaining in the pulp. It can be seen that the unconsumed xanthate remaining in the pulp after the grinding phase was consumed during the slurry transfer process. However, after N_2 sparging the measured xanthate was found to be higher than the remaining xanthate after slurry transfer indicating a reversible process. It is also important to note that the unconsumed xanthate (after 30 min N_2 sparging – 0.4au) is only slightly reduced after flotation with N_2 (Test-7 0.27au).

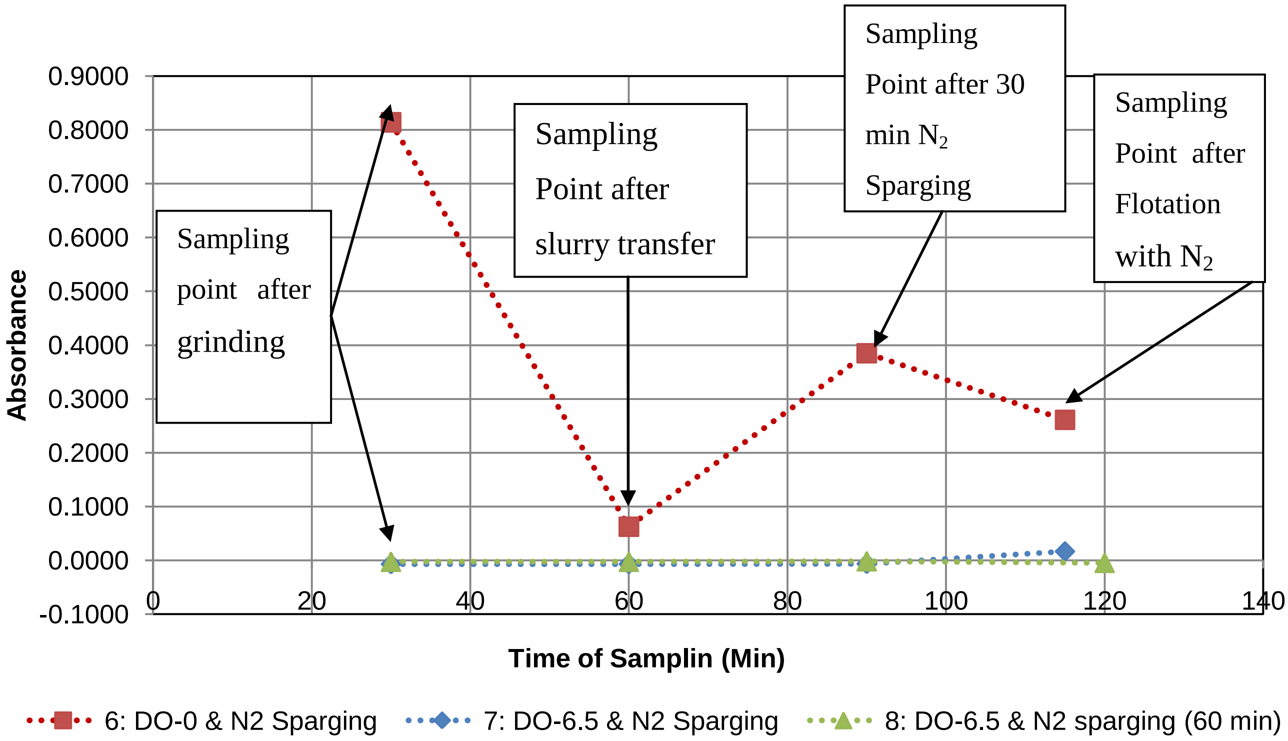

Figure 4.37: Residual concentration of xanthate left into the solution at different time interval of the test

4.6 Varying xanthate addition points at DO concentration of 0 and 6.5 ppm

In the tests shown in the previous two sections, xanthate was added into the mill. In this Section tests were performed by varying the grinding conditions in the total absence of oxygen i.e. DO-0 (Test-9) and in an oxygen environment i.e. DO-6.5 (Test-10) and then adding xanthate in the cell. The results were compared with the cases where xanthate was added in the mill (Test-1 and Test-3). Table 4.9 shows the resultant pulp readings recorded for the Magotteaux Mill discharge under the specified test conditions. The Eh, pH and DO profiles recorded during grinding are shown in Appendix-1. It is to be noted that an additional conditioning time of 2 min was incorporated after xanthate addition into the cell. No additional conditioning time was allowed when xanthate was added in the mill.

Table 4.9: Variation of pulp conditions during flotation by varying the flotation gases

Test. number	Grinding/ Flotation conditions			Pulp conditions during Grinding	
	Grinding Conditions	X^- addition pt.	Conditioning time	Eh mV (SHE)	pH
1	DO-0.0	Mill	-	-160 to -1800 mV	9.2-9.35
3	DO-6.5	Mill	-	230 to 245 mV	9.0-9.2
9	DO-0.0	Cell	2 Min	-160 to -180 mV	9.2-9.35
10	DO-6.5	Cell	2 Min	230 to 245 mV	9.0-9.2

4.6.1 Recovery time data

Figure 4.38 show the cumulative solid recovery-time results for the tests conducted under the specified grinding and flotation conditions. It can be seen that the amount of solid recovered after the first float can be seen in the overall solid recovery. Xanthate addition into the cell produces higher initial as well as overall solid recovery when the ore was ground at a DO concentration of 0 ppm. When the ore was ground at a DO concentration of 6.5 ppm, although there was an initial difference in the solid recovery by the end of flotation solid recovery was very similar and essentially independent of xanthate addition point.

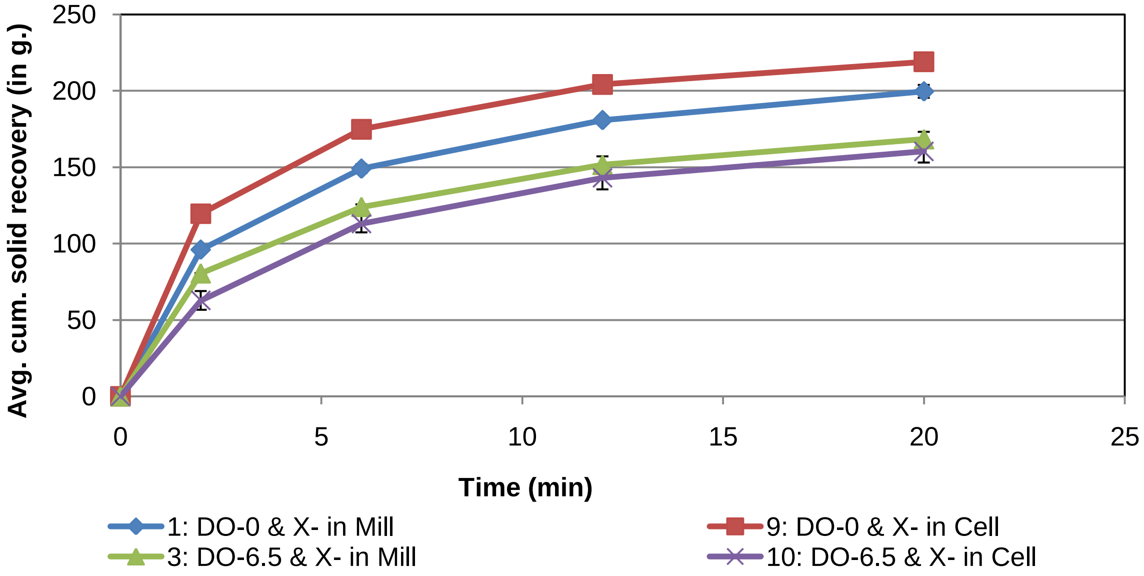

Figure 4.38: Average cumulative solid recovery vs. time plot at varying xanthate addition point

Figure 4.39 show the cumulative water recovery-time results for the tests conducted under the specified grinding and flotation conditions. It can be seen that the xanthate addition point did had an effect on the overall water recovery when the ore was ground at a DO concentration of 0 ppm. However, there was virtually no difference in the overall water recovery when the ore was ground at a DO concentration of 6.5 ppm.

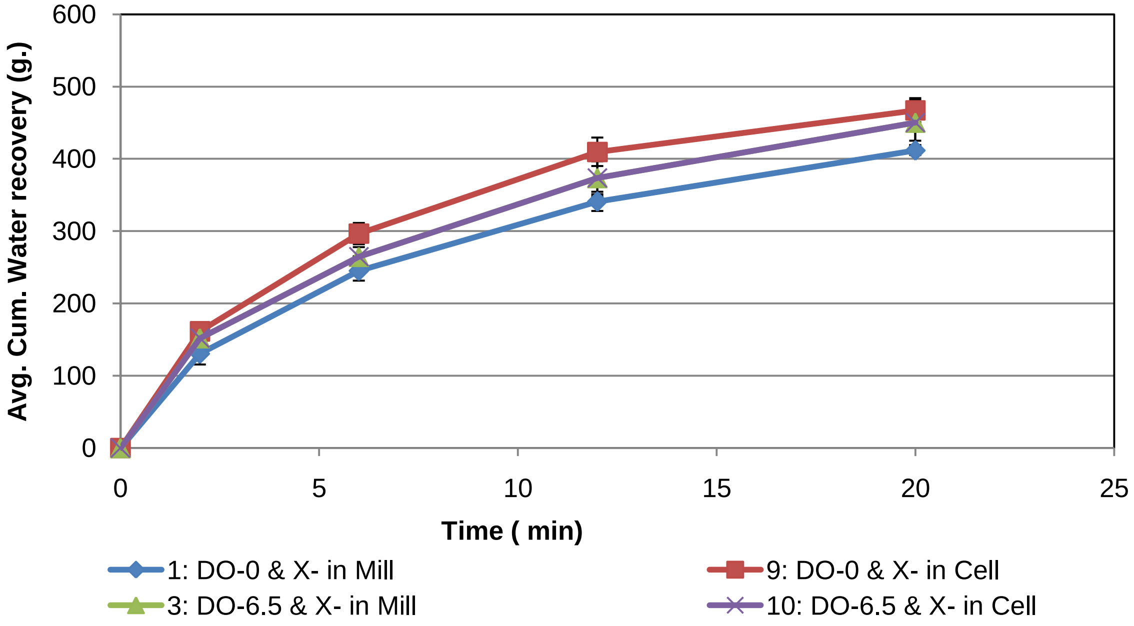

Figure 4.39: Average cumulative water recovery vs. time plot at varying xanthate addition point

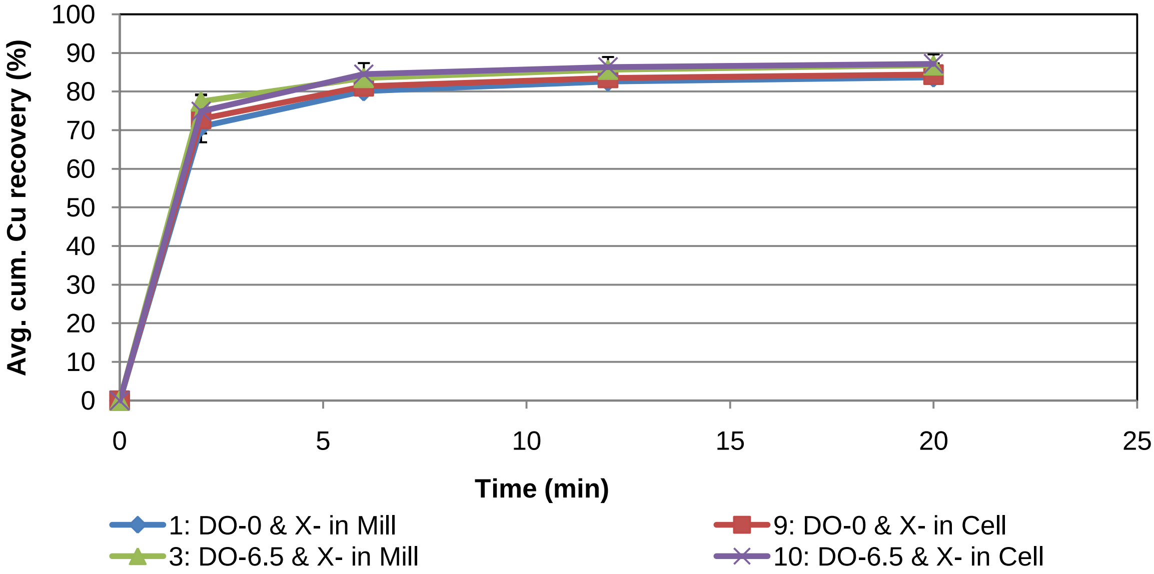

Figure 4.40 shows the cumulative Cu recovery-time results for the tests conducted under the specified grinding and flotation conditions. It can be seen that varying the xanthate addition point within different grinding environments had little effect on the floatability of Cu.

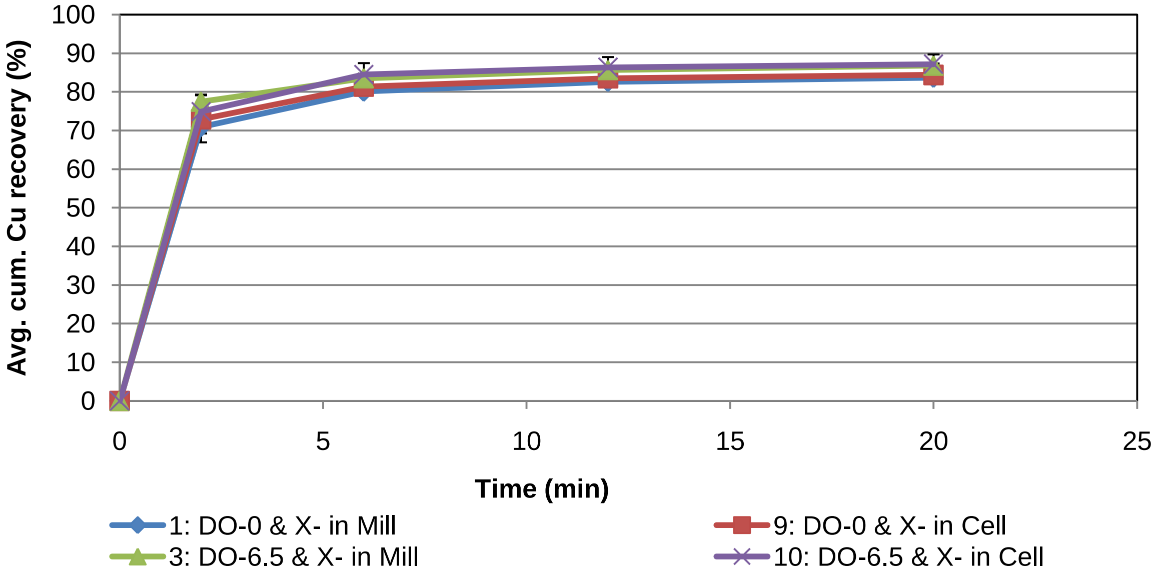

Figure 4.40: Average cumulative Cu recovery vs. time plot at varying xanthate addition point

Figure 4.41 shows the cumulative Ni recovery-time results for the tests conducted under the specified grinding and flotation conditions. It can be seen that the Ni recovery at the end of flotation was more or less independent of the xanthate addition point but was mostly dependent on the grinding environment.

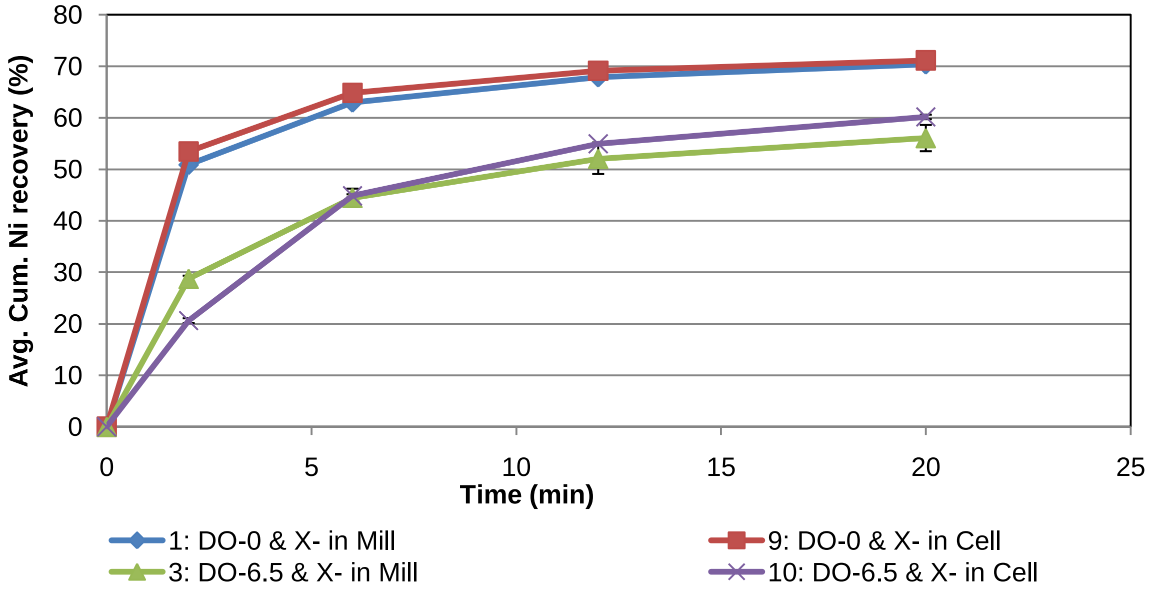

Figure 4.41: Average cumulative Ni recovery vs. time plot at varying xanthate addition point

Figure 4.42 shows the cumulative Po recovery-time results for the tests conducted under the specified grinding and flotation conditions. It can be seen that when xanthate was added into the cell, it produced a higher overall Po recovery and was independent of the grinding environment.

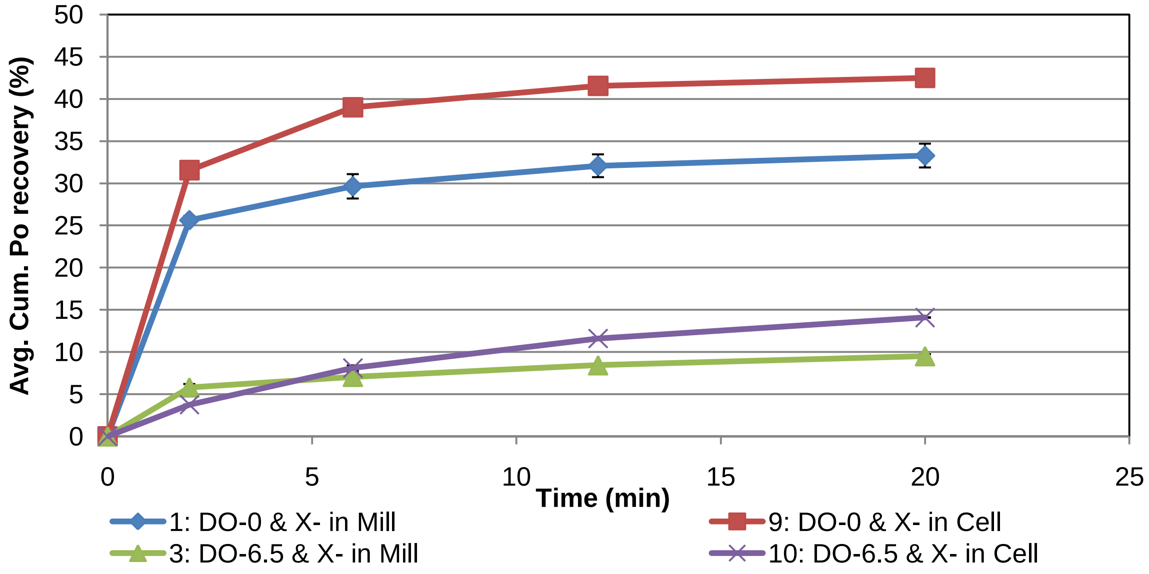

Figure 4.42: Average cumulative Po recovery vs. time plot at varying xanthate addition point

4.6.2 Solid Recovery data

The final solid and water recoveries for different grinding and flotation conditions are shown in Figure 4.43. It can be seen that there was a substantial increase in the amount of solid recovered when the ore was ground at DO concentration of 0 ppm and xanthate was added into the float cell (Test-9). This is to be compared with the test in which xanthate was added into the mill (Test-1) under similar grinding conditions. However, when the slurry was ground at DO concentration of 6.5 ppm, the amount of solid recovered was very similar irrespective of whether the xanthate was added in the mill or cell (Test-3 and Test-10). The maximum recovery of water was recorded in Test-9 and water recovery was found to be the least in Test-3. The major effect was clearly the DO level rather than the location of the xanthate.

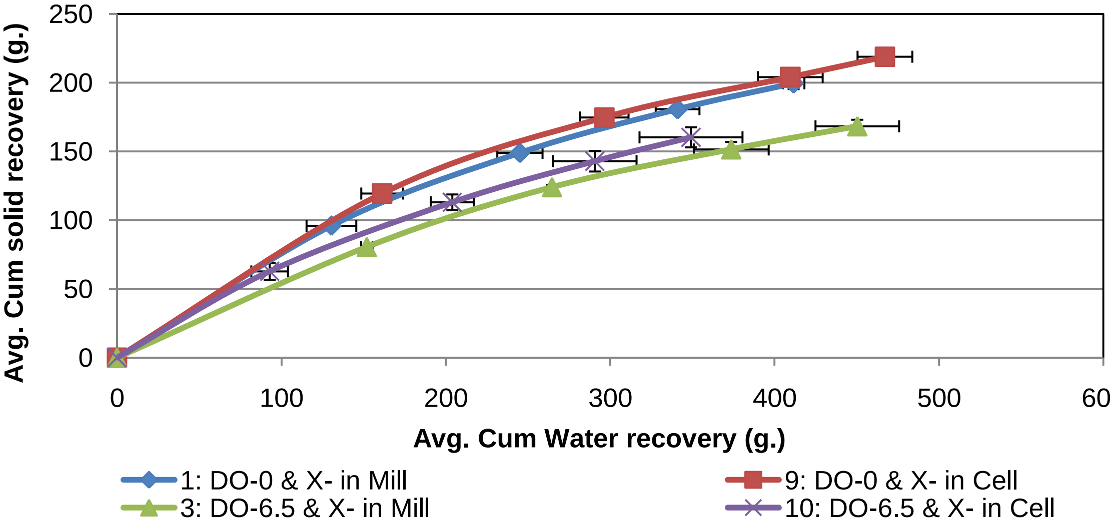

Figure 4.43: Average cumulative solid-water recovery graph with varied xanthate addition point

4.6.3 Grade-recovery data

Figure 4.44 shows the cumulative grade-recovery results for the tests conducted under the specified grinding and flotation conditions. It can be seen that the grade– recovery curves of the four tests were divided into two categories i.e. grinding at DO-0 (Test-1 and Test-9) and grinding at DO-6.5 (Test-3 and Test-10). Although the Cu recoveries under all the specified test conditions were similar, there was a significant difference in the grade between the two categories. Varying xanthate addition points did not produce any significant change in the overall grades and recoveries of Cu and again DO levels during grinding had the major impact.

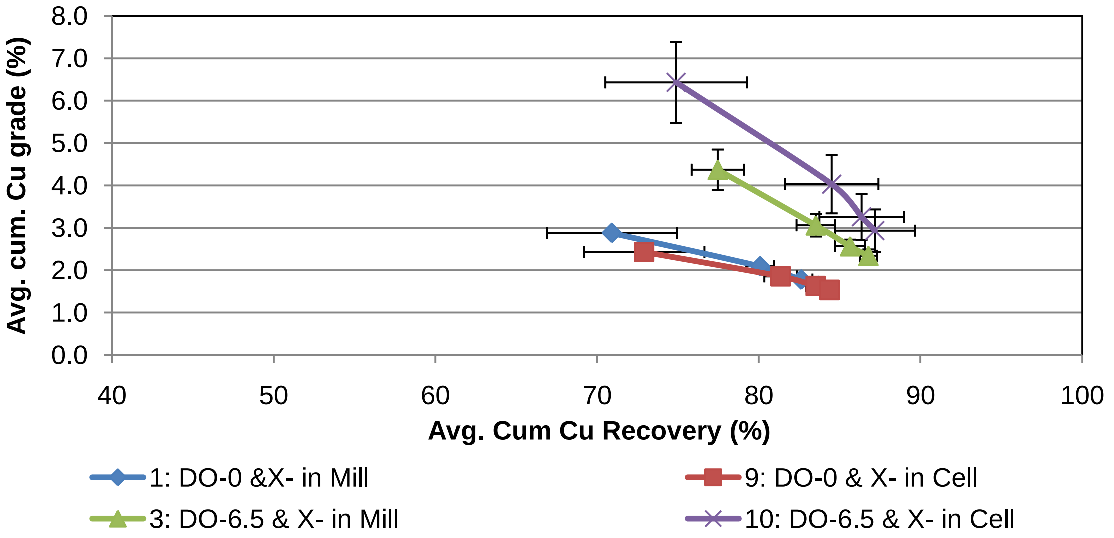

Figure 4.44: Average cumulative Cu grade-recovery graph with varied xanthate addition point

Figure 4.45 shows the cumulative Ni grade-recovery results for the tests conducted under the specified grinding and flotation conditions. Again, in all cases, a higher oxygen concentration during the grinding stage caused a significant deterioration in the performance and was independent of the xanthate addition point. Ni grade–recovery curves can be divided into two categories as specified above. The recoveries of Ni for the two categories followed the same trend. In the case of Test-9, the recovery was higher as compared to Test-1. However, in the case of DO-6.5, the order of recovery was reversed. Ni recovery was found to be lowest in Test-3. The grade of Ni was highest in Test-10 and lowest in Test-9.

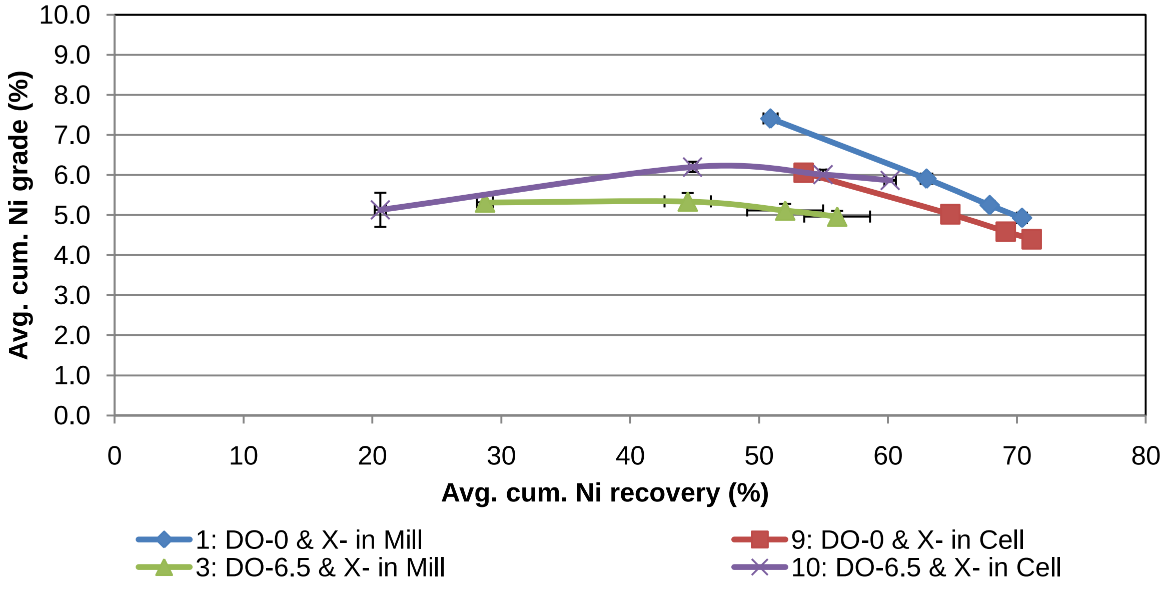

Figure 4.45: Average cumulative Ni grade-recovery graph with varied xanthate addition point

Figure 4.46 shows the cumulative Po grade-recovery results for the tests conducted under the specified grinding and flotation conditions. As can be seen, the presence of oxygen during the grinding stage produced extremely poor grade–recovery curves compared to test conducted in the absence of oxygen (DO-0). Po grade–recovery curves can be also divided into two categories as in the case of Ni. It can be seen that the addition of xanthate into the cell in each case had given a higher grade and recovery.

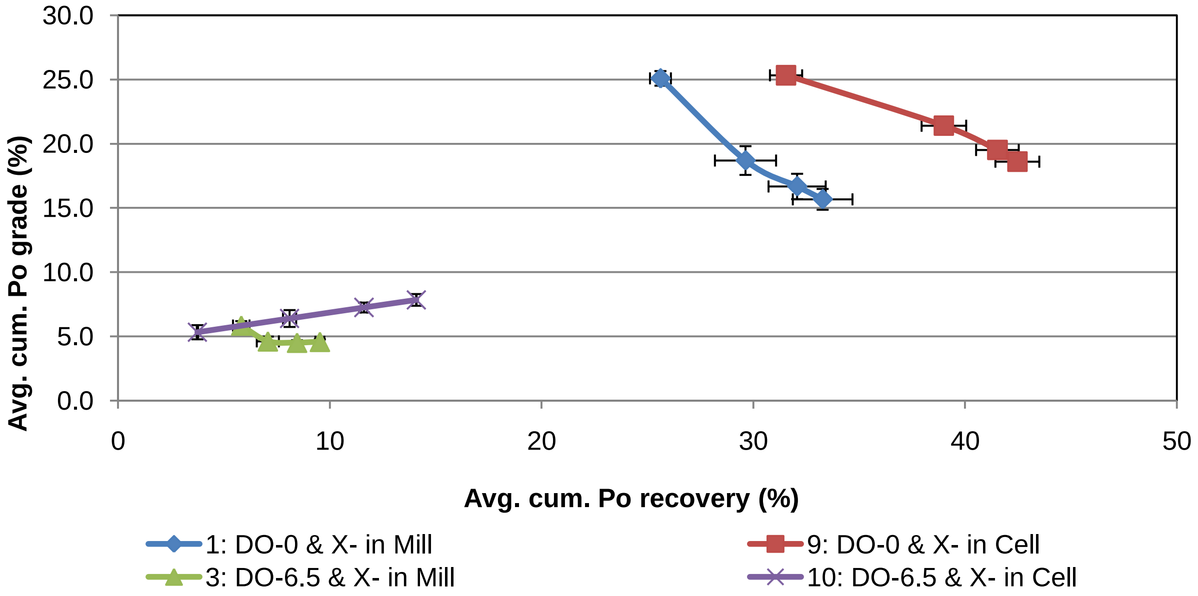

Figure 4.46: Average cumulative Po grade-recovery graph with varied xanthate addition point

4.6.4 Kinetic analysis of flotation data

Table 4.10 shows the kinetic analysis results of the tests conducted at DO concentration of 6.5 and 0, while changing the xanthate addition point. It can be seen that the kinetic parameters (ks, kf and Øs) of the Cp remained almost unaffected by the change in the xanthate addition point. In case of Pn, the rate of flotation of the fast floating component remained unchanged in case of Test-1 and test-9 but there were differences in this rate between Test-3 and Test-10. The fraction of slow floating component of Pn shows only marginal differences in Test-1 and Test-9, but there were notable differences between Test-3 and Test-10. The rate constant of the slow floating component of Po is negligible in all the cases. However, the rate constant of the fast floating component in Test-1 and Test-9 lies on the same line but in case of test-3 and test there was a huge difference in the rate of slow floating component. There was also a big difference between the slow floating fraction of Po in Test-1 and Test-9. Further there were also a notable difference between slow floating fraction of Test-3 and Test-10.

Table 4.10: Kinetic analysis of batch flotation test results based on Kelsall model

Test Number	Cp			Pn			Po		
	ks	kf	Øs	ks	kf	Øs	ks	kf	Øs
Test-1	0.01±0.00	1.11±0.35	0.21±0.01	0.02±0.00	0.86±0.01	0.40±0.00	0.00±0.00	1.07±0.33	0.72±0.02
Test-3	0.01±0.00	1.38±0.03	0.18±0.02	0.01±0.00	0.50±0.04	0.57±0.03	0.00+0.00	1.09±0.03	0.94±0.01
Test-9	0.01±0.00	1.16±0.18	0.20±0.01	0.01±0.00	0.90±0.02	0.37±0.00	0.01±0.00	0.83±.01	0.62±0.01
Test-10	0.01±0.00	1.11±0.10	0.16±0.03	0.01±0.00	0.23±0.00	0.43±0.01	0.00+0.00	0.14±0.03	0.87±0.01

4.7 Varying Eh through pH control at DO-0 and no gas control

In Section 4.4, it was observed that the grade and recovery was dependent on Eh (ORP) of the pulp. Further, the addition of lime on plant is mainly to improve the grade of the valuable minerals and enhance the selectivity (Sutherland and Wark, 1955). Keeping this in mind, the tests which gave maximum recovery in Section 4.4 (i.e. Test-1) and normal milling conditions (No gas control during grinding i.e. DO-5.5) were chosen, in order to compare the effect of pH, its influence on the Eh of the pulp and consequently on the floatability of the valuable minerals. Table 4.11 shows the resultant pulp chemistry readings recorded at the specified test conditions. The Eh, pH and DO profiles recorded during grinding are shown in Appendix-1. It is to be noted that a slightly higher pH was recorded when the ore was ground at DO concentration of 0 ppm as compared to DO concentration of 5.5 ppm.

Table 4.11: Resultant pulp chemical readings recorded in the Magotteaux Mill discharge

Test number	Test Condition/ Name	DO concentration	Eh (ORP)	pH
1.	pH-9.2 and DO-0	0	-160 to -180 mV	9.2-9.3
11.	pH-10 and DO-0	0	-180 to -205 mV	10.2-10.4
12.	pH-11 and DO-0	0	-205 to -230 mV	11.2-11.6
13.	pH-9.2 and DO-5.5	5.0 to 5.5	220 to 230 mV	9.0-9.2
14.	pH-10 and DO-5.5	5.0 to 5.5	195 to 190 mV	9.95- 10.1
15.	pH-11 and DO-5.5	5.0 to 5.5	150 to 140 mV	10.95-11.2

4.7.1 Varying pH at DO concentration of 0 ppm

4.7.1.1 Recovery time results

Figure 4.47 shows the cumulative solid recovery-time results for the tests conducted at DO-0 and varying pulp pH. It can be seen that the solid recovered at pH-9.2 (Test-1) was significantly higher compared to pH-10 (Test-11) and pH-11 (Test-12).

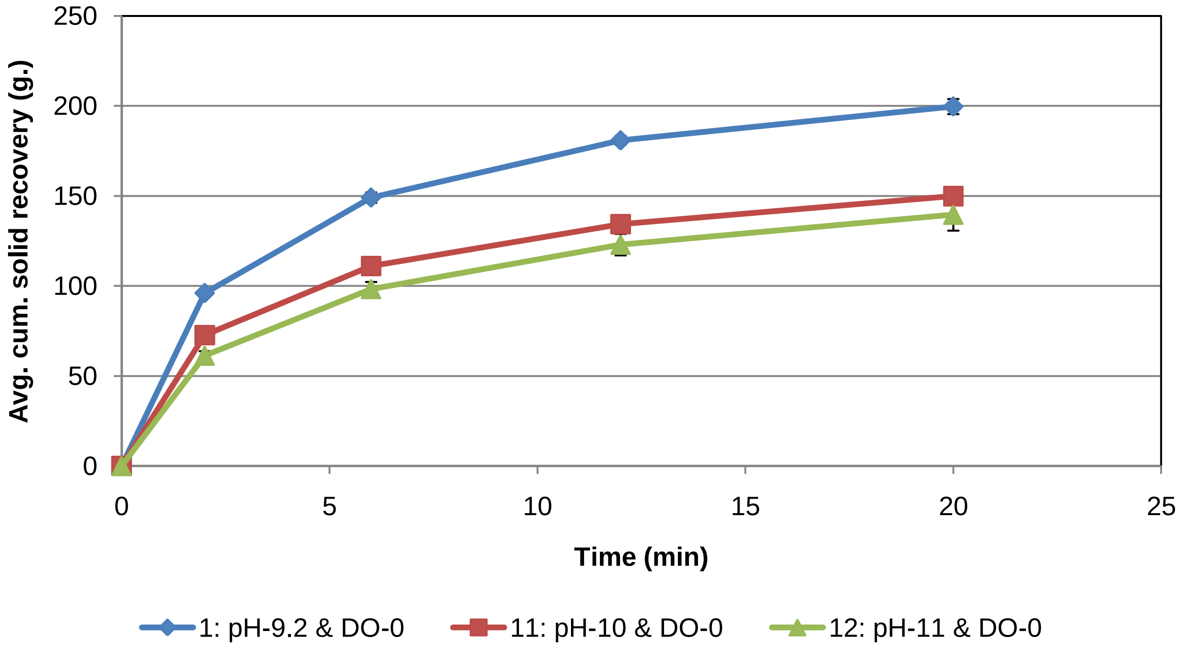

Figure 4.47: Average cumulative solid recovery vs. time plot at different pH and DO-0

Figure 4.48 shows the cumulative water recovery-time results for the tests conducted at DO concentration of 0 ppm and varying pulp pH. It can be seen that the water recovery in Test-12 was significantly lower compared to Test-1 and Test-11 which were almost identical.

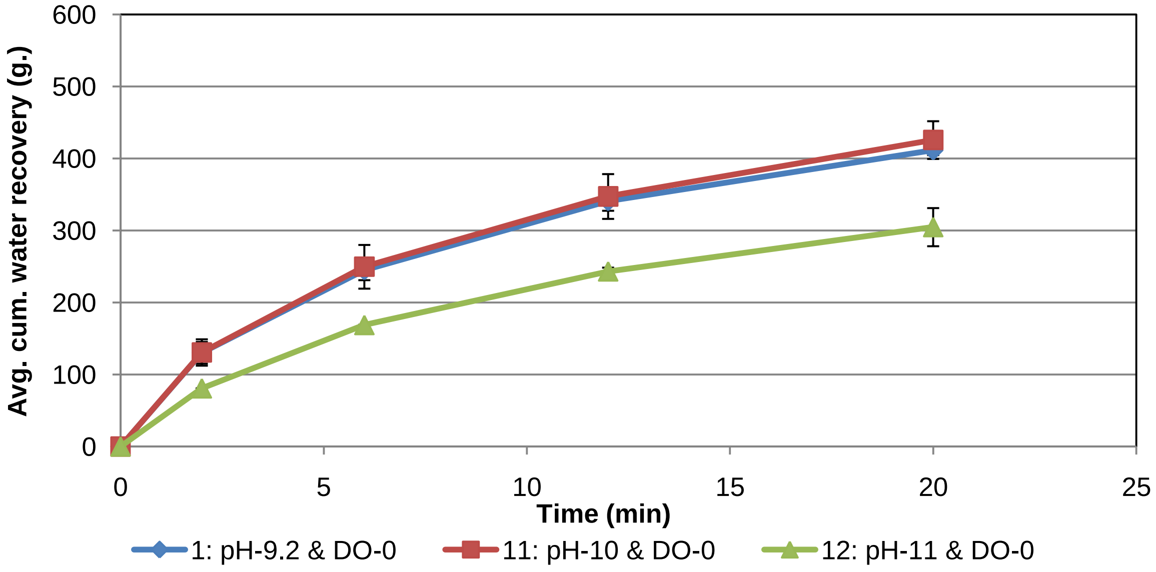

Figure 4.48: Average cumulative water recovery vs. time plot at different pH and DO-0

Figure 4.49 shows the cumulative Cu recovery-time results for the tests conducted at DO-0 and varying pulp pH. It can be seen that varying pulp pH had virtually no effect on the floatability of Cu.

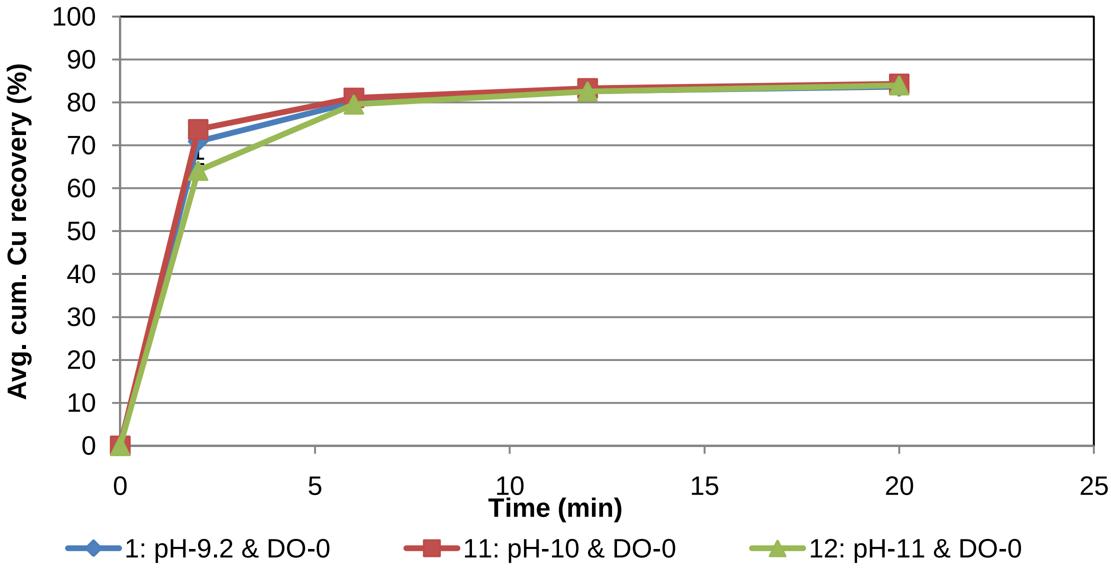

Figure 4.49: Average cumulative Cu recovery vs. time plot at different pH and DO-0

Figure 4.50 shows the cumulative Ni recovery-time results for the tests conducted at DO-0 and varying pulp pH. It can be seen that the overall Ni recovery in Test-11 and Test-12 were similar but lower than in the case of Test-1.

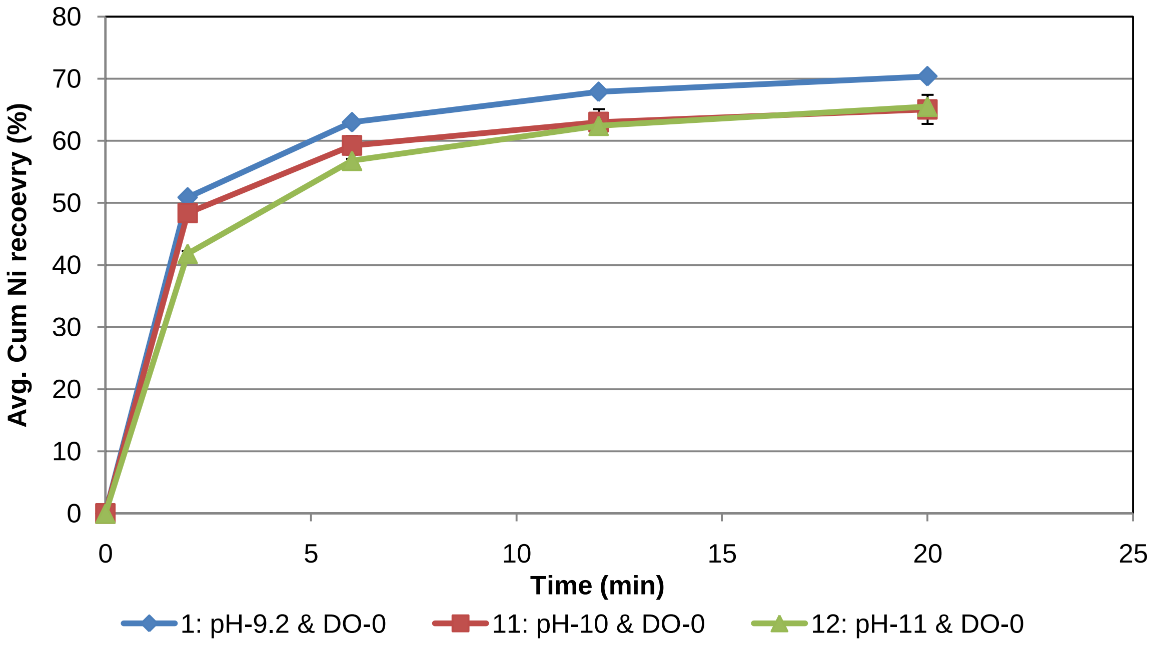

Figure 4.50: Average cumulative Ni recovery vs. time plot at different pH and DO-0

Figure 4.51 shows the cumulative Po recovery-time results for the tests conducted at DO-0 and varying pulp pH. The recovery at pH = 9.2 was much greater than for the higher pHs.

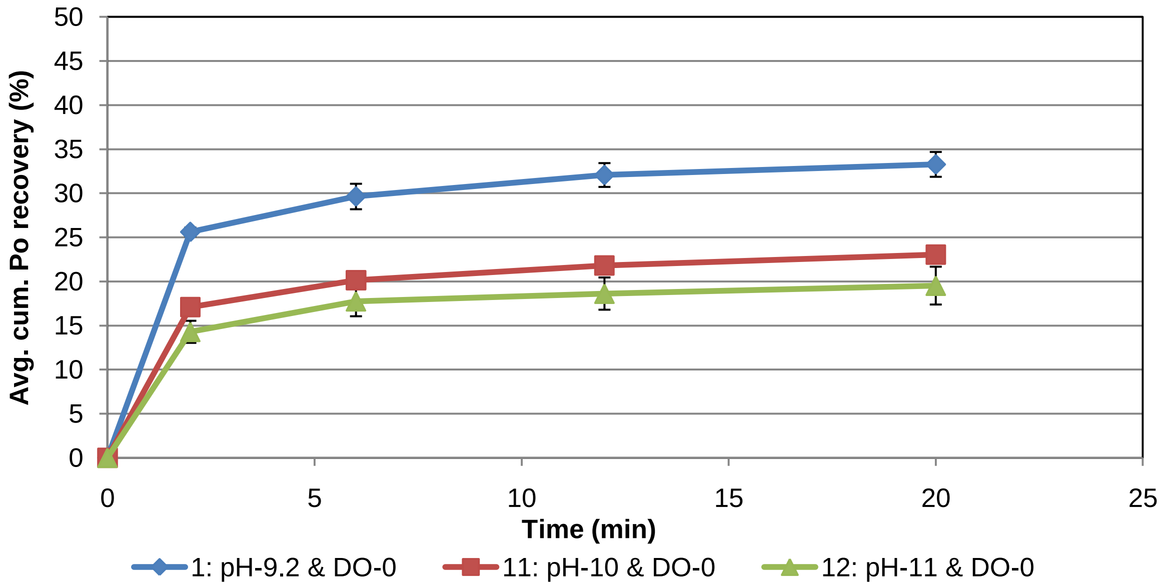

Figure 4.51: Average cumulative Po recovery vs. time plot at different pH and DO-0

4.7.1.2 Solid Recovery data

Figure 4.52 shows the final solid and water recoveries at DO concentration of 0 ppm and different pH conditions. These were the conditions which yielded the lowest Ni grades. It can be seen that the amount of solid recovered at the end of flotation was highest at pH-9.2 (Test-1) indicating an increase in non-selective solid pull. As the pH increases the solid recoveries continuously drop. However, the water recoveries did not show the same systematic change with the variation of pH.

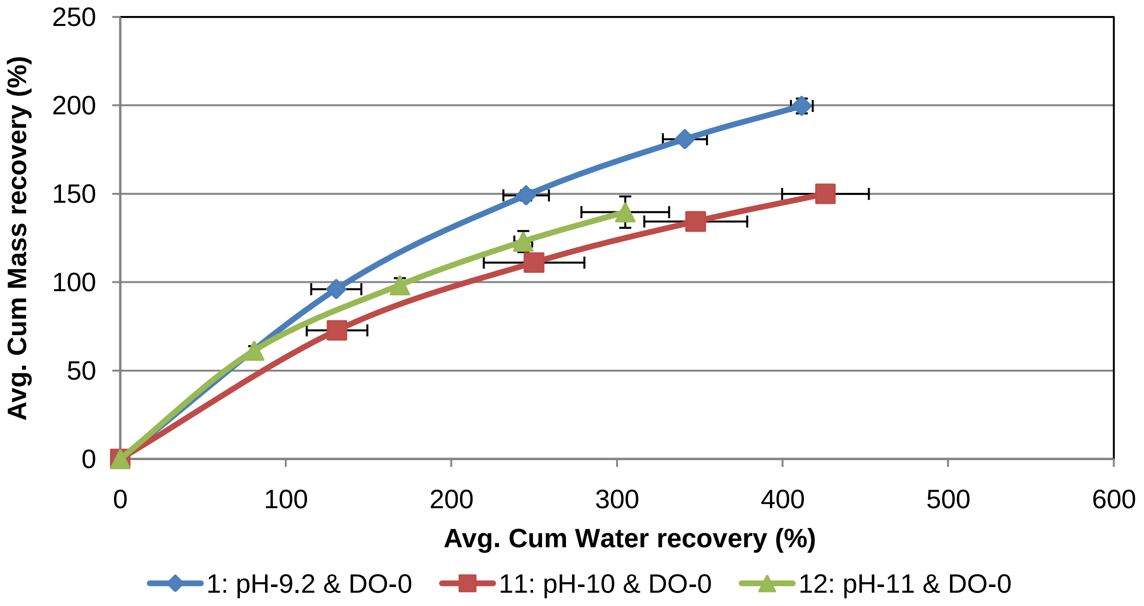

Figure 4.52: Average cumulative solid-water recovery graph at different pH and DO-0

4.7.1.3 Grade recovery data

Figure 4.53 shows the cumulative Cu grade–recovery at DO-0 and varying pH conditions. It can be seen that the overall recovery of Cu at different pH conditions varied in a narrow range. However, a significant improvement in the grade of Cu was observed with the increase of pH.

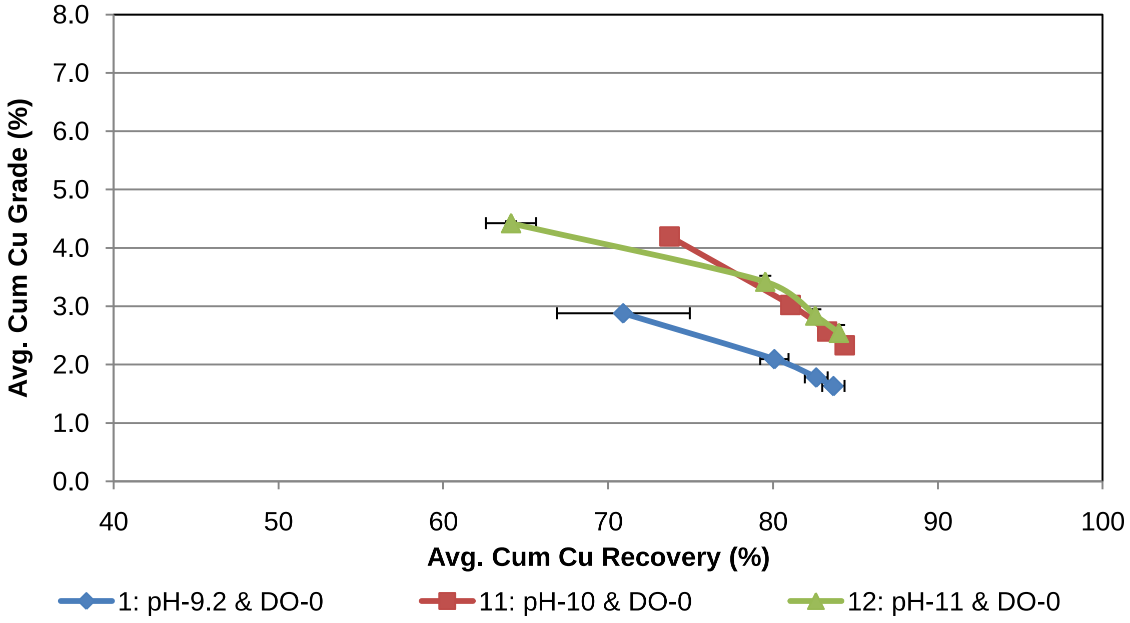

Figure 4.53: Average cumulative Cu grade-recovery at different pH and DO-0

Figure 4.54 shows the cumulative Ni grade–recovery at DO-0 and different pH values. At pH = 10 and 11 the recoveries were less than at pH = 9.2 but the grades marginally greater.

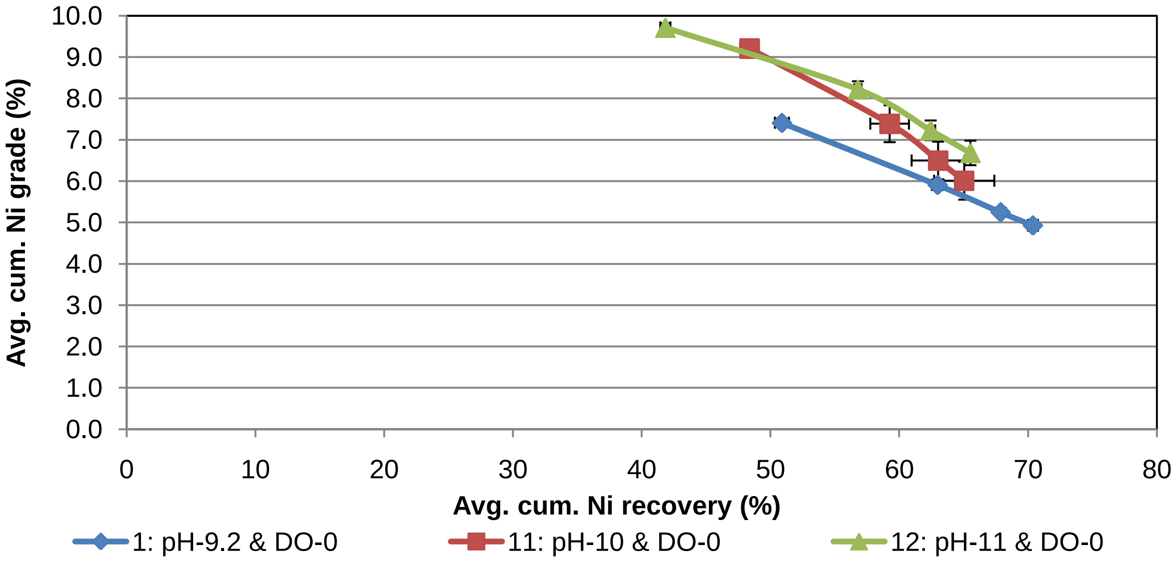

Figure 4.54: Average cumulative Ni grade-recovery at different pH and DO-0

Figure 4.55 shows the cumulative Po grade–recovery at DO-0 and different pH values. It can be seen that a higher pH at the grinding stage produced significantly poorer grades and recoveries of Po compared to pH-9.2.

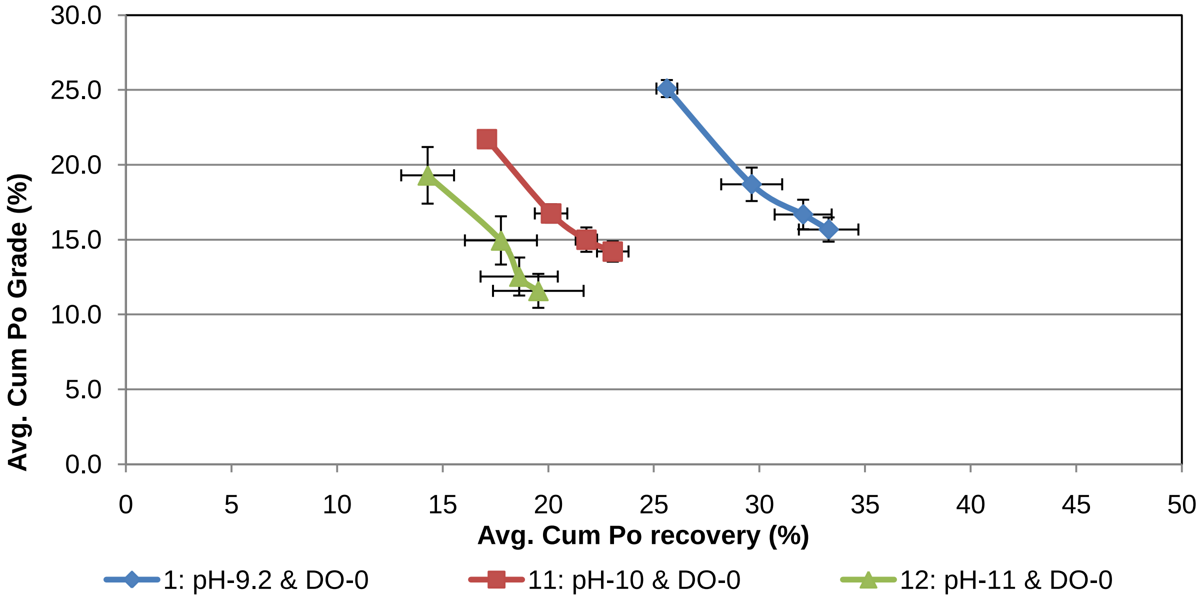

Figure 4.55: Average cumulative Po grade-recovery at different pH and DO-0

The effect of oxygen and pH during the grinding stage is evident in Figure 4.56 . As can be seen, the mixed potentials of the system are more cathodic at a higher pH. The variation in the pH produces a change in the Eh (SHE) of the pulp but they all fall within a very close range for each individual mineral. The change in pH did not have any significant effect on the recoveries of the Cu or Ni with a slight decrease in the latter case as pH increased from 9.2 to 10. There was a significant decrease in the Po recovery as the pH increased.

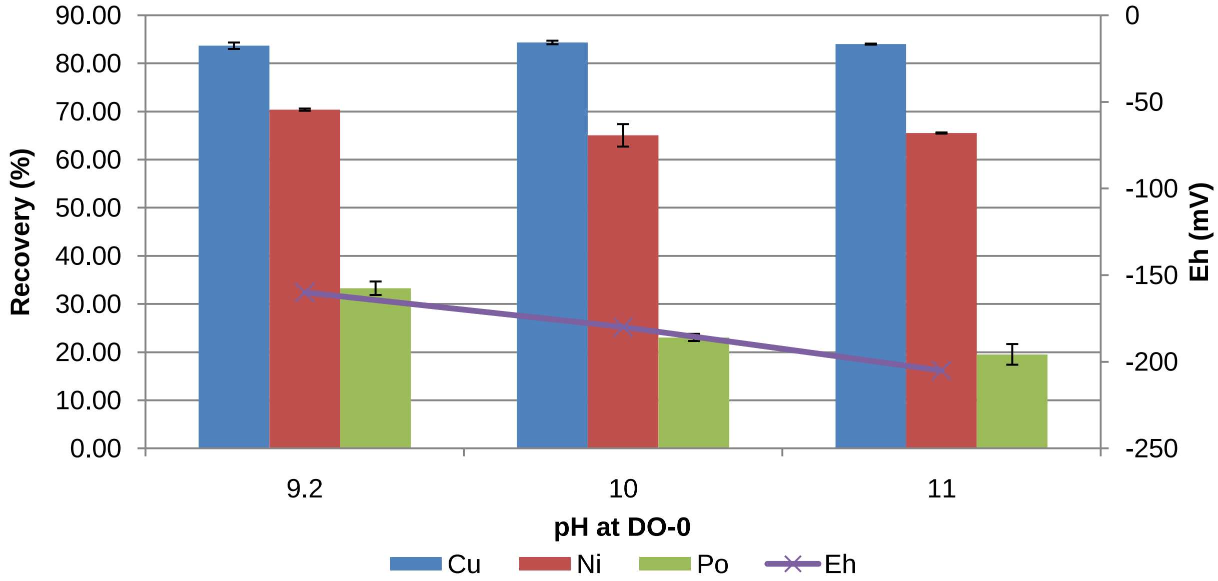

Figure 4.56: Variation of mineral recovery with respect to Eh by controlling pH at DO-0 during grinding

4.7.1.4 Kinetic analysis of flotation Results

Table 4.12 shows the kinetic analysis of the recovery-time data using Kelsall model. The most noticeable result was that the fast floating rate constant (kf) was lowest for all three minerals for Test-12 i.e. pH = 11. Apart from that there were also notable differences in the slow floating fraction of the Po at pH-10 and pH-11 in compared to pH-9.2.

Table 4.12: Kinetic analysis of batch flotation test results based on Kelsall model

Test Number	Cp			Pn			Po		
	ks	kf	Øs	ks	kf	Øs	ks	kf	Øs
1	0.01±0.00	1.11±0.35	0.21±0.01	0.02±0.00	0.86±0.01	0.40±0.00	0.00±0.00	1.07±0.33	0.72±0.02
11	0.01±0.00	1.16±0.01	0.20±0.00	0.01±0.00	0.88±0.01	0.43±0.01	0.00+0.00	1.04±0.01	0.81±0.01
12	0.02±0.00	0.88±0.08	0.22±0.00	0.01±0.00	0.68±0.03	0.46±0.01	0.00+0.00	0.85±0.01	0.83±0.01

4.7.2 Varying pH in the absence of gas control

4.7.2.1 Recovery time data

Figure 4.57 shows the cumulative solid recovery-time results for the tests conducted at DO concentration of 5.5 ppm and varying grinding pH. It can be seen that the amount of solid recovered followed a decreasing trend with the rising pH. Solid recovery was highest in Test-13 and lowest in Test-15.

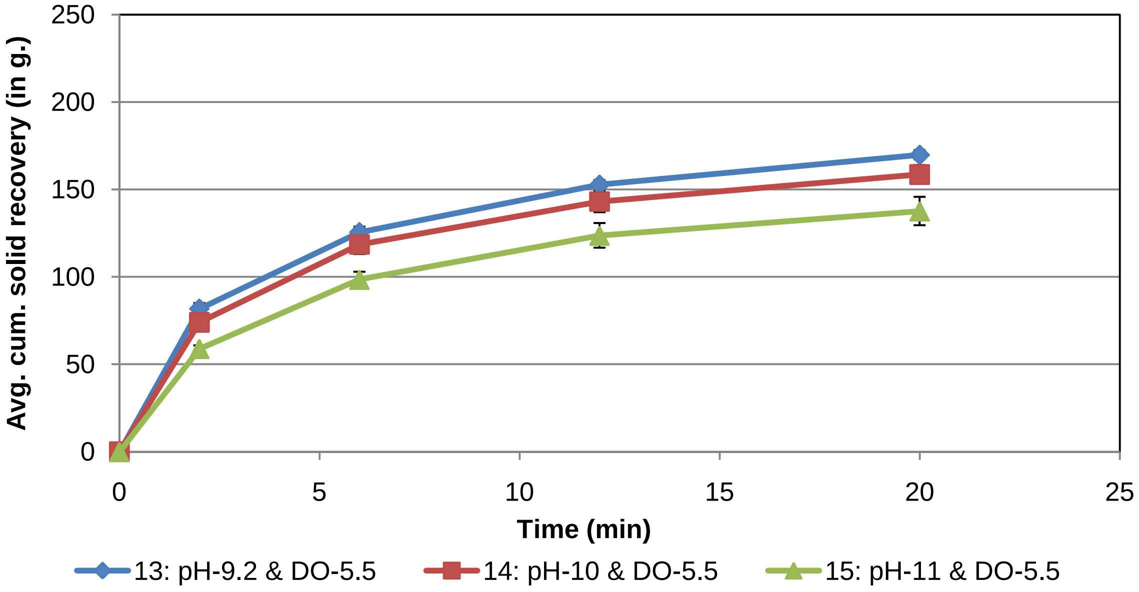

Figure 4.57: Average cumulative solid recovery vs. time plot at different pH and DO-5.5

Figure 4.58 shows the cumulative water recovery-time results for the tests conducted at DO concentration of 5.5 and varying pulp pH during grinding. It can be seen that the amount of water recovered in Test-13 and Test-15 lie in the same range. Water recovery hardly changed at different pHs.

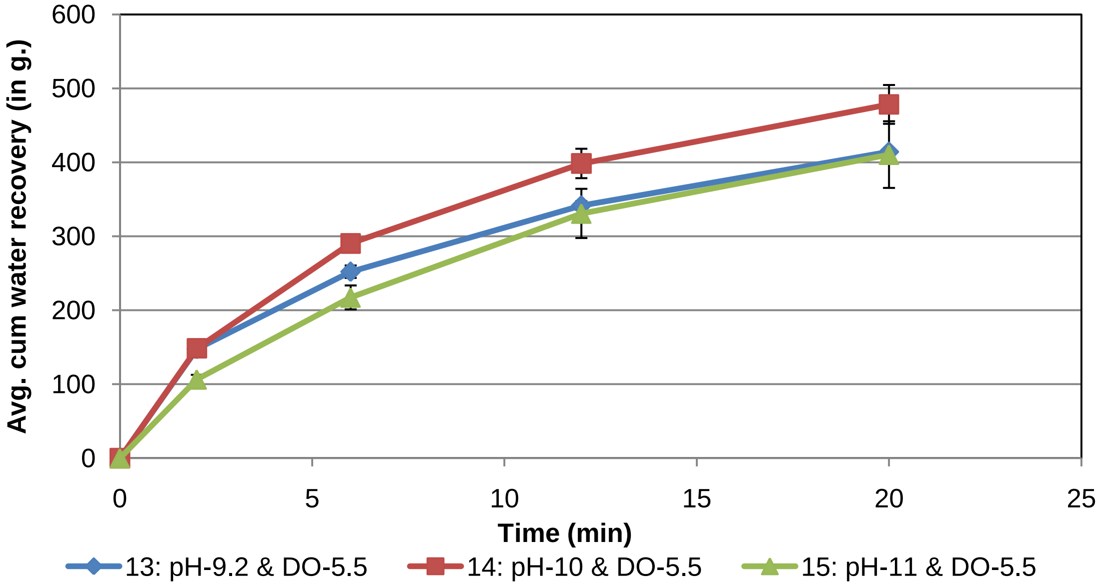

Figure 4.58: Average cumulative water recovery vs. time plot at different pH and DO-5.5

Figure 4.59 shows the cumulative Cu recovery-time plot for the tests conducted at DO concentration of 5.5 ppm and varying pulp pH during grinding. It can be seen that varying pulp pH had virtually no influence on the floatability of Cu.

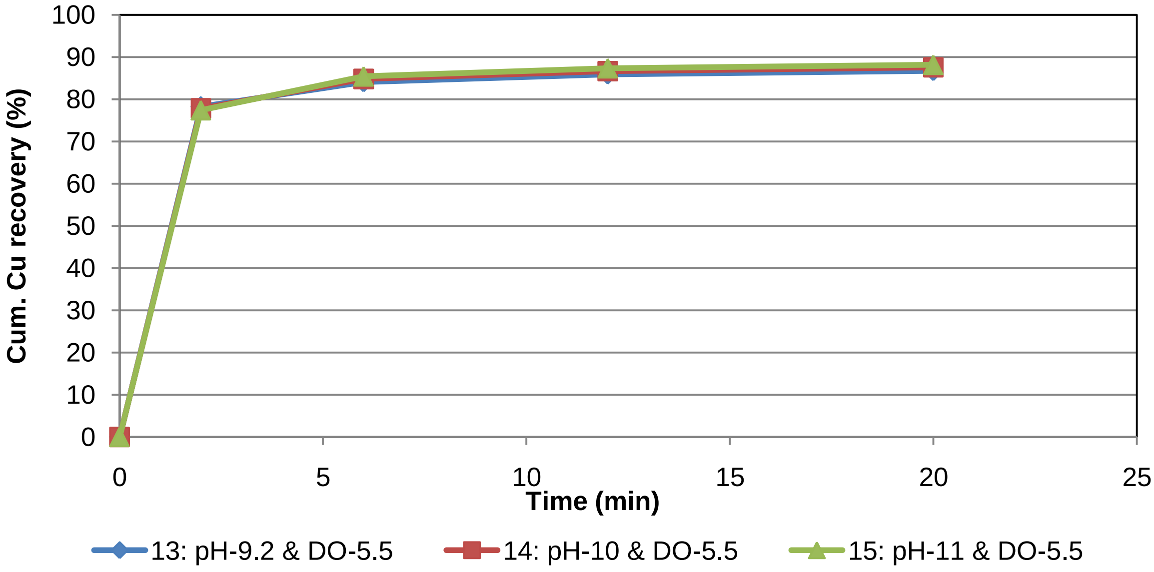

Figure 4.59: Average cumulative Cu recovery vs. time plot at different pH and DO-5.5

Figure 4.60 shows the cumulative Ni recovery-time results for the tests conducted at DO-5.5 and varying pulp pH. It can be seen that there were significant differences in the Ni recoveries, which appears to be related to the pH of the pulp with recoveries decreasing as pH increased.

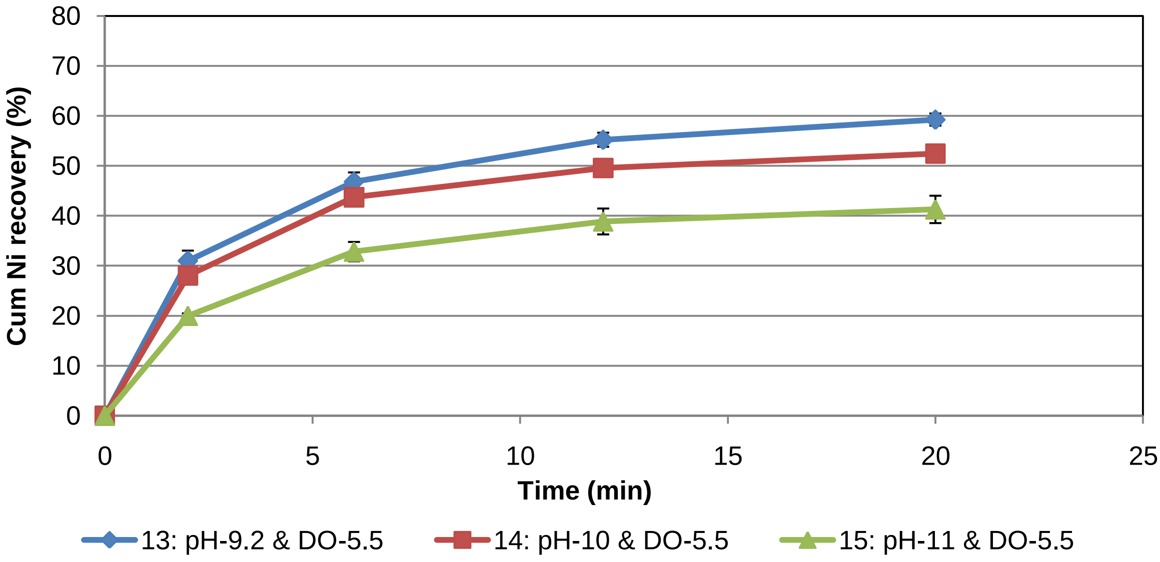

Figure 4.60: Average cumulative Ni recovery vs. time plot at different pH and DO-5.5

Figure 4.61 shows the cumulative Po recovery as a function of time for the tests conducted at DO concentration of 5.5 ppm and varying pulp pH. It can be seen that the Po recovery was lowest in Test-15 but in fact generally very low.

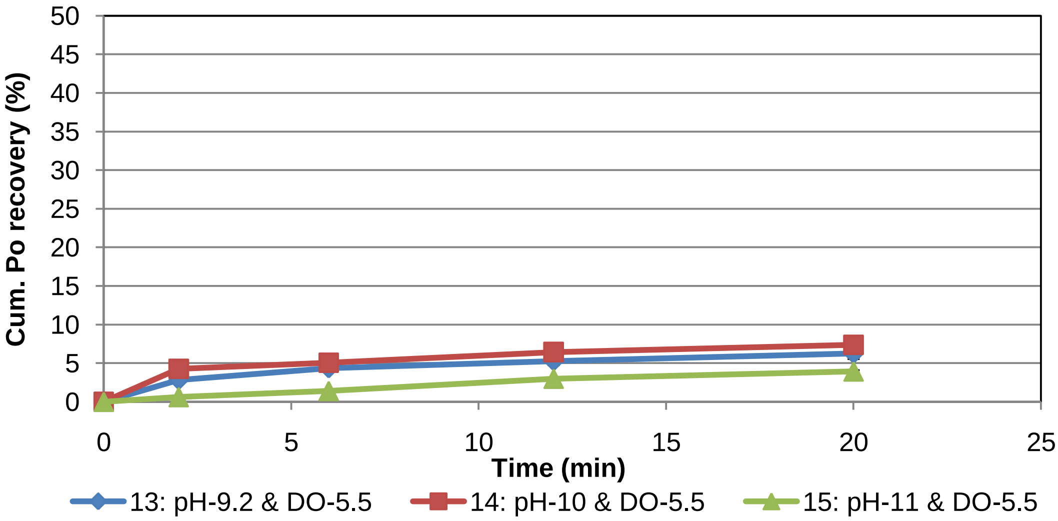

Figure 4.61: Average cumulative Po recovery vs. time plot at different pH and DO-5.5

4.7.2.2 Solid- water recovery data

Figure 4.62 shows the final solid and water recoveries at different milling pHs while the ore was ground at DO concentration of 5.5. It can be seen that there was a slight decreasing trend in the amount of solid recovered when the slurry was ground at a higher pH. However, water recoveries did not show any systematic change with the milling pH. Solid recovery was highest for Test-13 and lowest for Test-15.

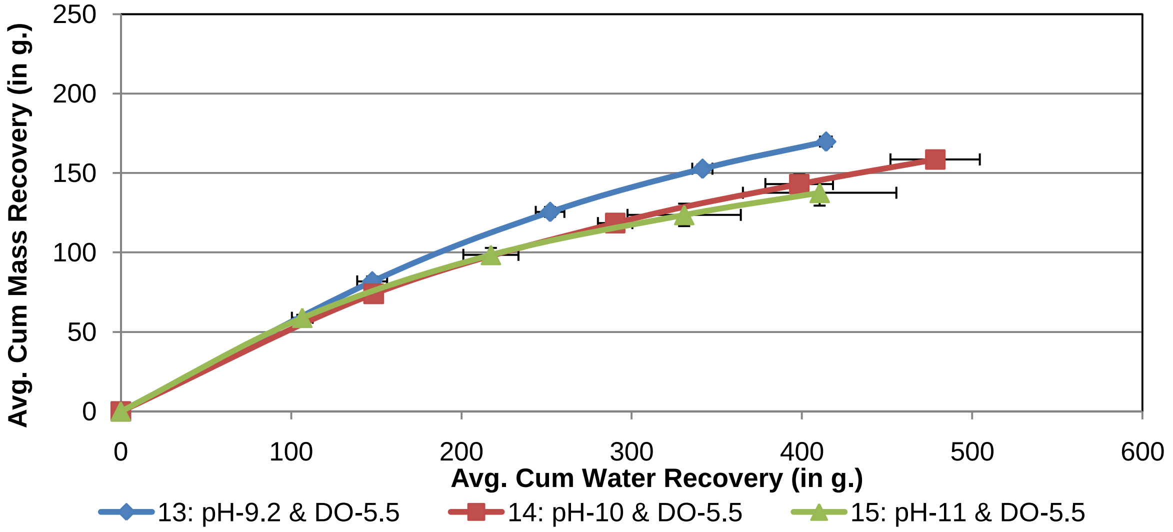

Figure 4.62: Average cumulative solid-water recovery graph at different pH in the mill

4.7.2.3 Grade-recovery data

Figure 4.63 shows the cumulative Cu grade–recovery performance at DO concentration of 5.5 while varying the pH. It can be seen that as the pH increases the grade of the Cu increases, while the recovery was more or less independent of the pH.

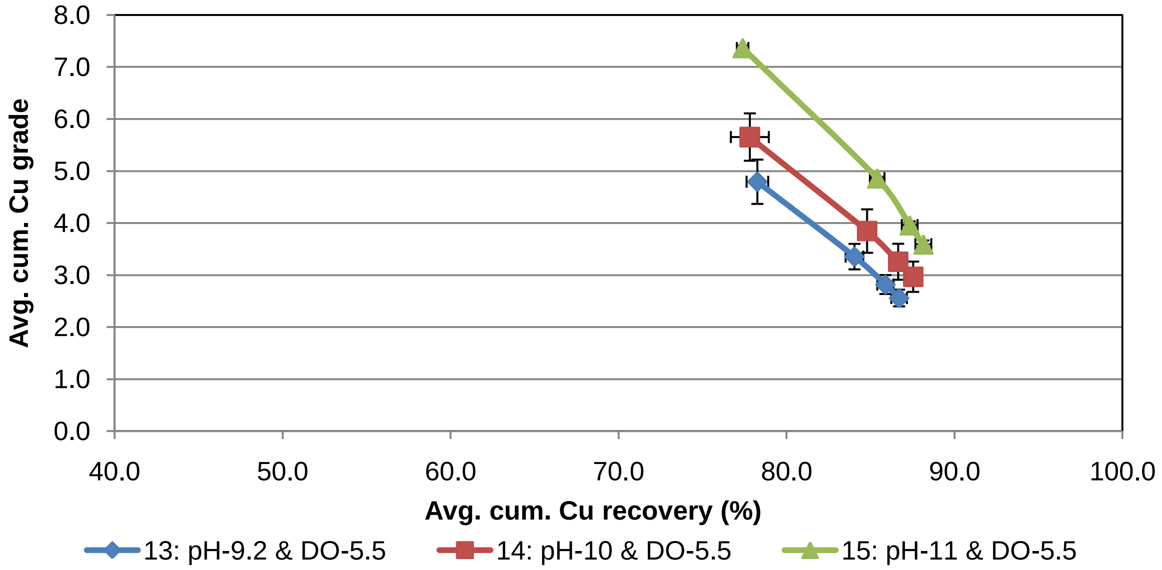

Figure 4.63: Average cumulative Cu grade-recovery at different pH in the mill

Figure 4.64 shows the cumulative Ni grade–recovery performance at DO concentration of 5.5 while varying the pH. In all cases, a higher pH during grinding caused a significant deterioration in the performance in comparison with the pH-9.2. The variation in the grade and recovery of the Ni was consistent with the variation in the pulp pH. The overall recoveries of the Ni in Test-14 and Test-15 were considerably lower than the recovery that was obtained in Test-3.

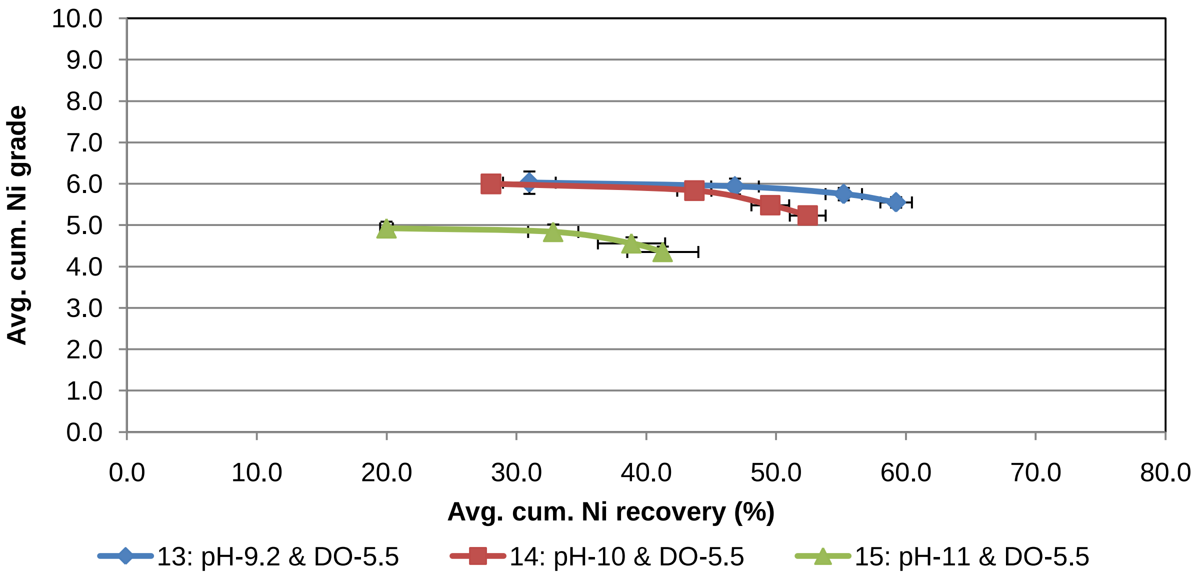

Figure 4.64: Average cumulative Ni grade-recovery at different pH in the mill

Figure 4.65 shows the cumulative Po grade–recovery performance at DO concentration of 5.5 while varying the pH. Clearly at this high DO level the grades and recoveries were very low for all pHs with recoveries being about 5-8% and grades about 4%.

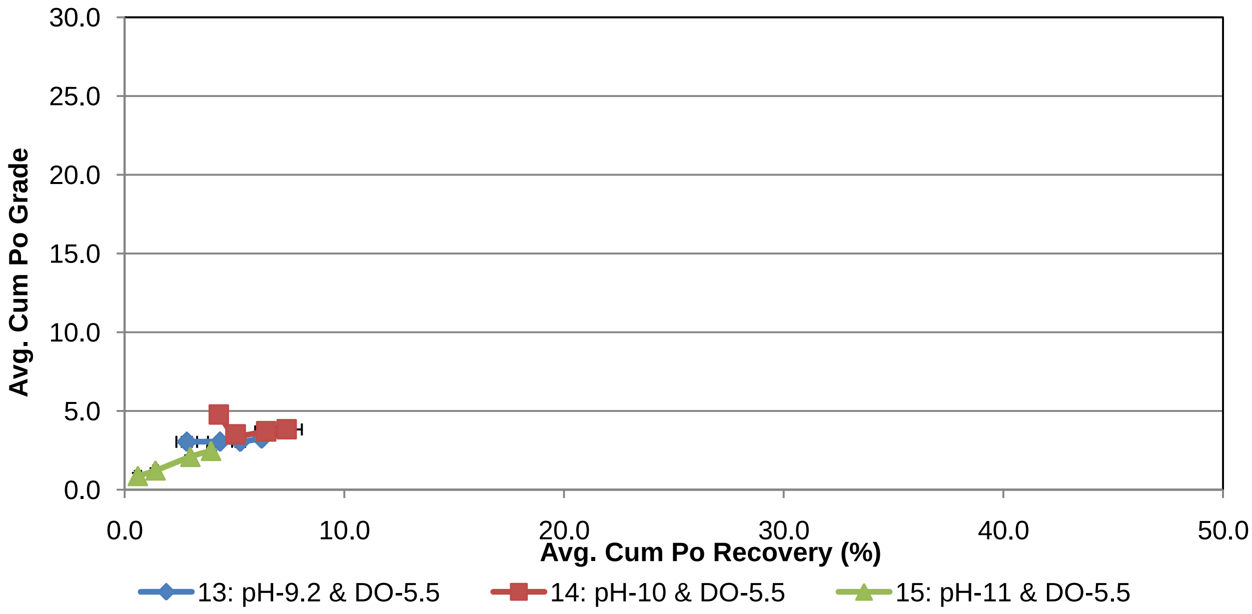

Figure 4.65: Average cumulative Po grade-recovery at different pH in the mill

The effect of pH control during the grinding stage on the valuable mineral recovery and Eh is shown in

Figure 4.66. It can be seen that at a higher pH, the mixed potentials or Eh (SHE) of the system were more anodic than at pH-9.2. Cu recovery was virtually unaffected with the variation of pH during the grinding stage. However, a higher pH during the grinding stage resulted in a significant decrease in the recovery of Ni and already observed the recoveries of Po were always very low.

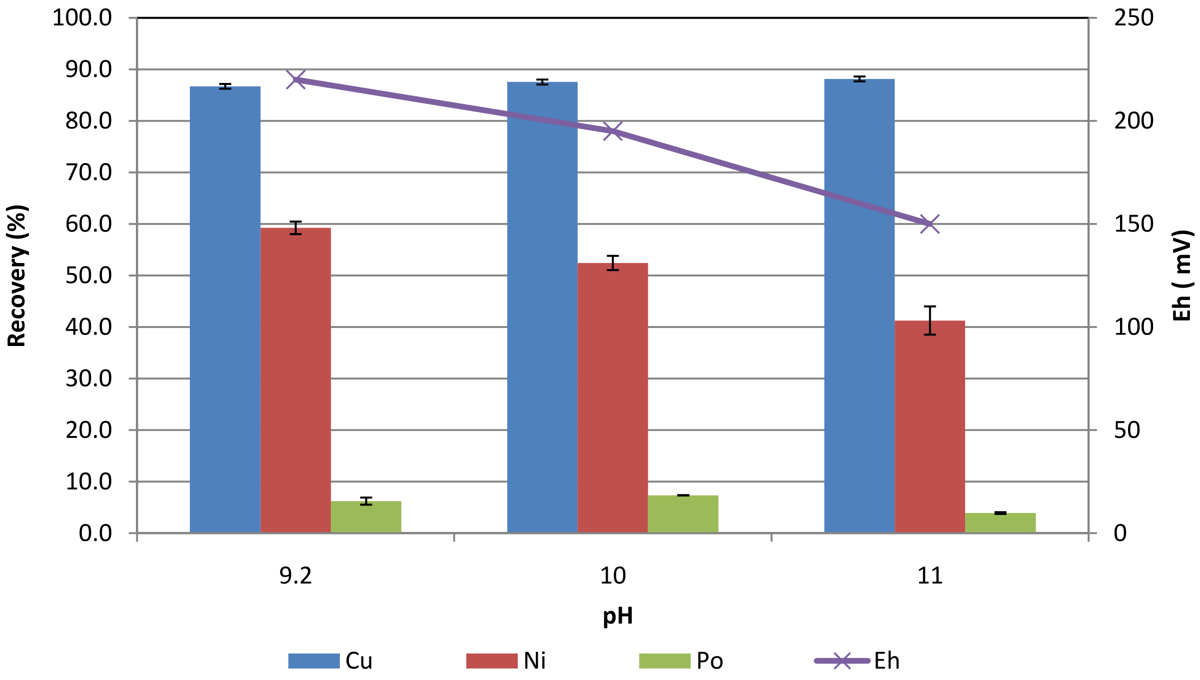

Figure 4.66: Variation of the floated element recovery with respect to Eh by controlling pH during grinding and DO-5.5

4.7.2.4 Kinetic analysis of flotation results

Table 4.13 shows the kinetic analysis of the recovery-time data using the Kelsall model. The most noticeable differences are that at pH=11 and DO=5.5 the Po was very slow floating (kf 0.05min^{-}1) and the Cp floated the slowest compared to pH=9.2 and 10. Interestingly the Pn showed a slightly higher kf value at pH = 11 but this was also the condition with the lowest slow floating fraction.

Test Number	Cp			Pn			Po		
	ks	kf	Øs	ks	kf	Øs	ks	kf	Øs
13	0.01±0.00	1.39±0.01	0.17±0.01	0.02±0.00	0.53±0.03	0.56±0.02	0.00+0.00	1.19±0.11	0.96±0.00
14	0.01±0.00	1.29±0.00	0.16±0.00	0.01±0.00	0.48±0.01	0.56±0.02	0.00+0.00	1.19±0.00	0.96±0.01
15	0.02±0.00	1.21±0.06	0.16±0.00	0.01±0.00	0.68±0.03	0.46±0.01	0.00+0.00	0.05±0.00	0.96±0.02

Table 4.13: Kinetic analysis of batch flotation test results based on Kelsall model

4.7.3 Xanthate adsorption data

Figure 4.67 shows the absorbance of xanthate using UV spectroscopy at different sampling times at DO-0 concentration. This represents a direct measure of the amount of residual xanthate in the pulp. It is noted here that the amount of xanthate remaining in the solution at a higher pH (Test-12 and Test-13) was almost double that of Test-3. However, the xanthate measurement after flotation shows that all the xanthate was consumed during 20 min of flotation

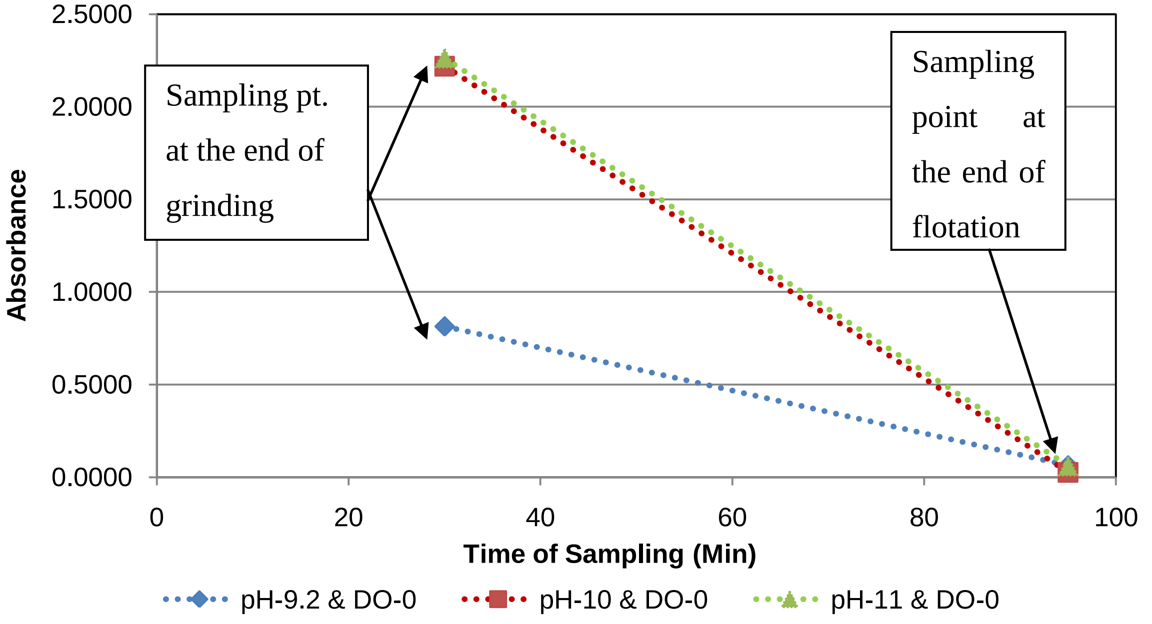

Figure 4.67: Residual concentration of xanthate left into the solution at different time interval

5 DISCUSSION

The purpose of this Chapter is to relate the results and findings of this study with those obtained by other researchers and try to fill the knowledge gap of the subject. In addition to that, the results which come out of this study are also discussed and the possible mechanisms are proposed to explain these findings. Some of the confirmatory tests results are also discussed along with the main test work in this section in order to validate proposed mechanisms.

As shown in the beginning of the Chapter 4, the reproducibility of data was good and reasonable interpretations can be made with reliability. As discussed earlier in Chapter 4 the reproducibility (cf. Section 4.3) of a batch flotation data depends on several factors and froth stability is one of the most important ones which were also observed in the current test work. In the case of batch flotation test work, previous studies had been done on investigating DO control or pulp potential control in a flotation cell (Kelebek and Nanthakumar, 2007; Klymowsky, 1968). The present study is unique in the sense that the DO concentration was measured and controlled in the grinding stage as well as in the flotation stage.

DO control during the grinding and flotation stages is a challenging task. However, with the help of the Magotteaux mill, it has become possible to control the grinding DO at laboratory scale. Further, in a real ore system such as the Cu-Ni sulfide ore used in the present study, data interpretation is more challenging as the ore may contain more than one valuable mineral. Most of the studies in the past were either performed with a single mineral system or with a mixture of two minerals and the xanthate concentration was measured and the DO level was controlled (Bozkurt et al, 1998; Buckley and Woods, 1991; Khan and Kelebek, 2004; Legrand et al, 2005b).

This chapter begins with a summary of the key findings of each section followed by a discussion of the results of the DO controlled grinding experiments. The maximum and minimum DO concentration conditions are then discussed along with the varying grinding and flotation conditions. The results of the tests done under normal milling conditions i.e. no gas control conditions are then discussed. Finally a detailed discussion of the selectivity between the Pentlandite (Pn) and Pyrrhotite (Po) is discussed. The possible mechanisms that may be occurring are then proposed.

5.1 Key Findings

Before discussing the results of this research in detail it is useful to summarize the main findings of the research. Details of the conditions for each test referred to below can be found in Chapter 3 and on the fold out at the back of the thesis.

5.1.1 Varying Dissolved oxygen of the pulp

- Pn and Po gave higher recoveries when ground at a DO concentration of zero.
- Chalcopyrite (Cp) recovery remained almost unaffected by DO except in the case when continuous N_2 purging (Test-1) occurred. However the grade varied across the tests performed (cf. Section 4.4).
- Xanthate adsorption results of Section 4.4 showed that the residual xanthate at the start of grinding was not consumed during grinding at a DO concentration of 0 ppm, but almost all xanthate was consumed during the slurry transfer from the mill to the cell.
- It was difficult to establish the optimum oxygen level for xanthate adsorption in such a system, because even after 5 min of grinding at DO-1, all the xanthate was consumed.
- Pn as well as Po grade and recovery decreased with an increase in Eh. Hence Eh may be a good indicator of Po and Pn grade and recovery.

5.1.2 Varying sparging and flotation gases

- The residual xanthate remaining after grinding was consumed during the slurry transfer, which took about 30 minutes. However after N_2 sparging, the xanthate concentration in the pulp increased after slurry transfer.
- Solids and water recovery were very similar for all the tests except for Test-6.
- Test-6, in which the ore was ground at DO-0 and sparged with N2 after slurry, was the most detrimental for the overall flotation of the sulfide minerals.
- Test-6 was most detrimental for Cp flotation and Test-7 was most detrimental for the Pn.

- There were variations in the grade of Cp over all the test conditions in Section 4.5, which can be correlated with the variation in the Pn and Po recovery of the respective test conditions.

5.1.3 Varying xanthate addition point

- Pn had a higher grade and recovery in Test-1 compared to Test-9.
- Cp grade decreased when xanthate was added to the cell compared to the mill.
- Cp recovery was slightly higher in Test-3 and 10 compared to Test-1 and 9, which supports the necessity of an oxidizing environment for the flotation of Cp.
- Test-3 and 10 gave the lowest Pn as well as Po recovery, which was an indication that excess oxygen during grinding was harmful for the flotation of Pn as well as Po.
- Addition of xanthate into the cell decreased the selectivity between the Pn and the Po flotation.
- Oxidation at the grinding stage had a major impact on the floatability of Po as well as Pn and was independent of the xanthate addition point. The effect was much more prominent in Po.
- Test-10 gave the maximum grade of Pn, although recovery was lower than Test-1 and 9, which may be due to diminished floatability of Po in Test-10.

5.1.4 Varying Eh through pH control

- As pH increases, the recovery of Pn decreased but the grade increased.
- Cp recovery almost remained unaffected.
- As the pH increased, the solids and water recoveries decreased and the lowest solids and water recoveries were observed at pH-11.
- At pH-11 some of the xanthate remains unconsumed in the mill.
- Eh control through pH control was not a useful tool to control the grade and recovery for such a system.
- Some species present in the mineral, mill or grinding media consumed the xanthate at low pH and not at high pH.

5.2 Effect of Dissolved oxygen at grinding on flotation

The primary aim of this project was to evaluate the relationship between the effects of a change in pulp chemistry in the mill and the resulting flotation of valuables in a Cu-Ni sulfide ore. This study included measuring the concentration of xanthate in the pulp after various treatments. Initially, the test work focused on relating the rate of xanthate consumption to the pulp DO concentration. The residual xanthate measurement at DO-0 (Test-1) as shown in Figure 4.18 indicated that the xanthate concentration in the pulp at the start of the grinding phase remained the same throughout the grinding phase. The xanthate was not consumed until the grinding phase was over due to the absence of oxygen during the grinding stage. This clearly shows the role of oxygen in xanthate adsorption. These findings are in line with the literature, viz. that most of the xanthate is consumed through the dixanthogen route, which is accompanied by the reduction of oxygen at the mineral surface (cf. Chapter-2). It can be seen in Figure 4.18 that during slurry transfer from the mill to the flotation cell, the residual xanthate is consumed. This might be either due to the contact of atmospheric oxygen with the slurry or due to the addition of oxygenated wash water.

The test work conducted at DO-1 (Test-2) for the residual xanthate measurement in slurry has shown that it was very difficult to relate the rate of xanthate adsorption with the pulp DO concentration. Later attempts were also made to establish the rate of the xanthate adsorption as specified in the confirmatory tests (See Appendix-1). These tests did not give any satisfactory results to explain xanthate adsorption kinetic measurements using the Magotteaux mill. However, it is to be noted here that during the confirmatory tests, the adsorption/chemical reaction of the minerals present in the ore with the xanthate may be a reversible reaction and N_2 purging appeared to cause desorption of the xanthate that had previously adsorbed/reacted (See Appendix-1). Furthermore, some of the important findings of the tests described in Section 4.4 laid the foundation for the overall test program conducted in this study.

As can be seen from Figure 4.13 the mass of water recovered at varying grinding DO concentrations did not vary much. However, the mass of solids recovered to the concentrate increased greatly when the ore was ground at a DO concentration of 0 ppm (Test-1). The extra solids recovered in Test-1 may be either due to true flotation or entrainment. It is to be noted here that the amount of water recovered in a batch flotation test is an indication of the froth stability and consequently of the amount of entrained material recovered, if the other test conditions such as the solids density and the particle size distribution were kept constant.

However, similar water recovery in all tests (Test-1, 2 and 3) made it clear that the extra solid recovered in the concentrate at DO-0 (Test-1) was due to true flotation and not entrainment (Wiese, 2009).

There are two zones in the flotation system, the pulp zone and the froth zone. The role of the froth zone is to enable the upgrading of the valuable materials reporting to the concentrate by controlling the entrained gangue. The amount of water recovered in a concentrate, is an indication of the froth stability and, in turn, of the amount of solids recovered through entrainment. However, entrainment is not directly affected by changes in the mineral surface properties which in the present study are strongly influenced by the procedure used in the grinding stage. So, the higher solids per unit water recovered in Test-1 could be due to a pulp phase effect and not a froth phase effect. Entrainment could increase the solids recovery as well as water recovery in the same proportion. However, similar water recovery in all the specified conditions (as shown in Figure 4.13) indicates that the increased solids recovery is probably not due to entrainment.

It was observed that the bubble collapse rate was higher in case of Test-1 compared to Test-2 and Test-3. As discussed earlier, it was not due to froth phase effects but rather it was a pulp phase effect which was a function of the grinding process. The pulp environment created during the grinding stage may have promoted the formation of highly hydrophobic particles - bubble collisions during the flotation stage and allowed for the successful attachment of the valuable hydrophobic particles to the bubble and the subsequent transport of these mineral laden bubbles to the froth phase. All the particles which attached at the air/water interface have a major influence on the froth stability. The increased bubble collapse rate as observed in Test-1 might be due to the strongly hydrophobic particles which may have been generated due to lack of media-mineral galvanic interactions and these particles are capable of destabilizing the froth by bridging the froth films and collapsing the bubbles (Harris, 2010).

Grade–recovery relationships are a key indicator to judge the performance of any flotation experiment. In the current work, the Po as well as Pn grade–recovery performance was found to deteriorate considerably when oxygen was present during grinding. The effect is much more pronounced on the recovery of Po than the Pn. However, the effect of oxygen level during the grinding stage did not have much effect on the floatability of Cp. The results are consistent with the literature which has shown the relative ease of individual mineral floatability in the processing of Cu-Ni ores to follow the order; Cp > Pn > Po (Kelebek, 1993). There could be many factors that are responsible for this behaviour of the sulfide minerals. From an electrochemical point of view, in general, it is known that mild oxidation of the sulfide mineral surface is required for effective collector action and excessive oxidation is detrimental to collector action (Hu, 2009).

As can be seen in Test-1, the recovery of the Cp is relatively low compared to that observed in Test-2 and Test-3. The lower recovery of the Cp in Test-1 case may be due to the lack of oxygen in the pulp. This is consistent with other findings which have shown that Cp retains its relatively strong hydrophobicity upon sufficient aeration of the pulp but that the absence of DO during grinding and flotation reduces its flotability (Kelebek, 1993; Klymowsky, 1968). The decrease in the Cp recovery in Test-1 (DO-0) was only marginal compared to Test-2 (DO-1) and Test-3 (DO-6.5). However, the increase in the recovery of the Pn and Po in Test-1 compared to Test-2 and Test-3 was significantly high. The recovery of the Pn and Po was lowest in the Test-3 compared to Test-1 and Test-2. This may be due to the rapid oxidation of Po compared to the Pn. This is consistent with the findings of (Legrand et al, 2005a), which showed that once both Pn and Po surfaces were covered with thin FeOOH layers their behaviour with the reagents would be similar and their separation would be difficult. The reason for the significant increase in the recovery of the Pn and Po may be the addition of xanthate to the mill where xantahte adsorption may take place prior to oxidation (in Test-1) and resulted in a significant increase in the recovery of the Pn. This may be the reason that the addition of xanthate at the milling stage is common practice (Legrand et al, 2005a) by the xanthate adhering to the fresh surfaces immediately upon exposure to these surfaces in the separation of Pn and Po. In this study the Cp recovery remains almost unaffected over all DO concentration tests while only the grade varies. The most important factor responsible for the decrease in the grade is the dilution of the concentrates owing to the enhanced flotation of Pn and Po.

As far as chemical metastability of sulfide minerals is concerned, the formation of elemental sulphur/polysulfides through the oxidation of the metal deficient surface is highly relevant to the current study. The nature and growth characteristics of oxidation layers have been described by many researchers as discussed in section-2.3.4. They form complex structures in patches or uniform layers, which are subject to change during interactions in the grinding and flotation environment. Grinding is the first stage where the liberated surface comes into contact with the oxygen and/or chemicals (collector in this case) and changes the mineral surface properties. The enhanced recovery of the Po and Pn at DO-0 (Test-1) can be explained by the formation of elevated amounts of elemental or metastable sulphur species in the absence of oxygen during the grinding stage. In the absence of oxygen the elemental sulphur which forms at the mineral surface can cause the mineral surface to be highly hydrophobic. This finding is consistent with that made by (Harris and Finkelstein, 1975b), viz. that the elemental sulphur formed at the mineral surface is highly hydrophobic and remains stable for a long time and increases the mineral floatability.

The flotation response of sulfide minerals depends on their oxidation characteristics or the surface properties of the mineral at different stages of mineral processing operations. In the froth flotation process, grinding of the ore prior to flotation is a crucial step due to the fresh surface generated at this stage, which is then susceptible to immediate oxidation and/or alteration. A greater extent of oxidation, of the ore at higher DO concentrations (Test-3) probably explains the higher redox values and the poor recovery of Pn. At higher DO concentrations both Pn and Po surfaces may get heavily oxidized even though the SIBX was present to react as in Test-3. In this case the surface product on both Pn and Po mineral may be oxides or oxyhydroxides (Legrand et al, 2005b). When the oxygen concentration is decreased to DO-0, there was a dramatic increase in the grade and recovery of the Pn and Po, and this may be due to a decrease in the surface FeOOH present on the mineral surfaces.

The mechanism of oxidation of Po and Pn as found in the literature proposes (Mycroft et al, 1995; Pratt et al, 1994) that the initial oxidation of Po and Pn happens through the diffusion of iron from the outermost layers of the solid lattice to form a Fe^{3+} hydroxyl-oxide or hydrated oxide at the air/solid interface, via Fe^{2+} oxidation. However, there is no appreciable diffusion of oxygen into the interior, nor appreciable diffusion of sulphur to the surface. Molecular oxygen, adsorbed onto the mineral surface, is quickly reduced to form FeOOH. The rate of formation of the overlayer decreases with time, probably as a result of slower iron diffusion through the thickening of the passivating FeOOH overlayer and/or inhibited electron transfer as a result of low Fe^{2+} abundance in the FeOOH layer. The reason for the rapid oxidation of the Po compared to the Pn is due to the higher rate of Fe diffusion through the structural vacancies Po. As observed by Mosses et al. (1987) the rate of diffusion is higher in the case of Po due to high spin Fe in Po as compared to low spin Fe in Pn

As can be seen from the stability diagram shown in Figure 5.1 of Pn, it was stable only at a low partial pressure of oxygen, which may be the case at a DO concentration of 0 ppm. It is to be noted here that the partial pressure of oxygen in the slurry is a measure of the DO concentration (MS, 2001). However, in Test-3 the slurry had a higher partial pressure of oxygen, which may have resulted in a low Ps_2 value (point A in Figure 5.1). This may have removed the Pn from the stability region, and resulted in its oxidation into Violarite ($FeNi_2S_4$) and FeOOH (Legrand et al, 2005a; Vaughan, 1989). This was produced through the oxidation of Fe^{2+} to Fe^{3+}, which was not possible in the absence of oxygen. However, during the time of slurry transfer, the slurry came into contact with atmospheric oxygen and as a result the surface may have been oxidized and elemental sulphur may have formed resulting in the improved grades and recoveries of the Pn and the Po.

At a relatively low DO concentration as in Test-2, the floatability of the Po decreased significantly. However, the decrease in the Pn recovery was only marginal. This may be due to lower FeOOH formation on the Pn surface which is less susceptible to oxidation as compared to the Po. Similar behaviour of these minerals was also noticed by (Legrand et al, 2005a) in their surface analysis experiment of these minerals where they observed that at relatively low concentrations of oxygen only small increases in the FeOOH on the Pn occurred whereas there was a remarkable increase in the FeOOH on Po. Apart from that, at low oxygen concentrations such as the case of Po in a nitrogen atmosphere, dixanthogen would not form on the mineral surfaces and xanthate ions would replaces the hydroxyl ions (Rao and Finch, 1991). Further, the FeOOH film became thermodynamically unstable at low oxygen concentrations and resulted in better selectivity between the Pn and Po.

The kinetic model used to analyse of the test data showed that the fraction of the fast floating particles increased with the decrease in the DO concentration during the grinding stage in the case of Po and Pn. As shown in Table 4.3 shows the results obtained in the kinetic analysis of the flotation results obtained conducted at different DO concentrations. The Kelsall first order kinetic model was used for this analysis. It can be seen that the rate constant for the slow floating component of the ore was about 2 orders of magnitude lower when compared to the fast floating component and remains unchanged through the set of tests. However, the rate constant for the fast floating component of the ore, k_f, changes due to the change of the grinding conditions. The chalcopyrite was always the fastest floating mineral. The rate of flotation of the fast floating Pn was not much different to that of the Po. The most significant differences were seen in the fraction of the slow floating components (Øs) of the different minerals in the different grinding environments. The slow floating fractions of the Cp remained unchanged through the course of changing the grinding environment (Øs =0.17-0.21). However, the changes in the grinding environment resulted in a significant change in the slow floating fraction of the Pn (Øs =0.40-0.57) and even more so for Po (Øs =0.72-0.94).

Table 4.3, in the case of Po, the fraction of slow floating particles increased significantly even when the oxygen was controlled as in Test-2 (DO-1). This was also evident in the recovery time plot of Po. From the kinetic analysis results, it could be seen that at higher DO concentrations (Test-3), the fraction of slow floating Po is very high (viz. 96 %) and the rate constant of the slow floating fraction Po is very low. Thus, the amount of fast floating fraction in this case would be 4 % (100-96) However, only 6-10 % of the Po has reported to the concentrate. Thus, the extra 2 to 4% may be either due to entrapment or entrainment but not due to true flotation. As the water recovery remains almost the same at all test conditions, the entrainment should remain the same. The variations in the Po recovery may have been due to its assemblages with the Pn and Cp i.e. it may be either due to entrapment or from the un-liberated Pn and Cp.

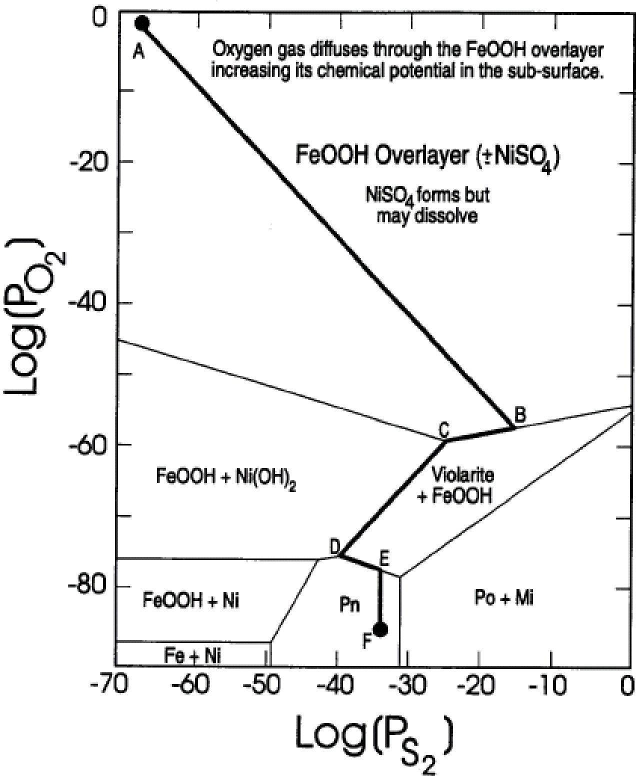

Figure 5.1: Stability diagram for Pn and its secondary alteration products, plotted as log (*P*O2) vs. log (*P*S2). The thick solid line shown on the diagram shows a proposed reaction path for pentlandite which is exposed to air saturated solutions (Legrand et al, 2005b)

These observations suggested that un-oxidised slurries had a population of particles not only with highly floatable character (due elemental sulphur formation) but also particles that had a weakly floatable character (due to entrapment or association with the other naturally floatable gangue) that may be caused by over oxidation. The former tended to dilute the concentrate grades while the latter limited the overall recovery, being responsible for the majority of Pn and Po losses. Higher DO concentrations (Test-3) at the grinding stage rendered Po and Pn minerals hydrophilic. As a result these hydrophilic particles remained unattached after collision with bubbles and were therefore not transported to the froth phase and resulted in a consequent loss in the recovery of the Pn and Po.

5.2.1 Grinding in N_2 environment

As soon as the ore comes in contact with the atmospheric oxygen and water it starts weathering as discussed in section **Error! Reference source not found.**. Although, during the mining operation the ore is in contact with the atmospheric oxygen, the ore may come into contact with water for the first time in the grinding stage. Freshly exposed mineral surfaces (Pn, Po and Cp in this case) at this stage may undergo the dissolution followed by oxidation depending upon the grinding environment. Much research has been carried out to understand the behaviour of Po because of its potential hazard to the environment through Acid Mine Drainage (AMD). Po dissolution may start once it comes into contact with air and water during the grinding stage. However, in the absence of oxygen as in DO-0 tests (Test-1, 5, 6 and 9) the dissolution of the Po may be completely impeded, and if the dissolution occurs, it may release Fe^{2+} onto the surface without the release of electrons, which followed the reduction of polysulfide to sulfides according to reaction 5.1 (Thomas et al, 1998) and further to the sulphate.

$$S_n^{2-} + 2\,(n-1)e^- \rightarrow nS^{2-} \qquad (5.1)$$

However, oxidation may not occur in the absence of oxygen as shown in Tests-1, 5, 6 and 9. (Knipe et al, 1995) have also confirmed this in a study which showed that when the Po was exposed to deoxygenated water no evidence of oxidation was found although it is difficult to relate the DO concentration of the plant water with the flotation performance without surface analysis. However, in the present study the rate of flotation of Pn and Po seemed to be related to the DO concentration of the synthetic plant water used.

It is to be noted here that in the Test-5, 6 and 9, the grinding conditions were kept the same as in the Test-1 which was discussed earlier but, the flotation conditions were varied to test the variability of the flotation performance. It can be seen from the solids - water recovery plots from these tests that the amount of water recovered in Test-6 and Test-9 were relatively high compared to Test-1 and Test-5. As explained earlier the amount of water recovered in a batch flotation test is an indication of the froth stability and consequently the amount of entrainment. The solids in the concentrate were highest in Test-9 and lowest in Test-5. The differences in the solids recovery can be explained by the strong hydrophobicity of the particles as described previously. However, it is to be noted here that in Test-9, the solids in the concentrate increased in the same proportion as the water recovery. The extra solids recovered in this case may be through entrainment as well as through true flotation. This may suggest that addition of xanthate in the cell (Test-9) may result in an increased entrainment compared to the xanthate in the mill (Test-1).

According to the hypothesis proposed in the present study the separation of Pn from Po by flotation could be improved by exposing the ore to xanthate adsorption prior to oxidation, or removal of the FeOOH overlayer by deoxygenating the slurry because once the FeOOH layer forms on the mineral surface both Pn and Po respond similarly to collector adsorption. Keeping this in mind, N_2 bubbling tests were carried out to find out whether deoxygenating the slurry could enhance the selectivity between the Pn and Po. The Selectivity Index values (cf. section 5.4), showed that deoxygenating the slurry did enhance the selectivity as observed in Test-6 when compared with the Test-1. However, it can be seen here that although the selectivity is relatively high when sparging and floating the slurry with N_2, the overall recoveries of Pn as well as Cp were very low and hence this treatment may not be a good option for operational practice.

The reason for the low recovery in Test-6 may be due to the absence of sufficient oxygen. As in this case, N_2 may purge oxygen from the pulp at various stages of grinding and flotation. This may have reduced xanthate adsorption as well as inhibiting mild oxidation by preventing oxygen reduction reaction (See, reaction 2.1, Chapter-2). Although different mechanisms and pathways of oxygen reduction have been proposed by many researchers as discussed in Chapter-2, the role of oxygen in a flotation pulp is still not fully understood. The complete removal of oxygen from the pulp at various stages could affect other mechanisms which may be the case in Test-6. One of the most important roles of oxygen is the production of elemental sulphur on the mineral acting as the anode (and possible natural or collectorless floatability) and its complete removal at various stages may result in the loss of valuable minerals recovery. The idea of using nitrogen has been referred to by many investigators (Abramov and Avdohin, 1998) have, for example, described the use of various gases in copper/molybdenum separation. They found that the use of N_2 depressed the Cp and also lowered the consumption of the reducing reagent and so reduced reagent costs. These researchers recommended the use of N_2, whenever reducing conditions are beneficial. In these applications the use of nitrogen was reported to have cut reagent costs by half in the separation of the Cp from molybdenum. Other studies have also shown that deoxygenated solutions may hinder the Cp-xanthate contact and thus no adsorption of xanthate was able to take place on Cp in the absence of oxygen (Klymowsky, 1968).

The recovery of the Cp was found to be more or less similar in all the tests (Test-1, 5 and 9) except in Test-6. The reason for this may have been because of the non- reactivity of the xanthate at low Eh and the absence of oxygen. As N_2 was used throughout in Test-6, it can be inferred from the findings of Test-6 that the use of N_2 inhibited the collector/mineral interaction. As shown above previous work has shown that the use of N_2 inhibits the (pure) mineral collector interaction. In the present work the use of N2 was tested for an ore during batch flotation and as shown in Figure 4.31 in Test-6, the adsorbed (reacted) xanthate was desorbed as the slurry was sparged with N_2. The increase in xanthate concentration may be due to desorption of some weakly physically adsorbed xanthate. However, some of the xanthate was consumed during the processes of grinding and flotation. The consumed xanthate may not be present in the form of dixanthogen but, depending upon the conditions, may be present as other xanthate derived species such as xanthic acid, monothiocarbonate ion, metal xanthates, or perxanthate ions (Rao and Leja, 2004). Not all of these species may be responsible for the hydrophobicity and consequently the floatability of the mineral. The most important species for the hydrophobicity of the mineral is dixanthogen. It can be also noted here that there was a significant increase in the slow floating fraction of the Cp in Test-6 which may be due to the loss of the natural floatability of the Cp in this case. Cp is the anomalous mineral in the sulfide mineral series, as it has the highest natural floatability but not the lowest susceptibility to oxidation (Klymowsky, 1968).

The initial objective of the test work using nitrogen was to assess whether its use would prevent the flotation of Po by reducing the pulp potential and the DO content thereby reducing the extent of Po-collector interaction. As reported in the literature (Rao and Leja, 2004) the non-selective flotation of Pn from Po can be significantly reduced if flotation is conducted with nitrogen instead of air because the reaction of the Po with xanthate requires a potential of 200 mV and its flotation is reduced by lowering the pulp potential to 120 mV by the use of N_2 (McGill unpublished data; (Rao and Leja, 2004)). Although as shown in section 4.5.1.3 the use of N_2 reduced the floatability of the Po it also reduced the recovery of Cp and Pn. The results of section 4.5.1.3 (especially the comparison of Test-1 and Test-6) were different to what has been previously reported for PGM ore i.e. the use of N_2 as a flotation gas enhanced the recovery of Pn (Buswell, 2002). In most of the previous studies the researchers were not controlling the DO concentration of the pulp during the grinding stage. As a result the DO available at grinding stage may be reduced (cf. reaction, 2.1; Chapter-2) and the mineral surface oxidized to elemental sulphur. The elemental sulphur may have provided active sites for better flotation in all the previous studies. As discussed previously oxygen starts playing a role from the commencement of the grinding process and, as seen in 4.4.5, even exposure to oxygen during the time of slurry transfer from mill to cell results in total xanthate consumption. Control of the pulp chemistry at the grinding stage is a crucial aspect of the mineral processing operation of the Cu-Ni sulfide ore and if the grinding stage is not controlled even subsequent bubbling with N_2 scarcely makes much difference although without analyzing the mineral surface it is not possible to confirm the exact mechanism of reduced flotation in Test-6. It is clear from the present study that complete absence of oxygen is detrimental to the flotation of the valuable mineral of a Cu-Ni sulfide ore.

Several researchers (Becker, 2009; Johnson and Munro, 2008; Spira and Rosenblum, 1974) have specified the importance of DO control on the selective flotation of Pn from Po. Air sparging (Test-5) results have shown that the floatability of the Po decreased with air sparging. Air sparging can be used as a depressant for Po in plant practice, if the plant configuration allows extra conditioning or sparging tanks. As can be seen from Test-5, the effect of air sparging was only significant in the case of Po and this may be due to the high reactivity of the magnetic Po, this form of the mineral having been confirmed through XRD analysis. The differences in the flotation performance of Po, Pn and Cp as seen in the air sparging tests may be due to differences in their relative catalytic activity with oxygen.

According to current electrochemical knowledge of flotation, when the rest potential of the mineral is more anodic than the redox potential for the xanthate-dixanthogen couple, dixanthogen would be the expected product at the mineral surface. The rest potential order is given as Cp > Pn > Po (Becker, 2009). As Eh or ORP of the pulp increases, the recovery of the valuable mineral decreases, however, Cp is an exception to this. As can be seen from

Table-4.12, the pulp potential in Test-6 was much lower at the various stages of grinding and flotation than that required for the formation of dixanthogen. The pulp potential dropped with the use of N_2, which ruled out the formation of dixanthogen and consequently depressed the valuable minerals (Allison et al, 1972, Woods, 1973, 1976). The reaction product of xanthate as discussed by many researchers (Bozkurt et al, 1998; Hodgson and Agar, 1989; Khan and Kelebek, 2004) would have been dixanthogen, which was responsible for the hydrophobicity of Po, Pn and Cp. The formation of dixanthogen however, was not feasible at the potential used in the current study.

As discussed in Section 2.9.1 and 2.9.2. the Po and Pn show their natural floatability at pulp potentials of 250 to 350 mV and -150 mV (SHE) respectively but in Test-6 after N_2 sparging the Eh of the pulp was lower than these values and hence the formation of the elemental sulphur through the dissolution/hydrolysis and/or mild oxidation of the mineral may also have become difficult and the minerals were not able to show natural floatability at the measured pulp potential. Further in the complete absence of oxygen the Cp did not show its natural floatability. The mineral surface was neither oxidized at the grinding stage nor at the flotation stage. A similar explanation may be given for the loss of the natural floatability as well as the collector induced floatability of Pn and Po.

Results of the batch flotation tests of section 4.6 showed that once the surface properties of the minerals were changed during the grinding stage, the floatability of the mineral was diminished and cannot be subsequently enhanced much by the addition of chemicals. Overall recovery of the Po was significantly lower in Test-1 compared to Test-9; however the difference in the recovery of the Pn was only marginal. Of the three major sulfide minerals (Cp, Pn, and Po), Cp floatability was enhanced by oxidation, while the floatabilities of the other two sulfide minerals (Pn and Po) diminished due to oxidation at the grinding stage.

Since most of the Cp, Pn and Po were found to be in the liberated form as confirmed by QEMSCAN data, the floatability of the Cp, Pn and Po in this study is largely independent of mineral association. The relative ease of the individual mineral floatability in the processing of Cu-Ni ores, as was observed in different test conditions at DO-0, follows the sequence Cp> Pn> Po. A similar trend was observed in all cases irrespective of whether the xanthate was added into the mill or cell. Floatability was largely dependent upon the grinding environment rather than xanthate addition point. However, it can be seen from the grade - recovery data that when the ore was ground at a DO concentration of 0 ppm, it not only increased the recovery of the Pn but also of the Po. This is in agreement with the literature that the behaviour of Po is similar enough to that of Pn and an increase in the recovery of the Pn would occur at the cost of its grade (recovery of Po) (Buckley and Woods, 1985; Legrand et al, 2005a; Legrand et al, 2005b).

When grinding the ore at a DO concentration of 0 ppm, addition of xanthate into the cell led to an increase in the overall recovery of Po by 10 %. This can also be seen in the kinetic analysis of the data which showed that the change in the xanthate addition point from mill to cell led to an increase in the fast floating fraction by 10 %. The significant increase in the recovery of the Po while adding xanthate into the cell may be due to the availability of more xanthate adsorbing sites and consequently an increase in the population of the hydrophobic particles. However, the increase in the overall recovery of Pn, when xanthate was added into the mill compared to the cell was only 1 %. The differences in the behaviour of both of the minerals may be due to differences in their xanthate adsorption mechanisms. The reaction mechanisms of collector adsorption on Po and Pn, as discussed in Section 2.11.2 require the presence of oxygen as an electron acceptor (Hodgson and Agar, 1989). However, xanthate adsorption still occurs even at a DO concentration of 0 ppm as shown in Section 4.7.3. This may be either due to oxidative dissolution or superficial oxidation of the Po (Rao and Finch, 1991; Thomas et al, 2001). Among the minerals (Pn, Po and Cp) considered in the present study, Po is known to be very susceptible to superficial oxidation or oxidative dissolution. As a results of this, Fe^{2+} ions react with the water giving the $Fe(OH)^+$ species (5.2).

$$\mathrm{Po[Fe^{2+}] + H_2O \rightarrow Po[Fe(OH)^+] + H^+} \qquad (5.2)$$

These species serve to attract the anionic X^- through the columbic attraction forces and an initial physical adsorption of xanthate takes place according to the reaction shown in (5.3). This species may form even at the very initial stages of reaction through the adsorption of xanthate ions even without charge transfer.

$$\mathrm{Po[Fe(OH)]^+ + X^- \rightarrow Po[Fe(OH)]^+X^- \rightarrow Po[Fe(OH)X]} \qquad (5.3)$$

Once the xanthate species are physically on the Po surface, chemisorption forces are likely to come into action as well. Po may have xanthate adsorbed species on the surface during the grinding stage even in the absence of oxygen. As shown by (Wang et al, 1989), these Fe^{2+} species are metastable and may be converted into the Fe^{3+} counterparts through transformation steps during slurry transfer (5.4):

$$Po[Fe(OH)X] + OH^- \rightarrow Po[Fe(OH)_2X] + e^- \quad (5.4)$$

Ferric hydroxyl xanthate is a highly stable species under alkaline conditions at lower potential than that at which dixanthogen is stable. The residual xanthate left in solution during the grinding stage may have been consumed through dixanthogen formation (5.5) and (5.6) during the slurry transfer and flotation with air (Khan and Kelebek, 2004):

$$Po[Fe(OH)_2X] + X^- \rightarrow Po[Fe(OH)_2X\text{-}X] + e^- \quad (5.5)$$

$$Po[Fe(OH)_2X\text{-}X] + X\text{-} \rightarrow Po[Fe(OH)_2X\text{-}X_2] + e^- \quad (5.6)$$

The formation of dixanthogen was interrelated with the mineral oxidation/oxidative dissolution reaction for the Po. This may not be the case for the Pn. As established in the literature**.** Chemisorption of the xanthate was not related with the hydroxylation effect on Pn as on Po (Khan and Kelebek, 2004). In the case of Pn xanthate ions may be chemisorbed probably at the Ni sites and able to induce hydrophobicity as discussed in Section 2.9.6.

5.2.2 Effect of pH when grinding in N_2 environment

One objective of this study was to investigate methods that could be used to separate the Pn from Po without compromising the recovery of the Pn and Cp. Nickel producers have been using a number of different strategies, sometimes in combination, to reject Po. These include raising the pH of flotation to partially suppress Po floatability (Klymowsky, 1968) and introducing separate Po rejection circuits which by and large also exploit the fact that Po floats poorly in alkaline solutions. Magnetic separation has been also used in some plants to remove the magnetic Po from feed or concentrate streams (Klymowsky, 1968) However, none is entirely satisfactory, as high levels of Po rejection are invariably accompanied by unacceptable Pn losses due to similarity in the structure and surface properties of the Pn and Po. However, as noted in the previous sections, the presence of oxygen during the grinding stage resulted in a significant decrease in the Po recovery due to the oxidation of the Po. Another means of increasing the rate of oxidation was by increasing the pH (Test-11 and 12), as this would result in more hydroxyl groups present in solution. Po is known to be more reactive sulfide mineral present in the Nkomati ore used in this study and it would also be expected to be the first to be affected by oxidation and thus the first sulfide to be depressed by oxidation due to increase of pH. This should lead to improved selectivity of Pn over Po.

It can be seen from recovery-time plot of section 4.6.1 that there was a notable difference in the overall water recovery between Test-1, 11 and 12. The lowest water recovery recorded in

Test-12 may be due to lower froth stability. However, the solids recovery plot showed that the amount of solids recovered to the concentrate was higher in the case of Test-1 compared to Test-11 and Test-12. The recovery - time plot showed that an increase in the pH resulted in a decrease in the solids recovery as well as in the rate of flotation. This suggests that oxidation carried out in conjunction with pH modification is much more selective in terms of which mineral is affected first. This can also be seen from the recovery - time plot of the Po which shows that the decrease in the solids recovery of the concentrate is proportional to the drop in the recovery of the Po. This shows that operating at a pH above the natural pH of the ore i.e. >9.2, may results in an increase of the hydroxyl groups present in solution. This will accelerate the oxidation of the different sulfides present in the pulp starting with the most reactive sulfide, viz. Po. This will result in a relatively greater selectivity of Pn at higher pH values.

It was noted in Section 5.1.1 that there was a significant variation in the recovery of the Pn and Po with the variation of the Eh. The floatability of the Po and Pn was quite high when the ore was ground in a cathodic environment. Pulp potential is an important electrochemical parameter that can be correlated with flotation results and it may determine the condition of the sulfide surface and the prediction of regions of optimal flotation. From the previous section it was hypothesized that the variation of the pH may have resulted in a shift in the Eh value towards more cathodic and consequently may result in improved flotation selectivity of the Pn and Cp. The data appears to support the hypothesis that an increase in the pH did result in an increase in the selectivity between the Pn and Po because of the precipitation of the $Fe(OH)_2$ and $Fe(OH)_3$ on Po surface which would result in a decrease in the recovery of the Po. However, Cp recoveries were found to be independent of pH in this study. It is to be further noted here that it is not only the pH that was controlled in this case but also the DO concentration. These two parameters together have a major influence on the Eh value of the system. It is important to note that in the present study the pH was in the alkaline range. Under acidic conditions elemental sulphur may form and render the Cp hydrophobic, (Gardner and Woods, 1979a) on the other hand (Ackerman et al, 2000) found that the recovery of Cp decreased continually as pH increased from 5 to 10.5. This was not observed in the present study where the pH was changed from 9 to 11 and Cp floatability was found to be independent of the pH.

In the present study lime, which was used as a pH modifier, may act as a "deactivator" and suspension of calcium hydroxide particles in a saturated aqueous solution may cause heavy metal ions to precipitate from the slurry. These heavy metal ions may activate Po and may prevent their selective depression from Cu-Ni sulfide minerals. The surface activity of a mineral at a particular pH can be determined by the Eh-pH diagram and zeta potential measurement of the associated ions. The surface chemistry of most minerals is affected by the pH e.g., in general minerals develop a positive surface charge under acidic conditions and a negative charge under alkaline conditions. Since each mineral's surface charge changes from negatively-charged to positively-charged at some particular pH, it is possible to manipulate the attraction of collectors to their surfaces by pH adjustment. At alkaline pH's there may be competition between the OH^- of the pH modifier and X^- of the SIBX for the mineral surface and depending upon the activity of the mineral, the selectivity between the valuable minerals and gangue minerals can be enhanced. Hydroxyl ions present at higher pH values can also modify the electrical double layer and zeta potential surrounding the mineral particles, and hence the hydration of the surfaces and their floatability is affected. With SIBX as collectors, at higher pH values (Test-12) Po may be depressed but has no impact on the floatability of Cp (Sutherland and Wark, 1955).

There are also other, more complex effects due to pH that change the way that particular collectors adsorb on mineral surfaces. Po, Pn and Cp minerals present in Nkomati ore may, when surface oxidation/ or dissolution occurs, leave different ions in the pulp (such as Fe^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}) during the grinding and flotation stage. Depending upon the grinding environment and availability of the xanthate during grinding, iron may form different compounds. The formation of ferric xanthate was reported very early by (Gaudin and Fuerstenau, 1976). (Wang et al, 1989) have studied in detail the chemistry of iron-xanthate compounds based on the thermodynamic calculations of iron-containing sulfide mineral flotation systems and have discussed in detail the formation of xanthate-iron complexes at different Eh-pH values of the pulp.

Residual xanthate measurement results at different pH conditions had shown that at higher pH (pH-10 and pH-11) the amount of residual xanthate immediately after the grinding phase over was almost double compared to that at pH = 9, i.e. the natural pH of the ore. This difference in the residual xanthate measurement can infer that some of the species in the ore or grinding media may be reacting at pH = 9 and may form some complex such as $Fe(OH)X$, $Fe(OH)X_2$. However, at higher pH values this complex formation is inhibited.

A confirmatory test (cf. Water test in Appendix-1) was carried out in order to measure the consumption of xanthate in the system and this showed that, in the absence of ore, the grinding media did not consume the xanthate and the natural pH of the system remained approximately 9. It is thus clear that it is the mineral and not the grinding media which is having the major effect on xanthate consumption. Detailed Eh, pH and DO values for this test can be found in Appendix-1.

Another test (cf. Lime test in Appendix-1) was carried out in which the ore was ground at DO concentration of 0 ppm and a sample of pulp was taken at the end of grinding. Further, 32 g of lime was pumped into the grinding chamber and the DO concentration was brought down to 0 ppm and a sample of pulp was collected for residual xanthate measurement. The test results showed that the residual xanthate concentration was double after the lime addition. It can be inferred from these findings that the reactions between xanthate and the ions (derived from ore) present in the system are reversible and at higher pH, OH^- preferably reacts with the ions present in the ore.

Speciation diagrams were used to identify the xanthate consuming species of the system (Rao and Leja, 2004). Figure 5.2 shows the speciation diagram of Cu^{2+}. It can be seen from this figure that Cu^{2+} ions in the pulp mostly precipitated as $Cu(OH)_2$ in the pH range of 9 to 11 and that hence they could not be reacting with xanthate at pH 9.2. Similarly from Figure 5.3 and Figure 5.4 it can be seen that the dissolved Ni^{2+} and Fe^{3+} will also precipitate as $Ni(OH)_2$ and $Fe(OH)_3$ in pH range of 9 to 11. However, it can be seen from Figure 5.5 that the Fe^{2+}, which was not oxidized to Fe^{3+} (due to reducing environment or in the absence of DO), may react with xanthate at pH-9 but may form $Fe(OH)_2$ at pH-11, thus resulting in an increase in the residual xanthate concentration in the pulp.

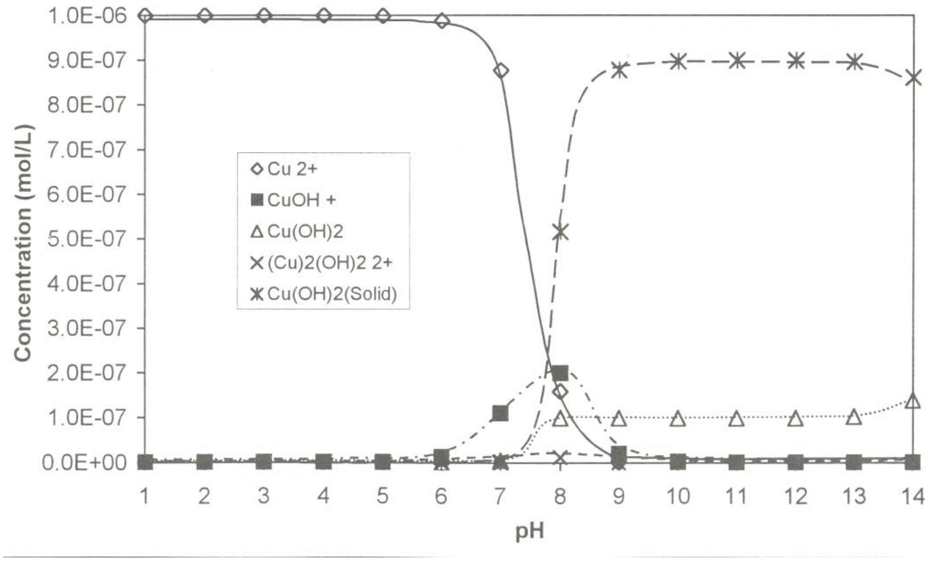

Figure 5.2 Speciation diagram for Cu^{2+} (Rao and Leja, 2004)

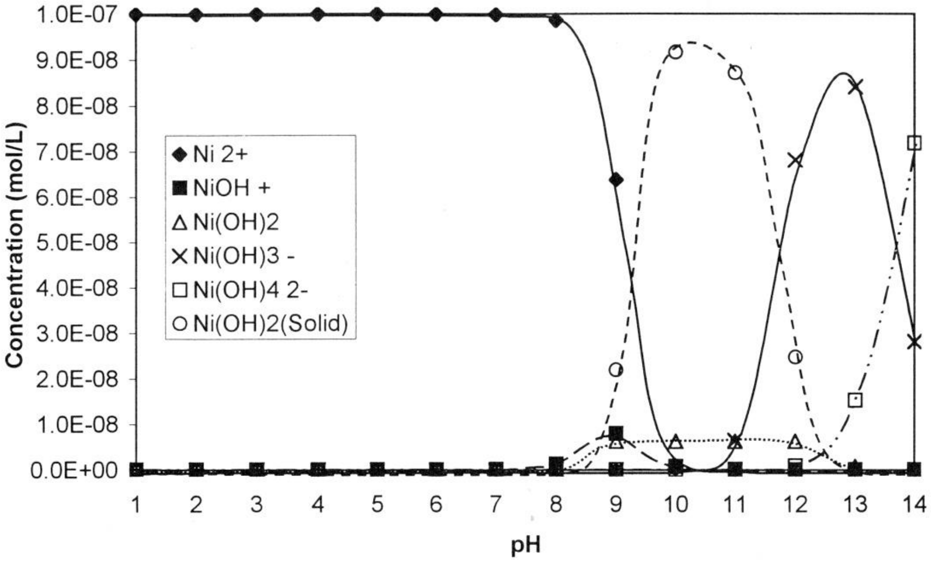

Figure 5.3: Speciation diagram for Ni^{2+} (Rao and Leja, 2004)

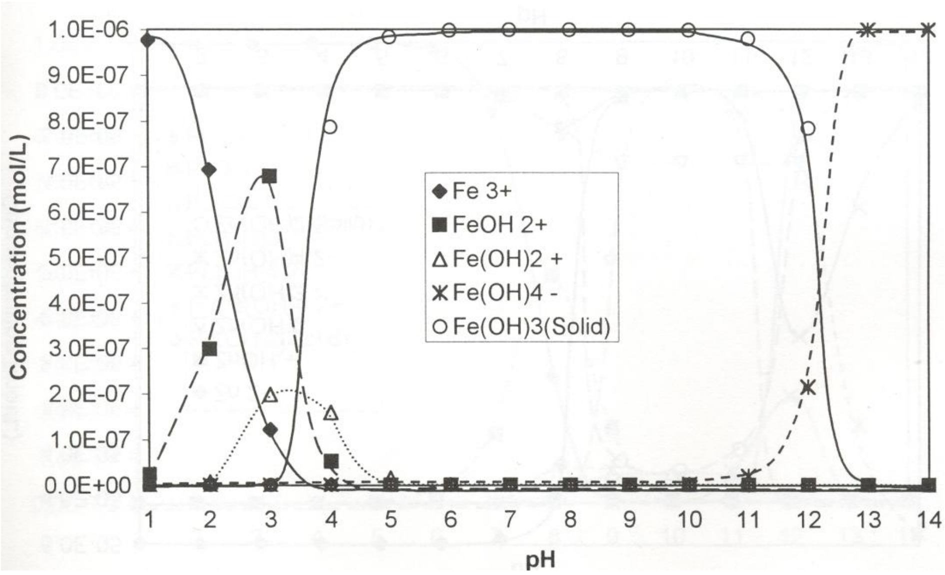

Figure 5.4: Speciation diagram for Fe^{3+} (Rao and Leja, 2004)

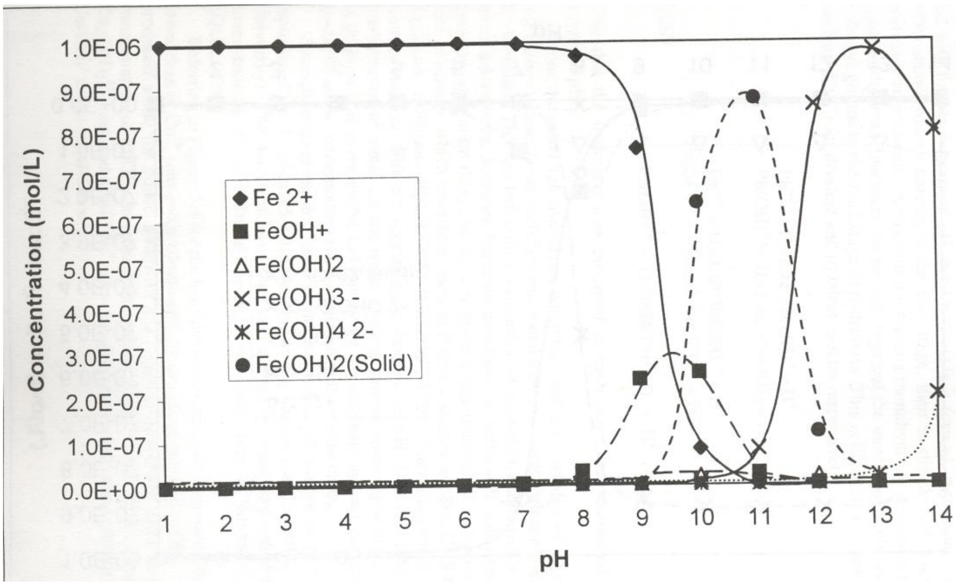

Figure 5.5 Speciation diagram for Fe^{2+} (Rao and Leja, 2004)

5.2.3 Grinding in air

During mining sulfide minerals come into contact with air and as a consequence oxygen begins playing its role through weathering/oxidation of the sulfide. The ore comes into contact with water during wet grinding and water will start acting as a chemical and the surface properties of the minerals will be affected first through dissolution then by oxidation. Po dissolution may start after it comes in contact with air and water during grinding. The pH conditions are equally important for the dissolution of the Po. In the present study the pH was kept in the alkaline range and Po may dissolve more slowly in alkaline conditions and oxidative dissolution may take place according to the reactions (5.2) and (5.3) (Thomas, Skinner and Smart, 2001):

$$MS \rightarrow M^{2+} + S^{2-} \tag{5.7}$$

$$\text{Surface} > S^{2-} + 4H_2O \rightarrow SO_4^{2-} + 8H+ + 8e- \tag{5.8}$$

$$\text{The overall reaction is: } 2O_2 + 4H_2O + 8e- \rightarrow 8OH- \tag{5.9}$$

During flotation dissolution and oxidation proceed together in the mineral slurry and oxygen may act as an ultimate oxidant for the sulfide minerals in plant water. While using normal plant water (DO concentration of 6 to 7 ppm) as in Test-3 and Test-10, oxygen is acting as a primary oxidizing agent for the conversion of Fe^{2+} to Fe^{3+} ((Belzile et al,, 1997; De Haan, 1991; Lowson, 1982), which implies that sulfide oxidation occurs when dissolved or gaseous oxygen is present in the plant water. In Test-3 and Test-10, the oxidation reaction may proceed as (5.10) (Nicholson and Scharer, 1994):

$$Fe_{1-x}S + (2- ½\, x)\, O_2 + xH_2O \rightarrow (1-x)\, Fe^{2+} + SO_4^{2-} + 2xH^+ \tag{5.10}$$

The oxidation of Fe^{2+} produces Fe^{3+} which may precipitate out of solution at high pH as in this study at higher DO concentrations (Test-3 and Test-10) and form ferric hydroxide.

$$Fe^{2+} + ¼\, O_2 + 2H^+ \rightarrow Fe^{3+} + ½\, H_2O \tag{5.11}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3\,(S)} + 3H^+ \tag{5.12}$$

Fe^{3+} can in turn oxidize more Po and generate more acidity, as observed during grinding in Test-3 and Test-10 which may proceed through the following reaction:

$$Fe_{1-x}S + (8- 2x)\, Fe^{3+} + 4H_2O \rightarrow (9-3x)\, Fe^{2+} + SO_4^{2-} + 8H^+ \tag{5.13}$$

Results of the batch flotation test shows that once the surface property of the mineral is changed through (oxidization) at the grinding stage, the floatability of the mineral will diminish (reduced recovery) and at a later stage it cannot be enhanced much by the addition of chemicals.

As can be seen from the results of Section 4.6.3 the recovery of the Pn and Po decreased significantly when the ore was ground at a DO concentration of 6.5 (Test-3 and Test-10) and addition of xanthate in the flotation cell made only a marginal difference. Overall recovery of the Pn as well Po was significantly lower when the ore was ground at a DO concentration of 6.5 ppm compared to DO concentration of 0 ppm. Of the three major sulfide minerals present in the ore (Cp, Pn, and Po), Cp floatability was enhanced by the oxidation but the other two sulfide minerals floatability diminishes due to oxidation during grinding.

The recovery of the Cp is relatively low when the ore was ground at a DO concentration of 0 ppm compared to DO concentration 6.5 ppm. However, the decrease in recovery is only marginal and should be offset against the advantage of an increase in the recovery of the Pn and Po. This may be due to the rapid oxidation of Po compared to the Pn. This shows that once both Pn and Po surfaces are oxidised probably due to coverage with thin FeOOH layer, their behaviour with the reagents would be similar and their separation would be difficult. This may be the reason that the addition of xanthate at the milling stage is advantageous since it enables their immediate attachment to fresh surfaces.

As discussed earlier the mechanism of the oxidation of the Po and Pn is proposed to occur through the diffusion of iron from the outermost layers of the solid lattice to form a Fe^{3+} hydroxyl-oxide or hydrated oxide at the air/solid interface, via a Fe^{2+} oxidation (Buckley and Woods, 1985). Fe diffuses from the bulk to the surface and is oxidized. There is no appreciable diffusion of oxygen into the interior, nor appreciable diffusion of sulphur to the surface. Molecular oxygen, adsorbed onto the mineral surface, reacts with the surface iron species to form FeOOH. The rate of formation of the overlayer decreases with time, probably as a result of slower iron diffusion through the thickening passivating FeOOH overlayer and/or inhibited electron transfer as a result of low Fe^{2+} abundance in the FeOOH layer. The reason for the rapid oxidation of the Po compared to the Pn may be due to the higher rate of Fe diffusion through the structural vacancies of Po. As already noted, Mosses et al. (1987) observed that the rate of diffusion is higher in the case of Po due to high spin Fe in Po compared to low spin Fe in Pn.

When grinding the ore at a DO concentration of 6.5 ppm, the addition of xanthate in the cell leads to an increase in the overall recovery of the Po by 5 % compared to the addition of xanthate in the mill. This can also be seen in the kinetic analysis of the data as well which showed that the change in the xanthate addition point from mill to cell led to a decrease in the slow floating fraction of the Po. The significant increase in the recovery of the Po when adding xanthate into the cell compared to mill may be due to the availability of more sites more amenable to xanthate adsorption. This may result in an increase in the population of the hydrophobic particles. However, the increase in the overall recovery of Pn, when xanthate was added into the mill compared to the cell was 4 % when the ore was ground at a DO concentration of 6.5 ppm.

Comparison of the two test conditions as shown in Section 4.5.2, Test-3 (flotation in air) and Test-7 (flotation in N_2) shows that sparging with N_2:

a) did not make any significant difference to the reduction of the pulp potential
b) very quickly reduced the DO content
c) strongly promoted the flotation of Po but had no influence on Cp and Pn

Considering either the collector-mineral interactions or the mineral-mineral galvanic interactions for the system studied, in both cases observations (a) and (b) are consistent with observation (c). According to the electrochemical theory of mineral-mineral interactions in a reducing environment (in the absence of oxygen), the oxidation of the noble mineral (Po in this case) diminished and the formation of hydrophilic ferrous hydroxide on the mineral surface was retarded and consequently resulted in the improved floatability of the noble mineral. It can also be noted here that there was a significant drop in the recovery of the Pn due to reduced mineral-mineral galvanic interactions. These findings are in line with the findings of (Bozkurt et al,, 1998) who showed that due to galvanic interactions between Po and Pn, the floatability of the Pn increased while the floatability of the Po decreased.

The kinetic analysis (cf. Section 4.5.2) showed that there was no change in the slow floating fraction of the Cp when the pulp was sparged with N_2 after grinding in the presence of air. However, there was a slight increase in the slow floating fraction of the Pn and a slight decrease in the slow floating fraction of Po. Overall, there were only marginal differences in the rate of the valuable mineral recovery through the adjustment of the pulp chemistry during the flotation stage. As discussed earlier, during grinding, the DO had a crucial role to play since this is the stage in which the fresh surfaces are generated and are able to come into contact with atmospheric oxygen and once this has occurred, pulp chemistry adjustments made at a later stage hardly made any difference.

5.3 Effect of pH on grinding in the absence of gas control

In normal plant operation, would be difficult to control the DO concentration in the mill. However, recording the pulp potential during grinding stage at DO-1 (Test-2) showed that decreased DO concentration in the mill resulted in a decreased pulp potential. The pulp potential can be adjusted by various means in the pulp. In the current study lime was used to vary the pulp potential. Lime (CaO or $Ca(OH)_2$) is the most widely used as a pH modifier, largely for economic reasons in mining industry. The pulp potential measured during grinding showed that increasing pH in the mill also resulted in a decrease in the pulp potential. The pulp potentials measured during grinding (Test-2 and Test-15) were similar but the variations in the recoveries of the Pn between the two cases were entirely different. The reason for the difference in the behaviour may be the availability of the Ca^{2+} ions at higher pH. The calcium ion often interacts with mineral surfaces to change their flotation behaviour. In some cases the calcium ions have beneficial effects while in other cases they may change the flotation in undesirable ways as in this case (Hodgson and Agar, 1989).

In the current study it was found that the Pn as well as Po recovery decreased with the increase in pH. However, the effect on the recovery of the Cp was only marginal. The overall recovery of the Pn and Po was significantly lower at DO-5.5 than at the same pH and at a DO concentration of 0 ppm. The DO concentration of the mill discharge in plant practice as well as in normal laboratory testing depends upon the type of grinding media used and this will affect the recovery of the valuable minerals. However further work is needed in order to evaluate the effect of grinding media at different DO concentrations. Nevertheless it can be established from the current results that controlling the pulp chemistry during grinding is important in managing grade-recovery performance on the plant. Apart from that, the test work conducted in the laboratory at normal milling conditions may be different from the actual plant practice (Greet et al,, 2004). In order to compare the effect of a chemical (collector or depressant) during grinding with a view to implementing procedures into plant practice, proper measurement of the pulp chemistry conditions is important.

Po tends to be thermodynamically and kinetically unstable in a flotation related conditions (Garrels, 1990). It is generally accepted that during flotation in acidic conditions at low oxidation potentials (achieved, for example, by sparging with nitrogen), the surface products of Po oxidation are sulphur-rich intermediates and/or elemental sulphur, which accounts for the naturally hydrophobic Po surface. However, in alkaline solutions (as shown in section 4.7.2), under relatively high oxidation potential as in normal grinding operation (open to the atmosphere) the surface may be covered by ferric hydroxide, resulting in a hydrophilic surface. It is evident from the Eh-pH diagram (Garrels, 1990) that Po is finally oxidized to hematite and sulphur under conventional flotation conditions. The oxidation kinetics of Po and the oxidation products at the surface depend on:

- Surface area of the Po
- Oxidation potential/ DO concentration
- Solution pH

Initial oxidation or hydrolysis of the process as found by (Khan and Kelebek, 2004) proceeds through reaction (5.14). Po is a metal deficient mineral and after this reaction the metal deficiency of the Po surface is further increased and iron may precipitate as a ferric hydroxide. The resulting surface of Po is considered to have heterogeneous character, showing patch-wise surface and depending upon the surface orientation and collision with the bubbles, the particle may either report to the concentrate or tailings (Khan and Kelebek, 2004).

$$Po[Fe_{1-x}S] + 3yOH^- = Po[Fe_{(1-x+y)}S + (y-z)Fe(OH)_3] + zFe(OH)_3 + 3ye^- \qquad (5.14)$$

In addition to the surface oxidation, at higher pH such as in Test-15, lime would also add extra hydroxide ions into the pulp and result in increased ferric hydroxide formation and consequently a significant drop in the recovery of the Po. In the case of Pn and Po, the presence of iron oxide/hydroxides is always a dominant factor, although accumulation of activating metal ions, such as nickel and copper, on their surfaces are also critical as shown by XPS, IR spectroscopy, TOF-SIMS and surface extraction studies by many researchers (Bozkurt et al,, 1998; Buckley and Woods, 1991; Malysiak et al,, 2002). The drop in the recovery of the Pn as recorded in Test-15 was significant and therefore raising the pH in normal plant operating condition cannot be utilized to depress the Po.

Electrochemical studies have shown that, it would be possible to optimise flotation performance by the control of the oxidation-reduction potential as measured in the flotation pulp (Ekmekçi et al,, 2005). However, this study has shown that Eh measurement can be used as a diagnostic tool for the plant performance but that it is essentially a measure of a combination of the effects of DO and pH which remain as major control parameters.

5.4 The Pn-Po Selectivity

Different authors have used different techniques to define the selectivity between two minerals (Pn and Po). However, the plot between the recovery of Pn and Po is the most popular in literature in defining the selectivity of the Pn and Po (Kelebek, 1993; Kelebek and Nanthakumar, 2007). The plot of Pn and Po recovery is shown in Figure 5.6. It can be established from this figure that the lower the slope of the Pn/Po curve, the higher is the selectivity. As discussed earlier, the Pn grade–recovery performance deteriorates considerably in the presence of oxygen during the grinding stage. Therefore, the tests where the recoveries of the Pn were less than 60 % were not included in Figure 5.2 and only tests having more than 60 % Pn recoveries were included to determine the best condition for the selectivity. The selectivity between the two minerals as can be defined as the lower the slope of the Pn/Po curve the higher is the selectivity. The most important factor responsible for the decrease in the grade of the Pn was the dilution of concentrates due to the enhanced flotation of Po.

The selectivity of the Pn over Po can also be defined in terms of the parameters of kinetic model and this is done using the concept of the Selectivity Index (SI). The parameters of Kelsall's unmodified two component equation (Kelsall, 1961) have been used in the current study in defining the Selectivity Index. Hence, the selectivity index (SI) for Pn is defined as the ratio of all kinetic variables of Pn and Po as shown in the equation (Kelebek and Nanthakumar, 2007):

$$SI = \frac{Pn\ [ks\ X\ kf\ X\ (1-\O s)]}{Po\ [ks\ X\ kf\ X\ (1-\O s)]} \qquad (5.1)$$

where, kf is the rate constant of the fast floating fraction, ks is the rate constant of the slow floating fraction and Øs is the fraction of the slow floating component of the mineral. On subtracting, the slow floating fraction from unity the fraction of fast floating fraction can be obtained. These parameters were calculated in Chapter 4 and it has been directly used in order to calculate the SI value.

E.g. The calculation of the SI value for Test-1 can be shown here;

For, Pn;		ks:	0.015	for Po;	ks:	0.004
		kf:	0.86		kf:	1.07
		Øs:	0.40		Øs:	0.72

Therefore

$$SI = \frac{0.015\ X\ 0.86\ X\ (1-0.40)}{0.004\ X\ 1.07\ X\ (1-0.72)}$$

$$= \quad 7.13$$

The SI value of the Pn over Po at different test conditions based on Kelsall's unmodified two-component equation (Kelsall, 1961) are shown in the Table 5.1. It is a measure of how well Pn floats relative to Po (Hay, 2008). It can be seen from Table 5.1 that the SI increased significantly from Test-1 to Test-2 due to a significant drop in the recovery of the Po as compared to Pn. It can be said from these findings that, Po was more prone to oxidation than the xanthate adsorption reaction. In a limited supply of oxygen the rate of oxidation of Po was faster in compared to the Pn and xanthate adsorption would be the preferred reaction on Pn and oxygen reduction on Po (Bozkurt et al,, 1998). The fast rate of oxidation of Po may enhance the rate of FeOOH formation at the Po surface. The higher the rate of formation of FeOOH, lower the hydrophobicity and the lower the recovery or rate of flotation. However, at higher DO concentrations such as in Test-3, the SI as well as the recovery of the Pn was low in compared to Test-2, which showed that grinding at higher DO concentrations was not only detrimental for the recovery of the Pn but it also reduced the selectivity between the Pn and Po.

Table 5.1: Floated Mineral and selectivity Index at different test numbers

Test No.	1	2	3	5	6	7	9	10	11	12	13	14	15
Pn recovery	70.39	65.42	56.05	68.99	46.03	43.22	71.14	60.16	65.05	65.53	59.25	52.44	41.28
Po recovery	33.28	13.34	9.53	29.82	16.41	11.77	42.47	14.09	23.06	19.53	6.24	7.38	3.93
SI	7.13	34.58	22.84	10.44	16.75	7.11	5.56	29.41	10.15	24.96	83.48	20.58	665.94

When grinding the ore at DO concentration 0 ppm, varying flotation conditions such as used in Test-5 and 6 resulted in an improvement in the selectivity but at the cost of Pn. When air was used as a sparging gas, it resulted in a significant drop in the recovery of the Po but the drop in the recovery of the Pn was only marginal. The decrease in the Po recovery resulted in an increase in the selectivity between Pn and Po and consequently an increase in the SI from 7.13 to 10.44. Air sparging in this case (Test-5) may be acting essentially as a depressant for Po. However, when N_2 is used as a sparging and flotation gas (Test-6), this resulted in an increase in the SI but the decrease in the recovery of the Pn is much more pronounced and cannot be promoted as an acceptable pathway for the improvement of the selectivity. Table 5.1 shows that when xanthate was added into the flotation cell (Test-9) instead of mill (Test-1), it gave the lowest selectivity of all the tests in this study. In Test-9, the recovery of the

Po was highest. This observation may be used to establish that addition of xanthate in the cell is recommended in plant practice, where Po is the valuable mineral.

The variation of the pH at a DO concentration of 0 ppm showed that the selectivity increased significantly when the ore was ground at higher pH values such as in Test-11 and Test-12. The SI and Pn recovery showed that increasing the pH from 9.2 to 10 resulted in a significant drop in the recovery of the Pn as well Po but raising the pH afterwards selectively depressed the Po and resulted in an increase in the SI to 25.0. However, it can be seen from Figure 5.6 that Test-2 gave a better performance than Test-12 with more or less similar Pn recoveries. These findings suggest that DO control during the grinding stage could be used as a better depressant in compared to pH control.

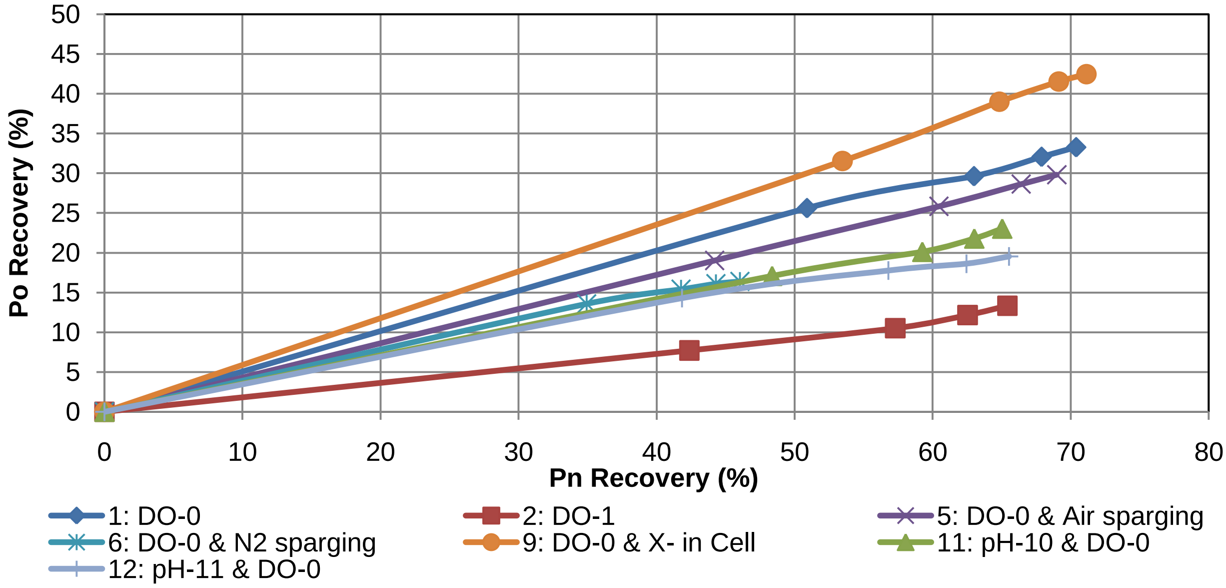

Figure 5.6: Pn and Po recovery comparison for the best selectivity point at a DO-0

In the test conditions other than DO-0, though the SI values were quite high the overall recovery of the Pn was quite low except in DO-1 (Test-2). All of the test work conducted in this study could be broadly divided into two categories, namely inert environment and air environment. Considering the tests where the ore was ground at DO-6.5 conditions (Test-3, -7 and -10), irrespective of the flotation conditions, the SI values were quite high. The reason for the higher SI values may be due to the high reactivity of the Po, and it being so prone to oxidation, which has been discussed previously in detail.

In the case of Test-13, 14 and 15 (no gas control DO-5.5), which was considered to be normal plant operation conditions, though the SI values were quite high, the recovery of the Pn were very low. Further varying pH at normal plant operating conditions during the grinding stage resulted in a drop in the recovery of both Pn and Po. The SI value was very high in the case of pH-11 (Test-15) but again the Pn recovery in this case was quite low. The main reason for the lower Pn and Po recovery at pH-11 may have been due to the non reactivity of the xanthate, which was confirmed by the residual xanthate measurement at pH-11. These findings are in line with the literature that the conversion of the xanthate to dixanthogen is not feasible at pH-11.

6 CONCLUSIONS

The primary aim of this project was to study the relationship between the effects of a change in pulp chemistry in the mill , as determined by measuring the pH, DO and Eh, and the resulting flotation behaviour of the minerals in a chalcopyrite-pentlandite-Po ore. A review of the literature indicated that there appeared to be very little published work on quantifying the relationship between the effect of dissolved oxygen, pH, xanthate adsorption and ORP simultaneously. In the present study, a highly instrumented laboratory scale Magotteaux mill was used to investigate the above interactions. The Magotteaux mill was specifically designed for the comparison of different grinding media and to mimic plant conditions in the laboratory. As extensive research has proven that 21 % Cr grinding media may give optimum plant performance when compared to other grinding media types (forged steel and 15% Cr). The objective set for this study was to use 21 % Cr grinding media and manipulate the grinding environment to improve further flotation performance. A Pt electrode was used to measure the redox potential (Eh). Studies were carried in which the dissolved oxygen levels in the mill were varied between 0 and 6.5 and the pH was varied between 9 and 11.

The main findings in this study were:

- The complete absence of oxygen (DO-0) in the mill during grinding resulted in residual xanthate remaining in the slurry after grinding. However, this residual xanthate was consumed during slurry transfer from the mill to the cell.
- Increasing the dissolved oxygen concentration to a value of 6.5 resulted in a lower grade and recovery of the Pn and Po but the recovery of the Cp was optimum in the present study.
- Increasing the pH of the pulp from the natural value of the ore i.e. 9 to 11 at a DO concentration of 0 ppm resulted in a decrease in the recovery of the Po. However, the recovery of the Pn and Cp remained similar to that obtained at pH 9.
- When the pulp was transferred from the mill to the flotation cell the DO level increased by up to 2 ppm values. This was accompanied by a change in the Eh from -170 mV to -30 mV.
- When the transferred slurry was purged with nitrogen in the flotation cell it was observed that, the xanthate level increased to the pre-grinding value. The recovery of all the valuable sulphide minerals (Cp, Pn and Po) was lowest in this test.

- The pulp potential (Eh) measurement during grinding at a DO concentration of 1 ppm (Test-2) and pH-11 with no gas control (Test-15) were more or less similar but the variations in the recovery of the Pn between these two tests was significant. This confirms that the Eh measurement can be used as a diagnostic tool for process control in plant practice but it is also important to consider the means of Eh control.
- The slower rate of oxidation of Pn and faster rate of oxidation of Po (as observed after the analysis of the batch flotation data using the Kelsall model) may be used as a tool for the development of separation processes for these minerals.
- It is hoped that the relative rates of oxidation/alteration of these two minerals on combination with the control of the DO concentration of the pulp can be used as tool for the separation of the Pn from Po, further study is required to better understand this process.

It became clear in this study that the presence of oxygen was critical to the consumption of xanthate which is consistent with the general literature. However a noteworthy observation related to the apparent reversibility of xanthate consumption when the ore was ground at a DO concentration of 0 ppm.

There are many proposals that a flotation system can be controlled by controlling the Eh value. However the present study has shown that controlling a combination of DO and pH is of critical importance and there was no clear trend observed in the relationship between the Eh value (which was a consequence of the DO and pH value) and flotation behavior of the different minerals.

With respect to the flotation behavior of the three minerals monitored in this study, it was observed that Cp grades and recoveries were not strongly influenced by the change in grinding enviroment. Pn and Po‘s flotation behavior was strongly influenced by DO concentration of the pulp, however, the effect of DO is much more pronounced on Po compared to Pn. Determining the Selectivity Index values showed that, the selectivity between these two minerals can be improved by grinding the ore at low DO concentration (DO-1).

This study represents one of the first investigations at laboratory scale of the effect of DO and pH in the mill on the subsequent flotation behavior. The study revealed that establishing a sound experimental procedure in such a system was a non-trivial exercise but that having achieved this as shown in the various sets of reproducibility results it was possible to begin to unravel the complex set of effects on the various minerals in the ore used in the study. The study did not involve changing the milling media from high chrome content balls to for example mild steel or ceramic media. Such studies would represent an excellent development of this study.

7 RECOMMENDATIONS

On the basis of the contributions and findings from this study, recommendations for future wok in this field are listed below:

1. Investigations using the Magotteaux Mill should be conducted using PGM ores milled for different DO concentrations to establish to what extent the recovery of the sulfide minerals varies among different DO concentrations. Concentrates from DO-0 tests should be submitted for PGM analysis in order to determine its effect on the recovery of PGMs as the PGM's are associated with the Po and Po recovery was found to be optimum in this case.
2. In order to understand completely, the effect of oxygen on xanthate adsorption and floatability of valuable minerals. A system is needed where the contact of oxygen during slurry transfer and flotation could be avoided.
3. In order to use Electrode potential as a tool for flotation control, different types of electrodes such as; Ion selective electrode, Mineral electrode, pH electrode, dissolved oxygen electrode separately as well as in combination should be tested at the grinding as well as the flotation stage.
4. The effect of grinding media should be tested at different DO concentration because it may be possible that in the case of Nkomati ore, Forged steel grinding media may perform better as it creates a reducing environment during grinding through the consumption of the DO present in the pulp.

8 BIBLIOGRAPHY

Abramov, A.A. and Avdohin, V.M. 1998. *Oxidation of sulfide minerals in beneficiation processes.* CRC.

Ackerman, P.K. and others. 2000. Use of xanthogen formates as collectors in the flotation of copper sulfides and pyrite. *International journal of mineral processing.* 58(1-4):1-13. [Online]. Available:

Adam, K., Natarajan, K.A. and Iwasaki, I. 1984. Grinding media wear and its effect on the flotation of sulfide minerals. *International journal of mineral processing.* 12(1-3):39-54.

Allison, S.A. and others. 1972. A determination of the products of reaction between various sulfide minerals and aqueous xanthate solution, and a correlation of the products with electrode rest potentials. *Metallurgical and materials transactions B.* 3(10):2613-2618.

Anon 2010. *Galvanic interaction.* [Online]. Available: http://www.miningbasics.com/galvanic-interactions [2010, April/05].

Avotins, P.V., Wang, S.S., Nagaraj, D.R. 1994. Recent advances in sulfide collector development. *Reagents for better metallurgy.*

Becker, M. 2009. The mineralogy and crystallography of pyrrhotite from selected nickel and PGE ore deposits and its effect on flotation performance. P.hD. University of Pretoria.

Belzile, N. and others. 1997. Acid mine drainage in the Sudbury area, Ontario. *Environmental geology of urban areas.geological association of canada, st.JohnÕs canada.* :223–226.

Biegler, T., Rand, D.A.J. and Woods, R. 1975. Oxygen reduction on sulphide minerals part I. Kinetics and mechanism at rotated pyrite electrodes. *Journal of electroanalytical chemistry.* 60(2):151-162.

Bowers R. L., Smit, D.S. 2008. Process development of the Nkomati PCMZ base metal sulphide ore. [Online]. Available: .

Bozkurt, V., Xu, Z. and Finch, J.A. 1998. Pentlandite/pyrrhotite interaction and xanthate adsorption. *International journal of mineral processing.* 52(4):203-214.

Bradford, L. and others. 1998. The development of the proposed milling circuit for the Nkomati main concentrator plant. *Minerals engineering.* 11(12):1103-1117.

Buckley, A.N. and others. 2003. Interaction of thiol collectors with pre-oxidised sulfide minerals. *International journal of mineral processing.* 72(1-4):163-174. [Online]. Available: .

Buckley, A.N., Hamilton, I.C. and Woods, R. 1988. Studies of the surface oxidation of pyrite and pyrrhotite using X-ray photoelectron spectroscopy and linear potential sweep voltammetry. *Int. Symp. On Electrochemistry in Mineral and Metal Processing II.* P.E. Richardson and R. Woods, Eds.The Electrochemical Society. 234.

Buckley, A.N. and Woods, R. 1985. X-ray photoelectron spectroscopy of oxidised pyrrhotite surfaces. *Applications of surface science.* 20(4):472-480.

Buckley, A.N. and Woods, R. 1991. Surface composition of pentlandite under flotation-related conditions. *Surface and interface analysis.* 17(9):675-680. [Online]. Available: .

Buckley, A.N. and Woods, R. 1997. Chemisorption—the thermodynamically favoured process in the interaction of thiol collectors with sulphide minerals. *International journal of mineral processing.* 51(1-4):15-26.

Buswell, A.M. and others. . 1998. The use of electrochemical measurements in the characterisation of flotation pulp chemistry on laboratory and plant scale.

Buswell, A.M. and Nicol, M.J. 2002. Some aspects of the electrochemistry of the flotation of pyrrhotite. *Journal of applied electrochemistry.* 32(12):1321-1329.

Chander, S. 1991. Electrochemistry of sulfide flotation: Growth characteristics of surface coatings and their properties, with special reference to chalcopyrite and pyrite. *International journal of mineral processing.* 33(1-4):121-134.

Chander, S. 2003. A brief review of pulp potentials in sulfide flotation* 1. *International journal of mineral processing.* 72(1-4):141-150.

Chander, S. and Fuerstenau, D.W. 1974. The effect of potassium diethyldithiophosphate on the electrochemical properties of platinum, copper and copper sulfide in aqueous solutions. *Journal of electroanalytical chemistry.* 56(2):217-247.

Chander, S. and Fuerstenau, D.W. 1983. Electrochemical flotation separation of chalcocite from molybdenite. *International journal of mineral processing.* 10(2):89-94.

Clark, L.C.,Jr and others. 1953. Continuous recording of blood oxygen tensions by polarography. *Journal of applied physiology.* 6(3):189-193. [Online]. Available:

Cook, M.A. and Nixon, J.C. 1950. The Theory of Water-Repellent Films on Solids Formed by Adsorption from Aqueous Solutions of Heteropolar Compounds. *The journal of physical chemistry.* 54(4):445-459.

Cook, M.A. and Wadsworth, M.E. 1957. Hydrolytic and ion pair adsorption processes in flotation, ion exchange and corrosion. *Proceedings.* Butterworths Scientific Publications. 228.

Cullinan, V.J. and others. 1999. Investigating fine galena recovery problems in the lead circuit of Mount Isa Mines Lead/Zinc Concentrator part 1: Grinding media effects. *Minerals engineering.* 12(2):147-163. [Online]. Available: .

De Haan, B. 1991. A review of the rate of pyrite oxidation in aqueous systems at low temperature. *Earth-science reviews.* 31(1):1-10.

E.J.B. 2009. *MAG011-09-MNL-165-1 - Experion PKS User Training Manual.* 1. South Australia: MANTA CONTROLS PTY LTD.

Ekmekci, Z. and Demirel, H. 1997. Effects of galvanic interaction on collectorless flotation behaviour of chalcopyrite and pyrite. *International journal of mineral processing.* 52(1):31-48. [Online]. Available: .

Ekmekçi, Z. 2009. Electrochemistry in sulphide mineral flotation: Hacettepe university mining engineering department, division of mineral processing.

Ekmekçi, Z. and others. 2005. The value and limitations of electrochemical measurements in flotation of precious metal ores. *Minerals engineering.* 18(8):825-831.

Fairthorne, G., Fornasiero, D. and Ralston, J. 1997. Effect of oxidation on the collectorless flotation of chalcopyrite. *International journal of mineral processing.* 49(1-2):31-48.

Finch, J.A. and Labonté, G. 1989. Verification of electrodes for pulp potential measurement. *Minerals engineering.* 2(4):557-564.

Fornasiero, D., Montalti, M. and Ralston, J. 1995. Kinetics of adsorption of ethyl xanthate on pyrrhotite: in situ UV and infrared spectroscopic studies. *Journal of colloid and interface science.* 172(2):467-478. [Online]. Available: .

Fuerstenau, M.C. and Sabacky, B.J. 1981. On the natural floatability of sulfides. *International journal of mineral processing.* 8(1):79-84.

Fuerstenau, M.C. 1976. Flotation : A.M. Gaudin memorial volume. *A.M Gaudin Memorial Flotation Symposium.* 1976. M.C. Fuerstenau and A.M. Gaudin, Eds. New York: American Institute of Mining, Metallurgical and Petroleum Engineers, Inc.

Gardner, J.R. and Woods, R. 1979a. An electrochemical investigation of the natural flotability of chalcopyrite. *International journal of mineral processing.* 6(1):1-16.

Gardner, J.R. and Woods, R. 1979b. A study of the surface oxidation of galena using cyclic voltammetry. *Journal of electroanalytical chemistry.* 100:447-459.

Garrels, R.M. 1990. *Solutions, minerals and equilibria.* Boston ; London: Jones and Bartlett.

Gaudin, A.M. and Fuerstenau, M.C. 1976. *Flotation : A. M. Gaudin memorial volume.* Society of Mining Engineers of AIME. Mineral Processing Division ed. New York: American Institute of Mining, Metallurgical, and Petroleum Engineers.

Gauert, C. 2001. Sulphide and oxide mineralisation in the Uitkomst Complex, South Africa: origin in a magma conduit. *Journal of african earth sciences.* 32(2):149-161.

Gebhardt, J.E.S., K.B. 1988. Effect of solution composition on redox potentials of platinum and sulfide mineral electrodes. *Proceedings of the Symposium on Electrochemistry in Mineral and Metal Processing II. Eds. PE Richardson and R. Woods, The Electrochemical Society, Atlanta, GA, May.* 15.

Glasstone, S. 1942. *An introduction to electrochemistry.* Princeton: D Van Nostrand Co.

Grano, S. 2009. The critical importance of the grinding environment on fine particle recovery in flotation. *Minerals engineering.* 22(4):386-394. [Online]. Available: .

Grant, S. 2010. Re : Troublshootings of the Mill. Australia. J. Mishra.

Greet, C. 2010. Re: Regarding the troubleshootings of the mill. Australia. J. Mishra.

Greet, C.J. 2008. The significance of grinding environment on the flotation of UG2 ores. *The journal of the southern african institute of mining and metallurgy.* 6:9. [Online]. Available: .

Greet, C.J. and others. 2004. The Magotteaux Mill®: investigating the effect of grinding media on pulp chemistry and flotation performance. *Minerals engineering.* 17(7-8):891-896. [Online]. Available: .

Guy, P.J. and Trahar, W.J. 1984. The effects of oxidation and mineral interaction on sulphide flotation. *Flotation of sulphide minerals.* :91-110.

Hamilton, I.C. and Woods, R. 1981. An investigation of surface oxidation of pyrite and pyrrhotite by linear potential sweep voltammetry. *Journal of electroanalytical chemistry.* 118:327-343. [Online]. Available: .

Hamilton, I.C. and Woods, R. 1986. Surfactant properties of alkyl xanthates. *International journal of mineral processing.* 17(1-2):113-120.

Harris, G.H., Ackerman, P.K. and Aplan, F.F. 1988. Google Patents.

Harris, P.J. 2010. Water recovery. South Africa. J. Mishra.

Harris, P.J. and Finkelstein, N.P. 1975a. Interactions between sulphide minerals and xanthates, I. The formation of monothiocarbonate at galena and pyrite surfaces. *International journal of mineral processing.* 2(1):77-100.

Harris, P.J. and Finkelstein, N.P. 1975b. Interactions between sulphide minerals and xanthates, I. The formation of monothiocarbonate at galena and pyrite surfaces. *International journal of mineral processing.* 2(1):77-100.

Hay, M.P. 2008. Optimising froth condition and recovery for a nickel ore. *Minerals engineering.* 21(12-14):861-872.

Hayes, R.A. and Ralston, J. 1988. The collectorless flotation and separation of sulphide minerals by Eh control. *International journal of mineral processing.* 23(1-2):55-84.

Healy, T.W. and Trahar, W.J. 1989. Challenges in sulfide flotation fundamentals. *Challenges in mineral processing, SME/AIME, littleton.* :3-13.

Heimala, S., Jounela, S. and Saari, M. 1988. Flotation control with mineral electrodes. 1713–1718.

Heimala, S.O. and Saari, K.M.J. 1992. Google Patents.

Heiskanen, K., Kirjavainen, V. and Laapas, H. 1991. Possibilities of collectorless flotation in the treatment of pentlandite ores. *International journal of mineral processing.* 33(1-4):263-274.

Heyes, G. and Trahar, W. 1984. The flotation of pyrite and pyrrhotite in the absence of conventional collectors. *Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing.* Industrial Electrolytic Division, Energy Technology Group. 219.

Hintikka, V. and others. 1996. Continuous classifying laboratory mill--New possibilities for research work* 1. *Minerals engineering.* 9(11):1157-1164. [Online]. Available: .

Hodgson, M. and Agar, G.E. 1984. An electrochemical investigation into the natural flotability of pyrrhotite. *Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing.* Industrial Electrolytic Division, Energy Technology Group. 185.

Hodgson, M. and Agar, G.E. 1989. Electrochemical investigations into the flotation chemistry of pentlandite and pyrrhotite: process water and xanthate interactions. *Can.metall.Q.* 28(3):189-198.

Hu, Y. 2009. *Electrochemistry of flotation of sulphide minerals.* 1st ed. New York: Springer.

Huang, G. and Grano, S. 2005. Galvanic interaction of grinding media with pyrite and its effect on flotation. *Minerals engineering.* 18(12):1152-1163. [Online]. Available: .

Huang, G. and Grano, S. 2006. Galvanic interaction between grinding media and arsenopyrite and its effect on flotation:: Part I. Quantifying galvanic interaction during grinding. *International journal of mineral processing.* 78(3):182-197. [Online]. Available: .

Huang, G., Grano, S. and Skinner, W. 2006. Galvanic interaction between grinding media and arsenopyrite and its effect on flotation: Part II. Effect of grinding on flotation. *International journal of mineral processing.* 78(3):198-213.

Iwasaki, I. and others. 1988. Nature of corrosive and abrasive wear in ball mill grinding. *International journal of mineral processing.* 22(1-4):345-360.

Janetski, N.D., Woodburn, S.I. and Woods, R. 1977. An electrochemical investigation of pyrite flotation and depression. *International journal of mineral processing.* 4(3):227-239.

Johnson, N.W. 2002. Practical aspects of the effect of electrochemical conditions in grinding mills on the flotation process. *Proceedings of Flotation and Flocculation: From Fundamentals to Applications* J. Ralston, J. Miller and J. Rubio, Eds. Australia: University of South Australia. 287.

Johnson, N.W. and Munro, P.D. 2008. **Methods for assigning domains in the primary sulfide zone of a sulfide ore body**. ***Proceedings 9th International Congress for Applied Mineralogy***. AusIMM, Ed. Australia: AusIMM Australia. 597. [Online]. Available: .

Jones Sean, C.F. and Smart Timothy, J. 1992. Compositional and structural alteration of pyrrhotite surfaces in solution: XPS and XRD studies. *Applied surface science.* 55(1):65-85. [Online]. Available: .

Jones, M.H. and Woodcock, J.T. 1978. Evaluation of ion-selective electrode for control of sodium sulfide additions during laboratory flotation of oxidized ores. 87:C99.

Jones, M.H. and Woodcock, J.T. 1979. Control of laboratory sulphidization with a sulphide ion-selective electrode before flotation of oxidized lead-zinc-silver dump material. 6(1):17.

Jones, M.H. 1991. Some recent developments in the measurement and control of xanthate, perxanthate, sulphide, and redox potential in flotation. *International journal of mineral processing.* 33(1-4):193-205.

Junior, A. and others. 2006. Study of galvanic interactions between Pyrite and Arsenopyrite through electrode potential and contact angle measurement. *61 DG Congresso Anual da Associacao Brasileira de Metalurgia e Materiais: 61 st Annual ABM International Congress.* Associacao Brasileira de Metalurgia e Materiais, Centro de Informacao/Library, Rua Antonio Comparato, 218, Sao Paulo SP, 04605-030, Brazil,. [Online]. Available: .

Kelebek, S. 1993. The effect of oxidation on the flotation behaviour of nickel–copper ores. *XVIII Mineral Processing Congress. Sydney.* 999–1005.

Kelebek, S. and Nanthakumar, B. 2007. Characterization of stockpile oxidation of pentlandite and pyrrhotite through kinetic analysis of their flotation. *International journal of mineral processing.* 84(1-4):69-80.

Kelebek, S., Wells, P.F. and Fekete, S.O. 1996. Differential flotation of chalcopyrite, pentlandite and pyrrhotite in Ni-Cu sulphide ores. *Canadian metallurgical quarterly.* 35(4):329-336.

Kelsall, D.F. 1961. Application of probability in the assessment of flotation systems. *Transactions of the institution of mining and metallurgy.* 70(3):191-204.

Khan, A. and Kelebek, S. 2004. Electrochemical aspects of pyrrhotite and pentlandite in relation to their flotation with xanthate. Part-I: Cyclic voltammetry and rest potential measurements. *Journal of applied electrochemistry.* 34(8):849-856.

King, R.P., Editor. 1982. *The Principles of flotation.* South African Institute of Mining and Metallurgy.

Klimpel, R.D. 1984. Froth Flotation: The kinetic approch. *Proceedings of Mintek 5.* Johannesburg: Mintek. 5.

Klymowsky, I.B. 1968a. *The role of oxygen in xanthate flotation of galena, pyrite, and chalcopyrit.* --. Montreal: .

Klymowsky, I.B. 1968b. *The role of oxygen in xanthate flotation of galena, pyrite, and chalcopyrit.* --. Montreal: .

Knipe, S.W. and others. 1995. X-ray photoelectron spectroscopic study of water adsorption on iron sulphide minerals. *Geochimica et cosmochimica acta.* 59(6):1079-1090.

Koryta, J. 1986. Ion-selective electrodes. *Annual review of materials science.* 16(1):13-27.

Kowal, A. and Pomianowski, A. 1973. Cyclic voltammetry of ethyl xanthate on a natural copper sulphide electrode. *Journal of electroanalytical chemistry.* 46(2):411-420.

Kuopanportti, H. and others. 2000. A model of conditioning in the flotation of a mixture of pyrite and chalcopyrite ores. *International journal of mineral processing.* 59(4):327-338.

Lambert, S. 2010. Presentation at University of Cape Town: Research activities in the Center for Mineral Research, University of Cape Town.

Laskowski, S.L. 2005. Flotation: MMPE 333, Lecture Notes.

Legrand, D., Bancroft, G. and Nesbitt, H. 2005a. Oxidation of pentlandite and pyrrhotite surfaces at pH 9.3: Part 2. Effect of xanthates and dissolved oxygen. *American mineralogist.* 90(7):1055. [Online]. Available: .

Legrand, D., Bancroft, G. and Nesbitt, H. 2005b. Oxidation/alteration of pentlandite and pyrrhotite surfaces at pH 9.3: Part 1. Assignment of XPS spectra and chemical trends. *American mineralogist.* 90(7):1042. [Online]. Available: .

Legrand, D.L., Bancroft, G.M. and Nesbitt, H.W. 1997. Surface characterization of pentlandite, (Fe,Ni)9S8, by X-ray photoelectron spectroscopy. *International journal of mineral processing.* 51(1-4):217-228.

Lowson, R.T. 1982. Aqueous oxidation of pyrite by molecular oxygen. *Chemical reviews.* 82(5):461-497.

Majima, H. 1969. How oxidation affects selective flotation of complex sulfide ores. *CAN MET QUART.* 8(3):269-273.

Majima, H. and Takeda, M. 1969. Electrochemical studies of the xanthate-dixanthogen system on pyrite. *Transactions.* 244:431.

Malysiak, V. and others. 2002. Pentlandite-feldspar interaction and its effect on separation by flotation. *International journal of mineral processing.* 66(1-4):89-106.

Martin, C.J. and others. 1991. Review of the effect of grinding media on flotation of sulphide minerals. *Minerals engineering.* 4(2):121-132.

Moses, C.O. and others. 1987. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochimica et cosmochimica acta.* 51(6):1561-1571.

Mycroft, J.R., Nesbitt, H.W. and Pratt, A.R. 1995. X-ray photoelectron and Auger electron spectroscopy of air-oxidized pyrrhotite: Distribution of oxidized species with depth. *Geochimica et cosmochimica acta.* 59(4):721-733. [Online]. Available: .

Nakazawa, H. and Iwasaki, I. 1986. Galvanic contact between nickel arsenide and pyrrhotite and its effect on flotation. *International journal of mineral processing.* 18(3-4):203-215.

Nanthakumar, B. and Kelebek, S. 2007. Stagewise analysis of flotation by factorial design approach with an application to the flotation of oxidized pentlandite and pyrrhotite. *International journal of mineral processing.* 84(1-4):192-206.

Natarajan, K.A. 1992. Ball wear and its control in the grinding of a lead-zinc sulphide ore. *International journal of mineral processing.* 34(1-2):161-175.

Natarajan, K.A. and Iwasaki, I. 1972. Eh measurements in hydrometallurgical systems. 252:437-437–439.

Natarajan, K.A. and Iwasaki, I. 1984. Electrochemical aspects of grinding media-mineral interactions in magnetite ore grinding. *International journal of mineral processing.* 13(1):53-71.

Nicholson, R.V. and Scharer, J.M. 1994. Laboratory studies of pyrrhotite oxidation kinetics. *ACS Symposium Series.* ACS Publications. 14.

Nixon, J.C. 1957. Proceedings of the 2nd International Congress on Surface Activity. 369.

Pearse, M.J. 2005. An overview of the use of chemical reagents in mineral processing. *Minerals engineering.* 18(2):139-149.

Pecina-Trevino, E.T., Uribe-Salas, A. and Nava-Alonso, F. 2003. Effect of dissolved oxygen and galvanic contact on the floatability of galena and pyrite with Aerophine 3418A. *Minerals engineering.* 16(4):359-367. [Online]. Available: .

Peng, Y. and others. 2003. Control of grinding conditions in the flotation of chalcopyrite and its separation from pyrite. *International journal of mineral processing.* 69(1-4):87-100. [Online]. Available: .

Plaksin, I. and Bessonov, S. 1957. Role of gases in flotation reactions. *Proceedings.* Butterworths Scientific Publications. 361.

Pozzo, R.L. and Iwasaki, I. 1989. Pyrite-Pyrrhotite Grinding Media Interactions and Their Effects on Media Wear and Flotation. *Journal of the electrochemical society.* 136:1734.

Pratt, A.R., Muir, I.J. and Nesbitt, H.W. 1994. X-ray photoelectron and Auger electron spectroscopic studies of pyrrhotite and mechanism of air oxidation. *Geochimica et cosmochimica acta.* 58(2):827-841. [Online]. Available: .

Ralston, J. 1991. Eh and its consequences in sulphide mineral flotation. *Minerals engineering.* 4(7-11):859-878.

Rand, D.A.J. and Woods, R. 1984. Eh measurements in sulphide mineral slurries. *International journal of mineral processing.* 13(1):29-42.

Rantapuska, S.V. and Heimala, S.O. 1990. Google Patents.

Rao, M.L.B., Damjanovic, A. and Bockris, J.O.M. 1963. Oxygen Adsorption Related to the Unpaired d-electrons in Transition Metals. *The journal of physical chemistry.* 67(11):2508-2509.

Rao, S.R. 1971. *Xanthates and related compounds.* M. Dekker New York.

Rao, S.R. and Finch, J. 1988. Galvanic interaction studies on sulphide minerals. *Can.metall.Q.* 27(4):253-259. [Online]. Available: .

Rao, S.R. and Finch, J.A. 1991. Adsorption of amyl xanthate at pyrrhotite in the presence of nitrogen and implications in flotation. *Canadian metallurgical quarterly.* 30(1):1-6. [Online]. Available: .

Rao, S.R. and Finch, J.A. 1988. Galvanic interaction studies on sulphide minerals. *Can.metall.Q.* 27(4):253-259. [Online]. Available: .

Rao, S.R. and Leja, J. 2004. *Surface chemistry of froth flotation.* 2nd ed. New York: Kluwer Academic/Plenum Publishers.

Ravitz, S.F. and Porter, R.R. 1933. Oxygen Free Flotation I: Flotation of Galena in Absence of Oxygen. *Amer.inst.min.metall.engrs, tech.publ.* 513:17.

Rey, M. and Formanek, V. 1960. Some factors affecting the selectivity in the differential flotation of lead-zinc ores in the presence of oxidized lead minerals. *Proceedings of 5th Int. Miner. Process. Congress, Inst. Min. Metall., London.* 343.

Richardson, P.E. and others. 1994. The photoelectrochemistry of galena. *International journal of mineral processing.* 41(1-2):77-97.

Ruonal, M., Heimala, S. and Jounela, S. 1997. Different aspects of using electrochemical potential measurements in mineral processing. *International journal of mineral processing.* 51(1-4):97-110.

Salamy, S.G. and Nixon, J.C. 1953. The application of electrochemical methods to flotation research. *Recent developments in mineral dressing.* :503-516.

Salamy, S.G. and Nixon, J.C. 1954. Reaction between a mercury surface and some flotation reagents: and electochemical study. I. Polarization curves. *Australian journal of chemistry.* 7(2):146-156.

Sato, M. 1960. Oxidation of sulfide ore bodies. II. Oxidation mechanisms of sulfide minerals at 25 C. *Economic geology and the bulletin of the society of economic geologists (US).* 55.

Slater, R. 2006. *Nkomati site visit.* Africa: ARM Platinum, Lion ore.

Spira, P. and Rosenblum, F. 1974. The oxygen demand of flotation pulps. *6th Annual Meeting of the Canadian Mineral Processors. CIM, Ottawa.* 74–106.

Sutherland, K.L. and Wark, I.W. 1955. *Principles of flotation.* Melbourne: Australasian Institute of Mining and Metallurgy.

Taggart, A.F. and Behre, H.A. 1945. *Handbook of mineral dressing, ores and industrial minerals.* New York; London: J. Wiley and sons, inc.; Chapman and Hall, limited.

Theart, H.F.J., de Nooy, C.D. 2001. The Platinum Group Minerals in two parts of the Massive Sulphide Body of the Uitkomst Complex, Mpumalanga, South Africa. *South african journal of geology.* 104(4):287. [Online]. Available: .

Thomas, J.E. and others. 1998. The role of surface sulfur species in the inhibition of pyrrhotite dissolution in acid conditions. *Geochimica et cosmochimica acta.* 62(9):1555-1565. [Online]. Available: .

Thomas, J.E., Skinner, W.M. and Smart, R.S.C. 2001. A mechanism to explain sudden changes in rates and products for pyrrhotite dissolution in acid solution. *Geochimica et cosmochimica acta.* 65(1):1-12.

Thornton, E. 1973. The effect of grinding media on flotation selectivity. *Proceedings 5th Annual Meeting of Canadian Mineral Processors, Dept of Energy, Ottawa, pp224-239.*

Tolun, R. and Kitchener, J.A. 1964. Electrochemical study of the galena-xanthate-oxygen flotation system. *Trans.IMM.* 73:313–322.

Urbano, G. and others. 2008. Pyrite− Arsenopyrite Galvanic Interaction and Electrochemical Reactivity. *The journal of physical chemistry C.* 112(28):10453-10461. [Online]. Available: .

Vathsala and Natarajan, K.A. 1989. Some electrochemical aspects of grinding media corrosion and sphalerite flotation. *International journal of mineral processing.* 26(3-4):193-203.

Vaughan, D.J. 1989. Surface alteration of pentlandite and spectroscopic evidence for secondary violarite formation. *Mineralogical magazine.* 53:213-222.

Walker, J. 1997. *Nkomati low on costs, high on returns.* company digest. Business Times.

Wang, X., Eric Forssberg, K.S. and Bolin, N.J. 1989. Thermodynamic calculations on iron-containing sulphide mineral flotation systems, I. The stability of iron-xanthates. *International journal of mineral processing.* 27(1-2):1-19. [Online]. Available: .

Wiese, J.G. 2009. Investigating depressant behaviour in the flotation of selected Merensky ores.

Wills, B.A. and others. 2006. *Wills' mineral processing technology : an introduction to the practical aspects of ore treatment and mineral recovery.* 7th ed. Amsterdam ; Boston, MA: Elsevier/BH.

Wolmarans, E. and Morgan, P. 2009. *Milling circuit selection for the Nkomati 375 ktpm concentrator: transaction paper.*

Woods, R. 1971. Oxidation of ethyl xanthate on platinum, gold, copper, and galena electrodes. Relation to the mechanism of mineral flotation. *The journal of physical chemistry.* 75(3):354-362.

Woods, R. 2003. Electrochemical potential controlling flotation. *International journal of mineral processing.* 72(1-4):151-162.

Woods, R. and others. 1992. Ethyl xanthate chemisorption isotherms and Eh-pH diagrams for the silver + water + ethyl xanthate system. *Journal of electroanalytical chemistry.* 328(1-2):179-194.

Woods, R. and others. 1994. Chemisorption of ethyl xanthate on copper electrodes. *International journal of mineral processing.* 42(3-4):215-223.

Woods, R., Constable, D.C. and Hamilton, I.C. 1989. A rotating ring disc electrode study of the oxidation of sulfur(-II) species on gold and sulfide minerals. *International journal of mineral processing.* 27(3-4):309-326.

Yelloji Rao, M.K. and Natarajan, K.A. 1988. Influence of galvanic interaction between chalcopyrite and some metallic materials on flotation. *Minerals engineering.* 1(4):281-294.

Yelloji Rao, M.K. and Natarajan, K.A. 1989. Effect of galvanic interaction between grinding media and minerals on sphalerite flotation. *International journal of mineral processing.* 27(1-2):95-109.

Yelloji Rao, M.K. and Natarajan, K.A. 1990. Effect of electrochemical interactions among sulphide minerals and grinding medium on the flotation of sphalerite and galena. *International journal of mineral processing.* 29(3-4):175-194.

Yuan, X.M., Pålsson, B.I. and Forssberg, K.S.E. 1996. Flotation of a complex sulphide ore II. Influence of grinding environments on Cu/Fe sulphide selectivity and pulp chemistry. *International journal of mineral processing.* 46(3-4):181-204. [Online]. Available: .

Zachwieja, J.B. and others. 1989. Correlation between the surface composition and collectorless flotation of chalcopyrite. *Journal of colloid and interface science.* 132(2):462-468. [Online]. Available: .

Zhou, R. and Chander, S. 1989. Effect of pretreatment on EH response of a gold electrode. :57-64.

Zhou, R. and Chander, S. 1991. Comparison of gold, platinum and sulfide ion selective electrodes as sensors for Eh measurement in sulfide solutions. 8(2):91-96. [Online]. Available: http://www.scopus.com.ezproxy.uct.ac.za/record/display.url?eid=2-s2.0-0026157640andorigin=inwardandtxGid=m83AaQrdrAECW5_uBP4vpr8%3a14.